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Design, optimization, and characterization of hybrid composite structural batteries

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**Design, optimization, and characterization of hybrid
composite structural batteries**

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Abstract

This thesis focuses on the design, development, and characterization of a multifunctional structural battery composed of glass fiber-reinforced polymer (GFRP) as the structural shell and electrical insulator, aluminum and copper alloys as current collectors coated with a lithium iron phosphate (LFP) cathode and a graphite anode, respectively, and a structural solid-state electrolyte. Several key actions have been undertaken throughout this work to enable the system to simultaneously store energy and bear mechanical loads, offering potential for lightweight structural energy storage solutions.

The first part of this thesis presents a comprehensive literature review covering the objectives of structural batteries, their various types along with advantages and disadvantages, key mechanical and electrochemical performance metrics, physical and chemical characterization techniques, and multifunctionality metrics. It concludes with a review of different types of electrolytes and a detailed discussion of the multifunctional properties and the trade-off between load-bearing capability and ionic conductivity in composite polymer electrolytes.

In the second part, the interfacial bonding between the GFRP shell and the metallic current collectors—which critically influences both mechanical durability and electrochemical performance—is evaluated and improved. First, Mode I interlaminar fracture toughness was tested using double cantilever beam (DCB) specimens, and various surface treatments were applied to the aluminum and copper alloys to enhance adhesion. These treatments included mechanical abrasion, alkaline etching, phosphoric acid treatment, and sol-gel anodizing. The results were compared with a baseline configuration without treatment, and also with an all-GFRP configuration. Surface roughness and surface energy were measured to better understand the role of surface modification. Additionally, the Mode II interlaminar fracture toughness was measured using the modified transverse crack tension (mTCT) specimens. Following the best surface treatment identified from the DCB study, the influence of this treatment and compressive transverse stresses on interfacial fracture behavior under Mode II loading was examined. The results were compared with the baseline configuration (without treatment or compressive stress) and the all-GFRP configuration. The dominance of mode II loading, using the modified transverse crack tension specimens was verified using the virtual crack closure technique. For the designed configurations, an analytical, closed-form solution to obtain the mode II interlaminar fracture toughness equation was derived, and verified numerically, considering residual thermal stresses and elastic mismatch. Crack initiation and propagation mechanisms were identified using digital image correlation (DIC), and the surfaces of the aluminum and copper alloys were analyzed after mTCT tests using scanning electron microscopy (SEM) to assess the effectiveness of surface treatments and the impact of transverse pressure.

The third part focuses on the development of the core component of the battery: the structural electrolyte. First, the most compatible polymer and solvent with epoxy to achieve multifunctional performance were identified by testing different polymers. Accordingly, thermoplastic polymers

including polyethylene oxide (PEO), polyvinyl alcohol (PVA), and polyvinyl acetate (PVAc) were each blended with thermosetting epoxy resin using various solvents. Potentiostatic electrochemical impedance spectroscopy (PEIS), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) were used to evaluate ionic conductivity, thermal stability, and mechanical properties, respectively. Based on these evaluations, PVA was identified as the most suitable thermoplastic when combined with epoxy to form a heat-resistant polymer host. Second, the amount of lithium salt (LiTFSI) and alumina (Al_2O_3) nanofillers was optimized to obtain a composite polymer matrix with multifunctional performance. Finally, using the optimized formulation ($\text{PVA}_{0.34}/\text{epoxy}_{0.14}/\text{LiTFSI}_{0.32}/\text{Al}_2\text{O}_{30.2}$), a structural electrolyte was fabricated by reinforcing it with woven glass fiber and evaluated through PEIS, DMA, TGA, tensile testing, and charge/discharge tests in half-cell and full-cell assemblies to assess its electrochemical and mechanical performance.

Finally, in the fourth part of the thesis, a complete structural battery was fabricated using the previously developed components. The battery features a quasi-isotropic lay-up GFRP shell bonded with aluminum and copper alloy current collectors, treated with sol-gel on the GFRP side, and coated with LFP cathode and graphite anode on the structural electrolyte side. Classical laminate theory was used to determine the best lay-up repetition of GFRP to ensure symmetric flexural stiffness. Mechanical performance was assessed using quasi-static indentation tests on both sides of the battery, with results benchmarked against equivalent hybrid structures and an all-GFRP configuration. Computed tomography (CT) imaging was employed to characterize internal damage across the different configurations. Energy storage performance was evaluated using PEIS and charge–discharge cycling and compared with coin cell configurations and state-of-the-art structural batteries. Finally, the multifunctionality of the system was assessed. The results demonstrated that the hybrid structural battery effectively combines load-bearing capability with energy storage, highlighting its potential for lightweight multifunctional applications.

Keywords: Structural Batteries. Hybrid laminates. Interlaminar fracture toughness. Composite polymer electrolytes. Quasi Static Indentation. Charge/Discharge.

Resumo

Esta tese aborda o design, desenvolvimento e caracterização de uma bateria estrutural multifuncional composta por um invólucro estrutural em polímero reforçado com fibra de vidro (GFRP), que funciona simultaneamente como estrutura mecânica e isolante elétrico, coletores de corrente em ligas de alumínio e cobre revestidos, respectivamente, com um cátodo de fosfato de ferro e lítio (LFP) e um ânodo de grafite, e um eletrólito estrutural em estado sólido. Várias ações fundamentais foram realizadas ao longo deste trabalho com o objetivo de permitir que o sistema armazene energia e suporte cargas mecânicas em simultâneo, oferecendo um elevado potencial para soluções de armazenamento de energia estrutural e leve.

A primeira parte da tese apresenta uma revisão bibliográfica abrangente, abordando os objetivos das baterias estruturais, os vários tipos existentes com as respectivas vantagens e desvantagens, as principais métricas de desempenho mecânico e eletroquímico, técnicas de caracterização física e química, e métricas de multifuncionalidade. Conclui com uma revisão dos diferentes tipos de eletrólitos e uma discussão detalhada das propriedades multifuncionais e do compromisso entre a capacidade de suporte de carga e a condutividade iônica em eletrólitos poliméricos compósitos.

Na segunda parte, a ligação interfacial entre o invólucro em GFRP e os coletores de corrente metálicos — que influencia de forma crítica a durabilidade mecânica e o desempenho eletroquímico — é avaliada e melhorada. Primeiramente, a tenacidade à fratura interlaminar no modo I foi avaliada utilizando o ensaio 'double-cantilever beam' (DCB), tendo sido aplicados diversos tratamentos de superfície às ligas de alumínio e cobre para melhorar a adesão, incluindo abrasão mecânica, ataque alcalino, tratamento com ácido fosfórico e anodização por sol-gel. Os resultados foram comparados com uma configuração de referência sem tratamento e com uma configuração totalmente em GFRP. Foram também medidas a rugosidade e a energia superficial para compreender melhor o efeito da modificação superficial. Em segundo lugar, a tenacidade à fratura interlaminar no modo II foi avaliada através do ensaio de tração com fissura transversal modificada (mTCT). Após identificar o melhor tratamento de superfície no estudo DCB, foi analisado o impacto deste tratamento e de tensões transversais compressivas no comportamento interfacial sob carregamento em modo II. Os resultados foram comparados com a configuração de referência (sem tratamento nem tensão compressiva) e com a configuração toda em GFRP. A predominância do modo II de carregamento, utilizando provetes modificados de tração com fissura transversal, foi verificada através da técnica de fecho virtual da fissura. Para as configurações concebidas, foi deduzida uma solução analítica em forma fechada para obter a equação da tenacidade à fratura interlaminar em modo II, a qual foi verificada numericamente, considerando as tensões térmicas residuais e o desajuste elástico. Os mecanismos de iniciação e propagação da fissura foram analisados com correlação digital de imagem (DIC), e as superfícies das ligas de alumínio e cobre foram examinadas por microscopia eletrônica de varrimento (SEM) após os ensaios mTCT para avaliar a eficácia dos tratamentos e o efeito da pressão transversal.

A terceira parte centra-se no desenvolvimento do componente central da bateria: o eletrólito estrutural. Em primeiro lugar, o polímero e o solvente mais compatíveis com a epóxi para alcançar um desempenho multifuncional foram identificados através do teste de diferentes polímeros. Assim, polímeros termoplásticos como o polietileno óxido (PEO), álcool polivinílico (PVA) e acetato de polivinilo (PVAc) foram misturados com resina epóxi termoendurecível utilizando diversos solventes. As propriedades de condutividade iônica, estabilidade térmica e propriedades mecânicas foram avaliadas com espectroscopia de impedância eletroquímica (PEIS), análise termogravimétrica (TGA) e análise mecânica dinâmica (DMA), respetivamente. Com base nestas avaliações, o PVA foi identificado como o termoplástico mais adequado para formar, em conjunto com a epóxi, uma matriz resistente ao calor. Em seguida, otimizou-se a quantidade de sal de lítio (LiTFSI) e de nanopartículas de alumina (Al_2O_3) para obter uma matriz polimérica compósita com desempenho multifuncional. Por fim, utilizando a formulação otimizada ($\text{PVA}_{0.34}/\text{epóxi}_{0.14}/\text{LiTFSI}_{0.32}/\text{Al}_2\text{O}_{30.2}$), foi fabricado um eletrólito estrutural reforçado com fibra de vidro entrelaçada e avaliado através de PEIS, DMA, TGA, ensaios de tração e testes de carga/descarga em células semi-completas e completas, a fim de avaliar o seu desempenho electroquímico e mecânico.

Finalmente, na quarta parte da tese, foi fabricada uma bateria estrutural completa com os componentes desenvolvidos anteriormente. A bateria apresenta um invólucro em GFRP com empilhamento quase isotrópico, ligado a coletores de corrente em alumínio e cobre tratados com sol-gel no lado do GFRP e revestidos com cátodo de LFP e ânodo de grafite do lado do eletrólito estrutural. A teoria clássica das lâminas foi utilizada para definir a melhor repetição do empilhamento do GFRP, garantindo à flexão fletora simétrica. O desempenho mecânico foi avaliado com ensaios de indentação quase-estática em ambos os lados da bateria e comparado com estruturas híbridas equivalentes e uma configuração apenas em GFRP. A tomografia computadorizada (CT) foi usada para caracterizar danos internos nas diferentes configurações testadas. O desempenho no armazenamento de energia foi avaliado através de PEIS e ciclos de carga-descarga, sendo comparado com configurações em célula tipo “coin” e com baterias estruturais de última geração. Por fim, foi avaliada a multifuncionalidade do sistema. Os resultados demonstraram que a bateria estrutural híbrida combina eficazmente capacidade de suporte mecânico com armazenamento de energia, evidenciando o seu potencial para aplicações leves e multifuncionais.

Palavras-chave: Baterias estruturais. Laminados híbridos. Tenacidade à fratura interlaminar. Eletrólitos poliméricos compósitos. Indentação quasi-estática. Carga/Descarga.

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*“A hundred times every day I remind myself that my inner and outer life are based on the labors
of other men, living and dead.”*

Albert Einstein

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Document notation

Abbreviations and Acronyms

EV	Electric vehicles
IEA	International Energy Agency
GFRP	Glass Fiber Reinforced Polymer
CFRP	Carbon Fiber Reinforced Polymer
VARI	Vacuum-Assisted Resin Infusion
UAV	Unmanned Aerial Vehicle
PAN	Polyacrylonitrile
LFP	LiFePO ₄
PANI	Polyaniline
SBE	Structural battery electrolyte
SPE	Solid polymer electrolytes
PEO	Polyethylene oxide
FML	Fiber Metal Laminates
CE	Coulombic Efficiency
OCV	Open Circuit Voltage
ICA	Incremental Capacity Analysis
DVA	Differential Voltage Analysis
DIC	Digital Image Correlation
ILSS	Interlaminar Shear Strength
SPM	Scanning probe microscope
DCB	Double Cantilever Beame
ENF	End Notched Flexure
mTCT	modified Transverse Crack Tension
ECT	Edge Crack Torsion
NVH	Noise and vibration harshness
LDV	Laser scanning Doppler vibrometry
DMA	Dynamic mechanical analysis
SEM	Scanning electron microscopy
FIB	Focused ion beam

NDT	Non-Destructive Testing
AE	Acoustic Emission
UT	Ultrasonic Testing
XCT	X-ray Computed Tomography
TEM	Transmission electron microscopy
AFM	Atomic force microscopy
SPM	Scanning probe microscopy
XCT	X-ray computed tomography
FT-IR	Fourier transform infrared spectroscopy
XRM	X-ray microscopy
XAS	X-ray absorption spectroscopy
HAADF-STEM	High-angle annular dark-field scanning transmission electron microscopy
ECT	Edge Crack Torsion
PE	Polyethylene
PVdF	Polyvinylidene fluoride
PVdF-HFP	Polyvinylidene fluoride-hexafluoropropylene
PMMA	Polymethyl methacrylate
PVC	Polyvinyl chloride
PVA	Polyvinyl alcohol
PVAc	Polyvinyl acetate
PAA	Polyacrylic acid
PAN	Polyacrylonitrile
PCL	Polycaprolactone
PC	Polycarbonate
PS	Polystyrene
T _g	Glass transition temperature
RT	Room temperature
PMS	Polymethyl methacrylate-co-styrene
PP	Polypropylene
ILs	Ionic liquids
CNTs	Carbon nanotubes
GO	Graphene oxide
NMP	N-Methyl-2-pyrrolidone
DMSO	Dimethyl sulfoxide
TGA	Thermogravimetric analyses
SPVA-Li	lithium sulfonated polyvinyl alcohol
LbL	layer-by-layer
VCCT	Virtual Crack Closure Technique
CSI	Coherence Scanning Interferometry
CAA	Chromic acid anodizing

PAA	Phosphoric acid anodizing
CLT	Classical Laminate Theory
MBT	Modified Beam Theory
CV	Coefficient of variation
OWRK-model	The Owens, Wendt, Rabel, and Kaelble method
TCT	Transverse Crack Tension
PVC	Polyvinyl Chloride
PVA	Polyvinyl Alcohol
PVAc	Polyvinyl Acetate
PEO	Polyethylene Oxide
PVdF	Polyvinylidene Fluoride
PMMA	Polymethyl Methacrylate
Chitosan	Chitosan
STA	Simultaneous Thermal Analysis
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis
PEIS	Potentiostatic Electrochemical Impedance Spectroscopy
DMA	Dynamic Mechanical Analysis
CCCV	Constant current–constant voltage
CTE	Coefficient of thermal expansion
GLARE	Glass Laminate Aluminum Reinforced Epoxy
QSI	Quasi-static indentation
CT	Computed tomography
DMSO	Dimethyl sulfoxide
LFP	Lithium iron phosphate
SEI	Solid electrolyte interphase
CE	Coulombic Efficiency

List of Symbols

T_g	Glass transition temperature
T_m	Melting points
E	Young's modulus
σ_u	Ultimate tensile strength
ν	Poisson's ratio
K_{IC}	Fracture toughness of polymers
σ	Ionic conductivity
M_w	Molecular weight
E	Young's modulus

E_1	Young's modulus in the longitudinal (fiber) direction
E_2	Young's modulus in the transverse and thickness direction
ν_{12}	Poisson's ratio of composite lamina
G_{12}	Shear modulus of composite lamina
ν	Poisson's ratio of isotropic materials (e.g. metal)
σ_y	Yield strength
h_m	Thicknesses of the metal
h_c	Thicknesses of the composite
E_x^f	Longitudinal flexural stiffness of the composite
A	Extensional stiffness matrix
B	Bending-extension coupling matrix
D	Bending stiffness matrix
N	In-plane force resultants
M	Bending moment resultants
A^*	Extensional compliance matrix
B^*	Bending-extension compliance matrix
D^*	Bending compliance matrix
ε^0	Mid-plane strain vector
$\bar{k}$	Mid-plane curvature vector
ε	General strain
G_I	Energy release rate for mode I (opening mode)
G_{II}	Energy release rate for mode II (sliding mode)
G_{III}	Energy release rate for mode III (tearing mode)
X_{Li}	Internal nodal force at crack-tip node in x-direction
Y_{Li}	Internal nodal force at crack-tip node in y-direction
Z_{Li}	Internal nodal force at crack-tip node in z-direction
u_{Li}	Displacement of top-face adjacent node Li in x-direction
v_{Li}	Displacement of top-face adjacent node Li in y-direction
w_{Li}	Displacement of top-face adjacent node Li in z-direction
u_{Li}^*	Displacement of bottom-face adjacent node Li^* in x-direction
v_{Li}^*	Displacement of bottom-face adjacent node Li^* in y-direction
w_{Li}^*	Displacement of bottom-face adjacent node Li^* in z-direction
Δa	Element size at the crack tip
b	Width of the specimen
F	Applied opening load
δ	Load-point vertical displacement
$ \Delta $	Effective crack length accounting for crack-tip rotations (in MBT)
σ_s	Surface free energy of metal surfaces
θ	Contact angle of the liquid droplet on the surface
σ_l	Surface tension of the liquid
σ_{sl}	Interfacial tension between liquid and solid
θ	Contact angle between liquid and solid
S_a	Surface roughness
A	Area of the sample for roughness test in the xy-plane
z	Height of each point of the sample in roughness test
G_{IC}	Critical interlaminar fracture toughness of mode I
α	Thermal expansion coefficient of isotropic material
α_1	Thermal expansion coefficient in the longitudinal direction

α_2	Thermal expansion coefficient in the transverse direction
σ_{33}	Applied compressive pressure
F_b	Axial load of each bolt
T_b	Torque applied to the bolt
n	Total number of bolts
l	Length of each rubber insert
D	Diameter of the bolt
κ	Torque coefficient
σ_∞	Far-field axial stress
P	Far-field axial load
h_t	Total thickness of the laminate
E_c	Young's modulus of the composite in the longitudinal direction
ϕ	Thickness fraction of the uncut plies relative to the total thickness
E_m	Young's modulus of the metal layer
α_m	Thermal expansion coefficient of the metal layer
h_m	Thickness of the metal layer
E_c	Longitudinal Young's modulus of the composite
α_c	Longitudinal thermal expansion coefficient of the composite
h_c	Thickness of the composite layer
a	Crack length
l	Total length of the considered segment of the mTCT specimen for derivation of the equation
W	Total external work
U	Total strain energy
j	Number of cracks in the laminate
σ_1	Axial stress in mTCT
E_{eq}	Equivalent Young's modulus of the hybrid beam
ϕ_m	Thickness fraction of the metal layer in mTCT
ϕ_c	Thickness fraction of the composite layer in mTCT
ΔT	Temperature difference between test and curing conditions
T_{test}	Testing temperature
T_{curing}	Curing temperature
α_{eq}	Equivalent thermal expansion coefficient of the hybrid beam
$\sigma_{T,m}$	Thermal stress in the metal
$\sigma_{T,c}$	Thermal stress in the composite
$\sigma_{M,m}$	Mechanical stress in the metal
$\sigma_{M,c}$	Mechanical stress in the composite
A	Contact area between the electrode and the thin film
t	Thickness of the thin film
R_b	Bulk resistance of the polymeric films
$\tan \delta$	Loss factor
E'	Storage modulus
E''	Loss modulus
l_e	Element size along the crack propagation direction (0.5 mm)
N_e	Number of elements within the cohesive zone
δ	Indentation displacement
δ_f	Indentation displacement at failure

d_1	Dent depth measured after the test
d_7	Dent depth measured seven days after the test
E_T	Total energy up to the maximum load
E_A	Absorbed energy up to the maximum load
m	Weight
V	Volume
F_f	Load at failure
$\bar{F}_f$	Load density at failure
$\bar{E}$	Tensile stiffness density
$\bar{E}_{SB}$	Energy density of the structural battery
$\bar{P}_{SB}$	Power density of the structural battery
$\bar{Q}_{Ch}$	Charge capacity density
$\bar{Q}_{Dch}$	Discharge capacity density
CE	Coulombic efficiency
η_s	Structural efficiency coefficient
η_b	Energy efficiency coefficient
η_{mf}	Multifunctional efficiency
$\bar{\sigma}$	Specific strength
$\bar{E}_e$	Energy density

Part I

Literature review and theoretical background

Chapter 1

Introduction to structural batteries

1.1 Definition and motivation

Sustainable development refers to meeting the needs of the present without compromising the ability of future generations to meet their own needs. It encompasses three main dimensions: economic, social, and environmental sustainability. Balancing these three pillars is essential for long-term global well-being ([Güney \(2019\)](#)). A critical component of sustainable development is addressing how we obtain and use energy. Energy powers nearly every aspect of modern life—from homes and transportation to industry and communication ([Sartori and Hestnes \(2007\)](#); [Clark \(1975\)](#)). The way we generate and consume energy has a profound impact on the environment, economy, and society. Therefore, rethinking our energy sources is essential for building a more sustainable future. Energy sources can be broadly classified into two categories: non-renewable and renewable ([Adedoyin et al. \(2020\)](#)). Non-renewable energy sources—such as coal, oil, and natural gas—are finite and cannot be replenished within a human timescale. These fossil fuels currently meet the majority of the world’s energy demand. However, their extraction and use have several downsides. They contribute significantly to greenhouse gas emissions, leading to climate change, air pollution, and environmental degradation. Additionally, reliance on these depleting resources raises concerns about energy security and economic volatility ([Rahman and Alam \(2022\)](#)). In contrast, renewable energy sources—including solar, wind, hydropower, biomass, and geothermal energy—are naturally replenished and have a minimal environmental footprint. These sources are clean, abundant, and sustainable over the long term. They help reduce carbon emissions, decrease dependence on fossil fuels, and promote energy security. Transitioning to renewable energy is therefore a key step toward achieving sustainable development. By shifting to cleaner, more sustainable sources of energy, societies can meet their current energy demands while safeguarding the planet for future generations ([Adams et al. \(2018\)](#); [Østergaard et al. \(2022\)](#)). Despite these advantages, renewable energy sources also face a major challenge—they depend on weather conditions, geographic location, and daily cycles. For example, solar panels generate electricity only when there is sufficient sunlight, and wind turbines are effective only when there’s enough wind. This inconsistency creates a mismatch between energy supply and demand. To

solve this problem, energy storage systems such as batteries are essential. They store extra energy produced during low-demand periods and release it when demand is high (Enasel and Dumitrascu (2025)). In addition, batteries are a key part of renewable-powered transportation, especially electric vehicles (EVs), which are crucial in the global effort to reduce carbon emissions (Biswas et al. (2022); Manzetti and Mariasiu (2015); Mohammadi and Saif (2023)). Tesla, a leading EV manufacturer, has achieved a high level of production automation in its battery pack technology. Table 1.1 provides information on various Tesla models, including battery pack weight, overall vehicle weight, as well as gravimetric and volumetric energy densities. Notably, in some models such as the Model 3 and Model Y, the battery pack accounts approximately for the 30% of the vehicle's total weight (Mohseni et al. (2023)).

Table 1.1: The specifications of the battery pack used in Tesla vehicles (Mohseni et al. (2023))

Specification	Model S and X	Model 3 and Y
Battery weight (kg)	480 kg	771 kg
Car weight (kg)	2061-2450	1800-2000 kg
Volumetric energy density (Wh/L)	675	689 Wh/L
Gravimetric energy density (Wh/kg)	250	300 Wh/kg

At the end of 2020, 10 million electric vehicles (EVs) were on the world's roads, marking a 41% increase in registrations, despite the global downturn in car sales caused by the COVID-19 pandemic. However, the risk of fire incidents has also grown alongside the rapid adoption of EVs (Zhu (2023)). As highlighted in the 2021 Global EV Outlook by the International Energy Agency (IEA), the number of electric vehicles on the road is expected to surge to 145 million by 2030 (Dioha et al. (2022)). This growth is anticipated to accelerate even further in the next decades. A critical question now arises: how can this large-scale transition to electric vehicles be ensured as both safe and efficient? Will the continued use of large, heavy, and potentially hazardous batteries remain the norm, or is a safer, more efficient alternative on the horizon? Structural batteries are innovative multifunctional devices that integrate energy storage directly into the vehicle's structure, allowing it to store energy and bear mechanical loads simultaneously (Liu et al. (2009); Kalnaus et al. (2021); Raju et al. (2025)). The ultimate goal is to integrate structural batteries into the vehicle structure instead of using bulky and heavy battery packs, which helps reduce overall vehicle weight, improve energy efficiency, and enhance safety by lowering the fire risks typically associated with traditional battery systems (Danzi et al. (2021b); Murugan et al. (2025); Siraj et al. (2023)). Therefore, structural batteries offer a promising solution to the challenges posed by the expanding EV market.

1.2 Types of structural batteries

In the last decade, three approaches have emerged for designing weightless and volume-saving structural batteries, broadly referred to as *embedded batteries*, *multi-functional materials*, and

combination of embedded batteries and multifunctional materials, as illustrated in Figure 1.1.

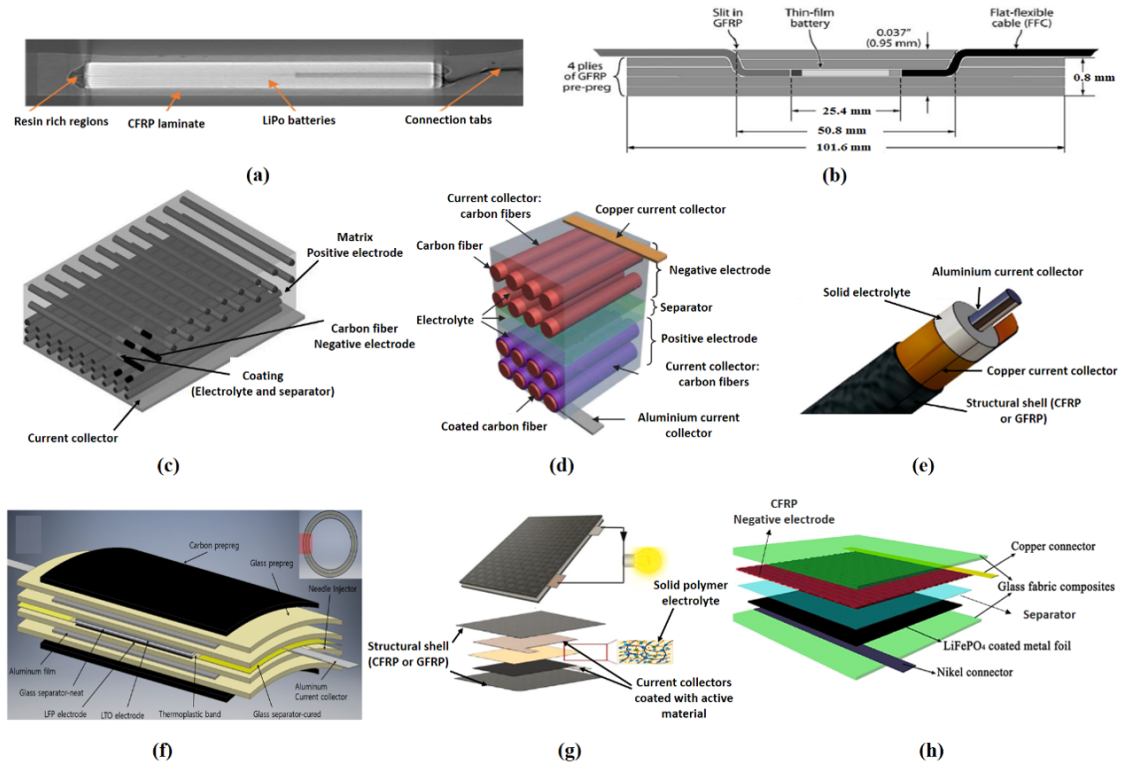


Figure 1.1: Different types of structural batteries: (a) LiPo-embedded structural batteries (Pattarakunnan et al. (2020)); (b) Thin-film lithium-ion batteries embedded in GFRP (Gasco and Feraboli (2014)); (c) Multifunctional materials with matrix cathode (Xu and Varna (2020)); (d) Multifunctional materials with coated carbon fiber cathode (Carlstedt et al. (2022)); (e) Coaxial laminate structural battery (Danzi et al. (2021a)); (f) Tubular laminate structural battery (Pyo et al. (2021)); (g) Flat-laminate structural battery with solid polymer electrolyte (Fu et al. (2022)); (h) Flat-laminate structural battery with carbon negative electrode (Zhao et al. (2020)).

1.2.1 Embedded structural batteries

In embedded batteries, the central part performs the electrochemical function, while the shell primarily handles mechanical loads. One type within this category of structural batteries involves integrating a commercially available lithium-ion battery into composite structures such as glass fiber-reinforced polymer (GFRP) or carbon fiber-reinforced polymer (CFRP) (see Figure 1.1 (a)). These embedded batteries typically consist of a sandwich or laminate configuration, with the central section containing lithium-ion batteries such as LiPo pouch cells or thin-film Li-ion batteries (Pattarakunnan et al. (2020)). In some studies, the integration between the battery and structural layers was enhanced by using interlocking rivets. For example, Ladpli et al. (Ladpli et al. (2019)) demonstrated that the rivet topology significantly improves mechanical properties such as bending stiffness and shear strength. However, it was also found to have a negative impact on the electrochemical performance. Thin-film lithium-ion batteries, with a thickness of approximately 0.15

mm, represent another category of lithium-ion batteries known for their high flexibility. They can be easily shaped into complex geometries and integrated into CFRP or GFRP laminates to create embedded batteries (see Figure 1.1 (b)). The thin-film batteries are embedded between composite layers without the need to cut the prepreg material or apply additional adhesive. However, some small splits may be necessary to accommodate connection tabs or wires. The composite laminates are fabricated using the Vacuum-Assisted Resin Infusion (VARI) method. In this design of embedded batteries (Figures 1.1 (a) and 1.1 (b)), the central part does not bear mechanical load and the composite structure itself does not contribute to electrochemical storage, thereby limiting the potential for weight savings. As a result, this design primarily optimizes volume rather than weight (Pattarakunnan et al. (2020)). Despite these limitations, this approach offers certain advantages. Most notably, commercial lithium-ion batteries have undergone significant improvements over the years: their electrochemical performance has been optimized, manufacturing costs reduced, and, since no modifications to battery components are required, the risk of compromising battery performance is minimal (Kalnaus et al. (2021)). Several studies have explored the application of this technique in systems such as spacecraft, underwater vehicles, and other platforms where weight reduction is critical (Kalnaus et al. (2021); Thomas et al. (2013); Pogue et al. (2008)). For example, a study conducted in 2002 demonstrated that embedding LiPo cells into the upper wing of an unmanned aerial vehicle (UAV) increased its flight endurance by approximately 26% (Pogue et al. (2008)). However, this type of embedded battery presents several critical drawbacks. First, since these batteries are not structurally load-bearing, their mass does not contribute to the mechanical integrity of the system. Second, the curing temperatures required for the composite materials and adhesives—typically above 100 °C—exceed the safe operating temperature range of lithium-ion batteries, which is generally below 60 °C. This thermal mismatch necessitates process modifications, such as pre-curing the composite prior to battery integration or employing resins with lower curing temperatures. Third, pouch-type lithium-ion batteries inherently exhibit low mechanical properties. Deformation of their active layers can result in mechanical failure, degradation of electrochemical performance, or in severe cases, short circuits and potential fire hazards (Danzi et al. (2021b)). Fourth, recent research indicates that embedding Li-ion batteries within composite laminates can degrade mechanical performance due to the inferior properties of the batteries compared to the removed composite material (Pattarakunnan et al. (2020, 2019)). In some cases, the integration process and the presence of the battery packaging can even initiate damage, such as delamination at the battery-composite shell interface (Attar et al. (2020)).

1.2.2 Multifunctional materials

In the second approach, known as “multi-functional materials,” the fibers and matrix of the composite not only act as the core components of the battery and perform electrochemical functions but also simultaneously carry mechanical loads (Chaudhary et al. (2024); Biswas et al. (2022); Bouton et al. (2024); Asp et al. (2019); Xu and Varna (2020)) (see Figures 1.1 (c) and 1.1 (d)). This approach relies on using multifunctional anodes, cathodes, and electrolytes that serve both electrochemical and mechanical roles. Recent studies highlight the high mechanical strength and

electrochemical performance of carbon fibers, making them promising candidates for use as anodes in structural batteries. Carbon fibers, due to their high theoretical capacity and mechanical strength, are well-suited for this application. The capacity of carbon fiber depends on the manufacturing process. Continuous carbon fibers are typically produced from either pitch or polyacrylonitrile (PAN) precursors (Wang et al. (2018b); Qin et al. (2012)). While pitch-based fibers have traditionally been used in battery manufacturing, research has shown that the disordered structure of PAN-based fibers is more favorable for lithium-ion intercalation. This makes PAN-based fibers suitable for applications where both strength and stiffness are critical, such as in structural composite batteries (Kjell et al. (2011); Jacques et al. (2013)). Experimental studies have demonstrated that carbon fibers with intermediate modulus and high capacity—such as IMS65 and T800—feature a disordered structure with nanocrystals. These nanocrystals provide additional sites for ion deposition, enhancing Li-ion intercalation and making these fibers strong candidates for anodes. In contrast, high-modulus, low-capacity fibers like M60J have a more ordered structure that limits intercalation, making them less suitable as anode materials (Hagberg et al. (2016); Jin et al. (2020)). Among the popular PAN-based carbon fiber grades—T300, T800, M40, M46, UTS50, IMS65, and UMS45—IMS65 stands out with the highest mechanical strength (6 GPa) and the highest capacity (360 mAhg^{-1}) (Kjell et al. (2011)). In structural batteries, the tensile strength of carbon fibers is influenced by the degree of lithiation during charging and cycling. A significant reduction in tensile strength—up to 40%—can occur during lithiation, and this strength loss is only partially reversible. This degradation has been attributed to a high concentration of defects introduced during cycling. Other interesting materials for structural battery anodes include carbon nanotube sheets, nanofoam sheets, and activated carbon-based fabrics (Jacques et al. (2014)). In contrast to the relatively high-studied multifunctional anodes, research into multifunctional cathode materials remains limited. While standard carbon fiber tows are used for anodes, cathode carbon fibers must be integrated with lithium oxide particles to facilitate effective electrochemical reactions. For instance, Bouton et al. coated carbon fibers with lithium oxide particles such as LiFePO_4 (LFP) to create a structural cathode. They identified an optimal carbonization temperature of approximately 450°C and reported a specific capacity of 100 mAhg^{-1} at C/10 (Bouton et al. (2019); Hagberg et al. (2018)). Another example of a multifunctional cathode involves the integration of conjugated polymers, such as polyaniline (PANI), with aramid nanofibers and carbon nanotubes. One study reported this composite achieving a theoretical capacity of 147 mAhg^{-1} , a Young's modulus of 4 GPa, and a tensile strength of 40 MPa (Flouda et al. (2020)). To fully harness the multifunctional potential of carbon fibers, they must be combined with a suitable matrix (electrolyte) that can bear mechanical loads and form a stable interface with other components, while also ensuring efficient lithium-ion transport. Although liquid electrolytes are widely used in lithium-ion batteries due to their high ionic conductivity, they have several drawbacks—such as their inability to bear mechanical loads, leakage issues, safety concerns, and the requirement for protective casings. These limitations have led researchers to investigate appropriate structural battery electrolytes (SBEs) for multifunctional systems (Ihrner et al. (2017)). To date, various strategies have been explored to develop effective SBEs. These include the use of solid poly-

mer electrolytes (SPEs) and particulate composites composed of polymers combined with ion-conducting ceramics or glass phases to achieve higher mechanical strength (Kalnaus et al. (2021); Tenhaeff and Kalnaus (2015)). Another approach involves creating structural electrolytes by embedding cross-linked polymers, such as polyethylene oxide (PEO), within woven glass fiber mats. Additionally, two-phase bicontinuous material systems—spongy polymer matrices filled with liquid electrolytes—have also been investigated (Gienger et al. (2015)).

Using multifunctional carbon fiber-based electrodes might also present some drawbacks. Hedayati et al. (Hedayati et al. (2025)) proposed a multiphysics modeling framework that sequentially couples the electrostatic and mechanical behaviors of structural supercapacitors made from carbon fiber-reinforced polymer electrolytes. They highlighted the critical influence of fiber spatial arrangement and volume fraction on both mechanical stiffness and electrochemical performance. As illustrated in Figure 1.2, increasing the number of fibers in the x -direction—where the added fibers are positioned farther from the separator—resulted in only a minimal improvement in capacitance. In contrast, increasing the number of fibers in the y -direction, thereby placing more fibers closer to the separator, led to a substantial increase in capacitance. Furthermore, they demonstrated that only about half of the carbon fiber surface area—the side facing the separator—significantly contributes to the electrochemical function, while the opposite side has a negligible effect on capacitance. From the electrochemical standpoint, because the distance between electrodes is critical, fibers closer to the separator—and thus nearer to the opposite electrode—contribute more substantially to electrochemical performance. This drawback of carbon fiber-based multifunctional materials motivated the selection of flat-type electrodes in this study due to their superior electrochemical characteristics.

1.2.3 Combination of multifunctional materials and embedded battery

Another type of structural battery is a combination of multifunctional materials and embedded batteries. This technique does not use commercial batteries; instead, the entire structural battery—including the battery-functioning components such as the cathode, electrolyte, anode, and current collectors—is manufactured using a step-by-step approach. All components are embedded into a structural shell made of GFRP or CFRP (Ladpli et al. (2019); Pattarakunanan et al. (2020); Ye et al. (2024)). Since some of the central components that provide electrochemical function also bear part of the mechanical load, they are considered multifunctional materials. In this approach, some researchers use carbon fiber (as the anode) or structural electrolyte as multifunctional materials, while on the other side employing a metallic foil coated with a cathode material like LFP, all enclosed within a fiber-reinforced polymer such as GFRP (Lawcock et al. (1997); Xu et al. (2022); Zhao et al. (2020)). In Figure 1.1 (h), carbon fiber is used as the negative electrode, serving both structural and electrochemical functions, and all components are embedded in a GFRP shell (Zhao et al. (2020)). As another example, in the structural batteries shown in Figures 1.1 (e) and 1.1 (g), the central parts perform electrochemical functions, while the solid-state electrolyte, in addition to its electrochemical role, also carries part of the mechanical load. The electrochemical components are embedded inside CFRP or GFRP (Danzi et al. (2021a); Fu et al. (2022)). This promising

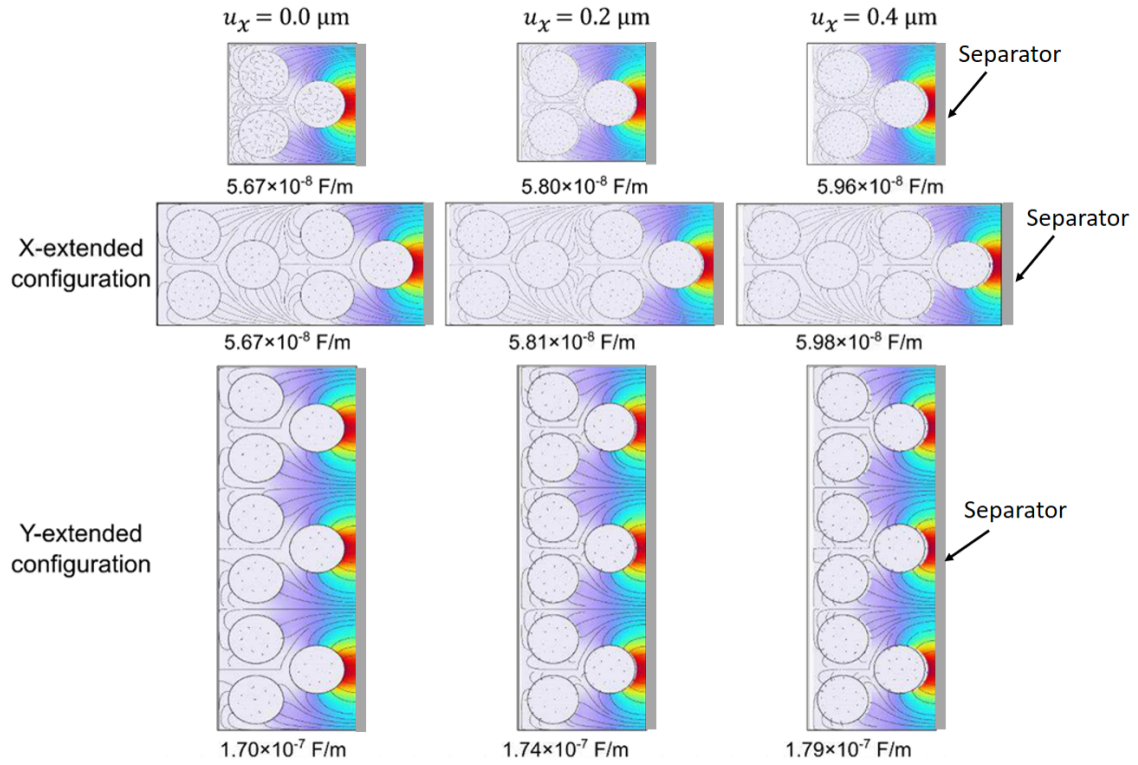


Figure 1.2: Impact of carbon fiber positioning relative to the separator on capacitance in structural supercapacitors (Hedayati et al. (2025)).

method allows all components to be fabricated together, enabling the structure to be manufactured in various forms and shapes, providing a smooth laminate. Several types of these structural batteries have already been developed, including coaxial laminated types (Figure 1.1 (e)), tubular laminated types (Figure 1.1 (f)), and flat laminated types (Figures 1.1 (g) and 1.1 (h)).

Chapter 2

Literature review on metrics and characterization techniques of structural batteries

To date, high-performance thermoset composite laminates have played a crucial role in enhancing the structural integrity and performance of vehicles in both the aerospace and automotive sectors. In aircraft such as the Boeing 787, Airbus A350, and Airbus A380, major components like the fuselage, the wing, and the tail assembly are primarily constructed from composites ([Krueger and Bergan \(2024\)](#)). Similarly, in the automotive sector, composites are extensively used in body panels ([Khan et al. \(2024\)](#)), chassis ([C. England et al. \(2010\)](#); [Ahamed and Natrayan \(2022\)](#)), suspension components ([Kuhn et al. \(2020\)](#)), interior parts ([Hoffmann et al. \(2021\)](#)), crash structures ([Godara and Nagar \(2020\)](#)), and wheels ([Dhas et al. \(2023\)](#)). Alternatively to the more traditional polymeric composites, fiber metal laminates (FMLs) become a popular hybrid structures made of metals, such as aluminum sheets, bonded to fiber-reinforced composites, like glass or carbon fiber. This combination offers a lightweight and tough material by merging the benefits of both ductile metals and high stiffness composites. GLARE, the most common FML in aerospace, is a combination of glass fiber and aluminum layers. It is used in the upper fuselage, as well as the wing and tail edges of the Airbus A380, due to its outstanding performance characteristics, including high strength-to-weight ratio, impact resistance, fatigue strength, and fire resistance ([Wu and Yang \(2005\)](#)). This configuration holds promise for the outer layers of structural batteries, as they usually require a metallic current collector, such as aluminum, and an insulating layer. Given the strength, fire resistance, and insulating properties of GFRP, combining it with metallic current collectors could create an effective shield for structural batteries ([Niazi et al. \(2024\)](#)). Composite structures have been designed to withstand various loads, including tensile, compressive, bending, fatigue, shear, and torsional stresses, due to aerodynamic forces, weight, and impacts ([Jerome \(2001\)](#)). Figure 2.1 shows the typical loads encountered by both airplanes and cars. Structural batteries must first have effective mechanical properties to withstand various external loads as well as internal stresses from expansion and contraction during charge and discharge cycles ([Larsson et al.](#)

(2023); McDowell et al. (2013, 2016); Zhang et al. (2021a); Jacques et al. (2013)). Additionally, they should offer competitive energy storage capabilities, including reasonable cycle life, power density, and energy density. Each of these aspects is evaluated through different tests and metrics which are thoroughly explained in the next sections. Although not discussed here, it is worth mentioning that other important metrics for structural batteries include the sustainability of materials, scalability, cost per kilowatt-hour (kWh), cost per unit weight/volume, manufacturing expenses, regulatory approval, and compliance with safety standards. Thermal management is also crucial for maintaining performance, extending cycle life, and ensuring safety. Several comprehensive review articles have thoroughly explored thermal management systems in conventional lithium-ion batteries (Zichen and Changqing (2021); Kim et al. (2019); Jiang et al. (2020a)), which can serve as guidance for structural batteries.

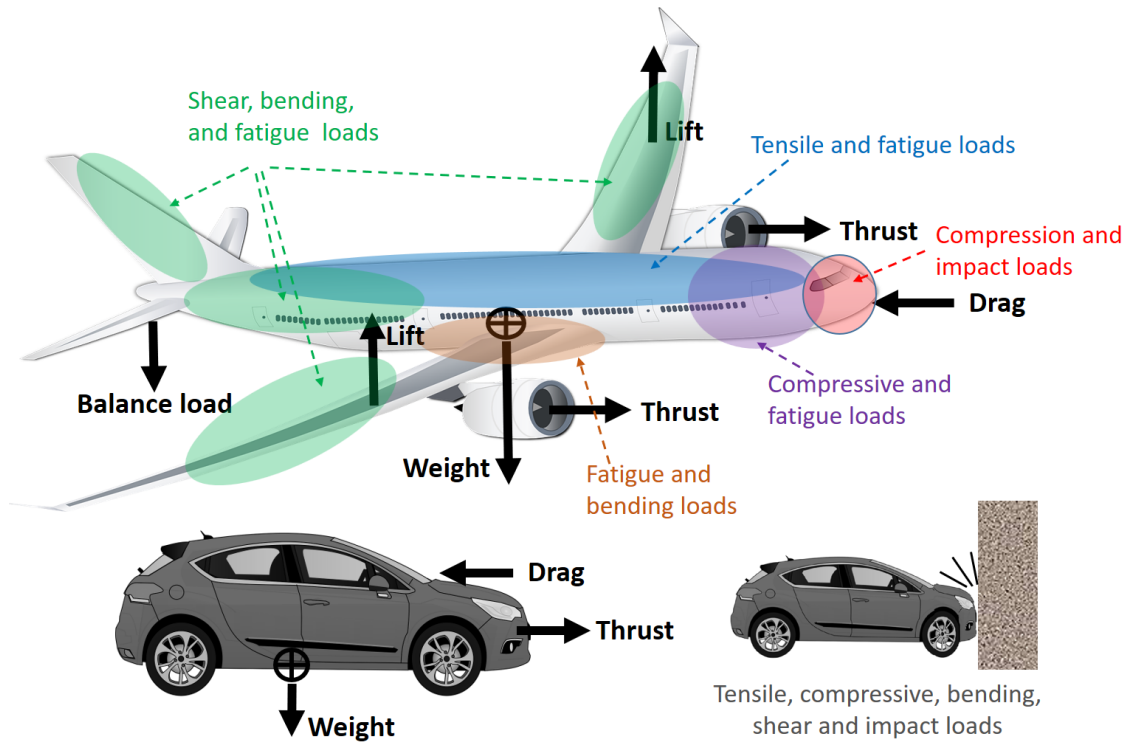


Figure 2.1: Schematic of loading on plane and car (Jerome (2001)).

The design of structural batteries requires a simultaneous evaluation of both mechanical performance and energy storage capability. The next section begins by focusing on energy storage metrics, reflecting the primary function of structural batteries. Subsequently, key design parameters for composite-based structural batteries will be discussed, addressing both electrochemical and mechanical aspects. Following this, a set of experimentally derived mechanical performance metrics will be introduced. Next, physical and chemical characterization techniques will be presented. The discussion will conclude with an overview of multifunctionality metrics.

2.1 Energy storage metrics

Modern lithium-ion batteries demonstrate remarkable energy storage capabilities, with energy densities reaching up to 250 Wh/kg and volumetric densities as high as 450 Wh/L in LiCoO₂/graphite cells. Power densities can peak at 3000 W/kg in lithium iron phosphate (LiFePO₄) (LFP)/graphite cells. Furthermore, lithium titanate (Li₄Ti₅O₁₂)-based batteries can achieve an exceptional cycle life of over 20,000 cycles (Thackeray et al. (2012); Barai et al. (2019)). These properties serve as key performance metrics and benchmarks for designing structural batteries. In addition to energy and power density, and cycle life, other critical factors such as fast-charging capability, capacity fade rate, Coulombic Efficiency (CE), and self-discharge rate are essential considerations in the development of structural batteries, which will be also discussed in the following subsections.

2.1.1 Energy Density

Energy density, measured in terms of energy per kilogram (gravimetric) or per unit volume (volumetric), is a critical metric for energy storage of structural batteries. When using structural batteries, not only is the traditional battery pack removed, but parts of the vehicle's structure, such as body panels, are replaced with multifunctional, lightweight components. Current state-of-the-art structural batteries have achieved energy densities of approximately 24 Wh/kg (Asp et al. (2021)). This structural battery design used T800Sc carbon fibers as both electrodes and current collectors, serving as a structural framework that hosts lithium-active materials. The battery was assembled by placing the components in a laminated film and sealing it under vacuum heat. Further improvements were demonstrated by Siraj et al. (2023), where a vacuum infusion technique was applied to manufacture similar structural batteries using T800Sc carbon fiber. By modifying the separator material, they achieved higher energy densities of 25.9 Wh/kg when using Whatman GF/A (thickness of 185 μm) as the separator, and 48 Wh/kg using a GF plain weave separator (thickness of 70 μm).

2.1.2 Power density, fast charging, and cycle life

To enhance mobile power sources, the battery must enable fast charging and deliver high power over a long cycle life. The development of fast-charging batteries is poised to revolutionize the electric vehicle (EV) industry. Tesla's battery packs can currently deliver a peak charging power of 120 kW at a voltage of 480 VDC. At this rate, it takes about 30 minutes to charge an EV for 300–400 km of driving, which is still slower compared to refueling a conventional internal combustion engine vehicle, which only takes around 5 minutes (Lu and Chen (2020)). Current state-of-the-art structural batteries, manufactured using a vacuum infusion technique with a 70 μm GF plain weave separator and T800Sc carbon fiber as the negative electrode, achieve a power density of approximately 12.4 W/kg (Siraj et al. (2023); Gray et al. (2024)). Evaluating fast-charging batteries involves considering three critical metrics simultaneously: (1) charge time, (2) specific energy gained, and (3) the number of cycles the battery can endure under fast charging

conditions. Additional critical metrics, such as lower internal resistance, higher ionic conductivity, and superior electrical conductivity, directly influence the fast-charging capabilities, power density, and cycle life of batteries. These factors are essential for minimizing energy loss in the form of heat and ensuring optimal battery performance. Ideally, a fast-charging battery should achieve 240 Wh/kg of energy after a 5-minute charge. This can be accomplished by charging a 300 Wh/kg battery to 80% State Of Charge (SOC). Additionally, this performance should be sustained over a lifetime of more than 2,000 cycles, with each cycle involving a fast charge (Wang et al. (2022a)). Conventional batteries, which rely on diffusion-limited redox reactions, typically experience slow charging times, often taking hours. Pseudocapacitive materials, however, combine the benefits of supercapacitors and batteries, offering the potential for high energy density along with high power density and fast charging (Choi et al. (2020)). For EV applications, it is crucial that batteries maintain at least 80% of their nominal capacity throughout their operational life. Most EV batteries are designed to last between 1,000 to 2,000 charge cycles, translating to approximately 12 to 16 years of use, depending on driving habits and environmental conditions (Lu and Chen (2020); Pesaran et al. (2023)). However, for aerospace applications, this lifespan is insufficient. Primary structural components in aircraft, such as wings and fuselage sections, are engineered to last the full operational lifetime of the aircraft—typically around 30 years—without replacement (EASA). Structural batteries for aerospace would not only need to retain their energy storage capabilities over decades but also meet stringent safety, durability, and load-bearing requirements, as they form integral parts of the aircraft's critical structures.

2.1.3 Capacity fade rate and Coulombic efficiency

Capacity fade rate refers to the gradual loss of a battery's capacity to store and deliver energy over time, typically measured as a percentage of capacity lost per cycle or per unit of time. Coulombic Efficiency (CE) is used to estimate the cycling life of the battery as it indicates the loss of Li^+ ions during each cycle. CE is the ratio of the discharge capacity to the charge capacity of a specific electrode within a cell. Since capacity is determined by the total charge flow to and from the electrode, and the batteries are typically limited by the cathode, CE can be expressed as the ratio of the number of Li^+ ions or electrons returning to the cathode to the number departing from it in a complete cycle (Xiao et al. (2020); Yao et al. (2021)). The equation for CE reads:

$$\begin{aligned}
 CE &= \frac{\text{Discharge capacity}}{\text{Charge capacity}} \\
 &= \frac{\text{Total number of } \text{Li}^+ \text{ ions back to cathode}}{\text{Total number of } \text{Li}^+ \text{ ions departing from cathode}} \\
 &= \frac{\text{Total number of } \text{e}^- \text{ back to cathode}}{\text{Total number of } \text{e}^- \text{ departing from cathode}}
 \end{aligned} \tag{2.1}$$

Commercial lithium-ion batteries exhibit very high Coulombic efficiency (CE), typically exceeding 99.9% under standard operating conditions, which implies capacity fade of only a few

percent over hundreds of cycles (Hobold et al. (2021)). Some state-of-the-art structural batteries demonstrate comparable CE values; for example, carbon-fiber-based structural lithium-ion batteries reported by Chaudhary et al. (2024) show CE values fluctuating around 100% during cycling.

2.1.4 Self-discharge rate

Self-discharge refers to the gradual loss of energy from a charged storage device without being connected to an external circuit. This phenomenon can result from various factors, including internal or external electron leakage, reactions between electrodes and electrolytes, partial dissolution of active materials, and electrode degradation. Two common methods for assessing self-discharge behavior are float current measurements and Open Circuit Voltage (OCV) measurements. In float current measurements, a small, constant current is applied to counteract the self-discharge and maintain a fully charged state. The variation in this current over time provides insights into the self-discharge mechanism. In contrast, the OCV method involves charging the device and then monitoring the change in its potential over time while it is in an open circuit state. To further explore self-discharge and degradation mechanisms, Incremental Capacity Analysis (ICA) and Differential Voltage Analysis (DVA) are often used. The review by Babu et al. (Babu (2024)) offers insights into these phenomena.

2.2 Design considerations

A wide range of design parameters influences the mechanical behavior of composite-based devices such as structural batteries. Examples of these parameters include fibers orientations, fiber volume fraction, number of layers, stacking sequence—which refers to how the orientation of fibers relative to loading direction change—the individual mechanical properties of fibers and matrix, the dimensions of each component, and the fracture toughness between fibers and matrix. These parameters greatly affect the device's response to external loading, deflection, and cycle life (Sihn et al. (2007); Nikbakt et al. (2018)). For instance, the orientation of fibers significantly influences the stiffness in composite materials. Usually there is a U-shaped relationship between Young's modulus and fiber orientation as shown in Figure 2.2 (a). The Young's modulus is at its maximum at a 0-degree orientation relative to the loading direction (representing E_1), reaches its minimum at a 45-degree orientation (corresponding to G_{12}), and experiences a slight increase at a 90-degree orientation, which reflects E_2 . In contrast, as shown in Figure 2.2 (b), a linear relationship exists between fiber volume fraction and Young's modulus, where an increase in fiber content leads to an increase in the stiffness of the composites (Wang et al. (2014a)).

Amacher et al. (Amacher et al. (2014)) conducted extensive experimental characterization to investigate the effect of the ply size on the mechanical properties of composite laminates. The thickness of the ply ranged from 30 μm to 250 μm . They found that thinner layers significantly enhance mechanical performance under various loading conditions. They delay or nearly suppress transverse cracking and delamination growth, particularly in hot and wet conditions. In addition, thinner plies improve fatigue life and ultimate strength. Under impact, the 30 μm thin-ply laminate

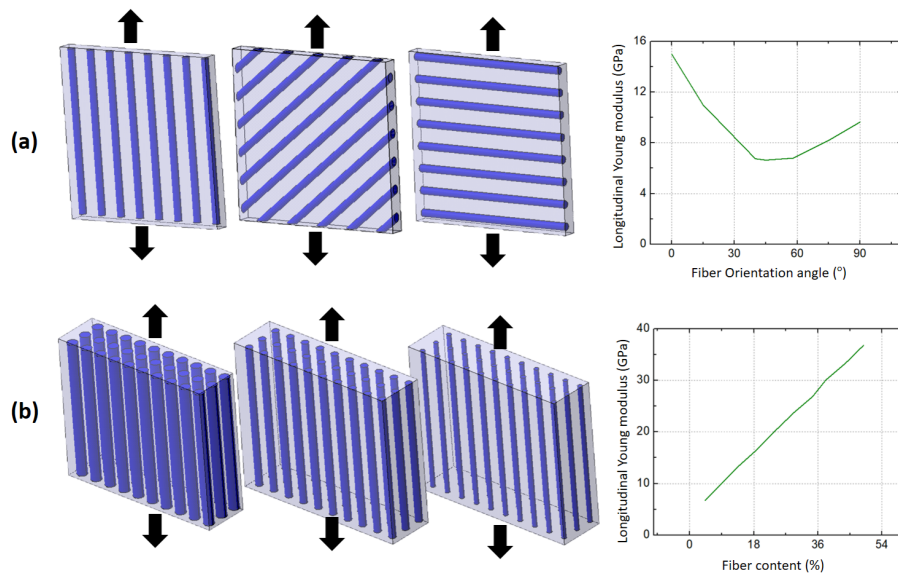


Figure 2.2: Effect of fiber orientation and fiber content on Young's modulus of composites (Wang et al. (2014a)): (a) Effect of fiber orientation; (b) Effect of fiber content.

exhibited quasi-brittle failure with extensive translaminal cracking, whereas a ply thickness of 100 μm was found to be optimal in minimizing the projected damage area. These considerations are crucial for the design of structural batteries, whether the fiber is used as an electrode or as part of the shell, since the propagation of cracks and delamination can compromise mechanical integrity and also degrade electrochemical performance.

2.3 Mechanical metrics

The review by Juner Zhu (Zhu (2023)) discusses various mechanical models and tests for conventional lithium-ion batteries. This section examines the range of tests and metrics, encompassing both the well-established methodologies discussed in the existing literature and the often overlooked but critical metrics necessary to advance structural batteries in aerospace and automotive applications. The total macro-mechanical tests of the structural batteries are shown in Figure 2.3.

Figure 2.4 illustrates several mechanical tests performed on the state-of-the-art structural batteries to evaluate their load-bearing performance. Figure 2.4(a) shows a tensile test on an embedded Li-ion battery, where Pattarakunnan et al. (2020) reported reductions in tensile modulus and strength due to the presence of rigid cells within carbon-fiber laminates. Figure 2.4(b) depicts a micro-tester used to apply tensile loads during electrochemical cycling, enabling analysis of the interaction between mechanical strain and lithium intercalation at the fiber scale (Jacques et al. (2012)). Figure 2.4(c) shows a compression test on battery-embedded laminates (Attar et al. (2020)), while Figure 2.4(d) presents a three-point bending test to assess flexural stiffness and strength (Danzi et al. (2021a)). Figure 2.4(e) demonstrates impact testing, which evaluates energy absorption, damage propagation, and residual electrochemical performance (Fu et al. (2022)). Finally, Figure 2.4(f) illustrates noise and vibration harshness (NVH) testing, used to measure

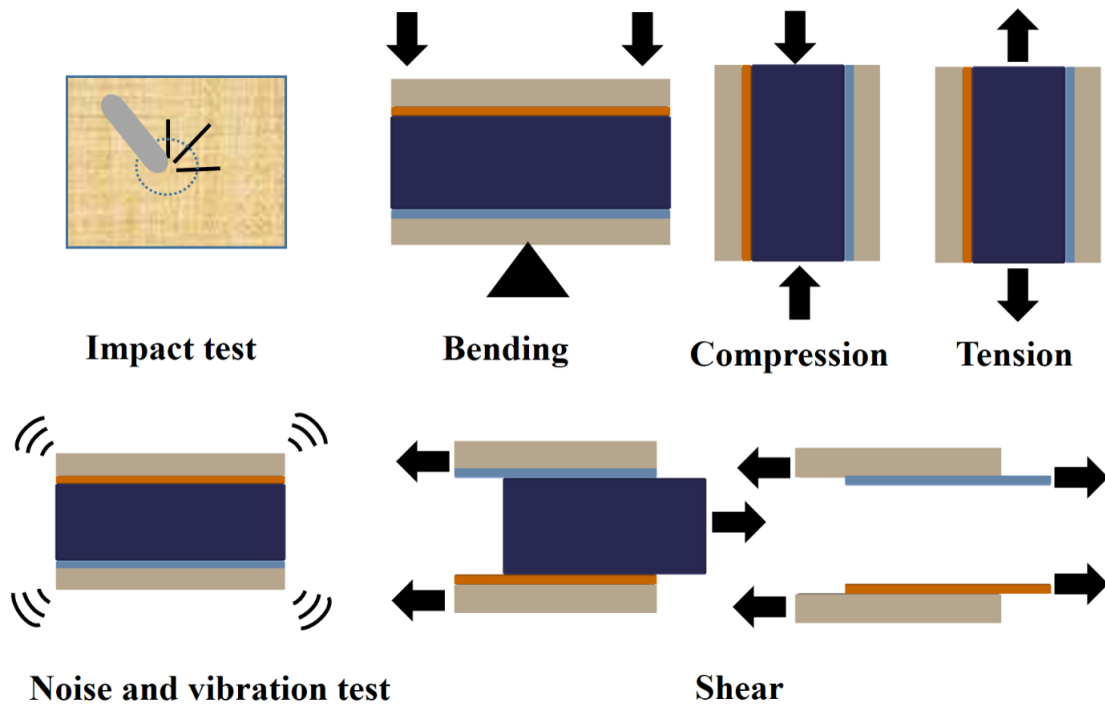


Figure 2.3: Macro-mechanical tests of structural batteries.

changes in modal frequencies and damping due to embedded batteries (Galos et al. (2019)). In the following subsections, all important mechanical tests for evaluating structural batteries are discussed, and the standard test methods for each are presented.

2.3.1 Tensile test

Tensile tests generate stress-strain diagrams that are used to determine properties such as yield strength, tensile strength, and stiffness of the structural battery. This single test also assesses the battery's ductility by measuring elongation at break, indicating how much the battery can stretch before breaking (Ashby et al. (2013)). Standards test method such as ASTM D638 and ISO 527 have provide guidance to perform tensile test in composite materials and have been guiding re-searchers to test structural batteries in tension (Pattarakunnan et al. (2020); Gunji et al. (2024); Jiang et al. (2023); Laurin et al. (2024)). ASTM D882 is a standardized test method designed for measuring the tensile properties of thin polymer films, including rectangular-shaped polymer electrolyte films. ASTM E345 is a test method used for tension testing of metallic foils, such as aluminum and copper current collectors. It is important to note that various types of premature failures can affect the test results of structural batteries when tested as a whole device. For example, delamination between layers—such as between the electrodes and the electrolyte, or between the electrodes, and current collectors—can impact the stress-strain results (Qi et al. (2024)). Another potential issue is the breakage or cracking in weaker layers, such as the electrodes (anode and cathode) or electrolyte, or the yielding of the current collector, particularly in pure metallic foils. These premature failures can lead to a reduction in stiffness and strength because the layers

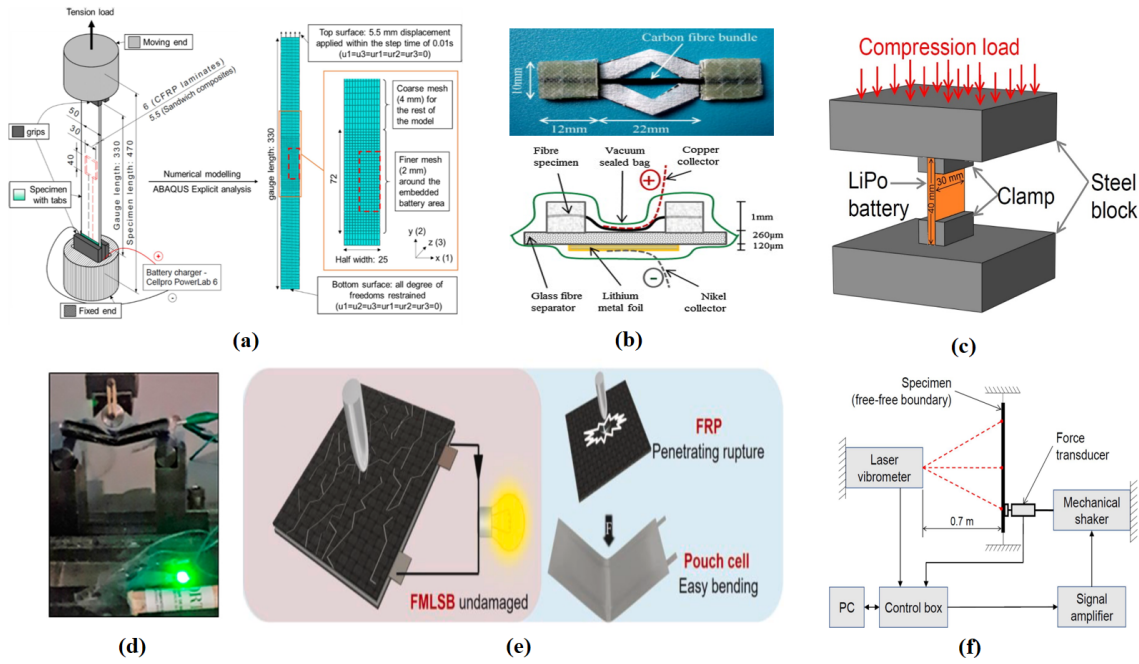


Figure 2.4: Mechanical tests on structural batteries: (a) Tensile test on an embedded battery ([Pat-tarakunnnan et al. \(2020\)](#)); (b) Schematic of a micro-tester used to measure tensile load during cycling ([Jacques et al. \(2012\)](#)); (c) Compression test ([Attar et al. \(2020\)](#)); (d) Three-point bending test ([Danzi et al. \(2021a\)](#)); (e) Impact test ([Fu et al. \(2022\)](#)); (f) Noise and vibration harshness (NVH) test ([Galos et al. \(2019\)](#)).

are no longer working together effectively ([Kashtalyan and Soutis \(2000\)](#); [Li et al. \(2023b\)](#)). The test can also be performed on a single component. For instance, Liu et al. conducted a tensile test on structural cathode ([Liu et al. \(2009\)](#)). Jacques et al. ([Jacques et al. \(2012\)](#)) used a micro tensile tester equipped with a 10 mm travel extensometer to measure the effect of electrochemical cycling on the tensile properties of carbon fibers used in structural lithium-ion composite batteries. They employed Micro-test software from Deben UK to acquire load, extension, and time data during tensile tests, carried out until specimen failure. The tensile load was measured both before and after cycling using the test set up shown in Figure 2.4 (b). Additionally, they used a modified microtester to in-situ measure the expansion percentage, which was calculated as the change in tensile load divided by the tensile stiffness of the carbon fiber ([Jacques et al. \(2013\)](#)). As a reference for structural batteries that could potentially be replaced with GLARE in aerospace applications, typical GLARE exhibits a minimum ultimate tensile strength of around 600 MPa, a yield strength of approximately 250 MPa, and a stiffness of about 50 GPa ([Wu and Yang \(2005\)](#)). Liu et al. ([Liu et al. \(2009\)](#)) designed a structural electrode using carbon nanofibers, achieving a tensile modulus of 0.5 GPa and a maximum tensile strength of 5 MPa before failure. When surface-modified carbon nanofibers were used, the tensile modulus increased to 0.65 GPa, and the strength improved to 12 MPa. The full battery incorporating these materials exhibited a tensile modulus of 3.1 GPa. Asp et al. ([Asp et al. \(2021\)](#)) developed a structural battery using T800Sc carbon fibers, which served as both the negative electrode and current collector. The positive side

was composed of LFP (LiFePO_4)-coated aluminum foil. The battery was assembled by vacuum-sealing layered components within a laminated film. This design achieved an elastic modulus of 25 GPa and a tensile strength exceeding 300 MPa. Guocheng Qi et al. (Qi et al. (2024)) used LFP coated on carbon fiber, a carbon fiber anode, and a structural electrolyte, achieving a Young's modulus of 31.6 GPa and a strength of 313 MPa for their structural battery.

2.3.2 Compression test

Compression test of structural batteries provides key properties such as compressive strength and compressive modulus. The compressive strength of structural batteries is typically evaluated using ASTM D7137 (Attar et al. (2020)). Testing solid state polymer electrolyte can be performed following ASTM standard D695 (Javaid and Ali (2018)). NASA's short block compression fixture, or anti-buckling guides, is typically used to prevent buckling during testing (Shalouf et al. (2014)). Buckling refers to sudden lateral failure of a structure under compressive stress, influenced by various composite parameters, including the aspect ratio of the laminate, boundary conditions, fiber orientation, and stacking sequence. Maximizing the critical buckling load is crucial to enhancing structural stability. Some review works, including (Nikbakt et al. (2018); Praveen A et al. (2018); Leissa (1987)), discuss various factors that affect the buckling and post-buckling behavior of composite laminates. These reviews also explore different methods to improve the critical buckling load, which could be valuable for composite-based structural batteries. For example, factors such as coupon's aspect ratio, fiber orientation, axial compression, thermal environment, and the presence of imperfections (e.g., delamination) significantly influence the buckling behavior of laminated composite shells (Praveen A et al. (2018); Khayal (2017)). Compression-compression fatigue tests are additional evaluations that can be performed on structural batteries to assess their fatigue behavior under compressive loading. During compression testing, digital image correlation (DIC) (Shalouf et al. (2014)) can be employed to monitor lateral strains and detect potential issues such as interface cracks, delamination, matrix cracking, or local buckling. The carbon fiber embedded with a LiPo battery, developed by Attar et al. (Attar et al. (2020)), achieved a compression modulus of 34 GPa and a compression strength of 166 MPa. In contrast, pure carbon fiber laminate showed superior properties, with a compression modulus of 41.5 GPa and a compression strength of 293 MPa.

2.3.3 Bending test

Bending stiffness measures the resistance of the laminate to bending and is influenced by the Young modulus of the material and the moment of inertia. The Three-Point Bending test and the Four-Point Bending test are commonly used for structural batteries to measure their flexural strength, stiffness, and failure mechanisms under bending loads (Thomas et al. (2019)). Standard test methods such as ASTM D7264, ASTM D790, and ISO 14125 are used to measure the bending properties of composite structural batteries (Adam et al. (2018); Petersen et al. (2022); Zhao et al. (2020); Mao et al. (2025); Dong and Chen (2023); Galos et al. (2020)). For sandwich beam

structural batteries, ASTM D7250 has been used to determine flexural stiffness and shear stiffness (for Testing and Materials (2006); Singh et al. (2015)).

2.3.4 In-plane shear test

Shear analysis of structural batteries is essential for evaluating their mechanical integrity and performance under shear loads. This test gives key properties such as shear strength and shear modulus which are critical for understanding the laminate's ability to resist shearing forces. Common methods for conducting these tests include the short beam shear test and the V-notched beam shear test. To evaluate the shear properties of polymer matrix composite materials and structural batteries, several standardized test methods can be employed, including ASTM D3518 (Javaid and Ali (2018); Snyder et al. (2015); Han et al. (2024); Qian et al. (2013)) and ASTM C273. Qi et al. (Qi et al. (2024)) fabricated a structural battery using a carbon fiber anode, a LiFePO_4 -loaded carbon fiber cathode, and a glass fiber separator, encapsulated with GF/Vinyl Ester prepreg. The battery exhibited an in-plane shear modulus of 392 MPa, a shear strength of 4 MPa, a tensile modulus of 31.6 GPa, and a tensile strength of 313.6 MPa. Javaid et al. (Javaid and Ali (2018)) developed a structural battery using resin infusion with a woven carbon fabric anode, a lithium cobalt oxide/graphene nanoplatelet cathode, an aluminum current collector, and a polymer electrolyte, achieving a shear strength of 0.75 GPa.

2.3.5 Impact and quasi-static indentation test

Impact tests and quasi-static indentation (QSI) are fundamental mechanical characterization techniques used to evaluate the damage tolerance and energy absorption capabilities of materials and structures, particularly under out-of-plane loads such as tool drops, maintenance mishandling, or localized stresses. Impact resistance refers to a structure's ability to absorb energy and resist fracture when subjected to sudden forces. The ASTM D7136/D7136M standard outlines a drop-weight impact test method commonly used to assess the damage resistance of fiber-reinforced polymer matrix composites (Fu et al. (2022)). Following impact testing, it is common to perform compression-after-impact (CAI) tests according to ASTM D7137 to measure the residual compressive strength of the specimen and evaluate its structural performance after damage at different impact energy levels (Wang et al. (2025a)).

QSI testing, involves applying a slow and controlled load to simulate and analyze damage mechanisms that occur sequentially during impact events. This method provides detailed insights into damage initiation and progression. It is standardized under ASTM D6264/D6264M for composite laminates and is widely used to evaluate their response to out-of-plane loading (Wagih et al. (2016a,b)). However, standardized QSI procedures for hybrid fiber-metal laminates are currently lacking, and to date, no QSI studies have been reported on complex multilayered systems such as structural batteries.

2.3.6 Interlaminar fracture toughness test

Structural batteries are composed of multiple layers made of different materials, each with distinct properties, such as the structural shell, metallic current collectors, electrodes, and electrolyte. Good bonding between these layers is crucial; otherwise, the elastic mismatch and differing thermal expansion coefficients between the layers and particles can lead to crack propagation under internal (due to charge/discharge) and external loading at various levels, including the nano, micro, and macro scales. This crack propagation can compromise both the structural integrity and electrochemical efficiency of the system (Niazi et al. (2024)). Therefore, similar to monolithic composite structures, the interfacial properties of structural batteries can be evaluated at three scales: 1) nano-scale, 2) micro-scale, and 3) macro-scale. Nano-scale measurements typically involve pulling out a single fiber using techniques such as nano-indentation technique (Zhang et al. (2015a); Gaitanelis et al. (2025)).

Micro-scale tests include fiber fragmentation, single fiber pull-out, and fiber push-out tests. At the macro-scale, methods like the short beam shear test (following ASTM D2344/ISO 14130) and fracture toughness tests such as Double Cantilever Beam (DCB) (following ASTM D5528/ISO 15024), End Notched Flexure (ENF) (following ASTM D7905/ISO 15114), and Mixed-Mode Bending (MMB) (following ASTM D6671 / D6671M) are used to measure the interlaminar fracture toughness (Huang et al. (2021); Prabhakar et al. (2026)). In the macro level, the interlaminar fracture toughness involves a combination of three fracture modes: opening mode (Mode I), shearing mode (Mode II), and tearing mode (Mode III). The DCB test is widely used to experimentally measure resistance to crack propagation in mode I—opening mode— loading. For Mode II interlaminar fracture toughness, the modified Transverse Crack Tension (mTCT) (Scalici et al. (2016)) and ENF using ASTM D7905/D7905M tests are extensively used. The Edge Crack Torsion (ECT) test is utilized to measure Mode III interlaminar fracture toughness (Ratcliffe (2004)). Various techniques can enhance mechanical or chemical adhesion between composites and metals in hybrid configurations, as well as between fibers and matrix materials in composites. Some of these methods may prove practical for use in structural batteries. For example, surface treatments like mechanical abrasion, chemical etching, plasma treatments, and anodizing increase surface roughness and introduce reactive sites that promote bonding (Niazi et al. (2024); Lin et al. (2020)). Coupling agents, such as silanes and Sol-Gel, can also chemically bridge dissimilar materials, improving adhesion (Niazi et al. (2024)). Additionally, primers and adhesives can strengthen bonding in certain applications (Lima et al. (2024)). Interfacial engineering techniques, such as fiber coatings, optimize load transfer at the interface (Xiong et al. (2021)). Micro/nano-structuring, including laser texturing, can increase surface area and enhance mechanical interlocking (Lambiase et al. (2023)). When choosing any of these treatments for structural batteries, careful selection based on their specific application and their effect on the electrochemical and mechanical performance of the battery is essential. For instance, some treatments may form oxide layers on metallic current collectors, which although they improve mechanical bonding between metal and the other side material, these oxides may also inhibit electron flow, making such treatments unsuitable for

interfaces between electrodes and current collectors. As another example, silanes, as well as certain primers and adhesives, might not be conducive to permit electrons flow. These methods might be practical in applications where electron flow should be inhibited, such as between the current collector and the structural shell (Niazi et al. (2024)). Jin et al. (Jin et al. (2021)) designed a tree-root-like lamination at the electrode/separator interface, which improved bonding and load transfer between different layers of the battery components. This design also allowed the cell to retain more 95% of its capacity for up to 500 cycles.

2.3.7 Noise and vibration test

Another challenge in structural batteries for vehicle design is to address noise and vibration harshness (NVH), with the primary goal of minimizing the acoustic noise and vibrations experienced by the occupants. Composites, especially sandwich structures, offer significant advantages in this area. They can be engineered to have superior vibration damping properties compared to steel and other conventional materials traditionally used in automobiles. In vehicle design, structural batteries must be engineered to match or surpass the vibration damping and noise reduction properties of traditional composites (Treviso et al. (2015); Li et al. (2022b)). The influence of embedding pouch cell lithium-ion batteries on the vibration and acoustic properties of carbon fiber laminates and sandwich panels were investigated by Galos et al. (Galos et al. (2019)). They used laser scanning Doppler vibrometry (LDV) which is presented in Figure 2.4 (f). They found that careful integration of LiPo within the structure is required to improve the vibration properties. The obtained results revealed that embedding batteries generally affect the damping ratio of the composite structures. If the battery is located at the vibrational nodal points, it can improve the vibration damping ratio. LiPo batteries also affected the acoustic properties of both the laminate and the sandwich. There are several standard test methods for noise and vibration testing of composite structures, which can be followed for structural batteries, in automotive applications. ASTM E756 is used to determine natural frequencies, damping factors, and mode shapes of these composite structures. For sound insulation properties, ASTM E90 can be followed, and ASTM D4728 can be used to evaluate how composite structures behave under random vibration conditions. ASTM D7028 is applicable for measuring the viscoelastic properties of composite materials, such as composite polymer electrolytes, through dynamic mechanical analysis (DMA). ISO 16750-3 is useful for assessing how the noise and vibration characteristics of composites change under varying environmental conditions, such as temperature and humidity. ASTM E756 can also be used to quantify the ability of composite materials to absorb and dissipate vibrational energy. Additionally, ISO 10534-2 is a test method used to determine how well a composite structure absorbs sound energy and contributes to noise reduction within a cabin.

2.4 Physical and chemical characterization techniques

The electrochemical performance of batteries, is significantly influenced by the interactions among various components, including the cathode, anode, and electrolyte (Johansen et al. (2023)). Sev-

eral reviews have discussed the characterization techniques employed in conventional batteries (Lu et al. (2017); Li et al. (2021); Zhao et al. (2018); Li et al. (2020); Shadike et al. (2018); Guo et al. (2023); Xiang et al. (2020)). These reviews explain various *ex situ*, *in-situ*, and *operando* characterization methods applicable to different types of batteries, including lithium-ion and sodium-ion batteries (Boebinger et al. (2020)). While many of these approaches are applicable to structural batteries—given the similarities in electrochemical active materials—this section will provide additional insights specifically tailored to the unique requirements of structural batteries.

For example, *in-situ* sensors and actuators have been integrated into structural batteries to continuously monitor the battery's state of charge (SoC) and its overall health (Ladpli et al. (2016)). For porous structures, traditional 2D scanning electron microscopy (SEM) imaging is often insufficient. Instead, a combination of focused ion beam and scanning electron microscopy (FIB-SEM) provides high-resolution 3D data (Duan et al. (2023)). Structural batteries, when subjected to external or internal loads, such as those caused by charge and discharge cycles, are vulnerable to several failure modes. Similar to composite laminates, these failure modes may include matrix (electrolyte) cracking, fiber breakage, delamination, and fiber-matrix shear failure (Xu and Varna (2020)). To evaluate these failure mechanisms, a combination of mechanical and Non-Destructive Testing (NDT) methods are needed. ASTM E2533 provides a practical guide for applying NDT methods to composite materials and structures in aerospace applications. Based on literature, Acoustic Emission (AE) (Samborski et al. (2024)), Ultrasonic Testing (UT) (Jodhani et al. (2023)), and thermography (Zhang et al. (2024); Chwał et al. (2024)) are commonly used to detect matrix cracking, while *in-situ* tensile testing with X-ray Computed Tomography (XCT) offers valuable insights into fiber characterization (Wang et al. (2024a); Jeon et al. (2014)). Delamination can be identified using non-destructive ultrasonic testing and hammer tap tests (Loganathan et al. (2018)).

SEM and transmission electron microscopy (TEM) can be used for observing morphology and microstructure (Liu et al. (2023a)). Atomic force microscopy (AFM) is effective for studying surface topography and interfacial properties at the nanoscale (Huang et al. (2021)). Scanning probe microscopy (SPM) techniques are also useful for analyzing fiber-electrolyte matrix interactions and for detecting defects such as voids, cracks, or delaminations within the composite structure (Farokh Payam and Passian (2023)). Additionally, techniques like X-ray computed tomography (XCT), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), X-ray microscopy (XRM), X-ray absorption spectroscopy (XAS), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) can be used to provide chemical composition, atomic bonding, and high-resolution mapping of composite structures.

2.5 Multi-functionality metrics

2.5.1 Multi-functionality efficiency

The structural efficiency coefficient (η_s) is calculated as the ratio of the specific strength (σ) or specific stiffness (E) of the structural batteries to that of conventional composite materials (Snyder

et al. (2015); Asp and Greenhalgh (2014)):

$$\eta_s = \frac{\bar{\sigma}_{SB}}{\bar{\sigma}_{Composite}} \quad \text{or} \quad \eta_s = \frac{\bar{E}_{SB}}{\bar{E}_{Composite}} \quad (2.2)$$

Similarly, the energy efficiency coefficient (η_b) is calculated as the ratio of the energy density ($\bar{E}$) or power density ($\bar{P}$) of the structural batteries to that of conventional batteries:

$$\eta_b = \frac{\bar{E}_{SB}}{\bar{E}_{Battery}} \quad \text{or} \quad \eta_b = \frac{\bar{P}_{SB}}{\bar{P}_{Battery}} \quad (2.3)$$

The multifunctional efficiency (η_{mf}) is defined as:

$$\eta_{mf} = \eta_s + \eta_b \quad (2.4)$$

For the system to be multifunctional, the multifunctional efficiency must satisfy the condition:

$$\eta_{mf} > 1 \quad (2.5)$$

2.5.2 Weight saving

The total mass of a system with an energy storage component (m_{tot}) is the sum of the structural mass (m_s) and battery pack mass (m_b), adjusted by a multifunctionality factor (Kalnaus et al. (2021)).

$$m_{tot} = m_s + (1 - \eta_s) \times \frac{m_b}{\eta_b} \quad (2.6)$$

The weight saving percentage is calculated as follows:

$$\text{Weight saving (\%)} = (\eta_s + \eta_b - 1) \frac{m_{mf}}{(m_s + m_b)} \times 100 \quad (2.7)$$

$$m_{mf} = \min\left(\frac{m_b}{\eta_b}, \frac{m_s}{\eta_s}\right) \quad (2.8)$$

Chapter 3

Literature review on electrolytes for structural batteries

3.1 Overview of electrolyte types

In structural batteries, a suitable electrolyte is needed that can bear mechanical loads and form a stable interface with other components, while also ensuring efficient lithium-ion transport. The mechanical properties of the electrolyte is particularly important, as it help accommodate internal stresses caused by volumetric changes during charge and discharge cycles (Luo et al. (2016); Jia et al. (2019); Yu et al. (2017); Dong et al. (2023)). Although liquid electrolytes are widely used in lithium-ion batteries due to their high ionic conductivity, they have several drawbacks—such as their inability to bear mechanical loads, leakage issues, dendrite formation, safety concerns, and the requirement for protective casings. These limitations have led researchers to investigate appropriate electrolytes for multifunctional systems such as structural batteries (Ihrner et al. (2017)).

To date, various methods have been explored to develop suitable electrolytes for structural batteries, with a major focus on solid-state electrolytes. Solid-state electrolytes can be categorized as inorganic (such as crystalline, glass, or glass-ceramic), organic (such as polymers), or composites of inorganic and organic materials (Lv et al. (2019); Goodenough and Braga (2018); Cheng et al. (2021)). Inorganic electrolytes exhibit high ionic conductivity; however, challenges such as poor interfacial contact, fragility, and hygroscopicity affect their application (Meesala et al. (2017)). On the other hand, organic electrolytes provide good interfacial contact but have low ionic conductivity. One way to overcome these challenges is by designing composite solid-state electrolytes, such as composite polymer electrolytes (CPEs), which combine the advantages of two-phase or multiphase components (Lv et al. (2019)). These consist of polymers combined with ion-conducting ceramic or glass phases (Kalnaus et al. (2021); Tenhaeff and Kalnaus (2015)).

Two-phase bicontinuous material systems—consisting of spongy polymer matrices infused with liquid electrolytes—have also been investigated in the context of structural batteries to combine the high ionic conductivity of liquid electrolytes with the mechanical integrity provided by the solid polymer framework (Gienger et al. (2015); Schneider et al. (2019)). In this concept, the

polymer sponge forms a continuous load-bearing network, while the interconnected liquid phase enables efficient ion transport throughout the structure. Building on this approach, Asp and co-workers demonstrated that such bicontinuous architectures can achieve a favorable balance between electrochemical performance and mechanical stiffness, making them promising candidates for multifunctional energy-storing composite materials (Larsson, Carl and Larsson, Fredrik and Xu, Johanna and Runesson, Kenneth and Asp, Leif E (2025); Austin (2022)).

Another promising approach is reinforcing the polymer electrolyte or composite polymer electrolyte with the glass fiber, which not only provides higher and more uniform mechanical properties but also retains the electrochemical advantages of composite polymer electrolytes. In the following state-of-the-art sections, the types of polymers used in composite polymer electrolytes, their thermo-electro-mechanical properties, the effects of different additives, the trade-offs between mechanical properties and ionic conductivity, and their manufacturing techniques are discussed. Additionally, current manufacturing techniques along with their advantages and limitations are discussed. Eventually, it highlights strategies to overcome the mechanical–ionic conductivity trade-off, including the use of self-healing networks, functional fillers, and engineered architectures.

3.2 Multifunctionality of composite polymer electrolytes

3.2.1 Overview of polymer types

Composite polymer electrolytes are promising in the context of structural batteries because they can facilitate efficient ionic conductivity through good interfacial contact and chemical stability with electrodes, while also providing sufficient mechanical strength to endure internal and external stresses (Fu et al. (2024a); Zhang et al. (2023a)). However, a trade-off often exists between their mechanical robustness and electrochemical performance, making it essential to carefully balance these properties for optimized multifunctionality (Snyder et al. (2007); Silva et al. (2024)). CPEs primarily consist of a polymer matrix integrated with ionic conductors, such as salts and ionic liquids, as well as organic or inorganic nano-fillers and other additives. The polymer serves as the fundamental component, providing structural integrity and facilitating efficient ion conduction (Goodenough and Braga (2018); Cheng et al. (2021)). Polymers have diverse applications, including in supercapacitors (Yan et al. (2023); Shekh et al. (2024)), fuel cells (Wang et al. (2025b)), dye-sensitized solar cells (Bella et al. (2014)), rechargeable batteries (Yee et al. (2022)), electrochemical sensors (Bagherzadeh et al. (2022)), analogue memory devices (Ling et al. (2007)), and electrochromic windows (Lim et al. (2023)). Polymers are classified into three main groups: thermoplastics, thermosets, and elastomers. Thermoplastics melt when heated and are divided into two subgroups: amorphous and semi-crystalline. Amorphous polymers remain disordered upon solidifying, while semi-crystalline thermoplastics have both crystalline and amorphous phases, held together by secondary forces (Oseli et al. (2020); Boyer (1968)). Various thermoplastic polymers are used in battery electrolytes, including polyethylene oxide (PEO) (Li et al. (2019)), polyethylene

(PE) (Sherazi et al. (2008)), polyvinylidene fluoride (PVdF) (Ma et al. (2022a)), polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) (He et al. (2023)), polymethyl methacrylate (PMMA) (Balakrishnan et al. (2023)), polyvinyl chloride (PVC) (Guo et al. (2024)), polyvinyl alcohol (PVA) (Liao et al. (2015)), polyvinyl acetate (PVAc) (Song et al. (2024)), polyacrylic acid (PAA) (Wang et al. (2022b)), polyacrylonitrile (PAN) (Hu et al. (2024a)), polycaprolactone (PCL) (Bharti et al. (2021)), polycarbonate (PC) (Chen et al. (2021a)), polystyrene (PS) (Chen and Hong (2001)), and chitosan (Zhang et al. (2021b)), among others. Thermosets have very low ionic conductivity due to extensive cross-linking and restricted polymer chain mobility. This limitation makes them unsuitable as the primary host for electrolytes, despite their favorable thermomechanical properties. However, blending thermosets with thermoplastics presents a promising approach for creating polymer electrolytes that leverage the advantages of both types of polymers (Yao et al. (2019); Sequeira and Santos (2010); Niazi et al. (2026)). Elastomers, characterized by their low degree of cross-linking and high stretchability, are particularly well-suited for use in flexible and wearable energy storage devices (Oseli et al. (2020); Fu et al. (2024b)).

3.2.2 Thermo-electro-mechanical properties of polymers

Thermoplastic polymers are frequently used in composite polymer electrolytes due to their high ionic conductivity (Reinoso and Frechero (2022)). These polymers become more ductile and deformable at elevated temperatures as intermolecular forces weaken. As the temperature decreases, they transition from a ductile to a glassy state, a change defined by the glass transition temperature (T_g), which varies depending on the polymer type, structure, crystallinity, and composition. Table 3.1 lists the T_g , melting points (T_m), mechanical properties—including Young's modulus (E), tensile strength (σ_u), Poisson's ratio (ν), and fracture toughness (K_{IC})—of some thermoplastic polymers.

3.2.2.1 Effect of molecular weight

In the late 20th century, significant advancements were made in understanding how polymer molecular weight influences their mechanical and thermal properties (Nunes et al. (1982); Martin et al. (1972); Smith et al. (1982); Bersted and Anderson (1990); Beevers and White (1960); Flory (1945); Termonia et al. (1985)). Literature consistently demonstrates that polymer stiffness increases with higher molecular weight, while crystallinity generally decreases. Strength tends to rise with increasing molecular weight until it reaches a threshold, after which it stabilizes (Fatou and Mandelkern (1965); Martin et al. (1972)). Elongation typically increases with higher molecular weight. Figure 3.1 illustrates the relationships between mechanical and thermal properties and the molecular weight of several thermoplastic polymers. Specifically, Figure 3.1 (a) shows the relationship between Young's modulus and molecular weight for PEO, indicating that Young's modulus increases from 30 MPa to 650 MPa as molecular weight rises from 3,000 g/mol to 1,500,000 g/mol (Jee et al. (2013)). Figure 3.1 (b) depicts the tensile strength of PS, which exhibits a linear relationship with molecular weight up to 160,000 g/mol before stabilizing (Martin et al. (1972)).

Table 3.1: Thermal and mechanical properties of thermoplastic polymers.

Polymer	T_g (°C)	T_m (°C)	E (GPa)	σ_u (MPa)	ν	K_{IC} (MPa·m ^{0.5})
PEO (Li et al. (2024a); Jee et al. (2013))	-64	65	0.03–0.6	–	–	–
PVdF (Li et al. (2024a); Saghafi et al. (2020); Ren et al. (2017))	-40	171	1.8–3	30–50	0.4	–
PVdF-HFP (Li et al. (2024a); Gradišar Centa et al. (2022); Peng et al. (2019))	-90	135	2	31	–	–
PMMA (Li et al. (2024a); Kim et al. (1988); Seitz (1993); Mizutani (1987))	105	–	1.6–3.2	49–90	0.35–0.37	1.7
PVC (Seitz (1993); Fang et al. (2014); Major and Lang (2003))	85	160–190	2.6	48	0.38	1–7.5
PVA (Sharma et al. (2015); Gupta et al. (2009))	62.4	184–212	4.4	77.4	–	–
PVAc (Vrsaljko et al. (2008); Hess (2011))	35	120	0.28	–	–	–
PAA (Ounifi et al. (2021); Ofem et al. (2021))	44.5	147.2	2.42	58.15	–	–
PAN (Li et al. (2024a); Tang et al. (2021))	125	317	–	–	–	–
PCL (Bassi et al. (2011); Carmona et al. (2015); França et al. (2016))	-60	58	0.238	13.7	–	–
PC (Seitz (1993); Kim et al. (1988))	150	–	2.3	62	0.38–0.4	3
PS (Seitz (1993); Kim et al. (1988); Vrsaljko et al. (2008))	100	240	2.8–3.3	52–76	0.35	2.2
Chitosan (Dresvyanina et al. (2018); Lazaridou and Biliaderis (2002))	140–150	–	1.6	100	–	–

Figure 3.1 (c) demonstrates that crystallinity in polyethylene decreases with increasing molecular weight at both room temperature (RT) and 130 °C, showing a similar trend at both temperatures (Fatou and Mandelkern (1965)). Figure 3.1 (d) illustrates the direct linear increase in elongation of PVC with higher molecular weight (Nunes et al. (1982)). Regarding thermal properties, both T_g and T_m of polymers typically increase with molecular weight until reaching a threshold, after which these properties stabilize (Daniels and Collins (1979); Beevers and White (1960); Novikov and Rössler (2013)). Figures 3.1 (e) and 3.1(f) show that the T_g and T_m of PVC and polypropylene (PP) rise with molecular weight up to approximately 10,000 g/mol, after which they stabilize. This trend is also observed for polymethyl methacrylate-co-styrene (PMS) and PS, continuing up to a molecular weight of 100,000 g/mol, and for PEO, up to 8,000 g/mol (Daniels and Collins (1979); Jee et al. (2013); Beevers and White (1960); Novikov and Rössler (2013)).

3.2.2.2 Effect of temperature

The mechanical properties of thermoplastic polymers are significantly influenced by temperature. As temperature increases, molecular movement also increases, allowing molecules to reposition within the constraints of neighboring molecules and the material structure. This phenomenon, known as segmental mobility, results in volume expansion (Carraher Jr (2017)). The expansion creates additional space for molecular motion, which accelerates time-dependent behaviors such as creep and relaxation under external loads (Krempl and Khan (2003)). Rapid cooling can hinder

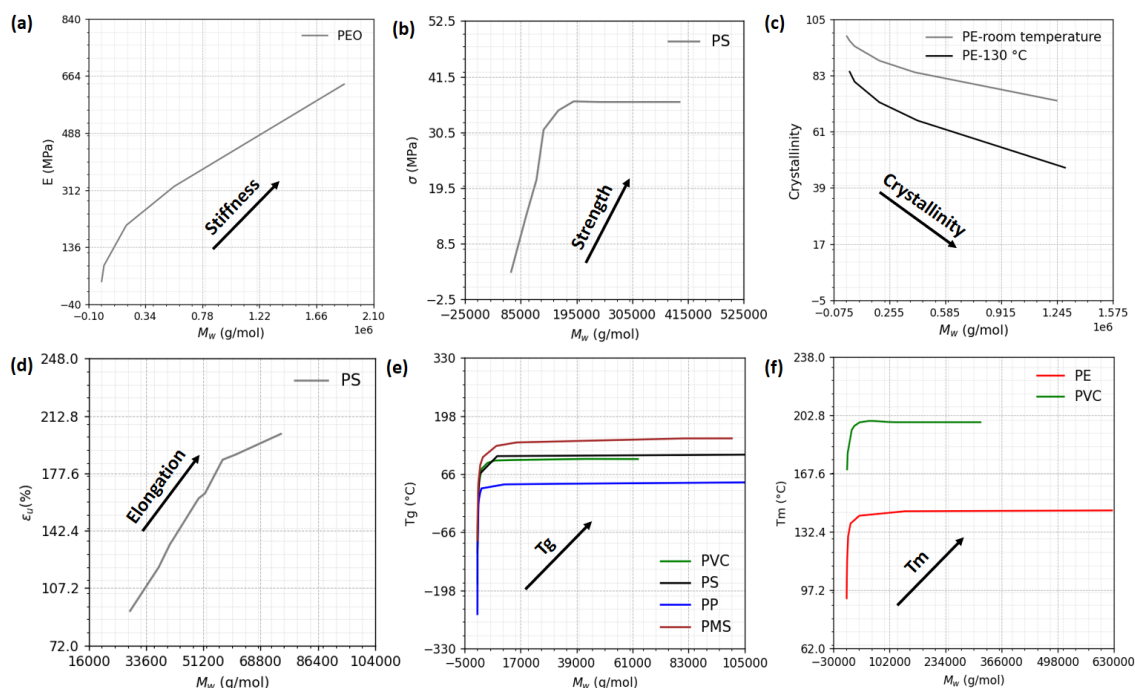


Figure 3.1: Effect of molecular weight on mechanical and thermal properties of thermoplastic polymers: (a) Young's modulus (E) of PEO (after [Jee et al. \(2013\)](#)); (b) Tensile strength (σ_u) of PS (after [Martin et al. \(1972\)](#)); (c) Crystallinity of polyethylene (PE) (after [Fatou and Mandelkern \(1965\)](#)); (d) Ultimate elongation (ϵ_u) of PVC (after [Nunes et al. \(1982\)](#)); (e) Glass transition of several polymers (after [Novikov and Rössler \(2013\)](#); [Beevers and White \(1960\)](#); [Daniels and Collins \(1979\)](#)); (f) Melting point of PE and PVC (after [Godovsky et al. \(1972\)](#); [Daniels and Collins \(1979\)](#)).

adequate molecular adjustments, leading to internal stresses and aging. Consequently, products made from these polymers may deform or develop cracks over time, even in the absence of external forces ([Struik \(1977\)](#); [Dean et al. \(1998\)](#)). Figure 3.2 illustrates the relationship between temperature and the mechanical properties of various thermoplastic polymers. In Figure 3.2 (a), the Young's modulus of PMMA shows a nearly linear decrease with increasing temperature, reflecting the softening phase of thermoplastic polymers in response to temperature variations ([Cheng et al. \(1990\)](#)). Figure 3.2 (b) depicts the degree of crystallinity of polyethylene at different molecular weights versus temperature, indicating that crystallinity decreases with increasing temperature for the same molecular weight. Furthermore, polymers with higher molecular weights exhibit lower crystallinity compared to those with lower molecular weights, as discussed in subsection 3.2.2.1. Figure 3.2 (c) shows the Poisson's ratio for PVC and PC, which increases with temperature up to the melting point, with a notable jump at the melting point ([Seitz \(1993\)](#)). Finally, Figure 3.2 (d) illustrates the fracture toughness of PMMA as a function of temperature, revealing that fracture toughness initially increases with rising temperature, peaks near the glass transition temperature, and then gradually decreases with further increases ([Mizutani \(1987\)](#); [Kim et al. \(1988\)](#)).

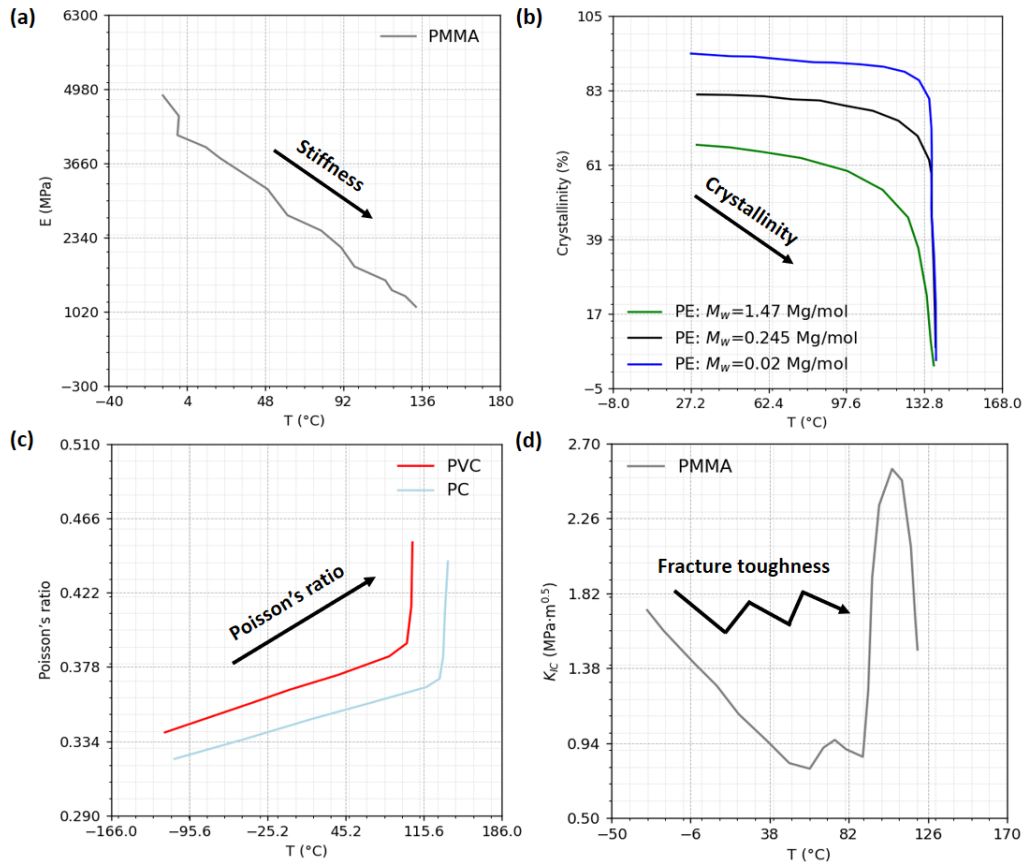


Figure 3.2: Effect of temperature on mechanical properties of thermoplastic polymers: (a) Young's modulus of PMMA (loading rate of 220 N.s⁻¹) (after [Cheng et al. \(1990\)](#)); (b) Crystallinity of Polyethylene (after [Fatou and Mandelkern \(1965\)](#)); (c) Poisson's ratio of PVC and PC (after [Seitz \(1993\)](#)); (d) Fracture toughness of PMMA (loading rate of 2.2 N.s⁻¹) (after [Mizutani \(1987\)](#)).

3.2.2.3 The time-dependent behavior of polymers

Unlike metals and ceramics, thermoplastic polymers exhibit both solid-like behavior (reversible) and fluid-like behavior (irreversible). This unique duality arises from their unbounded morphological structure ([Oseli et al. \(2020\)](#); [Landel and Nielsen \(1993\)](#)). These polymers undergo time-dependent changes in response to constant external loads, classifying them as viscoelastic or time-dependent materials ([O'dowd and Knauss \(1995\)](#)). Generally, higher strain rates result in increased stiffness and greater resistance to deformation. At faster strain rates, polymer chains have less time to rearrange, leading to a stiffer response. Additionally, the shorter duration of stress application hinders permanent deformation, requiring higher stress levels for plastic deformation to occur ([Şerban et al. \(2013\)](#)). Qin et al. ([Qin et al. \(2023\)](#)) conducted uniaxial tensile tests on PEO film, varying temperatures from 20 °C to 40 °C and strain rates from 0.001 s⁻¹ to 0.01 s⁻¹, to explore the viscoelastic-plastic characteristics of the PEO polymer. Figures 3.3 (a) and 3.3 (b) illustrate the effects of strain rate and temperature on the mechanical properties of the samples. As the strain rate increases, both Young's modulus and yield strength rise. Conversely, higher temperatures lead to decreases in both Young's modulus and yield strength of PEO. An empirical study by Teymoory

et al. (Teymoory et al. (2025)) investigated polymer composites with lithium salt and conductive fillers, and quantified complex viscosity and storage/loss modulus over temperature and frequency. Their results showed that salt addition tended to lower viscosity by enhancing chain mobility, while fillers (especially in networks) sharply increased viscosity and viscoelastic response, particularly at low frequencies. In another study, Rasul et al. (Rasul et al. (2022)) investigated PVdF-HFP composite polymer electrolytes incorporating aligned boron nitride (BN) nanosheets, fabricated via direct ink writing. They demonstrated that the addition and alignment of BN nanosheets enhanced mechanical strength, structural integrity, and rheological performance, providing empirical insights into the viscoelastic behavior of these composites. Specifically, the BN nanosheets restricted polymer chain mobility and formed aligned networks during printing, which increased the storage modulus, improved elasticity, and slowed stress relaxation under load. These effects collectively indicate that filler content and processing can modulate creep, stress relaxation, and overall viscoelasticity, which are critical for the performance and safety of lithium-metal batteries.

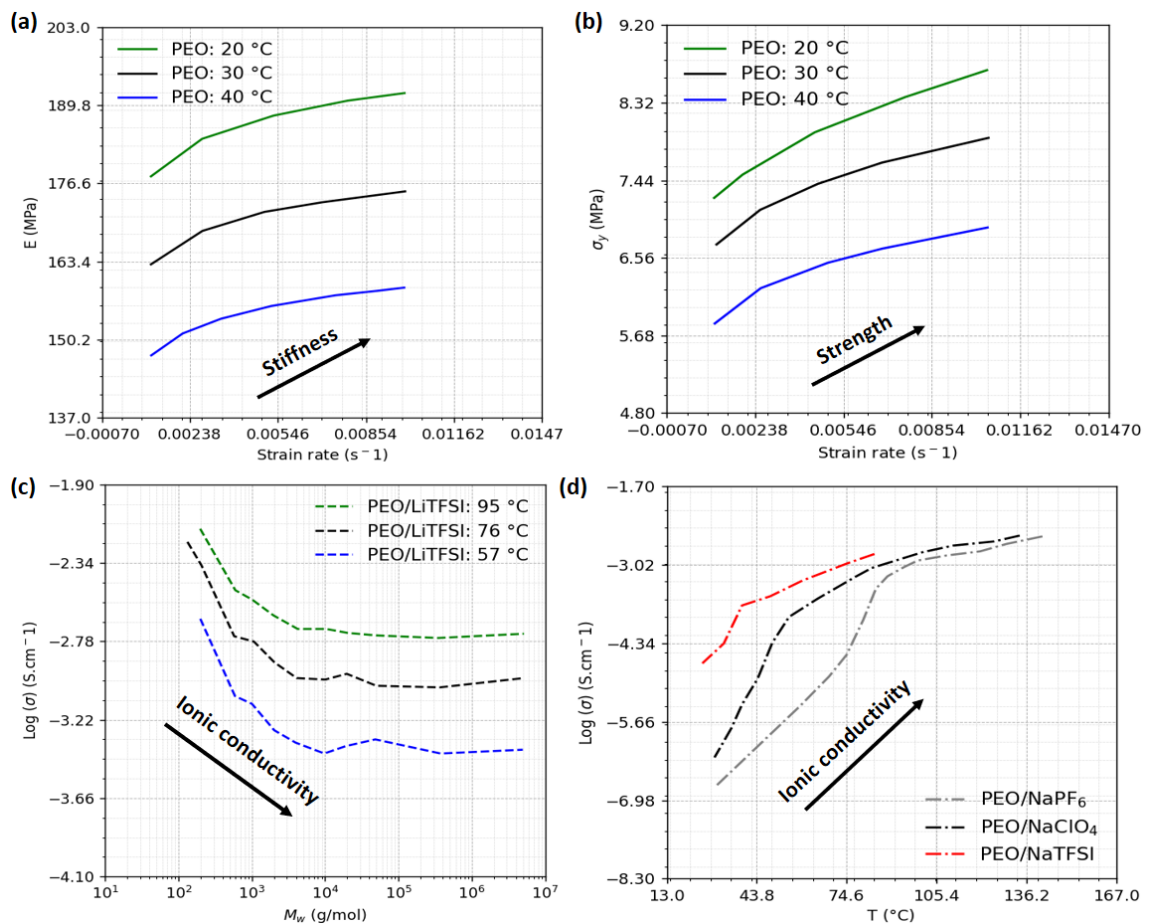


Figure 3.3: (a) Strain rate-dependence of Young's modulus of PEO film (after Qin et al. (2023)); (b) Strain rate-dependence of Yield strength of PEO film (after Qin et al. (2023)); (c) Effect of the molecular weight of PEO on the ionic conductivity of PEO/LiTFSI electrolytes (after Teran et al. (2011)); (d) Temperature dependence of ionic conductivity in different PEO/sodium salt electrolytes (after Wang et al. (2019)).

To characterize the time-dependent mechanical behavior of polymers, a wide range of experimental rheological techniques and constitutive models are available. Linear viscoelastic properties are commonly measured using dynamic mechanical analysis (DMA), stress–relaxation and creep–recovery tests, and small-amplitude oscillatory shear (SAOS). These measurements are often combined with time–temperature superposition to generate relaxation spectra (Ricarte and Shanbhag (2024)). On the modeling side, classical viscoelastic models such as the Maxwell, Kelvin–Voigt, and standard linear solid models are frequently used for qualitative discussions (Sclarsky et al. (2016)). More recently, fractional-order extensions of these models (e.g., fractional Zener or fractional Maxwell formulations) have been shown to fit polymer and epoxy relaxation data with fewer parameters and to provide improved extrapolation beyond the fitted window (Alves (2025)). Beyond these purely mechanical approaches, more physics-based continuum models have been proposed to capture the coupled behavior of functional polymers. For instance, Mohrle et al. (Mohrle, Daniel O and Schammer, Max and Becker-Steinberger, Katharina and Horstmann, Birger and Latz, Arnulf) treated the polymer as a highly elastic backbone, incorporating time-dependent viscous relaxation through a dissipation potential, enabling the prediction of creep, stress relaxation, and swelling induced by ionic transport in a thermodynamically consistent manner. Fractional viscoelastic models provide a powerful framework for describing the time-dependent mechanical behavior of complex soft materials. Bonfanti et al. (Bonfanti et al. (2020)) reviewed how fractional calculus can capture broad distributions of relaxation times, producing power-law stress relaxation and creep responses commonly observed in heterogeneous polymer systems. While their work did not focus specifically on composite polymer electrolytes, the framework is particularly relevant for such materials, where the presence of fillers and salts can introduce multi-scale interactions and non-exponential relaxation processes. Applying fractional viscoelastic models to CPEs could therefore help predict stress relaxation, creep, and overall time-dependent mechanical performance, complementing the experimental rheological studies described above.

3.2.2.4 Ionic conductivity in polymer electrolytes

Before incorporating additives, the polymer host of the electrolyte must effectively dissolve salts and form polymer-salt complexes. It should also exhibit chemical and electrochemical stability to maintain the electrolyte's integrity while providing adequate physical support for the structural integrity of the composite electrolyte (Zhang et al. (2017); Li et al. (2024a)). Polymer electrolytes form complexes through reactions between alkali metal salts and active groups of polar or Lewis acid-base sites present in the polymer host, such as C=O , C-O- , P- , N- , S- , and $\text{C}\equiv\text{N}$ (Li et al. (2023c)). These reactions occur thermodynamically only when the Gibbs energy of salt solvation in the polymer exceeds the lattice energy of the corresponding salt. Effective solvation requires a high concentration of polar groups on the polymer chain, moderate cohesive energy, and high flexibility (i.e., a lower glass transition temperature) of the polymer host (Aziz et al. (2018)). Polymer electrolytes exhibit ionic conduction through a combination of localized motion within polymer segments and the exchange of ions via hopping between coordinating sites. These

processes occur both within and between polymer chains and can vary with time and temperature (Wang et al. (2021)). Ionic conduction is heavily dependent on polymer chain mobility, which is influenced by T_g . Below T_g , polymer chains become rigid and immobile, resulting in nearly zero ionic conductivity in amorphous polymers. However, above T_g , local polymer chain motion becomes liquid-like and rapid, facilitating ionic conductivity. Notably, only the amorphous phase of polymers undergoes the glass transition, since the crystalline regions are already solid and ordered. Above the T_g and below the T_m , the amorphous phase becomes rubbery while the crystalline regions remain solid. Upon reaching the melting temperature, the crystalline regions also melt, and the polymer becomes a viscous melt (Li et al. (2023c)). While traditional literature suggests that segmental motion does not occur in crystalline structures, recent evidence challenges this view. Studies indicate that crystalline complexes can form cylindrical tunnels, which may exhibit superior ionic conductivity compared to amorphous structures (Li et al. (2023c)).

The molecular weight of polymers significantly affects their ionic conductivity; higher molecular weights generally lead to increased chain entanglement and reduced segmental mobility, delaying ion transport through the polymer matrix. According to the work of Shi and Vincent (Shi and Vincent (1993)), there is a correlation between ionic conductivity (σ) and molecular weight, as shown in Eq. (3.1):

$$\sigma = \sigma_0 + \frac{K}{M_w} \quad (3.1)$$

Here, σ_0 is the transport related to segmental motion, while the $\frac{K}{M_w}$ term represents transport involving coupled polymer chains and coordinated ions. The inverse relationship in the second term $\left(\frac{1}{M_w}\right)$ illustrates the heightened friction encountered by diffusing polymer chains as molecular weight increases, according to the Rouse model (Zimm (1956)). The constant K represents the impact of molecular weight on ionic conductivity, with higher K values indicating higher sensitivity to changes in molecular weight. Figure 3.3 (c) shows the ionic conductivity of PEO/LiTFSI blends across different molecular weights of PEO at three temperatures: 57 °C, 76 °C, and 95 °C, highlighting an inverse correlation with molecular weight (Ruiz et al. (2012)). Figure 3.3 (d) illustrates a direct correlation between temperature and the ionic conductivity of PEO incorporated with different sodium salts, indicating that ionic conductivity increases with rising temperature for all compositions (Noor et al. (2017); Wang et al. (2019)).

3.2.3 Effect of different additives

A diverse array of additives, including ionic conductors (e.g., salts and ionic liquids), nanofillers, and thermoset polymers (e.g., epoxy), are integrated into CPE formulations to enhance their electrochemical and mechanical properties. The effectiveness of these additives is influenced by factors such as size, porosity, concentration, surface area, and their interaction with the polymer host (Ngai et al. (2016); Chen et al. (2004)). The following subsections discuss their impact on the mechanical and electrochemical properties of CPEs.

3.2.3.1 Effect of salts

In lithium-ion batteries, various salts such as LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 , LiCF_3SO_3 , and LiTFSI are commonly used in polymer electrolytes (Li et al. (2023c); Hu et al. (2024b)). Salts with larger anions typically exhibit better solubility and dissociation in the polymer matrix, which increases the release of free Li cations and enhances ionic conductivity. Among these, LiTFSI stands out for its particularly promising properties in polymer electrolytes (Li et al. (2023c)). The intrinsic stability of salts, both alone and in combination with the polymer, is crucial for the overall stability of composite polymer electrolytes. Long Hu et al. (Hu et al. (2024b)) review the decomposition temperatures of various salts, examining their behavior in the presence and absence of polymers. Regarding the relationship between salt concentration and ionic conductivity, increasing salt levels generally enhance conductivity by improving ion mobility. However, this trend often plateaus at a certain concentration, beyond which additional salt may lead to reduced conductivity. This decline can result from factors such as ion-ion interactions, polymer-salt interactions, and phase separation (Konwar et al. (2021); Ravikumar et al. (2018); Arya and Sharma (2018); Du et al. (2012)). Figure 3.4 (a) illustrates the relationship between ionic conductivity and the amount of LiBF_4 in PVdF-HFP/ LiBF_4 electrolytes. The results show that ionic conductivity increases with salt content up to 30 wt%, after which it declines (Ataollahi et al. (2012)). Another study identified 8 wt% LiBF_4 as the optimal concentration for PVA-PMMA/ LiBF_4 electrolytes (Rajendran et al. (2003)). Figure 3.4 (b) illustrates the homogeneous phase at this optimal concentration and potential phase separation when salt concentration exceeds this level in polymer electrolytes. While blending salt with polymers enhances ionic conductivity in composite polymer electrolytes (CPEs), it compromises mechanical properties, reducing stiffness, deformability, and tensile strength. Figures 3.4 (c) and 3.4 (d) present findings by Qin et al. (Qin et al. (2023)) on the viscoelastic-plastic characteristics of PEO/ LiTFSI electrolytes at various LiTFSI concentrations, measured at 30 °C and strain rates from 0.001 to 0.01 s^{-1} . The results indicate that salt addition degrades mechanical properties; as salt concentration increases from a 1:20 to a 1:16 ratio, both Young's modulus and yield strength significantly decrease due to the plasticizing effect of LiTFSI . The authors note that LiTFSI reduces the crystallinity, melting temperature, and enthalpy of PEO polymers.

3.2.3.2 Effect of ionic liquids

The incorporation of ionic liquids (ILs) into composite polymer electrolytes significantly affects their ionic conductivity and mechanical properties. Low to moderate IL concentrations enhance ionic conductivity by improving ion mobility and reducing polymer crystallinity through a plasticizing effect (Tang et al. (2016)). However, when IL concentrations exceed an optimal level, ionic conductivity can decline due to phase separation (Chaurasia et al. (2011); Ramesh et al. (2011)). Mechanically, ILs lower Young's modulus and yield strength while increasing deformability. Therefore, optimizing IL content is essential for balancing electrochemical performance and mechanical properties. Andrew et al. (Westover et al. (2014)) examined the effect of EMIBF₄

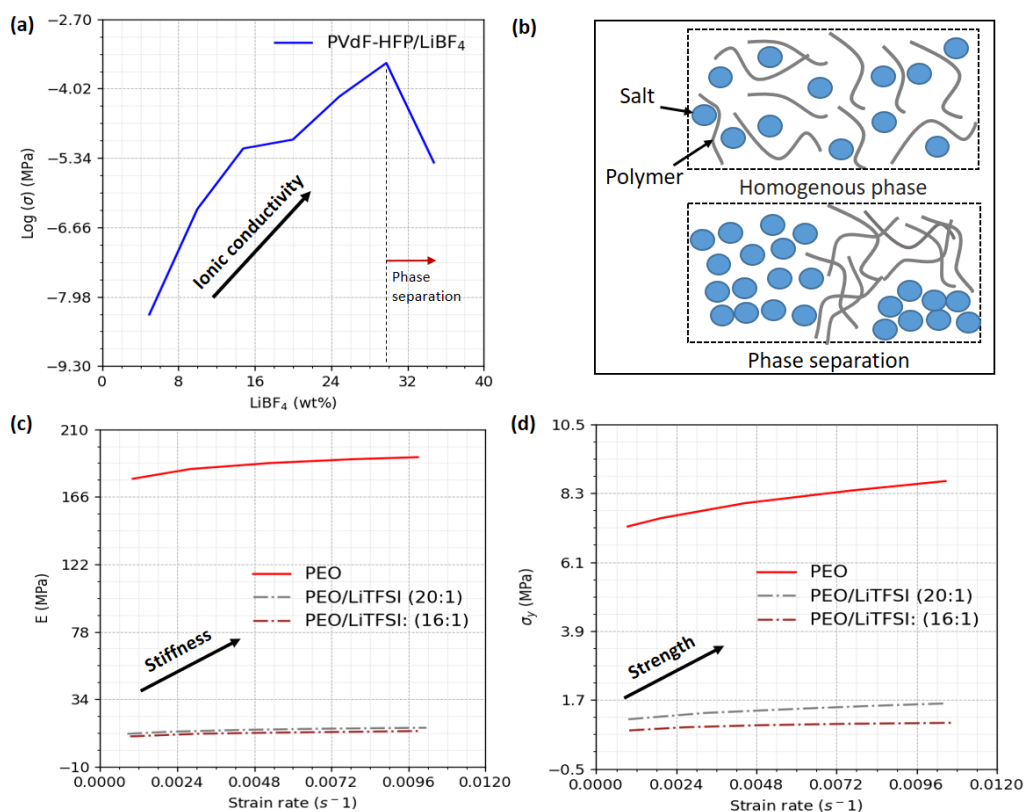


Figure 3.4: Effect of salt on composite polymer electrolytes: (a) Effect of concentration of LiBF_4 salt on the ionic conductivity of PVdF-HFP electrolyte (after [Ataollahi et al. \(2012\)](#)); (b) Schematic of homogeneous phase and phase separation in polymer electrolytes; (c) Young's modulus vs. strain rate of PEO/LiTFSI film with different concentrations of LiTFSI salt (after [Qin et al. \(2023\)](#)); (d) Yield strength vs. strain rate of PEO/LiTFSI film with different concentrations of LiTFSI salt (after [Qin et al. \(2023\)](#)).

ionic liquid concentration on the mechanical and electrochemical properties of PEO thin films, as illustrated in Figure 3.5. In Figure 3.5 (a), lower ionic liquid (IL) concentrations lead to increased elongation and yield strength. Figure 3.5 (b) indicates that higher IL concentrations boost ionic conductivity but reduce crystallinity. Figure 3.5 (c) compares EMIBF₄, LiPF₆, and I₂/LiI at a constant PEO/ionic liquid ratio of 5:1, revealing that EMIBF₄ offers superior mechanical properties, including greater stiffness, strength, and elongation, compared to the other ionic liquids. Additionally, Figure 3.5 (d) shows that Young's modulus, yield strength, and ultimate strength inversely relate to IL concentration.

3.2.3.3 Effect of nano-fillers

Nano-fillers enhance both ionic conductivity and mechanical strength of CPEs. They can be divided into two main categories based on their ion transport characteristics: passive inorganic nano-fillers and active inorganic nano-fillers. Passive nano-fillers improve ionic conductivity by increasing free volume, accelerating segmental dynamics, and delaying polymer crystallization,

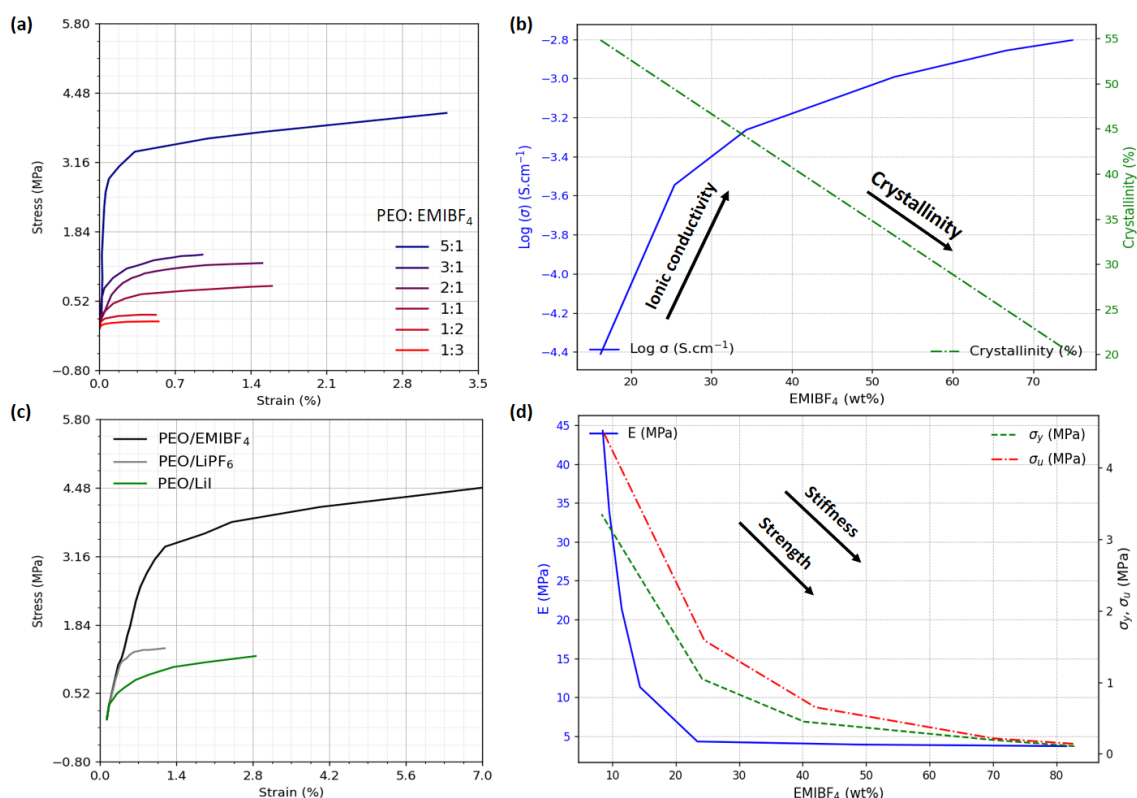


Figure 3.5: Effect of ionic liquids on the mechanical and electrochemical properties of PEO films (after Westover et al. (2014)): (a) Effect of EMIBF₄ concentration on stress-strain behavior (PEO/EMIBF₄ ratios are labeled); (b) Ionic conductivity and degree of crystallinity vs. percentage of EMIBF₄; (c) Effect of different ionic liquids (PEO/IL ratio of 5:1) on stress-strain behavior of thin film; (d) Effect of EMIBF₄ concentration on Young's modulus (E), yield strength (σ_y), and ultimate tensile strength (σ_u).

which lowers the glass transition temperature. According to Lewis acid-base theory, the specific surface of passive nano-fillers interacts with ion pairs, promoting their dissociation and increasing the availability of free Li⁺ ions for conduction. Additionally, these fillers provide migration sites where acidic sites attract anions and basic sites attract cations. This interaction can enhance ionic conductivity by two orders of magnitude (from 10⁻⁶ S.cm⁻¹ to 10⁻⁴ S.cm⁻¹) compared to pure polymer systems. Common passive fillers include TiO₂, SiO₂, Al₂O₃, ZnO₂, palygorskite, nanoclay, and carbon-based materials like carbon nanotubes (CNTs) and graphene oxide (GO) (Saleh et al. (2020); Shen et al. (2021); Liu et al. (2020a)). Active nano-fillers offer benefits such as enhanced electrochemical stability, reduced flammability, and improved cycling performance. Their large surface areas inhibit polymer chain crystallization during synthesis, promoting the formation of an amorphous polymer phase along the filler surfaces, which enhances ion transport through increased segmental motion of polymer chains (Shen et al. (2021); Liu et al. (2020a)). In lithium-ion battery research, several active nano-fillers have been used in CPEs, including Li₁₀GeP₂S₁₂ (LGPS), Li₇La₃Zr₂O₁₂ (LLZO), Li_{0.33}La_{0.56}TiO₃ (LLTO), and Li_{1+x}Al_xTi_{2-x}(PO₄)₃ (LATP) (Shen et al. (2021); Yu et al. (2021)). Chen et al. (Chen et al. (2018)) developed a CPE by blending PEO,

LiTFSI, and the ceramic active nano-filler, LLZTO, at varying concentrations of 10%, 50%, and 80%. These compositions were categorized as ceramic-in-polymer (10 wt% LLZTO), intermediate (50 wt% LLZTO), and polymer-in-ceramic (80 wt% LLZTO), as shown in Figure 3.6 (a). The results indicated that the addition of 10% nano-fillers significantly enhanced cycle stability, ionic conductivity, and discharge capacity compared to 50% or 80% fillers. Furthermore, the presence of 10% fillers notably reduced the resistance of the polymer electrolyte compared to the PEO/LiTFSI electrolyte without fillers. The results, including ionic conductivity and discharge capacity, are illustrated in Figures 3.6 (b) and 3.6 (c). Notably, both CPE systems with 10% and 50% LLZO filler exhibited remarkable deformability; however, the introduction of 80% LLZO filler resulted in cracking when the thin film was bent. These findings highlighted that increasing the concentration of LLZO ceramic fillers in PEO compromised the inherent mechanical deformability of the CPE. Xintong et al. (Mei et al. (2020)) investigated the impact of various percentages of LLZTO in PEO/LiClO₄/LLZTO electrolytes. The crystallinity of the thin film showed an inverse relationship with LLZTO content up to 50%; as LLZTO increased, crystallinity decreased. In higher than 50%, crystallinity increased with additional LLZTO, displaying a plateau with a direct relationship, as depicted in Figure 3.6 (d). The results also indicated that higher temperatures led to lower crystallinity. Conversely, the trend for ionic conductivity was reversed, as shown in Figure 3.6 (e). Ionic conductivity increased with the addition of LLZTO until it reached 50% and then decreased, indicating a negative effect of LLZTO on ionic conductivity. Higher temperatures corresponded to higher ionic conductivity. The findings suggested that the optimal percentage of LLZTO filler was 50%, achieving lower crystallinity and higher ionic conductivity across various temperatures. In another study, Jee et al. (Jee et al. (2013)) examined the mechanical properties of PEO/nanodiamond (ND) composite thin films with varying nanodiamond percentages. Figure 3.6 (f) illustrates a linear relationship between the Young's modulus of the thin films and the amount of nanodiamond fillers. The authors noted that Young's modulus adhered to the rule of mixtures, which states it is directly proportional to the mechanical properties of the polymer and the filler, as well as their respective proportions. They also mentioned that any non-linear dependencies, if present, depend on the unique interactions between the polymer, filler, and potential aggregation of nano-fillers. Zhang et al. (Zhang et al. (2011a)) investigated the effect of SiO₂ nano-wires on the mechanical and electrochemical properties of PVdF-HFP polymer films, testing various concentrations (0 wt%, 2 wt%, 6 wt%, and 10 wt%). The stress-strain graphs shown in Figure 3.6 (g) reveal that the addition of 10 wt% SiO₂ nano-wires significantly increased stiffness and strength compared to lower concentrations. Additionally, Figure 3.6 (h) illustrates the relationship between ionic conductivity and temperature, demonstrating that 10 wt% SiO₂ nano-wires enhanced ionic conductivity relative to lower percentages. Consistent with previous discussions, their findings indicate that ionic conductivity increases with rising temperature across all samples. Figure 3.6 (i) presents cross-sectional SEM images of composite polymer membranes with different proportions of SiO₂ nano-wires.

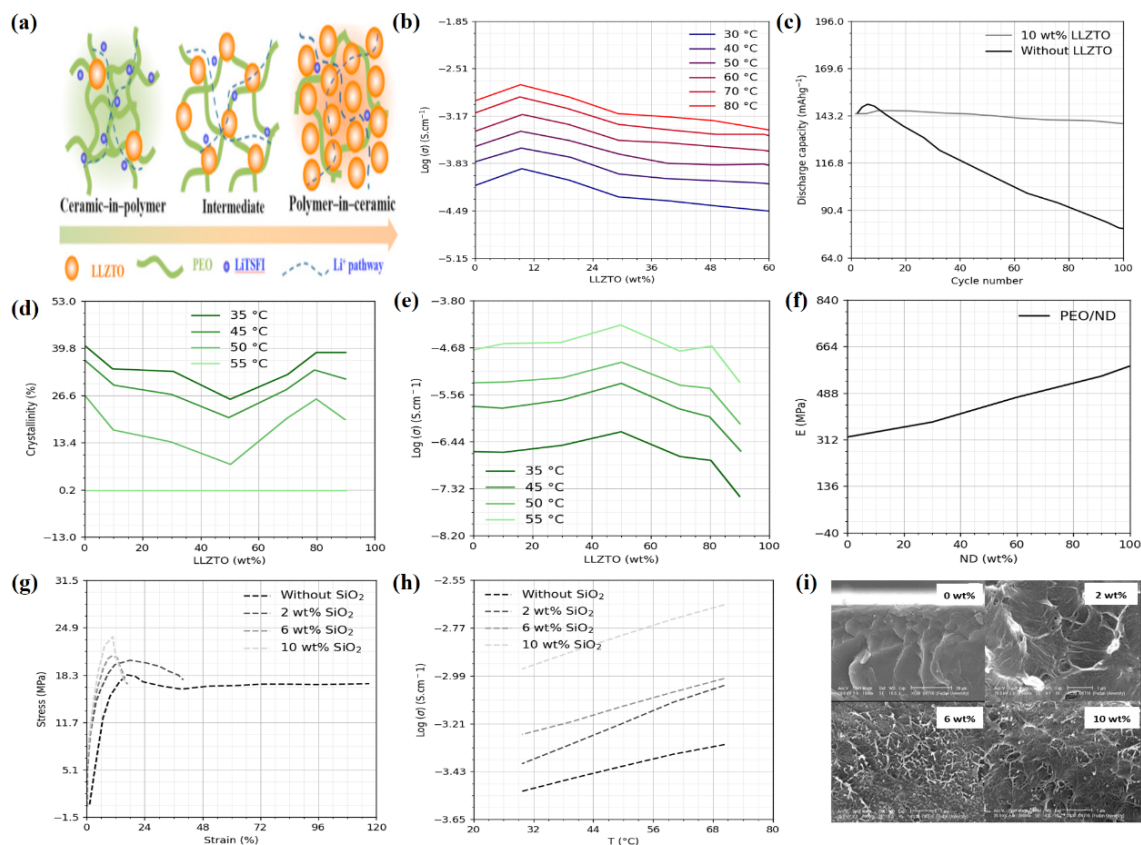


Figure 3.6: Effect of nano-fillers on electrochemical and mechanical properties of composite polymer electrolytes: (a) Ceramic-in-polymer, intermediate, and polymer-in-ceramic concepts (Chen et al. (2018)); (b) Effect of LLZTO on ionic conductivity of PEO/LiTFSI/LLZO (after Chen et al. (2018)); (c) Discharge capacity of PEO/LiTFSI/LLZO (after Chen et al. (2018)); (d) Effect of LLZTO on crystallinity of PEO film (after Mei et al. (2020)); (e) Effect of LLZTO on ionic conductivity of PEO film (after Mei et al. (2020)); (f) Effect of nanodiamond (ND) on Young's modulus of PEO film (after Jee et al. (2013)); (g) Effect of SiO₂ nano-wires on stress-strain behavior of PVdF-HFP polymer film (after Zhang et al. (2011a)); (h) Effect of SiO₂ nano-wires on ionic conductivity of PVdF-HFP polymer film (after Zhang et al. (2011a)); (i) Scanning electron microscope images of PVdF-HFP/SiO₂ (after Zhang et al. (2011a)).

3.2.3.4 Effect of thermoset polymers

Thermoset polymers like epoxy possess excellent thermomechanical properties, high corrosion resistance, and low shrinkage, but their significant cross-linking limits ion mobility, resulting in lower ionic conductivity than thermoplastics. Pure epoxy generally exhibits ionic conductivity below 10^{-12} S/cm at room temperature. Combining thermoset and thermoplastic polymers can create polymer electrolytes that leverage the strengths of both materials. The first notable attempt was by Chiang et al. in 1987 (Chiang et al. (1987)), who blended epoxy (Bisphenol-A) with PEO and lithium perchlorate (LiClO₄). They found that up to 30 wt% epoxy did not significantly reduce ionic conductivity compared to pure PEO while enhancing the mechanical strength of the thin films; however, exceeding this threshold decreased ionic conductivity. Figure 3.7 (a) illustrates the

inverse relationship between ionic conductivity (σ) and Young's modulus (E) concerning epoxy concentration. In another study, biphasic epoxy was integrated into a liquid electrolyte composed of EMIMBF₄ and LiTFSI, with thin films created via thermally initiated phase separation. Figures 3.7 (b) and 3.7 (c) show that increasing epoxy concentration enhances Young's modulus, tensile strength, and maximum elongation while decreasing ionic conductivity. These results emphasize the necessary trade-offs between mechanical and electrochemical properties when using epoxy in electrolytes.

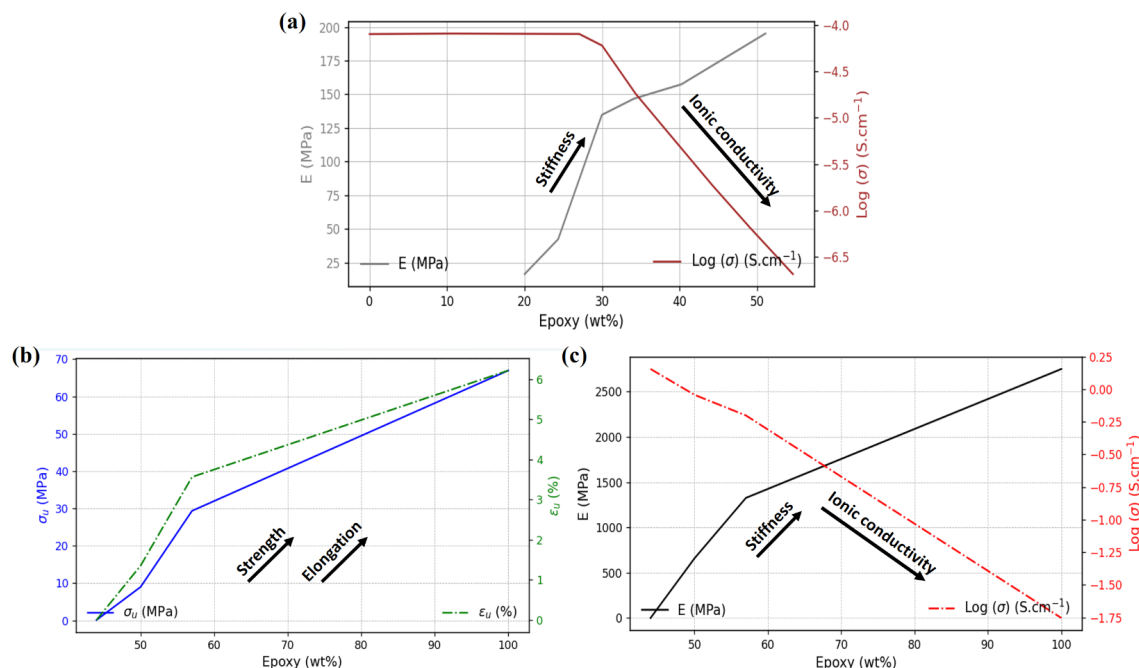


Figure 3.7: (a) Effect of epoxy concentration on Young's modulus and ionic conductivity of PEO/epoxy/LiClO₄ electrolyte (after [Chiang et al. \(1987\)](#)); (b) Effect of epoxy concentration on tensile strength (σ_u) and maximum elongation (ϵ_u) of biphasic epoxy/liquid electrolyte (after [Raja et al. \(2023\)](#)); (c) Effect of epoxy concentration on Young's modulus and ionic conductivity of biphasic epoxy/liquid electrolyte (after [Raja et al. \(2023\)](#)).

3.2.4 Manufacturing techniques

3.2.4.1 Solution casting

In this method, the solvent is selected based on its compatibility with the polymer and other additives. The choice of solvent significantly shapes the molecular arrangement of polymer hosts, leading to variations in amorphous structures that impact both electrochemical ([Dohrn et al. \(2021\)](#); [Hansen \(1995\)](#)) and mechanical properties ([Khan et al. \(2007\)](#)). Initially, the polymer is dissolved in the selected solvent to create a homogeneous solution. Additional components, such as salts and fillers, can also be incorporated. The solution is poured or spin-coated onto a glass or silicon mold. The solvent is then evaporated under controlled conditions, either in a vacuum chamber or ambient atmosphere, resulting in a thin, uniform film ([Mei et al. \(2023\)](#)), which is subsequently

sandwiched between electrodes. Incomplete drying can leave residual solvent in the thin film, significantly impacting its T_g . For instance, water lowers the T_g of hydrophilic polymers due to its low glass transition temperature of approximately -138 degrees Celsius (Chu and Berner (1993)). Generally, increased solvent content in polymers correlates with a decrease in the T_g of the thin film (Khan et al. (2007)). The solvent casting process may entrap significant amounts of solvent, particularly when using high-boiling solvents like N-Methyl-2-pyrrolidone (NMP) and Dimethyl sulfoxide (DMSO). Additionally, exposure to atmospheric moisture or absorption of extra solvents during storage can exacerbate solvent entrapment in composite polymer electrolytes. Residual solvent affects molecular shape and mobility, thereby influencing mechanical properties (Khan et al. (2007)) and ionic conductivity through its plasticizing effect (Foran et al. (2020)). Conversely, low-boiling solvents like methanol and water can be removed more easily, resulting in brittle thin films with higher strength (Khan et al. (2007)). Despite the critical role of solvent content in the thermo-electro-mechanical characteristics of CPEs, there has been a notable lack of reporting on solvent content in solid-state polymer electrolytes over the past four decades.

3.2.4.2 Solvent-free methods

Solvent-free methods like hot pressing, melt mixing, and thermal extrusion, which utilize heat and pressure, are commonly employed to prepare composite polymer electrolytes (Cai et al. (2019); Li et al. (2022c)). Figure 3.8 (a) illustrates the thermal-extrusion process. Solvent-free method offers several advantages over conventional solution casting technique, including environmental friendliness by removing the need for organic solvents and reducing associated environmental impacts; a simplified process by directly mixing components without solvent evaporation or removal steps; enhanced safety by eliminating risks associated with volatile organic solvents; and improved mechanical properties, resulting in CPEs with higher tensile strength and stiffness due to more efficient polymer chain alignment and interfacial interactions. However, solvent-free methods have limitations such as restricted processability for high-viscosity polymers, reduced control over morphology and microstructure compared to solution casting, and challenges in achieving uniform component distribution within the CPE matrix, potentially leading to phase separation and diminished performance (Liu et al. (2023b); Li et al. (2022c)). Li et al. (Li et al. (2022a)) compared the properties of CPEs produced by thermal-extrusion processing (TE-CPE) and conventional solution casting (SC-CPE). Their assessment, as shown in Figure 3.8, revealed that the thermal-extrusion method achieved high specific capacity (Figure 3.8 (c)) and similar ionic conductivity to solution casting (Figure 3.8 (d)), with distinct structural differences seen in scanning electron microscope images (Figure 3.8 (b)). Testing of symmetric lithium cells demonstrated that the solvent-free method operated for over 3700 hours, retaining 78.1% discharge capacity after 380 cycles. Thermogravimetric analyses (TGA) of both techniques are shown in Figure 3.8 (e). The elimination of residual solvent increased the tensile strength of the solvent-free membrane to 3.85 MPa, three times that of solution casting membranes (Figure 3.8 (f)).

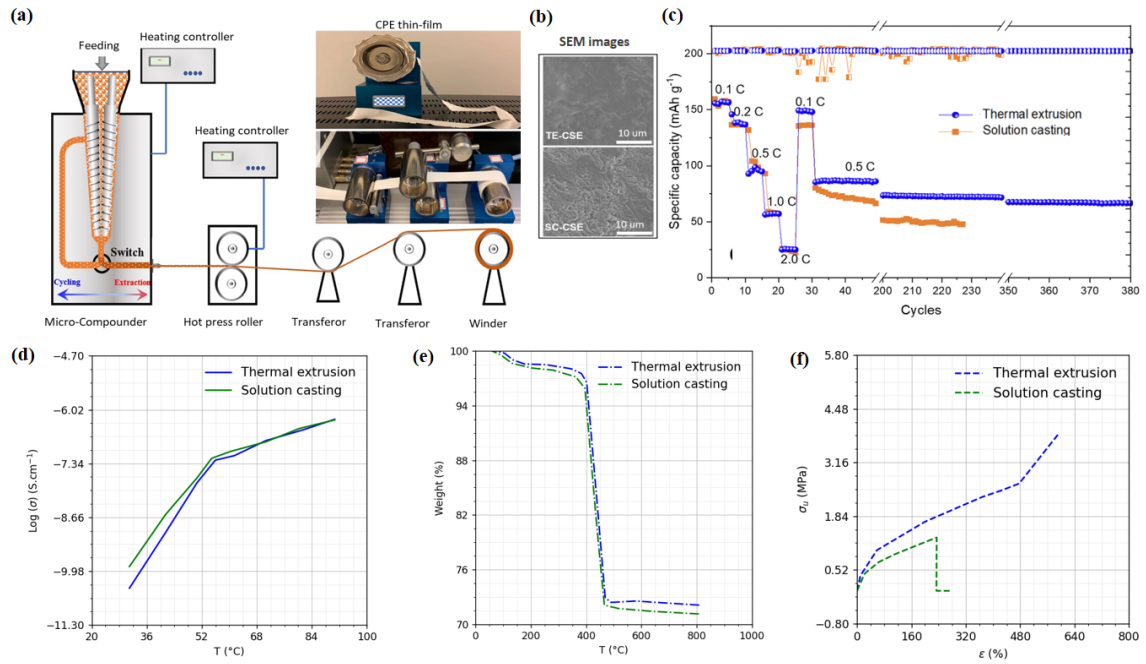


Figure 3.8: Solvent-free thermal-extrusion method (after Li et al. (2022a)): (a) Process of CPE manufacturing; (b) SEM images; (c) Specific capacity versus number of cycles; (d) Ionic conductivity; (e) TGA (f) Tensile strength versus elongation.

3.2.4.3 Phase inversion method

The phase inversion method, shown in Figure 3.9 (a), is used to manufacture polymer electrolyte membranes with various functionalities by transforming a homogeneous polymer solution from liquid to solid. A polymer solution is cast onto a glass or Teflon substrate, then immersed in a non-solvent bath (e.g., water), inducing rapid precipitation and forming an asymmetric surface structure. The process is influenced by the composition of the casting solution and additives (Liu et al. (2018); Deng et al. (2024)). Kim et al. (Kim et al. (2006)) performed a comparative analysis of the phase inversion technique and the conventional solution casting method for synthesizing composite polymer electrolytes based on PVdF-HFP with varying concentrations of titania (TiO_2) nanocrystalline particles. The ionic conductivity of the resulting electrolytes is presented in Figure 3.9 (b). Phase inversion polymer electrolytes demonstrated superior electrochemical properties, including enhanced ionic conductivity, greater electrochemical stability, and improved interfacial stability compared to solution-casting thin film electrolytes. Surface and cross-sectional images of both techniques, shown in Figure 3.9 (c), reveal that the phase inversion membranes have a distinct porous structure, highlighting the unique morphology produced by this method.

3.2.4.4 Electrospinning method

The electrospinning method offers superior chemical stability, increased porosity, and enhanced performance. In this technique, a polymer is dissolved in a suitable solvent to create a solution, into which ionic conductive fillers are dispersed or dissolved. This solution is loaded into a syringe

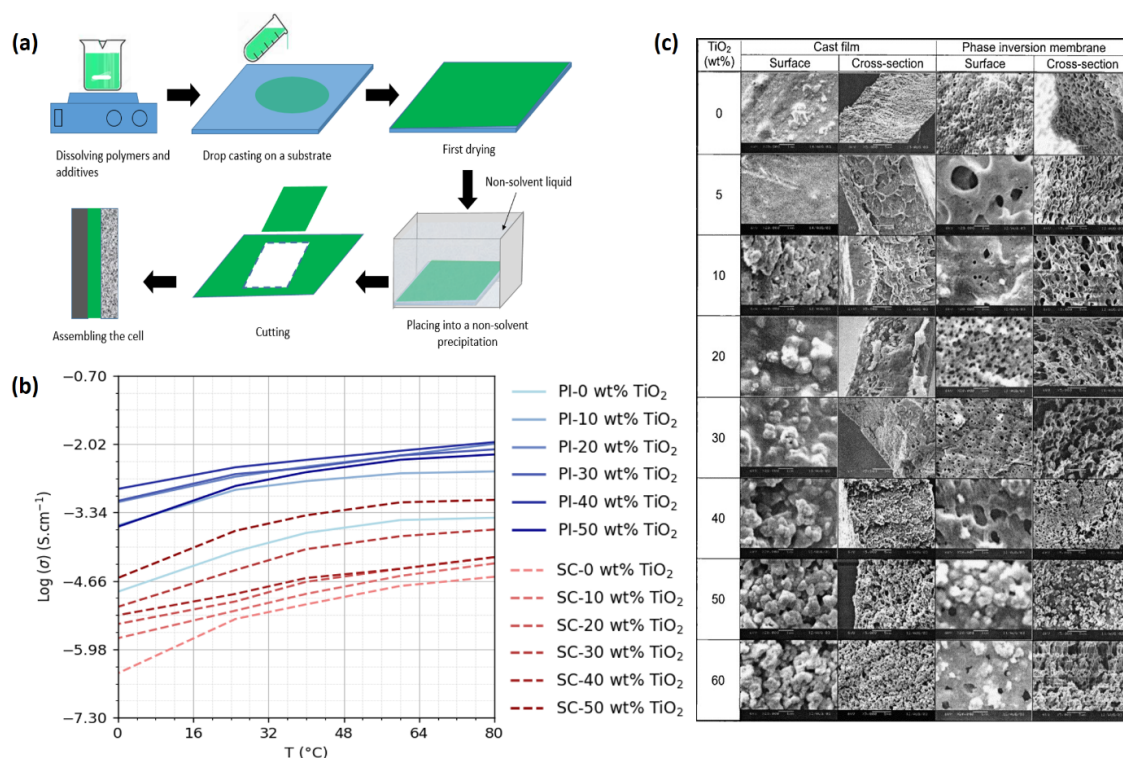


Figure 3.9: Phase inversion method: (a) Procedures of manufacturing thin film; (b) Comparison of ionic conductivity between phase inversion (PI) method and solution casting (SC) technique for PVdF-HFP/ TiO_2 films with various TiO_2 content (after Kim et al. (2006)); (c) Scanning electron microscope images of both techniques (Kim et al. (2006)).

connected to a high-voltage power supply. When high voltage is applied, a Taylor cone forms at the syringe tip, propelling a charged jet of the polymer solution towards a grounded collector. As the jet travels, the solvent evaporates, resulting in the formation of fine polymer fibers intertwined with the embedded fillers (Sood et al. (2016); Maurya et al. (2019); M. Shanthi et al. (2018)). Figure 3.10 (a) shows the electrospinning device used in the study (Li et al. (2023a)). Shanthi et al. (M. Shanthi et al. (2018)) conducted a comparative analysis of the electrospinning and solution casting techniques for synthesizing PVdF-HFP/LiTFSI composites with various nano-fillers, including TiO_2 , SiO_2 , and fumed TiO_2 . The comparative mechanical analysis is presented in Figures 3.10 (b) and 3.10 (c). CPEs produced via electrospinning exhibited significantly improved mechanical properties across all samples compared to those produced by solution casting. The inclusion of fumed TiO_2 resulted in a notable increase in tensile strength, surpassing the improvements observed with TiO_2 and SiO_2 fillers when compared to composites without nano-fillers. Additionally, the electrospinning technique effectively reduced dendrite formation on the lithium anode, providing exceptional chemical stability even after more than 100 cycles.

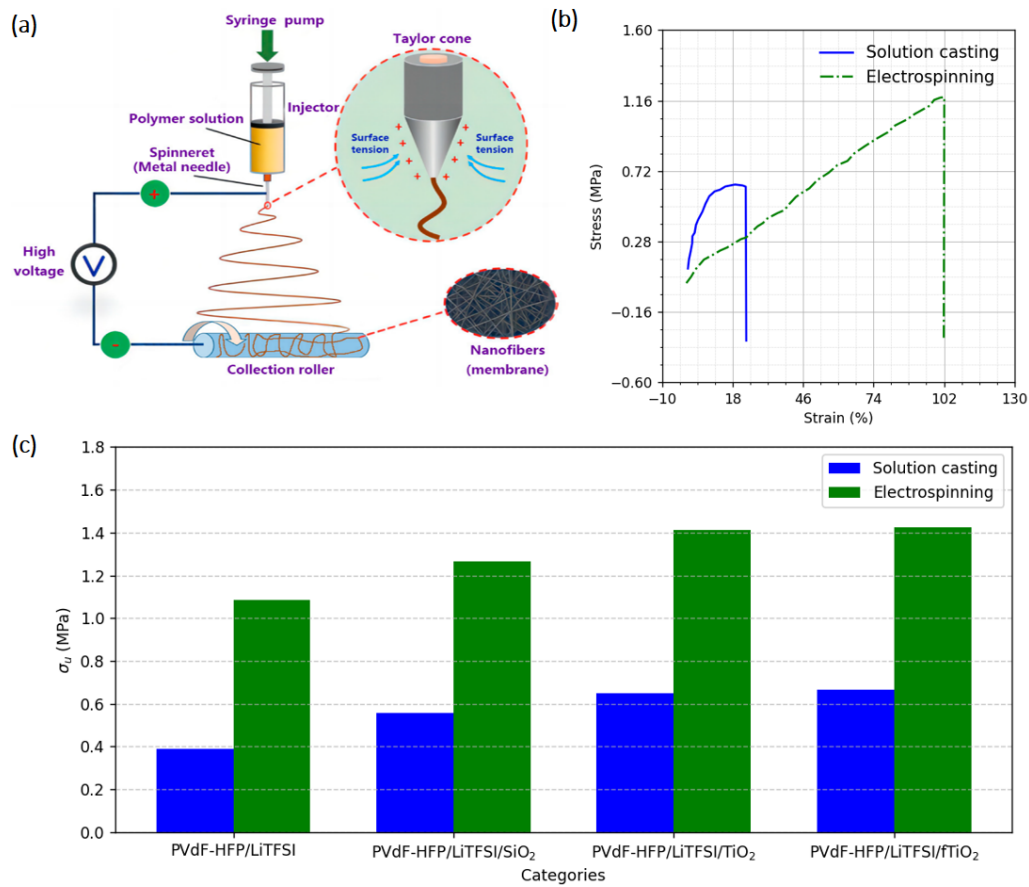


Figure 3.10: (a) The electrospinning technique (Li et al. (2023a)); (b) Comparison between stress vs. strain of electrospinning method and solution casting technique for PVdF-HFP/LiTFSI/TiO₂ (after M. Shanthi et al. (2018)); (c) Tensile strength of PVdF-HFP/LiTFSI with various nano-fillers (after M. Shanthi et al. (2018)).

3.2.4.5 In-situ polymerization method

The in-situ polymerization method involves dispersing fillers and additives into a solution of precursor monomers, followed by the polymerization of the monomers through standard polymerization reactions (Wang et al. (2024b); Zheng et al. (2022)). This method can be implemented using the indirect approach, direct separator deposition approach, and direct separator-free deposition approach (shown in Figure 3.11) (Vijayakumar et al. (2021); Wu et al. (2023)). The indirect approach may lead to poor interfacial contact; however, in the direct separator deposition and direct separator-free deposition approaches, voids may appear in the final cell due to dead volume within the electrode. These voids do not contribute to charge storage and can negatively impact the overall efficiency of the cell. In-situ polymerization begins with a common initial step across all approaches, where a precursor solution is prepared. This solution consists of polymerizable monomers/oligomers, a conducting salt, and an appropriate initiator. Additional components, such as plasticizers and fillers, may be added to modify the physicochemical and electrochemical properties, including interphase formation. The second step involves the indirect deposition method,

which includes drop-casting the precursor solution onto an external substrate, followed by polymerization with heat to form a thin film that is then sandwiched between electrodes (Figure 3.11 (a)) (Vijayakumar et al. (2021); Ma et al. (2022b)). In the direct deposition by separator-assisted approach (Figure 3.11 (b)), the cell is first sandwiched with a separator, and the precursor solution is poured onto the cell to fill the separator. Afterward, the cell is heated, allowing the solution to polymerize inside the sealed pouch cell, thereby ensuring enhanced electrode-electrolyte interfacial contact during fabrication. It is crucial to select appropriate monomers and initiators to avoid gas production or side reactions that could lead to bubble formation, pressure build-up, or undesirable interactions with cell components during fabrication or operation. One drawback of the separator-assisted method is the dead weight and inactive ion conduction areas introduced by the supporting separators, which are typically made from materials like cellulose, glass fiber, or PVdF. Alternatively, pre-soaking separators in the precursor can be replaced with a filling method (Ma et al. (2022b)). In the third method, known as the separator-free direct deposition approach (Figure 3.11 (c)), the precursor solution is drop-casted directly onto one of the electrodes, followed by polymerization and heating before being sandwiched into the cell. This approach completely eliminates the dead weight of reinforcing separators (Vijayakumar et al. (2021); Ma et al. (2022b)).

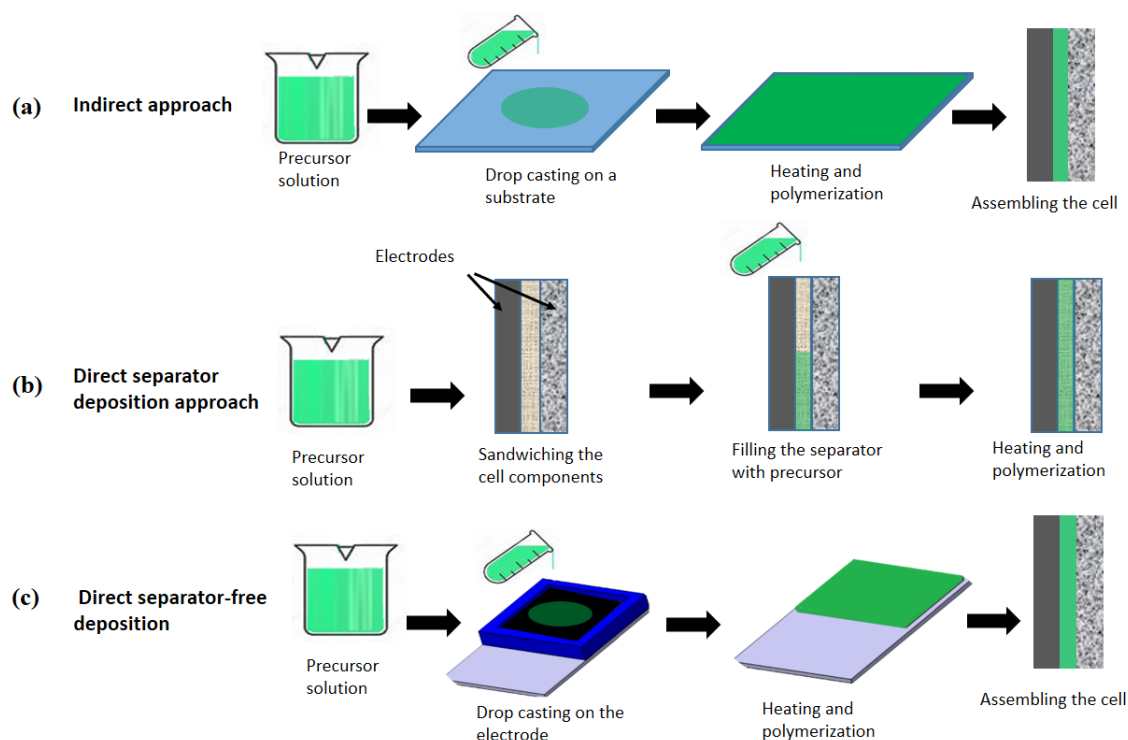


Figure 3.11: Different approaches of in-situ polymerization method: (a) Indirect approach; (b) Direct separator deposition approach; (c) Direct separator-free direct deposition.

Hu et al. (Hu et al. (2022)) investigated the effects of lithium sulfonated polyvinyl alcohol (SPVA-Li) as an organic filler and SiO_2 as an inorganic filler in PEO polymer using two methods: in-situ polymerization and solution casting. They found that a composite with 10% of each filler

achieved the highest conductivity of $0.33 \text{ mS}\cdot\text{cm}^{-1}$ ($-3.48 \log (\text{S}\cdot\text{cm}^{-1})$), as shown in Figure 3.12 (a). Ionic conductivity tests revealed that films produced via in-situ polymerization had superior conductivity compared to those made by conventional solution casting (Figure 3.12 (b)). Figures 3.12 (c) and 3.12 (d) illustrate the capacity-cycle number and stress-strain properties, highlighting the advantages of in-situ polymerization. The authors attributed these improvements to hydrogen bonds formed between SPVA-Li and SiO_2 particles with PEO polymers, which disrupted PEO chain organization, resulting in lower crystallinity and higher ionic conductivity. They also noted that in-situ polymerization facilitated stronger chemical and mechanical interactions between fillers and polymers compared to conventional methods, suggesting promising prospects for composite solid polymer electrolytes.

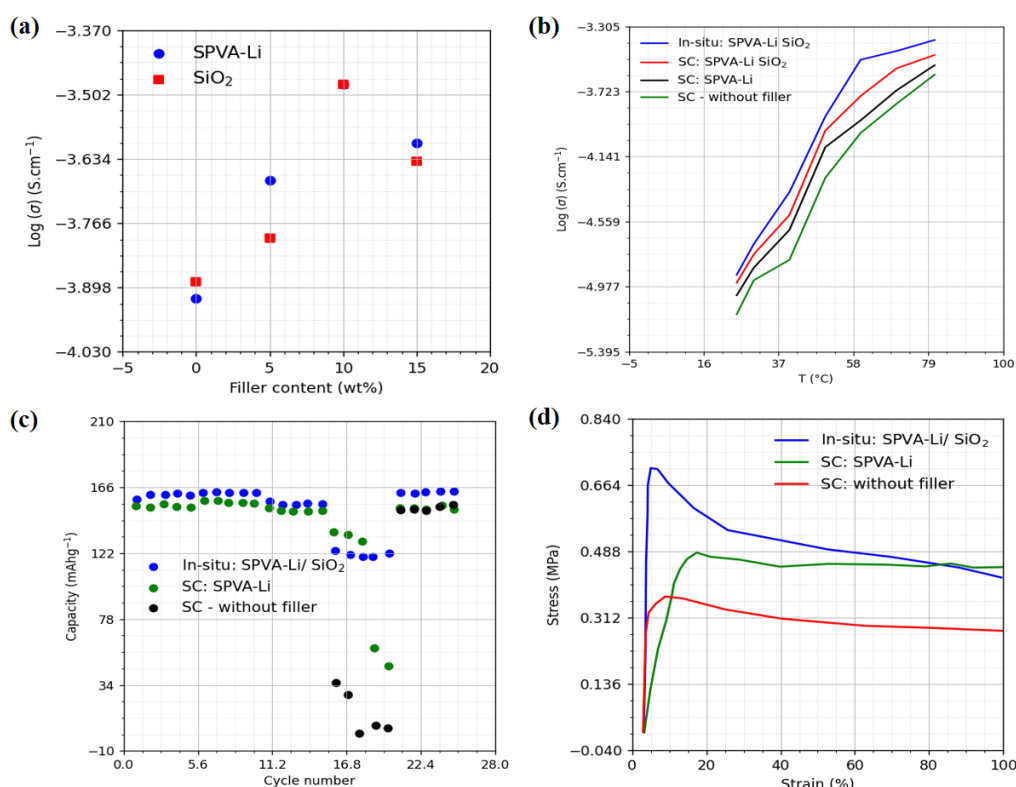


Figure 3.12: Comparison of Electrochemical and Mechanical Properties of PEO Composite Films Prepared via In-Situ Polymerization and Solution Casting (after Hu et al. (2022)): (a) Effect of SPVA-Li and SiO_2 fillers on ionic conductivity (in-situ polymerization); (b) Ionic conductivity comparison between in-situ polymerization and solution casting; (c) Capacity vs. cycle number comparison for both techniques; (d) Stress-strain comparison for both techniques.

3.2.4.6 Layer-by-layer assembly method

The layer-by-layer (LbL) assembly method, also known as multilayer membranes, provides precise control over the structure and properties of thin films. This technique retains the superior attributes of each layer while mitigating their shortcomings, resulting in excellent uniformity, minimal crystallinity, and high ionic conductivity (Branco et al. (2016); Nguyen et al. (2011); Tan et al.

(2023); Cui and Lee (2016)). LbL assembly can be achieved through electrostatic interactions or hydrogen bonding. In the electrostatic approach, successive layers are formed by immersing the substrate in solutions of oppositely charged polyelectrolytes. Conversely, the hydrogen bonding method is suitable for compounds with hydrogen-donor and hydrogen-acceptor groups. The choice of polyion pairs in the electrostatic method is critical, as it influences the retention of mobile ions and ionic mobility within the assembled films, which is affected by cross-linking density (Lowman et al. (2004)). Some researchers have combined hydrogen bonding and electrostatic interactions to leverage the benefits of both methods (Nguyen et al. (2011)). Both methods utilize a sequential deposition process to build alternating layers on a substrate, resulting in a multilayered composite polymer structure. Initially, the substrate may undergo pretreatment to ensure a hydrophilic surface. A solution of polyelectrolytes—polymers with ionic groups—along with additives, salts, or ionic liquids, is then deposited. Following deposition, the substrate is rinsed in a pH-adjusted DI water bath (Srivastava and Kotov (2008); Yuan et al. (2020)). The substrate is subsequently immersed in solutions containing polyelectrolytes, electrolytes, and materials that can interact via hydrogen bonding or electrostatic interactions, followed by another rinse in a pH-adjusted DI water bath. This layer-by-layer assembly process can be repeated as needed to achieve the desired number of layers and optimize the properties of the composite electrolyte (Cui and Lee (2016)). The general procedures of the LbL manufacturing method are shown in Figure 3.13.

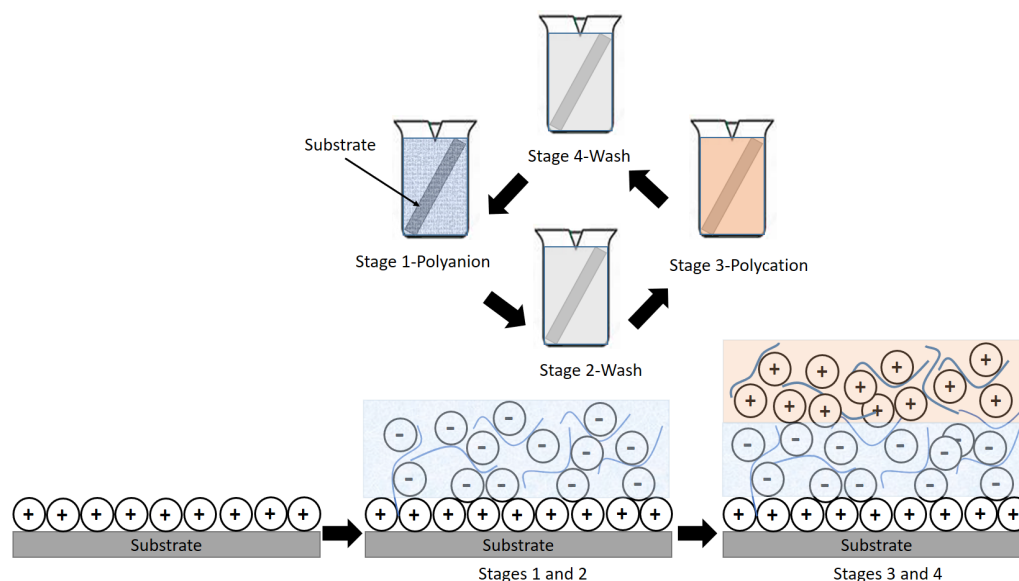


Figure 3.13: Procedures of layer-by-layer assembly method.

3.2.5 Summary of the key consideration of composite polymer electrolytes

In summary, as shown in Figure 3.14, higher molecular weight polymers and thermoset additives improve mechanical properties but reduce ionic conductivity. Conversely, ionic conductors and elevated temperatures enhance ionic conductivity but may compromise mechanical strength. Nano-fillers have the potential to boost both mechanical and ionic properties. Additionally, as

thoroughly discussed in previous subsections, various manufacturing techniques exist for producing composite polymer electrolytes, each with its own advantages and disadvantages. Selecting a manufacturing method involves trade-offs, where certain factors are prioritized at the expense of others. Achieving an optimal balance between mechanical and electrochemical properties is crucial when designing composite polymer electrolytes for multifunctional energy storage systems. Table 3.2 summarizes the advantages and disadvantages of various methods for manufacturing composite polymer electrolytes.

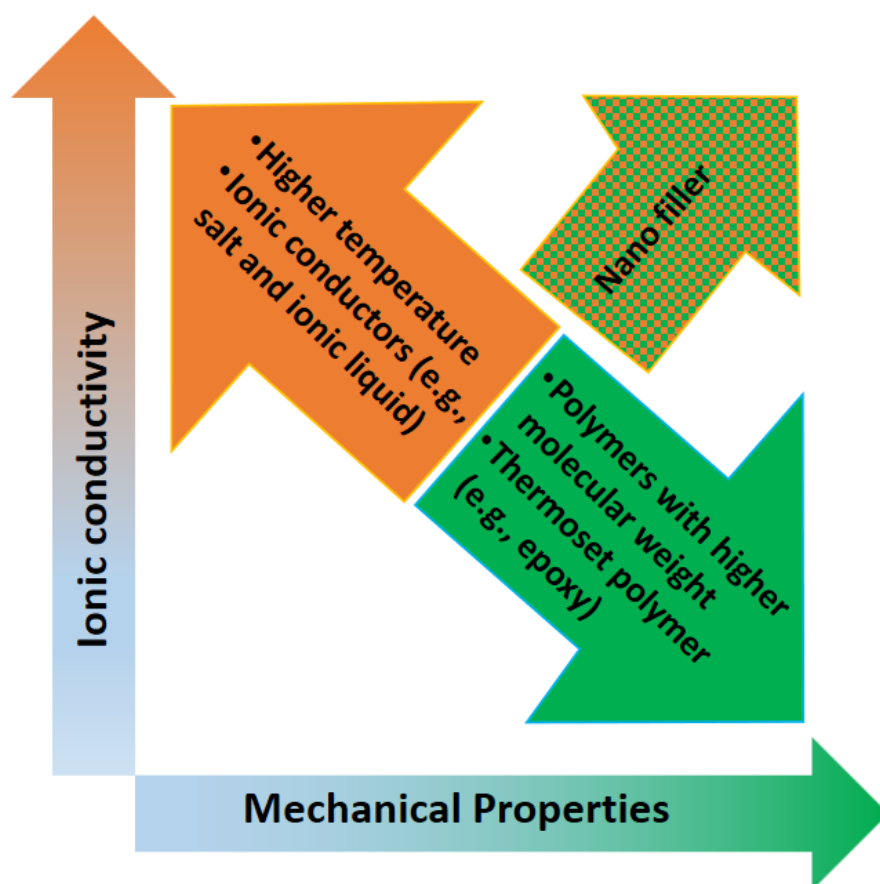


Figure 3.14: Effect of different parameters on the electrochemical and mechanical properties of composite polymer electrolytes.

Table 3.2: Manufacturing techniques of composite polymer electrolytes.

Technique (Ref.)	Advantages	Disadvantages
Solution casting (Khan et al. (2007) ; Chu and Berner (1993))	Versatility Homogeneous dispersion Scalability	Solvent handling Drying time Solvents volatilizing Low mechanical properties Poor interfacial contact
Solvent-free (Li et al. (2022c) ; Liu et al. (2023b) ; Foran et al. (2020))	Safety High mechanical properties Cost-effective Stability Dendrite-free	Limited application Processing challenges Poor micro-structure control Uneven particles dispersion
Phase inversion (Liu et al. (2018) ; Kim et al. (2006) ; Deng et al. (2024))	Multi-functionality Porosity control Stability	Solvent handling Solvent entrapment Complexity
Electrospinning (Sood et al. (2016) ; Maurya et al. (2019) ; M. Shanthi et al. (2018))	High surface area Control over morphology Enhanced performance High mechanical properties Stability	Equipment complexity Limited scalability
In-situ polymerization (Hu et al. (2022) ; Fu et al. (2021) ; Sun et al. (2021) ; Wang et al. (2024b) ; Vijayakumar et al. (2021) ; Wu et al. (2023) ; Ma et al. (2022b))	Good contact High ionic conductivity Good particles interactions	Reaction kinetics Void formation Dead-weight Solvents volatilizing
Layer-by-layer (Branco et al. (2016) ; Nguyen et al. (2011) ; Tan et al. (2023) ; Cui and Lee (2016) ; Lowman et al. (2004) ; De-Longchamp and Hammond (2003))	Thin thickness Mechanical properties Uniformity	Time-consuming Limited thickness Limited ion conductivity Water entrapment

3.2.6 Approaches to overcome the load-bearing–ionic conductivity trade-offs

Future work will focus on decoupling mechanical properties from ionic conductivity and overcoming the classic trade-off through novel material compositions, innovative architectures, and advanced techniques. For example, multi-objective optimization strategies should be developed to achieve an optimal, user-defined balance between electrochemical and mechanical performance. Below, we outline several approaches—emphasizing materials, compositions, and architectures—some of which have already been initiated.

3.2.6.1 Advanced networks

Exploring new additives with stimuli-responsive or self-healing properties could result in composite polymer electrolytes that adapt their mechanical and electrochemical properties based on external conditions, such as temperature changes or mechanical stress. Dynamic covalent or supramolecular networks (e.g., vitrimers and hydrogen-bonding polymers) can impart self-healing toughness without impeding ionic motion (Zhao *et al.* (2023); Gu *et al.* (2022)). For instance, Chen *et al.* (Chen *et al.* (2023)) developed a polymer network (PDDP) incorporating both hydrogen-bonding urea groups and dynamic disulfide bonds. This design enabled rapid self-healing at approximately 28 °C and yielded an ionic conductivity of $1.13 \times 10^{-4} \text{ S cm}^{-1}$ at the same temperature. Katcharava *et al.* (Katcharava *et al.* (2023)) reported a self-healable and conductive poly(ionic liquid) (PIL) electrolyte composed of pyrrolidinium-based repeating units. Similarly, Zhou *et al.* (Zhou *et al.* (2019)) introduced ureido-pyrimidinone (UPy) groups-quadruple hydrogen-bonding moieties-on SiO_2 fillers to create physically crosslinked supramolecular networks within a polymer matrix, achieving a mechanically robust, self-healing electrolyte with an ionic conductivity of $8.0 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C. In addition, block copolymer design-combining one block with a high glass-transition temperature (to provide stiffness) and a soft, ionic conductive block-enables microphase-separated structures. Such materials form interconnected ionic channels within a reinforcing matrix. By adjusting block lengths and crystallinity, the trade-off between conductivity and modulus can be overcome (Cao *et al.* (2020a); Varghese *et al.* (2025); Melodia *et al.* (2023); Zhang *et al.* (2011b); Wanakule (2010)). Embedding ion-conducting moieties directly into the polymer backbone can further enhance salt dissociation, increase Li^+ transference number, and raise ionic conductivity (Hou *et al.* (2023a); Wang *et al.* (2023)). Because this approach can also soften the polymer, co-optimization with fillers or crosslinks may be required to maintain mechanical integrity. Future research also could focus on designing polymers with tailored molecular weights to achieve specific combinations of mechanical and electrochemical properties.

3.2.6.2 Functional fillers

Reinforcing fillers such as nanofibers, whiskers, or two-dimensional (2D) nanosheets can considerably increase mechanical strength. For example, poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) nanofibers embedded in a PEO matrix acted as a rigid scaffold: they suppressed PEO crystallinity and increased the Young's modulus nearly 14-fold, while simultaneously enhancing Li^+ conductivity by facilitating smoother ion transport along the nanofibers. This result highlights how fibrous backbones can overcome the usual strength and conductivity trade-off (Du *et al.* (2024)). Oriented filler networks (e.g., vertically aligned ceramic columns or nanowire forests) can also create continuous ion pathways without sacrificing mechanical properties (Zhang *et al.* (2018)). Liu *et al.* (Liu *et al.* (2017)) demonstrated that aligning ion-conducting nanowires within a polymer matrix yields a composite with ionic conductivity an order of magnitude higher than that of composites containing randomly dispersed nanowires or particles. In addition, fillers whose surfaces interact with Li^+ can improve both ionic conductivity and mechanical properties of the

electrolyte. For instance, Wang *et al.* (Wang *et al.* (2020)) reinforced PEO with two-dimensional layered double hydroxide (LDH) nanosheets, achieving enhanced ionic conductivity and mechanical stability.

3.2.6.3 Architectures

Creating distinct but interpenetrating phases is a powerful way to decouple functions. For example, a two-step RIPS process (using a sacrificial porogen) can yield a rigid porous scaffold (polymer/resin) infiltrated by a conductive liquid/salt network (Adak *et al.* (2024)). Furthermore, future composites may exploit spatial gradients to localize properties. For example, an electrolyte could have two stiff skins and a soft, highly conductive core, like those in composite sandwich panels (Zenkert (1997)). For example, using corrugated or honeycomb structures with high strength polymers, filled with liquid or gel-state electrolyte, can create a structural electrolyte with high mechanical and electrochemical properties. The general strategy is to combine a stiff component that maintains shape with a soft, mobile phase that provide ionic conductivity. In addition, controlling morphology (droplet size, pore size, domain shape) using characterization and modeling (e.g. X-ray tomography, simulations) will guide the engineering of pore geometry to align with ionic pathways and mechanical load paths.

3.3 Glass fiber-reinforced composite polymer electrolytes matrix

Glass fiber separators, known for their excellent electrical insulation, high porosity, mechanical robustness, thermal and chemical stability, and excellent wettability, which could lead to large electrolyte intake and consequently high ionic conductivity, playing a crucial role in enhancing battery performance and cycle life (Zhu *et al.* (2016); Zhang *et al.* (2015b); Chen *et al.* (2021b); Gao *et al.* (2015)). The incorporation of polymer electrolytes into these separators provides a class of glass fiber-reinforced polymer (GFRP) structural electrolytes, which offer enhanced multifunctional properties. For example, Zhang *et al.* (Zhang *et al.* (2021c)) developed glass fiber reinforced with PEO/ionic liquid and achieved an ionic conductivity of 1.6×10^{-4} S/cm with 25 wt% ionic liquid, along with a tensile strength of 36 MPa and stiffness of 0.81 GPa. However, their method does not result in a fully solid-state electrolyte. In another study, Dong *et al.* (Dong *et al.* (2021)) manufactured a structural electrolyte using PEO, LiTFSI, LATP fillers, and glass fiber, obtaining a stiffness of around 1.2 GPa, a tensile strength of 33.1 MPa, and an ionic conductivity of 6.3×10^{-5} S/cm.

Chapter 4

Research gaps and motivation of this study

Despite growing interest in structural batteries as multifunctional systems that combine mechanical and electrochemical performance, several critical gaps remained unaddressed in the literature. This study aimed to bridge these gaps through a multidisciplinary approach that advances both the understanding and the practical development of structural battery components and architecture.

1. Lack of critical reviews on metrics of structural batteries and multifunctionality of composite polymer electrolyte

While several review studies have proposed individual solutions for structural batteries, a consolidated critical review focusing on appropriate mechanical and electrochemical performance metrics for evaluating structural batteries is absent. Additionally, the multifunctionality of composite polymer electrolytes—particularly the complex trade-offs between mechanical integrity and electrochemical performance—has not been thoroughly examined. This thesis addresses both aspects by providing an in-depth literature review, offering guidance for researchers aiming to optimize dual-performance of structural batteries.

2. First use of high-performance alloys as current collectors

Existing literature and commercial applications typically employ pure aluminum and copper foils as current collectors, materials that lack sufficient mechanical strength for structural load-bearing. This study pioneers the use of aerospace-grade alloys such as Al2024-T3 and copper heat-treated alloy (Cu110), offering superior mechanical properties and compatibility with composite layers.

3. First evaluation of interlaminar fracture toughness between GFRP and current collectors for structural batteries

The bonding interface between GFRP and metal current collectors is critical for multifunctional performance of structural batteries, yet no studies have quantified the interlaminar fracture toughness, particularly for copper alloys. This thesis is the first to evaluate and improve bonding behaviors using various surface treatments, identifying the optimal method for symmetric and high-fracture toughness in structural batteries.

4. Influence of transverse compressive stress on mode II fracture behavior

The effect of transverse compressive stress on mode II interlaminar fracture toughness in hybrid joints of structural batteries is studied for the first time. In addition, a novel equation is derived for calculating mode II fracture toughness in hybrid laminates in modified transverse crack tension (mTCT) test, accounting for both elastic and thermal expansion coefficient mismatches between the composite shell and the current collectors.

5. Novel structural electrolyte

Epoxy resins, with high thermal resistance, have not been fully explored as multifunctional components in structural batteries. This study introduces a novel composite polymer electrolyte formulation that combines a heat-resistant epoxy, thermoplastic polymer, lithium salt, and nano-ceramic fillers (Al_2O_3), reinforced with woven glass fiber fabric. This dual-purpose matrix serves both as a solid-state electrolyte and as a structural component, offering optimized electrochemical and mechanical properties. The specific composition and structural integration presented here are new contributions to the field. Additionally, traditional solution casting techniques for polymer electrolytes often suffer from poor interfacial contact and delamination. This research introduces an enhanced processing method involving an additional heat-and-pressure-assisted step. This process improvement significantly enhances bonding quality and structural cohesion between the electrolyte and the electrodes, marking a novel advancement in structural electrolyte fabrication.

6. First quasi-static indentation testing of structural batteries

This study performs the first quasi-static indentation tests on multifunctional structural battery laminates, benchmarking against traditional GFRP structures and equivalent hybrid laminate. The tests provide valuable insight into damage tolerance and energy absorption under mechanical loading. In addition, this research presents design methodologies to achieve symmetrical bending stiffness

The overview diagram showing the rest of this thesis workflow is illustrated in Figure [4.1](#).

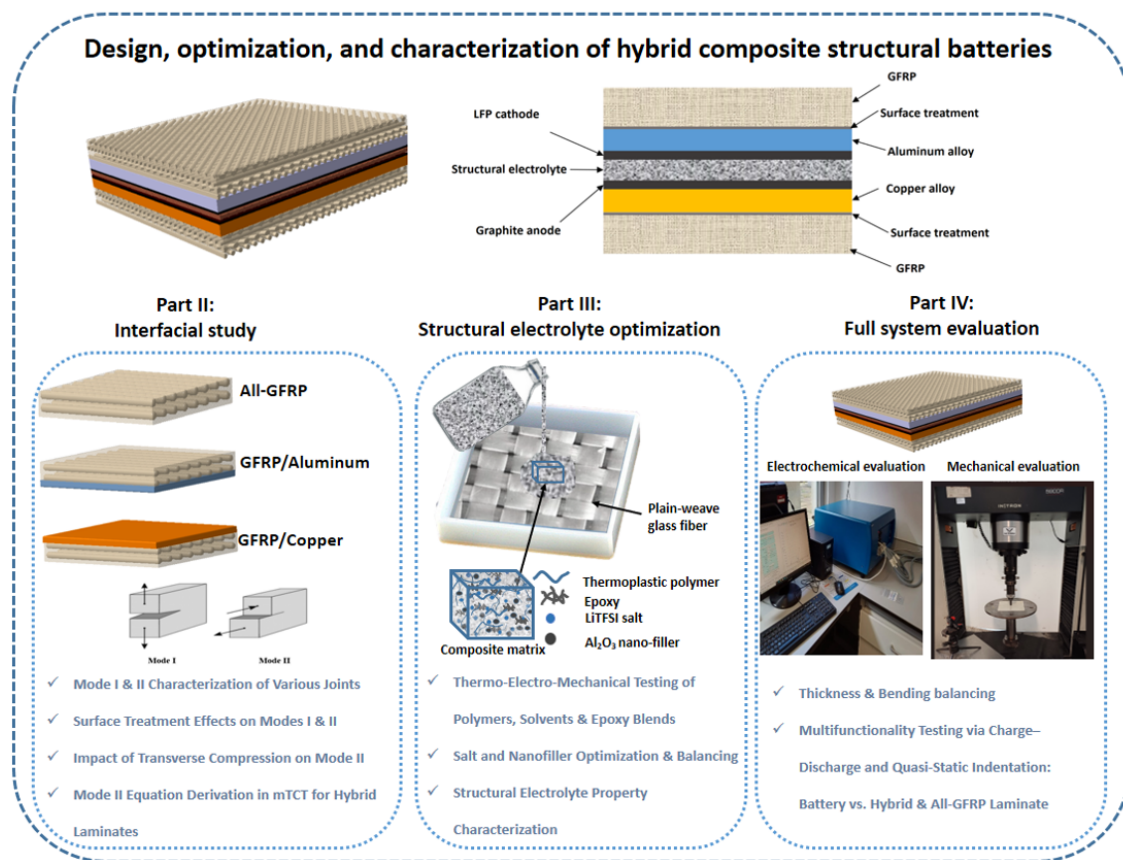


Figure 4.1: Overview Diagram of this thesis: Part II – Interfacial study of structural batteries, Part III – Structural electrolyte optimization and characterization, Part IV – Full system evaluation

Part II

Interfacial study of composite joins used in structural batteries

Chapter 5

Mode I interlaminar fracture toughness study

In this chapter, the effect of various surface treatments on the mode I interlaminar fracture toughness of two hybrid configurations used in structural batteries—GFRP/aluminum laminate and GFRP/copper laminate—is examined. The surface treatments include sulfo-ferric etching, NaOH/HNO₃ etching, and Sol-Gel anodizing for aluminum 2024-T3, and FeCl₃/HCl/Glycerol treatment and Sol-Gel anodizing for copper alloy. The results are compared with untreated conditions and with the baseline all-GFRP configuration. GFRP/metal coupons are designed to achieve pure mode I interlaminar fracture toughness in DCB tests, and the designs are verified using the Virtual Crack Closure Technique (VCCT). The surface characterization of the metals is performed using contact angle tests to estimate the surface free energy, while Coherence Scanning Interferometry (CSI) is used to measure the surface roughness and topography.

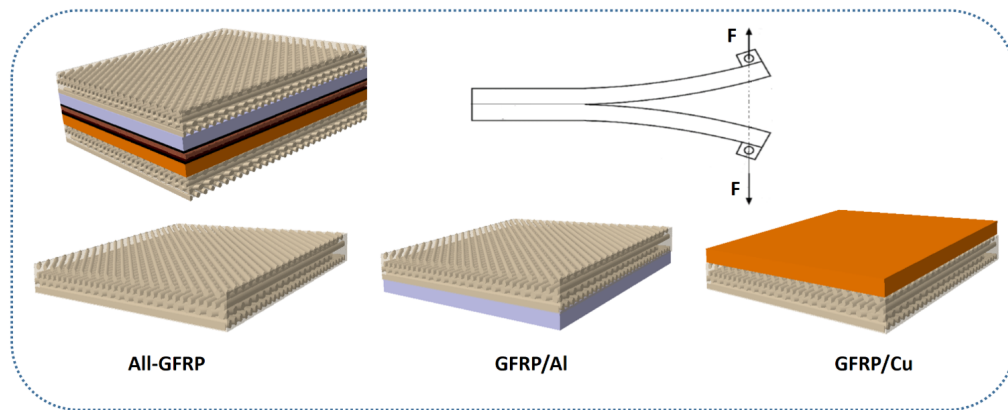


Figure 5.1: Mode I interlaminar fracture toughness study of composite joints used in structural batteries.

5.1 Introduction

In different types of structural batteries, the GFRP stands out as a promising candidate, either as the structural shell for embedding the battery or as an insulating cover for hosting the multifunctional system, due to its excellent mechanical and insulating properties (Qiu (1995)). However, the bonding between GFRP and the current collectors is a concern due to the material discontinuity and the stiffness mismatch that make the interface layer prone to crack nucleation and propagation. This issue can compromise both the structural integrity and the electrochemical efficiency of the system (Moyer et al. (2020a); Di Mauro et al. (2023); Chen et al. (2020a)). In the realm of electrochemical performance, delamination between the composite shell and current collectors causes the system to lose its compactness and strength, compromising the support for the core components of the battery against internal loads caused by charge/discharge cycles (McDowell et al. (2013, 2016); Zhang et al. (2021a)). This may affect the bonding between internal layers, such as electrodes and electrolytes, thereby degrading the cell electrochemical efficiency. Therefore, identifying effective methods to enhance the interlaminar fracture toughness between current collectors and the composite shell is crucial for achieving an efficient energy storage system. Nowadays, aluminum and copper are essential current collectors in batteries, valued in commercial markets due to their electrochemical stability, low cost, abundance, and excellent electrical properties (Jeong et al. (2022); Zhu et al. (2023a)). Aluminum serves as the current collector for the cathode, while copper serves this role for the anode in many commercial battery packs, and these assignments are not interchangeable (Jeong et al. (2022)). When assessing the fracture toughness of bonding between these metals and composite laminate for structural battery applications, simultaneous study of both current collectors is required for evaluating the performance, integrity, and identifying potential weaknesses. Due to the poor adhesive properties of the bare metals, surface treatment prior to bonding is required to enhance interfacial adhesion through mechanical interlocking and by increasing the number of active chemical sites at the metal-composite interface (Ochoa-Putman and Vaidya (2011)). Regarding the aluminum alloy, to date, several methods have been used to improve the surface morphology: mechanical abrasion and grit-blasting, alkaline etching, acidic etching, and anodizing (Park et al. (2010)). Mechanical abrasion and grit-blasting increase the surface roughness, improving the mechanical interlocking between the metal layer and the composite laminate (Aghamohammadi et al. (2018); Lawcock et al. (1997)). The alkaline and acidic etching enhance the adhesion by altering the surface chemical composition and by creating a strong adherent porous oxide layer (Hu et al. (2019); Joshi et al. (2011); Jin et al. (2020)). It has been reported that chemical treatments with NaOH/HNO₃ cause a chemical attack by dissolving the native oxide layer and particles of the aluminum, providing more appropriate layer for bonding with composite (Gonzalez-Canche et al. (2018); Zain et al. (2014)). In addition, some electrochemical methods such as Forest Product Laboratory etching (FPL-etching) (McGarel et al. (1986)), sulfoterric etching (P2-etching) (Prolongo and Ureña (2009); Aghamohammadi et al. (2018)), chromic acid anodizing (CAA) (İlhan and Gürbüz (2021); Critchlow et al. (2006)), and phosphoric acid anodizing (PAA) (Davis et al. (1982); Hardwick et al. (1986)) have been referred as effective

treatments that enhance interfacial bonding of composite and aluminum through making porous nanostructure on the metal surface. For several years after 1950, FPL-etching was very popular in the aerospace industry, however, the use of toxic chromium compounds (e.g. hexavalent chromium) in the treatment process restricted its application in many countries. Therefore, sulfo-ferric etching (P2-etching) was developed in the 1970s as a less toxic alternative with a similar performance (Barkhimer et al. (2015)). During the last ten years, a user-friendly Sol-Gel based technique, with good chemical stability, has been widely used in aerospace field as a potential technique to mitigate the negative effects that are associated with service surface treatments, and to protect metals from common problems such as corrosion, fouling, and wearing (Seifzadeh and Golmoghani-Ebrahimi (2012); Park et al. (2018); Voevodin et al. (2001)). Regarding the copper, E 407–99 standard suggests several chemical treatments. For example, Ferric chloride (FeCl_3) is indicated for small-scale etching process (Çakır et al. (2005)). But less information are currently available in the literature.

The interlaminar fracture of bonded joints is usually a combination of three fracture modes: opening mode (Mode I), shearing mode (Mode II) and tearing mode (Mode III). The Double Cantilever Beam (DCB) test has been extensively used to experimentally measure the mode I critical strain energy release rate (G_{IC}) for symmetric adherents (same material and same thickness) (Cabello et al. (2017); Shi et al. (2023); Todo and Jar (1998)). Due to the high application of FMLs in many areas such as aerospace (Prasad and Wanhill (2017); Asundi and Choi (1997); Sinmazçelik et al. (2011); Niazi and Sadr (2022)) automotive (Heggemann and Homberg (2019)), and multi-functional structural energy devices (Fu et al. (2022)), the interlaminar fracture properties between composite and metal adherents (usually with different thickness) has attracted recent studies (Banea et al. (2018); Wang et al. (2018a); Mujika et al. (2023); Shanmugam et al. (2019); Koord et al. (2023)).

This chapter focuses on assessing the impact of various surface treatments on the mode I interlaminar fracture toughness of two FML configurations deemed suitable for structural batteries: GFRP/Al and GFRP/Cu. The treatments applied to aluminum 2024-T3 included sulfo-ferric acidic etching (P2-etching), NaOH/HNO₃ chemical etching, and Sol-Gel anodizing. For copper, the treatments comprised FeCl_3/HCl /Glycerol chemical etching and Sol-Gel anodizing. The results were subsequently compared with untreated conditions and the symmetric all-GFRP laminates. The hybrid DCB configurations were initially designed using theoretical approaches found in the literature for bi-material systems. These designs were numerically verified by studying the mode mixity at the crack tip using the VCCT. For each treatment, the surface free energy was measured using contact angle tests. Moreover, surface roughness and topography were obtained using the CSI method.

5.2 Materials and method

5.2.1 Materials

The high-strength aluminum alloy Al2024-T3 and copper alloy Cu110-H02, both with a thickness of 2 mm, were sourced from McMaster-Carr. E-glass PPG-600T-15 μ -25 gsm-300 mm-TP736LT was used as the thin-ply lamina. The mechanical properties of the E-glass fiber lamina were calculated using the rule of mixtures and are shown in Table 5.1. The mechanical properties of the aluminum alloy and copper alloy are shown in Table 5.2, where E_1 is Young's modulus in the longitudinal (fiber) direction, E_2 is Young's modulus in the transverse and thickness direction, and ν_{12} and G_{12} are the Poisson's ratio and shear modulus, respectively. E and ν represent the Young's modulus and Poisson's ratio of the metals. The parameters σ_y and σ_u represent the yield strength and ultimate tensile strength of the metals, respectively.

Table 5.1: Mechanical properties of E-Glass Lamina.

E_1 (GPa)	E_2 (GPa)	ν_{12}	G_{12} (GPa)
40	6.43	0.298	2.735

Table 5.2: Mechanical properties of metals.

Material	E (GPa)	ν	σ_y (MPa)	σ_u (MPa)
Aluminum 2024-T3	73	0.33	316	457
Copper 110-H02	117	0.3	261	289

5.2.2 Pretreatment

After cutting the aluminum and copper sheets to the specified dimensions of the DCB specimens (200 mm $\times$ 25 mm) using a 5-axis DMG-DMU-60eVo CNC machine, surface treatments as outlined in Table 5.3 were applied. The procedures for each treatment are detailed in the following subsections.

Table 5.3: The selected surface treatments for metals.

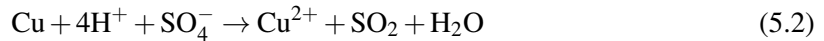
Metals	Surface Treatments
Aluminum	Without treatment
	P2-etching
	NaOH/HNO ₃
	Sol-Gel
Copper	Without treatment
	FeCl ₃ /HCl/Glycerol
	Sol-Gel

Before starting any treatment, all metal substrates were cleaned using a soft sponge, soap, and water to remove dust and contaminants originating from manufacturing processes. This was followed by rinsing with deionized water and drying at 40 °C in an oven for 1 hour. Each substrate

surface was then cleaned with acetone and dried at room temperature. Subsequently, the substrates were manually sanded using 800-grit sandpaper, followed by cleaning with acetone and drying at room temperature. It's worth noting that all configurations, including those labeled "without treatment," incorporate a preliminary step for surface pretreatment to ensure proper cleaning of the metal substrates.

5.2.3 P2-etching of aluminum

Following the procedure specified in (Barkhimer et al. (2015); Wegman and Van Twisk (2012)), P2-paste was made by mixing 5 g of concentrated sulfuric acid, 2 g of 75% ferric sulfate, and 10 g deionized water. After pretreatment of the aluminum substrates, the P2 solution was applied on their surfaces and then left at room temperature for 25-30 minutes. The sulfuric acid in the P2 paste resulted in the following chemical reactions, on the aluminum and copper components of the aluminium substrates:



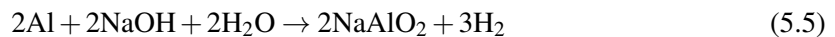
The reaction continues with ferric sulfate of P2-paste, where ferric sulfate make pitting of the alloy surface, leading to non-uniform attack at specific areas (Barkhimer et al. (2015)).



Afterwards, the substrates were cleaned with deionized water and dried at room temperature.

5.2.4 Chemical etching of aluminum with NaOH-HNO₃

Following the procedure specified in (Gonzalez-Canche et al. (2018)) and (Zain et al. (2014)), after pretreatment, the aluminium substrates were immersed in NaOH (5%) solution for 5 minutes, forming sodium aluminate (NaAlO₂) and hydrogen gas according to etching reaction:



Afterward, the substrates were cleaned by rinsing with deionized water. During this step, NaAlO₂ hydrolyzed in the presence of water, resulting in Al(OH)₃ as shown in Eq. (5.6).



Then, during the drying step (at 40°C for one hour), aluminum quickly oxidized to aluminum oxide (Al_2O_3), as shown in Eq. (5.7), forming a thin (approximately 10 nm), unstable layer that can result in poor bonding if cured with the composite at this stage (see Figure 5.2 (a)).



Finally, the aluminum substrates were immersed in a 30% weight nitric acid (HNO_3) solution for 45 seconds to clean the metallic unstable particles on the surface, resulting in a new rough layer of Al_2O_3 that is appropriate to be bonded to the composite (Gonzalez-Canche et al. (2018); Zain et al. (2014)). Subsequently, the substrates were rinsed with deionized water at room temperature. The substrates were then dried in an oven at 40°C for one hour (see Figure 5.2 (b)).

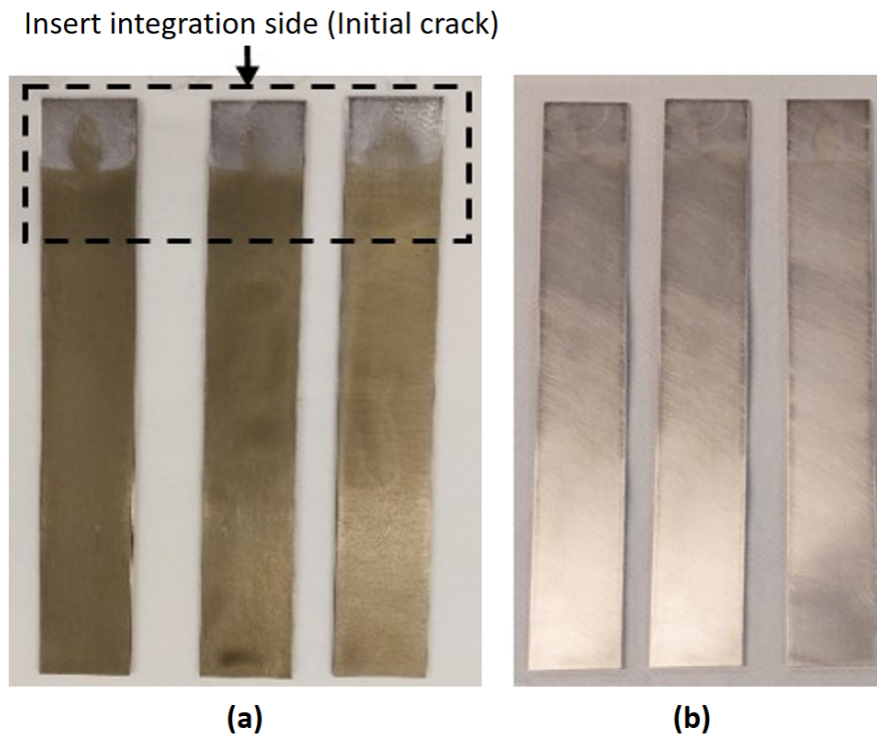


Figure 5.2: Chemical etching of aluminum with NaOH-HNO_3 .

5.2.5 Sol-Gel anodizing of aluminum and copper

Sol-Gel anodizing was performed using the 3M-AC-130-2 aerospace sealant, which consists of Part A—a water solution containing propyl alcohol, zirconium n-propoxide, acetic acid, and water—and Part B, GTMS—a blend of 3-glycidoxy propyl-trimethoxysilane and methyl alcohol (see Figure 5.3). The Sol-Gel paste was prepared by mixing Part A and Part B in compliance with the supplier's recommended ratio of 49.2:1.06, until a transparent and homogeneous solution was achieved. Following pretreatment of aluminum and copper substrates, the Sol-Gel solution was applied uniformly to cover their entire surface area. Subsequently, the substrates were air-dried at room temperature for approximately one hour. This treatment involves the growth of metal-oxo

polymers through hydrolysis (Eq. (5.8)) and condensation (Eq. (5.9)), resulting in the formation of a thin, inorganic zirconium oxide film incorporated with epoxy-silane on the metal surface (Park et al. (2018); Voevodin et al. (2001); Rider et al. (2005)).

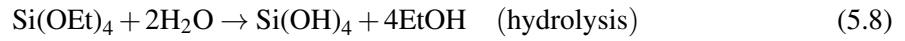
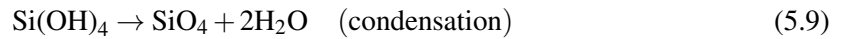
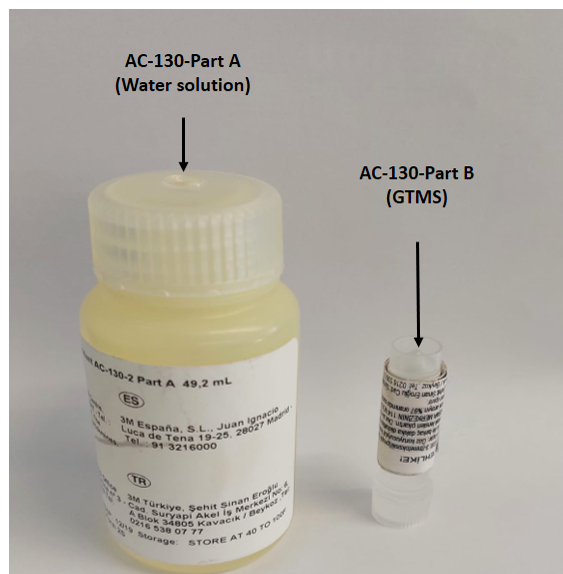


Figure 5.3: Sol-Gel components.

5.2.6 Chemical etching of copper with $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$

According to ASTM E 407–99 standard, a mixture was prepared by combining 1 g of ferric chloride (FeCl_3), 2 mL of HCl , 10 mL of glycerol, and 3 g of deionized water. The components were stirred until a homogeneous solution was achieved. Following the pretreatment stage of copper substrates, the solution was applied to their surface using a swab for 60 seconds (see Figure 5.4). Subsequently, the treated substrates were rinsed with warm deionized water and then air-dried at room temperature for approximately one hour.

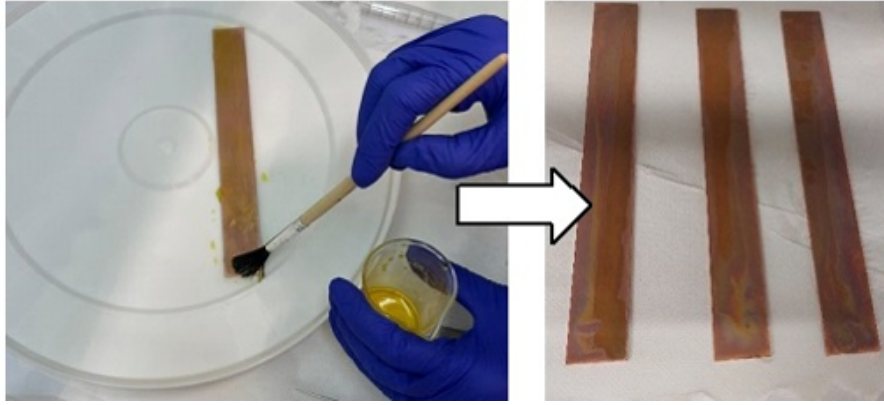


Figure 5.4: chemical etching of copper alloy with $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$.

5.2.7 Designs of hybrid DCBs

As discussed in the literature, for asymmetric DCBs, achieving pure mode I interlaminar fracture toughness typically requires matching the flexural stiffness of the two arms. Otherwise, shear stress in the interface of dissimilar adherents results in a mixed-mode loading scenario (Ouyang et al. (2011); Wang et al. (2018a); Gong et al. (1999)). Ouyang et al. (Ouyang et al. (2011)) developed an accurate method to estimate the thickness of each arm in bi-material DCB systems under pure mode-I loading. Their theoretical approach suggests that the condition $Eh_m^2 = E_x^f h_c^2$, where E is the Young's modulus of the metal arm, h_m and h_c are the thicknesses of the metal arm and composite arm, respectively, and E_x^f is the longitudinal flexural stiffness of the composite arm, minimizes the effects of shear stresses and results in a pure mode-I loading scenario. This method was validated by numerical and experimental studies (Ouyang et al. (2011); Wang et al. (2018a)). In this study, by applying this condition ($Eh_m^2 = E_x^f h_c^2$) and using the classical laminate theory, the thickness of the composite arms for both hybrid configurations (GFRP/Al and GFRP/Cu) was determined based on the specified thickness of the metal arms. The longitudinal flexural stiffness of composite arm, E_x^f , can be obtained by using (Wang et al. (2018a)):

$$E_x^f = \frac{12}{(h_c^3)D_{11}^*} \quad (5.10)$$

where D_{11}^* is the element at the first row and first column of $[D]^*$, which can be calculated by using the classical laminated plate theory (Eq. (5.11)).

$$\begin{bmatrix} \epsilon^0 \\ \bar{k} \end{bmatrix} = \begin{bmatrix} A & B \\ B & D \end{bmatrix}^{-1} \begin{bmatrix} N \\ M \end{bmatrix} = \begin{bmatrix} A^* & B^* \\ B^* & D^* \end{bmatrix} \begin{bmatrix} N \\ M \end{bmatrix} \quad (5.11)$$

The ABD-matrix in Classical Laminate Theory (CLT) serves as a fundamental tool for determining the mid-plane strains ϵ^0 and curvatures $\bar{k}$ resulting from applied in-plane loads N and bending moments M . It is composed of three submatrices: A , the extensional stiffness matrix; B , the bending-extension coupling matrix; and D , the bending stiffness matrix. These matrices collectively describe how the laminate resists deformation under mechanical loading. By inverting

the ABD-matrix, the corresponding compliance matrices A^* , B^* , and D^* are obtained, which relate applied forces and moments to resulting strains and curvatures. The strain vector ε^0 includes the mid-plane normal and shear strains, while $\bar{k}$ represents the laminate curvatures. The terms h_m and h_c denote the thicknesses of the metal and composite layers, respectively. Additionally, E_x^f represents the longitudinal flexural stiffness of the composite, and E is the Young's modulus of the material. The resulting configurations were numerically tested in Abaqus (Hibbitt et al. (2002)) to ensure there was no plastic yielding in the metal arms during quasi-static fracture testing. The final designed configurations are presented in Table 5.4, and shown in Figure 5.5.

Table 5.4: Configuration of GFRP/Al and GFRP/Cu laminates.

	GFRP/Al	GFRP/Cu
Lay up of GFRP	$[0^\circ/45^\circ/90^\circ/-45^\circ]_{20S}$	$[0^\circ/45^\circ/90^\circ/-45^\circ]_{25S}$
h_c (mm)	4	5
h_m (mm) [theoretical thickness]	2 [1.99]	2 [1.96]
E_x^f (MPa)	18106	18022

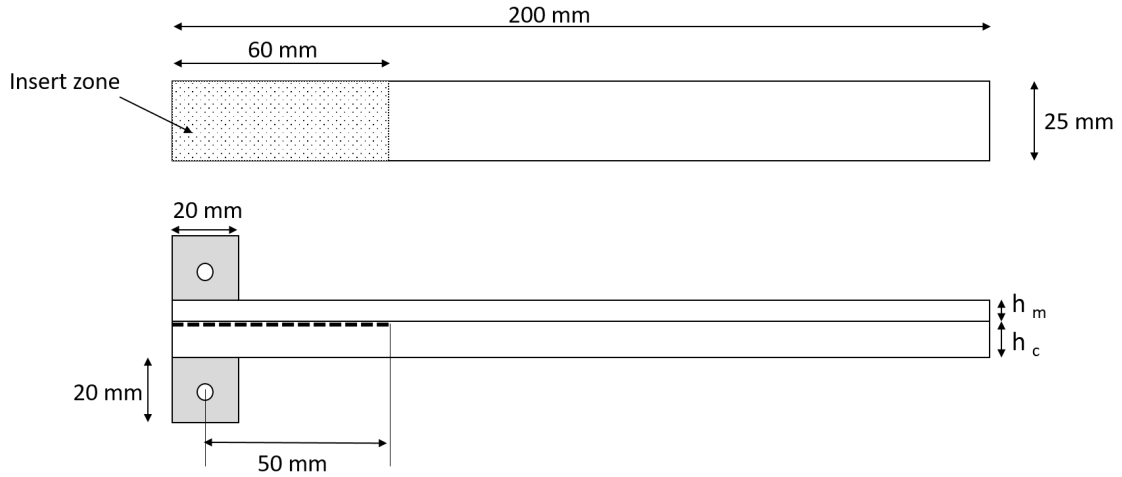


Figure 5.5: Dimensions of the DCB specimens.

5.2.8 Verification of the numerical methodology

In order to check the accuracy of the numerical methodology, two DCB simulations, a symmetric DCB and an asymmetric hybrid DCB, were modeled in Abaqus to verify the fracture behaviour of the DCB joints, methodology, elements, boundary condition with reference results from the literatures. The symmetric DCB used in Turon Travesa et al. (2006) was modeled by using incompatible C3D8I solid elements with size of between 0.5 mm and 2 mm, and COH3D8 cohesive elements with size of 0.5mm. A thickness of 0.01 mm was used for the interface elements. In second verification, an asymmetric hybrid DCB with configuration of steel/GFRP and dimension and the properties used in Wang et al. (2018a) was simulated using the same element type and

size as in the previous simulation. The illustrated results of Figure 5.6 shows a good agreement between the current approach and reference results.

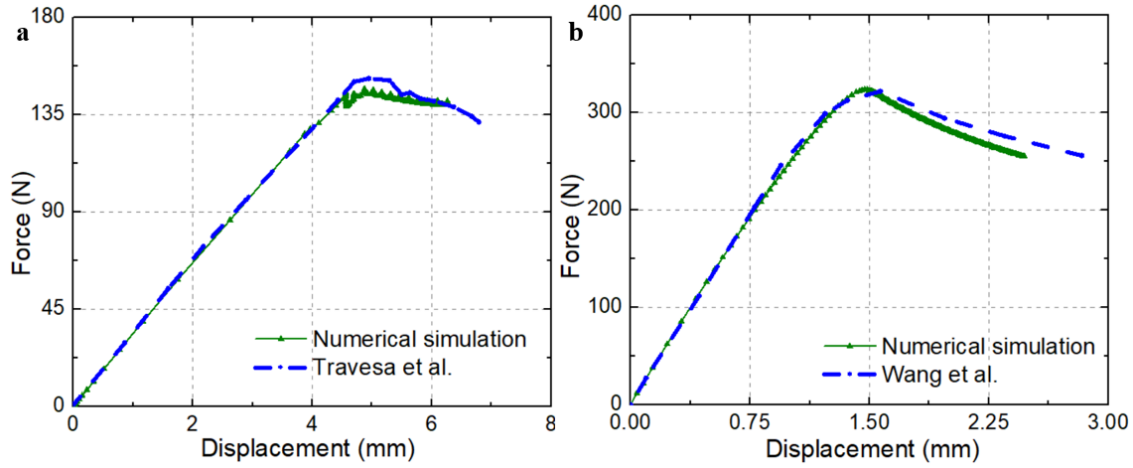


Figure 5.6: Verification of the numerical simulations: (a) Symmetric DCB (Turon Travesa et al. (2006)); (b) Asymmetric hybrid DCB (Wang et al. (2018a)).

5.2.9 VCCT validation of the designed DCBs

The 3D-VCCT was employed to calculate mode-mixity and determine the energy release rate profiles at the crack tip line (Rybicki and Kanninen (1977)). The model was defined as linear elastic. Both the GFRP and metal arms were modeled by properly partitioning a single part. To represent the initial crack, a seam was assigned to the relevant partition of pre-existing delamination. Figure 5.7 (a) illustrates the boundary conditions applied in the numerical models: on the crack side of the DCB, the outer edge of each adherend along the width were subjected to an opening displacement in out-of-plane direction. Figure 5.7 (b) shows the mesh configuration of the numerical models. C3D8I (8-node linear brick, incompatible modes) were employed for the finite element mesh. The first eight plies of the GFRP were modeled separately using partitions and each ply was meshed with one element through its thickness. Through the length of the specimen, the mesh size was varied from 0.25 mm near the crack tip to 2 mm in regions farther from the crack tip. For the thickness, except for the first 8 plies, the mesh size was varied from 0.25 mm to 0.5 mm. The element size through the width of the specimens was fixed at 0.25 mm. The total number of elements in the model was 314000. By obtaining the displacement of the nodes adjacent to the crack tip and using the nodal forces at the crack tip nodes, along with the equations of VCCT (Krueger, Ronald (2004)) (Eq. 5.12, Eq. 5.13, and Eq. 5.14), the contribution of each mode of interlaminar fracture toughness was determined.

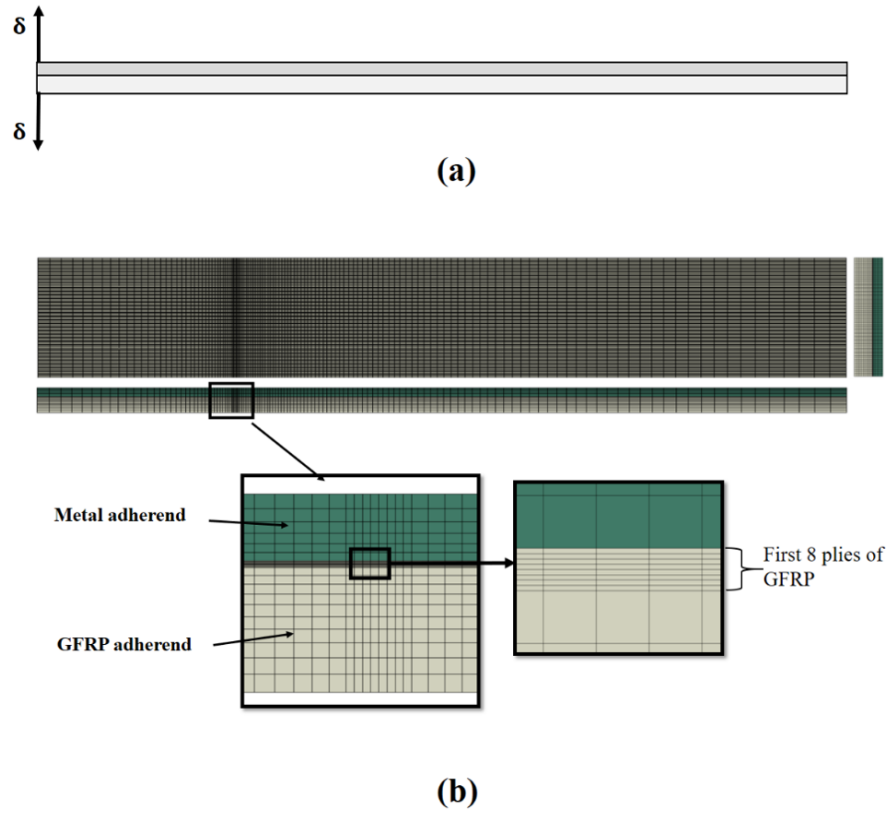


Figure 5.7: Finite element model of hybrid DCBs: (a) Boundary conditions; (b) Mesh overview.

According to the VCCT (Figure 5.8), when the crack propagates by a small increment of crack length, the released strain energy is equal to the required energy for closing the crack by the same length.

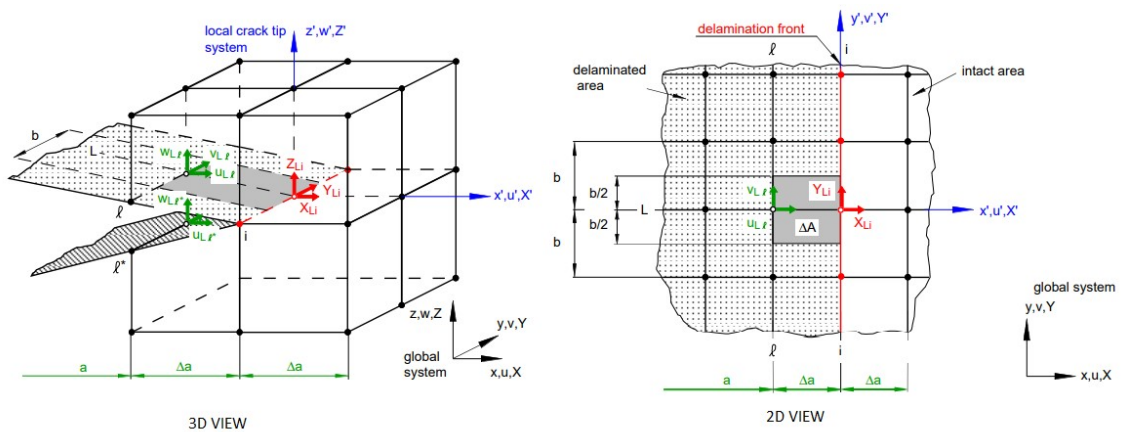


Figure 5.8: Nodal displacement in 3D element of VCCT model (Krueger, Ronald (2004)).

The energy release rates for mode I, mode II, and mode III components, denoted as G_I , G_{II} , and G_{III} , respectively, are calculated for three-dimensional solid elements with 8 nodes according

to the following equations:

$$G_I = \frac{1}{2\Delta a.b} Z_{Li}(w_{Li} - w_{Li}^*) \quad (5.12)$$

$$G_{II} = \frac{1}{2\Delta a.b} X_{Li}(u_{Li} - u_{Li}^*) \quad (5.13)$$

$$G_{III} = \frac{1}{2\Delta a.b} V_{Li}(v_{Li} - v_{Li}^*) \quad (5.14)$$

$$G_T = G_I + G_{II} + G_{III} \quad (5.15)$$

where X_{Li} , Y_{Li} and Z_{Li} represent the internal nodal forces acting at the crack-tip node along the x, y, and z direction. Also, u_{Li} , v_{Li} , w_{Li} , u_{Li}^* , v_{Li}^* , and w_{Li}^* are the displacements of the top face and lower face adjacent nodes Li and Li^* , respectively (see Figure 5.8). The element size at the crack tip, denoted as Δa , and b , representing the width of the specimen.

The energy release rates for mode I, mode II, and mode III components were calculated for GFRP/Al and GFRP/Cu laminates. Afterwards, the energy release rates were divided by the total energy release rate (the sum of all components) to calculate the relative contribution of each mode. Results for different crack lengths, including 50 mm, 60 mm, 70 mm, 80 mm, 90 mm, and 100 mm, are provided in Figures 5.9 and 5.10. For all crack lengths investigated, the findings indicated that the design of both hybrid laminates predominantly exhibits mode I behavior (around 97%), with mode II contributing approximately 3% and mode III less than 0.01%.

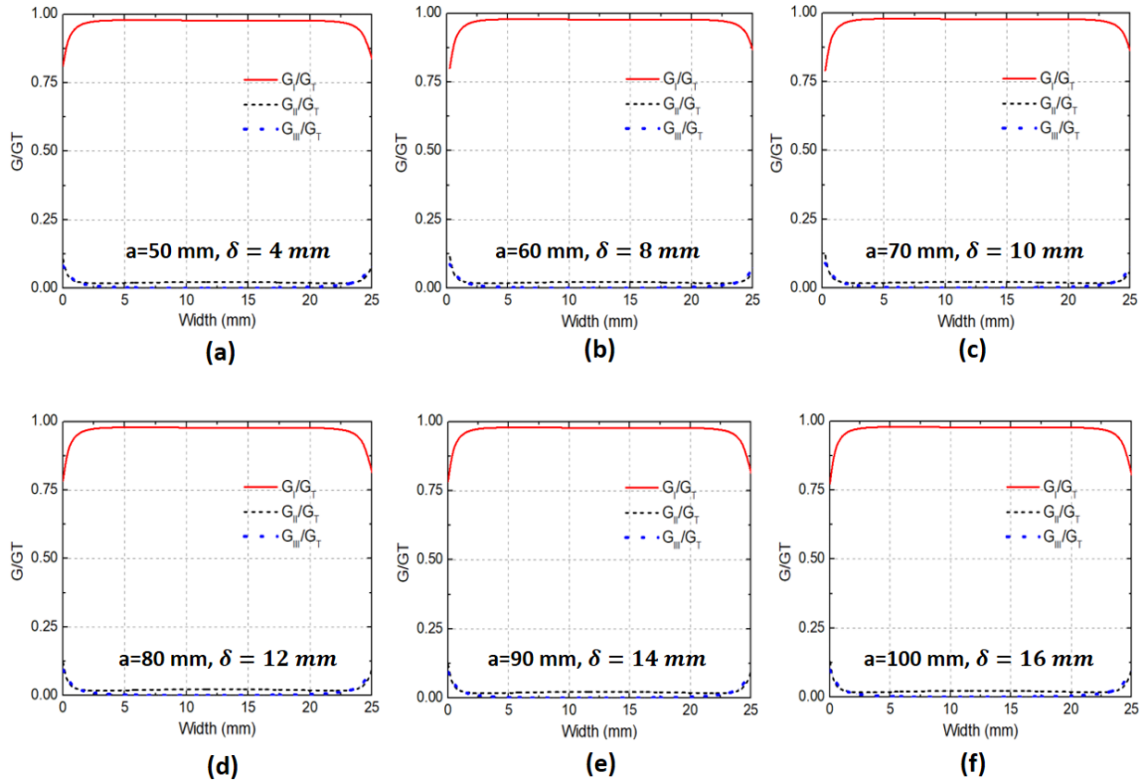


Figure 5.9: Mode mixity of GFRP/Al laminates with different crack lengths: (a) $a = 50$ mm; (b) $a = 60$ mm; (c) $a = 70$ mm; (d) $a = 80$ mm; (e) $a = 90$ mm; (f) $a = 100$ mm.

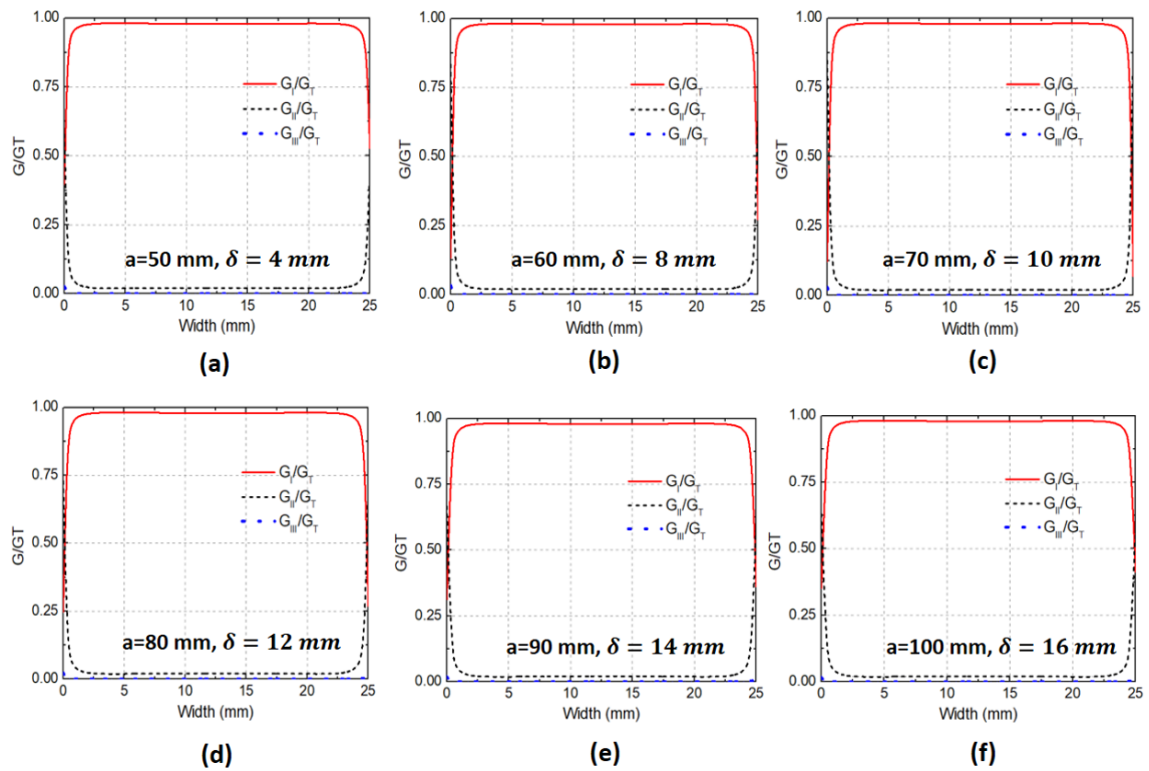


Figure 5.10: Mode mixity of GFRP/Cu laminates with different crack lengths: (a) $a = 50$ mm; (b) $a = 60$ mm; (c) $a = 70$ mm; (d) $a = 80$ mm; (e) $a = 90$ mm; (f) $a = 100$ mm.

5.2.10 Manufacturing DCB specimens and testing procedure

The procedures for manufacturing and testing the DCB specimens are illustrated in Figure 5.11. The GFRP laminates were manufactured through hand layup and cut using a roller cutter, aligning it with metal sheets as a reference and adopting the dimensions of the DCB specimen ($200 \text{ mm} \times 25 \text{ mm}$) (see Figure 5.11 (a)). The insert was manufactured from an Upilex film with a thickness of $25 \text{ }\mu\text{m}$, simulating an initial artificial crack of approximately 50 mm . The metal adherends were co-cured with the GFRP laminate using a hot press at a pressure of 25 bar and temperatures specified by the supplier ($1 \text{ hour at } 70^\circ\text{C}$ and $3 \text{ hours at } 100^\circ\text{C}$) (see Figure 5.11 (b)). After curing, the thickness of the hybrid laminate was measured to be 5.7 mm for GFRP/Al and 6.6 mm for GFRP/Cu. To prepare the specimens for DCB tests, parallelepipedal steel blocks were used (Figure 5.11 (c)). These blocks measured $25 \text{ mm} \times 20 \text{ mm} \times 20 \text{ mm}$ and had a central hole with a diameter of 6.2 mm . They were placed on the pre-crack sides of the specimens using an epoxy-based adhesive and a mould with appropriate reference pins to ensure alignment. The DCB tests were performed in compliance with the ASTM-D5528 standard test method. Quasi-static tests were conducted using a 1 kN load-cell tensile testing machine under displacement control at a rate of 1 mm/min (see Figure 5.11 (d)). Digital photos were made every two seconds by using Canon EOS 80D camera. The pre-crack was extended by 3 to 5 mm from the insert prior to testing, as recommend in the standard for inserts thicker than $13 \text{ }\mu\text{m}$. The crack length was calculated as the distance between the crack tip and the center-line of the pins of the blocks.

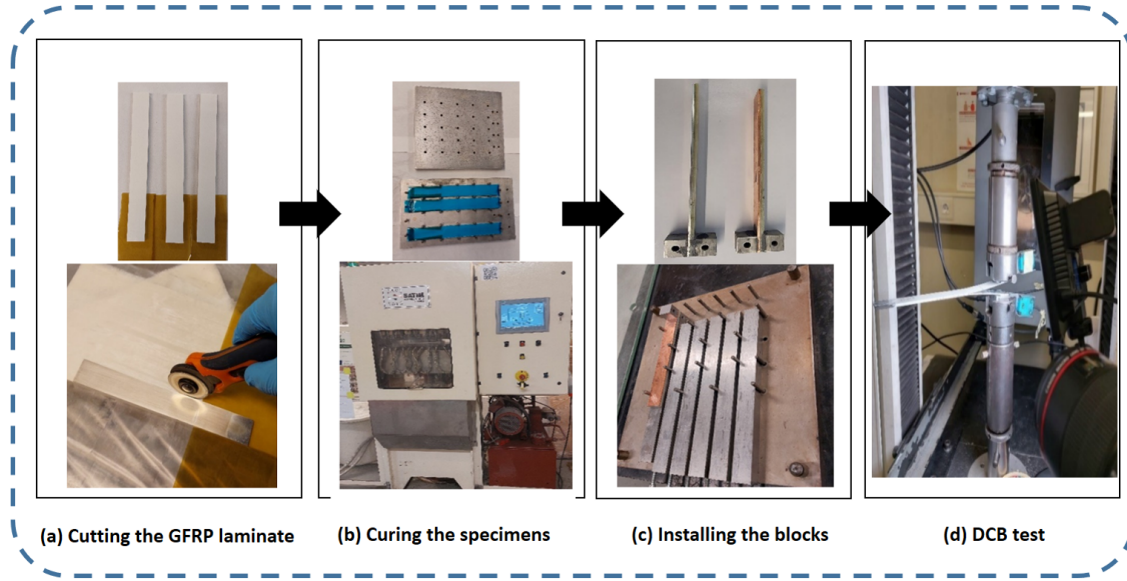


Figure 5.11: Procedures of manufacturing and testing hybrid DCB specimens: (a) Cutting the GFRP laminate and manufacturing DCB specimens; (b) Curing inside hot press; (c) Installation of blocks; (d) DCB test.

The mode I interlaminar fracture toughness of each specimen was measured using the Modified Beam Theory (MBT) based on the ASTM D5528 standard. Accordingly, the fracture toughness is given by:

$$G_I = \frac{3F\delta}{2b(a + |\Delta|)} \quad (5.16)$$

Where F is the applied opening load, δ is the load-point vertical displacement, and b is the specimen width. In the context of the MBT, $|\Delta|$ is used to define an effective crack length which accounts for non-zero rotations of the crack tip. The fracture toughness in each DCB test was determined by analyzing the stable part of the each resistance curve (R-curve). Three separate samples were examined for each configuration to assess setup repeatability. In the following subsections, the averages of the R-curve and load-displacement are presented for each group of specimens. Additionally, the coefficient of variation (CV) was calculated for each dataset to illustrate the extent of variation within each group of data, focusing on the stable plateau of the R-curve.

5.3 Results and discussion

5.3.1 Contact angle test

Contact angle tests were conducted on the surfaces of aluminum and copper substrates, each with dimensions of 25 mm × 40 mm, and subjected to various surface treatments as discussed previously. The experiments were carried out utilizing an OCA15 Neurtek goniometer, employing three distinct liquids: water, ethylene glycol 55%, and n-hexadecane. After adjusting the tester,

camera, and the substrate, a small droplet (around 5 μL) of each liquid was placed on the surface of the substrates, by using the dosing unit (see Figure 5.12).

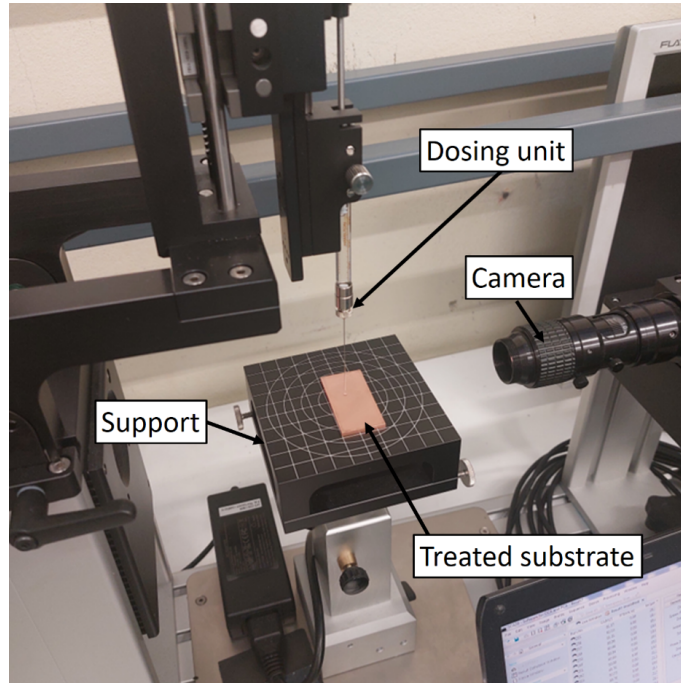


Figure 5.12: Contact angle test set-up.

The image of the droplet was captured using an optical camera. The static contact angle was measured by the SCA15 software after defining the base line of the surface and droplet shape of the liquid droplet. The Owens, Wendt, Rabel, and Kaelble method (OWRK-model) was used as a standard method for calculating the Surface Free Energy (σ_s) of metal surfaces from the contact angle (θ) (Owens and Wendt (1969); Loeb and Schrader (2013)). Accordingly, based on Young's equation, a relationship between the contact angle θ , the surface tension of the liquid σ_l , the interfacial tension σ_{sl} between liquid and solid, and the surface free energy σ_s of the substrate is established as:

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos \theta \quad (5.17)$$

OWRK-model, considers the geometric mean of the dispersive and polar parts of the liquid's surface tension σ_l and of the solid's surface free energy (σ_s) as the following equation:

$$\sigma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^d + \sigma_l^d} + \sqrt{\sigma_s^p + \sigma_l^p}) \quad (5.18)$$

By substituting this expression into Eq. (5.17) and using the surface tension of the liquids (shown in Table 5.5), the results for the polar and dispersive parts of the surface free energy were obtained. The overall surface free energy was determined by summing both the polar and dispersive components.

Table 5.5: Surface tensions of the different liquids used in contact angle test.

Liquid	σ_l (mJ/m ²)	σ_l^d (mJ/m ²)	σ_l^p (mJ/m ²)
Water	72.8	22.6	50.2
Ethylene glycol	48.8	32.8	16
n-hexadecane	27.5	27.5	0

The experimentally determined contact angle (θ), which is the angle between the metal-liquid interface and the liquid-gas interface, is shown in Table 5.6.

Table 5.6: Contact angle (θ) of aluminum and copper substrates with different treatments.

Metal	Surface treatment	Contact angle (degrees)		
		Water	Ethylene glycol	n-hexadecane
Al	Without treatment	97.6	66.9	14
	P2 etching	84.7	55.4	0
	NaOH/HNO ₃	56.4	39.6	0
	Sol-Gel	71.5	82.5	0
Cu	Without treatment	107.7	74.7	16
	FeCl ₃ /HCl/Glycerol	100.9	41.3	0
	Sol-Gel	83.5	53.9	0

Accordingly, $\theta = 0^\circ$ indicates the liquid completely wetted the substrate, $0^\circ < \theta < 90^\circ$ shows high wettability, $90^\circ < \theta < 180^\circ$ indicates low wettability of the surface.

Figure 5.13 shows the ethylene glycol droplet and its contact angles on aluminium and copper substrates treated with Sol-Gel anodizing. The image reveals that the copper substrate exhibited a lower contact angle, indicating higher wettability compared to the aluminum substrate under the same treatment condition. This enhanced wettability suggests potentially stronger adhesive bonding between the copper and the GFRP laminate compared to the one between aluminum and GFRP laminate.

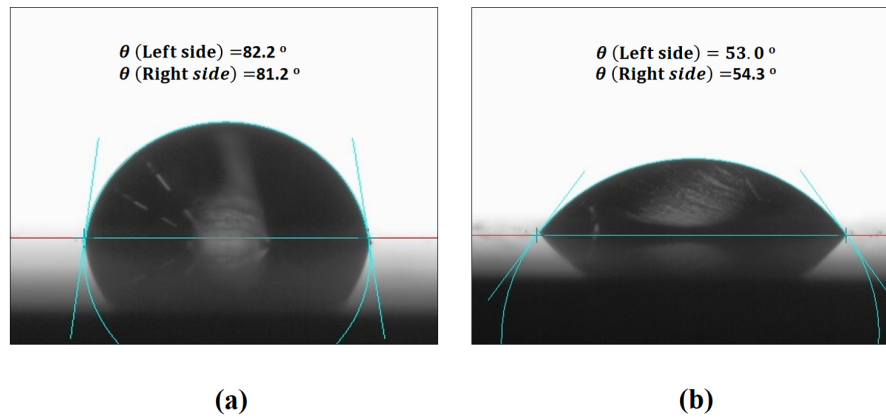


Figure 5.13: Ethylene glycol droplet on substrates with Sol-Gel anodizing treatment: (a) Aluminum substrate; (b) Copper substrate.

The surface free energy (σ_s) of various substrates, as presented in Table 5.7, reveals notable variations due to different chemical treatments. Chemical etching with NaOH/HNO₃ significantly affected the surface free energy of aluminum (43 mJ/m²), compared to untreated substrate (27.8 mJ/m²), Sol-Gel anodizing (30 mJ/m²), and P2-etching (31.8 mJ/m²). For copper, chemical etching with FeCl₃/HCl/Glycerol resulted in a higher surface free energy of 34.8 mJ/m², compared to untreated substrates (27 mJ/m²) and Sol-Gel anodizing (32.3 mJ/m²).

Table 5.7: Surface free energy of different substrates, σ_s (mJ/m²).

Surface Treatment	Aluminum	Copper
Without Treatment	27.8	27
P2-etching	31.8	-
NaOH/HNO ₃	43	-
Sol-Gel	30	32.3
FeCl ₃ /HCl/Glycerol	-	34.8

5.3.2 Surface roughness

Coherence Scanning Interferometry (CSI) was used to measure the surface roughness and topography with nanometric precision. The 3D surface characterization of the specimens was performed using a non-contact measurement system NPFLEX from Bruker. It is an optical unit with an XLWD Industrial Objective with 10 times magnification, a working distance of 34 mm, an aperture of 0.28 and an optical resolution based on Sparrow Criteria at 535 nm of 1 μ m. The vertical resolution was less than 15 nm.

Surface roughness parameter, S_a , directly influence the contact area and strength of mechanical interlocking between the metal and composite layers. Higher S_a values typically result in increased micro-asperities and contact points, enhancing the mechanical interlocking capability. This, in turn, improves the load transfer across the interface and contributes to the overall fracture toughness by resisting crack propagation (Gent and Lin (1990)).

The surface roughness measurement, S_a , was determined as the arithmetic mean of the absolute heights within a sampling area, $4.8 \text{ mm} \times 4.8 \text{ mm}$ square region extracted from the center of the specimen:

$$S_a = \frac{1}{A} \int |z(x,y)| dx dy \quad (5.19)$$

where A is the sampling area in the xy plane, and z is the height of each point of the sample.

The 2D profiles of the surfaces of both aluminum and copper, each subjected to different surface treatments, are shown in Figures 5.14 and 5.15, respectively.

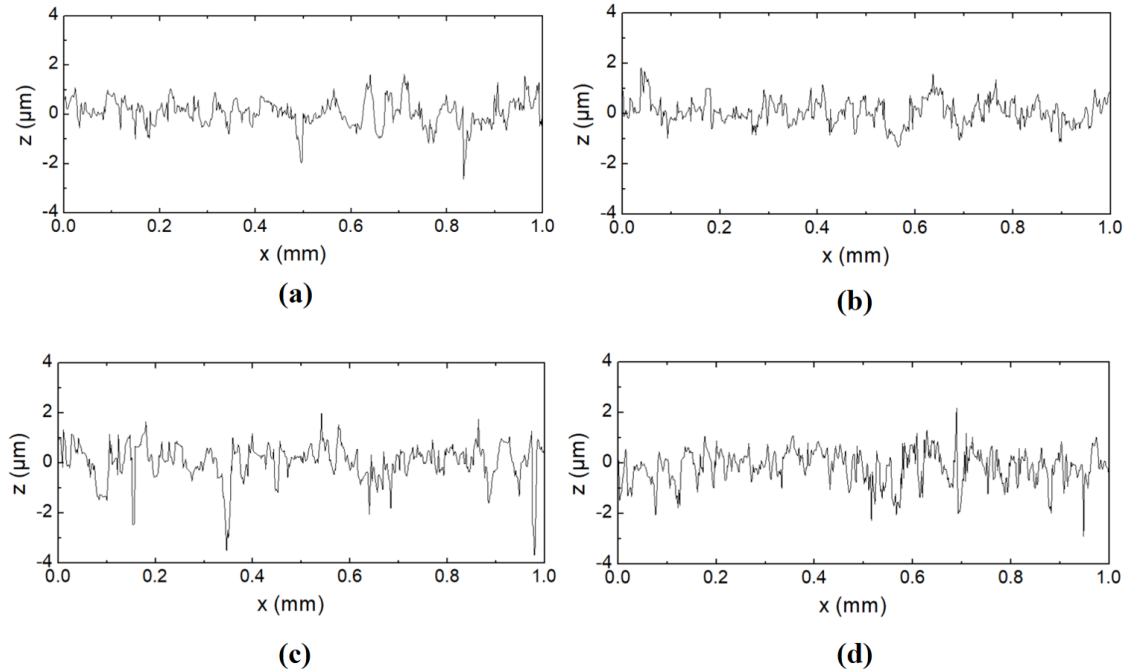


Figure 5.14: The 2D surface profiles of aluminum with different surface treatments: (a) Without treatment; (b) P2-etching; (c) NaOH/HNO₃; d. Sol-Gel anodizing.

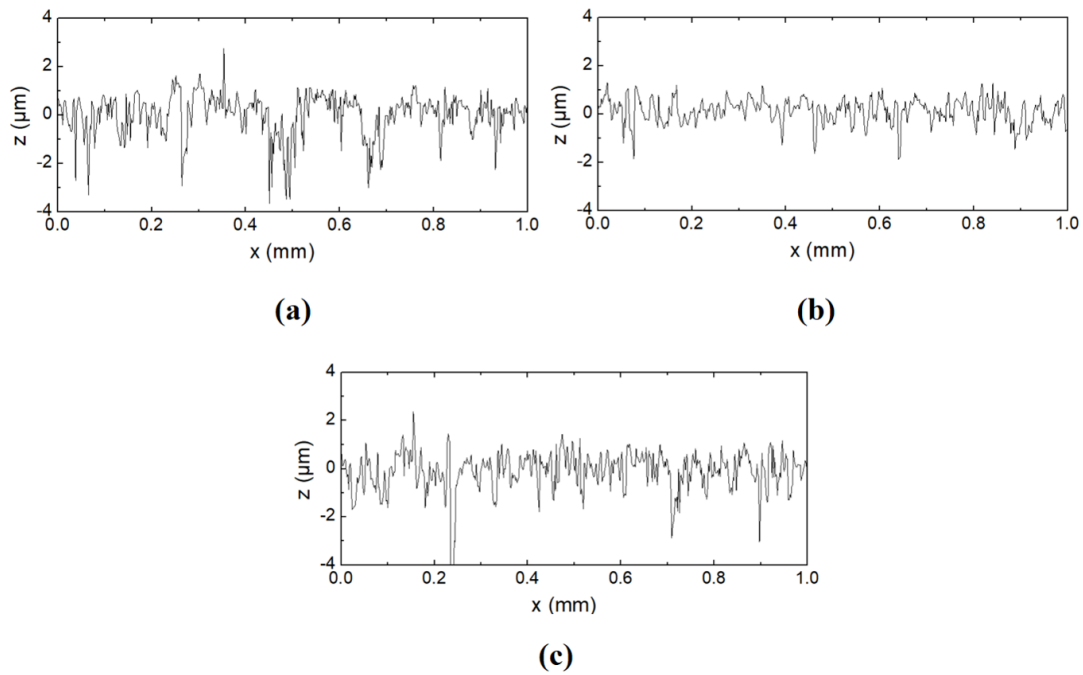


Figure 5.15: The 2D surface profiles of copper with different surface treatments: (a) Without treatment; (b) $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$; (c) Sol-Gel anodizing.

The surface roughness of different substrates is presented in Table 5.8. Accordingly, Sol-Gel anodizing had the strongest effect on the surface roughness of both substrates, especially the copper substrate with a peak of $0.71 \mu\text{m}$, whereas untreated copper displayed the lowest roughness of $0.41 \mu\text{m}$. NaOH/HNO_3 of aluminum and $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$ of copper substrates both resulted in similar surface roughness of $0.56 \mu\text{m}$. In the context of P2-etching of aluminum substrates, a noticeable reduction in roughness from $0.45 \mu\text{m}$ to $0.43 \mu\text{m}$ was observed in comparison to untreated specimens. This phenomenon arose from the chemical action induced by ferric sulfate and sulfuric acid during the etching process. This chemical interaction targeted and diminished the height of peak points, which were originally formed during the preliminary cleaning step with sanding paper in the pretreatment stage.

Table 5.8: Surface roughness of different substrates, $S_a(\mu\text{m})$.

Surface Treatment	Aluminum	Copper
Without Treatment	0.45	0.41
P2-etching	0.43	-
NaOH/HNO_3	0.56	-
Sol-Gel	0.62	0.71
$\text{FeCl}_3/\text{HCl}/\text{Glycerol}$	-	0.56

5.3.3 Mode I interlaminar fracture toughness of all-GFRP laminate

Thin-ply E-glass laminates were tested in DCB experiments with two distinct configurations: unidirectional $[0]_{72S}$ and quasi-isotropic $[0^\circ/45^\circ/90^\circ/-45^\circ]_{18S}$. The quasi-isotropic configuration,

strategically designed within the hybrid laminate to mitigate thermal residual stress, was selected for comparison with the ASTM D5528-standardized unidirectional configuration. This comparison aims to explore variations in crack propagation behavior between the two configurations. The R-curve and load-displacement data for both configurations are depicted in Figure 5.16. In this dataset, GG_UD refers to the curves associated with unidirectional GFRP samples, while GG_QI denotes the curves for quasi-isotropic GFRP specimens. The average G_{IC} values of both configurations, along with their relative CVs, are presented in Table 5.9. The unidirectional (UD) GFRP exhibited an average value of 0.86 N/mm for G_{IC} with a CV of 6%, while the quasi-isotropic (QI) configuration showed an average G_{IC} of 0.52 N/mm with a CV of 4%. A similar study conducted by Shokrieh and Heidari-Rarani (2011) reached the same conclusion, finding that unidirectional laminates result in higher G_{IC} values compared to multidirectional laminates. This difference can be attributed to the higher amount of fiber bridging observed in the unidirectional configuration, which originated not only from the first ply but also involved fiber bridging from adjacent plies near the interface (see Figure 5.17 (a)). In contrast, for the quasi-isotropic laminate, fiber bridging primarily arose from the first ply at the interface (see Figure 5.17 (b)).

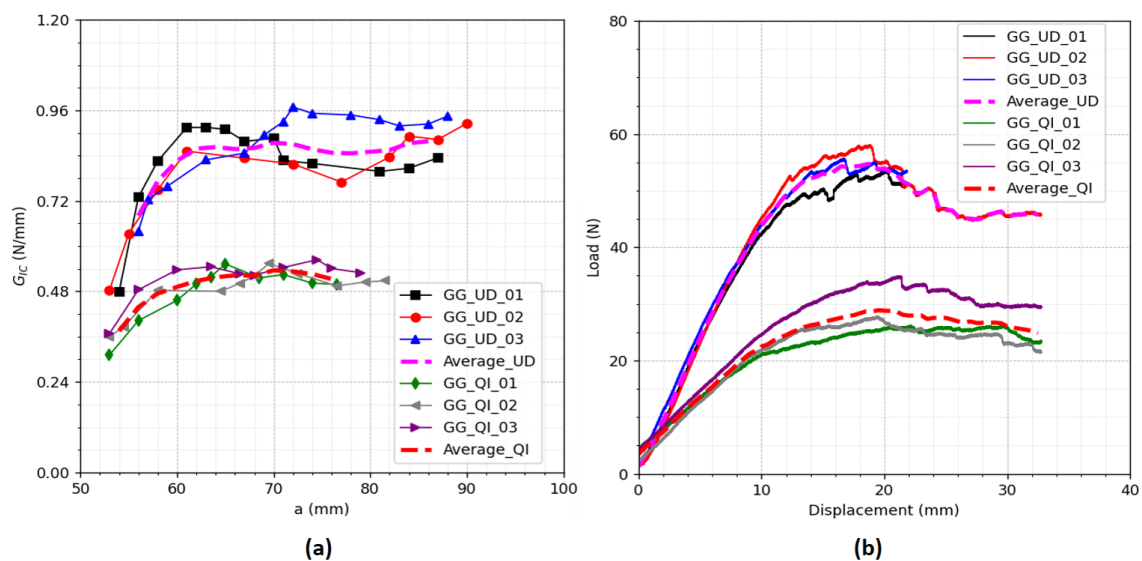


Figure 5.16: The fracture toughness results of all-GFRP laminate: (a) R-Curve; (b) Load-displacement.

Table 5.9: Average G_{IC} and CV of all-GFRP laminates.

	UD laminate ($[0]_{72S}$)	QI laminate ($[-45^\circ/90^\circ/45^\circ/0^\circ]_{18S}$)
G_{IC} (N/mm)	0.86	0.52
CV (%)	6	4

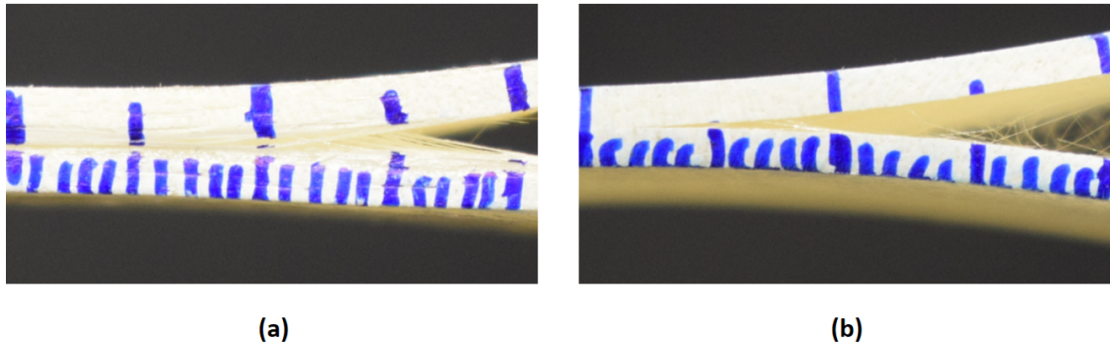


Figure 5.17: The lateral view of delamination propagation of all-GFRP laminates: (a) Unidirectional GFRP; (b) Quasi-isotropic.

5.3.4 Mode I interlaminar fracture toughness of GFRP/Al laminate

The R-curve and load-displacement behavior of GFRP/Al with different surface treatments on the aluminum are shown in Figure 5.18. The results show how different treatments of aluminum significantly influenced the R-curve shapes, indicating varied resistance to crack initiation and propagation at the interface.

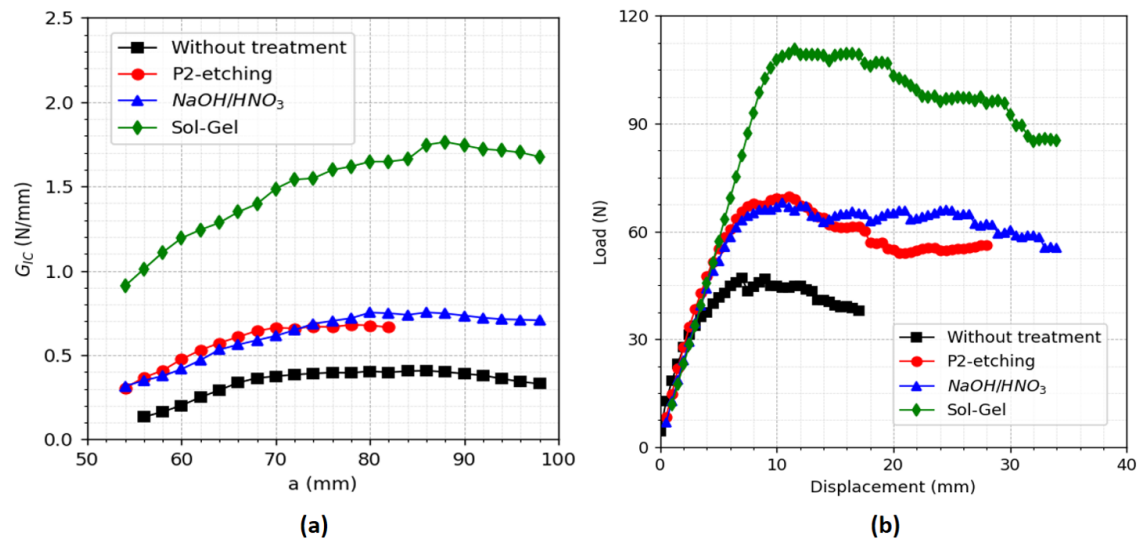


Figure 5.18: The fracture toughness results of GFRP/Al with different surface treatment on aluminum: (a) R-Curve; (b) Load-displacement.

The average G_{IC} values of different treatments, along with their relative CVs, are presented in Table 5.10. It is worth noting that for data sets with a CV greater than 15% (here without treatment and with NaOH/HNO₃ etching), three additional samples were tested (6 samples in total). However, since the CV did not change significantly in the new data set, the CV from the first data set was retained.

Table 5.10: Average G_{IC} and CV of hybrid GFRP/Al with different surface treatments.

	Without treatment	P2-etching	NaOH/HNO ₃	Sol-Gel
G_{IC} (N/mm)	0.37	0.66	0.73	1.73
CV (%)	40	4.2	47	7

Configurations with Sol-Gel anodizing treatment achieved the highest fracture toughness, with an average G_{IC} of 1.73 N/mm. In contrast, untreated samples had an average G_{IC} of 0.37 N/mm. Specimens with NaOH/HNO₃ treatment yielded a G_{IC} of 0.73 N/mm, while the ones with P2-etching resulted in G_{IC} of 0.66 N/mm. Notably, P2-etching and Sol-Gel anodizing configurations exhibited higher repeatability, with average CVs of 4.2% and 7%, respectively. In comparison, untreated samples and those subjected to NaOH/HNO₃ etching showed lower repeatability, with average CVs of approximately 40% and 47%, respectively.

Figure 5.19 provides a visual representation of the surface of both arms after debonding, as well as the lateral fracture morphology observed during the test, for each configuration of GFRP/Al. In this figure, for untreated specimens and NaOH/HNO₃ etched samples, two different examples are presented due to lower repeatability, showcasing different possible phenomena. Conversely, for P2-etched and Sol-Gel anodized samples, where there was higher repeatability and similar surface morphology, only one example is shown. Figures 5.19 (a) and 5.19 (b) display untreated specimens, highlighting different interface phenomena across samples. While the specimen presented in Figure 5.19 (a) exhibited poor bonding and straightforward crack propagation, resulting in lower G_{IC} , the specimen presented in Figure 5.19 (b) showed occasional crack jumping and significant fiber bridging, leading to higher G_{IC} . These differences explain the inconsistent behavior and repeatability observed. Figure 5.19 (c) depicts P2-etched specimens with increased fiber bridging and crack jumping, resulting in higher G_{IC} consistently among treated samples. Figures 5.19 (d) and 5.19 (e) illustrate NaOH/HNO₃ treated specimens, showing mixed results. While one sample had poor bonding at the interface, another showed extensive fiber bridging and crack jumping, contributing to higher G_{IC} . This variation indicated differences in treatment effectiveness and specimen behavior. Figure 5.19 (f) shows the outcomes of Sol-Gel anodizing treatment, highlighting features such as extensive fiber bridging, bifurcation, and widespread crack jumping across the entire surface of treated specimens. A similar fracture mechanism was observed in Lima et al. (2023). This treatment showed superior fracture toughness with more plies involved in failure compared to other treatments, indicating strong bonding between the aluminum and the GFRP arms when using this treatment.

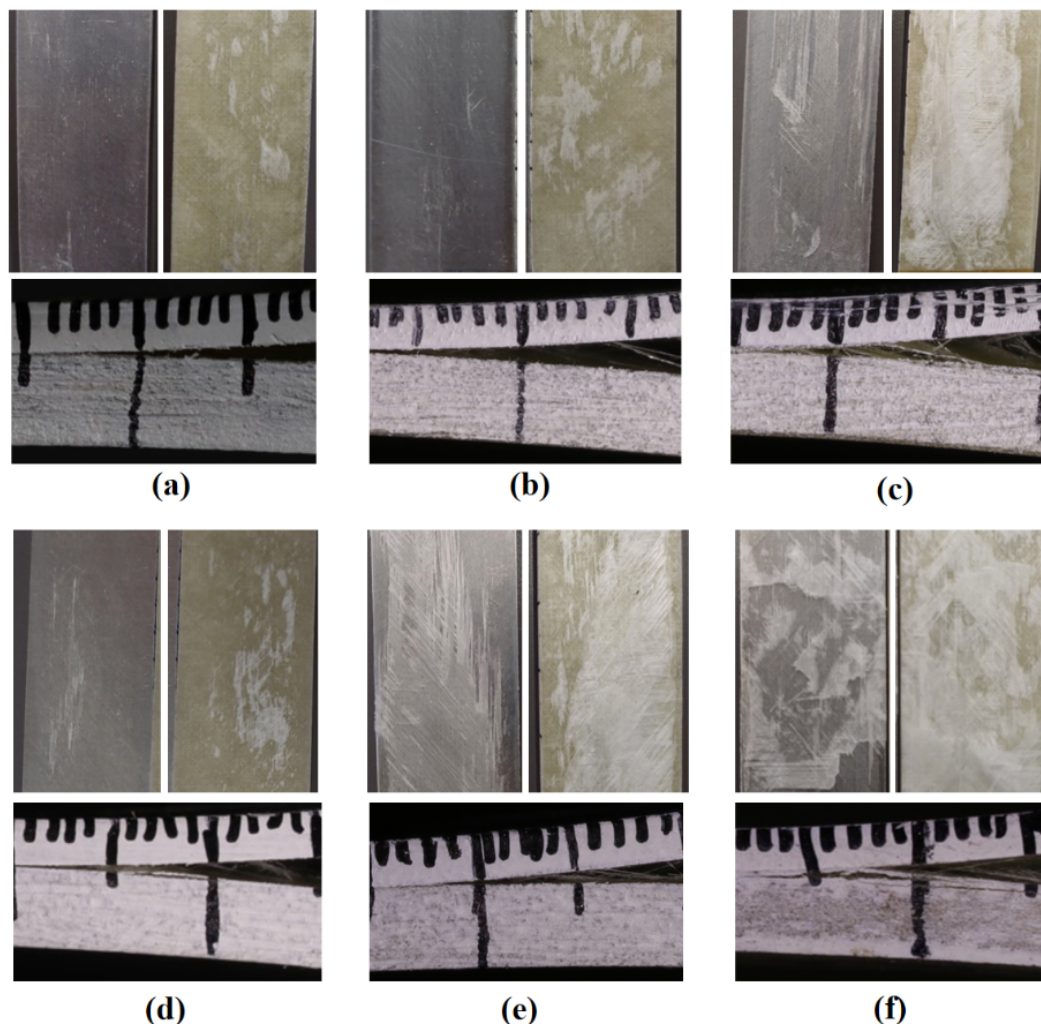


Figure 5.19: The surface morphology of GFRP and aluminum arms of GFRP/Al laminate with different surface treatment on aluminum (left side: aluminum , right side: GFRP), along with the lateral view of delamination propagation: (a) and (b) Without treatment; (c) P2-etching; (d) and (e) NaOH/HNO₃ treatment; (f) Sol-Gel anodizing.

5.3.5 Mode I interlaminar fracture toughness of GFRP/Cu laminate

The R-curve and load-displacement behavior of GFRP/Cu with various surface treatments on the copper are shown in Figure 5.20. As illustrated in this figure, different treatments applied to copper alloys considerably affect the shapes of the R-curves and the load-displacement behavior of GFRP/Cu, highlighting varying levels of resistance to crack initiation and propagation at the interface.

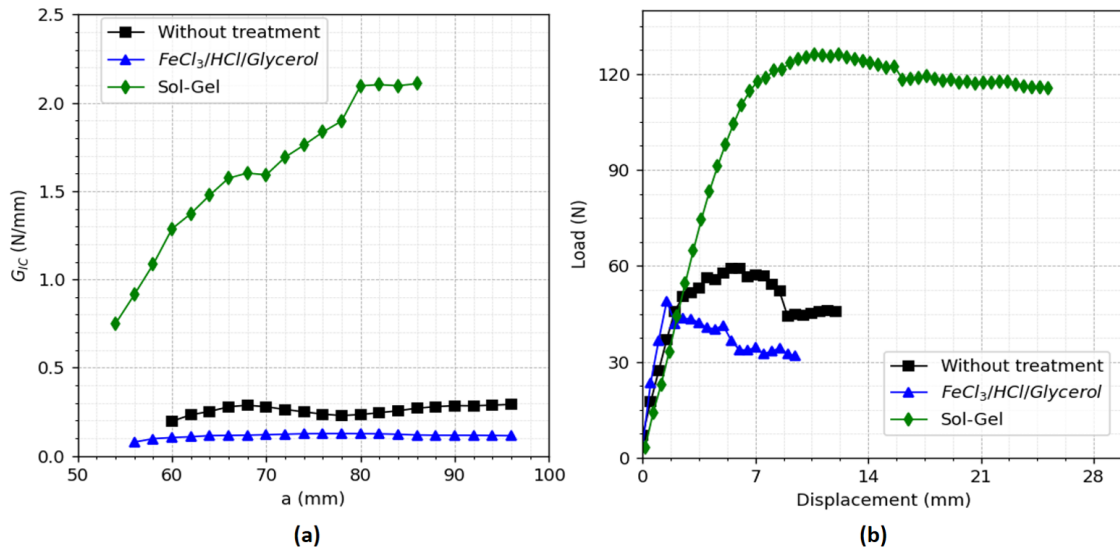


Figure 5.20: The fracture toughness results of GFRP/Cu with different surface treatment on copper: (a) R-Curve; (b) Load-displacement.

Based on the observation of the stable part of the R-curve in Figure 5.20 (a) (compiled in Table 5.11), specimens without surface treatment exhibited an average fracture toughness (G_{IC}) of 0.26 N/mm. However, the application of $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$ treatment to the copper resulted in a notable reduction of G_{IC} to 0.12 N/mm compared to the untreated configuration. Conversely, Sol-Gel anodizing of copper significantly enhanced the mode I fracture toughness of the hybrid laminate. For the untreated condition, which exhibited a coefficient of variation exceeding 42%, three additional samples were tested, resulting in a total of six samples. As this did not lead to a significant change in the CV, the value from the initial data set was retained. Figure 5.21 illustrates the surfaces of the copper and GFRP arms after debonding, as well as the lateral fracture morphology observed during the test, for each configuration of GFRP/Cu. Figure 5.21 (a) shows that the specimens without treatment exhibited small areas of crack jumping, with the remaining areas showing poor bonding. The lateral view also reveals occasional instances of fiber bridging amidst predominantly straightforward crack propagation. Figure 5.21 (b) shows the results of specimens treated with $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$. From the residual color traces of FeCl_3 on the GFRP surface, it is evident that this treatment resulted in the formation of an unstable layer on the copper surface. This instability contributed to the poor bonding. In this configuration, no fiber bridging or other secondary fracture mechanisms were observed. Figure 5.21 (c) depicts the results of Sol-Gel anodizing. Widespread crack jumping, fiber bridging, and bifurcation mechanisms across the entire area of the specimen indicate that this treatment created a superior bond between the metal and the composite. Consequently, it offered superior interlaminar fracture toughness by inhibiting crack initiation and propagation. In this particular configuration, when the total fracture toughness exceeded 1.8 N/mm, the metal underwent yielding, dissipating energy on plastic deformation. The fracture toughness continued to increase without stabilization due to metal yielding. Therefore, the total G_{IC} value for this treatment was conservatively considered as 1.8 N/mm. In terms of re-

peatability, specimens without treatment exhibited a high CV of 42%, indicating low consistency. In contrast, specimens treated with $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$ had a CV of 15%, while those treated with Sol-Gel demonstrated the highest repeatability with a CV of 4%.

Table 5.11: Average G_{IC} and CV of hybrid GFRP/Cu with different surface treatments.

	Without treatment	$\text{FeCl}_3/\text{HCl}/\text{Glycerol}$	Sol-Gel
G_{IC} (N/mm)	0.26	0.12	1.8
CV (%)	42	15	4

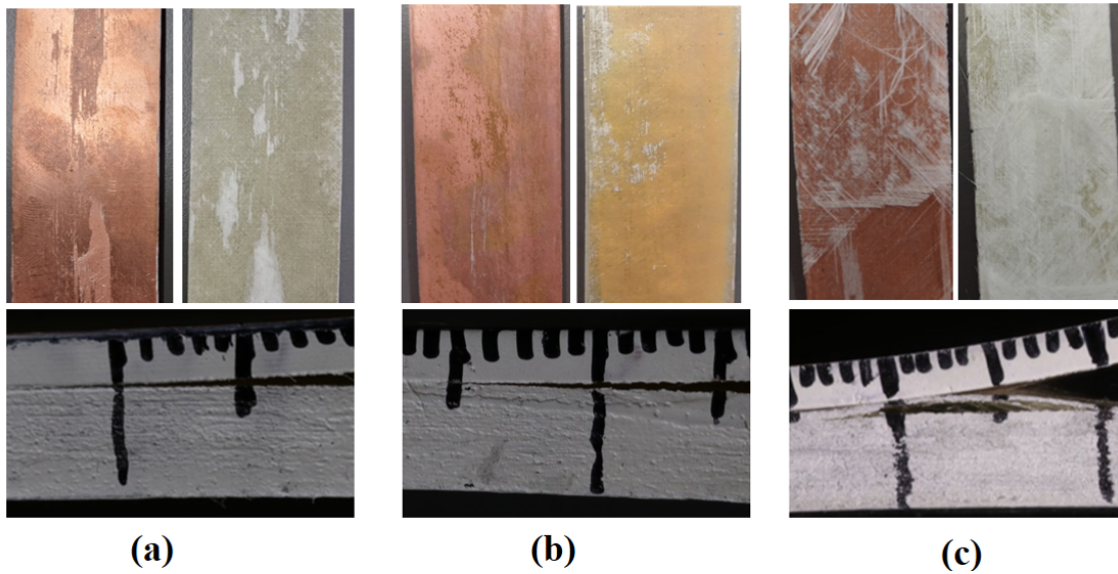


Figure 5.21: The surface morphology of GFRP and copper arms of GFRP/Cu laminate with different surface treatment on copper (left side: copper, right side: GFRP), along with the lateral view of delamination propagation: (a) Without treatment; (b) $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$; (c) Sol-Gel anodizing.

5.3.6 Key insights and patterns across treatments

In the previous subsections, the impact of various treatments on the surface free energy and surface roughness of aluminum and copper, as well as the interlaminar fracture toughness of GFRP/Al and GFRP/Cu laminates, were discussed in detail. In this subsection, the possible correlations between these parameters are discussed. The total results for the different configurations are shown in Figure 5.22. To highlight variations in different parameters within a single image and facilitate comparison, the focus has shifted from absolute surface free energy to considering the ratio of surface energy. This ratio was determined by dividing the surface energy of each treatment by that observed in the benchmark (without treatment) configuration. In general, surface roughness appeared to correlate with interlaminar fracture toughness. However, there was an exception: in the case of P2-etching, the roughness was slightly lower than that without treatment; however, the G_{IC} of P2-etching was approximately 2 times higher than that of the untreated samples. This can be attributed to the fact that both treatments were cleaned with sandpaper, and the P2-based treatment

possibly removing some of the surface roughness peaks. For specimens with Sol-Gel treatment, both the surface roughness and interlaminar fracture toughness were the highest in both configurations (GFRP/Al and GFRP/Cu), whereas the surface free energy was lower compared to other treatments. This indicates that surface free energy, which reflects the wettability of the surface, did not correlate with interlaminar fracture toughness. Another example is the $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$ treatment, which, despite having the highest surface free energy among copper treatments, exhibited the lowest interlaminar fracture toughness. Although this treatment enhanced wettability, it created an unstable layer on the copper surface. This instability resulted in poor bonding with the GFRP, leading to rapid delamination propagation during the DCB test without fiber bridging, consequently resulting in a low G_{IC} . This shows that achieving good wettability through metal surface treatment alone does not guarantee strong bonding in hybrid laminates. The stability and strength of the created layer on the metal surface after treatment are also crucial factors. The high mechanical interlocking and chemical bonding, along with the stability of the created layer on the metal surface provided by Sol-Gel anodizing, significantly enhanced the Mode I interlaminar fracture toughness of GFRP/Al and GFRP/Cu composites by inhibiting crack initiation and propagation. The R-curve analysis revealed a substantial increase in fracture toughness from 0.37 N/mm to 1.72 N/mm and from 0.26 N/mm to 1.8 N/mm for GFRP/Al and GFRP/Cu, respectively, in comparison to without treatment configuration. This treatment outperformed other chemical treatments such as P2-etching and NaOH/HNO_3 etching, and $\text{FeCl}_3/\text{HCl}/\text{Glycerol}$ treatment, underscoring its efficacy in improving the structural integrity of hybrid laminates for structural batteries applications. Furthermore, high repeatability was observed in Sol-Gel anodizing and P2-etching treatments, demonstrating the reliability of these methodologies. In contrast, specimens without treatment and NaOH/HNO_3 etching exhibited lower repeatability.

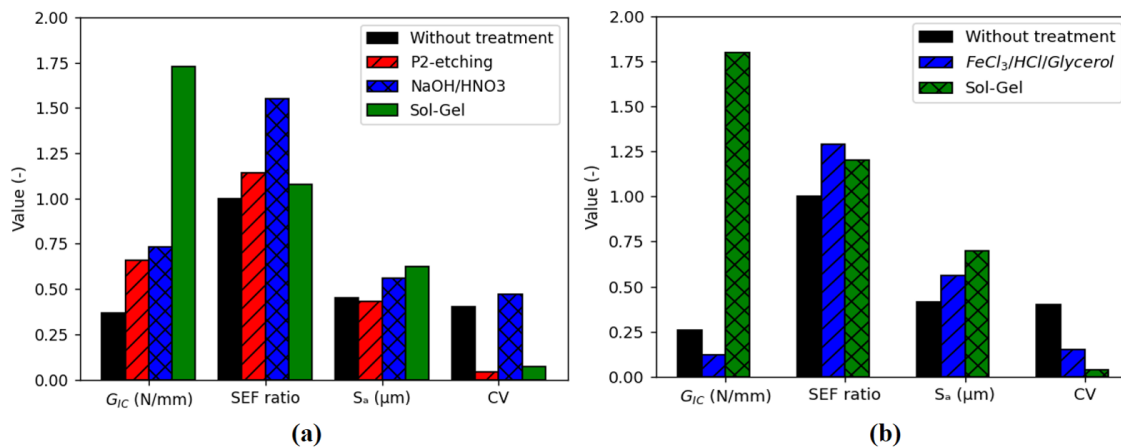


Figure 5.22: Comparison of different obtained parameters: (a) GFRP/Al; (b) GFRP/Cu.

It should be noted that the calculated mode I fracture toughness values were often affected by multiple secondary fracture mechanisms such as crack jumping and fiber bridging. Collectively, these factors indicate that the obtained values reflect structural properties rather than purely material properties, especially regarding effective treatments such as Sol-Gel anodizing. Despite

achieving consistent interlaminar fracture toughness across different samples with Sol-Gel treatment, these complexities in interlaminar fracture behaviour may pose challenges for numerical verification.

5.4 Conclusions

In this chapter, a comprehensive analysis of GFRP/Al and GFRP/Cu hybrid laminates with varying surface treatments on the metal was presented. Critical parameters such as surface free energy, surface roughness, and Mode I interlaminar fracture toughness were analyzed. The findings revealed that surface roughness of the metal generally correlates with interlaminar fracture toughness of hybrid laminates, although exceptions exist, such as with P2-etching. Sol-Gel treatment resulted in the highest surface roughness and superior interlaminar fracture toughness despite lower surface free energy. Conversely, the FeCl_3/HCl /Glycerol treatment of copper, despite enhancing surface free energy and thereby improving wettability, resulted in poor bonding with GFRP due to the formation of an unstable layer on the copper surface. These findings underscore that increased metal surface wettability alone doesn't not always guarantee effective bonding with composite laminate. Beside metal surface roughness, stability and strength of the created layer on the surface of metal are also critical factors for achieving robust bonding in hybrid laminates. Sol-Gel anodizing emerged as the best metal treatment, increasing the mode I fracture toughness of GFRP/Al and GFRP/Cu by about five and seven times, respectively, compared to the baseline configurations without treatment. This technique outperformed the chemical treatment methods such as P2-etching, NaOH/HNO_3 etching, and FeCl_3/HCl /Glycerol treatment. The remarkable repeatability observed in Sol-Gel anodizing and P2-etching treatments enhanced the reliability of these techniques. In contrast, untreated specimens and NaOH/HNO_3 etching presented challenges with lower repeatability, warranting caution when using these methods.

Chapter 6

Mode II interlaminar fracture toughness study

In this chapter, the modified transverse crack tension (mTCT) test was used to measure the mode II interlaminar fracture toughness of GFRP/current collector interfaces, with the current collectors being aluminum and copper. The dominance of mode II loading was confirmed using the virtual crack closure technique. For the designed configurations, an analytical closed-form solution was derived to obtain the mode II interlaminar fracture toughness in the mTCT test. This solution accounts for residual thermal stresses and elastic mismatch and was verified numerically. The effects of Sol-Gel surface treatment and compressive transverse pressure on mode II interlaminar fracture toughness were assessed and compared with untreated samples and an all-GFRP configuration. Digital image correlation technique was employed to accurately identify the onset of crack propagation of each specimen. Additionally, scanning electron microscopy images of the surfaces of the current collectors were taken after debonding to analyze the failure mechanisms.

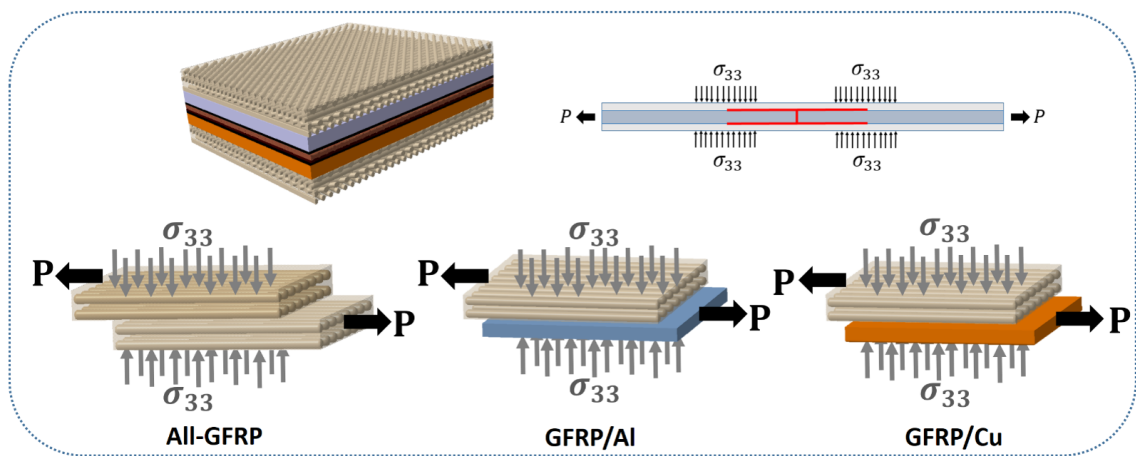


Figure 6.1: Effect of compressive transverse stress on mode II interlaminar fracture toughness of composite joints used in structural batteries.

6.1 Introduction

As explained in Section 5.1, the bonding between the GFRP shell and the aluminum and copper current collectors in structural batteries is crucial, as it significantly influences the system's multifunctionality (Moyer et al. (2020a); Di Mauro et al. (2023); Chen et al. (2020a)). Surface treatment of these current collectors before curing with the GFRP structural shell can also improve bonding. In the previous chapter, the effect of different surface treatments on mode I interlaminar fracture toughness was investigated. These treatments included sulfo-ferric etching, NaOH/HNO₃ etching, and Sol-Gel anodizing for aluminum 2024-T3, as well as FeCl₃/HCl/Glycerol treatment and Sol-Gel anodizing for copper alloy. The results demonstrated that the Sol-Gel anodizing significantly enhanced the mode I interlaminar fracture toughness of both configurations, increasing it fivefold for GFRP/Al and sevenfold for GFRP/Cu compared to untreated samples. This improvement was attributed to secondary damage mechanisms such as fiber bridging, crack jumping, and bifurcation. Sol-Gel anodizing also resulted in a higher reliability and repeatability compared to other treatments. Consequently, this treatment was concluded to be the best for improving the mode I interlaminar fracture toughness of these hybrid laminates. Therefore, in this chapter, the Sol-Gel anodizing treatment is used, and its effectiveness on mode II interlaminar fracture toughness is evaluated.

Structural batteries can be subjected to high transverse compressive stresses in transient phenomena (e.g. low-velocity impact), or when the structures are bolted together. In structural batteries, transverse compressive stress, whether applied through riveting, bolting, or resulting from natural dimensional changes during battery charge and discharge (Xiang et al. (2017); Lee et al. (2003)), can significantly increase the contact area between the electrodes and the solid electrolyte, which can improve capacity retention, cycle life, and energy density of structural batteries (Bhosale et al. (2021); Ladpli et al. (2019)). It has been reported that transverse compressive stress can enhance failure mechanisms and delay the onset of delamination in composite laminates (Yang et al. (2012); Ataş et al. (2012); Catalanotti et al. (2017); Cao et al. (2020b)). However, extent of improvement in the interfacial fracture toughness of hybrid laminates, including the GFRP/Al and GFRP/Cu configurations used in structural batteries is still unknown. Therefore, evaluating the interlaminar fracture toughness of the GFRP/current collector interfaces under compressive transverse stress is a crucial step in achieving the multifunctionality in structural batteries.

The Transverse Crack Tension (TCT) test has been used in previous studies as a experimental method for determining the mode II interlaminar fracture toughness of composite laminates under static and fatigue loading (Wisnom et al. (1995); Rans et al. (2015)). This test method offers advantages in terms of loading conditions (tensile loading) and simplicity, as the closed-form solution for data reduction requires only the maximum load and the geometric dimensions of the specimen (Wisnom (1992); Cui et al. (1994)). Although highly effective from a theoretical perspective, the experimental results of the TCT are significantly influenced by specimen geometry, local defects, and asymmetries. These factors lead to non-simultaneous propagation of the four cracks, invalidating the applicability of simple analytical models and, consequently, the test itself.

Moreover, crack propagation does not occur in pure mode II. For this reason, the modified TCT (mTCT) test was recently developed to avoid asymmetric crack propagation and a spurious mode I loading by introducing Teflon films as pre-cracks, thereby ensuring pure mode II loading (Scalici et al. (2016)). This modified method has been used in previous studies (Hahn et al. (2022); Pitarresi, Giuseppe and Scalici, Tommaso and Catalanotti, Giuseppe (2019); Pitarresi et al. (2018); Ke and van der Meer (2024); Scalici et al. (2025)).

In this chapter, the effects of compressive transverse stress and Sol-Gel surface treatment on the mode II interlaminar fracture toughness of GFRP/Al and GFRP/Cu are assessed using the mTCT technique. The results are compared with untreated samples and all-GFRP coupons. The chapter is structured as follows: Section 6.2 discusses the materials used and provides a detailed explanation of the experimental and numerical methods, including design procedures, numerical verification via the virtual crack closure technique (VCCT), surface treatment procedures, mTCT specimen manufacturing, and testing procedures. Additionally, it covers the digital image correlation (DIC) technique (Turner (2015)) and scanning electron microscopy (SEM). Section 6.3 begins with the derivation of an analytical equation for calculating the mode II interlaminar fracture toughness of hybrid laminates, taking into account the mismatch in elastic and thermal expansion coefficients of the materials. It then presents the results for the all-GFRP configuration, followed by those for GFRP/Al and GFRP/Cu hybrid laminates, and concludes with a comparative analysis of the results across these three configurations.

6.2 Materials and method

6.2.1 Materials

The high-strength aluminum alloy Al2024-T3 and the copper alloy Cu110-H02, both with a thickness of 4.8 mm, were sourced from McMaster-Carr. E-glass PPG-600T-15 μ -25 gsm-300 mm-TP736LT from NTPT was used as the thin-ply lamina. The mechanical properties of the aluminum alloy and copper alloy are shown in Table 6.1. Accordingly, E and ν are respectively the Young's modulus and the Poisson's ratio of the metals. The parameters σ_y and σ_u are the yield stress and the tensile strength, respectively, and α represents the thermal expansion coefficient. The mechanical properties of the E-glass fiber lamina are shown in Table 6.2, where E_1 is the Young's modulus in the longitudinal (fiber) direction, E_2 is the Young's modulus in the transverse and thickness directions, and ν_{12} and G_{12} are the Poisson's ratio and shear modulus, respectively. In addition, α_1 and α_2 represent the thermal expansion coefficient in the longitudinal and transverse directions.

Table 6.1: Mechanical properties of metals.

Material	E (GPa)	ν	σ_y (MPa)	σ_u (MPa)	α ($10^{-6}/K$)
Aluminum 2024-T3	73	0.33	316	457	23.2
Copper 110-H02	117	0.30	261	289	17

Table 6.2: Mechanical properties of E-Glass lamina.

E_1 (GPa)	E_2 (GPa)	ν_{12}	G_{12} (GPa)	α_1 ($10^{-6}/K$)	α_2 ($10^{-6}/K$)
40	6.43	0.298	2.735	7.12	36

6.2.2 mTCT design and VCCT Verification

The all-GFRP mTCT specimens were designed with a layup of $[0_n/0_{2n}/0_n]$ (Scalici et al. (2016)), where $n = 90$. The hybrid mTCT specimens were designed with configurations of GFRP/Al/GFRP and GFRP/Cu/GFRP, with the GFRP having a layup of $[0^\circ]_{90}$. The nominal dimensions of the mTCT specimens were 220 mm $\times$ 15 mm. The width of the mTCT specimen was based on the reference work on mTCT (Scalici et al. (2016)), while the length was conservatively increased by 20 mm to account for the gripping device. The dimensions of the specimen including the pre-cracked regions are shown in Figure 6.2. In contrast to previous work (Scalici et al. (2025)), the metallic layers were positioned at the center of the laminate to delay plastic deformation of the metal part during the quasi-static tensile test, which could pose a risk of interfering with the calculation of the interlaminar fracture energy toughness.

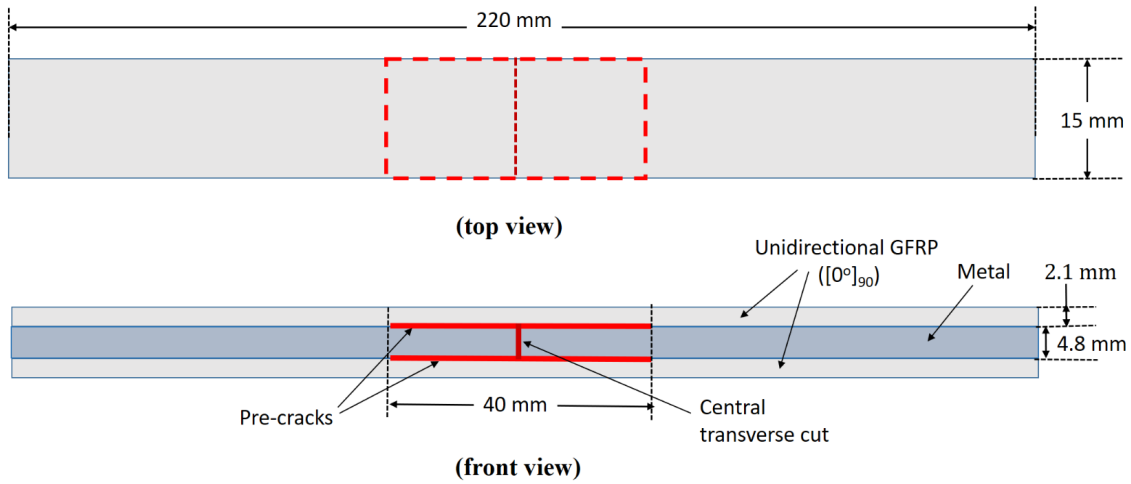


Figure 6.2: Dimensions of the mTCT specimens.

The resulting configurations of the hybrid laminates were numerically simulated in Abaqus (Hibbitt et al. (2002)) with a conservative assumption of $\mathcal{G}_H^c$ equal to 2 N/mm. This was done to ensure that no plastic yielding occurred in the metallic current collectors or any failure in the GFRP laminate occurs during the crack propagation stage of the quasi-static tests, accounting for the effect of compressive stress. The thicknesses of the metals were also chosen based on market availability. The numerical 3D virtual crack closure technique (VCCT) was also used to calculate mode-mixity and to determine the energy release rate profiles along the crack tip line (Rybicki and Kanninen (1977)). To reduce computational time, only one-eighth of the configuration was modeled and symmetric boundary conditions were applied to the models, as shown in Figure 6.3. Both the GFRP and the metal were represented by appropriately partitioning a single part in

Abaqus. For the pre-crack, a seam was assigned to the relevant partition to represent the initial crack. Both composite and metal were considered as linear elastic. In the material definition stage, the linear elastic properties of the GFRP laminate and the metal were specified. Additionally, the thermal expansion coefficient was defined isotropically for the metal and orthotropically for the composite material. The simulation process involved three sequential steps to accurately model the loading conditions on the specimen. The first step was a thermal analysis to replicate the natural cooling process, where the temperature was reduced from the curing temperature of 80°C to room temperature (20°C). This step aimed to capture the residual thermal stresses induced in the specimen due to differential thermal expansion between metal and composite. The second step involved a mechanical loading condition to simulate the compressive transverse stress applied to a square area around the crack tip, which extended 10 mm before and after the crack tip to replicate the experimental clamp pressure. The third step was a mechanical loading condition to simulate the tensile displacement loading. Displacement boundary conditions were applied on specimen to simulate the tensile loading. C3D8I (8-node linear brick, incompatible modes) elements were employed for the finite element mesh. Through the length of the specimen, the mesh size varied from 0.25 mm near the crack tip to 1 mm in regions farther from the crack tip. For the thickness, the mesh size was fixed at 0.25 mm, while for the width it was set at 0.5 mm. The total number of elements in the model was 43320. Figure 6.3 shows the mesh configuration of the numerical model, along with the graphical representation of the pre-cracked regions.

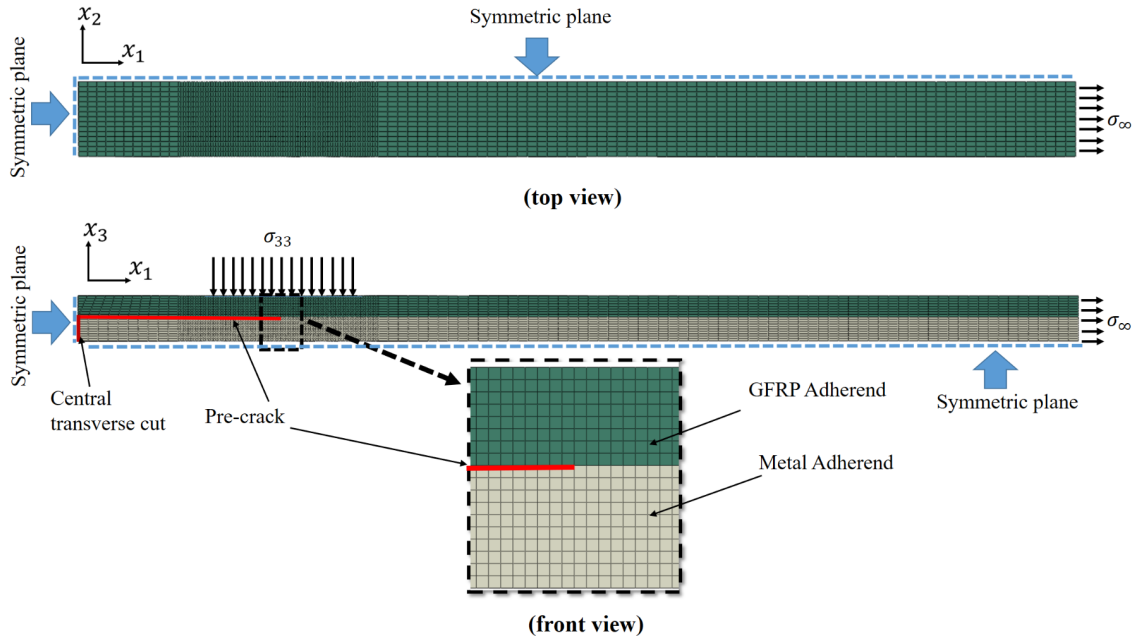


Figure 6.3: Finite element model of the mTCT specimens for VCCT verification.

By obtaining the displacement of the nodes adjacent to the crack tip and using the nodal forces at the crack tip nodes, along with the equations of VCCT shown in Subsection 5.2.9, the energy release rates for mode I ($\mathcal{G}_I$), mode II ($\mathcal{G}_{II}$), and mode III ($\mathcal{G}_{III}$) components were calculated and divided by the total energy release rate (the sum of all components, G_T) to calculate the relative

contribution of each mode. Figure 6.4 shows the contribution of each mode of interlaminar fracture toughness of GFRP/Al/GFRP and GFRP/Cu/GFRP for both cases: with and without compressive transverse stress. Here, b represents the width of the specimens. The total crack length was fixed at 40 mm. A tensile displacement of 0.2 mm, which corresponded to a tensile stress of 114 MPa and 127 MPa for the GFRP/Al/GFRP and GFRP/Cu/GFRP configurations, respectively, was applied to the models. In Figures 6.4 (a) and 6.4 (b), the models were analyzed without transverse stress, while in Figures 6.4 (c) and 6.4 (d), a transverse compressive stress of 90 MPa was applied to a square area around the crack tip. This area extended 10 mm before and after the crack tip to replicate the experimental setup. The results shown in Figures 6.4 (a) and 6.4 (b) indicate that for mTCT hybrid configurations without compressive transverse stress, approximately 97% of the behavior was contribution of mode II, with over 2% attributed to mode III, and less than 0.01% to mode I. However, the findings from Figures 6.4 (c) and 6.4 (d), where a compressive transverse stress of 90 MPa was applied, demonstrate that the contribution of mode II increased to over 99%. Additionally, the mode II curves in Figures 6.4 (c) and 6.4 (d) reveal that mode II behavior became more consistent across the specimen width. The compressive transverse stress effectively reduced the negative edge effects of the specimens on mode II interlaminar fracture toughness.

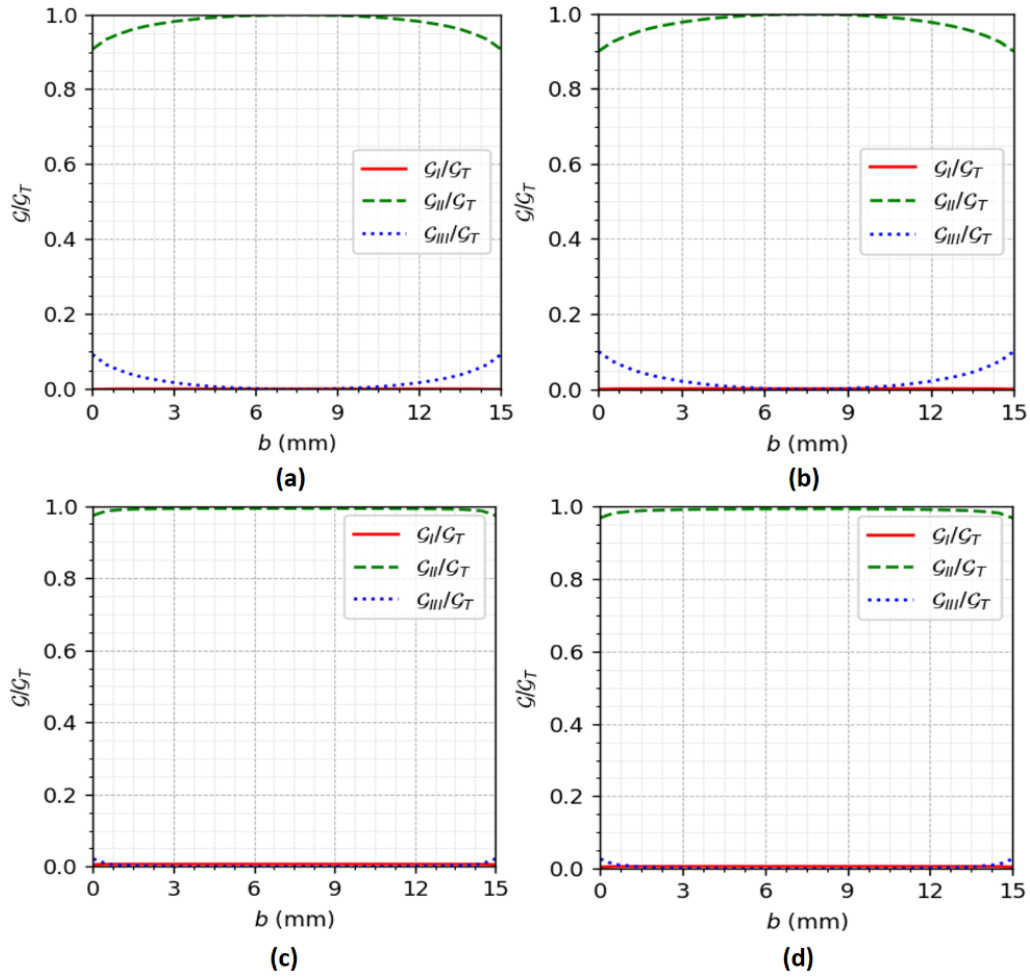


Figure 6.4: Mode mixity of the hybrid mTCT specimens with and without compressive transverse stress: (a) GFRP/Al/GFRP ($\sigma_{33} = 0$); (b) GFRP/Cu/GFRP ($\sigma_{33} = 0$); (c) GFRP/Al/GFRP ($\sigma_{33} = -90$ MPa); (d) GFRP/Cu/GFRP ($\sigma_{33} = -90$ MPa).

6.2.3 Surface treatment

After cutting the aluminum and copper sheets to half the specified dimensions of the mTCT specimens, measuring $110 \text{ mm} \times 15 \text{ mm}$, using a 5-axis DMG-DMU-60eVo CNC machine, Sol-Gel anodizing was performed on both surfaces of the aluminum and copper sheets. The procedures for cleaning stage and Sol-Gel treatment are detailed in the following subsections.

6.2.3.1 Cleaning stage

Before starting any treatment, all metal substrates were cleaned using a soft sponge, soap, and water to remove dust and contaminants originating from manufacturing processes. This was followed by rinsing with deionized water and drying at 40°C in an oven for 1 hour. Each substrate surface was then cleaned with acetone and dried at room temperature. Subsequently, the substrates were manually sanded using 800-grit sandpaper, followed by cleaning with acetone and drying at room temperature.

6.2.3.2 Sol-Gel anodizing

Sol-Gel anodizing was performed using the 3M-AC-130-2 sealant, which consists of Part A—a water solution containing propyl alcohol, zirconium n-propoxide, acetic acid, and water—and Part B, GTMS—a blend of 3-glycidoxy propyl-trimethoxysilane and methyl alcohol. The Sol-Gel paste was prepared by mixing Part A and Part B in compliance with the supplier's recommended ratio of 49.2:1.06, until a transparent and homogeneous solution was achieved (3M Company (2012)). Following pretreatment of aluminum and copper substrates, the Sol-Gel solution was applied uniformly to cover their entire surface area. Subsequently, the substrates were air-dried at room temperature for approximately one hour.

6.2.4 mTCT manufacturing procedure

The hybrid mTCT specimens were individually fabricated using a co-curing process with a hot press. Accordingly, the unidirectional GFRP laminates with a $[0]_{90}$ layup were manufactured using the hand layup process. An insert made from Upilex film with a thickness of $25\text{ }\mu\text{m}$, simulating initial artificial cracks approximately 40 mm in length, was placed over the GFRP, as shown in Figure 6.5. Two metal sheets, each with dimensions of half of the mTCT ($110\text{ mm} \times 15\text{ mm}$), which had already undergone the relevant cleaning and treatment (Figure 6.5 (a)), were arranged over the unidirectional GFRP laminate. The metal sheets were aligned so that their length was in the fiber direction of the GFRP laminate, and they were symmetrically positioned relative to the insert to ensure equal crack lengths on both sides of the mTCT specimen with respect to the center. The GFRP was then cut using a roller cutter, with the metal sheets serving as a reference. After this cut, the GFRP/metal was placed on the GFRP laminate to cut and manufacture the other side of the mTCT specimen (Figure 6.5 (b)). Three individual specimens were made for each configuration to assess the reliability of the method. The specimens were then covered with Teflon, arranged in an aluminum mold, and co-cured using a hot press at a pressure of 25 bar, with temperatures specified by the supplier (1 hour at 70°C and 12 hours at 80°C) (Figure 6.5 (c)). The alignment of the metal and composite parts was ensured throughout the curing process using alignment pins in the mold. After curing, the thickness of the hybrid mTCT laminates was measured to be 9 mm. The edges of the specimens were cleaned with sandpaper to remove excess matrix material and ensure a sharp, clean edge on the mTCT specimens. Finally, the specimens' lateral sides (thickness) were painted in two stages to prepare them for DIC imaging during testing. First, a white base coat was applied evenly, followed by the application of a high-contrast black speckle.

Regarding the all-GFRP configuration, the mTCT specimens were prepared by fabricating a single plate with Upilex inserts located in the designated position to simulate pre-cracks. After curing in hot press, the plate was then precisely cut using a 5-axis CNC machine in the dimension of mTCT specimens ($220\text{ mm} \times 15\text{ mm}$). The total thickness of the all-GFRP mTCT specimens after curing was 8.5 mm.

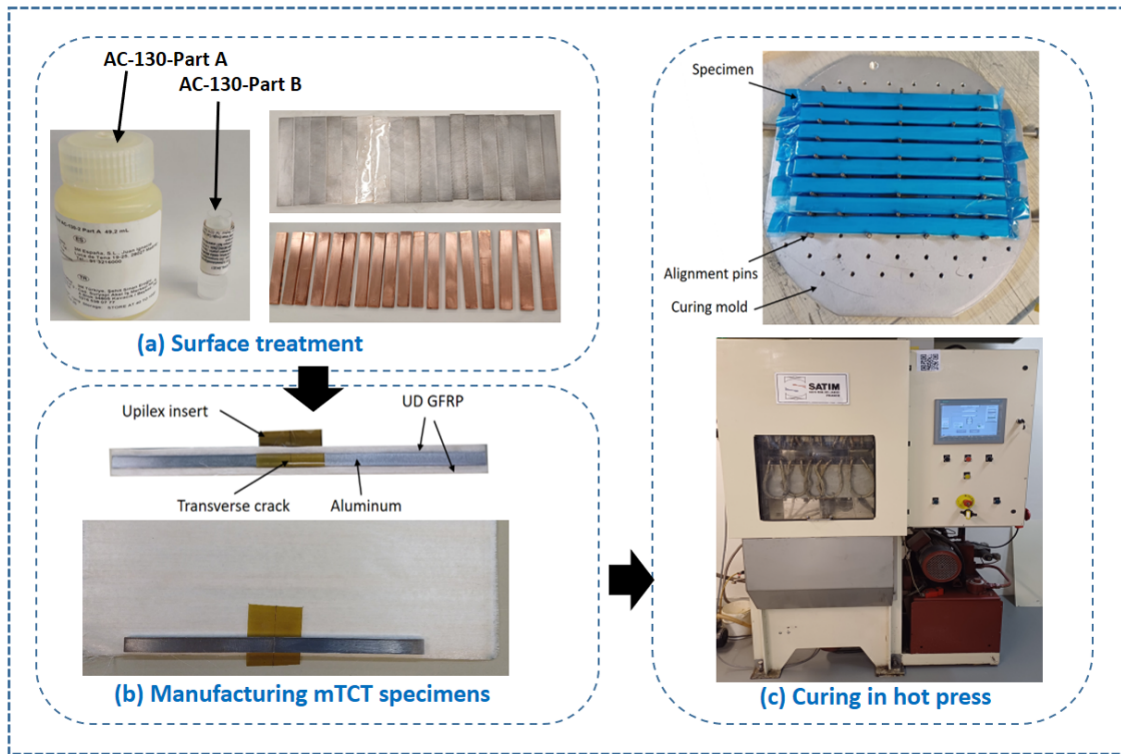


Figure 6.5: Manufacturing process of hybrid mTCT specimens: (a) Sol-Gel treatment of metal substrates; (b) Cutting GFRP and fabricating the mTCT specimens; (c) Arranging the specimens in the mould and curing them in a hot press.

6.2.5 mTCT testing procedure

Quasi-static tests were conducted using an INSTRON 5900R tensile testing machine with a 300 kN load cell, under displacement control at a rate of 1 mm/min. Digital images were recorded every two seconds by using a Canon EOS R7 camera. The test set up is shown in Figures 6.6 (a) and 6.6 (b). The compressive transverse stresses were applied using a clamp pressure device shown in Figure 6.6 (c). In this test set up, the specimen, marked as (1), was held in place by two sturdy steel grips (2) fastened with M10 bolts (3) spanning 100 mm across the central transverse crack. These grips were 25 mm thick to prevent any bending and ensure no additional forces affect the specimens. Each grip had a channel where the specimen was located, supported by two rubber inserts (4) per channel to effectively handle lateral loads on 20 mm of the specimen, with the crack tip at the center of this area. PTFE-coated glass strips of CHEMFAB CF205, with a friction coefficient of $\mu_s = 0.02-0.04$ (as specified by the manufacturer), were placed between the specimen and the grips. This PTFE-coated glass cloth reduces friction on the specimens, while the rubber inserts allow for uniform distribution of normal stresses over the area of interest, even in the presence of imperfectly aligned surfaces. On each side of each bolt, two series disk springs (5) were used to ensure applying constant load by the bolts during the test. Figure 6.6 (d) shows the loading and compressive transverse stress applied on the mTCT specimen. Regarding the 2D Digital Image Correlation technique, a 1280×1024 , 8-bit sensor and a camera noise of 0.7% was

used. A 50 mm F-mount lens was positioned at a 0.350 m imaging distance. The system captured two images at 1 Hz, with a pixel-to-mm conversion of 1 pixel = 0.085 mm. The region of interest (ROI) measured 100 mm $\times$ 80 mm. A subset size of 31 and a step size of 15 $\times$ 15 were applied to read the strain in the x_1 axis (length of the specimen).

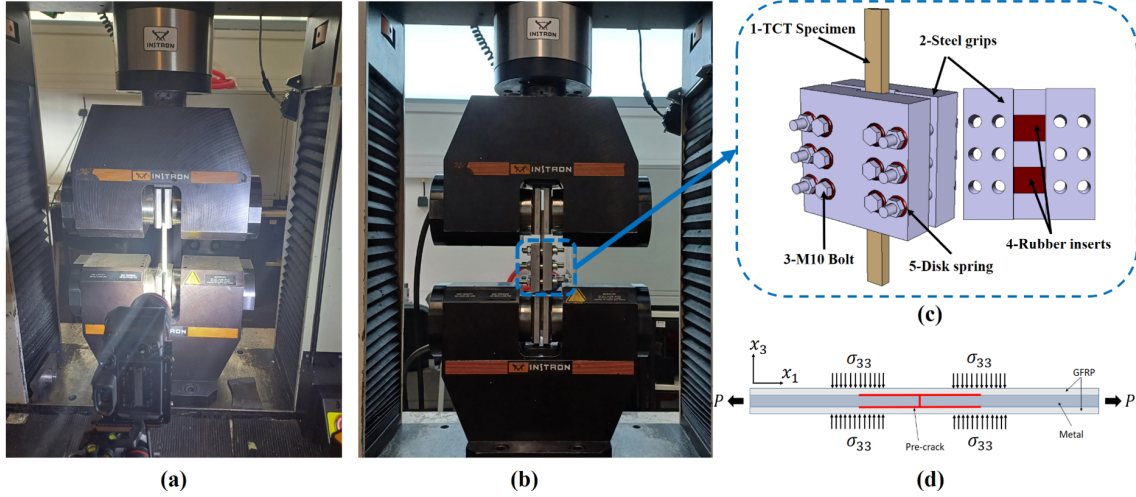


Figure 6.6: mTCT test set up with clamp pressure: (a) mTCT test set up without clamp pressure; (b) mTCT test set up with clamp pressure; (c) Clamp pressure; (d) Loading of mTCT specimen with compressive transverse stress.

Assuming that the bolts had the same preload, the lateral pressure, was calculated as:

$$-\sigma_{33} = \frac{F_b n}{2bl} \quad (6.1)$$

where σ_{33} is the applied compressive pressure, F_b is the axial load of each bolt, n is the total number of bolts, b is the width of the specimen, and l is the length of each rubber insert. Bolt torque was applied using a DB6N Tohnichi torque wrench, which had a precision of 0.1 N.m and a full scale of 10 N.m. The relationship between the axial load, F_b , and the torque applied to the bolt, T_b , was calculated as:

$$F_b = \frac{T_b}{\kappa D} \quad (6.2)$$

where D is the diameter of the bolt, and κ is the torque coefficient, usually taken as $\kappa = 0.2$ for steel bolts (Catalanotti et al. (2017)).

6.2.6 Surface topography characterization

The scanning electron microscope (SEM) images were captured using the Phenom XL to examine the surfaces of both aluminum and copper after debonding in the mTCT tests and to investigate the type of failures. The Phenom ProX was utilized to analyze the surface morphology and the composition of the materials. The images were taken at different points within an area of 1 cm², located 1 cm ahead of the initial crack tip at the center of the specimen width.

6.3 Results and discussion

This section begins with the calculation and derivation of the Mode II interlaminar fracture toughness of hybrid laminates, accounting for elastic mismatch and thermal expansion coefficient mismatch. The theoretical formulation is then verified. Subsequently, the experimental results for all-GFRP and hybrid GFRP/Al/GFRP and GFRP/Cu/GFRP laminates are presented, including the effect of transverse compressive stress, followed by a detailed discussion.

6.3.1 Mode II interlaminar fracture toughness calculation

The critical energy release rate for all-GFRP specimens was determined using Eq. 6.3 (Scalici et al. (2016)).

$$\mathcal{G}_{II} = \frac{\sigma_{\infty}^2 h_t}{4E_c} \left(\frac{1}{\phi} - 1 \right) \quad (6.3)$$

Here, $\sigma_{\infty} = \frac{P}{bh_t}$, where P is the far-field axial load, b is the coupon width, and h_t is the total thickness of the laminate. The Young's modulus of the composite in the longitudinal direction is denoted by E_c . The parameter ϕ represents the thickness fraction of the uncut plies relative to the total thickness.

Regarding the hybrid mTCT specimens, natural cooling after curing induces thermal residual stresses due to differences in the coefficients of thermal expansion between the GFRP laminate and the metal. Additionally, elastic mismatches between the GFRP laminate and the metals needed to be considered in the calculation of mode II interlaminar fracture toughness. Therefore, the mode II interlaminar fracture toughness, incorporating these factors for hybrid laminates, was analytically derived. As shown in Figure 6.7 (a), the hybrid mTCT specimen is subjected to a far-field load P . Assuming symmetric loading, geometry, and material conditions, with all four cracks propagating simultaneously, a pure Mode II loading scenario occurs in the laminate. As depicted in Figure 6.7 (b), half of the specimen is considered for derivation of the equation for mode II interlaminar fracture toughness. Here, E_m , α_m , and h_m represent the Young's modulus, thermal expansion coefficient, and thickness of the metal layer, respectively, while E_c , α_c , and h_c denote the longitudinal Young's modulus, longitudinal thermal expansion coefficient, and thickness of the composite, respectively. The parameters a and l represent the crack length and the total length of the considered segment of the specimen, respectively.

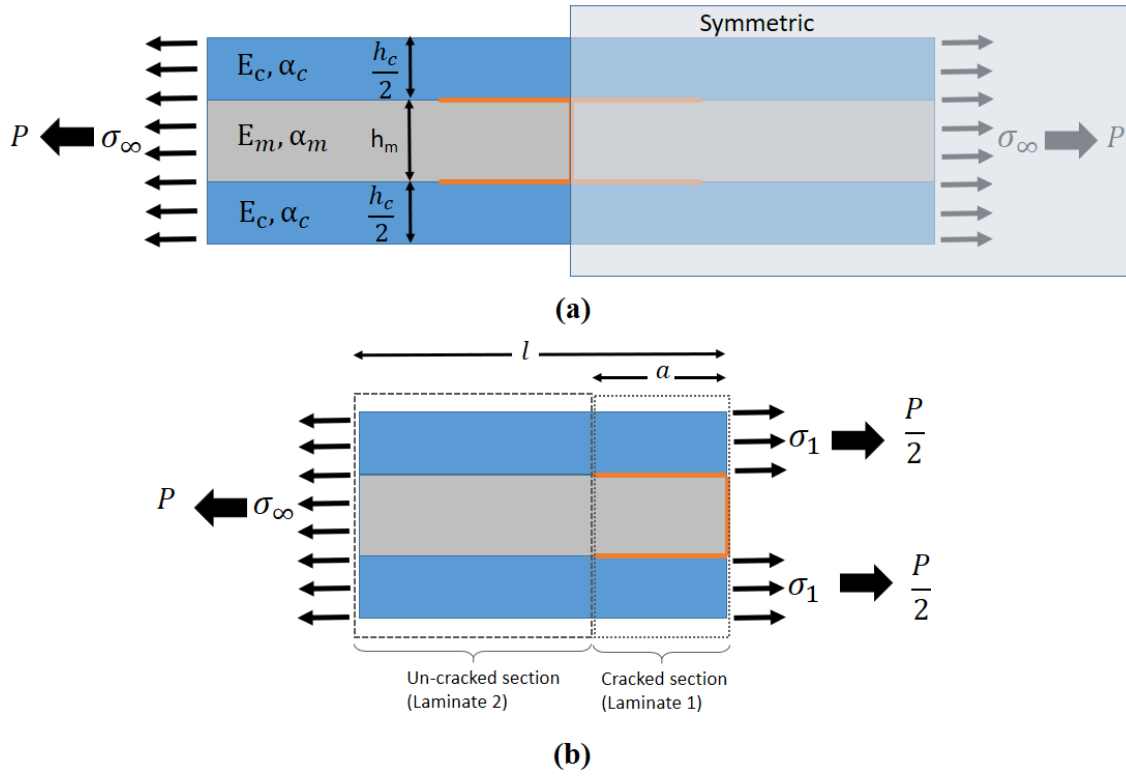


Figure 6.7: Hybrid mTCT configuration: (a) Full-model; (b) Considered half-model for $\mathcal{G}_{II}$ calculation derivation.

The energy release rate of a laminate with such cracks can be determined using the following equation (Williams (1987); Williams, JG (1988)):

$$\mathcal{G}_{II} = \frac{1}{bj} \left(\frac{dW(a)}{da} - \frac{dU(a)}{da} \right), \quad (6.4)$$

where W is the total external work, U is the total strain energy and j is the number of cracks in the laminate. For the derivation of $\mathcal{G}_{II}$, following assumptions are made: The uniaxial external load, P , is assumed to remain constant during the crack propagation over a length da . Both ends of the considered element are free to move, allowing the external load to perform work. It is assumed that the interfaces under consideration are subjected exclusively to shear loads, resulting in a pure mode II loading scenario. Eccentric loads, which can introduce additional normal stresses and consequently a mode I loading component, have been neglected in this derivation. Furthermore, it is assumed that all cracks present in the mTCT laminate propagate simultaneously. If asymmetric crack propagation occurs, due to thermal residual stresses, the contribution of mode I loading would need to be accounted for. The configuration and loading conditions are considered to be under plane stress, resulting in a uniaxial stress state. Consequently, only stresses in the x_1 -axis are assumed to contribute to delamination propagation.

As shown in Figure 6.7 (b), the part of the mTCT under consideration consists of two sections around the crack tip. The cracked section, referred to as laminate 1, has its parameters denoted

with subscript 1, while the uncracked section, named laminate 2, has its parameters denoted with subscript 2. While Nairn (Nairn (1997)) derived the general solution for the energy release rate of composites with residual thermal stresses, Fink (Fink (2010)) proposed closed-form solutions for the specific case of hybrid laminates. To accurately account for the influence of thermal residual stresses in the energy balance, it is necessary to separately calculate both the external work and the internal strain energy. The analytical solution used to calculate the energy release rate of hybrid laminates in the presence of thermal stresses follows Fink's work (Fink (2010)). The total work performed on the system can be determined using the following equation (Fink (2010)):

$$W(a) = P(\delta_{M,1} + \delta_{M,2} + \delta_{T,1} + \delta_{T,2}), \quad (6.5)$$

where $\delta_{M,1}$ and $\delta_{M,2}$, are respectively the displacements of laminate 1 and laminate 2 due to external mechanical load, and $\delta_{T,1}$ and $\delta_{T,2}$, are respectively the displacements of laminate 1 and laminate 2 due to thermal stress. These displacements can be calculated using the following equations:

$$\delta_{M,1} = \frac{\sigma_1 a}{E_c} = \frac{\sigma_\infty h_t a}{h_c E_c} \quad (6.6)$$

$$\delta_{M,2} = \frac{\sigma_\infty (l - a)}{E_{eq}} \quad (6.7)$$

$$\delta_{T,1} = \alpha_c \Delta T a \quad (6.8)$$

$$\delta_{T,2} = \alpha_{eq} \Delta T (l - a) \quad (6.9)$$

Here, σ_1 is the axial stresses of laminate 1. E_{eq} is the equivalent Young's modulus of the hybrid beam and can be calculated using $E_{eq} = E_m \phi_m + E_c \phi_c$, where ϕ_m and ϕ_c are the thickness fractions of the metal and the composite, respectively, and can be obtained by dividing their thickness to the total thickness of the hybrid beam. $\Delta T = T_{\text{test}} - T_{\text{curing}}$ represents the temperature difference between the test and curing conditions. The equivalent thermal expansion coefficient of the hybrid beam, α_{eq} , is obtained using:

$$\alpha_{eq} = \frac{E_m \alpha_m \phi_m + E_c \alpha_c \phi_c}{E_m \phi_m + E_c \phi_c} \quad (6.10)$$

Using $P = \sigma_\infty h_t b$, and substituting Eq. 6.6 to Eq. 6.9 into Eq. 6.5, the following equation can be obtained for the total work performed on the system shown in Figure 6.7 (b):

$$W(a) = \sigma_\infty h_t b \left(\frac{\sigma_\infty h_t a}{h_c E_c} + \frac{\sigma_\infty (l - a)}{E_{eq}} + \alpha_c \Delta T a + \alpha_{eq} \Delta T (l - a) \right) \quad (6.11)$$

Taking the derivative of $W(a)$ with respect to a :

$$\frac{dW(a)}{da} = bh_t \left(\frac{h_t}{h_c E_c} - \frac{1}{E_{eq}} \right) \sigma_\infty^2 + bh_t \Delta T (\alpha_c - \alpha_{eq}) \sigma_\infty \quad (6.12)$$

The total complementary strain energy of the segment under analysis, comprising the strain energies of the individual layers in both the delaminated and non-delaminated regions (laminate 1 and laminate 2), can be obtained using the following equation:

$$U(a) = U_1 + U_2 \quad (6.13)$$

The strain energy of each segment can be obtained using the following equation:

$$U_i = \frac{1}{2E_i} \sigma_i^2 V_i = \frac{1}{2E_i} \sigma_i^2 bh_i l_i \quad (6.14)$$

where σ_i represents the stresses on each laminate, V_i is its volume, and h_i and l_i are the thickness and length of each laminate, respectively. In laminate 1, the thermal stress between the metal and the composite layer is equal to zero, since the metal and composite are delaminated. The mechanical stress of laminate 1 can be obtained using $\sigma_1 = \sigma_\infty \frac{h_t}{h_c}$. Therefore, the total strain energy of laminate 1 can be obtained using the following equation:

$$U_1 = \frac{1}{2E_c h_c} \sigma_\infty^2 h_t^2 ba \quad (6.15)$$

Regarding the uncracked section (laminate 2), the total strain energy can be obtained using the following equation:

$$U_2 = \frac{b(l-a)}{2} \sum \frac{\sigma_k^2 h_k}{E_k} \quad (6.16)$$

Here, k corresponds to each material of laminate 2, which consists of composite and metal layers, and σ_k represents the sum of thermal and mechanical stresses in material k of laminate 2. The thermal stress of each material is obtained using the following equation:

$$\begin{aligned} \sigma_{T,m} &= E_m (\varepsilon - \alpha_m \Delta T) \\ \sigma_{T,c} &= E_c (\varepsilon - \alpha_c \Delta T) \end{aligned} \quad (6.17)$$

Here, $\sigma_{T,m}$ and $\sigma_{T,c}$ refer to the thermal stress in the metal and composite parts of laminate 2, respectively. The thermal compression loads of the composite part and the thermal tensile load of metal part are equal in magnitude but opposite in direction ($F_m = -F_c$). Therefore following equation can be written:

$$\sigma_{T,m} b h_m = -\sigma_{T,c} b h_c \quad (6.18)$$

Using Eq. 6.17 and Eq. 6.18, the following equation is obtained:

$$\varepsilon = \frac{E_m \alpha_m \phi_m + E_c \alpha_c \phi_c}{E_m \phi_m + E_c \phi_c} \Delta T = \alpha_{eq} \Delta T \quad (6.19)$$

Therefore, by substituting Eq. 6.19 into Eq. 6.17, the thermal stress of each material is obtained

using the following equation:

$$\begin{aligned}\sigma_{T,m} &= \Delta T E_m (\alpha_{eq} - \alpha_m) \\ \sigma_{T,c} &= \Delta T E_c (\alpha_{eq} - \alpha_c)\end{aligned}\quad (6.20)$$

The mechanical stress of the metal and composite parts of laminate 2 can be obtained using the following equation:

$$\begin{aligned}\sigma_{M,m} &= \sigma_\infty \frac{E_m}{E_{eq}} \\ \sigma_{M,c} &= \sigma_\infty \frac{E_c}{E_{eq}}\end{aligned}\quad (6.21)$$

Here, $\sigma_{M,m}$ and $\sigma_{M,c}$ represent the mechanical stresses in the metal part and composite part of laminate 2, respectively. By substituting Eq. 6.20 and Eq. 6.21 into Eq. 6.16, the following equation for the total strain energy of laminate 2 can be obtained:

$$\begin{aligned}U_2 &= \frac{bh_c E_c (l-a)}{2} \left(\Delta T (\alpha_{eq} - \alpha_c) + \frac{\sigma_\infty}{E_{eq}^2} \right)^2 \\ &\quad + \frac{bh_m E_m (l-a)}{2} \left(\Delta T (\alpha_{eq} - \alpha_m) + \frac{\sigma_\infty}{E_{eq}^2} \right)^2\end{aligned}\quad (6.22)$$

By substituting Eq. 6.15 and Eq. 6.22 into Eq. 6.13 and differentiating with respect to crack length a , the following equation can be obtained:

$$\begin{aligned}\frac{dU}{da} &= \frac{b}{2} \left(\frac{h_t^2}{E_c h_c} - \frac{E_c h_c}{E_{eq}^2} - \frac{E_m h_m}{E_{eq}^2} \right) \sigma_\infty^2 \\ &\quad - b \Delta T \left(\frac{E_c (\alpha_{eq} - \alpha_c) h_c}{E_{eq}} + \frac{E_m (\alpha_{eq} - \alpha_m) h_m}{E_{eq}} \right) \sigma_\infty \\ &\quad - \frac{\Delta T^2 b}{2} (E_c (\alpha_{eq} - \alpha_c)^2 h_c + E_m (\alpha_{eq} - \alpha_m)^2 h_m)\end{aligned}\quad (6.23)$$

Finally, the mode II interlaminar fracture toughness, $\mathcal{G}_{II}$, for a single crack can be obtained by substituting Eq. 6.12 and Eq. 6.23 in Eq. 6.4, resulting in the following equation:

$$\boxed{\mathcal{G}_{II} = \omega \sigma_\infty^2 + \gamma \Delta T \sigma_\infty + \lambda \Delta T^2}\quad (6.24)$$

The parameters ω , γ , and λ are calculated as follow:

$$\omega = \frac{h_t}{4} \left(\frac{1}{E_c \phi_c} - \frac{1}{E_{eq}} \right)\quad (6.25)$$

$$\gamma = \frac{h_t}{2} \left(\frac{(E_c \phi_c - E_{eq})(\alpha_{eq} - \alpha_c) + E_m \phi_m (\alpha_{eq} - \alpha_m)}{E_{eq}} \right)\quad (6.26)$$

$$\lambda = \frac{h_t}{4} (E_c \phi_c (\alpha_{eq} - \alpha_c)^2 + E_m \phi_m (\alpha_{eq} - \alpha_m)^2) \quad (6.27)$$

The verification of this equation was performed using the VCCT technique. Accordingly, both the GFRP/Al/GFRP and GFRP/Cu/GFRP configurations were selected and modeled in Abaqus following the procedure described in Section 6.2.2, with the exception of step 2 ($\sigma_{33} = 0$). By applying various displacements, the numerical values of $\mathcal{G}_{II}$ were determined and compared with the analytical solutions. The results are presented in Figure 6.8, which show good agreement between the numerical and analytical solutions.

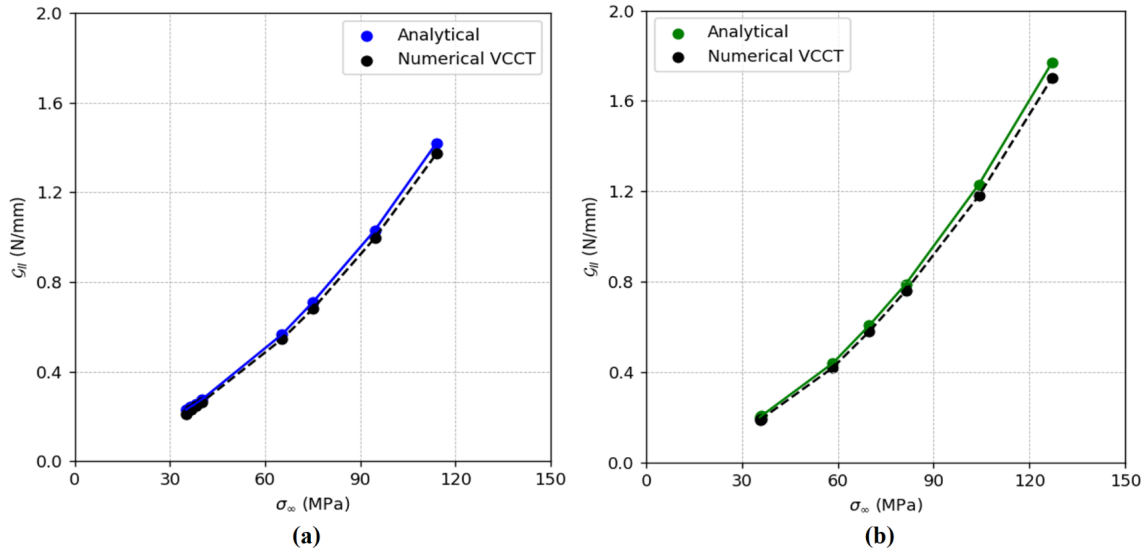


Figure 6.8: Numerical verification of the analytical equation: (a) GFRP/Al/GFRP configuration; (b) GFRP/Cu/GFRP configuration.

6.3.2 Mode II interlaminar fracture toughness of all-GFRP configuration

Figure 6.9 (a) shows the load-displacement behavior of the mTCT specimen with pure GFRP configuration ($[0_{90}/0_{180}/0_{90}]$) without transverse stress, with some points of interest highlighted. Figure 6.9 (b) presents DIC images of one side of the specimen at these corresponding points. The central transverse crack, pre-cracks, pre-crack limit, and propagated cracks are also shown in Figure 6.9 (b). The pre-crack limit marks the tip of the pre-cracks, beyond which crack propagation is monitored for the calculation of interlaminar fracture toughness. The tensile loading (Figure 6.9 (a)) can be divided into four distinct stages. The first stage is a linear elastic response observed between zero and 1.8 mm, during which the specimen experiences elastic strain and some resin pocket failures, although no crack propagation occurs as is shown in point P1 of Figure 6.9 (b). The second stage, from 1.8 mm to 2.3 mm, is characterized by the propagation of all four cracks in the specimen. The images in Figure 6.9 (b) show the lateral view of the specimen at some various peak-loads during this stage. At point P2, which corresponds to the first load drop, two cracks propagated simultaneously for approximately 5 mm. In point P3, one of these cracks extended to

the end of the specimen, while at point P4, the remaining crack on the other side propagated to the end. Although the cracks propagation had different timing, the difference between the peak-loads was less than 1 kN. In the third stage, the GFRP skin of the mTCT continues to elastically deformation until the final stage, where GFRP failure occurs (4 mm, 31.8 kN).

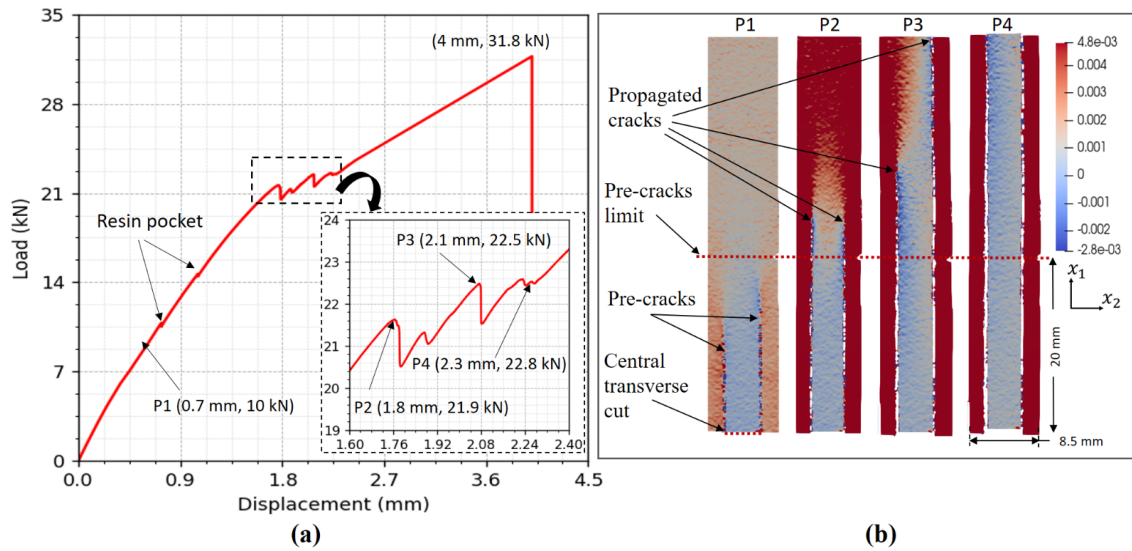


Figure 6.9: The mTCT results of the all-GFRP configuration with a layup of $[0_{90}/0_{180}/0_{90}]$: (a) Load-displacement curve; (b) DIC strain along the x_1 -axis.

Figure 6.10 shows the representative load-displacement curves of the specimens subjected to various compressive transverse stresses, including 0 MPa, 20 MPa, and 50 MPa. Higher compressive transverse stresses up to 70 MPa, 80 MPa, and 90 MPa were also tested; however, no delamination propagation was observed before GFRP failure. The results of Figure 6.10 show that higher transverse stress resulted in higher loads at which delamination propagation occurred. This demonstrates the effectiveness of transverse stress in delaying crack propagation in these specimens. The transverse stress delayed failure by inducing hydrostatic compressive stress within the resin at the interface and increasing the frictional resistance at the fractured interface. Figure 6.10 also shows that partial composite failure occurs above 34 kN, at a sufficient distance from the crack propagation zone, ensuring that this failure did not interfere with the interlaminar fracture toughness.

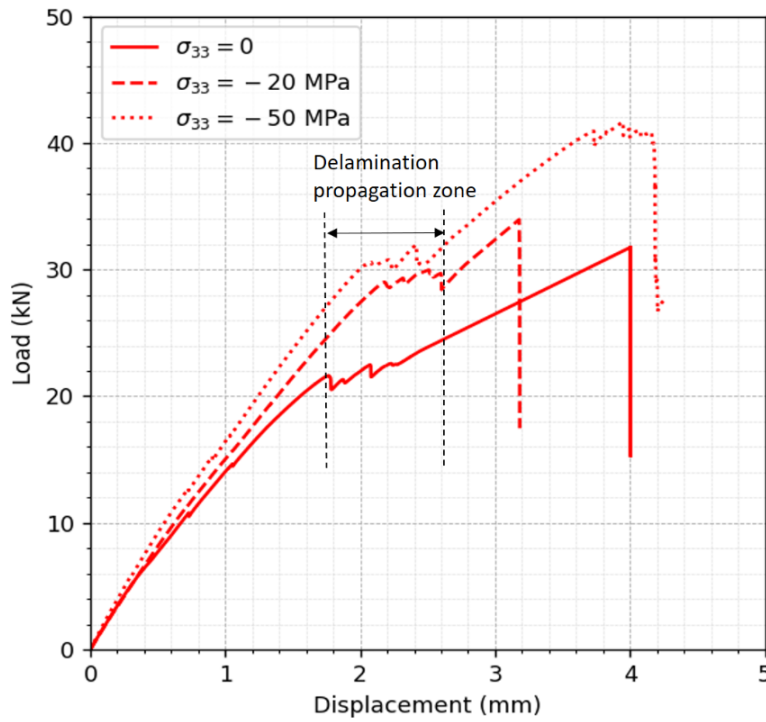


Figure 6.10: The mTCT results of all-GFRP configuration with layup of $[0_{90}/0_{180}/0_{90}]$ and different transverse stress.

The mode II interlaminar fracture toughness ($\mathcal{G}_{II}^c$), the corresponding peak load, and the coefficient of variation (CV) for each data set are presented in Table 6.3. For specimens without transverse pressure, $\mathcal{G}_{II}^c$ was measured to be 1.6 N/mm, with a CV of 15%. When a transverse stress of 20 MPa was applied, $\mathcal{G}_{II}^c$ increased to 2.71 N/mm, with a CV of 10%, representing a 70% improvement compared to the baseline without transverse stress. For a transverse stress of 50 MPa, $\mathcal{G}_{II}^c$ further increased to 3.17 N/mm, with a CV of 6%, indicating a twofold increase in interlaminar fracture toughness relative to the baseline.

Table 6.3: Mode II fracture toughness of all-GFRP ($[0_{90}/0_{180}/0_{90}]$).

σ_{33} (MPa)	Peak-load (kN)	Ave($\mathcal{G}_{II}^c$) (N/mm)	CV (%)
0	20.64	1.6	15
-20	28.93	2.71	10
-50	31.24	3.17	6

The results show that compressive stress increases the mode II interlaminar fracture toughness as the mechanisms of plastic deformation of the resin-rich zone present at the interface are affected by the hydrostatic component of the stress tensor. Similar observation of the effect of through-thickness stresses on the mode II fracture toughness were also reported in other studies (Catalanotti et al. (2017); Bing and Sun (2007); Li et al. (2008)). The relationship between mode II interlaminar fracture toughness ($\mathcal{G}_{II}^c$) can be expressed as the following relation (Catalanotti et al. (2017)):

$$\mathcal{G}_{II}^c = \mathcal{G}_{II0}^c (1 + \eta \langle -\sigma_{33} \rangle), \quad (6.28)$$

where $\langle \dots \rangle$ denotes the Macaulay brackets and η is an empirical parameter which is analogous to the internal friction enhancement. The relationship between $\mathcal{G}_{II}^c$, $\mathcal{G}_{II0}^c$ and transverse stress obtained from experimental data, along with the best fit of Eq. 6.28, is shown in Figure 6.11. The best fit was achieved with η set to 0.027. The R^2 value for the fit curve was calculated as 0.75. R^2 is a statistical measure that quantifies the proportion of the variance in the actual data that is explained by the fit curve. The slope of the curve is given by $\mathcal{G}_{II0}^c \eta$, which has been calculated to be 0.0432.

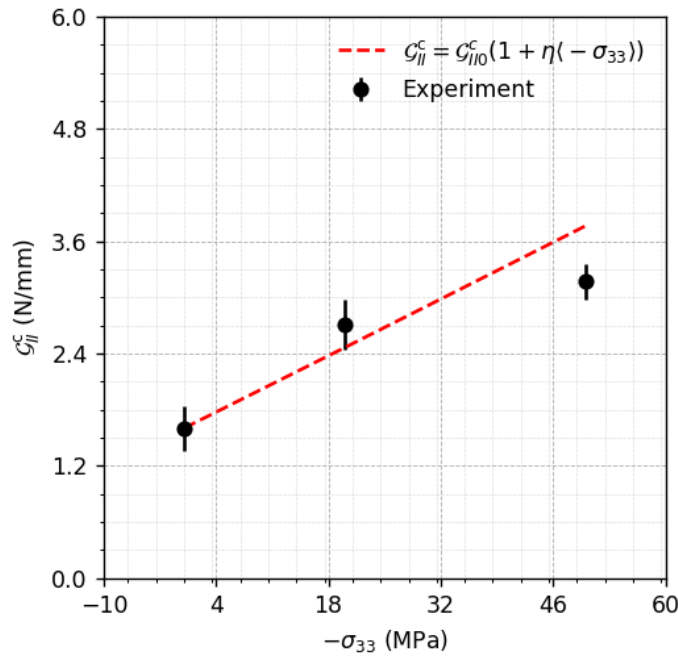


Figure 6.11: Mode II interlaminar fracture toughness vs. through-thickness stress of all-GFRP laminate ($[0_{90}/0_{180}/0_{90}]$), $\eta = 0.027 \text{ MPa}^{-1}$, $R^2 = 0.75$.

6.3.3 Mode II interlaminar fracture toughness of GFRP/Al joins

Figure 6.12 (a) shows the typical load-displacement behavior of the mTCT specimen with a GFRP/Al/GFRP configuration without transverse stress, highlighting specific points of interest, while Figure 6.12 (b) presents the DIC images of one side of the specimen at the specified points. The central transverse crack, pre-cracks, pre-crack limit, and propagated cracks are also shown in Figure 6.12 (b). The tensile loading behavior (Figure 6.12 (a)) can be divided into four distinct stages. The first stage is the linear elastic response observed between zero and 0.28 mm, during which the specimen experiences elastic strain, but no crack propagation occurs, as shown at point P1 in Figure 6.12 (b). The second stage, from 0.28 mm to 0.7 mm, is characterized by the propagation of all four cracks in the specimen. The images in Figure 6.12 (b) provide a lateral view of the specimen at various peak-loads during this stage. Point P2 corresponds to the first load drop,

during which one of the cracks propagated approximately 20 mm. At point P3, this crack fully propagated while the other crack propagated through most of its length. Finally, by point P5, both cracks were fully propagated. Between these points, other small peak-loads were observed, which are likely related to the behavior of the opposite side of the specimen which was not captured by the DIC images. This phenomenon indicates that the completion of crack propagation occurred at different times. This irregular behavior is attributed to the fact that, although the specimen was untreated, the cleaning process with sandpaper created variations in surface morphology at each interface. Even within the same interface, these morphological differences could exist at different points, leading to intermittent crack propagation. In the third stage, the GFRP skin of the mTCT continued to deform elastically until the final stage, where GFRP partly failed (39.2 kN). The load-displacement behavior and corresponding DIC images of the GFRP/Al/GFRP configuration with Sol-Gel anodizing are shown in Figure 6.13. The tensile loading was similar to the untreated configuration; however, the crack propagation phenomena occurred at higher loads. Specifically, the crack propagation stage was observed between a displacement of 0.63 mm (11.3 kN) and 1.6 mm (16.4 kN). As illustrated in Figure 6.13 (b), similar to the untreated configuration, the two interfaces exhibited different timings in crack propagation. This discrepancy highlights the different surface morphologies of the aluminum on each side, resulting from the cleaning process with sandpaper and the Sol-Gel anodizing treatment. These variations likely led to slight differences in interlaminar fracture toughness between the two sides or an uneven distribution of fracture toughness across different points on each interface. These conditions cause one side (which is metal/GFRP) to experience out-of-plane loading due to the presence of thermal residual stress, which, in turn, contributes to mode I fracture behavior during the propagation stage for both untreated and treated hybrid configurations. The mode II interlaminar fracture toughness for each configuration was conservatively calculated based on the first peak-load to ensure that the calculations were not affected by mode mixity.

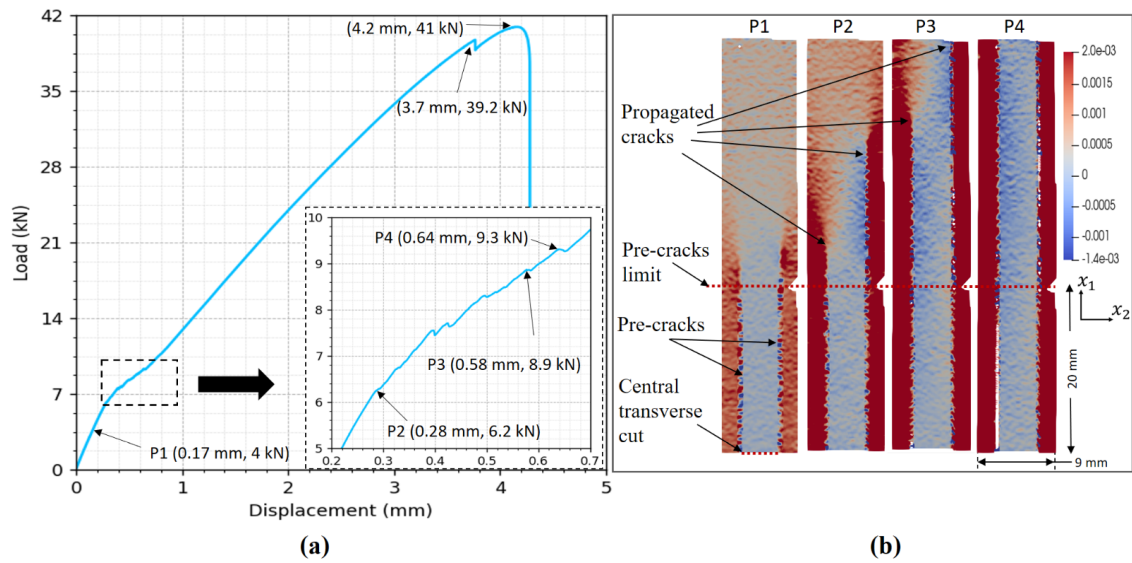


Figure 6.12: The mTCT results of GFRP/Al/GFRP configuration without treatment: (a) Load-displacement; (b) DIC strain along the x_1 -axis.

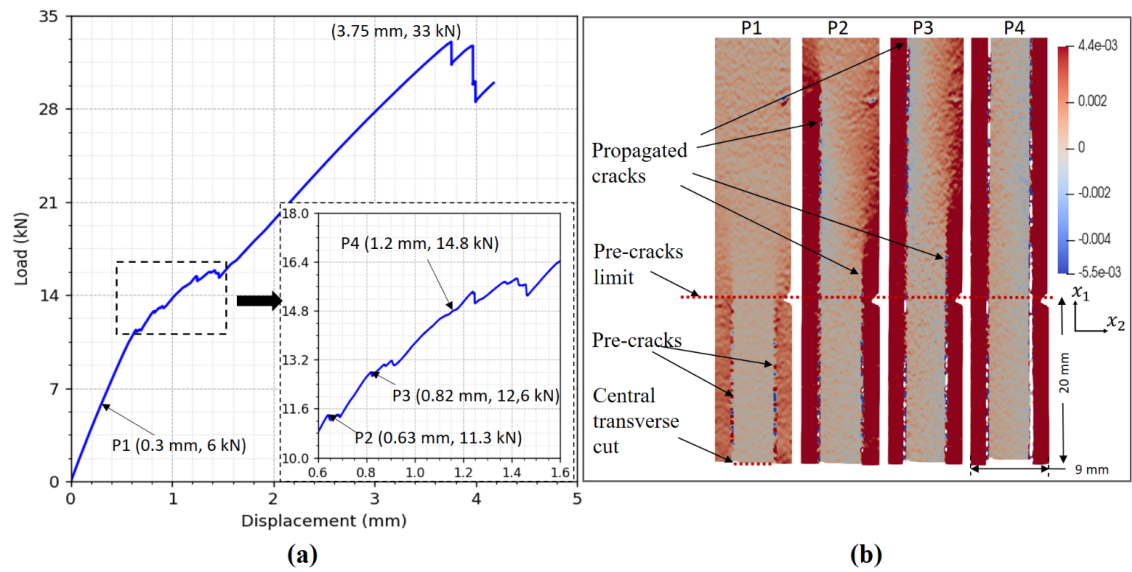


Figure 6.13: The mTCT specimens with GFRP/Al/GFRP configuration with Sol-Gel anodizing treatment: (a) Load-displacement; (b) DIC strain along the x_1 -axis.

Figure 6.14 shows the representative load-displacement curves of specimens subjected to various compressive transverse stresses, including 0 MPa, 50 MPa, and 90 MPa, for two different conditions: without treatment (Figure 6.14 (a)) and with Sol-Gel anodizing (Figure 6.14 (b)). The general behavior of the specimens under transverse stresses is similar to that observed without transverse stress; however, higher pressure led to higher load at which delamination propagation occurred. This demonstrates the effectiveness of transverse stress in delaying crack propagation in these specimens. Figure 6.14 demonstrates the load levels at which the composite begins to partially fail, as well as the instances of metal plastic yielding. The data indicate that partial composite

failure occurs above 40 kN for specimens without treatment and between 33 kN and 46 kN for specimens with Sol-Gel treatment, under different transverse stress levels. These failures occurred sufficiently far from the crack propagation zone, ensuring no interference with the interlaminar fracture toughness calculations.

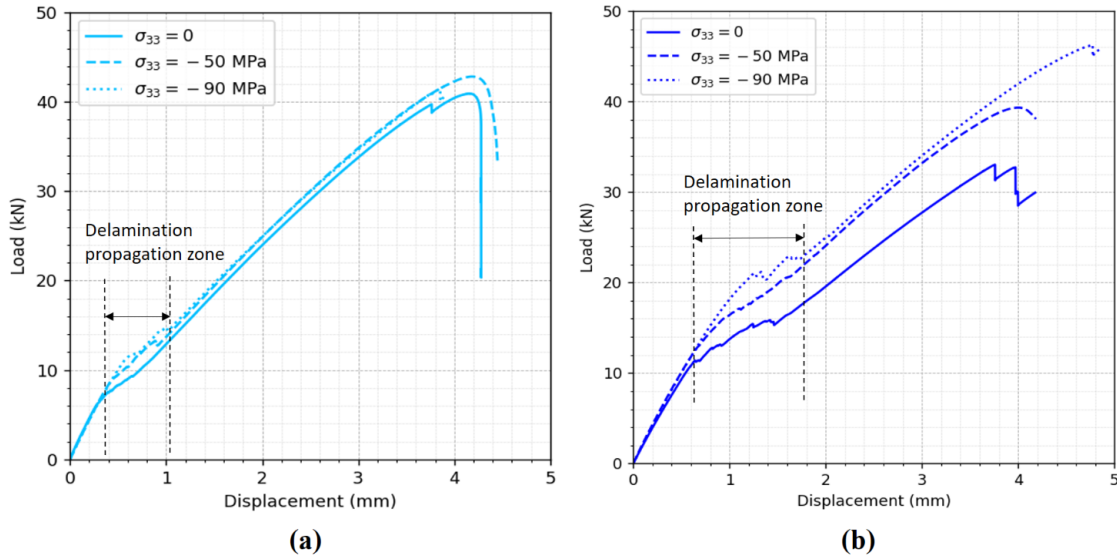


Figure 6.14: Load-displacement of GFRP/Al/GFRP with different transverse stress: (a) Without treatment; (b) With Sol-Gel anodizing.

A summary of the interlaminar fracture toughness measurements are shown in Table 6.4. The results show that GFRP/Al/GFRP configurations with Sol-Gel anodizing achieved a mode II interlaminar fracture toughness ($\mathcal{G}_{II}^c$) of 0.8 N/mm², around 150% improvement compared to the untreated configuration. When applying a transverse stress of 50 MPa, the $\mathcal{G}_{II}^c$ for the untreated specimens increased by approximately two times compared to those without transverse stress, whereas for the Sol-Gel anodized specimens, it increased by around 1.5 times. With a further increase in transverse stress to 90 MPa, the untreated specimens showed a three-fold increase in $\mathcal{G}_{II}^c$, and the Sol-Gel anodized specimens showed a 2.5-fold increase compared to those without pressure. As for reliability, all sets of configurations had a CV below 10%, demonstrating the repeatability of the set-up, clamp pressure device, and testing methodology.

Table 6.4: Mode II fracture toughness of GFRP/Al/GFRP configuration.

σ_{33} (MPa)	Treatment	Load (kN)	$\mathcal{G}_{II}^c$ (N/mm)	CV (%)
0	Without	6.025	0.31	2.6
	Sol-Gel	10.96	0.8	8
-50	Without	9.75	0.66	8.5
	Sol-Gel	14.22	1.24	10
-90	Without	11.95	0.93	6.4
	Sol-Gel	19.28	2.09	4.5

The relationship between mode II interlaminar fracture toughness ($\mathcal{G}_{II}^c$) and transverse stress,

along with the best fit of Eq. 6.28 for GFRP/Al/GFRP without treatment and with Sol-Gel anodizing of aluminum, is shown in Figures 6.15 (a) and 6.15 (b), respectively. The best fit was achieved with η values of 0.0219 MPa^{-1} and 0.0163 MPa^{-1} for the untreated and Sol-Gel anodized configurations, in turn. The slope of the curve ($\mathcal{G}_{II0}^c \eta$) for the untreated and Sol-Gel treated configurations were 0.0068 and 0.013, respectively. This indicates that the Sol-Gel treated configuration showed a higher slope with increasing transverse stress, suggesting that it was more affected by the transverse compression stress. The R^2 value for the fit curve was calculated as 0.999 for untreated samples, indicating a perfect match between the fit curve and the data. For the treated samples with Sol-Gel anodizing, the R^2 value was 0.93, suggesting that the fit curve explains 93% of the variability in the data.

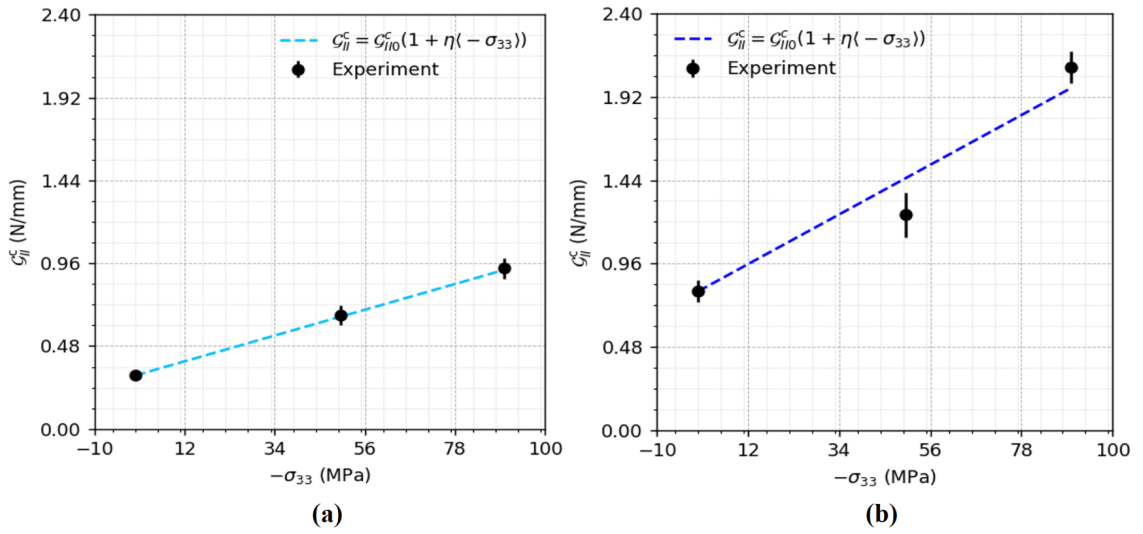


Figure 6.15: Mode II interlaminar fracture toughness vs. through-thickness stress of GFRP/Al/GFRP: (a) Without treatment ($\eta = 0.0219 \text{ MPa}^{-1}$, $R^2 \approx 1$); (b) Sol-Gel anodizing ($\eta = 0.0163 \text{ MPa}^{-1}$, $R^2 = 0.93$).

The SEM images in Figure 6.16 show the surface of both untreated and treated aluminum after debonding in the mTCT test with no transverse stress. The images were taken 10 mm after the initial crack tip in the middle of the specimen's width. The images revealed three different types of failure at the interface of aluminum and composite: adhesive failure, cohesive failure, and fiber debonding. Figures 6.16 (a), 6.16 (b), and 6.16 (c) depict samples without treatment, where adhesive failure was the most common type of failure observed. This indicates that debonding occurred primarily at the interface between the adhesive and aluminum, suggesting weak bonding between the metal and composite. Cohesive failure was also observed in a few areas (Figure 6.16 (b)). Figures 6.16 (d), 6.16 (e), and 6.16 (f) show the surface of aluminum treated with Sol-Gel anodizing. The treated samples had some cohesive failure and fiber debonding across the sample area. This suggests that the bond between the adhesive and substrates was stronger than the internal strength of the adhesive. These results demonstrate the effectiveness of Sol-Gel treatment in improving mode II interlaminar failure resistance in GFRP/aluminum configurations. In addition,

the composition analysis revealed that most of the surface of untreated aluminum contained only aluminum, copper, and magnesium, which are the primary components of Al2024-T3. However, on the surface of aluminum treated with Sol-Gel anodizing, silicon, oxygen, and carbon were also detected alongside these elements. This indicates the presence of components from the Sol-Gel paste and the resin of the GFRP on the aluminum surface after debonding, demonstrating the high stability and effectiveness of the Sol-Gel treatment.

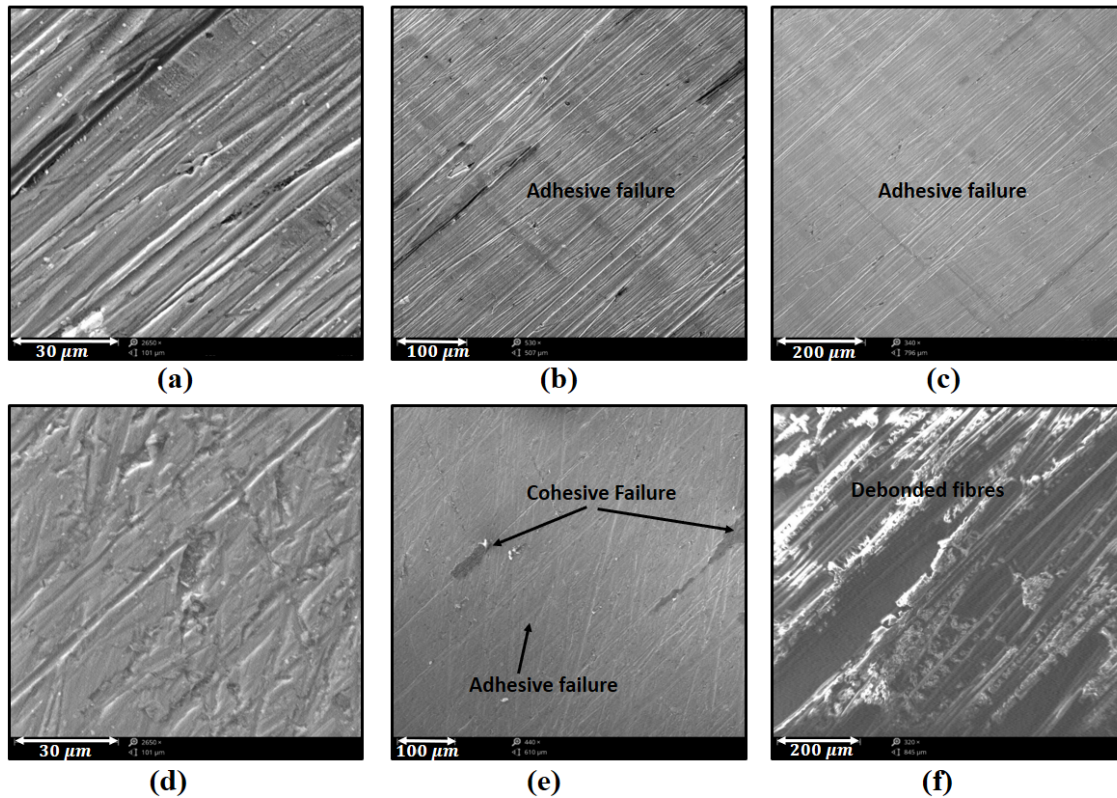


Figure 6.16: SEM images of the surface of aluminum without transverse compressive stress after debonding in mTCT tests: (a,b,c) Without treatment, (d,e,f) Sol-Gel anodizing.

The SEM images in Figure 6.17 show the surfaces of both untreated and Sol-Gel-treated aluminum after debonding in the mTCT test under a transverse compressive stress of 90 MPa. Figures 6.17 (a), 6.17 (b), and 6.17 (c) depict untreated samples, where adhesive failure was the most common failure mode observed. Compared to Figures 6.16 (a) to 6.16 (c), which shows specimens without compressive transverse stress, some cohesive failure can also be seen. This indicates weak bonding between the aluminum and the composite, even under compressive stress—though it is still better than in the absence of such stress. Figures 6.17 (d), 6.17 (e), and 6.17 (f) show SEM images of samples treated with Sol-Gel anodizing. These images reveal extensive fiber debonding and adhesive failure across most of the surface area. Compared to the Sol-Gel treated specimens without compressive stress (Figures 6.16 (d) to 6.16 (f)), the amount of fiber debonding is significantly higher.

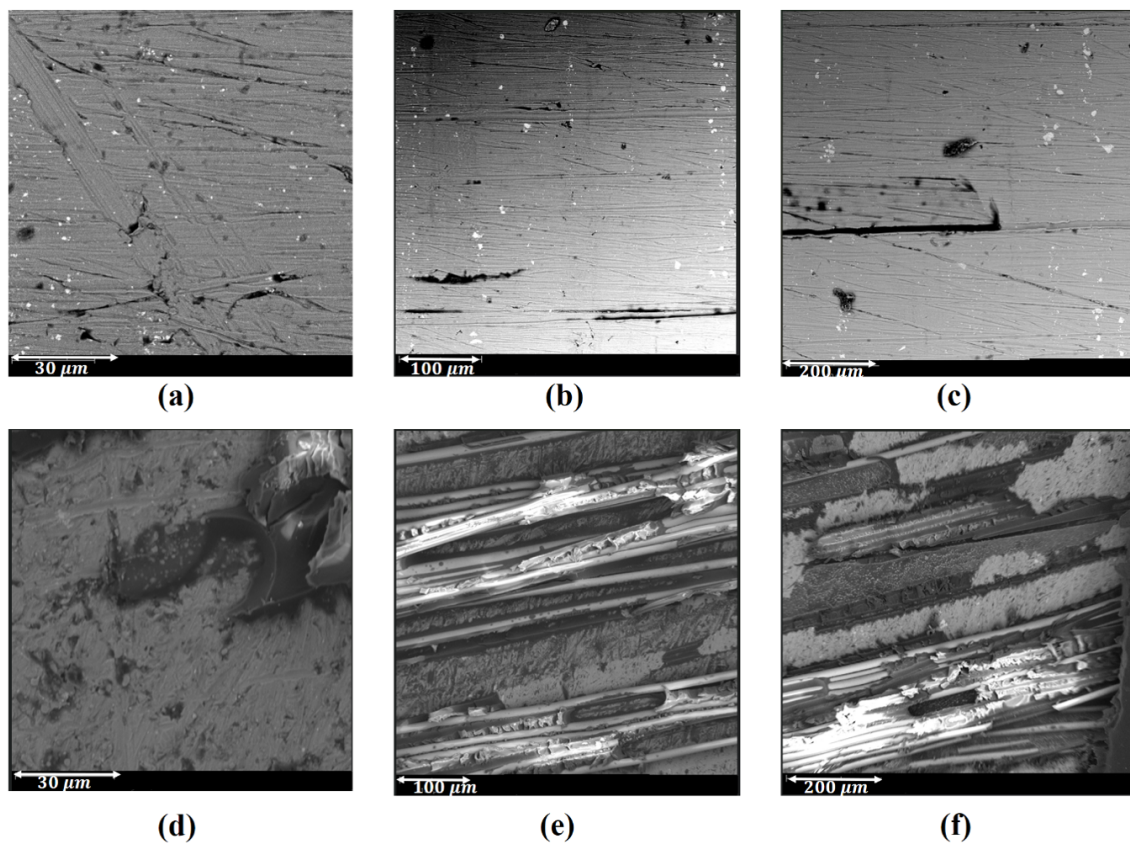


Figure 6.17: SEM images of the aluminum surface subjected to a transverse compressive stress of 90 MPa after debonding in mTCT tests: (a–c) Without treatment; (d–f) With Sol-Gel anodizing.

6.3.4 Mode II interlaminar fracture toughness of GFRP/Cu joints

The typical load-displacement behavior of the mTCT specimen with a GFRP/Cu/GFRP configuration without treatment and with no transverse stress is shown in Figure 6.18 (a), highlighting key points of interest, while Figure 6.18 (b) provides DIC images at these points. The central transverse crack, pre-cracks, pre-crack limit, and propagated cracks are also shown in Figure 6.18 (b). The tensile loading behavior can be divided into four stages. The first stage (up to 0.45 mm displacement) shows an elastic linear response, with no crack propagation. The second stage, from 0.45 mm to 0.9 mm displacement, corresponds to the propagation of all four cracks in the specimen. The DIC images in Figure 6.18 (b) provide details of the propagation. At point P2, which corresponds to the first load drop, one crack propagated approximately 15 mm. By point P3, another crack extended to the end of the specimen. Finally, at point P4, both cracks were fully propagated. This suggests that crack propagation completion occurred at varying loads, influenced by surface morphology and thermal residual stresses. The load-displacement behavior of the GFRP/Cu/GFRP configuration with Sol-Gel anodizing and with no transverse stress is shown in Figure 6.19, where the general behavior is similar to that of the untreated configuration. However, crack propagation occurred at higher loads, between 0.45 mm (10.5 kN) and 1.2 mm (15.2 kN) displacement. Similar to the untreated configuration, different timings in crack propagation were observed at the two interfaces, due to variations in surface morphology from both the cleaning stage and the Sol-Gel treatment. These variations caused slight differences in interlaminar fracture toughness in each interface and across a same interface. These conditions cause one side (metal/GFRP) to experience out-of-plane loads due to the presence of thermal residual stress, which consequently contributes to mode I fracture behavior during the propagation stage for both untreated and treated hybrid configurations. The mode II interlaminar fracture toughness was conservatively calculated from the first peak-load to avoid the influence of mode mixity.

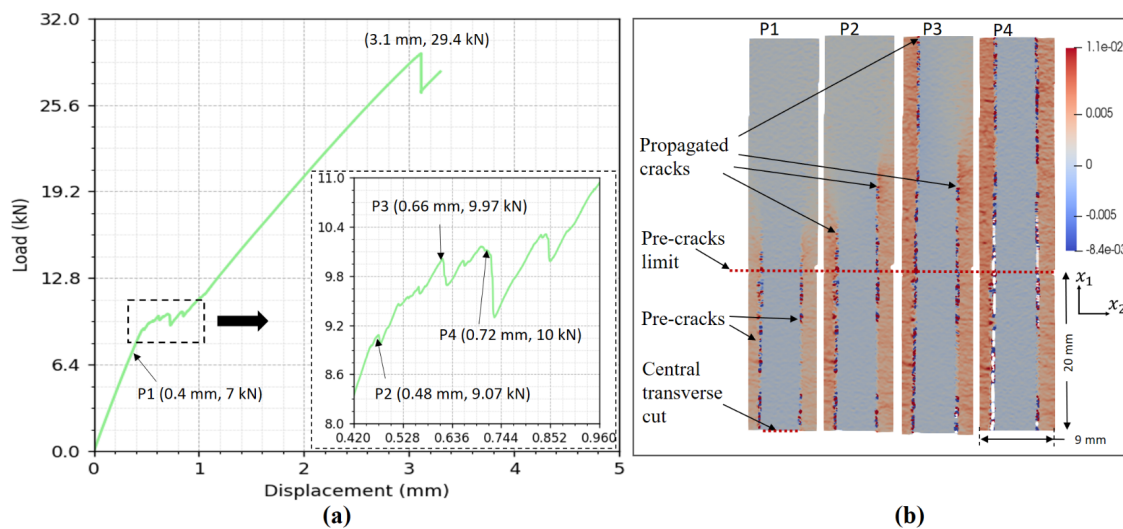


Figure 6.18: The mTCT results of GFRP/Cu/GFRP configuration without treatment: (a) Load-displacement; (b) DIC strain along the x_1 -axis.

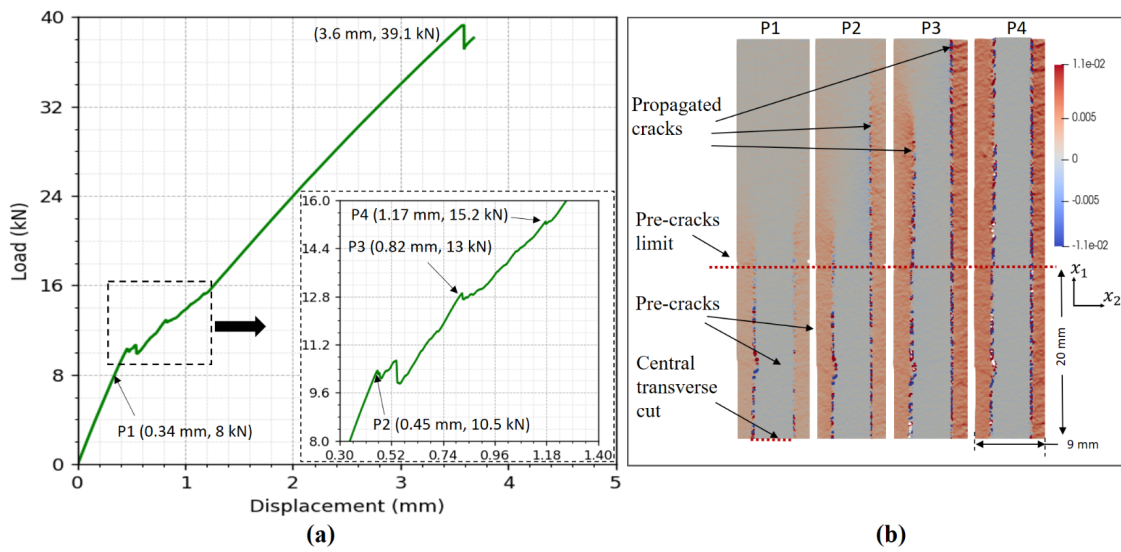


Figure 6.19: The mTCT results of GFRP/Cu/GFRP configuration with Sol-Gel anodizing: (a) Load-displacement; (b) DIC strain along the x_1 -axis.

Figure 6.20 presents the load-displacement curves of GFRP/Cu/GFRP specimens under varying transverse stresses of 0 MPa, 50 MPa, and 90 MPa, comparing untreated samples (Figure 6.20 (a)) with those treated with Sol-Gel anodizing (Figure 6.20 (b)). The results show increasing transverse stress resulted in higher loads for initiate delamination propagation. This highlights the effectiveness of transverse stress in delaying crack propagation in these configurations. Figure 6.20 illustrates the load levels at which the composite begins to partially fail, along with the instances of metal plastic yielding. The data show that partial composite failure occurs above 41 kN for untreated specimens and between 33 kN and 39 kN for specimens treated with Sol-Gel, under varying transverse stress levels. These failures occurred at a sufficient distance from the crack propagation zone, ensuring they did not interfere with the interlaminar fracture toughness calculations. A summary of the interlaminar fracture toughness measurements are presented in Table 6.5. The mode II interlaminar fracture toughness of untreated samples with no transverse stress was measured to be 0.53 N/mm. This value increased to 0.89 N/mm when Sol-Gel anodizing was applied, representing an improvement of approximately 70%. When a transverse stress of 50 MPa was applied to untreated samples, $\mathcal{G}_{II}^c$ was measured to be 1.08 N/mm, showing a twofold improvement compared to the no transverse stress condition. For the Sol-Gel anodized specimens, $\mathcal{G}_{II}^c$ reached 1.29 N/mm, reflecting a 50% improvement compared to the no transverse stress condition. With a further increase in transverse stress to 90 MPa, $\mathcal{G}_{II}^c$ of untreated specimens increased to 1.44 N/mm, nearly three times the value observed in the no transverse stress condition. For Sol-Gel treated specimens, $\mathcal{G}_{II}^c$ improved to 2.08 N/mm, more than twice the baseline value without transverse stress. Regarding the CV, both configurations exhibited values below 10%, confirming the consistency of the manufacturing and testing methodology.

The relationship between mode II interlaminar fracture toughness and transverse stress, along with the best fit of Eq. 6.28 for GFRP/Cu/GFRP with no treatment and with Sol-Gel anodizing,

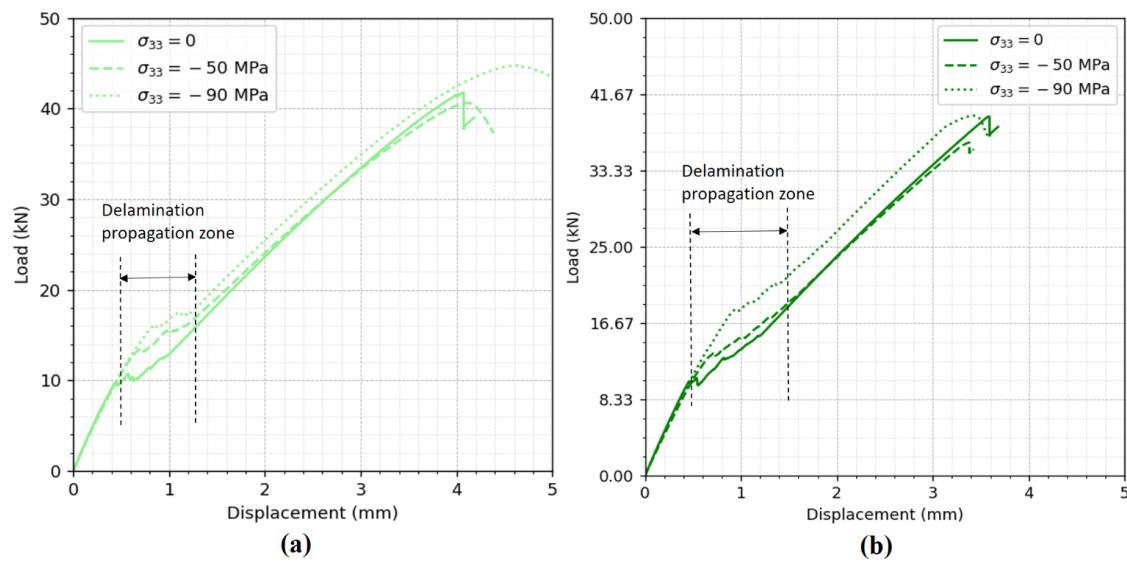


Figure 6.20: Load- displacement of mTCT specimens with GFRP/Cu/GFRP configuration: (a) without treatment, (b) Sol-Gel anodizing.

is shown in Figures 6.21 (a) and 6.21 (b), respectively. The best fit was achieved with η values of 0.0194 MPa^{-1} and 0.0133 MPa^{-1} for the untreated and Sol-Gel anodized configurations, respectively. The slope of the curve ($\mathcal{G}_{II0}^c \eta$) for the untreated and Sol-Gel treated configurations were 0.0103 and 0.0118, respectively. This suggests that the Sol-Gel treated configuration exhibited a slightly higher slope with increasing transverse stress, indicating that it was marginally more sensitive to the transverse stress. The R^2 value for the fit curve was calculated as 0.999 for untreated samples, indicating a very good match between the fit curve and the data. For the treated samples with Sol-Gel anodizing, the R^2 value was 0.92.

Table 6.5: Mode II interlaminar fracture toughness of GFRP/Cu/GFRP configuration.

σ_{33} (MPa)	Treatment	Load (kN)	$\mathcal{G}_{II}^c$ (N/mm)	CV (%)
0	Without	8.77	0.53	2.6
	Sol-Gel	11.77	0.89	9.7
-50	Without	13.1	1.08	8.5
	Sol-Gel	14.4	1.29	4.2
-90	Without	15.3	1.44	6.4
	Sol-Gel	18.7	2.08	7.1

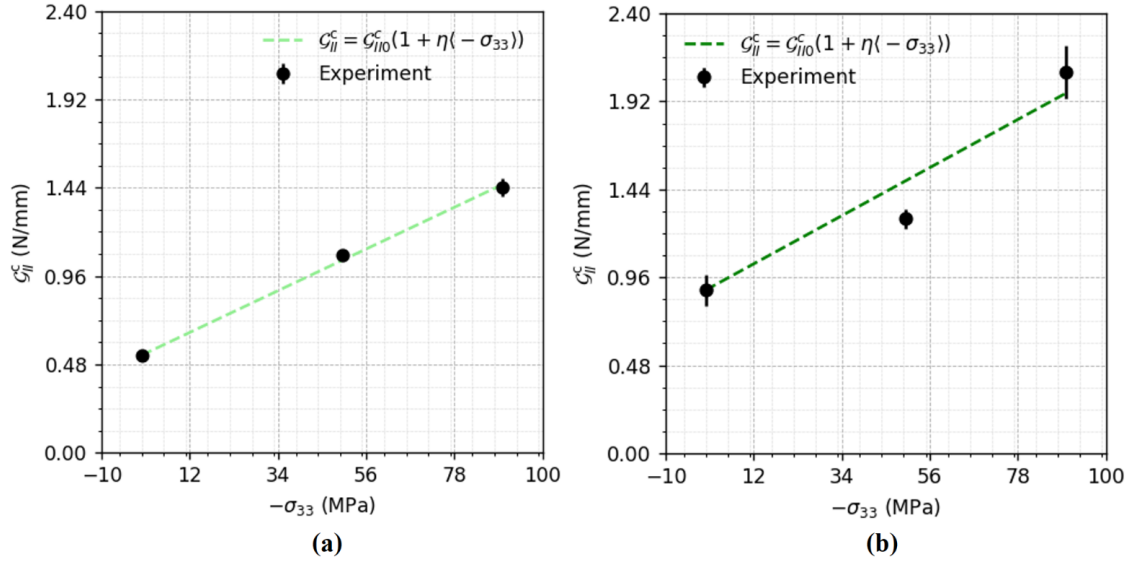


Figure 6.21: Mode II interlaminar fracture toughness vs. through-thickness stress of GFR-P/Cu/GFRP, (a) Without treatment ($\eta = 0.0194 \text{ MPa}^{-1}$, $R^2 \approx 1$), (b) Sol-Gel anodizing ($\eta = 0.0133 \text{ MPa}^{-1}$, $R^2 = 0.92$).

Figure 6.22 shows SEM images of the surface of copper with and without treatment after debonding in the mTCT test with no transverse stress. The images were taken 10 mm after the initial crack tip in the middle of the specimen's width. Figure 6.22 (a) shows the untreated sample, where adhesive failure was the most common type of failure observed, suggesting weak bonding between the copper and composite. Cohesive failure was also noted in a few areas. Figure 6.22 (b) show the surface of copper with Sol-Gel treatment. The treated samples exhibited a larger portion of cohesive failure compared to the untreated samples. This suggests that the bond between the adhesive and substrates was stronger with Sol-Gel anodizing than without treatment. Additionally, the composition analysis of the copper surface revealed that the untreated sample contained only copper across most of the substrate surface, representing the pure material of the substrate. In contrast, the Sol-Gel-treated samples predominantly contained silicon, oxygen, and carbon on the copper surface. These elements, derived from the Sol-Gel paste and resin, indicate the high stability of the Sol-Gel treatment and the effectiveness of the bonding.

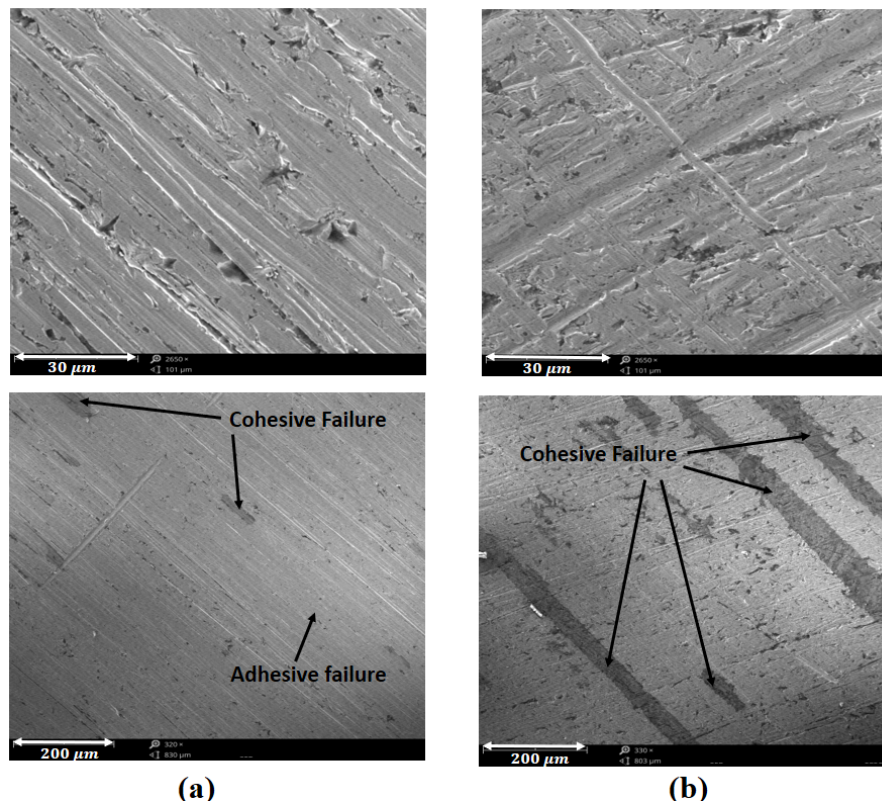


Figure 6.22: SEM images of the surface of the copper without compressive transverse stress, after debonding in mTCT tests: (a) Without treatment, (b) Sol-Gel anodizing.

Figure 6.23 presents SEM images of both untreated and Sol-Gel-treated copper surfaces following debonding in the mTCT test under a transverse compressive stress of 90 MPa. Figures 6.23 (a) to 6.23 (c) correspond to untreated specimens, where cohesive failure and fiber debonding are the predominant failure mechanisms observed. In comparison with the specimens tested without compressive stress (Figures 6.22 (a) to 6.22 (b)), a higher incidence of cohesive failure is evident, along with more pronounced fiber debonding. These observations indicate an improvement in the interfacial bonding between the copper and the composite material under transverse compressive loading. Figures 6.23 (d) to 6.23 (f) show SEM images of samples treated with Sol-Gel anodizing. These specimens exhibit widespread fiber debonding and adhesive failure across the majority of the surface. Relative to their counterparts tested without compressive stress (Figures 6.22 (c) to 6.22 (d)), the extent of fiber debonding is considerably increased, highlighting the influence of compressive loading on the failure characteristics of the treated interface.

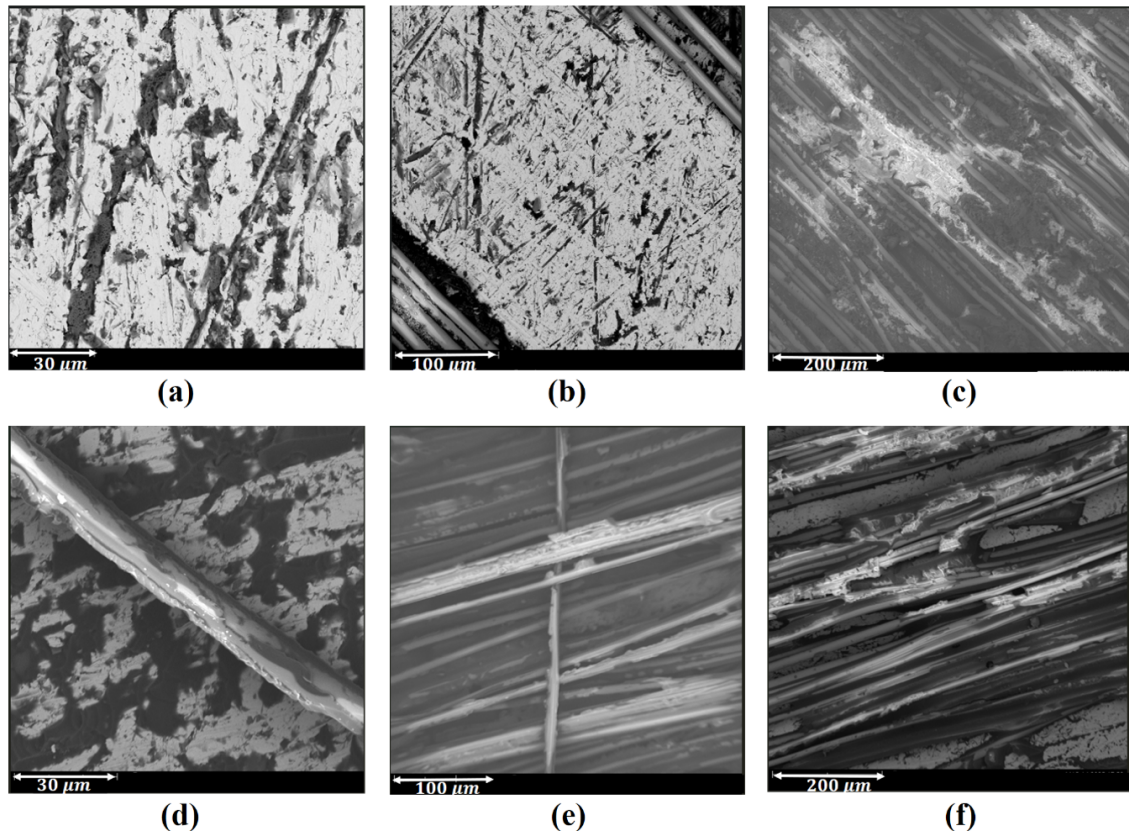


Figure 6.23: SEM images of the copper surface under a transverse compressive stress of 90 MPa after debonding in mTCT tests: (a–c) Without treatment; (d–f) With Sol-Gel anodizing.

6.3.5 Comparison between all-GFRP, GFRP/Al, and GFRP/Cu joints

The interlaminar fracture toughness values for different joints, including all-GFRP, GFRP/Al, and GFRP/Cu, are presented in Figure 6.24. The results reveal that, with no transverse stress, all-GFRP mTCT specimens exhibit a $\mathcal{G}_{II0}^c$ of 1.6 N/mm. In contrast, hybrid GFRP/Al laminates have values ranging from 0.31 N/mm (no treatment) to 0.8 N/mm (Sol-Gel treatment), while hybrid GFRP/Cu laminates range from 0.53 N/mm (no treatment) to 0.89 N/mm (Sol-Gel treatment). These results indicate that the all-GFRP configuration achieves nearly double the $\mathcal{G}_{II0}^c$ of the hybrid laminates with Sol-Gel treatment. Furthermore, both hybrid configurations exhibit almost identical $\mathcal{G}_{II0}^c$ values when treated with Sol-Gel anodizing. Without treatment, however, the GFRP/Cu configuration demonstrates higher interlaminar fracture toughness compared to GFRP/Al. These findings underscore the role of Sol-Gel treatment in enhancing bonding strength, leading to more symmetric and balanced adhesion in structural batteries.

Additionally, the $\mathcal{G}_{II}^c$ in all configurations increased with the application of transverse stress. However, all-GFRP specimens showed a greater increase compared to the hybrid laminates. Among the hybrid laminates, the Sol-Gel-treated configurations exhibited a higher improvement in $\mathcal{G}_{II}^c$ under transverse stress compared to untreated ones.

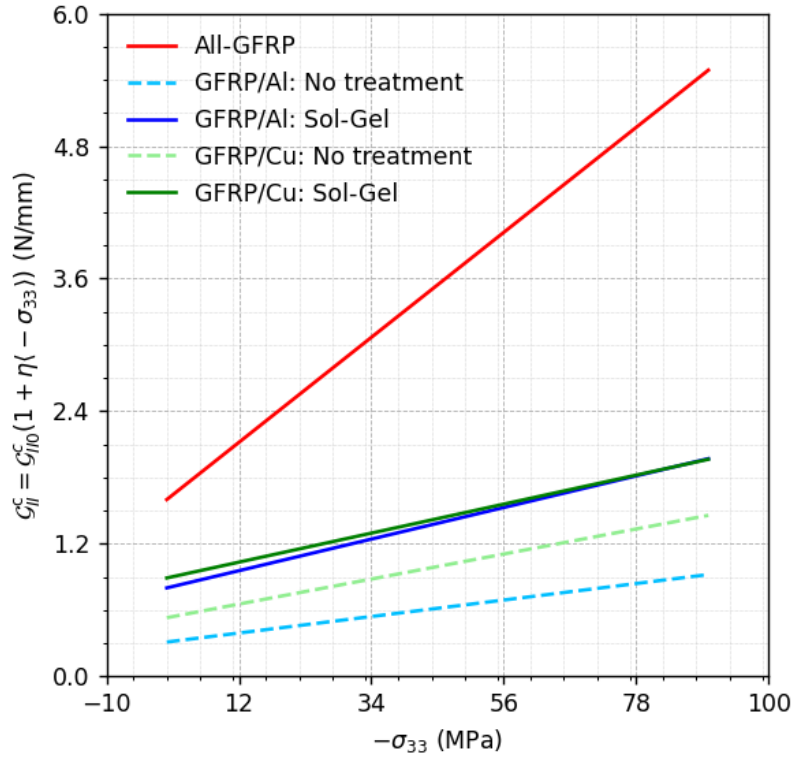


Figure 6.24: Mode II interlaminar fracture toughness of different configurations.

6.3.6 Comparison between numerical simulations, experimental data, and analytical results

In this section, both hybrid laminates, GFRP/Al/GFRP and GFRP/Cu/GFRP, without transverse stress were numerically simulated in Abaqus to discuss the numerical results of the hybrid mTCT specimen, and compare them with experimental data. To reduce computational time, only one-eighth of the model was simulated, and mesh and boundary conditions were similar to those in Subsection 6.2.2, but without compressive transverse stress ($\sigma_{33} = 0$). The delamination propagation was modeled using cohesive zone elements. For damage initiation, the stress-based quadratic initiation criterion (QUADS) was selected. Damage progression followed an energy-based linear softening law combined with mode-mixity behavior based on Benzeggagh and Kenane (Benzeggagh and Kenane (1996)), accounting for delamination mode interaction using the exponent η_{BK} . The stiffness of the cohesive elements was considered as 1×10^6 N/mm³ as was recommended by Turon et al. (2007) and Camanho et al. (2003). The strength of the interfacial cohesive layer for each experimentally obtained G_{IIC} was obtained by using the following equation obtained from Turon et al. (2007):

$$\bar{\tau}_N = \sqrt{\frac{9\pi E_c \mathcal{G}_I^c}{32l_e N_e}} \quad (6.29)$$

Here, E_c was considered as the longitudinal Young's modulus of the composite laminate. l_e is the size of the element along the direction of the crack propagation (0.5 mm), N_e is the number of

elements within the cohesive zone, which was chosen to be equal to 5 (Turon et al. (2007)). The effective strength in pure mode I, τ_N , was calculated as:

$$\tau_N = \min(\bar{\tau}_N, Y_T) \quad (6.30)$$

where $Y_T = 25$ MPa is the transverse tensile strength of the unidirectional GFRP laminate. The effective shear strength was calculated using (Turon et al. (2010)):

$$\tau_{sh} = \tau_N \sqrt{\frac{\mathcal{G}_{II}^c}{\mathcal{G}_I^c}} \quad (6.31)$$

The value of $\mathcal{G}_{II}^c$ was taken from the experimental part of this work, for both untreated samples and those with Sol-Gel anodizing. To select the appropriate value of $\mathcal{G}_I^c$, a logical approach was followed, guided by Chapter 5 (Niazi et al. (2024)). Specifically, the values for untreated samples were taken directly from the previous chapter. However, for the Sol-Gel-treated samples, since the $\mathcal{G}_I^c$ values were not purely Mode I, a value similar to $\mathcal{G}_{II}^c$ was selected. In summary, the parameters compiled in Table 6.6 were considered for this numerical simulation.

Table 6.6: Considered data for numerical simulation ($\mathcal{G}_I^c$ data were taken from Chapter 5 (Niazi et al. (2024))).

Configurations	Surface Treatment	$\mathcal{G}_I^c$ (N/mm)	$\mathcal{G}_{II}^c$ (N/mm)	τ_N (MPa)	τ_{sh} (MPa)	K (N/mm ³)
GFRP/Al/GFRP	Without treatment	0.37	0.31	25	23	10^6
	Sol-Gel	0.8	0.8	25	25	10^6
GFRP/Cu/GFRP	Without treatment	0.26	0.53	25	36	10^6
	Sol-Gel	0.89	0.89	25	25	10^6

Linear-elastic transverse-orthotropic material properties were defined for the composite plies, while the metal layers were modeled as linear-elastic isotropic material. Hard contact in the normal direction and frictionless contact in the transverse direction were chosen for the surface-to-surface contact in all pre-crack regions. Before the introduction of mechanical load, a thermal step was applied. The specimen was cooled from the curing temperature (80°C) to room temperature (20°C), resulting in residual thermal stress. Previously, in the material step, the thermal expansion coefficient of both the metal (as an isotropic property) and the composite (as orthotropic properties) were input. Regarding the cohesive zone part, the coefficient of thermal expansion (CTE) was considered to be isotropic and equal to the amount of CTE of composite laminate in the transverse direction. Both unidirectional composite laminate and metal were meshed using incompatible mode 8-node linear solid elements (C3D8I) with size of 0.5 mm. The cohesive zones were meshed using 8-node three-dimensional cohesive elements (COH3D8) with dimensions of 0.5 mm. The total number of elements were 42240. During the thermal analysis step in Abaqus, simply supported boundary conditions were applied to prevent unrealistic movements and ensure numerical stability, and were deactivated during the second step (mechanical tensile loading). In the second step, a displacement boundary condition was applied to both end of the specimen in

the length direction (X direction) to introduce tensile load. The comparison of experimental, numerical, and analytical results for both configurations are presented in Figures 6.25 and 6.26. The data show that the analytical results are in excellent agreement with the numerical simulations for both GFRP/Al/GFRP and GFRP/Cu/GFRP, with a deviation of less than 1%. When comparing the numerical results to the experimental data, the propagation initiation load for both approaches is closely aligned. However, some discrepancies still exist. This is because the numerical simulation was based on the average $\mathcal{G}_{II}^c$, which was derived from experimental data and exhibits a CV for each configuration. In contrast, the experimental results presented in Figures 6.25 and 6.26 correspond to only one of the three samples for each configuration. Therefore, the propagation initiation points in the numerical and experimental methods do not perfectly coincide. An important distinction between the numerical and experimental approaches lies in the idealization of the numerical model. In the numerical simulation, the system is assumed to be ideal, leading to stable and uniform crack propagation under constant loading. However, in the experimental setup, the hybrid laminate is not a perfect system. Slight variations in crack lengths, surface morphology of the metal across the laminate faces, and slight deviations from perfectly axial loading introduce additional complexities. Consequently, Mode I loading influences the experimental results, which is not captured in the idealized numerical model. As detailed in the experimental section of this study, $\mathcal{G}_{II}^c$ was conservatively calculated based on the first load peak (the initiation point of crack propagation) to minimize the effects of Mode I loading. The results validate the accuracy of the analytical calculations, numerical simulations, and the experimental methodology used in this study.

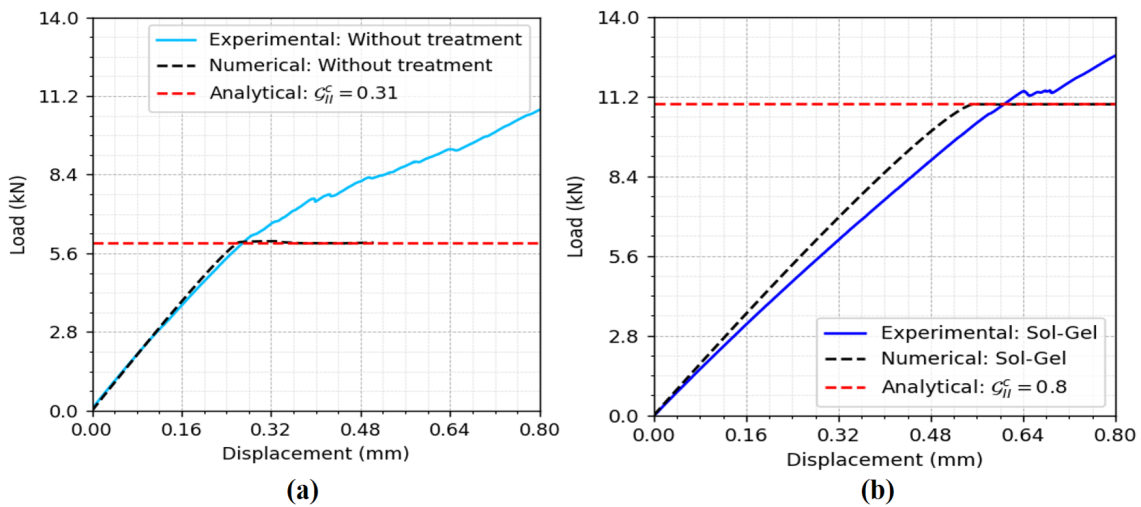


Figure 6.25: Comparison between experimental, numerical, and analytical results of GFRP/Al/GFRP: (a) Without treatment; (b) Sol-Gel anodizing.

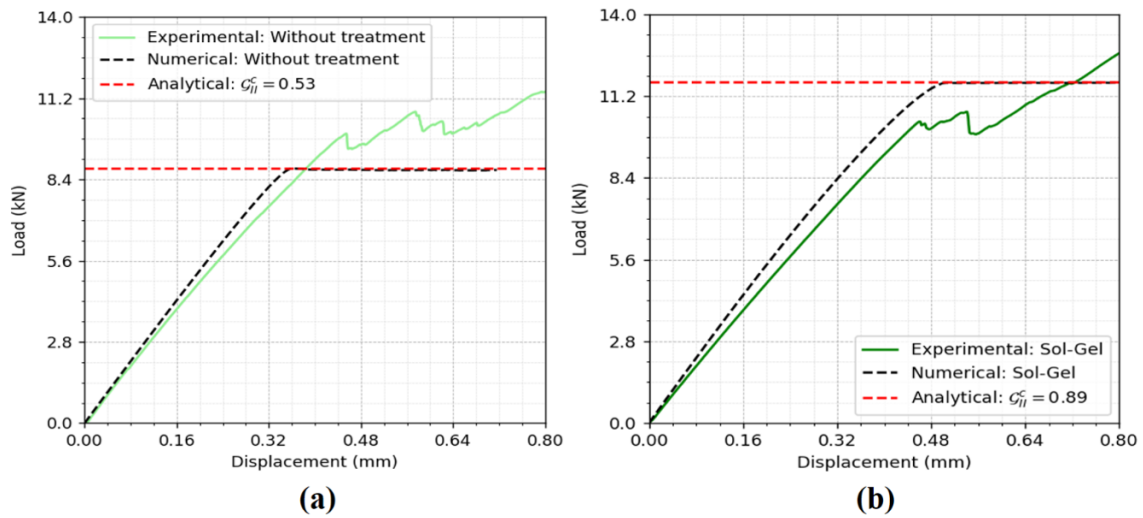


Figure 6.26: Comparison between experimental, numerical, and analytical results of GFRP/Cu/GFRP: (a) Without treatment; (b) Sol-Gel anodizing.

6.4 Conclusions

This chapter evaluated the bonding between three joints suitable for structural batteries including all-GFRP, GFRP/Al, and GFRP/Cu, with focus on the analysis of the mode II interlaminar fracture toughness using the mTCT test. An analytical equation was derived to calculate the mode II interlaminar fracture toughness of hybrid laminates, considering the mismatch in elastic and thermal expansion coefficients, and it was numerically verified using the Virtual Crack Closure Technique. The chapter examined the effects of Sol-Gel surface treatment and compressive transverse stress on the bonding performance. The results showed that the all-GFRP configuration demonstrated superior interlaminar fracture toughness, nearly double that of hybrid configurations. Among the investigated hybrid joints, Sol-Gel treatment significantly improved mode II interlaminar fracture toughness, yielding similar results for both GFRP/Al and GFRP/Cu, while untreated GFRP/Cu outperformed untreated GFRP/Al. This suggests that the Sol-Gel treatment not only enhances bonding but also leads to more symmetric bonding in the structural batteries. Moreover, in all configurations interlaminar fracture toughness values increased with the application of compressive transverse stress. However, the all-GFRP specimens exhibited a greater increase compared to the hybrid laminates. Among the hybrid laminates, the Sol-Gel-treated configurations showed a more significant improvement in fracture toughness under compressive transverse stress compared to the ones without treatment. Overall, these findings underscore the importance of both Sol-Gel surface treatment and compressive transverse stress in improving the mode II interlaminar fracture toughness of hybrid laminates for structural batteries applications.

Part III

Structural electrolyte

Chapter 7

Thermo-electro-mechanical characterization of thermoset/thermoplastic films

While thermoplastic polymers are commonly used in composite polymer electrolytes for load-bearing energy storage devices, they often lose mechanical strength when exposed to heat from internal reactions or external sources like sunlight. Incorporating heat-resistant thermoset polymers such as epoxy can mitigate this degradation and enhance their overall performance. This chapter investigate the thermo-electro-mechanical properties of thermoplastic/epoxy blends, employing three thermoplastic polymers—PEO, PVA, and PVAc. A modified solution casting technique that retains the benefits of the conventional method, while improving electrode/thin film contact is introduced. Thin films are fabricated using various solvents: dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), and water for PEO and PVA blends, and DMSO, NMP, and methanol for PVAc blends. Microscopy imaging is conducted to visualize surface morphology and identify potential phase separation. Simultaneous thermal analysis is employed to evaluate thermal properties, material degradation, and the presence of trapped solvent. Potentiostatic electrochemical impedance spectroscopy is employed to obtain Nyquist plots and determine the ionic conductivity. Dynamic mechanical analysis is used to obtain the thermo-mechanical properties. Blending epoxy with a thermoplastic polymer using a compatible solvent produces materials with high ionic conductivity and enhanced thermomechanical stability.

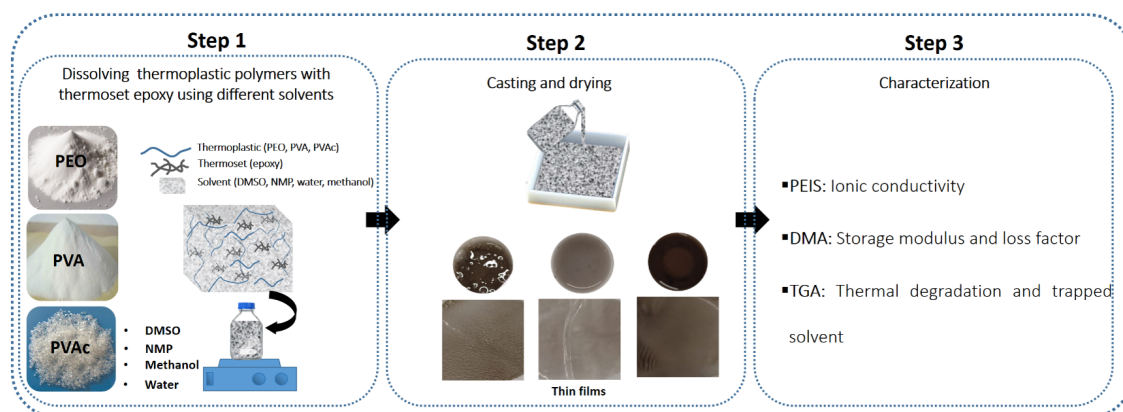
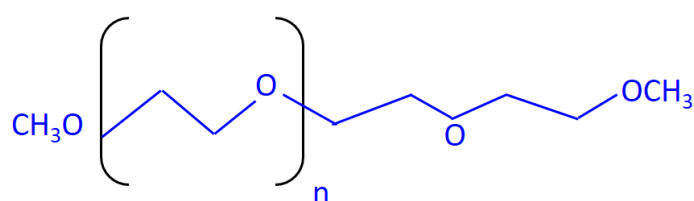


Figure 7.1: Thermo-electro-mechanical characterization of thermoset/thermoplastic films.

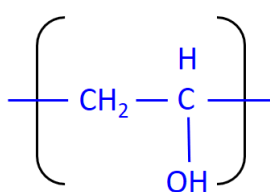
7.1 Introduction

Composite polymer electrolytes (CPEs), which combine organic polymers with inorganic salts and nano-fillers, offer significant advantages over single-phase solid-state and liquid-state electrolytes. These benefits include improved safety, flexibility, lower interfacial resistance, and reduced hygroscopicity (Natarajan et al. (2017); Zhao et al. (2021); Park et al. (2013); Cheng et al. (2021)). Furthermore, CPEs can serve a dual function in structural batteries by providing both ionic conduction and mechanical strength (Ihrner and Johansson (2017); ?; Niazi et al. (2025a)). State-of-the-art CPEs for lithium- and sodium-ion batteries have demonstrated ionic conductivities in the range of 10^{-2} to 10^{-5} S/cm (Li et al. (2024b); Yang (2002)), representing a significant enhancement over pure polymer films, which typically exhibit much lower conductivities on the order of 10^{-8} to 10^{-11} S/cm (Manjunath et al. (2015); Yang (2002)). For instance, PEO-based electrolytes incorporating ceramic nanoparticles (e.g., LLZO or LATP), cross-linked networks, and lithium bis(trifluoromethane)sulfonimide (LiTFSI) have demonstrated ionic conductivities exceeding 10^{-4} S/cm at ambient temperature (Meda et al. (2024)). Similarly, PVA-based composites functionalized with SiO_2 and combined with LiCl have achieved conductivities as high as 5.6×10^{-2} S/cm (Tang et al. (2025)), compared to pure PVA, which exhibits conductivities as low as 2×10^{-10} S/cm (Manjunath et al. (2015)). Despite these advancements, several key challenges remain—particularly for load-bearing applications such as structural batteries. One major issue is that thermoplastic polymers—widely used as hosts in CPEs due to their high ionic conductivity (Zakaria et al. (2023); Reinoso and Frechero (2022))—tend to soften at elevated temperatures, compromising the mechanical integrity of the CPEs (Şerban et al. (2013); Cheng et al. (1990)). While this softening enhances ionic conductivity, it is detrimental to the mechanical performance required for structural applications. On the other hand, thermoset polymers exhibit excellent thermal stability and stiffness due to extensive cross-linking, which limits chain mobility. Their irreversible curing process results in a robust, heat-resistant network. However, their low ion mobility makes them less suitable as primary hosts for ion transport (Costa et al. (2020)). A promising solution involves blending thermoplastics with thermosets, which can potentially combine the fa-

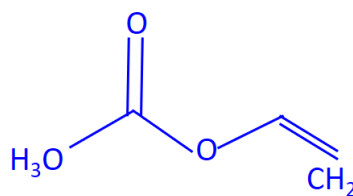
avorable mechanical properties of thermosets with the high conductivity of thermoplastics (Yao et al. (2019); Sequeira and Santos (2010); Meynie et al. (2004); Niazi et al. (2025b)). Various thermoplastic polymers have already been investigated for use in battery electrolytes, including polyvinyl chloride (PVC) (Yuan et al. (2025)), polyvinyl alcohol (PVA) (Zakaria et al. (2022)), polyvinyl acetate (PVAc) (Masoud et al. (2016)), polyethylene oxide (PEO) (Chang et al. (2023)), polyvinylidene fluoride (PVdF) (Varghese et al. (2023)), polymethyl methacrylate (PMMA) (Su et al. (1997)), and chitosan (Lasrado et al. (2020)), among others (Ngai et al. (2016)). Among these, PEO stands out for its semi-crystalline structure, excellent film-forming ability, and low glass transition temperature, making it especially flexible and highly suitable for complexation with metal salts (Andrews et al. (2018); Appetecchi et al. (2001); Young et al. (2014)). PVAc also serves effectively as a polymer host and plasticizer, offering strong ionic conductivity and mechanical properties at ambient temperatures, thanks to its ester-linked side chains and high dipole moment (Henry et al. (2002)). PVA, derived from the hydrolysis of PVAc, provides a valuable balance of mechanical strength, dielectric performance, environmental friendliness, and cost-effectiveness (Kassenova et al. (2022); Júnior and Boudinov (2023); Aziz et al. (2021)). Figure 7.2 shows the chemical structure of PEO, PVA, and PVAc.



(a) PEO



(b) PVA



(c) PVAc

Figure 7.2: Chemical structure of: (a) PEO (Braun and Meyer (2013)); (b) PVA (Gadhav (2023)); (c) PAVc (Gadhav (2023)).

Various techniques are used in the manufacturing of the polymeric thin films, such as solution casting (Makireddi et al. (2015)), solvent-free processing (Zhu et al. (2023b); Ten and Vermerris (2015)), phase inversion (Jamil et al. (2017)), electrospinning (Feng et al. (2010)), *in-situ* polymerization (Li et al. (2015)), and layer-by-layer deposition (Branco et al. (2016)). Solution casting

remains the most commonly used technique due to its simplicity, versatility, homogeneous dispersion, and scalability. However, this method suffers from limitations like poor interfacial contact, which reduces energy density (Li et al. (2022a)). More advanced techniques like *in-situ* polymerization can improve electrode-electrolyte interfaces, but they often introduce issues such as voids, dead weight, and poor control over uniformity during manufacturing (Li et al. (2022a); Vijayakumar et al. (2021)). This study addresses these limitations by introducing a modified solution casting approach that includes the initial fabrication of thin films using the conventional solution casting technique, followed by a wetting step with the same polymer solution composition, and *in-situ* drying of the film within the cell. These additional steps are designed to enhance electrode-electrolyte adhesion and improve interfacial contact. It is worth noting that in solvent-based fabrication methods such as solution casting, incomplete drying can result in residual solvents within the film. While such retention can lower the glass transition temperature and improve ionic conductivity, it may also compromise mechanical strength due to the plasticizing effect (Foran et al. (2020); Khan et al. (2007)). Therefore, solvent selection and accurate quantification of trapped solvent are essential when evaluating a film's electrochemical and mechanical properties (Barbosa et al. (2023); Dohrn et al. (2021); Hansen (1995); Al-Fakih et al. (2025)). In summary, this work investigates the thermo-electro-mechanical properties of blends composed of thermoplastic polymers (e.g., PEO, PVA, and PVAc) and epoxy, processed using a modified solution casting technique. A range of solvents was examined, including Dimethyl sulfoxide (DMSO), N-Methyl-2-pyrrolidone (NMP), and water for PEO and PVA blends, and DMSO, NMP, and methanol for PVAc compositions. This selection was based on their ability to dissolve the polymers and their differing polarity and boiling points. DMSO and NMP are polar aprotic solvents known for their strong solvating power and good compatibility with both thermoplastic and thermoset polymers, facilitating uniform film formation (Sherwood et al. (2016)). Methanol and water are polar protic solvents characterized by strong polarity and low boiling points. These properties make them advantageous for rapid solvent evaporation and cost-effective processing during thin-film formation (Mazzini et al. (2018); dos Santos Pereira (2023)). These solvents represent a range of physicochemical properties relevant to the dissolution and processing of the thermoplastic/thermoset blends. This study employed simultaneous thermal analysis (STA) techniques, including differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), to characterize the thermal behavior and degradation of the polymer compositions. The analysis included quantification of residual solvent content in each blend, as well as determination of key thermal properties such as decomposition temperature, glass transition temperature, and melting point. Potentiostatic electrochemical impedance spectroscopy (PEIS) was conducted to obtain Nyquist plots and calculate the ionic conductivity of the polymeric film systems. Additionally, the dynamic mechanical analysis (DMA) was used to evaluate thermomechanical properties, including storage modulus and viscoelasticity factor.

7.2 Materials and methods

7.2.1 Materials

In this study, PEO with a molecular weight of 2,000,000 was purchased from Sigma-Aldrich. PVA was sourced from Thermo Scientific, with a molecular weight range of 146,000-186,000 and a purity exceeding 99.3%. PVAc with a molecular weight of 170,000 was acquired from Thermo Scientific. The NMP solvent, supplied by Thermo Scientific, with a purity of 99%. DMSO was obtained from Labkem, while methanol was sourced from Fisher. The epoxy AS-89, was obtained from HBQUIMICA and constituted a two-component system. Part A functioned as the resin, while part B served as the hardener and was black in color, with a recommended mixing ratio of 100:45, as specified in the supplier data sheet. The detailed composition of both part A and part B, extracted from the supplier's data sheet, is presented in Table 7.1.

Table 7.1: Components of the thermoset epoxy.

Epoxy part	Components
Part A	Epichlorohydrin-formaldehyde phenol: $\geq 30\%$, $< 50\%$
	2,2-bis-[4-(2,3-epoxipropoxy)fenil]propano: $\geq 30\%$, $< 50\%$
	Reaction product of Epichlorohydrin/Bisphenol-A: $\geq 12.5\%$, $< 20\%$
	1,6-Hexamethylenediol diglycidyl Ether: $\geq 3\%$, $< 5\%$
	Silane, trimethoxy[3-(oxiranylmethoxy)propyl]: $\geq 1\%$, $< 3\%$
Part B	2-Propenenitrile, polymer with 1,3-butadiene, 1-cyano-1-methyl-4-oxo-4-[[2-(1-piperazinyl)ethyl]amino]butyl terminated: $\geq 30\%$, $< 50\%$
	Ethanamine, 2,2'-[1,2-ethanediylbis(oxy)]bis: $\geq 20\%$, $< 25\%$
	Phenol, 4,4'-(1-methylethylidene)bis-, polymer with N,N'-bis(2-aminoethyl)-1,2-ethanediamine and (chloromethyl)oxirane: $\geq 10\%$, $< 12.5\%$
	Fatty acids, C18-unsatd., dimers, polymers with tall-oil fatty acids and triethylenetetramine: $\geq 10\%$, $< 12.5\%$
	N'-(3-Aminopropyl)-N,N-dimethylpropane-1,3-diamine: $\geq 7\%$, $< 10\%$
	Polymer of MXDA: $\geq 3\%$, $< 5\%$
	m-Phenylenebis(methylamine): $\geq 0.25\%$, $< 0.5\%$
	3-aminometil-3,5,5-trimetilciclohexilamina: $\geq 0.25\%$, $< 0.5\%$

A summary of the various polymer compositions is provided in Table 7.2.

Table 7.2: Polymers and solvents used for manufacturing the thin films.

Polymers	Solvents	Epoxy (%)
PEO	DMSO, NMP, Water	0, 30
PVA	DMSO, NMP, Water	0, 30
PVAc	DMSO, NMP, Methanol	0, 30

7.2.2 Modified solution casting technique

In this study, the conventional solution casting technique was modified by introducing additional steps to improve the contact between electrodes and the thin film. The procedures of this technique are shown in 7.3. Similar to the conventional approach, the process began with the preparation

of the polymer solution using selected solvents and a magnetic stirrer. In this study, PEO was dissolved at 50°C for approximately 6 hours, while PVA was dissolved at 100°C for the same duration. PVAc required a temperature of 50°C for methanol and 90°C for DMSO and NMP. For epoxy-based compositions, parts A and B of the epoxy were mixed in a 100:45 ratio as recommended by supplier and then combined with the polymer solution in a 30:70 ratio, excluding the solvent's weight. The resulting mixtures were stirred for about 10 minutes to achieve homogeneous solution. Visual representations of the various polymer solutions are shown in Figure 7.4. The solutions then were poured into silicone molds and dried in a vacuum heat chamber at 80°C for 60 hours. After drying, the thin films were wetted on both sides with the same solution using a brush and assembled with electrodes, using a single spring clamp to apply sufficient pressure (about 0.7 bar) and ensure good contact during drying (see Figure 7.3). The solution used to wet the polymer film was identical to the solution employed in its preparation. For example, the PVA/epoxy film synthesized with DMSO was wetted using its corresponding solution blend (PVA/epoxy/DMSO). The assembly was then dried in a vacuum heat chamber at 80 °C for 12 hours. Finally, the assembly was sealed with a laminated film and tested. The electrodes were pure aluminum sheets, measuring 20×20 mm² and 0.5 mm thick. The aluminum sheets used as electrodes were originally covered with a thin protective Teflon layer by the supplier to prevent oxidation during storage and transport. Prior to use, this layer was carefully removed, and the sheets were rinsed with acetone. No additional surface treatment was applied, preserving consistent surface roughness and area to ensure reliable and comparable ionic conductivity measurements of the polymeric films.

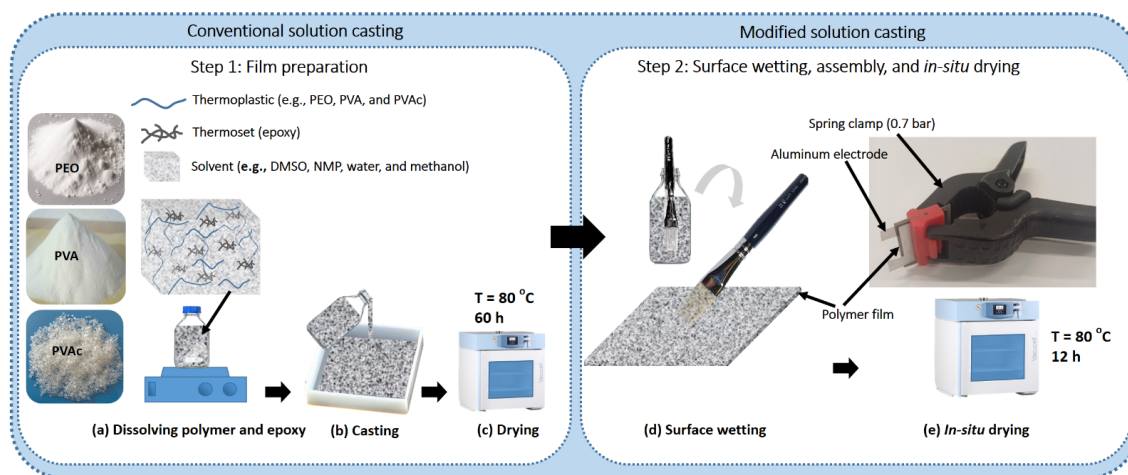


Figure 7.3: Procedures of modified solution casting method.

7.2.3 Simultaneous thermal analysis

In this study, the STA300 instrument from HITACHI with a platinum pan, shown in Figure 7.5, was used to perform simultaneous thermal analysis (STA) and characterize the physical and chemical properties of polymeric thin films. This involved examining factors such as melting point, glass

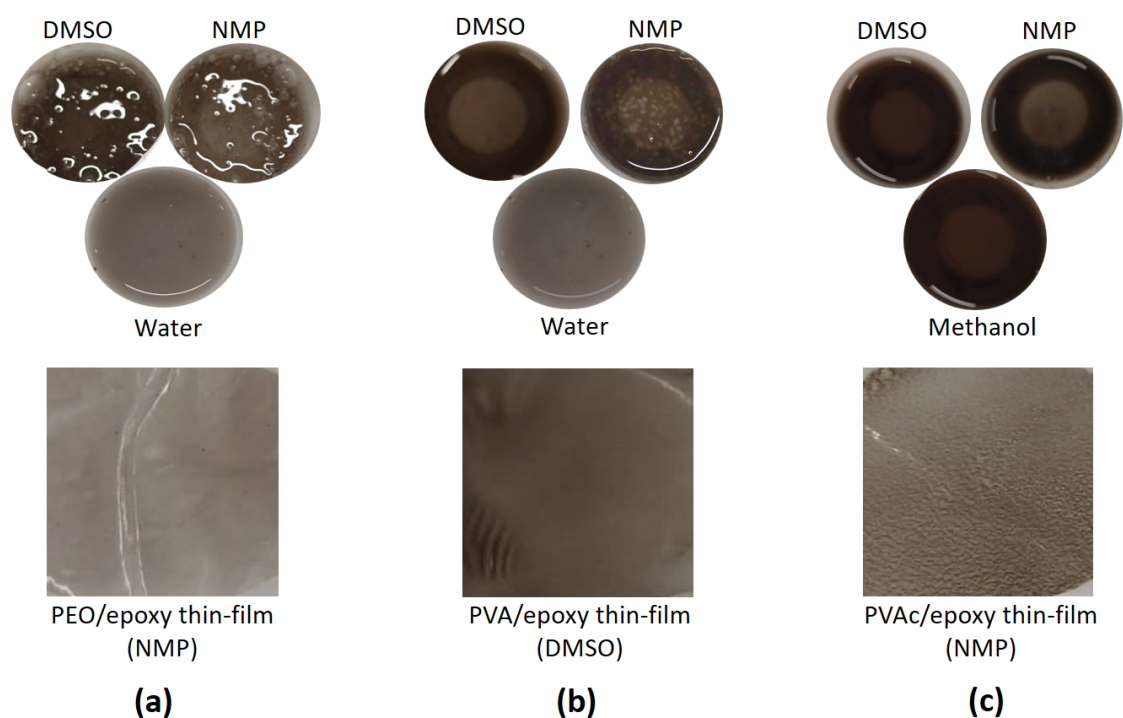


Figure 7.4: Visual comparison of various polymer solutions synthesized with different solvents: (a) PEO/Epoxy; (b) PVA/Epoxy; (c) PVAc/Epoxy.

transition temperature, evaporation, and decomposition behavior at various temperatures over time, employing two complementary thermal analysis techniques: differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TGA was further employed to determine the trapped solvents and moisture absorption of each composition. The tests were performed using a platinum pan, heating from 30 °C to 700 °C with a temperature ramp rate of 10 °C/min. A consistent nitrogen gas flow of 100 mL/min was maintained throughout the whole testing process. In the case of pure epoxy, the sample was derived from a fully cured epoxy block cured at room temperature for seven days. For the unsynthesized pure polymers, samples were directly obtained from the raw polymers supplied by the manufacturer.

7.2.4 Potentiostatic electrochemical impedance spectroscopy

The PEIS measurements were conducted using a Biologic VMP-300 potentiostat. The Nyquist plots of the solid polymer thin films were obtained through AC impedance spectroscopy, and the collected data post-processed using EC-Lab V11.52 software. All impedance spectra presented in this study were measured between the working and sense electrode (one of the aluminum electrodes) and the counter and reference electrode (another aluminum electrode). Due to the symmetric nature of the cells used, this configuration does not introduce any discernible differences in the impedance measurements. In this study, PEIS tests were performed using an amplitude of 10 mV across a frequency range spanning from 7 MHz to 1 Hz. Figure 7.6 depicts the Biologic tester.

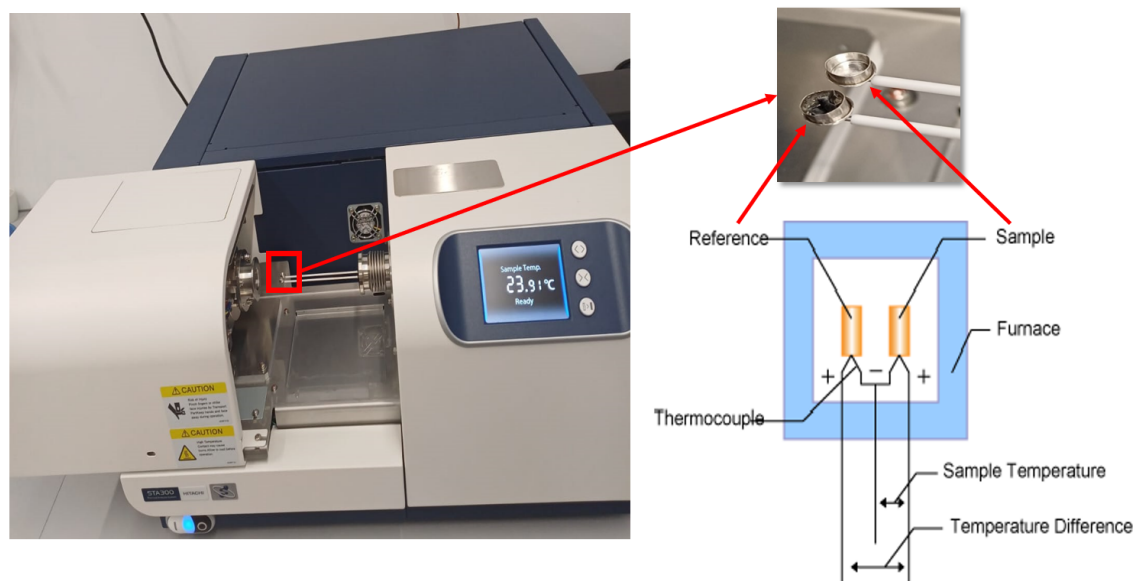


Figure 7.5: Thermal characterization of polymers by using STA300.



Figure 7.6: Measuring the PEIS of thin films using Biologic VMP-300.

7.2.5 Dynamic mechanical analysis

The DMA was performed using the DMA7100 tester from HITACHI. The analysis temperature ranged from 30 °C to a maximum of 150 °C. However, not all samples reached 150 °C; some ruptured earlier or reached the machine's maximum displacement limit. The tests were conducted at a frequency of 1 Hz with a heating rate of 5 °C/min. The sinusoidal oscillation amplitude was set to 10 μm . Figure 7.7 shows the DMA test set-up.

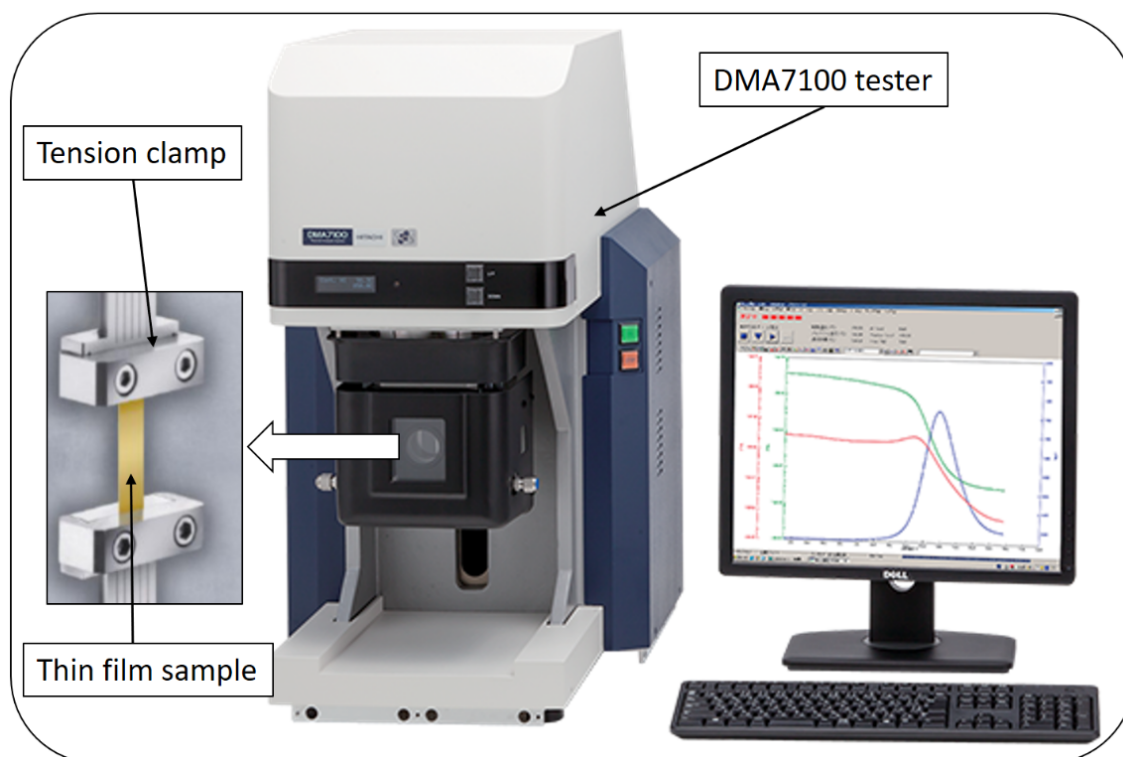


Figure 7.7: DMA7100 tester for measuring dynamic mechanical properties of thin films.

7.3 Results and discussion

7.3.1 Thermal analysis

7.3.1.1 PEO and PEO/epoxy thin films

The DSC and TGA curves of PEO and PEO/epoxy films, as well as pure PEO and pure epoxy, are shown in Figures 7.8 and 7.9. Figure 7.8 (a) illustrates that the crystalline portion of the PEO films consistently melted at 68 °C, regardless of the solvent used, which aligns with the literature (Polu et al. (2015); Nguyen et al. (2021)). However, the results for pure PEO, prior to synthesis, showed a melting point of approximately 75 °C. The lower glass transition temperature in the PEO films compared to pure PEO is attributed to the effect of trapped solvent. According to the literature, the presence of solvents generally decreases the glass transition temperature of the resulting polymer (Chu and Berner (1993)). The TGA curves shown in Figures 7.8 (b) and 7.9 (b) reveal a triphasic thermal decomposition pattern across all samples: the initial drying phase (below 212 °C for PEO and below 220 °C for PEO/epoxy), the pyrolysis and decomposition stage (212–450 °C for PEO and 220–500 °C for PEO/epoxy), and the subsequent carbonization phase (above 450 °C for PEO and above 500 °C for PEO/epoxy). The observed shift in thermal behavior between PEO and PEO/epoxy films highlights the influence of epoxy on the thermal stability of the resulting thin films. During the drying stage which is attributed to the vaporization of moisture and residual solvents, a mass loss of approximately 1 wt% was observed for PEO film synthesized

from water, while the ones dissolved using DMSO and NMP exhibited a higher mass loss of 5 wt% and 4 wt%, respectively. Figure 7.8 (b) shows that unsynthesized pure PEO, contained 0.1 wt% of moisture. During the intermediate stages of thermal degradation, a notable increase in mass loss was observed, corresponding to the pyrolysis and decomposition of the polymers. This stage was characterized by the breaking of the polymeric chains, release of volatile products, and the formation of smaller fragments. Approximately 92 wt% for PEO and 89 wt% for PEO/epoxy were attributed to this stage. As the temperature increased to 600 °C, the remaining material transitioned into a gaseous state through incineration. In the case of PEO/epoxy films, after heating up to 600 °C, around 9 wt% of residual carbonaceous material was left. Pure epoxy exhibited a higher content of residual carbonaceous material at 600 °C, with approximately 17 wt%. Figure 7.9 (b) reveals that the addition of epoxy to PEO didn't alter the melting point of the resulting films. The endothermic peak at 51 °C in the TGA curve of pure epoxy, shown in Figure 7.9 (a), corresponds to the glass transition temperature of the epoxy. This value is slightly lower than that reported in the supplier's data sheet (54 °C). The observed difference is attributed to the absorption of 2 wt% humidity, as evidenced by the drying stage in the TGA curve of the epoxy in Figure 7.9 (b).

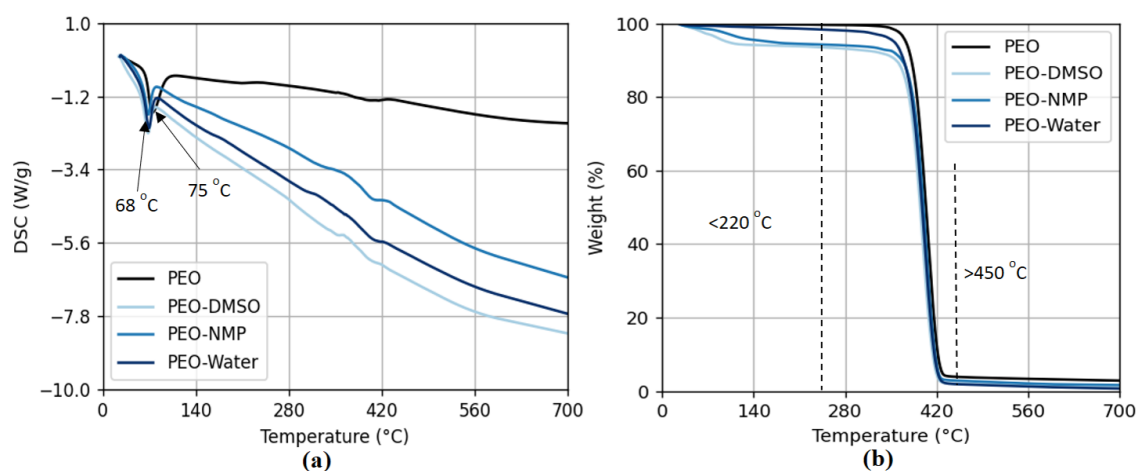


Figure 7.8: STA results of PEO compositions: (a) DSC of pure PEO and PEO films; (b) TGA of pure PEO and PEO films.

7.3.1.2 PVA and PVA/epoxy thin films

Figures 7.10 (a) and 7.10 (b) present the DSC and TGA curves of PVA films synthesized using various solvents. Figure 7.10 (a) indicates that the melting point of unsynthesized pure PVA is approximately 222 °C. The TGA curves depicted in Figure 7.10 (b) reveal a four-phase decomposition pattern consistent across all samples: the initial drying phase (below 200 °C), the first decomposition stage (200–350 °C), the second decomposition stage (350–500 °C), and the final carbonization phase (above 500 °C), which aligns with the thermal decomposition behavior of PVA polymer reported in the literature (Pandey et al. (2011)). During the drying stage (30 °C to 200 °C), mass losses of approximately 11wt%, 9wt%, and 10wt% were observed for PVA films

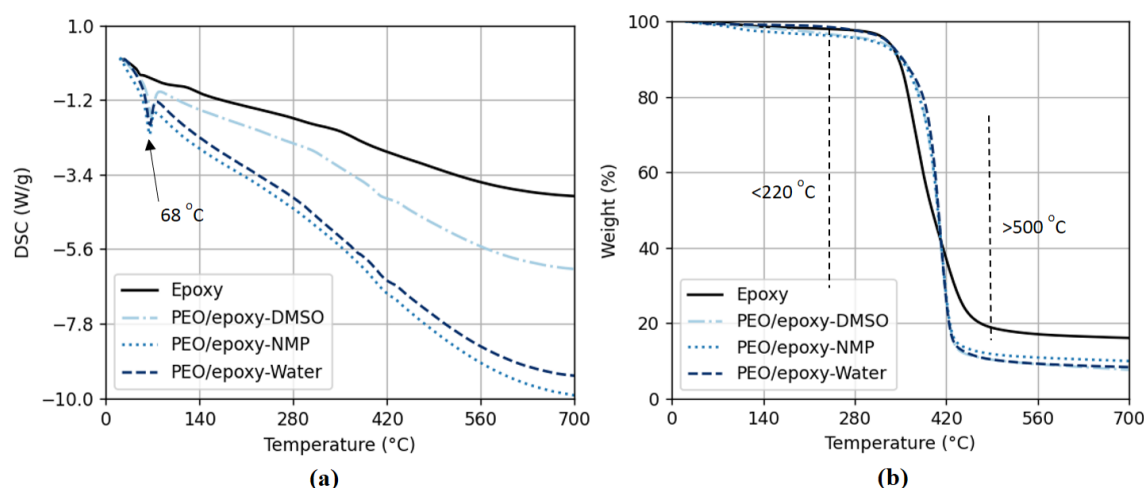


Figure 7.9: STA results of PEO compositions: (a) DSC of pure epoxy and PEO/epoxy films; (b) TGA of pure epoxy and PEO/epoxy films.

obtained from DMSO, NMP, and water solvents, respectively. This loss is attributed to the vaporization of moisture and residual solvents. In contrast, the TGA curve of unsynthesized pure PVA indicated a solvent evaporation of about 4.6wt%. According to the technical data sheet from the PVA supplier, approximately 2wt% is attributed to methanol within the polymer chain, resulting from the manufacturing and hydrolysis processes of the PVAc polymer. In the first decomposition stage (200–350 °C), a weight loss of approximately 60wt% was observed, attributed to the volatilization of organic compounds and the dehydration of the polymer's side chains. In the second decomposition stage, a weight loss of around 16wt% was associated with the degradation of the polymer's main chains. Similar findings were reported by Mohsin et al. (Mohsin et al. (2011)) for PVA plasticized with glycerol and by Sukudom et al. (Sukudom et al. (2019)) for pure PVA. Figures 7.11 (a) and 7.11 (b) illustrate the DSC and TGA curves of PVA/epoxy films. The TGA analysis of PVA/epoxy films, shown in Figure 7.11 (b), revealed a three-phase decomposition pattern consistent across all samples. This pattern includes the initial drying phase (below 200 °C), the decomposition stage (200–500 °C), and the final carbonization phase (above 500 °C). In the drying phase (below 200 °C), mass losses of approximately 20wt%, 10wt%, and 11 wt% were observed for films synthesized from DMSO, NMP, and water solvents, respectively. Figures 7.10 (a) and 7.11 (a) indicate that the melting points of both PVA and PVA/epoxy films, regardless of the solvent type used, consistently fall within a range of 216 °C to 220 °C. These values align with the melting temperature specified in the material data sheet (200 °C).

7.3.1.3 PVAc and PVAc/epoxy thin films

The DSC and TGA curves of PVAc and PVAc/epoxy films are shown in Figures 7.12 and 7.13, respectively. Figure 7.12 (a) displays an endothermic peak at around 38 °C for unsynthesized pure PVAc, corresponding to the glass transition temperature, which aligns with the literature (20–40 °C) (Wang et al. (2017)). In the case of the PVAc/epoxy blend, no endothermic peak was

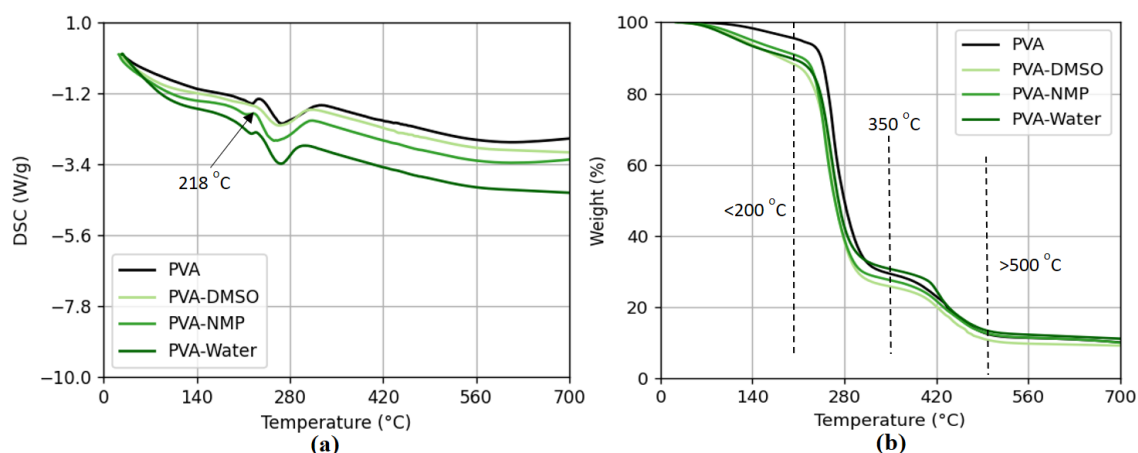


Figure 7.10: STA results of PVA compositions: (a) DSC of pure PVA and PVA films; (b) TGA of pure PVA and PVA films.

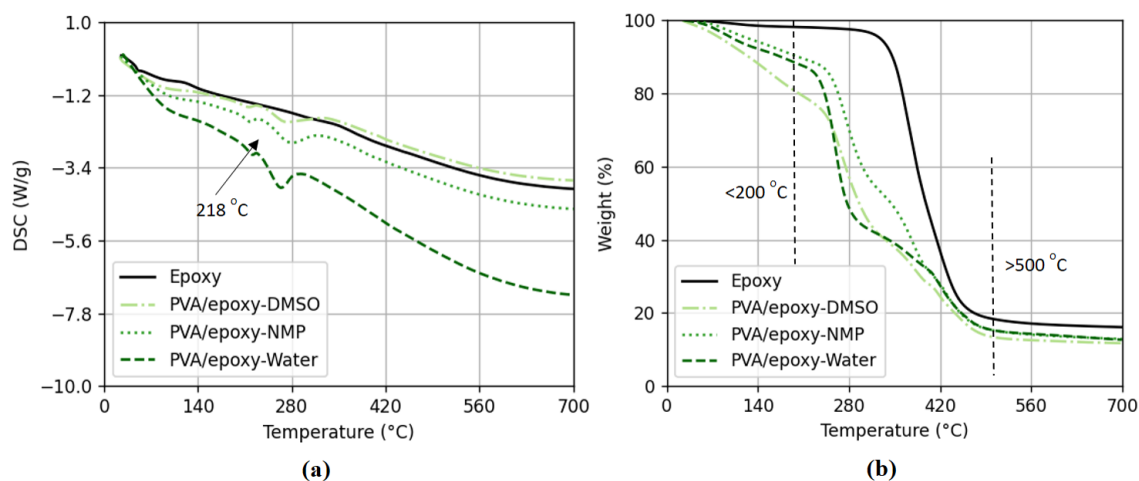


Figure 7.11: STA results of PVA compositions: (a) DSC of pure epoxy and PVA/epoxy films; (b) TGA of pure epoxy and PVA/epoxy films.

observed. The thermal degradation analysis revealed a four-phase decomposition pattern across all samples: the drying phase (30–250 °C), the first decomposition stage (250–400 °C), the second decomposition stage (400–500 °C), and the final carbonization phase (≥ 500 °C), which matches the literature on PVAc thermal decomposition ([Sameela et al. \(2023\)](#)). For PVAc films, approximately 4 wt% of the material remained as char, while for PVAc/epoxy films, the residual carbonaceous material and char constituted about 9 wt%. Examining the drying stage of PVAc films (shown in Figure 7.12 (b)), it can be observed that PVAc films synthesized with methanol retained 1 wt% residual solvent, whereas those produced with DMSO and NMP contained approximately 7 wt% of trapped solvent. In the case of the PVAc/epoxy film (illustrated in Figure 7.13 (b)), the thin film exhibited residual solvent levels of 1.2 wt% for methanol, and 4 wt% and 5 wt% for DMSO and NMP, respectively.

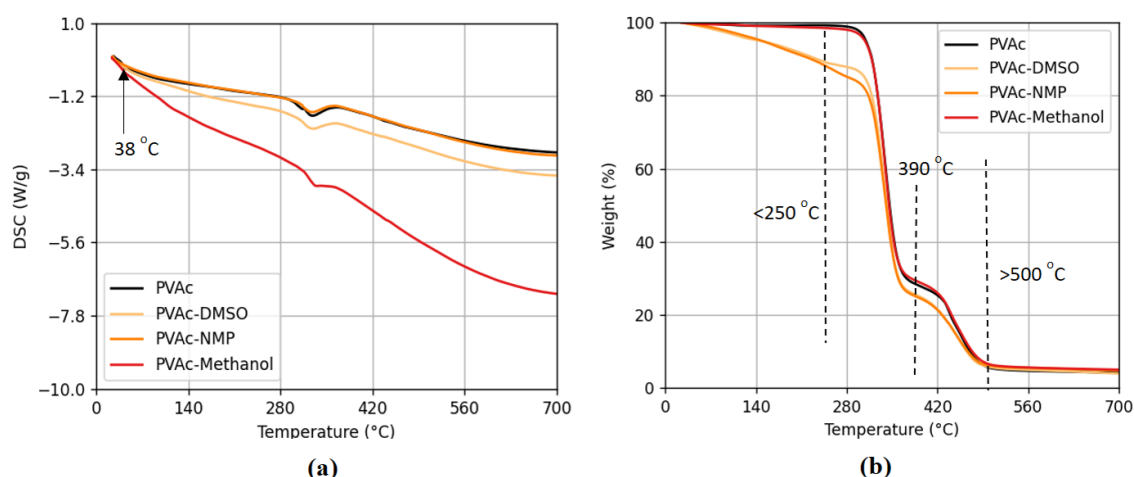


Figure 7.12: STA results of PVAc compositions: (a) DSC of pure PVAc and PVAc films; (b) TGA of pure PVAc and PVAc films.

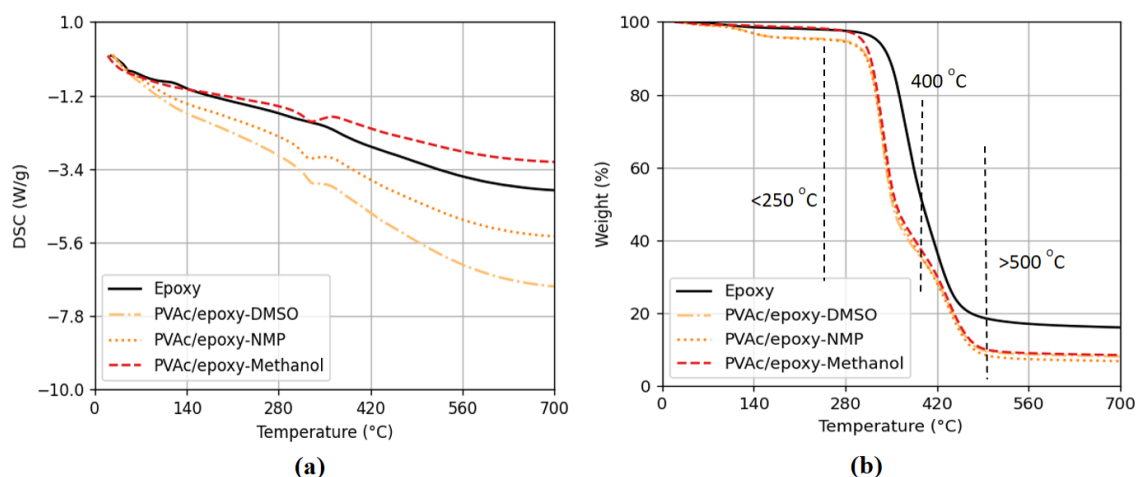


Figure 7.13: STA results of PVAc compositions: (a) DSC of pure epoxy and PVAc/epoxy films; (b) TGA of pure epoxy and PVAc/epoxy films.

7.3.2 Ionic conductivity

In this section, the Nyquist plots of the thin films obtained from PEIS measurements, along with the calculated ionic conductivity, are presented and discussed. The total resistance of the polymer films was extracted by fitting the data to an equivalent circuit model, with the Randles circuit providing the best fit. This total resistance was subsequently used to calculate the ionic conductivity. Figure 7.14 presents a comparison of the Nyquist plots and ionic conductivity between the current modified solution casting (MSC) technique and the conventional solution casting (SC) technique for PEO, PVA, and PVAc films synthesized using DMSO. The Nyquist plots have been normalized to a film thickness of 0.5 mm. Each plot shown in Figure 7.14(a) illustrates two distinct regions: (1) a high-frequency semicircle representing the overall resistance of the polymeric film, which is the sum of the bulk resistance (R_b) and the solid electrolyte interphase resistance (R_{SEI}); and

(2) a low-frequency inclined spike, indicative of the ionic-conducting nature of the polymer film with aluminum electrodes (Vadhva et al. (2021); Muchakayala et al. (2017); Tang et al. (2016)). The corresponding equivalent circuits for the films are shown at the top of Figure 7.14(a). When testing the polymeric films, the total resistance ($R_b + R_{SEI}$) is obtained from the intersection point between the low-frequency end of the semicircle and the high-frequency start of the inclined spike along the real axis. The ionic conductivity (σ) of the polymer thin films can then be determined using the following equation (Vadhva et al. (2021)):

$$\sigma = \frac{t}{A \cdot R_b} \quad (7.1)$$

Here, A is the contact area between the electrodes and the thin film, and t is the thickness of the thin film. The resulting values of the ionic conductivity are expressed in S/cm. The comparison of ionic conductivity between the two approaches is illustrated in Figure 7.14(b). The results show that, by using the MSC technique, the ionic conductivity of the three polymers—PEO, PVA, and PVAc—increased by factors of 10, 20, and 55, respectively, compared to the SC method. This improvement indicates a significant enhancement in interfacial contact between the electrode and polymer films achieved through the MSC method.

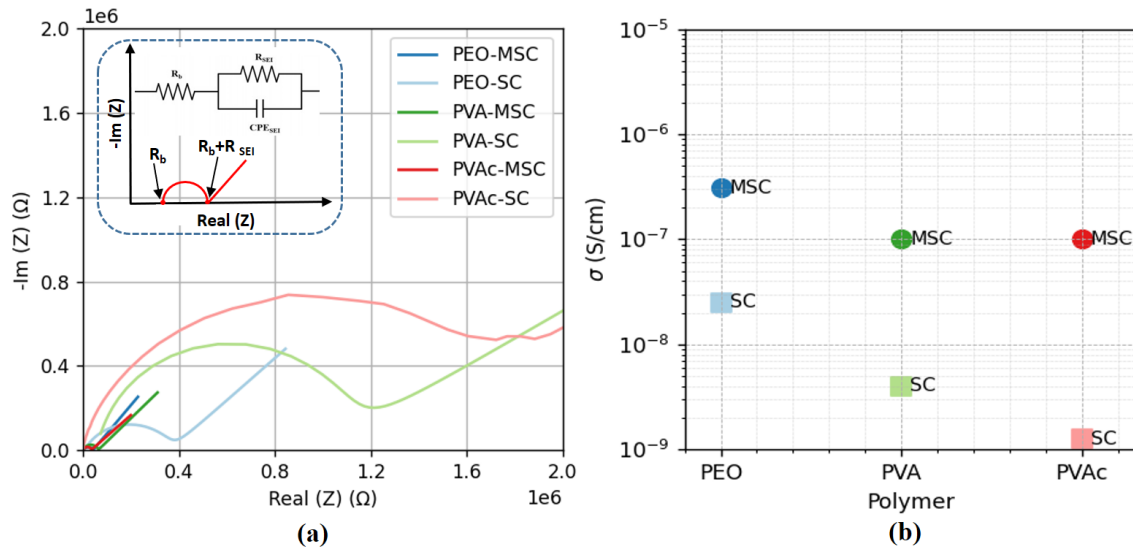


Figure 7.14: PEIS results of polymer films prepared with conventional solution casting technique (SC) and modified solution casting method (MSC): (a) Nyquist plot; (b) Ionic conductivity.

The room-temperature Nyquist plot of pure epoxy is shown in Figure 7.15, indicating very high resistance. It has also been reported in the literature that pure epoxy exhibits an ionic conductivity of less than 10^{-12} S/cm at room temperature (Chiang et al. (1987)).

The room temperature Nyquist plots and ionic conductivity for different thin films, each with a thickness of 0.5 mm, are shown in Figures 7.16, 7.17, and 7.18. These results highlight the distinctive effects of various solvents on individual polymers and their combinations with epoxy.

The ionic conductivity values, ranging from 2.4×10^{-6} S/cm to 1.8×10^{-8} S/cm, are summa-

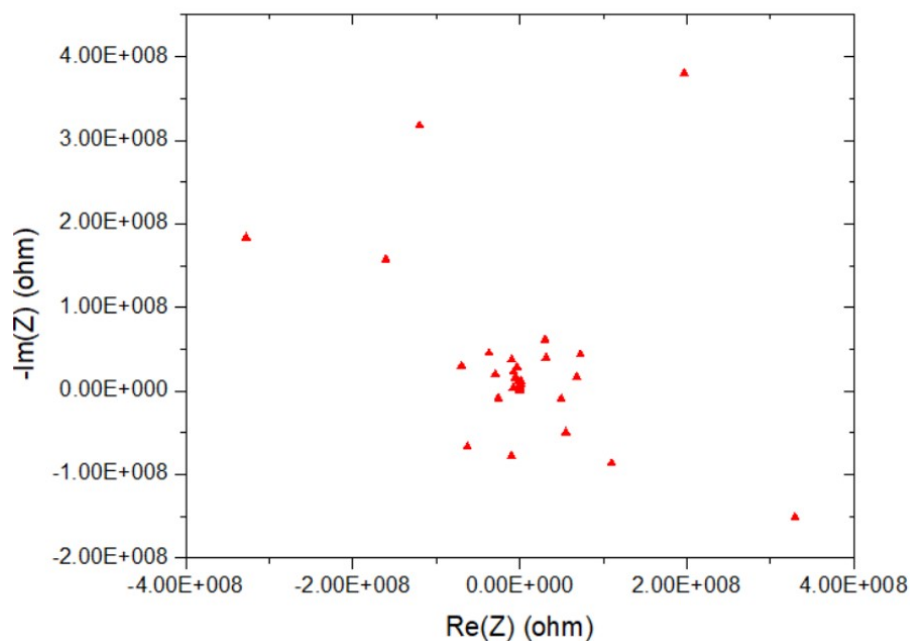


Figure 7.15: Nyquist impedance of cured pure epoxy at room temperature.

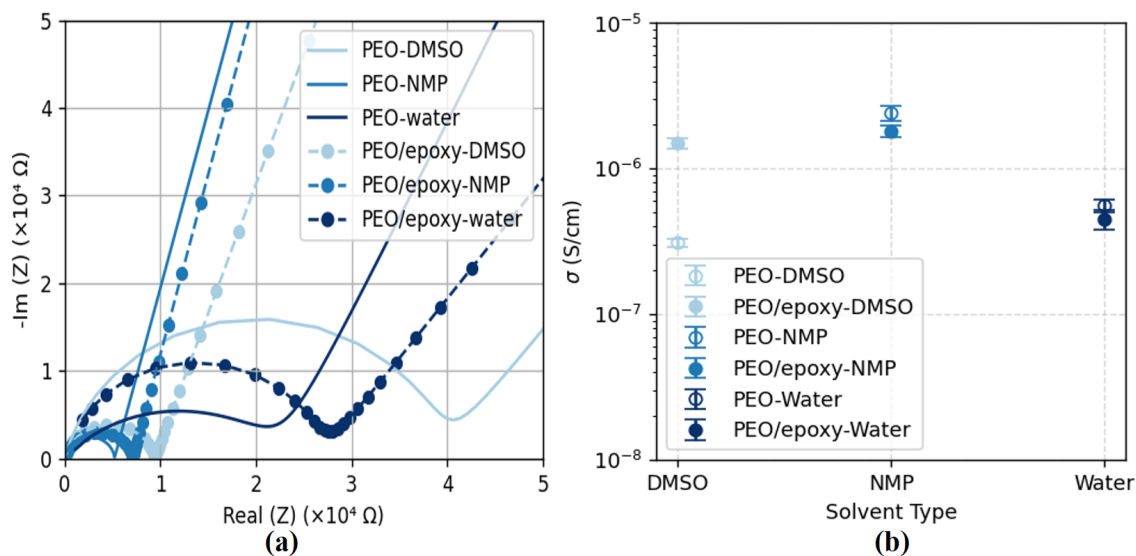


Figure 7.16: PEIS analysis of thin films: (a) Nyquist impedance plots of PEO films with and without epoxy; (b) Corresponding ionic conductivities of the same film systems.

ized in Table 7.3. For each composition, three samples were tested. The solvent content of each film and the coefficient of variation of the ionic conductivity for each sample group are also compiled in Table 7.3. These results highlight the distinctive effects of various solvents on individual polymers and their combinations with epoxy. In the PEO group, the ionic conductivity ranged from 3.1×10^{-7} S/cm with DMSO to 2.4×10^{-6} S/cm with NMP, consistent with literature values for PEO in the range of 10^{-6} to 10^{-8} S/cm (Zhang et al. (2021d)). Although films synthesized with

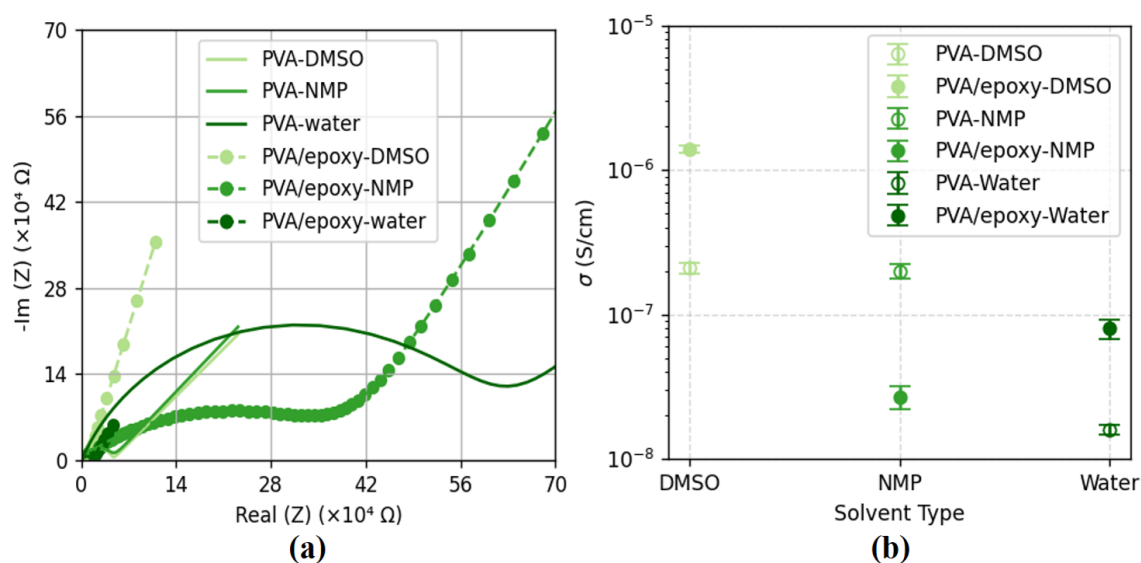


Figure 7.17: PEIS analysis of thin films: (a) Nyquist impedance plots of PVA films with and without epoxy; (b) Corresponding ionic conductivities of the same film systems.

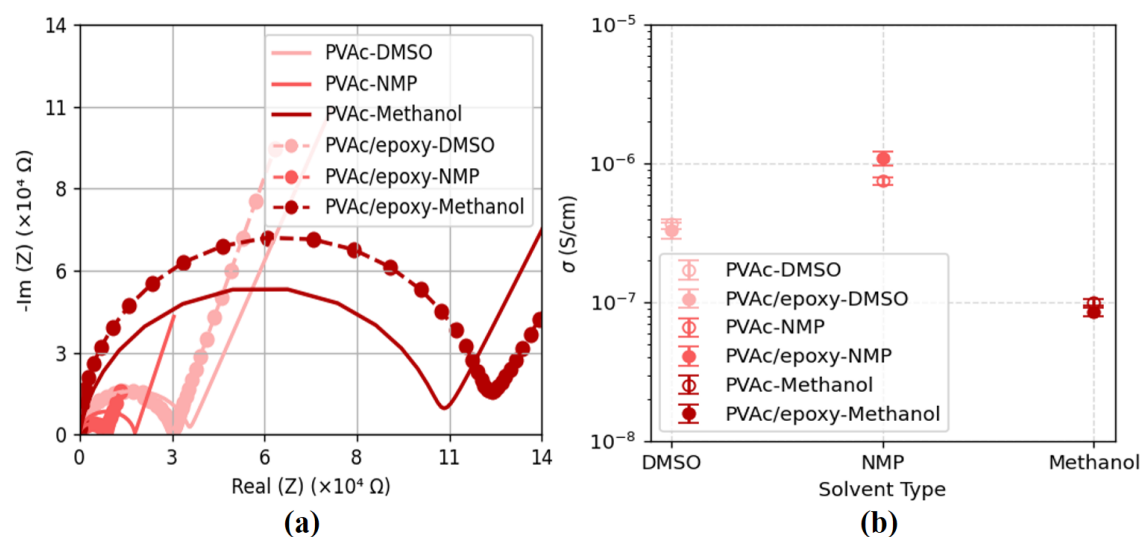


Figure 7.18: PEIS analysis of thin films: (a) Nyquist impedance plots of PVAc films with and without epoxy; (b) Corresponding ionic conductivities of the same film systems.

NMP exhibited the highest ionic conductivity, they also contained higher levels of trapped solvent, which may have contributed to the enhanced ionic conductivity values. In contrast, films synthesized using water showed the lowest amount of trapped solvent and, correspondingly, the lowest ionic conductivity in both PEO and PEO/epoxy systems, with values ranging from 4.5×10^{-7} S/cm to 5.6×10^{-7} S/cm.

The PVA group exhibited ionic conductivity values ranging from 1.6×10^{-8} S/cm in PVA films with 10 wt% trapped water to 1.4×10^{-6} S/cm in PVA/epoxy films containing 20 wt% trapped DMSO. These values are significantly higher than the ionic conductivity typically reported for PVA films, which is around 2.1×10^{-11} S/cm (Manjunath et al. (2015)). This enhancement is

attributed to the presence of residual solvent in the films, which acts as a plasticizer and facilitates the ion transport. It is worth noting that in the films synthesized with NMP, incorporating epoxy led to a more than sevenfold decrease in ionic conductivity, despite the PVA/epoxy films containing approximately 1 wt% more trapped solvent. This suggests a negative influence of epoxy on the ionic conductivity in the NMP system. The PVA/epoxy films synthesized using DMSO exhibited approximately sixfold higher ionic conductivity than their PVA counterparts. This enhancement cannot be attributed solely to the presence of epoxy, as the trapped solvent content in the PVA/epoxy films was nearly double that of the PVA films. For films synthesized with water, the PVA/epoxy compositions exhibited higher ionic conductivity compared to PVA films, which is attributed to their higher trapped solvent content. Regarding the PVAc films, DMSO and NMP solvents yielded ionic conductivities of the same order— 3.7×10^{-7} S/cm and 7.5×10^{-7} S/cm, respectively—despite both films having an identical trapped solvent content of 7 wt%. The ionic conductivities of PVAc and PVAc/epoxy films synthesized using DMSO were comparable, whereas in the NMP system, the PVAc/epoxy film exhibited an approximately 1.5-fold increase relative to the PVAc film despite containing less trapped solvent. The PVAc films synthesized using methanol exhibited an ionic conductivity of 1×10^{-7} S/cm, whereas the PVAc/epoxy films synthesized with the same solvent showed a lower conductivity of 8.6×10^{-8} S/cm. Despite containing the same amount of trapped solvent, this decrease in ionic conductivity is likely attributable to the presence of epoxy and its interactions within the polymer matrix.

Table 7.3: The room temperature ionic conductivity of different thin films.

Polymer	Solvent	0% epoxy			30% epoxy		
		Solvent (%)	σ (S/cm)	CV (%)	Solvent (%)	σ (S/cm)	CV (%)
PEO	DMSO	5	3.1×10^{-7}	6	4	1.5×10^{-6}	8
	NMP	6	2.4×10^{-6}	12	5	1.8×10^{-6}	9
	Water	2	5.6×10^{-7}	10	1.5	4.5×10^{-7}	15
PVA	DMSO	10	2.1×10^{-7}	9	20	1.4×10^{-6}	6
	NMP	9	2×10^{-7}	12	10	2.7×10^{-8}	18
	Water	10	1.6×10^{-8}	7	11	8×10^{-8}	16
PVAc	DMSO	7	3.7×10^{-7}	8	5	3.3×10^{-7}	13
	NMP	7	7.5×10^{-7}	6	5	1.1×10^{-6}	12
	Methanol	1	1×10^{-7}	5	1	8.6×10^{-8}	7

Figure 7.19, 7.20, and 7.21 present microscopy images of the top and bottom surfaces of the polymer films. The top view corresponds to the free surface of the polymer after drying, while the bottom view corresponds to the surface in contact with the silicon mold. The images reveal distinct surface morphologies influenced by both the solvent used and the presence of epoxy, with notable differences between the free and mold-contacting surfaces. Figure 7.19 shows that the solvent choice significantly affected the surface morphology of PEO/epoxy films. The PEO film prepared using DMSO (Figure 7.19(a)) exhibited a relatively smooth and homogeneous surface on both sides, with no visible phase separation or microstructural features, suggesting uniform sol-

vent evaporation and polymer crystallization. When epoxy was incorporated into the PEO matrix using DMSO (Figure 7.19(b)), the surfaces became slightly rougher, with minor inhomogeneities and some microstructural features, especially on the top surface. A more pronounced morphological change was observed when NMP was used as the solvent (Figure 7.19(c)), with both surfaces showing rougher and more irregular textures. Films cast from water (Figure 7.19(d)) showed the most irregular morphology, marked by significant phase separation between PEO and epoxy and an uneven surface texture on both sides. In all films, some epoxy and PVA particles were observed on the surface of the films, likely due to incomplete dissolution during processing. Figure 7.20 presents microscopy images of the top and bottom surfaces of PVA and PVA/epoxy films. The PVA film prepared using DMSO (Figure 7.20(a)) displayed smooth, homogeneous surfaces, indicative of uniform crystallization. Some undissolved PVA particles were visible on both sides. When blended with epoxy using DMSO solvent (Figure 7.20(b)), the films retained a relatively smooth texture, suggesting good miscibility between PVA, epoxy, and solvent. In the case of the PVA/epoxy film prepared using NMP (Figure 7.20(c)), both sides of the film exhibited similar, patterned textures. Films cast from water (Figure 7.20(d)) showed the most significant changes, with rougher and more granular top surface due to poor epoxy solubility in water compared to DMSO and NMP solvents. Some Epoxy and PVA particles were also observed on the surfaces of PVA/epoxy films; however, the epoxy particles were noticeably larger in the water-cast film. Figure 7.21 shows microscopy images of PVAc and PVAc/epoxy films. The PVAc film prepared using DMSO (Figure 7.21(a)) exhibited smooth and homogeneous surfaces. In the case of PVAc/epoxy film made using DMSO solvent (Figure 7.21(b)), pronounced surface roughness, spherulitic features, and irregular patterns appeared. In contrast, films cast using NMP (Figure 7.21(c)) remained relatively homogeneous, with smooth surfaces on both sides. When methanol was used as the solvent (Figure 7.21(d)), the surfaces appeared more heterogeneous. Notably, the methanol-based solution was not transparent, suggesting it may have broken down epoxy particles and dissolved them more aggressively into the thermoplastic polymer. This could be a contributing factor to the lower ionic conductivity observed in the corresponding film. Although surface morphology can directly affect ionic conductivity by reducing effective contact with the electrodes, the modified solution casting technique used in this work likely improved interfacial contact due to *in-situ* drying of polymer films inside electrodes, thereby mitigating a part of the negative impact of surface roughness and inhomogeneity.

7.3.3 Dynamic mechanical analysis

In this section, The thermo-mechanical tests using DMA tensile mode method was performed on each thin film. Each polymer composition was synthesized with its optimal solvent as identified in Subsection 7.3.2 —NMP for PEO and PVAc, and DMSO for PVA. The resulting thin films were dried in a vacuum heat chamber at 60 °C for six days. For each polymer composition, the DMA tests were performed on three samples, and the average of the thermomechanical results was considered as the final result. The thin films measured 20 mm in length, 6 mm in width, and had a thickness between 0.5 mm and 1 mm. Due to the influence of solvent on mechanical proper-

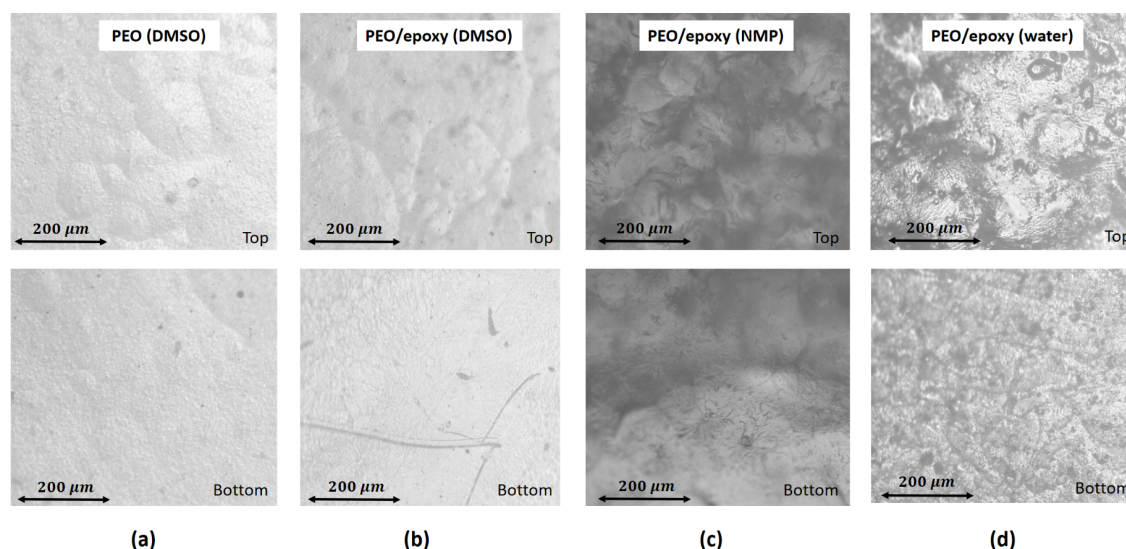


Figure 7.19: Microscopy images: (a) PEO film; (b) PEO/epoxy film (cast from DMSO); (c) PEO/epoxy film (cast from NMP); (d) PEO/epoxy film (cast from water).

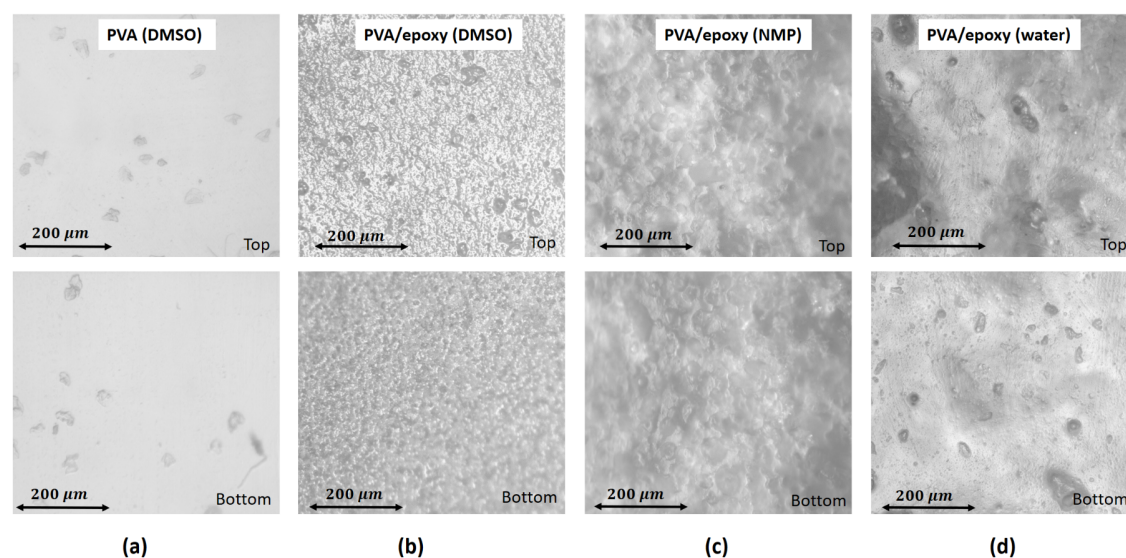


Figure 7.20: Microscopy images: (a) PVA film; (b) PVA/epoxy film (cast from DMSO); (c) PVA/epoxy film (cast from NMP); (d) PVA/epoxy film (cast from water).

ties, in this part of the study, the TGA tests were conducted again prior to the mechanical tests to determine the amount of trapped solvent in each polymer film. Results indicated solvent contents ranging from 1 wt% for PEO and PEO/epoxy to approximately 3.5 wt% for pure PVA. Additionally, PVA/epoxy and PVAc/epoxy, as well as pure PVAc, contained around 2 wt% solvents.

The thermomechanical properties of the thin films, including the storage modulus (E'), which indicates the stiffness of a material, and $\tan \delta$ (the loss factor), which is the ratio of the loss modulus (E'') to the storage modulus (E'), are shown in Figure 7.22. The storage modulus versus temperature of different polymers and the effect of epoxy on each polymer are shown in Figure 7.22 (a).

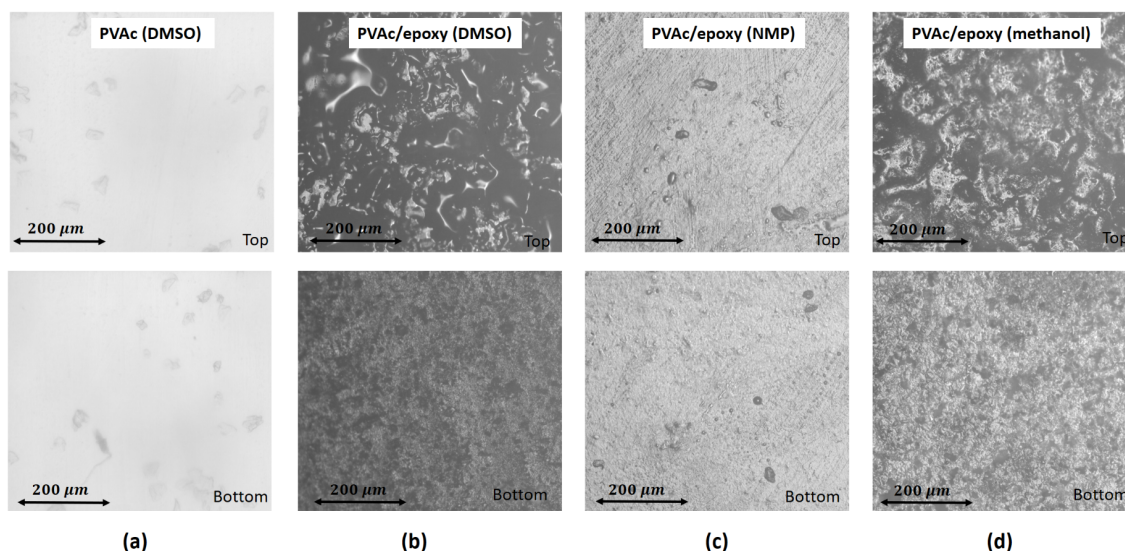


Figure 7.21: Microscopy images: (a) PVAc film; (b) PVAc/epoxy film (cast from DMSO); (c) PVAc/epoxy film (cast from NMP); (d) PVAc/epoxy film (cast from methanol).

The results indicate that PVA and PVA/epoxy thin films had the highest storage modulus compared to other thin films and could withstand higher temperatures. Additionally, the results highlight the impact of epoxy on the thermomechanical stability of PVA. The PVA/epoxy film retained 22 % of its storage modulus after heating up to 150 °C, while the PVA maintained only 5 % of E' . A 5% retention in storage modulus suggests significant softening of the polymer matrix, which may improve interfacial contact with electrodes under compression but could also raise concerns regarding mechanical stability under sustained load.

For PVAc in particular, the high $\tan \delta$ and low storage modulus reflect a highly viscoelastic nature. This could be beneficial in maintaining intimate contact with electrode surfaces during operation, but excessive damping may lead to energy dissipation and reduced mechanical integrity over time. The storage modulus of PVAc decreased considerably with heating from 30 °C to 40 °C, indicating high sensitivity of PVAc's stiffness to temperature. Adding 30 % epoxy resulted in a more stable plateau for the storage modulus at high temperatures. PVAc/epoxy withstood higher temperatures before rupture and maintained 5.4 % of the storage modulus after heating up to 100 °C, whereas, PVAc lost its rigidity entirely.

The results also show both PEO and PEO/epoxy thin films had a significant decrease in storage modulus as the temperature increased.

Figure 7.22 (b) shows the $\tan \delta$ versus temperature, reflecting the thin film's damping behavior and viscoelasticity. The results indicate that the PEO/epoxy thin film had a higher $\tan \delta$ at all temperatures compared to the PEO film. For the PEO thin film, $\tan \delta$ increased almost linearly with temperature. However, the $\tan \delta$ of PEO/epoxy thin film remained stable up to 50 °C, then increased linearly until 72 °C, and subsequently decreased linearly until the rupture point. Regarding the PVA and PVA/epoxy thin films, the results reveal that the $\tan \delta$ of the PVA/epoxy film is low and more stable across all temperatures compared to the pure PVA film. A peak at 138 °C

in the PVA curve is considered the melting point of the PVA. Finally, the notably higher $\tan \delta$ of PVAc indicates significantly greater viscoelastic behavior in this polymer compared to PVA and PEO films. The prominent peak observed at 32 °C corresponds to its glass transition temperature. Incorporating epoxy into PVAc led to enhanced thermomechanical stability and a reduced $\tan \delta$, signifying lower viscoelasticity compared to pure PVAc.

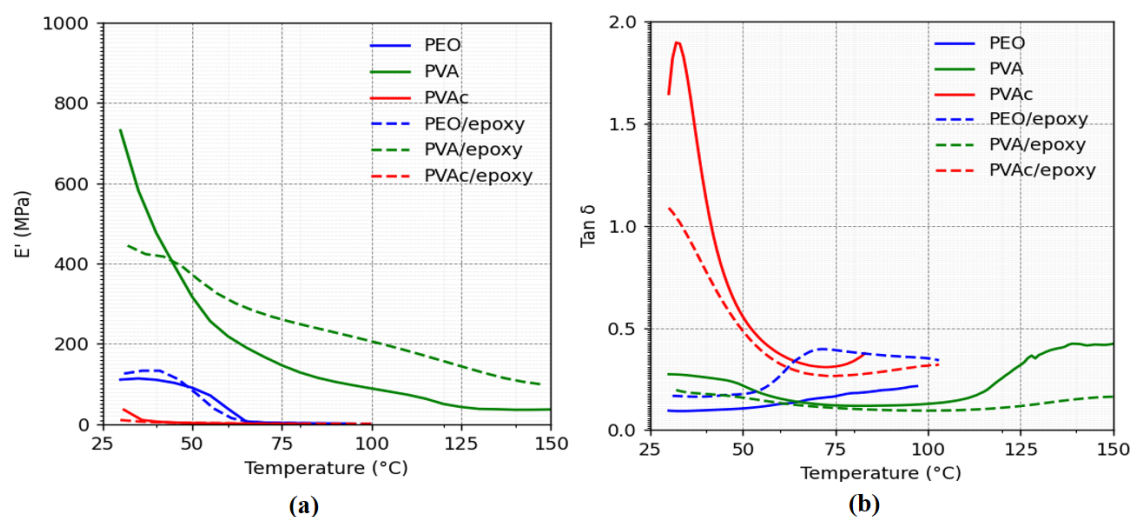


Figure 7.22: Thermomechanical properties of thin films: (a) Storage modulus (E') vs. temperature; (b) $\tan \delta$ vs. temperature.

7.4 Conclusions

In this chapter, blends of three thermoplastic polymers—PEO, PVA, and PVAc—with epoxy, prepared using different solvents, were tested to develop heat-resistant polymer hosts for composite polymer electrolyte applications. A modified solution casting technique was introduced, which involved *in-situ* drying of the film inside the cell assembly, combined with the application of pressure and heat to ensure good contact between the film and electrodes and enhance ionic conductivity. Thin films were fabricated using various solvents: DMSO, NMP, and water for PEO and PVA blends, and DMSO, NMP, and methanol for PVAc blends. Despite its intrinsically low ionic conductivity, thermoset epoxy, when blended with thermoplastic polymers using a compatible solvent, resulted in a composition with ionic conductivity comparable to that of neat thermoplastic polymers and enhanced thermomechanical properties. The results showed that NMP was the most effective solvent for achieving the highest ionic conductivity in PEO, PEO/epoxy, PVAc, and PVAc/epoxy blends, while DMSO proved optimal for PVA and PVA/epoxy compositions. However, the trapped solvent content was also a key factor contributing to the observed improvements. DMA tests demonstrated that incorporating epoxy into the polymeric films enhanced their thermomechanical properties. In the PEO composition, adding epoxy resulted in a higher storage modulus, though the loss factor ($\tan \delta$) also increased. In both PVA and PVAc, adding epoxy im-

proved thermomechanical stability, enhanced storage modulus retention at elevated temperatures, and decreased the loss factor.

Chapter 8

Optimization and characterization of a multifunctional structural electrolyte

In this chapter, a novel multifunctional structural electrolyte was developed using plain-weave glass fiber reinforced with a composite polymer matrix for load-bearing energy-storage applications such as structural batteries. The composite matrix comprised polyvinyl alcohol (PVA) blended with epoxy, LiTFSI salt, and Al_2O_3 at optimized ratios. A set of techniques was used to evaluate and optimize the thermo-electro-mechanical properties of the matrix, including dynamic mechanical analysis (DMA), potentiostatic electrochemical impedance spectroscopy (PEIS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The optimization revealed a clear trade-off: increasing salt content enhanced ionic conductivity but compromised mechanical properties, while the addition of nanofiller improved stiffness but reduced ionic conductivity. Based on multi-functional balancing, a matrix with a formulation of $\text{PVA}_{0.34}/\text{epoxy}_{0.14}/\text{LiTFSI}_{0.32}/(\text{Al}_2\text{O}_3)_{0.2}$ was obtained. The structural electrolyte, composed of glass fiber impregnated with the optimized matrix, was characterized using PEIS, DMA, tensile testing, and charge–discharge tests within lithium iron phosphate (LFP)/lithium metal and LFP/graphite cells. The electrolyte exhibited a storage modulus of 3 GPa, an ionic conductivity of 1.74×10^{-4} S/cm, a bulk stiffness of 1.82 GPa, and a tensile strength of 56.9 MPa. Full-cell testing demonstrated long cycle life and stable cyclability for approximately 240 cycles, maintaining a high coulombic efficiency of around 95% throughout cycling.

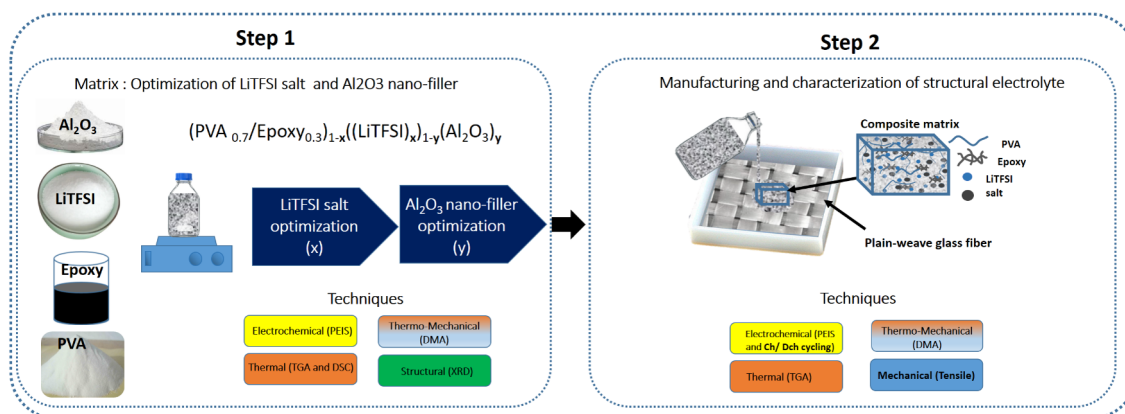


Figure 8.1: Schematics of the method for optimization of composite polymer matrix and structural electrolyte.

8.1 Introduction

Structural batteries are advanced systems that integrate load-bearing and energy storage functions into a single structure, reducing weight and improving efficiency in applications such as electric vehicles and aerospace (Asp et al. (2021); ?); Danzi et al. (2021b); Carlstedt et al. (2019); Yu, Xingwen and Manthiram, Arumugam (2021)). However, one of their main challenges is the development of a structural electrolyte that offers both high ionic conductivity and sufficient mechanical integrity (Siraj et al. (2023); Tavano et al. (2024); Demir et al. (2020); Fu et al. (2025)). Composite polymer electrolytes (CPEs) are promising candidates for structural battery applications due to their mechanical strength, flexibility, interfacial compatibility, ease of processing, and enhanced safety (Grundish et al. (2021); Yu and Manthiram (2021); Yu et al. (2022); Fu et al. (2024a)). However, because CPEs are typically based on thermoplastic polymer hosts, they tend to lose mechanical strength at elevated temperatures caused by internal electrochemical reactions or external environmental thermal exposure (e.g., sunlight). This limitation is addressed by incorporating heat-resistant thermoset polymers (e.g., epoxy) and carefully optimizing lithium salt and nanofiller concentrations to produce a composite electrolyte matrix with superior thermo-electro-mechanical performance. The optimized matrix is subsequently used to impregnate a glass fiber fabrics, thereby further improving thermal stability, load-bearing capability, and ionic conductivity. Additionally, a modified solution-casting approach (combining conventional solution casting with *in-situ* drying under pressure and heat) is employed to overcome the common limitation of poor interfacial contact encountered in conventional solution casting (Niazi et al. (2026)). Various thermoplastic polymers (e.g., PVC, PVA, PEO, PAN, PVdF, PMMA, and chitosan) have been used as electrolyte hosts (Liu et al. (2020b); Zhou et al. (2021); Herbers et al. (2023); Wang et al. (2014b); Zhou et al. (2022); Luo et al. (2023); Xu et al. (2018)). Among these, PVA stands out for its high dielectric constant, excellent mechanical properties, biodegradability, and cost-effectiveness (Hou et al. (2023b)). Thermoplastic hosts are favored in electrolytes for their high ionic conductivity (Reinoso and Frechero (2022)), but they tend to soften when heated. Although

this softening improves ionic conductivity at elevated temperatures, it significantly compromises mechanical performance. In contrast, thermoset polymers such as epoxy exhibit outstanding thermomechanical stability. However, extensive cross-linking in thermosets restricts the mobility of polymer chains and ions, resulting in very low ionic conductivity (typically below 10^{-12} S/cm at room temperature) (Costa et al. (2020)). Therefore, combining thermoset and thermoplastic polymers offers a promising strategy for creating a composite electrolyte matrix that leverages the strengths of both (Yao et al. (2019); Raja et al. (2024)). Salts and nanofillers strongly influence the electrochemical and mechanical properties of the composite polymer matrix. Initially, increasing lithium salt concentration enhances ionic conductivity by plasticizing the polymer and increasing ion mobility. However, beyond an optimal concentration, further salt addition leads to diminishing returns or reduced conductivity due to ion-pairing, polymer-salt complexation, and phase separation (Konwar et al. (2021); Ravikumar et al. (2018); Ataollahi et al. (2012); Li et al. (2023c); Hu et al. (2024b)). Salt content can also plasticize the polymer matrix and reduce its stiffness and tensile strength (Qin et al. (2023)). Inorganic nanofillers such as Al_2O_3 are commonly incorporated into polymer electrolytes to enhance their mechanical strength. However, their effects on polymer crystallinity and ionic conductivity can vary depending on several factors. Some studies have shown that when well dispersed, these rigid particles can disrupt polymer chain packing, increase the amorphous fraction, and lower the glass transition temperature, thereby enhancing segmental mobility and facilitating ion transport (Shen et al. (2021); Liu et al. (2024)). Conversely, other studies have demonstrated that nanofillers can also act as nucleating agents, promoting crystallization rather than suppressing it, which may slightly reduce ionic conductivity (Ding et al. (2024)). Optimizing the concentrations of both salt and filler is thus critical to balance mechanical integrity with electrochemical performance in structural battery applications. Several fabrication techniques exist for polymer electrolytes, including solution casting (Chen et al. (2020b)), solvent-free methods (Jiang et al. (2020b); Zhu et al. (2023b)), phase inversion (Kim et al. (2006)), electrospinning (Hong et al. (2018)), *in-situ* polymerization (Peng et al. (2024)), and layer-by-layer deposition (Branco et al. (2016)). Solution casting is widely favored for its simplicity, uniform dispersion, and scalability, but it often suffers from poor interfacial contact with electrodes, which can limit energy density. In contrast, techniques like *in-situ* polymerization can enhance the polymer-electrode interface by polymerizing the polymer electrolyte directly on the electrodes or within the cell. However, these methods may introduce issues such as voids, dead volume, and dead weight during manufacturing (Vijayakumar et al. (2021)). The previous chapter has shown that applying additional steps such as wetting the film and *in-situ* drying it in presence of heat and pressure can improve interfacial contact and ionic conductivity (Niazi et al. (2026)). In the previous chapter, different solvents (NMP, DMSO, water, and methanol) were used to dissolve PEO, PVA, and PVAc and to blend them with epoxy. Among these systems, PVA blended with epoxy using DMSO exhibited the best multifunctional thermomechanical properties and good ionic conductivity, comparable to that of thermoplastic hosts. In this chapter, a composite polymer electrolyte—comprising PVA blended with epoxy resin, LiTFSI salt, and Al_2O_3 nanofiller at optimized ratios—was first developed and then used as the polymer matrix and was reinforced

with a glass fiber to form a structural electrolyte. This chapter is structured as follows: Section 8.2 details the materials and techniques that have been used. Section 8.3 presents the results and discussion. The first part of Section 8.3 focuses on the optimization of the salt and nanofiller content to obtain the composite matrix. This optimization was guided by results from PEIS, DMA, TGA, differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The second part of Section 8.3 discusses the characterization of the structural electrolyte, which consists of the optimized polymer matrix reinforced with the glass fiber. The thermo-electro-mechanical properties of the structural electrolyte are evaluated using PEIS, DMA, TGA, and tensile testing to determine ionic conductivity, thermomechanical properties, solvent content, stiffness, strength, and failure strain. Furthermore, the structural electrolyte was tested electrochemically in both half-cell configurations—using commercial LiFePO_4 (LFP) foil as cathode and lithium metal as anode—and full-cell configurations with hand-made LFP coatings on aluminum foil and graphite coatings on copper foil.

8.2 Materials and methods

8.2.1 Materials

In this chapter of work, the matrix part of the structural electrolyte consisted of a blend of PVA, epoxy, LiTFSI salt, and Al_2O_3 nano-filler. The PVA had a molecular weight between 146,000 and 186,000, with a purity greater than 99.3%, and was sourced from Thermo Scientific. DMSO solvent, acquired from Labkem, was used to dissolve the polymer and mix the different additives. The epoxy AS-89, supplied by HBQUIMICA, was a two-component system: Part A served as the resin, and Part B as the hardener, with a recommended mixing ratio of 100:45, according to the supplier's datasheet. The LiTFSI salt, with a purity of 99%, was obtained from Acros Organics, while the Aluminum oxide (Al_2O_3) nano-filler (flash grade), with a particle size of 18–32 microns and a molecular weight of 101.96 g/mol, was supplied by Thermo Scientific. For the separator, a plain-weave glass fiber with a $[0^\circ/90^\circ]$ orientation, a ply thickness of $70\mu\text{m}$, and an areal weight of 0.008 g/cm^2 was used. In Figure 8.2, these materials—including PVA, epoxy components, LiTFSI salt, Al_2O_3 nanofiller, and plain-weave glass fiber—are shown.

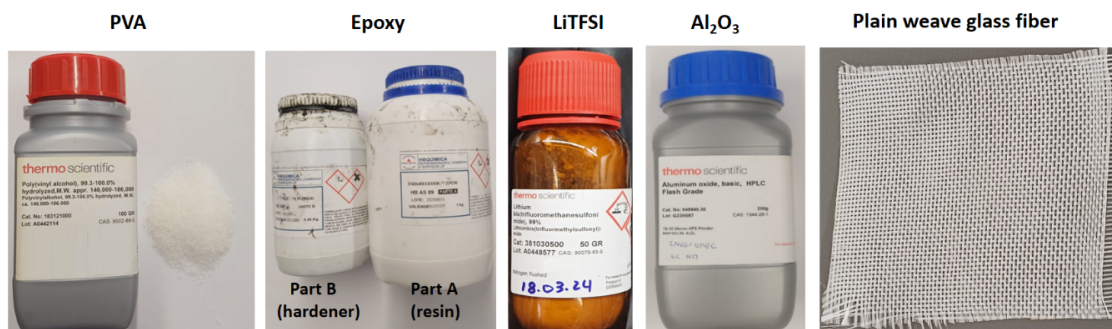


Figure 8.2: Schematics of the materials used for manufacturing the structural electrolyte.

Additionally, the commercial cathode foil, consisting of an aluminum substrate coated with lithium iron phosphate (LFP), was obtained from MTI Corporation. The foil had a total thickness of $84\text{ }\mu\text{m}$ and an areal density of approximately 13.5 mg/cm^2 , comprising 95.4% LFP by weight, with the remaining content consisting of PVdF and conductive carbon. LFP powder with an average particle size of $1.5\text{ }\mu\text{m}$ was procured from MSE Supplies. Graphite powder and conductive acetylene black (Super P) were sourced from Nanografi. The PVdF binder was also obtained from MTI Corporation. All components used to assemble the 2032 coin cells—including the positive case, negative case, spring, and spacer—were supplied by Nanografi.

8.2.2 Manufacturing thin films and structural electrolyte

In this study, a two-step progressive optimization process was conducted to identify the ideal matrix formulation. First, the optimal concentration of LiTFSI salt was determined to obtain desirable thermomechanical and electrochemical properties, using various characterization techniques. This optimal salt concentration was then used to establish the appropriate amount of Al_2O_3 nano-filler, employing the same evaluation methods. The modified solution casting technique presented in Chapter 7 (Niazi et al. (2026)) was used to fabricate the cells for PEIS tests. This method was introduced to address the poor interfacial contact between electrodes and thin films by incorporating a modified approach: the initial fabrication of thin films using the conventional solution casting technique is followed by a wetting step with the same polymer solution composition, and *in-situ* drying of the film within the cell. These additional steps were intended to enhance electrode–electrolyte adhesion and improve interfacial contact.

For the polymer host preparation, PVA was dissolved in DMSO at 100°C for 6 hours using a magnetic stirrer set to 400 RPM. For the epoxy preparation, parts A and B were mixed in a 100:45 ratio, in compliance with the supplier recommendation, and then combined with the polymer solution in a 30:70 ratio, excluding the solvent weight. The mixture was stirred for 10 minutes to ensure a homogeneous solution. In the first part of optimization, different percentages of LiTFSI salt (10%, 20%, 30%, 40%, 50%, and 60%) were mixed with the polymer solution using a magnetic stirrer at 60°C and 400 RPM for 1 hour. The resulting solutions were poured into silicone molds and dried in a vacuum heat chamber at 80°C for three days before testing.

For compositions containing nano-fillers, the previously prepared solution (using the best percentage of LiTFSI salt) was further modified by adding different percentages of Al_2O_3 (5%, 10%, 15%, and 20%). The solution was stirred for an additional 20 minutes to ensure uniform dispersion of the nano-filler. To prevent alumina from depositing during the drying stage, it was crucial to minimize the solvent usage, keeping it below 80%. The polymer dissolution process was conducted at 150°C , with gradual addition of PVA to the solvent to ensure effective dissolution using less solvent. The resulting solutions were poured into silicone molds and dried in a vacuum heat chamber at 80°C for three days, after which the films were tested accordingly. The optimized amounts of LiTFSI salt and Al_2O_3 nano-filler were then used to manufacture the structural electrolyte. This electrolyte was prepared using the PVA/epoxy polymer host in a 7:3 ratio, the optimized amounts of LiTFSI salt and Al_2O_3 nano-filler, and a single layer of plain weave glass fiber with a $[0^\circ/90^\circ]$

orientation and a thickness of 70 μm . A layer of glass fiber was placed on a silicone mold, and the prepared polymer solution was poured over it. The assembly was dried according to the same procedure as the thin films. The general schematic of the method for optimizing composite polymer matrix and structural electrolyte is shown in Figure 8.3. Step 3 is applied only for PEIS tests to improve the contact between electrodes and the electrolyte. In the following subsections, the techniques used to evaluate the polymer matrix and structural electrolyte are explained.

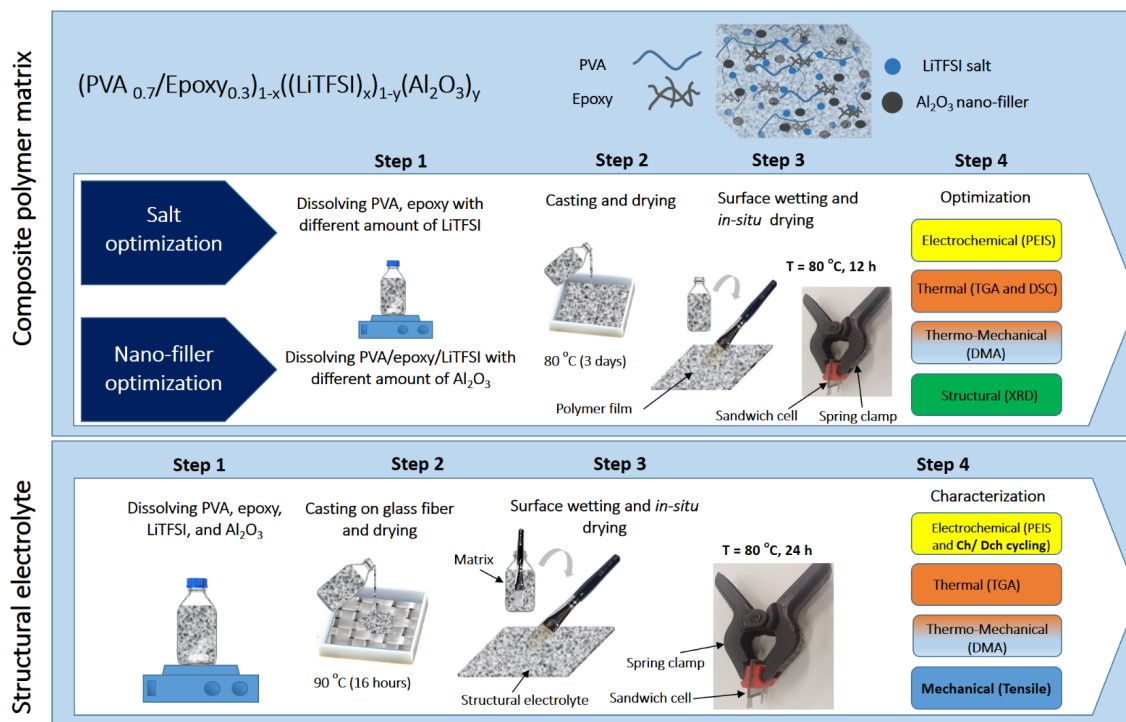


Figure 8.3: Schematics of the method for optimization of composite polymer matrix and structural electrolyte.

8.2.3 Potentiostatic electrochemical impedance spectroscopy test

To perform the PEIS test, after manufacturing the thin films, they were wetted on both sides with a solution matching their composition. They were then assembled with electrodes consisting of two aluminum sheets, each measuring 20 × 20 mm and 0.5 mm in thickness, coated with a 60 nm gold to prevent potential reactions between the aluminum and the electrolyte during drying and tested. Electrochemical impedance measurements were conducted using a Biologic VMP-300 potentiostat (see Figure 7.6). Nyquist plots of the thin films were generated through AC impedance spectroscopy, with data analysis carried out using EC-Lab V11.52 software. All impedance spectra presented in this study were recorded between the working/sense electrode (one of the coated aluminum electrodes) and the counter/reference electrode (the other coated aluminum electrode). PEIS tests were performed with a 10 mV amplitude relative to the Electrochemical Open Circuit Voltage (EOC), across frequencies ranging from 7 MHz to 1 Hz. Three samples were tested for each configuration to assess the repeatability of the methodology. Since the thin films had slight

variations in thickness, the measured Nyquist plots were normalized to a standard film thickness of 0.5 mm for comparison. Accordingly both the real and imaginary components of the impedance were multiplied by the factor $0.5/(\text{thickness of film in mm})$.

8.2.4 Dynamic mechanical analysis

DMA tests were conducted using the HITACHI DMA7100 tester (see Figure 7.7), in tension mode with temperatures from 25 °C up to 150 °C. The tests were performed at a frequency of 1 Hz and a heating rate of 5 °C/min. The sinusoidal oscillation amplitude was set to 10 μm . Three samples were tested for each configuration to assess the repeatability of the methodology. The thin films measured 12 mm in length, 6 mm in width, and had a thickness between 0.5 mm and 1 mm. Each rectangular sample was clamped in the sample holder and tightened to 3 N·m using a calibrated torque wrench at room temperature.

8.2.5 Thermogravimetric analysis

Thermogravimetric analyses were conducted using a HITACHI STA300 instrument (see Figure 7.5) to assess trapped solvents and moisture absorption in each composition. Testing was performed in a platinum pan, with the temperature gradually increasing from 30°C to 800°C at a rate of 10°C per minute. A constant nitrogen gas flow of 100 mL/min was maintained throughout the process.

8.2.6 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) analyses were conducted using a Q20 model calorimeter (TA Instruments) to determine heat flow, glass transition temperature, and melting point. Samples were tested in aluminum pans, with the temperature gradually increased from 0°C to 240°C at a rate of 10°C/min. A constant nitrogen gas flow of 50 mL/min was maintained throughout the process. All samples had a weight of approximately 9 mg.

8.2.7 X-ray Diffraction

X-ray diffraction (XRD) measurements were carried out using a PANalytical Empyrean diffractometer equipped with a Cu anode ($K_{\alpha} = 1.5406 \text{ \AA}$) operating at 30 kV and 55 mA. Scans were performed in reflection-transmission mode over a 2θ range of 10–90° with a step size of 0.026° using a continuous scan mode. A fixed divergence slit of 0.38 mm was used, and no monochromator was applied. Calibration offsets were applied to 2θ (-0.016°) and Omega (+0.0397°).

8.2.8 Tensile test

Quasi-static tensile tests of the structural electrolyte were performed following the ASTM D882 standard test method using a Mecmesin Universal Tensile Tester with a 1 kN load cell limit (see

Figure 8.4) to evaluate the mechanical properties of the structural electrolyte, specifically the stiffness, tensile strength, and failure strain. The tests were conducted at a rate of 1 mm/min. To evaluate the repeatability of the methodology, three samples were tested for each configuration. All samples were rectangular, with approximate dimensions of 8 mm in width, 0.3 mm in thickness, and 80 mm in length, with a grip-to-grip distance of 60 mm. The tensile tester recorded load versus time. Strain was directly determined using the cross-head displacement.

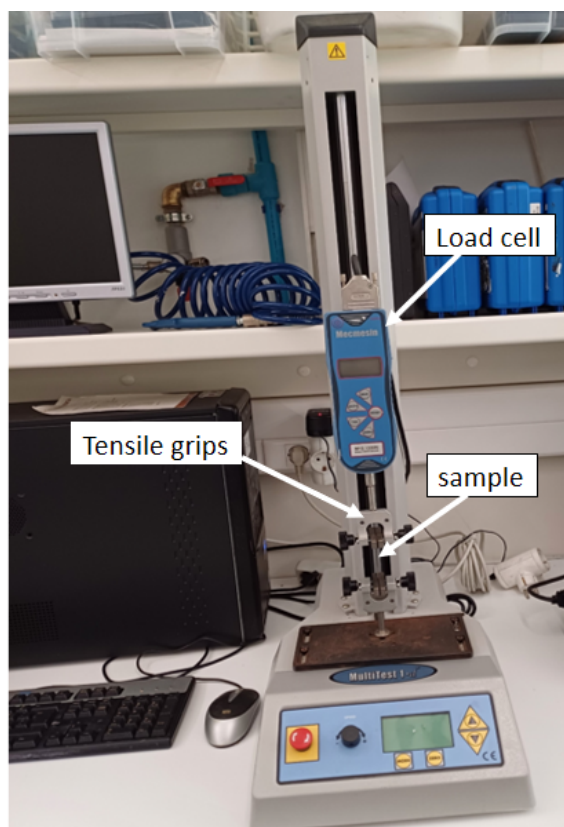


Figure 8.4: Mecmesin universal tensile tester used for quasi-static tensile testing of structural electrolytes.

8.2.9 Charge/discharge tests

The electrochemical performance of the structural electrolyte was evaluated in both half-cell and full-cell configurations. For the half-cell configuration, a 2032 coin cell was assembled using a commercial LFP foil as a cathode, the structural electrolyte, and a lithium metal anode. This configuration is hereafter referred to as cLFP/SE/Li. Both manufacturing and testing were performed at room temperature (18–22 °C). The cathode was cut with a diameter of 15 mm, resulting in an active LFP mass of 22.6 mg. Based on this mass and the manufacturer's specified cathode specific capacity of 150 mAh/g, the currents for different charge/discharge rates were calculated accordingly. The charge/discharge cycle tests were conducted using a Neware CT-4008Tn-5V20mA-164 battery cycler (Neware, Shenzhen, China). Each cycle consisted of constant current–constant

voltage (CCCV) charging, a one-minute rest, constant voltage (CV) discharging, and another rest period. The upper and lower cutoff voltages were set to 4.2 V and 2.8 V, respectively, in accordance with the literature (Lee and Park (2024)).

In the full-cell configuration, aluminum and copper foils were cut into 15 mm diameter discs and subsequently coated with LFP and graphite slurries, respectively. The coated foils were dried at 45°C for 12 hours. After drying the manufactured LFP foil had an areal density of 3 mg/cm² (80% LFP, 10% PVdF, 10% conductive carbon by weight). Structural electrolyte films were cut into 18 mm diameter discs. Following the modified solution casting technique, both sides of the electrolyte were wetted with the matrix solution before being assembled between the LFP and graphite electrodes. The resulting stack was clamped with a single spring clamp (0.7 bar) to ensure good contact and dried in a vacuum chamber at 45°C for 20 hours. After drying, the assembled layers were transferred to a glovebox for final coin cell assembly. Since the electrode foils had low thicknesses (less than 0.1 mm), two springs were used in the coin cell to ensure proper contact between the central active components. This configuration is hereafter referred to as LFP/SE/G. Figure 8.5 illustrates the experimental setup used for battery testing. The glovebox (Figure 8.5 (a)) provided an inert atmosphere for safe cell assembly and handling, while the Neware charge/discharge cycling tester (Figure 8.5 (b)), integrated with a temperature-controlled sandbox, was used to perform charge/discharge testing of the batteries under temperature-controlled condition. Figure 8.6 shows the individual components used in assembling a coin cell in half-cell LFP/Li metal configuration. The setup includes the LFP as working electrode, lithium metal as counter electrode, structural electrolyte, spacer, spring, and stainless steel casing.

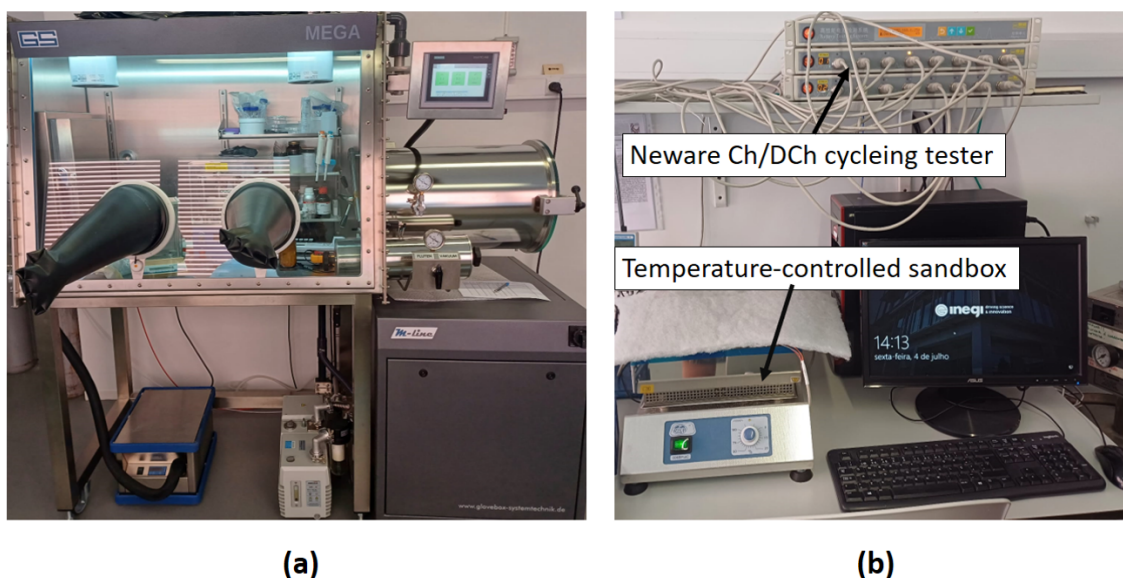


Figure 8.5: (a) Glovebox; (b) Neware charge/discharge cycling tester with temperature-controlled sandbox.

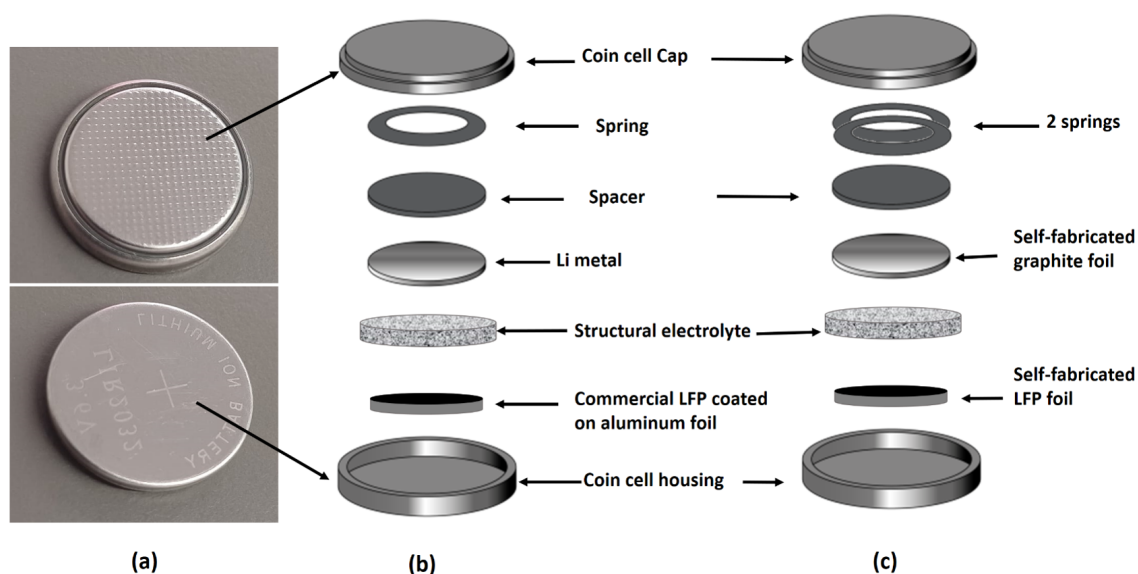


Figure 8.6: (a) Assembled coin cell; (b) Components of the coin cell in half-cell configuration; (c) Components of the coin cell in full-cell configuration.

8.3 Results and discussion

8.3.1 Composite polymer electrolyte: optimization of salt and nano-filler

8.3.1.1 Thermomechanical, thermogravimetric, and structural results

The thermomechanical and thermogravimetric results of polymeric films containing different amounts of LiTFSI and Al_2O_3 are shown in Figure 8.7. Figure 8.7(a) shows the results for PVA/epoxy films with varying concentrations of LiTFSI. As the LiTFSI salt content increases, the storage modulus decreases due to the plasticizing effect of LiTFSI, which is consistent with the literature (Qin et al. (2023)). In addition, thin films with lower LiTFSI concentrations exhibit a pronounced reduction in storage modulus as the temperature increases, indicating higher sensitivity to thermal softening. In contrast, films with higher LiTFSI concentrations also show modulus decrease at elevated temperatures; however, the reduction is notably smaller. This suggests that higher LiTFSI content contributes to improved thermo-mechanical stability of the polymer network, potentially through enhanced ionic crosslinking or increased salt-polymer interactions that reinforce the structural integrity of the material at high temperatures. For instance, in thin films containing 10 wt% LiTFSI, the storage modulus dropped from 85 MPa to 32 MPa upon heating to 150°C—a 62% decrease. In contrast, films with 40 wt% LiTFSI showed a less pronounced decline, from 10 MPa to 8.3 MPa, representing only a 17% decrease. Inside a polymer film, increasing temperature enhances the mobility of polymer chains, leading to a reduction in storage modulus. Interestingly, films with higher salt content exhibit a transient increase in storage modulus around 105 °C, possibly due to LiTFSI crystallization or the evaporation of trapped solvent, followed by a gradual decline as the temperature continues to rise.

Figure 8.7(b) display the TGA curves of PVA/epoxy films containing different amounts of LiTFSI

salt, demonstrating a four-phase decomposition pattern that is consistent across all samples: the initial drying phase (below 240 °C), the first decomposition stage (240–310 °C), the second decomposition stage (310–480 °C), and the final carbonization phase (above 480 °C). This four-stage decomposition closely resembles the thermal decomposition behavior of PVA polymer (Pandey et al. (2011)) and PVA/LiTFSI (Ek et al. (2017)). During the drying phase, the mass loss corresponds to the evaporation of solvent and moisture trapped in the material, with varying amounts depending on the LiTFSI salt concentration. The sample with 10 wt% LiTFSI salt showed a 10 wt% mass loss, while the samples with 20 wt%, 30 wt%, and 40 wt% LiTFSI salt exhibited mass losses of 13 wt%, 15 wt%, and 22 wt%, respectively. This trend indicates that increasing the LiTFSI salt concentration leads to greater retention of solvent and moisture, likely due to the hygroscopic nature of the salt or the increased complexity of the drying in compositions with higher salt content, which may enhance the potential for trapping more solvent.

Keeping constant the LiTFSI-to-PVA/epoxy ratio of 4:6, different Al₂O₃ nano-filler concentrations (5 wt%, 10 wt%, 15 wt%, and 20 wt%) were tested, with their DMA and TGA results shown in Figure 8.7(c) and 8.7(d).

Figure 8.7(c) illustrates the storage modulus as a function of temperature for the PVA/epoxy/LiTFSI films with varying Al₂O₃ content. Increasing the Al₂O₃ content generally led to a higher storage modulus, indicating enhanced mechanical stiffness. However, the relative decrease in storage modulus with increasing temperature also became more pronounced, suggesting reduced thermo-mechanical stability under elevated thermal conditions. In detail, by adding 5 wt% Al₂O₃, the storage modulus increases to 33.6 MPa at room temperature but drops by 80% to 6.1 MPa upon heating to 150°C. With 10 wt% Al₂O₃, the storage modulus of films increases to 41.7 MPa at room temperature and decreases by 82% to 7.2 MPa at 150°C. At 15 wt% Al₂O₃, the storage modulus rises further to 56 MPa but experiences a similar 82% reduction, falling to 10 MPa at 150°C. When the Al₂O₃ content is increased to 20 wt%, the modulus reaches 178 MPa but declines by 88%, dropping to 21 MPa at 150°C. Having 20 wt% Al₂O₃ resulted in a significant increase in stiffness, with the storage modulus reaching 178 MPa at room temperature—nearly 18 times higher than that of the film without any nano-fillers. At 150°C, the modulus remained 2.5 times higher (21 MPa) than that of the films without Al₂O₃. Remarkably, the storage modulus of thin films with 20 wt% Al₂O₃ at high temperatures (150°C) still exceeded the stiffness of the thin film without nano-filler at lower temperatures.

The TGA results shown in Figure 8.7(d) reveal a consistent five-phase decomposition pattern across all samples: the initial drying phase (below 100°C), the second drying phase (below 250°C), the first decomposition stage (250–360°C), the second decomposition stage (360–450°C), and the final carbonization (above 450°C). During the drying phase, mass losses of 28 wt%, 26 wt%, 21 wt%, and 25 wt% were observed, corresponding to the evaporation of solvent and moisture trapped in thin films containing 5 wt%, 10 wt%, 15 wt%, and 20 wt% nano-filler, respectively.

Ionic mobility is known to be enhanced by the segmental motion of the polymer host, with ionic conductivity occurring predominantly in amorphous regions of the material (Yang and Wu (2022); Yang, Chun-Chen (2004)). Here, DSC and XRD analyses (shown in Figure 9.9) were con-

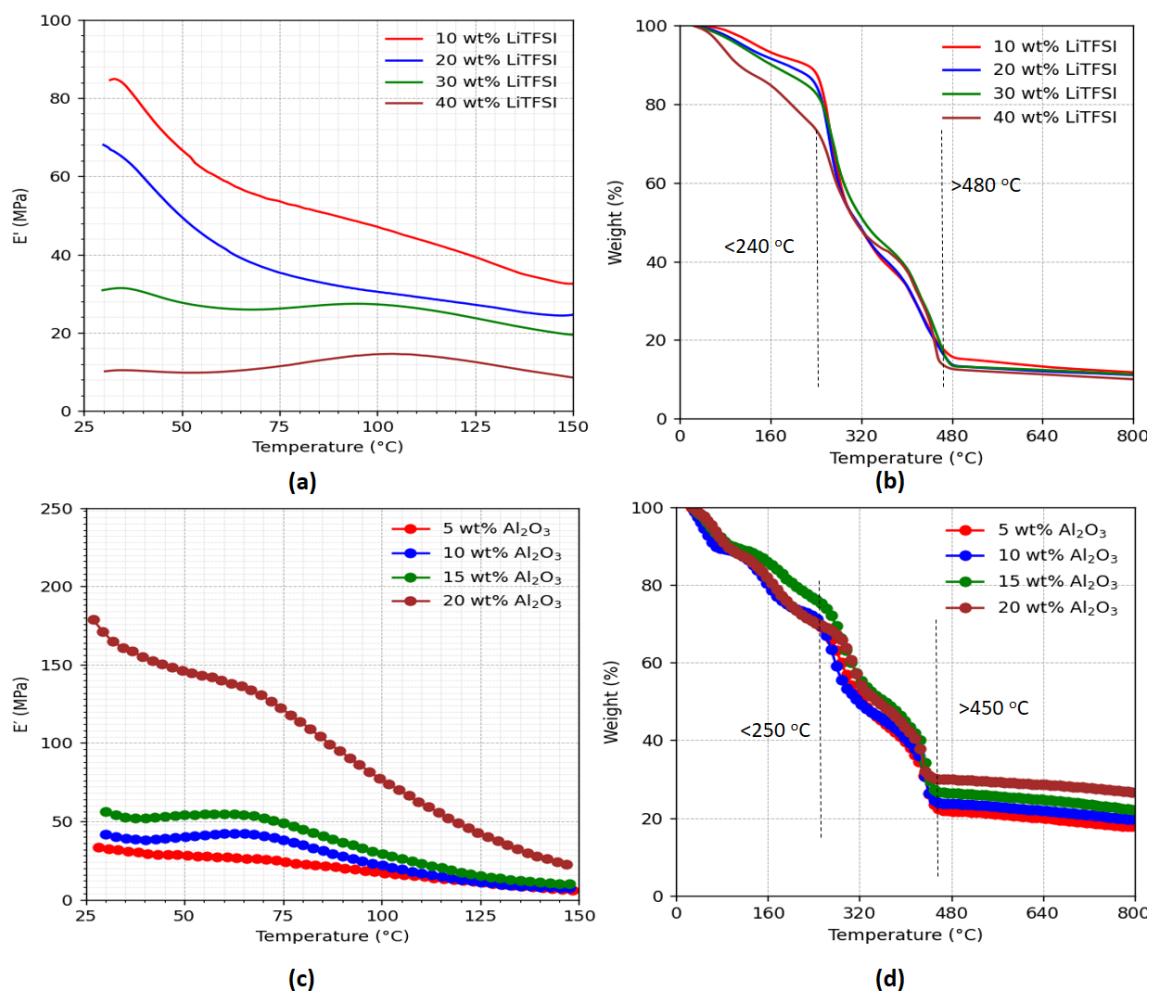


Figure 8.7: Thermomechanical and thermogravimetric results: (a) Storage modulus (E') and (b) TGA of PVA/epoxy films with different concentrations of LiTFSI; (c) Storage modulus (E') and (d) TGA of PVA/epoxy/LiTFSI films with different concentrations of Al₂O₃.

ducted to investigate how the amorphous phase evolves across different compositions. Figure 8.8 (a) presents the DSC analysis of the final matrix- $\text{PVA}_{0.34}/\text{epoxy}_{0.14}/\text{LiTFSI}_{0.32}/(\text{Al}_2\text{O}_3)_{0.2}$ - in comparison with neat epoxy, pure PVA, PVA/epoxy (with a ratio of 70:30), and PVA/epoxy/LiTFSI (with a LiTFSI-to-PVA/epoxy ratio of 40:60). The results showed that epoxy had a glass transition temperature (T_g) of 84 °C, with no melting point detected within the tested temperature range, consistent with the supplier's datasheet ([HBQUIMICA, LDA \(2011\)](#)). Pure PVA showed a T_g of 78 °C and a strong endothermic peak at 226 °C, corresponding to its melting point; literature reports a T_g of 87 °C and a melting point of 218.5 °C for pure PVA ([El-Sayed et al. \(2011\)](#)). The PVA/epoxy blend demonstrated a slightly lower T_g of 73 °C and a melting point of 221 °C. Incorporating LiTFSI into the PVA/epoxy system further reduced the T_g to approximately 42 °C and lowered the melting point to 162 °C. It has been widely reported that the addition of salts decreases the glass transition temperature. For instance, one study using LiTFSI and PVA with water as the solvent—with only 1% trapped solvent and 25 wt% salt concentration—observed a T_g of 58 °C ([Ek et al. \(2017\)](#)). In the present work, DMSO was used as the solvent, resulting in a higher residual solvent content of approximately 13%, and a salt concentration of 40 wt% was used; both factors contributed to the lower observed T_g . The matrix, consisting of the PVA/epoxy/LiTFSI blended with 20 wt% Al_2O_3 , exhibited a T_g near 46 °C, slightly higher than compositions without the nanofiller. These results indicate that the nanofiller increased the crystallinity of the polymer host, consistent with literature reports that the addition of fillers can enhance polymer crystallization ([Ding et al. \(2024\)](#)).

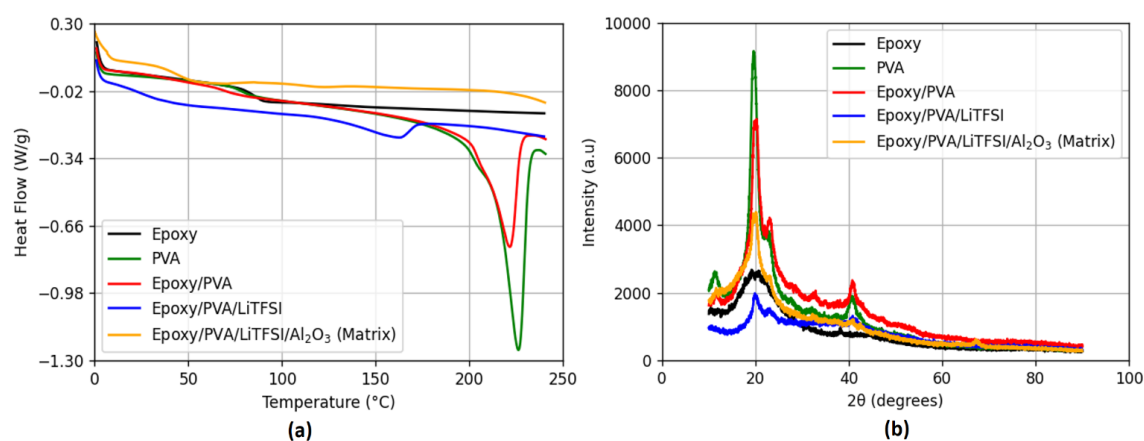


Figure 8.8: (a) DSC and (b) XRD of the matrix ($\text{PVA}_{0.34}/\text{epoxy}_{0.14}/\text{LiTFSI}_{0.32}/(\text{Al}_2\text{O}_3)_{0.2}$) compared with neat epoxy, pure PVA, PVA/epoxy, and PVA/epoxy/LiTFSI.

The XRD patterns (Figure 9.9(b)) further support these observations. Pure PVA exhibited the most prominent peak among the tested compositions at $2\theta = 19.5^\circ$, corresponding to its orthorhombic lattice and semi-crystalline nature, as reported in ([Alakanandana et al. \(2016\)](#)). Neat epoxy displayed a broad halo with very low-intensity features, characteristic of amorphous thermoset polymers ([Mustafa et al. \(2020\)](#)). When PVA was blended with epoxy, the peak intensity decreased compared to pure PVA, suggesting disruption of the PVA crystalline structure by epoxy.

Further addition of LiTFSI continued to reduce crystallinity. However, the addition of nanofillers in the matrix resulted in a sharper peak at $2\theta = 19.5^\circ$, indicating partial recrystallization.

8.3.1.2 Electrochemical results

Figure 8.9 visually compares PVA/epoxy polymer solutions with 40 wt%, 50 wt%, and 60 wt% LiTFSI. As shown in Figure 8.9(b) and 8.9(c), both the 50 wt% and 60 wt% concentrations exhibited phase separation during the drying stage. These results suggest that the salt concentration should not exceed 40 wt%.

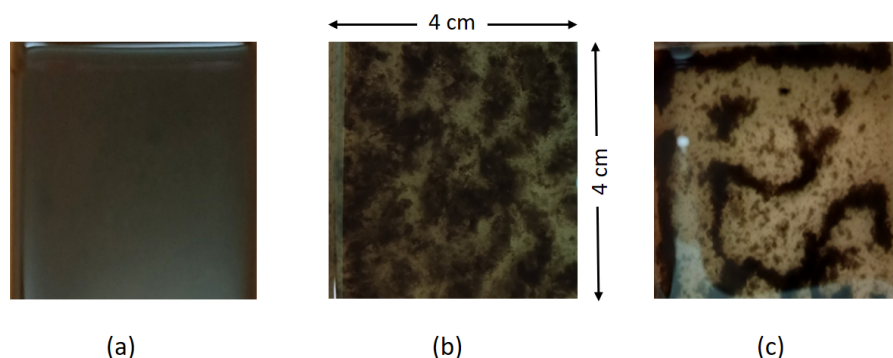


Figure 8.9: Schematic of the the PVA/epoxy/LiTFSI solutions: (a) LiTFSI: 40 wt%; (b) LiTFSI: 50 wt%; (c) LiTFSI: 60 wt%.

The Nyquist plots obtained from PEIS tests of different thin films are shown in Figure 9.3. Figure 9.3(a) to 9.3(d) shows the results of PVA/epoxy samples with different concentrations of LiTFSI (10 wt%, 20 wt%, 30 wt%, and 40 wt%), measured at four temperatures (25°C, 50°C, 75°C, and 100°C). The coefficient of variation (CV) for each dataset was calculated using the bulk resistance of each sample group at room temperature. The CV ranged from 5% to 10% across different compositions, indicating high repeatability. The results demonstrate that increasing the LiTFSI content leads to a decrease in resistance, with the 40 wt% sample showing the lowest bulk resistance. Moreover, increasing the temperature also reduces the overall resistance across all compositions. Considering that 40 wt% LiTFSI salt yielded the highest ionic conductivity without phase separation, the salt-to-PVA/epoxy ratio was maintained at 4:6 for the second part of the optimization, and the effect of different Al_2O_3 nano-filler concentrations (5 wt%, 10 wt%, 15 wt%, and 20 wt%) was assessed. The corresponding Nyquist plots at various temperatures (25°C, 50°C, 75°C, and 100°C) are shown in Figure 8.10(e) to 8.10(h). The CV for each dataset was calculated using the bulk resistance of each sample at room temperature. The values ranged from 3% to 15%, indicating high repeatability across different compositions.

The plots in Figure 8.10 display two distinct regions: (1) a high-frequency semicircle, which is assigned to the bulk resistance of the electrolyte and (2) an upward tilted straight line at low-frequency, corresponding to the ion migration and electrode-electrolyte interfacial effects. The bulk resistance (R_b) of the polymeric films was determined by the intersection of the low-frequency end of the semicircle with the high-frequency end of the straight line along the real axis (Muchakay-

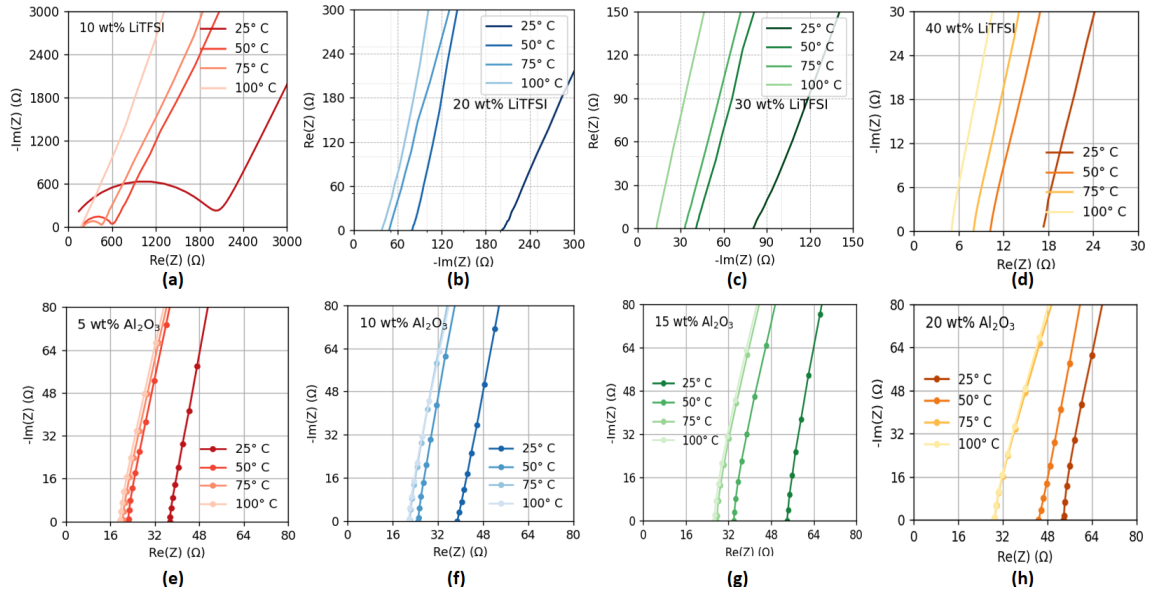


Figure 8.10: (a-d) Nyquist plots of PVA/epoxy films with different concentrations of LiTFSI at different temperatures: (a) 10 wt% LiTFSI, (b) 20 wt% LiTFSI, (c) 30 wt% LiTFSI, (d) 40 wt% LiTFSI; (e-h) Nyquist plot of PVA/epoxy/LiTFSI films with different amounts of Al_2O_3 at different temperatures: (e) 5 wt% Al_2O_3 ; (f) 10 wt% Al_2O_3 ; (g) 15 wt% Al_2O_3 ; (h) 20 wt% Al_2O_3 .

ala et al. (2017); Tang et al. (2016)). In films with lower resistance, such as those shown in Figure 8.10(b) to 8.10(h), no semicircle is visible. Therefore, the bulk resistance was obtained from the point where the impedance line intercepts the real axis. Eventually, the ionic conductivity (σ) of the polymer thin films can be calculated using Equation (8.1).

$$\sigma = \frac{t}{A \cdot R_b}. \quad (8.1)$$

where A represents the electrode-thin film contact area, and t is the film thickness.

Ionic conductivity values, expressed in S/cm, are presented in Table 8.1. The left side of the table shows the results of LiTFSI optimization, indicating that increasing the LiTFSI concentration enhances the ionic conductivity. For example, at room temperature, the conductivity at 10 wt% LiTFSI was 6.1×10^{-6} S/cm, which raised to 7.3×10^{-4} S/cm at 40 wt% LiTFSI. Additionally, the conductivity increases with temperature. For instance, at 20 wt% LiTFSI, it increased from 6.1×10^{-5} S/cm at 25°C to 3.3×10^{-4} S/cm at 100°C. The highest conductivity was observed at 40 wt% LiTFSI, where it ranged from 7.3×10^{-4} S/cm at 25°C to 2.5×10^{-3} S/cm at 100°C. Thus, both LiTFSI concentration and temperature showed a positive impact on ionic conductivity. The right side of Table 8.1 presents the ionic conductivity results for films containing different amounts of Al_2O_3 nano-filler at various temperatures, with the salt-to-PVA/epoxy ratio maintained at 4:6. The ionic conductivity values remained consistently in the range of 10^{-4} S/cm, indicating that the addition of nano-filler did not significantly alter the overall ionic conductivity; however, a slight negative effect can be observed with increasing Al_2O_3 content. For example, at room temperature, the results show that as the Al_2O_3 concentration increases from 5 wt% to 20 wt%,

the ionic conductivity decreases from 3.3×10^{-4} S/cm for 5 wt% nano-filler to 2.3×10^{-4} S/cm for 20 wt% nano-filler.

Based on the literature, the addition of fillers can enhance polymer crystallization, leading to ion trapping and a subsequent decrease in ionic conductivity (Ding et al. (2024)), which aligns with the DSC and XRD results shown in Figure 8.8. In addition, with higher amounts of nano-filler, the total concentration of salt in the film decreases. While the ratio of salt to PVA/epoxy was kept constant at 4:6, at a lower nano-filler concentration, such as 5 wt%, the salt constitutes 38 wt% of the film. However, at 20 wt% nano-filler, the salt content reduces to 32 wt% of the film. This reduction in salt concentration likely contributed to the slight decrease in ionic conductivity as the nano-filler content increases. A similar trend is observed at higher temperatures. Consistently, for each nano-filler concentration, the ionic conductivity increased with rising temperature. For instance, in thin films with 5 wt% Al_2O_3 , the ionic conductivity increased from 3.3×10^{-4} S/cm at 25 to 6.5×10^{-4} S/cm at 100.

Table 8.1: Ionic conductivity of PVA/epoxy-based films with varying LiTFSI and Al_2O_3 content at different temperatures.

LiTFSI optimization			Al_2O_3 optimization		
LiTFSI (wt%)	T (°C)	σ (S/cm)	Al_2O_3 (wt%)	T (°C)	σ (S/cm)
10	25	6.1×10^{-6}	5	25	3.3×10^{-4}
10	50	2.1×10^{-5}	5	50	5.6×10^{-4}
10	75	2.7×10^{-5}	5	75	6.1×10^{-4}
10	100	7.2×10^{-5}	5	100	6.5×10^{-4}
20	25	6.1×10^{-5}	10	25	3.2×10^{-4}
20	50	1.6×10^{-4}	10	50	5.0×10^{-4}
20	75	2.6×10^{-4}	10	75	5.7×10^{-4}
20	100	3.3×10^{-4}	10	100	5.8×10^{-4}
30	25	1.6×10^{-4}	15	25	2.3×10^{-4}
30	50	3.1×10^{-4}	15	50	3.7×10^{-4}
30	75	3.8×10^{-4}	15	75	4.5×10^{-4}
30	100	9.6×10^{-4}	15	100	4.7×10^{-4}
40	25	7.3×10^{-4}	20	25	2.3×10^{-4}
40	50	1.3×10^{-3}	20	50	2.8×10^{-4}
40	75	1.6×10^{-3}	20	75	4.3×10^{-4}
40	100	2.5×10^{-3}	20	100	4.4×10^{-4}

Figure 8.11 shows the ionic conductivity of PVA/epoxy/LiTFSI and PVA/epoxy/LiTFSI/ Al_2O_3 films at different temperatures.

8.3.1.3 Correlation and summary

In summary, the results from PEIS, DMA, TGA, DSC, and XRD were found to correlate with one another. PEIS results showed that increasing the amount of salt decreases bulk resistance, thereby increasing ionic conductivity. However, DMA results revealed that salt has the opposite effect on mechanical properties due to plasticization: increasing salt content reduces mechanical stiffness. This was further supported by DSC and XRD analyses, which showed that the addition of salt lowers both the glass transition temperature and the crystallinity of the polymer film—both

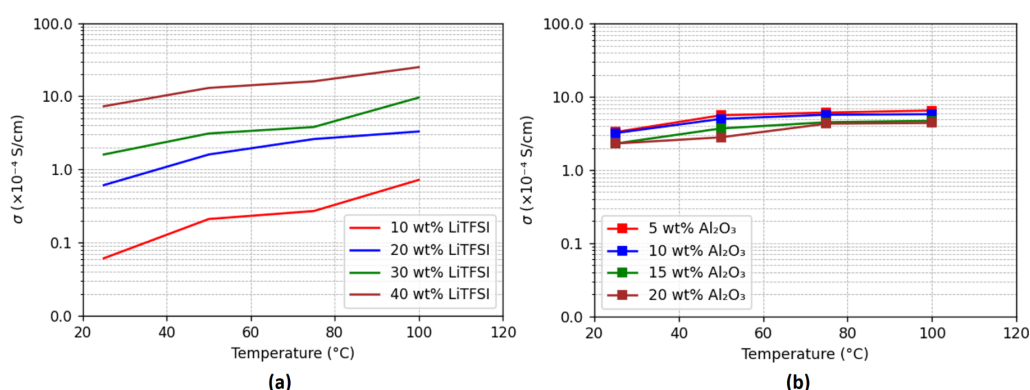


Figure 8.11: Ionic conductivity of thin films at different temperatures: (a) PVA/epoxy/LiTFSI with different concentrations of LiTFSI; (b) PVA/epoxy/LiTFSI/Al₂O₃ with different concentrations of Al₂O₃.

of which are commonly associated in the literature with enhanced ionic conductivity but reduced mechanical integrity. In addition, thin films with higher LiTFSI concentrations exhibited better thermo-mechanical stability, as evidenced by a smaller reduction in storage modulus at elevated temperatures.

Interestingly, this trend reversed upon the addition of nanofillers. PEIS and DMA results showed that nanofillers decrease ionic conductivity while enhancing mechanical properties. This observation was also consistent with DSC and XRD data, which indicated that the addition of nanofillers increases both T_g and crystallinity. Although increasing Al₂O₃ content improves the initial mechanical stiffness of the polymer films, as shown by a higher storage modulus, it also leads to a more significant decline in modulus with temperature—indicating reduced thermo-mechanical stability at elevated temperatures. Accordingly, 40% salt and 20% Al₂O₃ nanofiller, which were chosen as the best-optimized amounts for the matrix, were used in the structural electrolyte in the next step.

8.3.2 Structural electrolyte

8.3.2.1 Thermo-mechanical results

The manufactured structural electrolyte had a thickness of 0.3 mm and a density of 0.02 g/cm³. Compared to pure glass fiber, which has a density of 0.008 g/cm³, this indicates approximately 60 wt% polymer matrix. The mechanical, thermomechanical, and thermal properties of the structural electrolyte are shown in Figure 8.12. Figure 8.12(a) demonstrates the good flexibility of the manufactured structural electrolyte, which showed no damage under hand-bending. The Universal tensile tester and stress-strain curves for three structural electrolyte films are shown in Figure 8.12(b) and 8.12(c). As shown in Figure 8.12(b), the fracture point consistently appeared in the middle of the thin films, away from the grip clamps. The stress-strain curves in Figure 8.12(c) show a CV of approximately 3% for both the strain and stress axes, verifying the repeatability of the manufacturing and testing processes. The linear slope of these curves represents an average

Young's modulus (bulk stiffness) of 1.82 GPa. The maximum stress corresponds to an average tensile strength of 56.9 MPa, and the average failure strain for the group of samples was 3.12%. The thermo-mechanical properties of the structural electrolyte are shown in Figure 8.12(d) and 8.12(e). The CV of the three samples across different temperatures was approximately 5%. Figure 8.12(d) illustrates the storage modulus of the structural electrolyte as a function of temperature. At room temperature, the average storage modulus was 3.2 GPa, decreasing to approximately 1.1 GPa at 150°C, representing a 65% reduction. Compared to the optimized composite polymer electrolyte, at room temperature the storage modulus increased significantly from 178 MPa to 3 GPa, demonstrating more than a 16-fold improvement due to the inclusion of glass fiber. Comparing the results of Figure 8.12(d) at room temperature (25°C) with the stiffness obtained from Figure 8.12(c) reveals that the storage modulus from the DMA test is higher than the bulk stiffness measured in the tensile test, which was found to be 1.82 GPa—approximately 1.6 times lower than storage modulus. This discrepancy arises from differences in sample size between the two tests and the testing methods. While DMA offers insights into molecular and microstructural dynamics, the tensile test assesses the overall bulk properties of the material. Some studies have attempted to correlate the results of these two tests (Deng et al. (2007)). Figure 8.12(e) displays $\tan \delta$ versus temperature, representing the damping behavior of the structural electrolyte, which remained relatively stable across different temperatures. The value changed from 0.12 at room temperature to 0.15 at 150°C. Figure 8.12(f) shows the TGA of the structural electrolyte, demonstrating a four-phase decomposition pattern: the initial drying phase (below 250 °C), the first decomposition stage (250–320 °C), the second decomposition stage (320–460 °C), and the carbonization phase (above 460 °C). This decomposition behavior closely resembles the thermal decomposition of glass fiber-reinforced epoxy, as reported in the literature (Zaheer et al. (2018); Lim et al. (2012); Laoubi et al. (2014)). Comparison of the TGA curve of the structural electrolyte with that of the composite polymer matrix (Figure 8.7 (d)) reveals that the structural electrolyte exhibits higher thermal stability and resistance to heating, primarily due to the incorporation of glass fiber. The initial drying phase (below 250 °C) shows a 6 wt% mass loss, corresponding to the evaporation of solvent and moisture trapped in the structural electrolyte.

The microscopy images in Figure 8.13 reveal distinct morphological differences among the pure PVA film, PVA/epoxy film, the matrix (PVA/epoxy/LiTFSI/Al₂O₃), and the structural electrolyte (glass fiber reinforced with the matrix). The pure PVA film (Figure 8.13(a)) shows a smooth, featureless surface, indicating a homogeneous structure with low porosity. Adding epoxy (Figure 8.13(b)) results in microphase separation and a more complex, textured morphology. Further addition of LiTFSI and Al₂O₃ to the PVA/epoxy film—forming the matrix (Figure 8.13(c))—increases heterogeneity and surface roughness due to multiphase interactions. In Figure 8.13(d), the structural electrolyte appears more uniform and less phase-separated than the matrix. This may be attributed to the infiltration of the matrix into the glass fiber network, which could suppress surface phase contrast and smooth out visible heterogeneities.

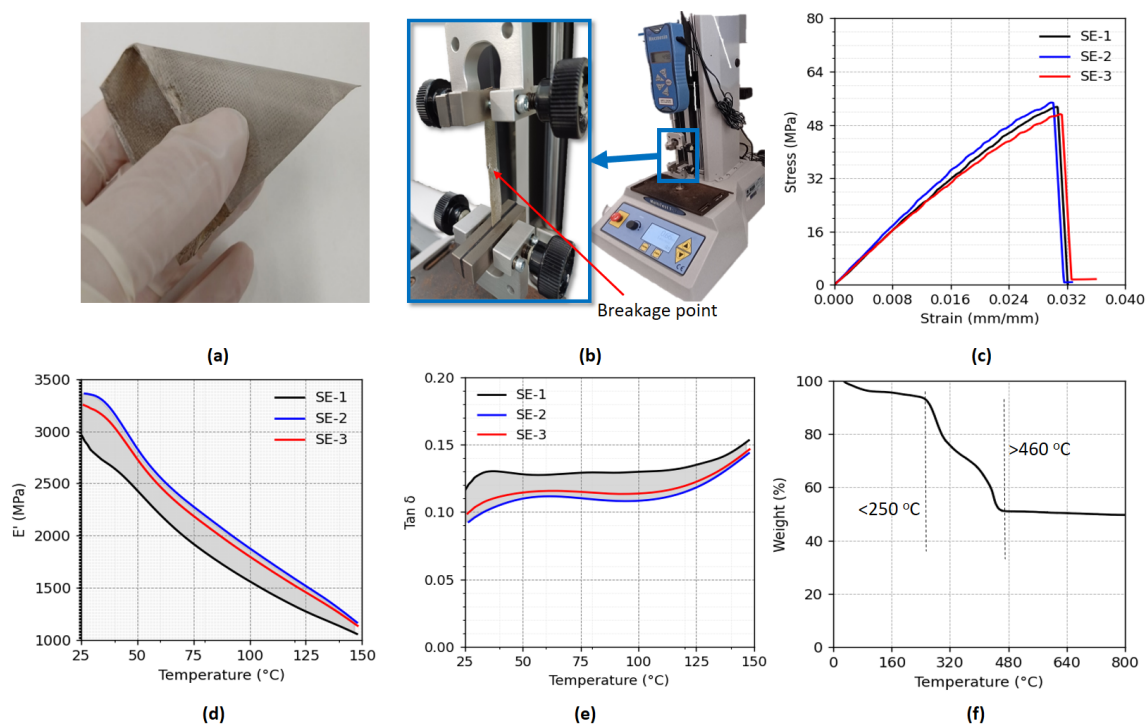


Figure 8.12: Mechanical, thermomechanical, and TGA results of the structural electrolyte (Glass fiber reinforced with $\text{PVA}_{0.34}/\text{epoxy}_{0.14}/\text{LiTFSI}_{0.32}/(\text{Al}_2\text{O}_3)_{0.2}$ matrix): (a) Structural electrolyte under hand-bending; (b) Universal tensile tester; (c) Stress versus strain; (d) Storage modulus (E'); (e) $\tan \delta$; (f) TGA results.

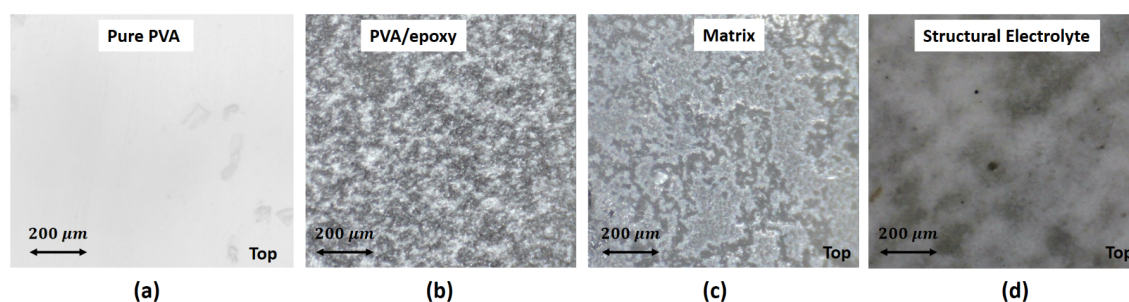


Figure 8.13: Microscopy images: (a) Pure PVA; (b) PVA/epoxy; (c) Matrix ($\text{PVA}_{0.34}/\text{epoxy}_{0.14}/\text{LiTFSI}_{0.32}/(\text{Al}_2\text{O}_3)_{0.2}$); (d) Structural electrolyte (Glass fiber reinforced with the matrix).

8.3.2.2 Electrochemical results

The overall electrochemical results of the structural electrolyte are shown in Figure 8.14. Figure 8.14(a) displays the Nyquist plots for one of the three tested samples at different temperatures in Au@Al/SE/Au@Al pouch cell configuration. Although the structural electrolyte samples had a thickness of 0.3 mm, the Nyquist plots were normalized to a thickness of 0.5 mm to ensure comparability with the polymer films discussed in previous section. The bulk resistance was obtained from the Nyquist plot using the same approach as for the polymer films, and the ionic conductivity of the membranes was calculated using Equation (9.1) and the results are shown in Figure 8.14(b). The CV of the tested samples ranged between 4% and 7% across different temperatures. At room temperature, the average ionic conductivity was found to be 1.74×10^{-4} S/cm, which is still close to the value for the optimized composite electrolyte from the previous section (2.3×10^{-4} S/cm). Upon increasing the temperature to 50°C, the ionic conductivity increased to 2.62×10^{-4} S/cm. Further heating to 75°C and 100°C resulted in conductivities of 3.8×10^{-4} S/cm and 5.9×10^{-4} S/cm, respectively.

Figure 8.14(c) presents the Nyquist plot of the structural electrolyte in half-cell cLFP/SE/Li configuration. The presence of two semicircles in the high- and mid-frequency regions corresponds to the resistance of the solid electrolyte interphase layer (R_{SEI}) and the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface, respectively. The relatively large diameter of the second semicircle indicates a high R_{ct} , suggesting sluggish electrochemical kinetics and interfacial polarization, likely contributing to the performance degradation. At low frequencies, the inclined line represents Warburg impedance, which reflects the diffusion of lithium ions within the electrode. The equivalent circuit of the cell was taken from (Vadhva et al. (2021)) and is shown in the upper part of Figure 8.14(b). The ionic conductivity of the cell can be calculated using Equation (8.1), with the total resistance being the sum of the bulk resistance (R_b), R_{SEI} , and R_{ct} (Vadhva et al. (2021)). The calculated ionic conductivity is 6.3×10^{-5} S/cm.

Figure 8.14(d) shows the galvanostatic charge-discharge (GCD)- voltage profiles of the half-cell (cLFP/SE/Li) at different cycles and current rates. The first and second cycles were conducted at a lower current rate (0.02C), while subsequent cycles were measured at 0.05C. The initial discharge capacity reaches approximately 150 mAh/g, indicating good initial electrochemical activity. However, as cycling progresses, both the charge and discharge capacities decrease noticeably, indicating a decline in capacity retention. The shape of the voltage profiles remains fairly stable in the early cycles, suggesting consistent electrochemical reactions, but the fading plateau region and shrinking capacity reflect increasing polarization and potential degradation of the electrode material over time. Figure 8.14(e) summarizes the cycling performance of the half-cell (cLFP/SE/Li) over eight charge-discharge cycles. The specific charge and discharge capacities decline progressively. Initially, the cell delivers a high charge capacity (~ 150 mAh/g) and discharge capacity (~ 145 mAh/g), indicating good electrochemical activity. However, both charge and discharge capacities decline over successive cycles, with the discharge capacity dropping to below 46 mAh/g by the eighth cycle. The Coulombic efficiency—calculated as the ratio of discharge to charge ca-

capacity density for each cycle (Xiao et al. (2020); Yao et al. (2021))—remains moderate, fluctuating between approximately 70% and 96%, suggesting that a portion of the charge is consistently lost to irreversible side reactions such as electrolyte decomposition or continuous SEI growth.

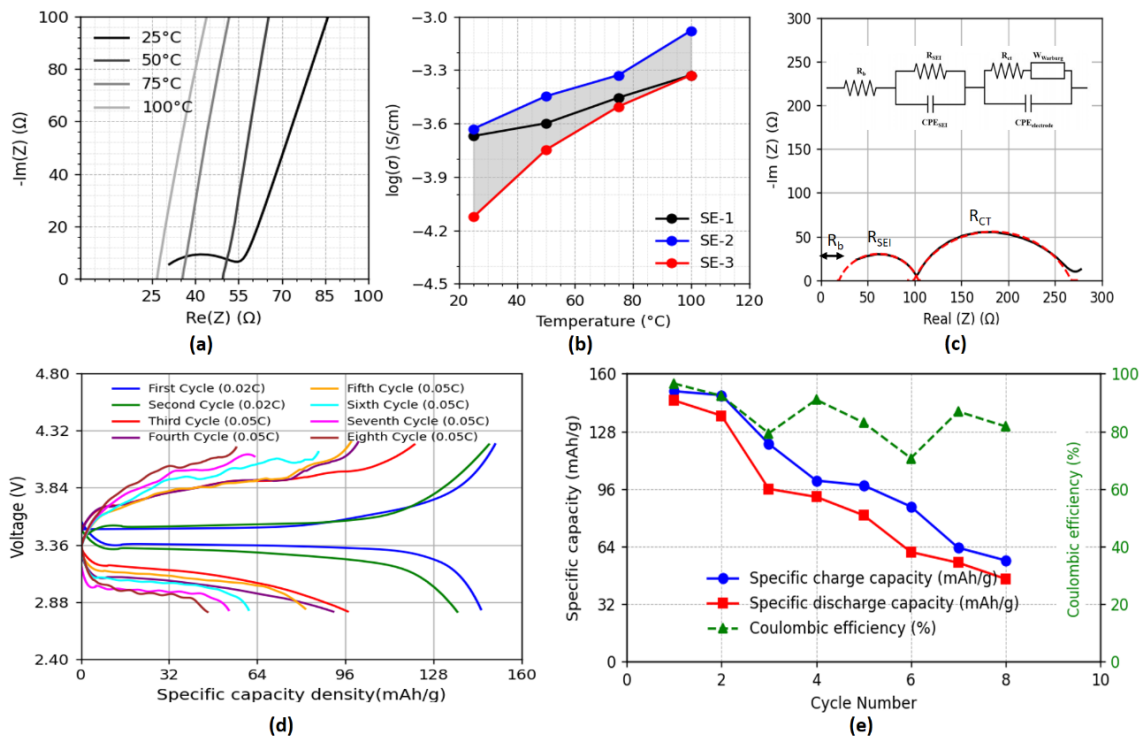


Figure 8.14: Electrochemical results of the structural electrolyte (glass fiber reinforced with $PVA_{0.34}/epoxy_{0.14}/LiTFSI_{0.32}/(Al_2O_3)_{0.2}$ matrix): (a) Nyquist plots in symmetric Au@Al/SE/Au@Al configuration; (b) Ionic conductivity in symmetric Au@Al/SE/Au@Al configuration; (c) Nyquist plot in half-cell cLFP/SE/Li configuration; (d) Voltage vs specific capacity of different cycles of the half-cell; (e) Specific capacity of charge and discharge of the half-cell.

The electrochemical performance of the full cell comprising a LFP-coated aluminum foil, structural electrolyte, and graphite-coated copper foil in coin cell configuration is shown in Figure 8.15. Figure 8.15(a) displays the Nyquist plot of the cell, which reveals a bulk resistance of 22Ω , a solid electrolyte interphase resistance of 17Ω , and a charge-transfer resistance of 14Ω , resulting in a total resistance of 53Ω . The ionic conductivity for this configuration was calculated using Equation 9.1 to be $3.2 \times 10^{-4} \text{ S/cm}$.

Figure 8.15(b) illustrates the voltage versus capacity density over 240 cycles at various current rates. The battery was initially cycled at 0.02C for two cycles, followed by six cycles at 0.05C, six cycles at 0.1C, ten cycles at 0.2C, ten cycles at 0.5C, and ten cycles at 1C. It was then returned to 0.1C for six cycles before undergoing long-term cycling at 1C for an additional 185 cycles. This sequence-reducing the current rate after high-rate cycling—was designed to evaluate the reversibility of the electrochemical behavior and determine whether the cell could recover its capacity. The battery was charged and discharged between 0 V and 2 V, which is lower than operating voltage range for commercial LFP/graphite cells. At 0.02C and 0.05C, the cell exhib-

ited a charge capacity of approximately 160 mAh/g and a discharge capacity of 155 mAh/g. At 0.1C, the charge capacity remained around 160 mAh/g, while the discharge capacity decreased to approximately 145 mAh/g. As the rate increased to 0.2C, the charge and discharge capacities dropped to 124 mAh/g and 110 mAh/g, respectively. Further increases in current rate to 0.5C and 1C led to a progressive reduction in capacity, with the charge/discharge capacities declining to 72/67 mAh/g and 50/47 mAh/g, respectively. To test reversibility, the cell was re-evaluated at 0.1C, where it delivered a charge capacity of approximately 158 mAh/g and a discharge capacity of 145 mAh/g—values closely matching obtained earlier at 0.1C results. This indicates good reversibility of the cell's electrochemical performance.

Figure 8.15(c) shows the long-term cycling performance at 1C over 180 cycles, where the charge and discharge capacities remained consistently close, demonstrating excellent cycling stability. Overall, the results indicate that the battery exhibits stable and repeatable behavior across different charge/discharge rates. As expected for solid-state batteries, capacity decreased with increasing current rate. Although the capacity retention declined to around 20% after 240 cycles, the Coulombic efficiency remained approximately 95% throughout the tests, indicating high electrochemical reversibility and stable cyclability of the cell.

To place these results in context, some recent studies are highlighted. In one study, PEO/LiTFSI/LZTO solid electrolytes were used in a Li/LiFePO₄ cell configuration, achieving a high capacity of 155.2 mAh/g at 0.5 C and 45 °C, with a capacity retention of 84.3% after 500 cycles (Lin et al. (2021)). The superior electrochemical performance of that system, compared to the current study, is attributed to the use of the PEO-based electrolyte, which—when combined with LiTFSI—has a glass transition temperature of approximately −40 °C and was tested at 45 °C. The combination of a polymer with a low glass transition temperature and testing at elevated temperature enhanced ionic conductivity and charge/discharge capacity. Other studies have also reported similarly superior results (Chen et al. (2020b); Xu et al. (2025); Wang et al. (2025c)). Although not explicitly discussed in these studies, the testing conditions suggest that mechanical properties were likely not the primary focus. In comparison, the current study focuses on both mechanical properties and energy storage functionality at room temperature, which is desirable for structural batteries. To achieve enhanced mechanical properties, a PVA-based polymer system was employed. When combined with epoxy and LiTFSI, this system exhibited a glass transition temperature of 42 °C, considerably higher than that of the PEO systems. Additionally, the system was tested at room temperature (18–22 °C), which is typical for structural battery operation. Therefore, the lower capacity retention observed in the current study is expected, given the focus on mechanical robustness alongside electrochemical performance.

The overall results of the structural electrolyte, including the ionic conductivity (σ), bulk stiffness (E), tensile strength (σ_u), failure strain (ϵ), storage modulus (E'), $\tan \delta$, and amount of trapped solvent (TS), are compiled in Table 8.2. The high mechanical properties, along with good ionic conductivity, demonstrate that the optimized structural electrolyte provides excellent multifunctionality, making it suitable for use in load-bearing energy storage devices. Compared to Zhang et al. (Zhang et al. (2021c)), who developed glass fiber reinforced with polyethylene oxide

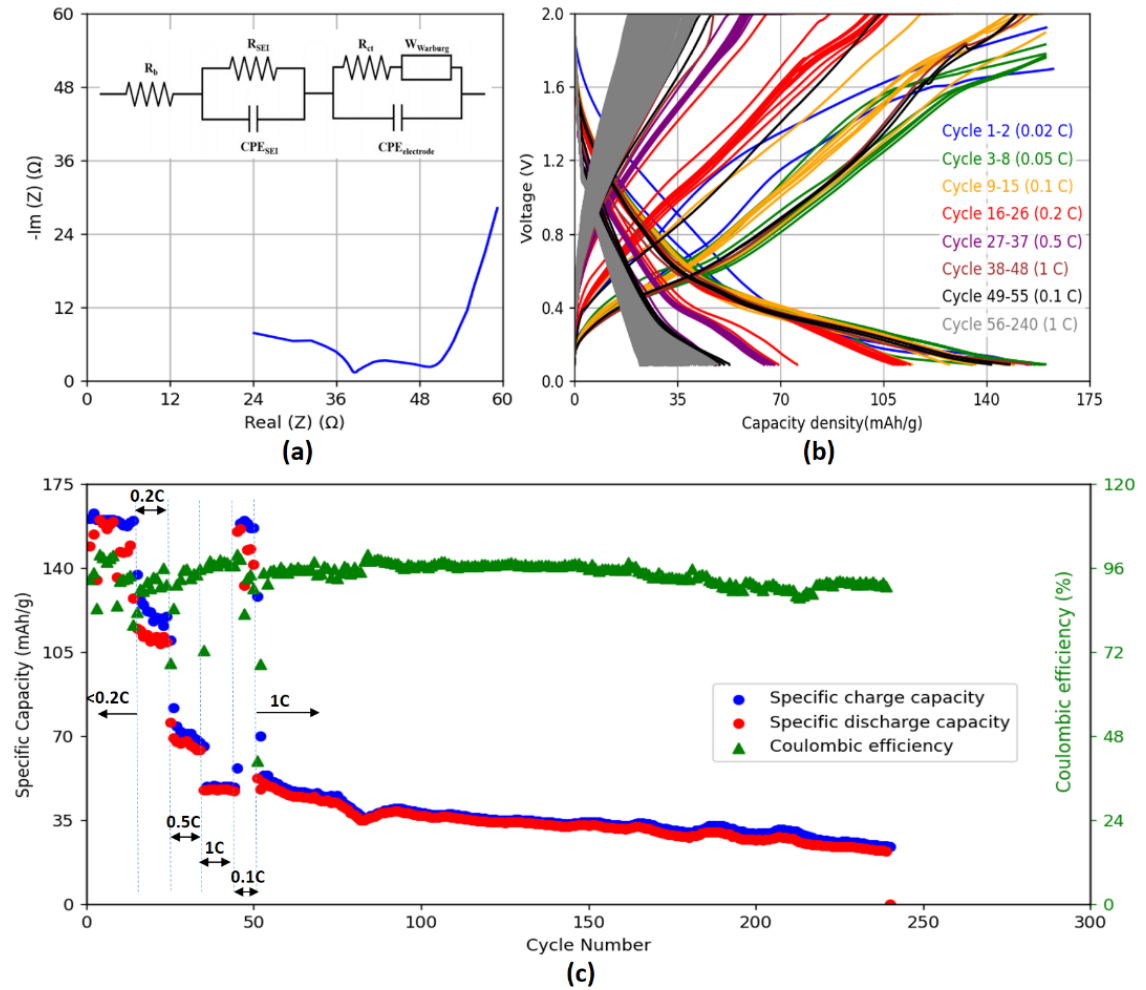


Figure 8.15: Electrochemical results of the structural electrolyte (glass fiber reinforced with a $\text{PVA}_{0.34}/\text{epoxy}_{0.14}/\text{LiTFSI}_{0.32}/(\text{Al}_2\text{O}_3)_{0.2}$ matrix) in the LFP/SE/G full cell configuration: (a) Nyquist plots; (b) Voltage vs. specific capacity for different cycles; (c) Cycle number vs. Specific capacity of charge and discharge, and Coulombic efficiency.

(PEO)/ionic liquid and achieved an ionic conductivity of 1.6×10^{-4} S/cm with 25 wt% ionic liquid, the current work reports a slightly higher ionic conductivity (1.74×10^{-4} S/cm) due to using a higher amount of LiTFSI salt compared to the amount of ionic liquid. Additionally, their method does not result in a fully solid-state electrolyte, whereas the current approach achieves a fully solid-state electrolyte with only 6 wt% trapped solvent. Zhang *et al.* (Zhang *et al.* (2021c)) obtained a tensile strength of 36 MPa and stiffness of 0.81 GPa, while the current method achieves a higher tensile strength of 56.9 MPa and stiffness of 1.82 GPa. In another work, Dong *et al.* (Dong *et al.* (2021)) manufactured a structural electrolyte using PEO, LiTFSI, LATP fillers, and glass fiber. They obtained a stiffness of around 1.2 GPa, a tensile strength of 33.1 MPa, and an ionic conductivity of 6.3×10^{-5} S/cm, which shows that both the mechanical properties and ionic conductivity of the current methodology are higher than in their work. These results confirm the suitability of the current optimized electrolyte for applications requiring high ionic conductivity and good mechanical properties across varying temperatures.

Table 8.2: The electro-mechanical properties of the structural electrolyte (glass fiber reinforced with PVA_{0.34}/epoxy_{0.14}/LiTFSI_{0.32}/(Al₂O₃)_{0.2} matrix).

T (°C)	σ (S/cm)	E (GPa)	σ_u (MPa)	ϵ (%)	E' (GPa)	Tan δ -	TS (wt%)
25	1.74×10^{-4}	1.82	56.9	3.12	3.2	0.113	6
50	2.6×10^{-4}	-	-	-	2.6	0.129	6
75	3.8×10^{-4}	-	-	-	2.1	0.129	6
100	5.9×10^{-4}	-	-	-	1.74	0.129	6

8.4 Conclusions

In this study, a structural electrolyte with remarkable mechanical properties and high ionic conductivity was successfully developed for load-bearing energy storage applications, such as structural batteries. A composite matrix with the formulation PVA_{0.34}/epoxy_{0.14}/LiTFSI_{0.32}/(Al₂O₃)_{0.2} was optimized and then reinforced with glass fibers, forming the structural electrolyte. The salt and nanofiller optimization results from PEIS, DMA, TGA, DSC, and XRD correlated with each other and collectively demonstrated a clear trade-off between ionic conductivity and mechanical properties in the composite matrix. While increasing salt content enhanced ionic conductivity by reducing bulk resistance, it compromised mechanical properties due to plasticization, as reflected in lower stiffness, reduced T_g , and crystallinity. Conversely, the addition of nanofiller reversed this trend-improving mechanical properties but reducing ionic conductivity by increasing both T_g and crystallinity. Notably, although nanofillers boost initial stiffness, they also decreased thermo-mechanical stability. These findings highlight the need for an optimized balance of salt and nanofiller concentrations to achieve desirable electrochemical and mechanical performance in composite polymer electrolytes. The structural electrolyte exhibited a bulk stiffness of 1.82 GPa, a tensile strength of 56.91 MPa, a failure strain of 0.0312, and a high ionic conduc-

tivity of 1.74×10^{-4} S/cm at room temperature. Additionally, it demonstrated a storage modulus of 3 GPa—a remarkable 16-fold improvement compared to the composite polymer electrolyte alone. Furthermore, the electrolyte maintained stable damping characteristics over a wide temperature range, from room temperature to 150°C. Electrochemical testing in a lithium iron phosphate (LFP) half-cell showed good initial performance with high initial charge and discharge capacity densities. The full cell of the structural electrolyte, paired with LFP and graphite, demonstrated long cycle life and good cyclability for approximately 240 cycles, maintaining a high coulombic efficiency of 96% throughout. Both charge and discharge capacity densities decreased with increasing C-rate, which is typical behavior for solid-state electrolytes.

Part IV

Full-system evaluation

Chapter 9

Manufacturing and evaluation of a fully integrated structural battery

This chapter presents the design, manufacturing, and evaluation of a hybrid multifunctional structural battery. The battery features a glass fiber-reinforced polymer shell bonded with surface-treated metallic current collectors, forming a mechanically robust structure. Lithium iron phosphate was used as the cathode, graphite as the anode, and a plain-weave glass fiber incorporating a composite polymer electrolyte matrix served as the structural solid-state electrolyte. The mechanical performance was assessed using quasi-static indentation tests on both sides of the structural battery, and results were benchmarked against equivalent hybrid structures and an all-GFRP configuration. Computed tomography imaging was employed to detect internal damage across the various tested configurations. Energy storage performance was evaluated using potentiostatic electrochemical impedance spectroscopy and charge–discharge cycling, and the results were compared with those of reference coin cells and state-of-the-art structural batteries.

9.1 Introduction

Structural batteries are innovative multifunctional devices that integrate energy storage directly into a vehicle's structure, enabling it to store energy while simultaneously bearing mechanical loads ([Liu et al. \(2009\)](#); [Kalnaus et al. \(2021\)](#)). Various strategies—or combinations thereof—have been explored to achieve this dual functionality. These include the use of solid-state or structural electrolytes ([Snyder et al. \(2007\)](#); [Niazi et al. \(2025a\)](#)), carbon fiber-based electrodes ([Chaudhary et al. \(2024\)](#); [Biswas et al. \(2022\)](#); [Bouton et al. \(2024\)](#)), and either embedding commercial batteries within GFRP or CFRP composites ([Pattarakunann et al. \(2020\)](#); [Ladpli et al. \(2019\)](#); [Rohatgi et al. \(2008\)](#); [Gasco and Feraboli \(2014\)](#)), or in-situ manufacturing of active battery components within structural shells made from GFRP or CFRP ([Danzi et al. \(2021a\)](#); [Asp, Leif E and Johansson, Mats and Lindbergh, Goran and Xu, Johanna and Zenkert, Dan \(2019\)](#)). The ultimate goal is to integrate these structural batteries directly into the vehicle's body, eliminating the need for bulky and heavy battery packs. This integration can reduce overall vehicle weight, improve energy

efficiency, and enhance safety by lowering fire risks typically associated with conventional battery systems (Danzi et al. (2021b); Murugan et al. (2025); Siraj et al. (2023)).

To date, fiber metal laminates (FMLs) have become a popular hybrid structural configuration made of metals, such as aluminum sheets, bonded to fiber-reinforced composites, like glass or carbon fiber. This combination offers a lightweight and tough material by merging the benefits of both metals and high stiffness composites. A well-known example of an FML is GLARE (Glass Laminate Aluminum Reinforced Epoxy), a hybrid laminate made of alternating layers of glass fiber-reinforced epoxy and aluminum. GLARE is widely used in the aerospace industry, particularly in the upper fuselage, wing, and tail edges of the Airbus A380, due to its excellent performance characteristics—such as high strength-to-weight ratio, impact resistance, fatigue strength, and fire resistance (Wu and Yang (2005)).

This GFRP/metal hybrid laminate is also a promising candidate for structural batteries, which typically require a metallic current collector—such as aluminum or copper—alongside an insulating layer that provides high strength, fire resistance, and electrical insulation, as offered by materials like GFRP (Niazi et al. (2024); ?). Therefore, by introducing electrochemical active layers—cathode, anode, and electrolyte—into the laminate stack, a new class of FMLs can be developed. Such FMLs would no longer have a single-function component but a multifunctional structure that, in addition to carrying mechanical loads, can also store energy.

While pure aluminum and copper foils have been consistently used as current collectors in both conventional liquid-state batteries and state-of-the-art structural batteries (Fei et al. (2021); Carlstedt et al. (2022); Yadav et al. (2022))—due to their excellent electrical, thermal, and electrochemical characteristics—their relatively low mechanical strength raises concerns about their suitability for structural battery applications (Jeong et al. (2022); De Matteis et al. (2012); Yuhang et al. (2023)). The development of structural batteries therefore demands more robust and multifunctional alternatives, such as alloy-based current collectors. For example, pure aluminum is relatively soft and ductile, resulting in significantly lower mechanical properties. In contrast, the aerospace-grade 2024-T3 aluminum alloy exhibits substantially higher strength, primarily due to the presence of alloying elements such as copper and manganese, combined with precise heat treatment processes. Despite the addition of these alloying elements, aluminum alloy 2024-T3 retains good electrical and thermal conductivity (Gao et al. (2022); Abdo et al. (2021); Zhang and Li (2023)).

According to literature, the multifunctionality assessment of structural batteries involves evaluating two key performance metrics: the multifunctional efficiency coefficient (η_{mf})—which uses stiffness (or strength) density, and energy (or power) density—and the weight-saving (Snyder et al. (2015); Asp and Greenhalgh (2014); Kalnaus et al. (2021)). However, it is important to note that this assessment does not fully capture the complexity of multifunctional performance. For instance, when evaluating mechanical properties, strength and stiffness alone may not be sufficient; characteristics such as impact resistance, damage tolerance, and failure mechanisms also play a crucial role. Similarly, for the energy storage aspect, additional metrics—such as capacity fade over cycles, cycle life, self discharge rate and coulombic efficiency—could be also considered to provide a more comprehensive multifunctional evaluation of the system (Wang et al. (2022a); Babu

(2024); Xiao et al. (2020); Yao et al. (2021)). To date, structural batteries have been mechanically tested using tensile (Pattarakunann et al. (2020); Liu et al. (2009); Jacques et al. (2012)), compressive (Attar et al. (2020); Shalouf et al. (2014)), bending (Danzi et al. (2021a); Adam et al. (2018); Zhao et al. (2020)), fatigue, shear (Javaid and Ali (2018)), and impact (Fu et al. (2022)) tests.

Quasi-static indentation (QSI) testing, which provides valuable insight into damage mechanisms resulting from out-of-plane loads—such as tool drops, maintenance mishandling, or concentrated stresses—is standardized under ASTM D6264/D6264M for composite laminates and has been widely used to assess the resistance of these laminates to such loads (Wagih et al. (2016a,b)). However, standardized methods are currently lacking for hybrid fiber-metal laminates (FMLs), and no QSI research has yet been reported on complex multilayered systems like structural batteries. Therefore, further investigation is necessary to understand the behavior of these multifunctional systems under quasi-static indentation loading. These tests mimic the low-velocity impacts that structural batteries may experience in service. By combining QSI with advanced imaging techniques such as x-ray computed tomography (CT), damage modes such as delamination, matrix cracking, or current collector yielding can be identified.

In this chapter, a structural battery was designed and manufactured using a GFRP shell, aluminum and copper alloys as current collectors, a conventional LFP cathode and graphite anode, and a previously developed glass fiber-based structural electrolyte. The batteries were tested under quasi-static indentation loading with varying denting displacements. Indentation responses from both sides of the battery were compared and they were further benchmarked against an equivalent hybrid laminate and an all-GFRP laminate. The associated failure mechanisms were detected using CT-scan imaging. Additionally, PEIS was performed to monitor changes in internal resistance and to detect the onset of short-circuit conditions after indentation tests. To evaluate the electrochemical performance of the structural batteries, charge–discharge testing and PEIS measurements were compared with those obtained from the equivalent and reference coin cells and state-of-the-art structural batteries. Finally, based on both mechanical and electrochemical results, the multifunctionality of the structural batteries was assessed and discussed.

9.2 Materials and methods

9.2.1 Materials

The high-strength aluminum alloy Al2024-T3 and copper alloy Cu110-H02, with thicknesses of 0.3 mm and 0.5 mm respectively, were sourced from McMaster-Carr. In both cases, the thinnest commercially available alloys were selected to enable the design and fabrication of a high-strength, lightweight structural battery, while also aligning with GLARE laminate thicknesses. In GLARE systems, it has been shown that a 0.3 mm thickness of aluminum offers improved energy absorption and reduced damage compared to other thicknesses (Kumar M and Mathivanan (2023); Niazi and Sadr (2022)). This approach aimed to maximize both the strength-to-volume and energy-to-volume ratios of the the designed structural battery.

The mechanical properties of the aluminum and copper alloys are presented in Table 9.1, where E and ν represent the Young's modulus and Poisson's ratio, respectively; σ_y is the yield stress, σ_u the ultimate tensile strength, and α the thermal expansion coefficient.

Table 9.1: Mechanical properties of metals.

Material	E (GPa)	ν	σ_y (MPa)	σ_u (MPa)	α ($10^{-6}/K$)
Aluminum 2024-T3	73	0.33	316	457	23.2
Copper 110-H02	117	0.30	261	289	17

The thin-ply lamina used was E-glass PPG-600T-15 μm -25 gsm-300 mm-TP736LT, supplied by NTPT. Table 9.2 summarizes the mechanical properties of the E-glass fiber lamina. In this table, E_1 refers to the Young's modulus in the longitudinal (fiber) direction, and E_2 applies to the transverse and thickness directions. The Poisson's ratio and shear modulus are denoted by ν_{12} and G_{12} , respectively. The thermal expansion coefficients in the longitudinal and transverse directions are indicated by α_1 and α_2 .

Table 9.2: Mechanical properties of E-glass lamina.

E_1 (GPa)	E_2 (GPa)	ν_{12}	G_{12} (GPa)	α_1 ($10^{-6}/K$)	α_2 ($10^{-6}/K$)
40	6.43	0.298	2.735	7.12	36

The structural electrolyte was composed of a polymer matrix and a plain-weave glass fiber with a $[0^\circ/90^\circ]$ orientation, a ply thickness of 70 μm , and an areal weight of 0.008 g/cm². The total thickness of the structural electrolyte was 0.3 mm and it contained 60 wt% polymer matrix (Niazi et al. (2025a)).

The polymer matrix was formulated using a blend of PVA, epoxy, lithium salt, and a nano-filler with the formulation PVA_{0.34}/epoxy_{0.14}/LiTFSI_{0.32}/(Al₂O₃)_{0.2}. The PVA, sourced from Thermo Scientific, had a molecular weight in the range of 146,000–186,000 and a purity exceeding 99.3%. Dimethyl sulfoxide (DMSO), purchased from Labkem, was used as the solvent to dissolve the polymer and facilitate mixing of the additives. The epoxy system (AS-89), provided by HBQUIMICA, consisted of two components: Part A (resin) and Part B (hardener), mixed in a 100:45 ratio as recommended by the manufacturer (HBQUIMICA, LDA (2011)). Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt with 99% purity was obtained from Acros Organics. The nano-filler, aluminum oxide (Al₂O₃) of flash grade with particle sizes between 18 and 32 microns and a molecular weight of 101.96 g/mol, was also supplied by Thermo Scientific.

The commercial cathode foil—an aluminum foil coated with lithium iron phosphate (LFP)—was sourced from MTI Corporation. According to the manufacturer's datasheet, it has an areal density of approximately 13.5 mg/cm² and a composition of 95.4% LFP, with the remaining constituents being PVdF and conductive carbon. The commercial anode foil—a copper foil coated with graphite—was sourced from MSE Supplies. According to the manufacturer's datasheet, it had a total thickness of 65 μm , with an active material layer thickness of 8 μm , an areal density of approximately 7.28 mg/cm², and a composition of 96% active graphite. LFP powder (parti-

cle size of $1.5\ \mu\text{m}$) was sourced from MSE Supplies. Graphite powder and conductive acetylene black—known as Super P—were obtained from Nanografi. The PVdF binder was sourced from MTI Corporation. The components of the 2032 coin cell—including the positive case, negative case, spring, and spacer—were all sourced from Nanografi.

The moisture-protective coating used was Marino Maritimo 3V3, a transparent polyurethane varnish formulated with marine alkyd resins.

9.2.2 Method

9.2.2.1 Structural battery design

When designing hybrid laminate structural batteries, due to poor bonding between current collectors and internal active layers, each structural side of the battery should exhibit minimal extension-bending coupling to prevent warping under tension. Additionally, after curing the structural batteries, during the cooling down stage, bending may occur in the GFRP/current collector layers due to the mismatch in thermal expansion coefficients between the GFRP and metallic current collectors. To mitigate these effects—which can lead to delamination between both sides of the battery and therefore within the internal layers and compromise the multifunctionality of the system—a quasi-isotropic symmetric layup of $[0^\circ/45^\circ/90^\circ/-45^\circ]_{\text{ns}}$ was selected for the GFRP shell on each side of the battery. This layup also promotes a more uniform distribution of thermal stresses across the GFRP laminates. Since aluminum and copper alloy sheets were sourced in the minimum commercially available thicknesses (0.3 mm for aluminum and 0.5 mm for copper) to ensure a thin and lightweight structure—and given their differences in both thickness and stiffness—the number of repetitions of the $[0^\circ/45^\circ/90^\circ/-45^\circ]$ layup was adjusted accordingly on each side of the battery. The GFRP layup on the aluminum side was designed as $[0^\circ/45^\circ/90^\circ/-45^\circ]_{5\text{S}}$, resulting in a total thickness of approximately 1 mm. On the copper side, a $[0^\circ/45^\circ/90^\circ/-45^\circ]_{3\text{S}}$ layup with a thickness of 0.6 mm was used to compensate for the greater thickness and stiffness of the copper. Further increasing the GFRP thickness on the aluminum side could have resulted in more balanced stiffness between both sides of the battery, but this was avoided to prevent an undesirable increase in the extension-bending coupling matrix of the overall structural battery laminate.

Figure 9.1 (a) presents a 3D schematic of the designed structural battery, Figure 9.1 (b) illustrates its internal lay-up configuration, and Figure 9.1 (c) shows the lay-up of the equivalent hybrid laminate used for comparison. To create the equivalent hybrid laminate, the battery electrochemical active components—cathode, electrolyte, and anode—were replaced with a mechanically representative structure: a 0.4 mm thick layer of symmetric, quasi-isotropic GFRP ($[0^\circ/45^\circ/90^\circ/-45^\circ]_{2\text{S}}$), matching the total thickness of the battery's active materials. Additionally, all-GFRP laminate with layup of $[0^\circ/45^\circ/90^\circ/-45^\circ]_{14\text{S}}$ was considered as another configuration for comparison with both the hybrid laminate and the structural battery. This also allowed examination of the behavior of thin-ply GFRP laminate under QSI testing.

The tensile stiffness and bending stiffness of the structural battery, hybrid laminate, and all-GFRP laminate were calculated using classical laminate theory (Barbero (2017)). As reported in a previ-

ous study (Niazi et al. (2025a)), the structural electrolyte was a plain-weave glass fiber reinforced composite polymer matrix with a thickness of 0.3 mm and a tensile stiffness of 1.82 GPa, and was considered as an isotropic layer in the calculation. The stiffness contributions of the cathode and anode layers were assumed to be negligible. For the structural battery, the tensile stiffness was 40.5 GPa, and the bending stiffness was 26.44 GPa. On the other hand, the hybrid laminate exhibited a tensile stiffness of 41.3 GPa and a bending stiffness of 27.2 GPa. In comparison, the all-GFRP laminate showed a tensile stiffness of 17.7 GPa and a bending stiffness of 18 GPa.

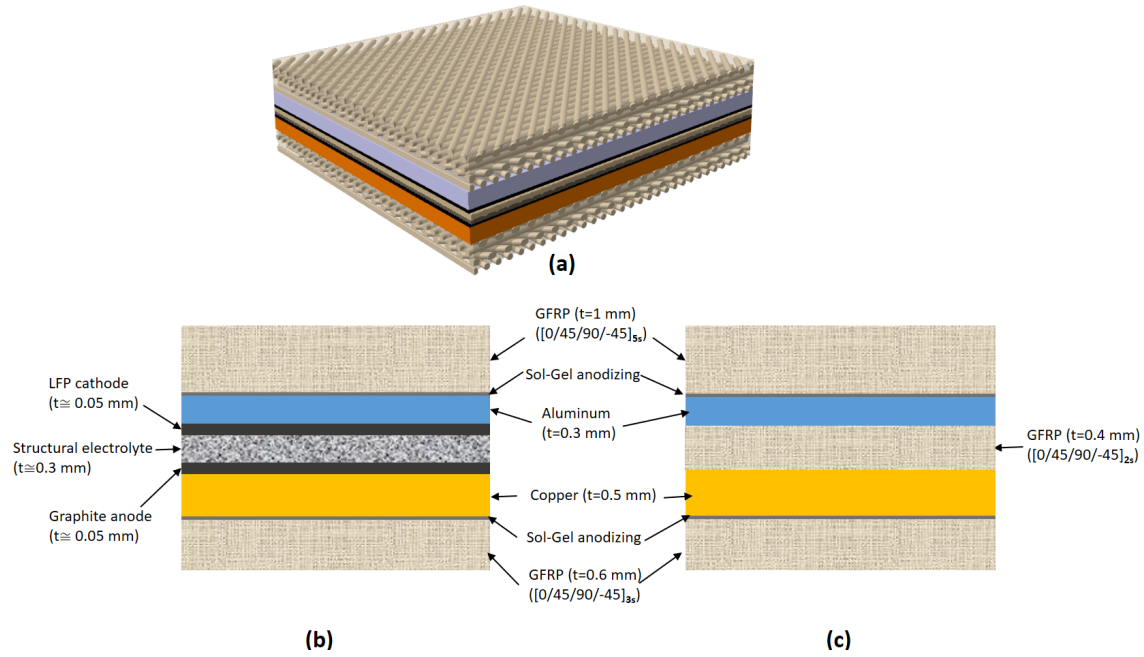


Figure 9.1: (a) 3D schematics of the designed structural battery; (b) Lay-up of the designed structural battery; (c) Lay up of the equivalent hybrid laminate.

9.2.2.2 Manufacturing

The structural batteries, equivalent hybrid laminates, and all-GFRP laminates—were fabricated with dimensions of $150 \text{ mm} \times 150 \text{ mm}$, in compliance with the ASTM D6264/D6264M standard. However, for structural batteries subjected exclusively to electrochemical tests, smaller dimensions of $20 \text{ mm} \times 20 \text{ mm}$ were used. The structural battery samples were designed with metallic current collectors featuring extensions measuring approximately 6 mm in width and 10 mm in length. These extensions were positioned beyond the edges of the laminate to allow for external electrical connections. The manufacturing process of the structural batteries is shown in Figure 9.2.

The structural electrolyte was prepared following Chapter 8 (Niazi et al. (2025a)) (Figure 9.2 (a)). After cutting the aluminum and copper alloy sheets to $150 \text{ mm} \times 150 \text{ mm}$ using a 5-axis CNC machine, Sol-Gel treatment was performed on surfaces of the aluminum and copper sheets at the GFRP interfaces side, following the methodology described in Chapters 5 and 6 (Figure 9.2 (b)).

Previously, the LFP cathode and graphite anode were coated on opposite sides of the aluminum and copper sheets, respectively, as shown in Figure 9.2 (c). The electrodes were then dried inside a vacuum chamber for 12 hours at 45°C. This relatively low drying temperature was chosen to prevent oxidation of the metallic current collectors, which could hinder electron flow and increase internal resistance.

Both the LFP cathode and graphite anode were prepared using N-methyl-2-pyrrolidone (NMP) as the solvent, with active material, carbon-conductive powder, and PVdF binder mixed in an 8:1:1 weight ratio. The mixtures were stirred using a magnetic stirrer at 400 rpm and 60°C for approximately 6 hours to ensure proper dissolution.

The structural electrolyte was wetted with a composite polymer matrix on both sides, then sandwiched between the aluminum alloy coated with LFP and the copper alloy coated with graphite. The structural electrolyte was approximately 1 mm larger than the metal components on each side to prevent short circuit. The resulting laminate was held using multiple spring clamps (with a pressure of 0.7 bar) and placed in a vacuum chamber for approximately 20 hours at 45°C to have additional drying and enhance interfacial bonding between the layers (Figure 9.2 (d)).

The GFRP laminates with layups of $[0^\circ/45^\circ/90^\circ/-45^\circ]_{3S}$ and $[0^\circ/45^\circ/90^\circ/-45^\circ]_{5S}$ with uncured prepregs were independently laminated using hand lay-up and then cut to the battery dimensions. The structural batteries were manufactured by sequentially stacking the following layers: a GFRP layer with a $[0^\circ/45^\circ/90^\circ/-45^\circ]_{5S}$ layup, the pre-assembled sandwich of electrodes and electrolyte (positioned with the aluminum side facing the GFRP), and another GFRP layer with a $[0^\circ/45^\circ/90^\circ/-45^\circ]_{3S}$ layup. The GFRP laminates were designed to be approximately 5 mm larger than the sandwich core on each side, in order to fully enclose the internal components.

The full stack was wrapped with Teflon and placed in an aluminum mold. Finally, to co-cure the stacks, the mold was placed inside a hot press at 25 bar, following the GFRP supplier's specifications for the low-temperature curing cycle: 1 hour at 70 °C and 12 hours at 80 °C (Figure 9.2 (e)). As discussed in (Qi et al. (2024)), controlling the applied pressure during fabrication promotes uniform material distribution, reduces porosity, and enhances interfacial bonding between components. In this study, a pressure of 25 bar was applied using a hot press; however, the full load was not directly transferred to the samples. To limit overpressure and ensure controlled compaction during curing, two metallic sheets were used as spacers. These spacers also ensured consistent sample thickness across all configurations. They had a thickness of 2.85 mm and dimensions of approximately 20 mm × 100 mm and were placed on both sides of the samples, positioned between the top and bottom plates of the aluminum mold. The spacer thickness accounted for the cured sample thickness (2.8 mm) as well as the top and bottom Teflon layers (with a thickness of 0.025 mm).

Two types of structural batteries were tested electrochemically: one without a moisture-protective coating on the GFRP skin, and another with a thin layer of moisture-protective material applied to further protect the structure from moisture absorption. The manufacturing process of the equivalent hybrid laminate involved sequentially stacking the following layers: a GFRP layer with a $[0^\circ/45^\circ/90^\circ/-45^\circ]_{5S}$ layup, an aluminum alloy layer treated with sol-gel on both sides, a GFRP

layer with a $[0^\circ/45^\circ/90^\circ/-45^\circ]_{2S}$ layup, a copper alloy layer treated with sol-gel on both sides, and a final GFRP layer with a $[0^\circ/45^\circ/90^\circ/-45^\circ]_{3S}$ layup. After curing, the thickness of the structural batteries, hybrid laminates, and all-GFRP laminates was measured to be 2.8 mm.

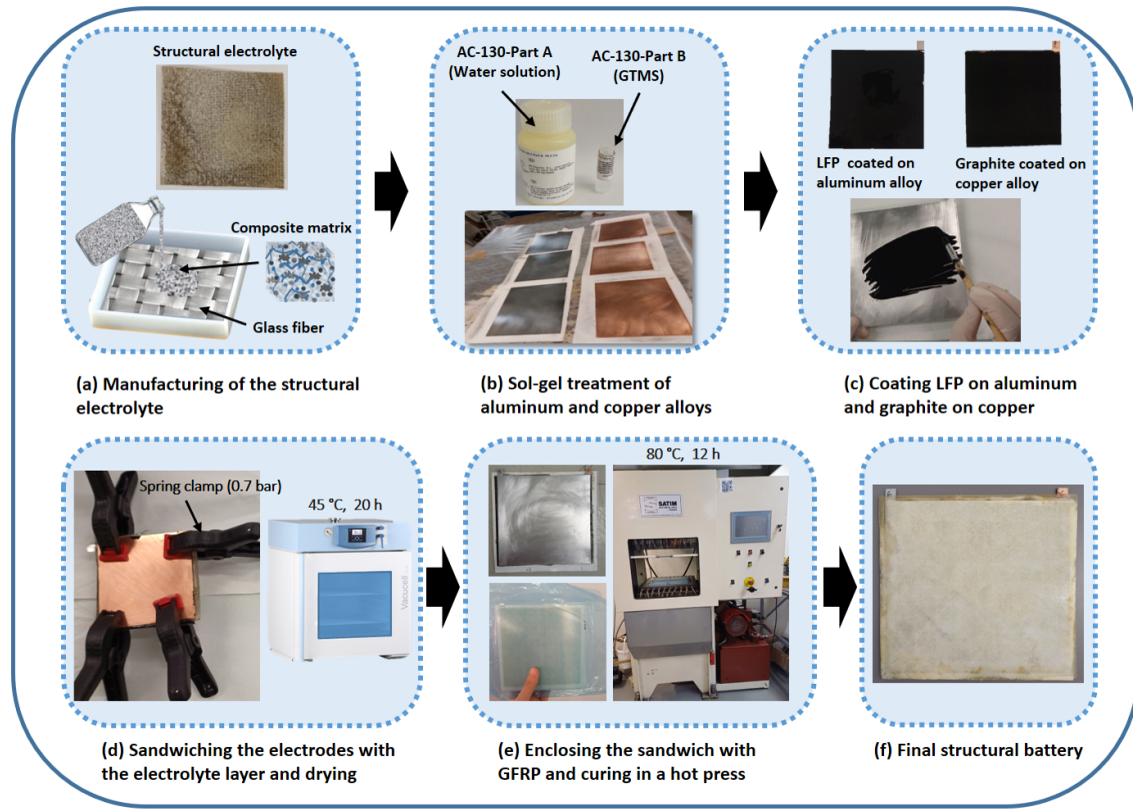


Figure 9.2: Schematic of the structural battery manufacturing process.

9.2.2.3 Quasi-static indentation test

The QSI tests were performed in compliance with the ASTM D6264/D6264M standard using the rigidly-backed configuration. The test setup is shown in Figure 9.3, illustrating the indenter, the specimen, and the support used during testing. The indenter had a hemispherical tip with a diameter of 13 mm, was made of hardened steel, and was heat-treated to achieve a hardness of 60 HRC. The support was a steel plate with a thickness of 20 mm. The tests were conducted using an Instron universal testing machine equipped with a 100 kN load cell. All tests were performed at room temperature (20 °C). The load was applied in displacement control mode at a rate of 0.25 mm/min.

According to the standard's procedure for rigidly-backed support, the samples were simply placed on the support such that the indenter was located at the center of the laminate. Each test continued until a previously specified indentation displacement was reached, after which the indenter was returned to the initial position. The depth of the indentations were immediately measured after unloading using a depth gauge with a spherical tip of 5 mm in diameter. Since both structural

batteries and hybrid laminates have asymmetric layups, indentation tests were performed on both sides for comparison. In this work, specimens with the GFRP/aluminum sequence facing the indenter are named the "Al-side," while those with the GFRP/copper sequence facing the indenter are referred to as the "Cu-side." To assess the relaxation behavior of the laminates, the depth of the indentations were also measured seven days after the QSI tests.

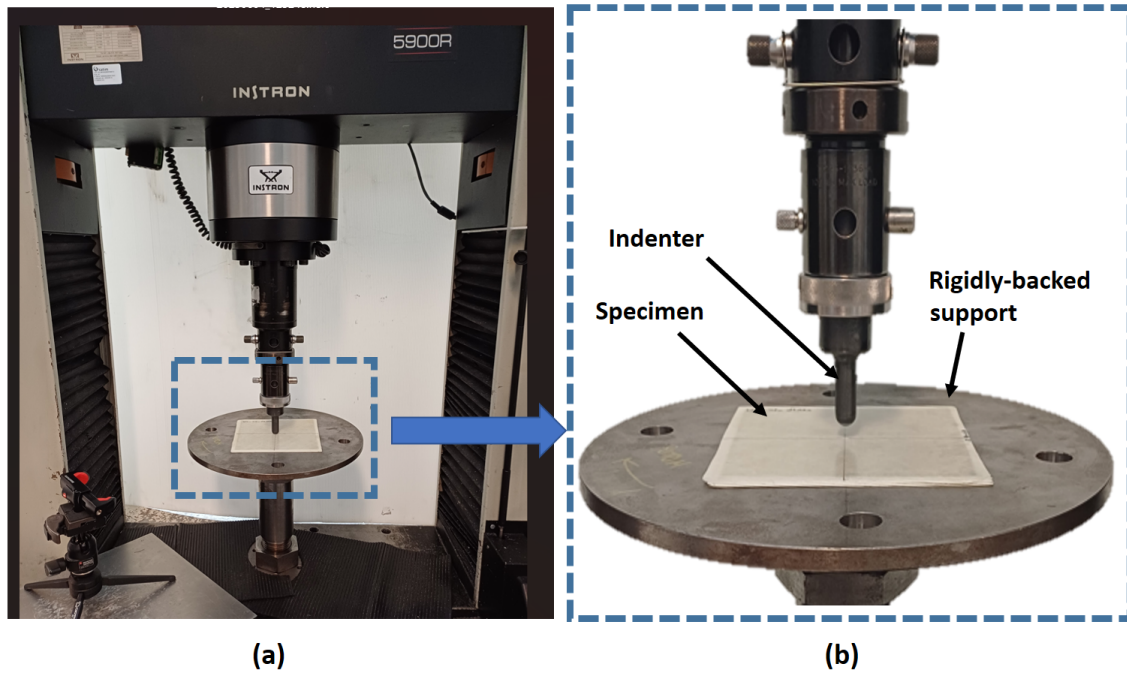


Figure 9.3: Schematics of quasi-static indentation test set up.

9.2.2.4 Computed tomography scanning

Computed tomography (CT) scans were conducted using a *ZEISS METROTOM 1500* system (see Figure 9.4 (a)), capable of operating at a maximum of 225 kV and 3000 μA , with a power limit of 500 W. All scans were performed using a consistent field of view (FOV) ranging from 40 mm $\times$ 40 mm to 50 mm $\times$ 50 mm around the indentation area. Image acquisition was carried out using *METROTOM OS* software, while *VGStudio* was used for image processing and evaluation. Scanning parameters were tailored to each sample type: structural battery samples were scanned at 180 kV and 410 μA ; hybrid laminate samples at 150 kV and 400 μA ; and all-GFRP samples at 150 kV and 156 μA . A uniform voxel size of 19.90 μm was used across all scans. As shown in Figure 9.4 (b), the specimen was mounted on the rotating sample platform using protective foam to hold it securely in place and to prevent any movement during scanning. The X-ray source emits a beam that passes through the specimen while it rotates. As the X-rays travel through the material, variations in absorption are captured by a digital detector positioned opposite to the source. These captured 2D projections are then reconstructed using dedicated software to generate a high-resolution 3D image of the specimen's internal structure.

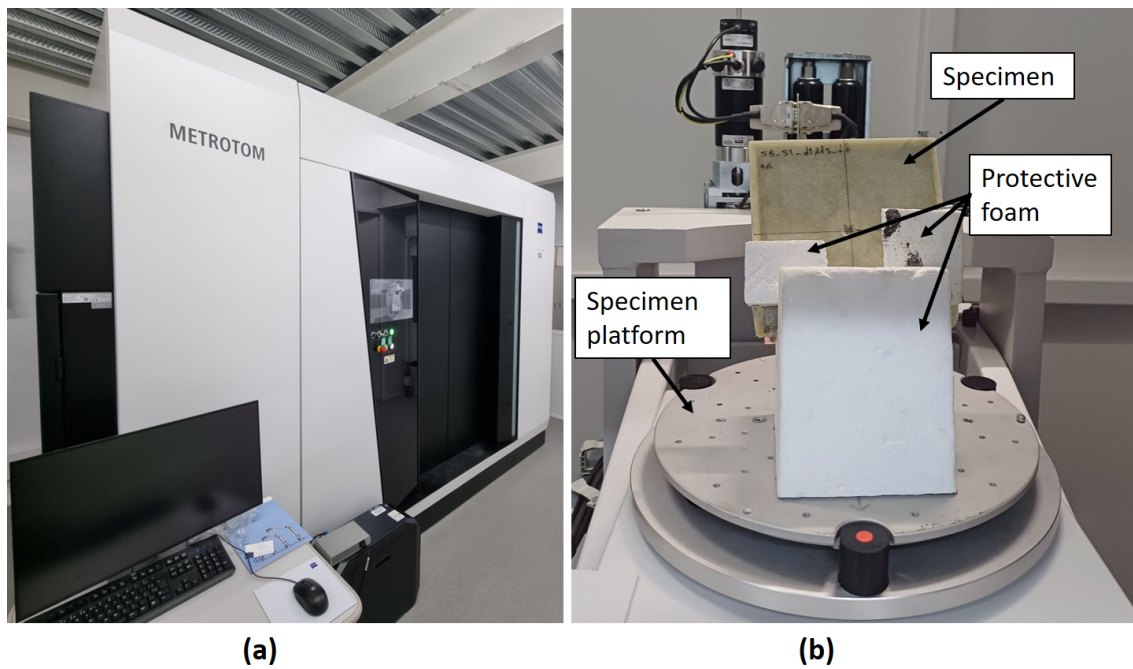


Figure 9.4: CT-scanning setup: (a) ZEISS METROTOM 1500; (b) Sample set-up for CT-scans.

9.2.2.5 Coin cell preparation

To systematically monitor changes and provide a detailed understanding of the electrochemical behavior of the structural battery, a series of tests were first conducted using coin cells, followed by testing of the full structural battery. Figure 9.5 illustrates the three coin cell configurations examined in this study. As shown in Figure 9.5 (a), the first configuration employed commercial LFP and graphite foils with a liquid electrolyte, serving as a baseline for comparison. Next, the structural electrolyte was tested in combination with the same commercial electrodes to evaluate its compatibility and performance (Figure 9.5 (b)). In both of these configurations, since the electrode foils had low thicknesses (less than 0.1 mm), two springs were used to compensate for the low thickness and to ensure proper contact between the central active components. The commercial cathode was punched into 15 mm diameter discs, yielding an active LFP mass of approximately 22.6 mg. Based on this mass and the manufacturer-specified specific capacity of 150 mAh/g for the cathode, the corresponding charge/discharge currents for various C-rates were calculated. The commercial graphite foil was cut into discs with a diameter of 14 mm. Figure 9.5 (c) shows the third coin cell configuration, in which LFP and graphite were coated onto aluminum and copper alloy substrates, respectively, and tested with the structural electrolyte. This setup was designed to evaluate the electrochemical performance of the active section of the structural battery. For electrode fabrication, the aluminum alloy was cut into 15 mm diameter discs and the copper alloy into 14 mm discs, which were then coated with LFP and graphite slurries, respectively, and dried at 45°C for 12 hours. Following a procedure similar to the structural battery preparation, the structural electrolyte was wetted with the matrix solution and assembled with the electrodes. The resulting stack was then dried for 20 hours at 45°C before being transferred to a glovebox for final

coin cell assembly. In this configuration, only one spring clamp was required to hold the stack and no spacer in the coin cell was used, due to the greater thickness of the alloy current collectors (0.3 mm for aluminum and 0.5 mm for copper).

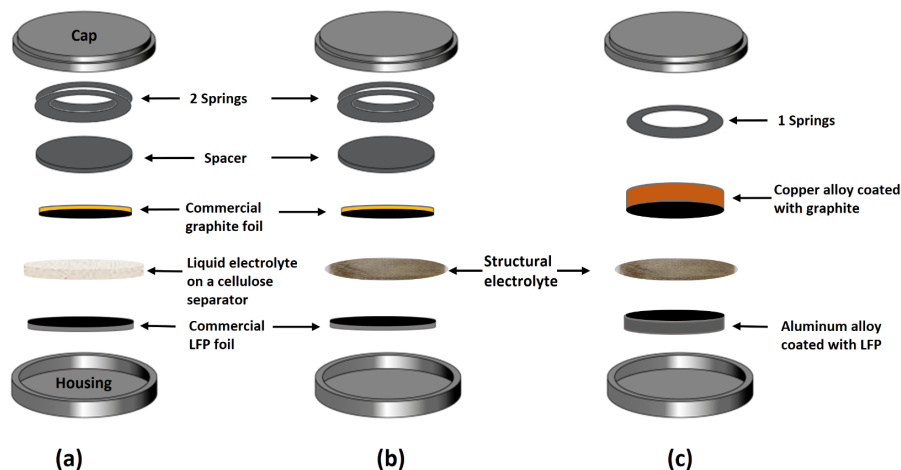


Figure 9.5: Different coin cell configurations: (a) Commercial electrodes with liquid-state electrolyte; (b) Commercial electrodes with structural electrolyte; (c) Aluminum alloy coated with LFP electrode paired with copper alloy coated with graphite and structural electrolyte.

9.2.2.6 Electrochemical tests

Electrochemical impedance measurements were performed using a Biologic VMP-300 potentiostat. Nyquist plots were obtained through AC impedance spectroscopy, and the resulting data were analyzed using EC-Lab V11.52 software. All impedance spectra were recorded between the working/sense electrode (cathode) and the counter/reference electrode (anode). PEIS tests were carried out with a 10 mV amplitude relative to the Electrochemical Open Circuit Voltage (EOC), over a frequency range of 7 MHz to 1 Hz.

Charge/discharge cycle tests were carried out using a Neware CT-4008Tn-5V20mA-164 battery cycler (Neware, Shenzhen, China). Each cycle consisted of constant current–constant voltage (CCCV) charging, followed by a one-minute rest, constant voltage (CV) discharging, and a second rest period. For the cells with commercial electrodes, the upper and lower cutoff voltages were set to 4.2 V and 2.2 V, respectively, in accordance with the literature (Lee and Park (2024)). For cells employing custom-made electrodes, including structural battery configurations, the cutoff voltage was determined based on the electrochemical behavior of the cell. Accordingly, the applied charge and discharge currents were calculated using the amount of cathode material and cathode capacity, and the designated C-rates. These currents were then applied to the system, while the corresponding voltage was continuously recorded.

All manufacturing and testing procedures were carried out at room temperature (18–22 °C). After the QSI tests, Nyquist plots obtained from PEIS measurements of the structural batteries were analyzed and compared to the pre indentation-tests data to evaluate the effect of indentation on internal resistance and to determine whether a short circuit had occurred.

9.3 Results and discussion

9.3.1 Quasi-static indentation results

The results of the quasi-static indentation tests—including load-displacement responses and CT-scan images—for different configurations are presented in Figures 9.6, 9.7, and 9.8. To evaluate how indentation affects these systems progressively, multiple indentation levels were tested. Specifically, four indentation levels were applied on the Al-side (0.75 mm, 1.2 mm, 1.55 mm, and 2.6 mm), while five levels were tested on the Cu-side and the all-GFRP samples (0.6 mm, 0.75 mm, 1.2 mm, 1.55 mm, and 2.6 mm). The additional 0.6 mm indentation level on the Cu-side and all-GFRP configurations was included to account for the thinner GFRP layer on the Cu-side compared to the Al-side in both hybrid configurations. These matching indentation levels across different configurations were used to enable comparison of the mechanical response and damage evolution under similar loading conditions.

The load–displacement responses shown in Figures 9.6 (a), 9.6 (c), 9.7 (a), and 9.7 (c) indicate that, across all indentation levels, the maximum load values are relatively similar between the Al-side and Cu-side for both the structural battery and hybrid laminate configurations. This suggests a symmetric mechanical response of the laminates regardless of the loading side. However, across all corresponding displacement levels, the hybrid laminates exhibit higher maximum loads compared to their structural battery counterparts. For example, at an indentation displacement of 1.55 mm, the hybrid laminate exhibits a reaction force of approximately 23 kN, whereas the structural battery reaches about 17 kN. Additionally, the load–displacement curves remain smooth and continuous up to around 1.55 mm of indentation for all configurations, showing no sudden load drops. This suggests that no immediate or catastrophic damage, such as assembly crushing or delamination, occurs up to that point. However, beyond 1.55 mm, the curves start to show discontinuities or sudden changes in slope, indicating localized failures due to transverse compressive cracking and tearing of the metal layers. In addition, the structural battery exhibits nearly symmetric behavior in terms of load response between Al-side and Cu-side indentations at the maximum displacement. In contrast, the hybrid laminate shows more noticeable variation depending on the loading side. The symmetric load response of the structural battery may be attributed to the damping behavior of the thermoplastic-based structural electrolyte which helps distribute stresses evenly across the laminate. Figure 9.6 (b), Figure 9.6 (d), Figure 9.7 (b), and Figure 9.7 (d) show the CT-scan images of the structural batteries and hybrid laminates at various indentation levels, used to evaluate internal damage evolution. It is worth noting that acquiring CT-scan images for these multilayer configurations was challenging due to the presence of materials with varying densities and X-ray absorption characteristics. The grayscale contrast in the images helps distinguish between individual layers—such as GFRP, aluminum, and copper—as well as identify different damage mechanisms. Typically, darker regions indicate lower-density materials, which could correspond to air gaps (e.g., delamination or cracks) or the structural electrolyte in the case of the structural battery configurations. The first CT images (at $\delta = 0$ mm in Figures 9.6 (b) and 9.7 (b)) serve as references, showing the undamaged structure prior to indentation. As indentation increases,

evidence of metal yielding, delamination, and fiber failure becomes more apparent. Among the different materials, copper—having the highest density—appears brightest in the CT images, particularly when plastically deformed. Aluminum appears slightly less bright, while lower-density layers such as GFRP and the structural electrolyte appear darker. Figure 9.6 (b) shows the structural battery at $\delta = 0$ mm, where the internal dark layer corresponds to the structural electrolyte, which had the lowest density (0.02 g/cm^3 (see Chapter 8 (Niazi et al. (2025a))). At $\delta = 0.75$ mm (Al-side indentation), both metal layers begin to yield, with the structural electrolyte still visible between them. At $\delta = 1.2$ mm, delamination between the top GFRP and aluminum layer becomes visible, likely due to GFRP relaxation. When indentation increases to $\delta = 1.55$ mm, the top GFRP layer breaks, and copper shows increased yielding, evidenced by higher brightness. At the maximum indentation level ($\delta = 2.6$ mm), the top GFRP, aluminum current collector, and internal layers—including cathode, structural electrolyte, and anode—are all visibly damaged, with copper yielding more significantly across its width. Figure 9.6 (d) shows indentation from the opposite side (Cu-side). Delamination begins at $\delta = 0.75$ mm, and although deformation continues with higher displacements, copper does not tear even at $\delta = 2.6$ mm. This contrasts with the Al-side, where aluminum tears at $\delta = 1.55$ mm. This behavior can be attributed to copper's higher stiffness and thickness compared to aluminum. As a result, when indentation is applied from the Cu-side, structural batteries exhibit less tearing and fiber breakage in the layers beneath copper, suggesting that copper provides a degree of protection to the underlying layers.

Figures 9.7 (b) and 9.7 (d) show the CT-scans of the hybrid laminate. In both Al-side and Cu-side indentations, delamination between copper and the internal GFRP layer is the most prominent, possibly due to the high stiffness of copper and post-indentation relaxation of the laminate. Similar to the structural battery results, the hybrid laminate samples indented from the Cu-side show less fiber breakage in the layers beneath copper. In contrast, Al-side indentation leads to aluminum tearing at $\delta = 1.55$ mm.

The QSI results for the all-GFRP configuration at various indentation displacements are presented in Figure 9.8. As shown in Figure 9.8 (a), the load-displacement response indicates that the maximum loads for each indentation level were slightly higher than those observed for the structural battery, but lower than those of the hybrid laminates. Up to an indentation displacement of 1.55 mm, the load response remained smooth and continuous, suggesting the absence of significant damage or sudden failure. However, at δ of 1.8 mm, a distinct load drop is observed, indicating the onset of major damage.

It is worth noting that the nonlinear load-displacement curves observed in the QSI tests are attributed to the use of a rigidly backed support. With each incremental increase in indentation, the underlying material becomes progressively densified and more resistant to further indentation. This results in increased local stiffness beneath the indenter and a corresponding reduction in the displacement rate under load, leading to a curved load-displacement trend.

Figure 9.8 (b) presents CT-scan images of the all-GFRP samples under varying indentation displacements. As the indentation displacement increases, a progressive densification of the laminate is observed beneath the indenter. This is evident from the increasingly brighter regions in the CT

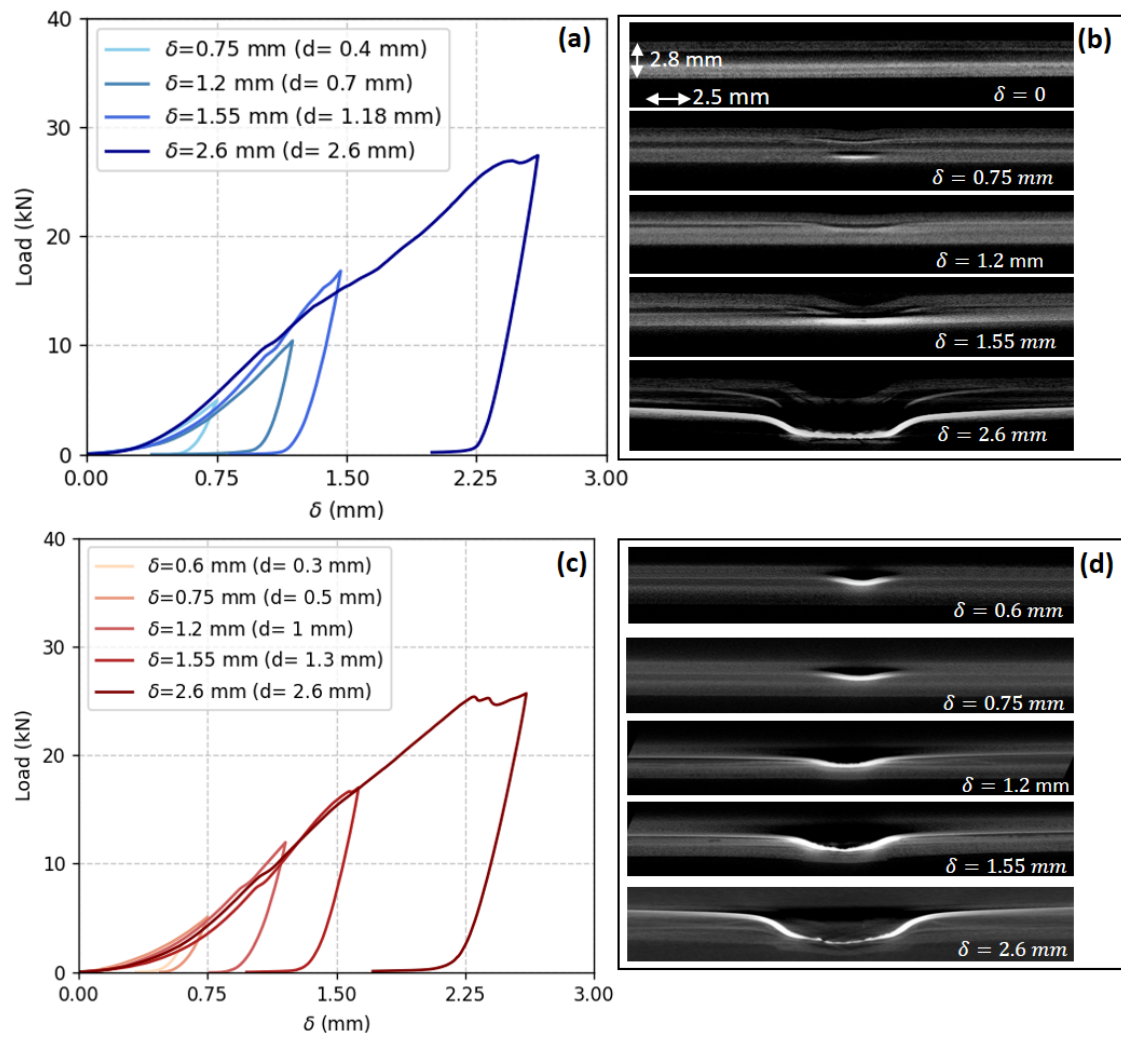


Figure 9.6: QSI results of the structural battery under different indentation levels: (a) Load-displacement results on Al-side; (b) CT-scans images on Al-side; (c) Load-displacement results on Cu-side; (d) CT-scans images on Cu-side.

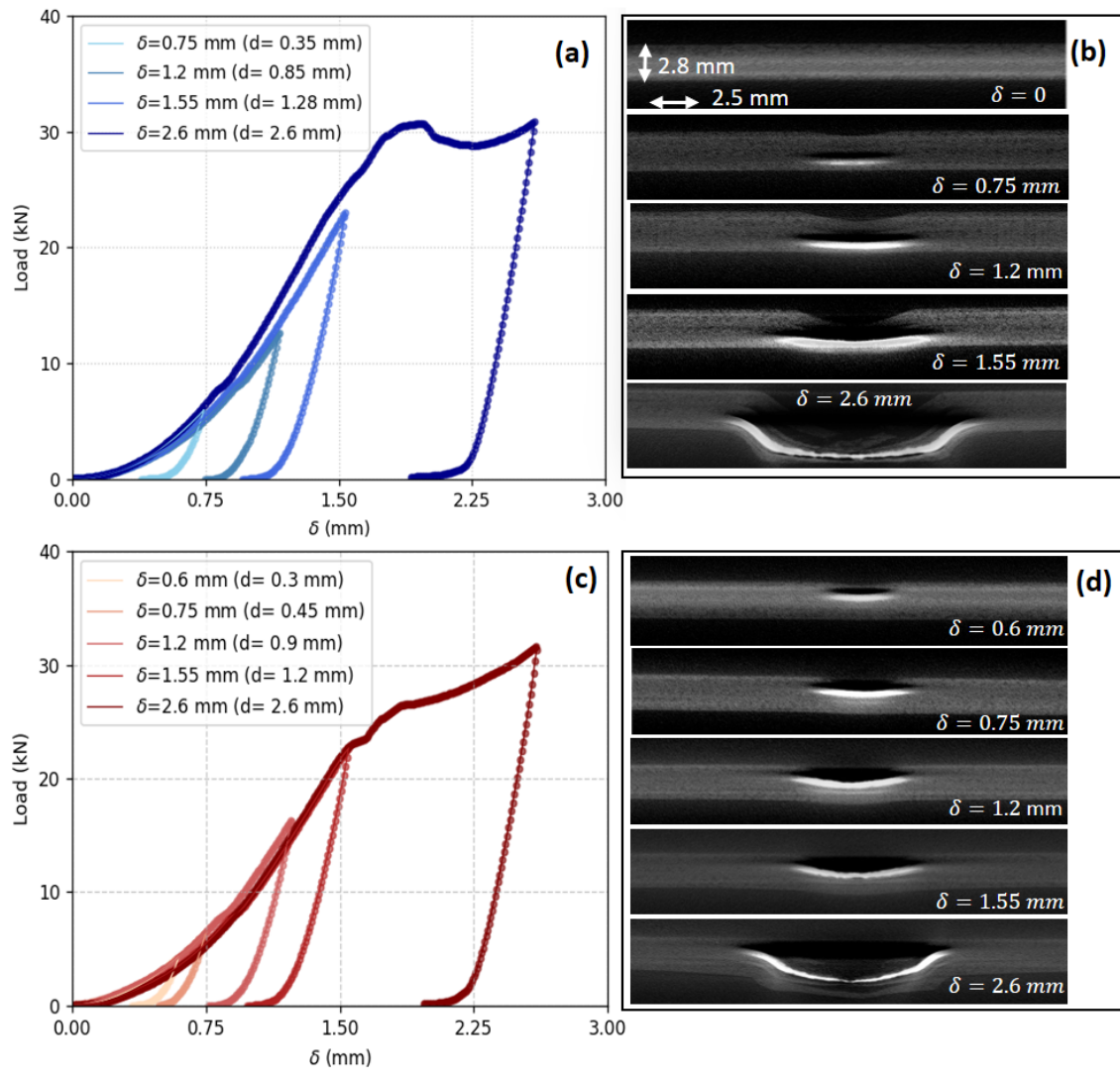


Figure 9.7: QSI results of equivalent hybrid laminate under different indentation levels: (a) Load-displacement results on Al-side; (b) CT-scans images on Al-side; (c) Load-displacement results on Cu-side; (d) CT-scans images on Cu-side.

images, which indicate higher material density due to localized compression. Up to an indentation of $\delta = 1.55$ mm, the compression remains distributed without severe internal damage. However, at $\delta = 2.6$ mm, fiber breakage and damage become visible on the bottom side of the laminate. No signs of delamination are apparent, likely due to the quasi-isotropic architecture of the thin-ply GFRP laminate, which enhances interlaminar fracture resistance (Balaga et al. (2025); Sebaey and Mahdi (2016)).

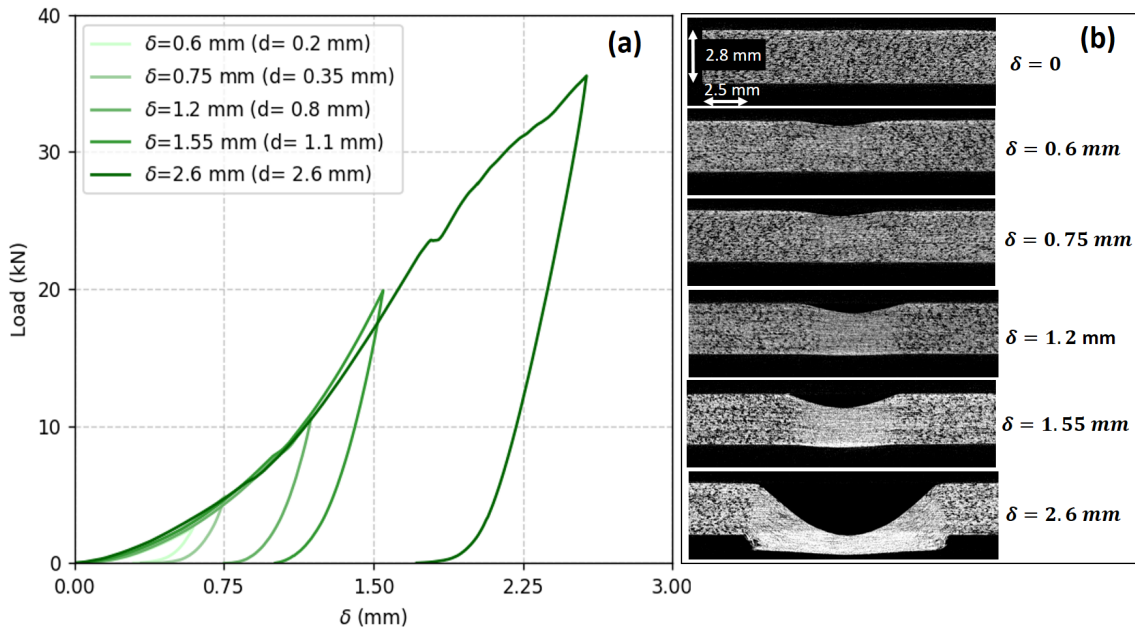


Figure 9.8: The QSI results of all-GFRP $[0^\circ/45^\circ/90^\circ/-45^\circ]_{14S}$ under varying indentation levels: (a) Load-displacement; (b) CT-scans images.

Figure 9.9 presents top-view images of various configurations after indentation. These include structural batteries indented from the Al-side (top row in Figure 9.9 (a)) and from the Cu-side (bottom row in Figure 9.9 (a)); hybrid laminates indented from the Al-side (top row in Figure 9.9 (b)) and Cu-side (bottom row in Figure 9.9 (b)); and all-GFRP samples (Figure 9.9 (c)). Images are shown at two indentation displacements, $\delta = 1.55$ mm and $\delta = 2.6$ mm, as the most severe damage occurred within this range. Although the CT-scan images did not completely capture delamination between layers—due to the limitation with multi-material densities—some delamination can be observed in Figure 9.9.

In the structural battery configuration (Figure 9.9 (a)), concentric delamination is visible around the indentation center: between the first GFRP layer and the aluminum layer when indented from the Al-side, and between the first GFRP and the copper layer when indented from the Cu-side. The delaminated area on the Al-side is approximately 1.5 times larger than that on the Cu-side.

Figure 9.9 (b) shows eccentric delamination around the indentation center in the hybrid laminate configuration. Delamination occurs between the first GFRP layer and the aluminum layer when indented from the Al-side, and between the first GFRP and the copper layer when indented from the Cu-side. At $\delta = 2.6$ mm, the delamination on the Al-side is significantly larger—about three

times—than that on the Cu-side.

Figure 9.9 (c) shows the all-GFRP samples under $\delta = 1.55$ mm and $\delta = 2.6$ mm indentation. While damage is visible at both levels, no delamination can be observed from these views.

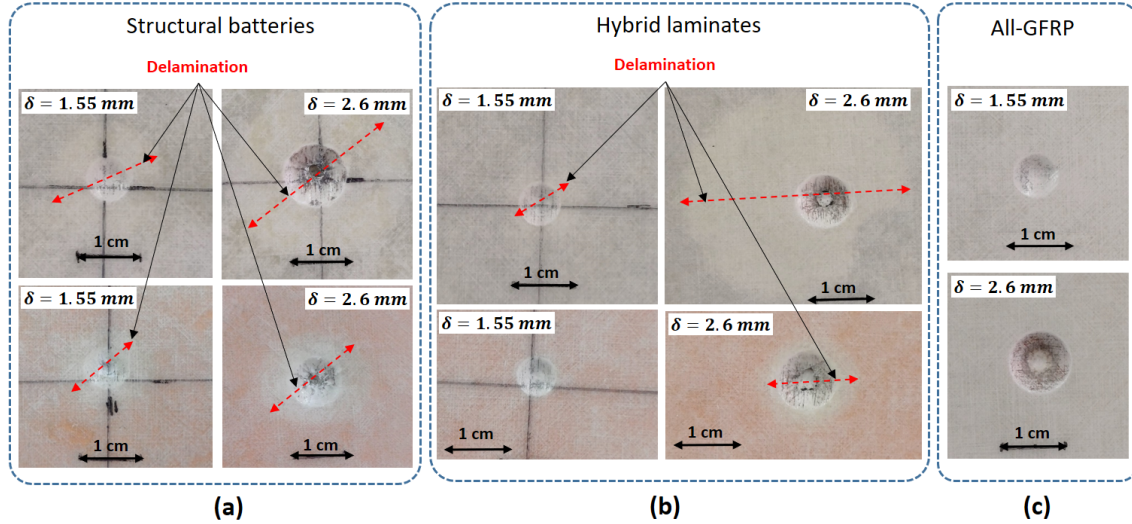


Figure 9.9: Top views of the different configurations with indentations of $\delta = 1.55$ mm and $\delta = 2.6$ mm: (a) Structural batteries (top = Al-side; bottom = Cu-side); (b) Hybrid laminate (top = Al-side; bottom = Cu-side); (c) All-GFRP.

The overall results for the three configurations—structural battery, hybrid laminate, and all-GFRP laminate—are summarized in Table 9.3. The table includes the following parameters for each indentation displacement (δ): dent depth measured after the test (d_1), dent depth measured seven days after the test, total energy up to the maximum load (E_T), and absorbed energy (E_A) up to the maximum load. The total energy was calculated as the area under the load-displacement curve during the loading phase of each indentation cycle. The inelastic (absorbed) energy, which represents the energy dissipated during a complete loading-unloading cycle, was determined as the area bounded between the loading and unloading curves for each indentation displacement. The indentation displacements (δ) were recorded from the point of initial contact, with a preload of 15–20 N applied to ensure proper contact between the indenter and the specimens. The dent depths measured after the test (d_1) in all tested configurations were consistently lower than the corresponding indentation displacements (δ). This reduction is attributed to the elastic recovery and relaxation behavior of the materials. Furthermore, the dent depths measured seven days after testing (d_7) were slightly lower than those recorded immediately after the test (d_1). This reduction is attributed to time-dependent relaxation or viscoelastic recovery of the materials. Notably, at an indentation displacement of 2.6 mm, the final dent depth was nearly equal to the applied displacement, and no significant recovery was observed even after seven days. This indicates that at this level, the deformation became fully plastic and permanent.

The results corresponding to the main failure events—including the indentation displacement at failure (δ_f), the load at the failure point (F_f), the total energy at failure (E_T), and the absorbed energy (E_A)—for all configurations are presented in Table 9.4. The results show that the hybrid

Table 9.3: Quasi-static indentation results of structural battery, hybrid laminate, and all-GFRP configurations.

Configuration	Ind. side	δ (mm)	d_1 (mm)	d_7 (mm)	E_T (J)	E_A (J)	E_A/E_T (%)
-	-						
Structural battery	Al-side	0.75	0.4	0.35	1.22	0.84	69.1
		1.2	0.7	0.6	3.94	3.05	77.3
		1.55	1.18	0.95	8.45	6.38	75.5
		2.6	2.6	2.6	33.74	29.51	87.5
	Cu-side	0.6	0.3	0.25	0.49	0.34	67.8
		0.75	0.5	0.3	1.37	0.96	69.6
		1.2	1	0.85	4.91	3.57	72.7
		1.55	1.3	1.1	10	7.86	78.5
		2.6	2.6	2.6	32.34	27.64	85.5
Hybrid laminate	Al-side	0.75	0.35	0.25	1.46	0.97	66.5
		1.2	0.85	0.65	4.91	3.41	69.4
		1.55	1.28	1.1	11.97	8.13	67.9
		2.6	2.6	2.6	44.75	39.41	88.1
	Cu-side	0.6	0.3	0.25	0.9	0.61	67.3
		0.75	0.45	0.42	1.75	1.22	69.7
		1.2	0.9	0.8	7.02	4.82	68.6
		1.55	1.2	1.1	12.04	8.33	69.2
		2.6	2.6	2.6	41.04	35.47	86.4
All-GFRP	–	0.6	0.2	0.1	0.52	0.32	62.4
		0.75	0.35	0.27	1.27	0.85	66.5
		1.2	0.8	0.61	4.21	2.97	70.4
		1.55	1.1	0.95	9.96	6.64	66.7
		2.6	2.6	2.6	38	29.13	76.6

laminate indented from the Cu-side experienced its main failure at an indentation displacement of 1.56 mm, with a corresponding load of 22.7 kN. Subsequently, the all-GFRP configuration failed at an indentation displacement of 1.8 mm, reaching a peak load of 23.6 kN at failure point. The hybrid laminate indented from the Al-side failed at a displacement of 1.96 mm and exhibited the highest load response among all configurations—30.8 kN. Interestingly, the structural battery configurations demonstrated delayed failure compared to the other setups. The specimen indented from the Al-side failed at 2.45 mm with a loading response of 27 kN, while the one indented from the Cu-side failed at approximately 2.3 mm with a loading response of 25.4 kN. These results shows very similar failure behavior in terms of both indentation displacement and load response, indicating a nearly symmetric mechanical performance of the designed structural battery under quasi-static indentation testing. The total energy and absorbed energy of different configurations are shown in Figure 9.10. The main failure of each configuration is also marked with an 'x' to better visualize the failure point of each configuration. From an energy point of view, structural batteries show the highest total energy and absorbed energy at failure compared to other configurations. This behavior may be attributed to the use of a thermoplastic-based matrix in the structural electrolyte. Thermoplastics generally exhibit higher damping capacity than thermosets and metals,

which can contribute to improved energy dissipation during impact or indentation. Additionally, positioning this thermoplastic-based layer in the core region may enhance through-thickness deformation resistance and delay damage propagation under indentation loading (Liu et al. (2020c); Kayaaslan et al. (2022)).

Table 9.4: Quasi-static indentation results for failure point of different configurations.

Configuration	Ind. side	δ_f (mm)	F_f (kN)	E_T (J)	E_A (J)	E_A/E_T (%)
Structural battery	Al-side	2.45	27	29.71	25.6	86.2
	Cu-side	2.30	25.4	25.8	21.10	81.8
Hybrid laminate	Al-side	1.96	30.7	26.45	21.11	79.8
	Cu-side	1.56	22.8	12.6	9.23	73.2
All-GFRP	-	1.8	23.6	14.74	10.1	68.4

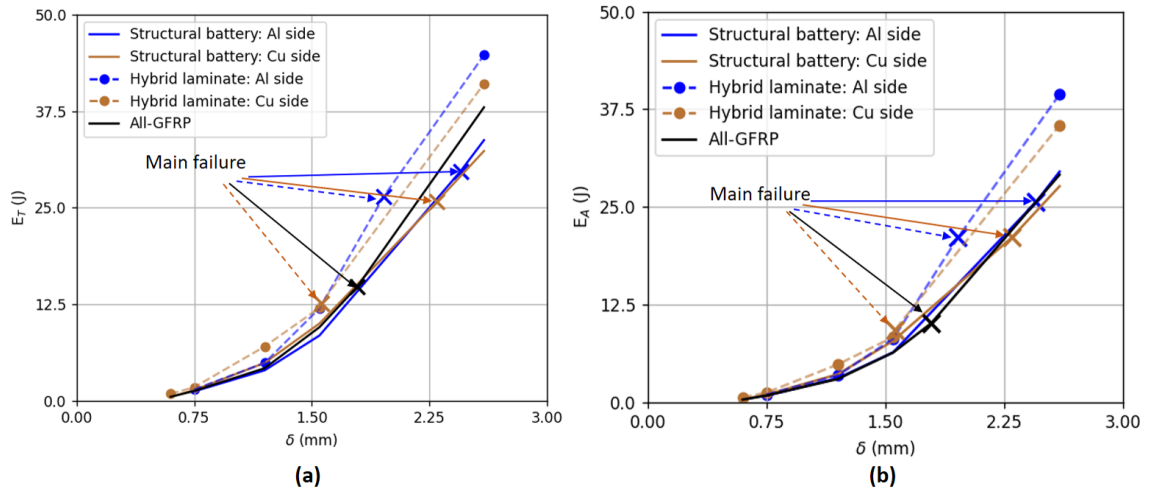


Figure 9.10: (a) Total energy; (b) Absorbed energy for different configurations under varying indenting displacements.

9.3.2 Electrochemical results

Figure 9.11 presents the Nyquist plots obtained from the PEIS tests for various configurations, including three types of coin cells and the structural battery. To enable direct comparison across configurations, the Nyquist plot of the structural battery was normalized to coin cell size by scaling the impedance (both axes) according to the ratio of the sample's area to that of the coin cell active components area. Additionally, each plot includes the equivalent circuit model-shown in the corresponding subfigure- used to analyze the impedance data, adapted from (Vadhva et al. (2021)).

Figure 9.11 (a) shows the Nyquist plot of the coin cell with liquid electrolyte and commercial LFP/graphite electrodes. The plot indicates a bulk resistance (R_b) of 16Ω and a single semicircle corresponding to the solid electrolyte interphase resistance (R_{SEI}), which was found to be 50Ω ,

resulting in a total resistance of 63 Ω . The ionic conductivity for this configuration, calculated using Equation 9.1, was 3×10^{-4} S/cm.

$$\sigma = \frac{t}{A \cdot R_t}, \quad (9.1)$$

where A is the contact area between the electrode and the electrolyte, t is the thickness of the separator or structural electrolyte, and R_t is the total resistance of the cell.

Figure 9.11 (b) shows the Nyquist plot of the coin cell with commercial electrodes and a structural electrolyte. The cell exhibited a bulk resistance of 54 Ω and two distinct semicircles: the high-frequency semicircle corresponds to the resistance of the solid electrolyte interphase layer (R_{SEI}), measured at 164 Ω , while the mid-frequency semicircle represents the charge-transfer resistance (R_{ct}) at the electrode–electrolyte interface, which was found to be 163 Ω . The total resistance was approximately 381 Ω . The ionic conductivity for this configuration was calculated to be 5×10^{-5} S/cm.

Figure 9.11 (c) shows the Nyquist plot of the coin cell with custom-made electrodes—LFP coated on an aluminum alloy and graphite on a copper alloy—paired with a structural electrolyte, simulating the electrochemically active part of the structural battery in a coin cell configuration. As shown in the figure, this configuration exhibits lower resistance compared to the other solid-state tested setups, due to the excellent contact between the active components. It had a bulk resistance of 40 Ω , a solid electrolyte interphase resistance of 32 Ω , and a charge-transfer resistance of 40 Ω , resulting in a total resistance of 112 Ω . The ionic conductivity was calculated to be 1.7×10^{-4} S/cm.

Figure 9.11 (d) shows the Nyquist plot of the structural battery. This configuration exhibited a bulk resistance of 25 Ω , SEI resistance of 62 Ω , and charge-transfer resistance of 215 Ω , resulting in a total resistance of 302 Ω . Using Equation 9.1, the ionic conductivity of the structural battery was calculated to be 6.5×10^{-5} S/cm. In general, the ionic conductivity results highlight that the coin cell with liquid electrolyte exhibited the highest ionic conductivity (3×10^{-4} S/cm). Among the solid-state configurations, the coin cell with custom electrodes and structural electrolyte demonstrated improved performance (1.7×10^{-4} S/cm) compared to the configuration with commercial electrodes, due to interface improvement during fabrication. The structural battery showed moderate ionic conductivity, lower than its coin cell counterpart.

Figure 9.12 shows the voltage–capacity density plots (Figures 9.12 (a) and 9.12 (c)), and the charge/discharge capacity density and coulombic efficiency versus cycle number (Figures 9.12 (b) and 9.12 (d)) for two coin cell configurations: one with commercial electrodes and liquid electrolyte, and the other with commercial electrodes and structural electrolyte. The results indicate that the cell with liquid electrolyte exhibited an initial charge capacity density of 175 mAh/g and a discharge capacity density of 100 mAh/g at a current rate of 0.02C. However, both the charge and discharge capacities declined progressively with further cycling. By the 10th cycle, as shown in Figure 9.12 (b), the cell's performance had significantly deteriorated, with both capacities approaching zero.

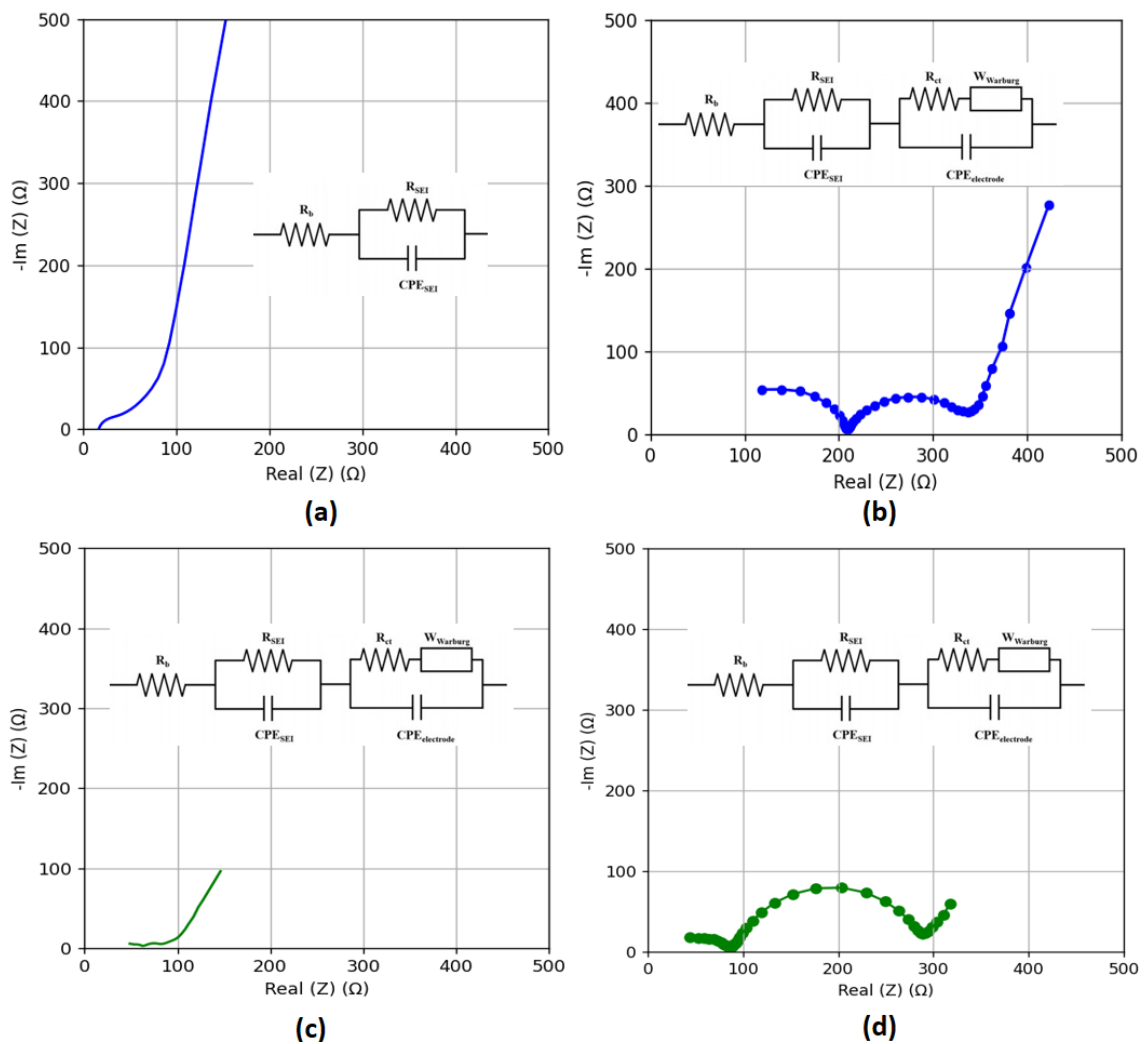


Figure 9.11: Nyquist plots of different configurations: (a) Coin cell with commercial electrodes and liquid electrolyte; (b) Coin cell with commercial electrodes and structural electrolyte; (c) Coin cell with custom-made electrodes and structural electrolyte; (d) Structural battery (normalized to coin cell dimensions).

Figures 9.12 (c) and 9.12 (d) present the electrochemical behavior of the coin cell with commercial electrodes paired with the structural electrolyte. Compared to the liquid-state configuration, this cell completed only 8 cycles. In the first cycle, the charge capacity reached 130 mAh/g, while the discharge capacity was limited to 30 mAh/g. Both capacities decreased rapidly in subsequent cycles, and the cell was fully degraded by the 8th cycle.

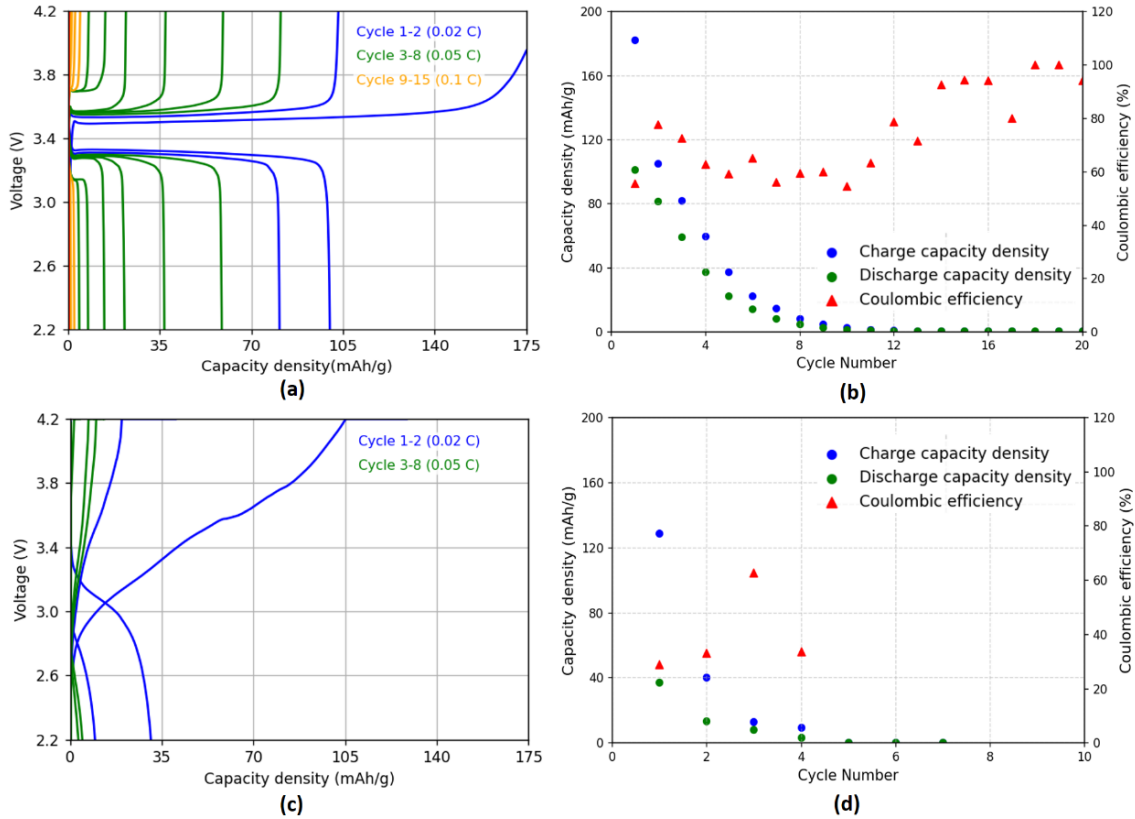


Figure 9.12: Electrochemical performance of coin cells with commercial electrodes: (a, b) liquid electrolyte; (c, d) structural electrolyte (normalized to coin cell dimensions).

The electrochemical results for the coin cell incorporating the central active components of the structural battery (aluminum alloy coated with LFP, structural electrolyte, and copper alloy coated with graphite) are shown in Figures 9.13. Figure 9.13 (a) displays the voltage versus capacity density over 550 cycles. The battery was tested under various current rates: two cycles at 0.02C, six cycles at 0.05C, six cycles at 0.1C, ten cycles at 0.2C, ten cycles at 0.5C, and ten cycles at 1C. Subsequently, it was tested at 0.1C for six cycles, followed by long-term cycling at 1C for approximately 500 cycles. This return from 1C to 0.1C, and then back to 1C, was performed to evaluate the reversibility of the electrochemical behavior and to assess whether the cell could recover its capacity after prolonged high-rate cycling. The cutoff voltage was determined based on the electrochemical behavior of the cell. Accordingly, the calculated C-rate current was applied during charge and discharge, while the corresponding voltage was continuously recorded based on the cell behavior. The results show that the battery exhibited repeatable behavior at various charge/discharge rates. The capacity density of both charge and discharge decreased with increas-

ing current rate, as expected for solid state batteries.

The Coulombic efficiency was calculated as the ratio of discharge capacity density to the charge capacity density for each cycle (Xiao et al. (2020); Yao et al. (2021)) and is shown in Figure 9.13 (b). It fluctuated around 100%, indicating high electrochemical reversibility during cycling.

The electrochemical performance of the full structural battery without a moisture-protective coating is presented in Figures 9.13 (c) and 9.13 (d). The battery followed the same sequence of charge/discharge testing as the coin cell configuration, although a fewer number of cycles were completed. Similar to their coin-cell counterparts, the cutoff voltage was determined based on the electrochemical behavior of the cell, which was measured between 0 and 2 V. Figure 9.13 (c) shows the voltage versus capacity density, with the battery charged and discharged between 0 and 2 V. Figure 9.13 (d) presents the charge and discharge capacity densities along with the Coulombic efficiency. For most cycles, the charge and discharge capacity densities were closely matched, resulting in a Coulombic efficiency of approximately 100%. At a rate of 0.02 C, the first charge cycle yielded a capacity density of 160 mAh/g, while the corresponding discharge capacity density was 82 mAh/g. In the second cycle, the charge capacity density dropped to around 120 mAh/g, while the discharge capacity increased to 104 mAh/g. The next six cycles were performed at a 0.05 C rate. In the first cycle at this rate, the charge and discharge capacity densities were 157 mAh/g and 110 mAh/g, respectively. Both values decreased over subsequent cycles, reaching 98 mAh/g (charge) and 95 mAh/g (discharge) by the eighth cycle. The cycling then continued at a 0.1 C rate for six additional cycles. During this stage, the charge capacity density decreased from 95 mAh/g to 75 mAh/g, while the discharge capacity density dropped from 85 mAh/g to 64 mAh/g. Subsequently, 10 cycles were conducted at a 0.2 C rate. The charge capacity density declined from 65 mAh/g to 30 mAh/g by the 24th cycle (10th at this rate), while the discharge capacity density decreased from 62 mAh/g to 24 mAh/g. Finally, the cell was tested at a 0.5 C rate for another 10 cycles. The charge capacity density dropped from 24 mAh/g to 6 mAh/g, and the discharge capacity density decreased from 26 mAh/g to 6 mAh/g.

Figure 9.14(a) shows the voltage versus capacity density of the full structural battery with a moisture-protective coating on the GFRP skin. At low current rates of 0.02C and 0.05C, the battery exhibited charge capacities of approximately 140 mAh/g and discharge capacities of about 110 mAh/g. At 0.1C, the charge capacity was around 70 mAh/g in the first cycle and decreased to 37 mAh/g after six cycles, while the discharge capacity dropped from approximately 55 mAh/g to 33 mAh/g over the same period. When the rate increased to 0.2C, both charge and discharge capacities decreased to around 30 mAh/g. Further increases in current rate to 0.5C and 1C resulted in progressive reductions in capacity, with charge and discharge values of approximately 20 mAh/g and 22 mAh/g, respectively. To assess reversibility, the cell was re-evaluated at 0.1C, where it delivered charge and discharge capacities of about 37 mAh/g and 33 mAh/g, respectively—values closely matching the earlier 0.1C results. This consistency indicates good electrochemical reversibility of the cell. Afterward, the cell was tested for extended cycling at 1C up to 550 cycles. Figure 9.14(b) presents the charge and discharge capacity profiles along with the Coulombic efficiency versus cycle number of the structural battery with protective moisture-protective coating,

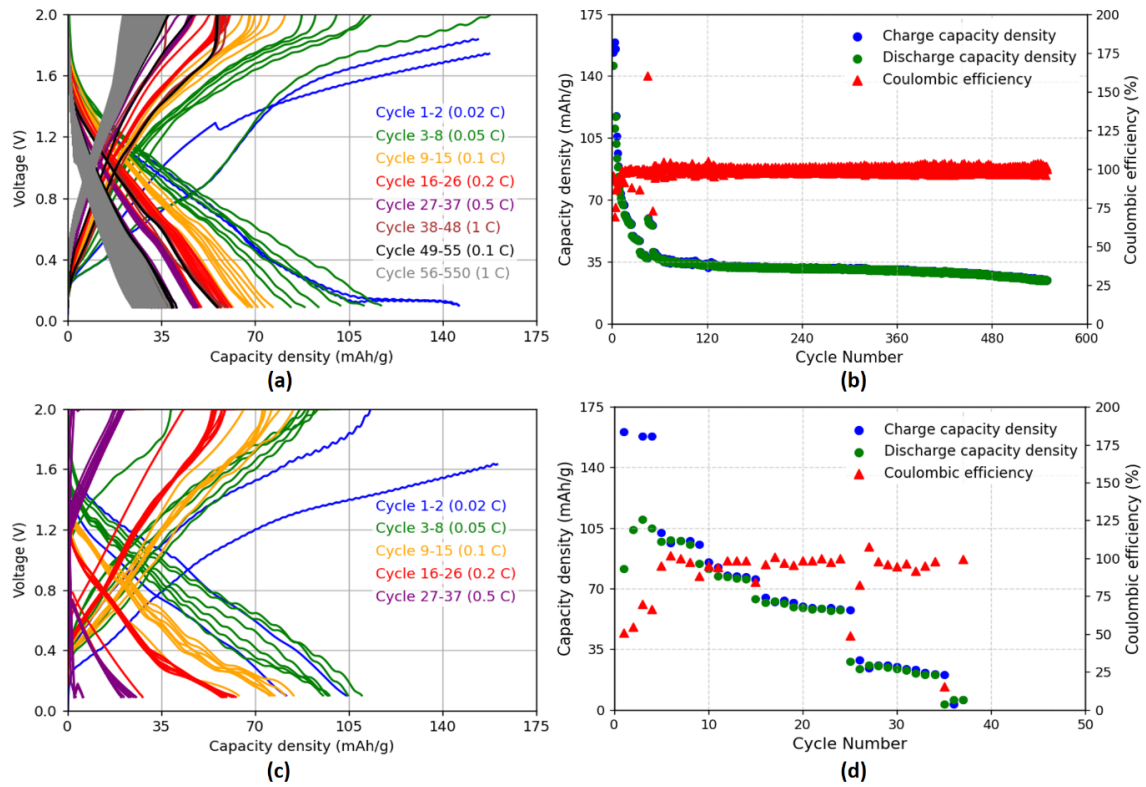


Figure 9.13: Electrochemical performance: (a,b) coin cell with central active components of the structural battery; (c,d) Full structural battery.

showing the long-term cycling performance at 1C for about 500 cycles (495 cycles). The charge and discharge capacities remained consistently close throughout the test, demonstrating excellent cycling stability. Overall, the results confirm that the structural battery exhibits stable and repeatable behavior across different charge/discharge rates. As expected for solid-state batteries, capacity decreased with increasing current rate. The Coulombic efficiency remained around 93% during cycling at 1C, indicating high electrochemical reversibility of the cell.

A comparison between the structural battery configuration shown in Figure 9.13 (without moisture-protective coating) and that shown in Figure 9.14 (with moisture-protective coating) highlights the positive effect of using the protective coating on battery performance. The first configuration, without the coating, cycled only 37 times and degraded quickly due to exposure to moisture. In contrast, with the moisture-protective coating, the battery cycled approximately 550 times and was still capable of continued operation.

9.3.3 Post-indentation and system multifunctionality

The Nyquist plots obtained from PEIS tests of the structural batteries before and after the QSI tests are shown in Figure 9.15. Figure 9.15 (a) presents the Nyquist plots for samples indented from the Al side. The results show that at a displacement (δ) of 1.2 mm, the resistance increased by approximately 1.5 times after indentation. At an indentation depth of 1.55 mm, the resistance de-

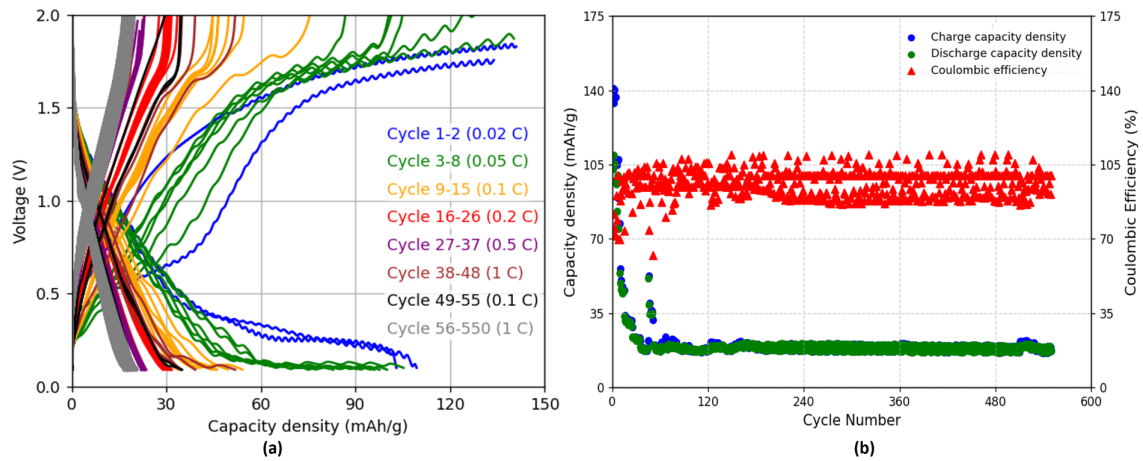


Figure 9.14: Electrochemical performance of the full structural battery with a moisture-protective coating: (a) voltage vs. capacity density; (b) capacity density and Coulombic efficiency vs. cycle number.

creased by about 10 times, while for the maximum indentation of 2.6 mm, the resistance increased around twofold.

Figure 9.15 (b) shows results for those structural batteries indented from the Cu side. The results show that the battery internal resistance increased by about 1.3 times when indented to $\delta = 1.2$ mm. When the indentation displacement reached 1.55 mm, the internal resistance decreased by around 4 times, and when the indentation was 2.6 mm, the resistance increased by about 2 times. These changes in resistance may also be attributed to intrinsic cell behavior over time, such as internal relaxation processes and evolution of the solid electrolyte interphase (SEI) layer, rather than solely to the QSI test. However, the considerable changes observed after the indentation at 1.55 mm suggest that mechanical effects may also contribute to impedance reduction, potentially due to improved contact or reduced distance between electrodes caused by the pressure during the QSI test. These Nyquist plots also confirm that no short circuit occurred inside the batteries after indentation tests, which may be attributed to the use of a structural electrolyte possessing high mechanical strength and robustness.

In Table 9.5, key mechanical properties—including weight (m), volume (V), indentation level at failure (δ_f), absorbed energy at failure (E_A), load at failure (F_f), load density at failure ($\bar{F}_f$), and tensile stiffness density ($\bar{E}$) of the structural battery and equivalent hybrid laminate—are compiled. The table also includes key electrochemical properties such as energy storage capabilities, energy density ($\bar{E}$), power density ($\bar{P}$), charge capacity density ($\bar{Q}_{Ch}$), discharge capacity density ($\bar{Q}_{Dch}$), and coulombic efficiency (CE) from the first cycle at a 0.02C rate for both the structural battery and the reference coin cell.

The structural battery designed for the QSI tests had the same dimensions—and thus the same volume—as the hybrid laminate. Nevertheless, it was lighter, with an average mass of 165 g compared to 176 g for the hybrid laminate. This result highlights the structural battery's ability to achieve multifunctionality while improving weight efficiency.

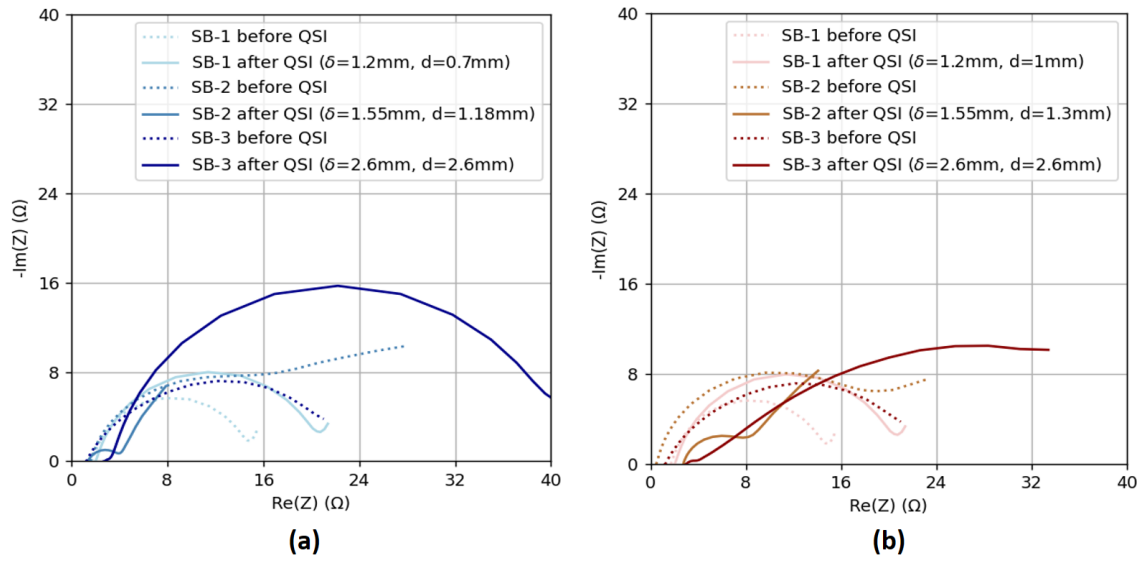


Figure 9.15: Nyquist plots of structural batteries before and after QSI tests: (a) Batteries indented from the Al-side; (b) Batteries indented from the Cu-side.

Mechanically, the main failure in the structural batteries—averaged across both sides—occurred at an indentation displacement of approximately 2.37 mm, absorbing 23.35 J of energy. In contrast, the hybrid laminate failed at a displacement of 1.76 mm and absorbed only 13.67 J. These results indicate that the structural battery failed at a higher displacement and dissipated more energy prior to failure, demonstrating enhanced damage tolerance and energy absorption capacity.

In the final column of Table 9.5, the mechanical properties of the structural battery are normalized by those of the hybrid laminate, while the electrochemical properties are normalized by those of the coin cell. The structural battery outperforms the hybrid laminate in terms of weight savings, delayed failure onset, and stiffness density, resulting in a lighter structure with improved damage resistance. Moreover, as previously noted, the structural battery exhibited symmetric dissipated energy.

In this work the energy density and power density were calculated using the total mass of the cathode. The calculated energy density ($\bar{E}_{SB}$) of the structural battery was 0.086 Wh/g (86 Wh/kg), and the power density ($\bar{P}_{SB}$) was 0.00172 Wh/g (1.72 W/kg). Regarding additional metrics, the structural battery demonstrated a higher cycle life and coulombic efficiency than the reference coin cell. In addition, although the charge capacity density of the structural battery (140 mAh g^{-1}) was lower than that of the reference coin cell (175 mAh g^{-1}), corresponding to approximately 80% of the reference value, the discharge capacity density was 110 mAh g^{-1} , which was higher than that of the coin cell (100 mAh g^{-1}).

9.3.3.1 Multi-functionality efficiency

The multifunctionality of the structural battery was evaluated using the efficiency framework proposed by Snyder et al. and Asp et al. (Snyder et al. (2015); Asp and Greenhalgh (2014)). This

Table 9.5: Summary of properties for different configurations: coin cell, hybrid laminate (HL), and structural battery (SB).

Domain	Metric	Coin Cell(ref)	HL(ref)	SB	SB/ref
Mechanical	m (g)	–	176	165	0.93
	V (cm ³)	–	63	63	1
	δ_f (mm)	–	1.76	2.37	1.34
	E_A (J)	–	13.67	23.35	1.71
	F_f (kN)	–	26.7	26.2	0.98
	$\bar{F}_f$ (kN/g)	–	0.15	0.16	1.07
	$\bar{E}$ (MPa/g)	–	234.66	245.45	1.05
Electrochemical	$\bar{E}_e$ (Wh/g)	0.34	–	0.11	0.32
	$\bar{P}$ (W/g)	6.8×10^{-3}	–	5.5×10^{-3}	0.8
	Cycle life	15	–	550	–
	$\bar{Q}_{Ch}$ (mAh/g)	175	–	140	0.8
	$\bar{Q}_{Dch}$ (mAh/g)	100	–	110	1.1
	CE (%)	57	–	93	1.63

framework quantifies the ability of a multifunctional system to simultaneously fulfil structural and energy storage functions relative to conventional single-function systems.

The structural efficiency coefficient (η_s) is defined as the ratio of the specific stiffness performance of the structural battery to that of the equivalent hybrid laminate:

$$\eta_s = \frac{\bar{E}_{SB}}{\bar{E}_{HL}}. \quad (9.2)$$

Based on the experimentally measured stiffness of the structural battery and the corresponding stiffness of the equivalent hybrid laminate, a structural efficiency coefficient of $\eta_s = 1.05$ was obtained, indicating structural over-performance relative to the reference material.

The energy efficiency coefficient (η_b) is defined as the ratio of the energy density of the structural battery to that of a coin cell reference, resulting in a value of $\eta_b = 0.32$.

$$\eta_b = \frac{\bar{E}_{e,SB}}{\bar{E}_{Battery}} \quad (9.3)$$

The overall multifunctional efficiency (η_{mf}) is defined as the sum of the structural and energy efficiency coefficients:

$$\eta_{mf} = \eta_s + \eta_b. \quad (9.4)$$

Substituting the obtained values yields

$$\eta_{mf} = 1.05 + 0.32 = 1.37. \quad (9.5)$$

A multifunctional system is considered advantageous when the multifunctional efficiency exceeds unity, i.e.,

$$\eta_{mf} > 1. \quad (9.6)$$

Since $\eta_{mf} = 1.37$, the developed structural battery satisfies the criterion for multifunctional-

ity, demonstrating that the combined structural and energy storage functions are delivered more efficiently than in an equivalent system composed of separate conventional materials.

9.3.3.2 Total mass and weight saving

Using calculated efficiency coefficients, the equivalent total mass of a conventional structure–battery system providing the same combined structural and energy storage functions as the structural battery was calculated as:

$$m_{\text{tot}} = m_{HL} + (1 - \eta_s) \frac{m_b}{\eta_b}, \quad (9.7)$$

where $m_{SB} = 165$ g is the physical mass of the structural battery and $m_{HL} = 176$ g is the mass of the equivalent hybrid laminate. The reference battery mass (m_b) was obtained by scaling the mass of a conventional coin cell using the ratio of the active material area of the structural battery (225 cm²) to that of the coin cell, resulting in $m_b = 215$ g.

The system-level weight saving is calculated using the following equation:

$$\text{Weight saving (\%)} = (\eta_s + \eta_b - 1) \frac{m_{mf}}{(m_{HL} + m_b)} \times 100 \quad (9.8)$$

$$m_{mf} = \min\left(\frac{m_b}{\eta_b}, \frac{m_{HL}}{\eta_s}\right) \quad (9.9)$$

which results in a 16% weight saving by replacing the structural battery with a conventional battery and an equivalent structure.

9.3.4 Comparison with state-of-the-art structural batteries

The main distinction between the present work and prior structural battery studies lies in the architecture and structural integrity of the system. Table 9.6 compares the present work with several representative studies, highlighting these differences. Building on previous proof-of-concept studies, the current work advances toward an engineering-scale, deployable structural battery designed for practical applications such as vehicle body components.

For example, Hu et al. (Hu et al. (2025)) and Asp et al. (Asp et al. (2021)) rely on laminated films—composed of thermoplastic polymer–metal–thermoplastic polymer composites—or tape to encapsulate the cells. Although these materials are suitable for sealing battery components, they are not true structural elements. Consequently, additional encapsulation or a separate structural shell is required for practical structural use. Other studies (Xu et al. (2022); Siraj et al. (2023)) embed batteries with laminated film covers inside GFRP or CFRP skins. However, epoxy or polyester resins used in these composites cure via crosslinking reactions that do not chemically bond with inert thermoplastic surfaces (Deng et al. (2015); Raos and Zappone (2021)), which can result in poor interfacial bonding and delamination between the laminated film and the skin, as well

as between internal layers such as the current collector and the laminated film, thereby compromising mechanical integrity. In contrast, the present work employs a GFRP skin with engineered thickness inspired by GLARE structures, combined with surface treated alloys and a transparent, moisture-protective coating for enhanced sealing, producing a fully integrated and mechanically robust architecture.

It is also noteworthy that prior studies typically report energy densities normalized by cell weight, which do not accurately reflect the total weight of a fully integrated load-bearing structure. In some cases, it is unclear whether the mass of laminated films or tapes was included. Therefore, the energy and power densities reported in these studies are not directly comparable to those of the present work, which represents a finalized structural architecture suitable for practical applications.

In addition, some previous designs, such as Moyer et al. (Moyer et al. (2020b)), used lithium metal anode, which, despite offering high energy density, pose safety risks in the event of structural fracture or failure. Other studies employ pure aluminum or copper foils as current collectors, which provide limited mechanical performance compared to the robust metallic alloys used in the present work. Specifically, Al2024-T3, inspired by the GLARE configuration used in the Airbus A380 (Hosseini-Toudeshky et al. (2025)), was integrated as the current collector for the cathode, together with Cu110-H02 alloy serving as the current collector for the anode. The structural battery has been tested under indentation loading and subsequently evaluated, demonstrating high damage tolerance and confirming its ability to operate safely under realistic mechanical stresses. Despite demonstrating a fully integrated and mechanically robust structural battery, the present work exhibits a relatively low nominal voltage (1.1 V), which results in a reduced power density compared to higher-voltage systems such as commercial or state-of-the-art cells (around 3.4 V) (Sharma et al. (2022)). Further studies are needed to enhance the electrochemical performance while preserving the structural integrity and high damage tolerance of the composite architecture.

Table 9.6: Comparison of present work with selected structural battery studies.

Property	This work	Hu et al. (2025)	Asp et al. (2021)	Moyer et al. (2020b)
Skin (shell)	GFRP with coating	Thermoplastic film & tape	Laminate film	CFRP
Electrodes	LFP/Graphite	LFP/lithium metal	LFP/CF	LFP/Graphite
Current collectors	Al/Cu alloys	CF/None	Aluminum foil/CF	CF
Damage tol.	High	-	-	-
Tensile modulus (GPa)	40.5	43.8	25	50
Bending stiffness (GPa)	26.4	-	-	-
E_{act} (Wh/kg)	110	96.9	106	-
E_{cell} (Wh/kg)	-	19.8	24	37
Cycle life (-)	550	>100	30	30
Multifunctionality index	1.37	1.59	-	-

9.4 Conclusions

In this chapter, a hybrid structural battery designed for load-bearing energy storage applications was developed and evaluated. The battery featured a GFRP shell bonded to Sol-Gel-treated aluminum and copper alloy current collectors coated with LFP cathode and graphite anode materials.

A structural electrolyte—consisting of a plain-weave glass fiber reinforced with a composite polymer matrix—was used as the core.

Mechanical performance was assessed using quasi-static indentation tests on both sides of the structural batteries, and the results were compared with equivalent hybrid laminate and all-GFRP samples. The structural batteries exhibited lower weight and higher stiffness density, as well as greater damage resistance compared to their hybrid laminate counterparts. They failed at greater indentation displacements and absorbed more energy before failure, indicating improved energy dissipation due to the thermoplastic-based electrolyte at their core. At maximum indentation, delamination in the structural battery was smaller and more concentric, whereas in the hybrid laminate it was larger and more eccentric.

Electrochemically, the structural battery outperformed a reference coin cell with liquid electrolyte in terms of cycle life and Coulombic efficiency, despite exhibiting lower energy density due to its lower nominal voltage. It achieved a Coulombic efficiency of over 90% and a cycle life of 550 when using a moisture-protective coating, whereas the uncoated cell completed only 37 cycles and degraded rapidly.

Post-indentation PEIS data on structural batteries revealed no short circuits and generally lower resistance, attributed to compaction due to indentation testing. The calculated multifunctional efficiency exceeded the critical threshold, confirming that the structural battery delivers net benefits in both structural integrity and energy storage. These results highlight its potential as a lightweight, damage-tolerant solution for multifunctional systems.

Part V

Conclusions and future works

Chapter 10

Conclusions

This thesis has presented the design, development, and thorough characterization of a multifunctional structural battery that integrates mechanical load-bearing capacity with energy storage capabilities. Through a systematic and multidisciplinary approach, the work addressed critical challenges in material selection, interfacial bonding, electrolyte formulation, and full-cell assembly for lightweight structural energy storage solution.

The first part laid a comprehensive theoretical foundation through an extensive literature review, mapping the evolution of structural batteries, key performance metrics of structural batteries, and the multifunctionality of composite polymer electrolytes. This background guided the subsequent experimental work, material selection and methodology.

In the second part, the interfacial bonding between the GFRP shell and metallic current collectors (aluminum and copper) was studied in detail. Surface treatments were shown to play a pivotal role in enhancing Mode I and Mode II interlaminar fracture toughness. Among the various techniques evaluated, Sol-Gel anodizing emerged as the most effective, significantly improving bonding strength and repeatability while maintaining compatibility with the GFRP composite. The application of compressive transverse stress further was shown to increase mode II interlaminar fracture toughness in different joints used in structural batteries.

The third part focused on the development of a multifunctional solid-state electrolyte. By blending thermoplastic polymers (PEO, PVA, PVAc) with a heat-resistance thermoset epoxy using optimized solvents, the best polymer host with enhanced thermomechanical and electrochemical performance was achieved. PVA emerged as the most compatible polymer due to its favorable balance of ionic conductivity and thermal stability when combined with epoxy. The subsequent optimization of lithium salt and alumina nanoparticle content led to the formulation of a composite matrix with high ionic conductivity and superior mechanical properties. Building upon this, a structural electrolyte was fabricated using the optimized matrix reinforced with plain-woven glass fiber. The resulting structural electrolyte exhibited a significant increase in both tensile strength and stiffness while maintaining high ionic conductivity and damping stability across a wide temperature range. Electrochemical testing in half-cell configuration confirmed its suitability for energy storage applications.

In the final part, all components were integrated into a complete hybrid structural battery. Featuring a quasi-isotropic GFRP lay-up, Sol-Gel-treated metallic current collectors, and the developed structural electrolyte, the battery was evaluated through mechanical quasi-static indentation testing and electrochemical charge/discharge and PEIS characterization. The structural battery showed superior properties: it was lighter, had higher stiffness density, and greater damage resistance due to the thermoplastic-based electrolyte core. It withstood larger indentation displacements and absorbed more energy before failure. Delamination was smaller and concentric in the structural battery, while larger and eccentric in the hybrid laminate. Electrochemically, the structural battery outperformed a reference coin cell with liquid electrolyte and commercial electrodes in cycle life and coulombic efficiency, though with slightly lower charge/discharge capacity densities. A coin cell using its active components achieved over 500 stable cycles with near-100% coulombic efficiency, despite capacity decline at higher current rates. Post-indentation PEIS showed no short circuits and generally lower resistance, due to compaction. The calculated multifunctional efficiency exceeded the critical threshold, confirming the structural battery's combined benefits in structural integrity and energy storage, and highlighting its potential for lightweight, damage-tolerant multifunctional systems.

This research demonstrated that the combined advantages of material innovation, interface engineering, and structural design can yield structural batteries with high mechanical durability and effective energy storage performance.

Chapter 11

Future perspectives

- Develop safe disassembly and recycling methods for structural batteries at end-of-life.
- Integrate structural batteries with embedded energy harvesting components (e.g., piezoelectric, photovoltaic) for self-sustaining multifunctional structures.
- Continue exploring thermoset polymers and discover new materials with high temperature resistance and superior thermo-electro-mechanical properties.
- Design polymers with tailored molecular weights to achieve specific mechanical and electrochemical properties.
- Explore novel additives and nanofillers with stimuli-responsive or self-healing properties to enable dynamic adaptation of composite electrolytes.
- Develop multi-objective optimization methods to balance electrochemical and mechanical performance optimally.
- Advance computational methods integrating multiscale modeling and experimental data to improve predictive accuracy.
- Utilize artificial intelligence and machine learning to simplify simulations, integrate computational methods, and accelerate material optimization.
- Develop self-healing materials and AI-driven autonomous optimization to enhance durability and performance through adaptive, self-regulating systems.
- Further refine structural electrolyte matrix compositions and test various nanofillers and salt types/concentrations to enhance ionic conductivity while maintaining or improving mechanical properties.
- Develop and evaluate thermoplastic/thermoset structural electrolyte matrices using alternative methods, especially solvent-free techniques.

- Explore alternative cathode and anode materials compatible with the structural electrolyte to increase energy and power density.
- Develop and test novel surface treatments or hybrid methods (e.g., sol-gel combined with chemical/plasma techniques) to improve metal/composite adhesion and durability.
- Develop electrically conductive treatments to enhance bonding between electrode particles and current collectors.
- Investigate simultaneous cyclic mechanical and electrochemical loading to assess long-term stability and failure modes.
- Develop predictive models coupling electrochemical and mechanical behavior under real-world conditions.
- Incorporate embedded sensors (strain gauges, impedance sensors) for in-situ real-time monitoring of mechanical damage and electrochemical degradation.
- Study the effects of humidity, temperature extremes, and UV exposure on structural battery performance and longevity.
- Extend multifunctionality to include thermal management and structural health monitoring alongside load-bearing and energy storage.

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Appendix A

Additional investigations and lessons learned

This appendix presents additional investigations that, although not directly used in the main content of the thesis, have influenced the overall approach and decision-making process. The lessons learned from these investigations are also discussed.

Aging and corrosion in current collector

Introduction

In the field of structural batteries, selecting an appropriate current collector requires a comprehensive evaluation of multiple factors, including mechanical properties, electrical and thermal performance, aging behavior, and overall stability. While traditional battery technologies commonly use pure metal foils—such as aluminum for cathode current collectors and copper for anode current collectors—due to their excellent electrical, thermal, and electrochemical characteristics, their relatively low mechanical strength raises concerns about their suitability for structural battery applications (Jeong et al. (2022); De Matteis et al. (2012); Yuhang et al. (2023)). For example, pure aluminum is relatively soft and ductile, resulting in significantly lower mechanical properties compared to aluminum alloys. In contrast, the aerospace-grade 2024-T3 aluminum alloy demonstrates much higher strength, primarily due to the presence of alloying elements such as copper and manganese, along with precise heat treatment processes (Gao et al. (2022)). Although aluminum alloy 2024-T3 contains alloying elements, it retains good electrical conductivity. However, its conductivity is slightly reduced compared to pure aluminum due to the presence of these alloying constituents (Zhang et al. (2023b)). A 2021 study by H.S. Abdo investigated the mechanical and electrical properties of aluminum alloys containing various alloying elements. The study included tensile testing, hardness measurements, and electrical resistivity analysis, with results compared against pure aluminum. The findings demonstrated that alloying elements such as copper and manganese significantly enhance mechanical strength, though they lead to a modest reduction in electrical conductivity. Notably, an increase in alloying content resulted in an improvement in yield strength of over 250%, while electrical conductivity decreased by approximately 14.6% (Abdo et al. (2021)). Regarding thermal properties, pure aluminum is well known for its high thermal conductivity, making it an excellent heat conductor. Although aluminum alloy 2024-T3 contains alloying elements, it still maintains relatively high thermal conductivity, albeit slightly lower than that of pure aluminum (Zhang and Li (2023)). Regarding corrosion resistance, both pure aluminum and the 2024-T3 aluminum alloy are susceptible to corrosion when exposed to harsh industrial environments without protection. Although pure aluminum is generally considered corrosion-resistant, it is prone to pitting corrosion, especially in battery applications where exposure to salts and chemicals is common (Jeong et al. (2022)). The 2024-T3 alloy, due to its copper content, is even more vulnerable to certain forms of corrosion, such as galvanic corrosion, when in contact with dissimilar metals or electrolytes (Spacht (1946)). Therefore, regardless of whether pure aluminum or the 2024-T3 alloy is used, implementing adequate corrosion protection is crucial to ensure the durability and reliability of energy storage systems. For anode current

collectors in structural battery applications, where both electrical conductivity and mechanical strength are essential, using a mechanically stronger form of copper can be beneficial. Although pure copper foils are commonly used due to their excellent electrical conductivity, replacing them with hardened copper alloy such as C110 H02 (Half Hard) sheets can improve the mechanical strength and overall integrity of the structural battery. C110 Copper H02 sheets provide enhanced mechanical properties, including higher tensile and yield strength, compared to pure copper foils. This improved mechanical strength contributes to greater structural stability and durability, which are crucial for structural batteries that must withstand mechanical loads and stresses. The use of coatings to prevent corrosion and reduce side reactions of pure metals and alloys is essential in structural batteries. Coatings serve as protective barriers, shielding battery components from corrosive environments and unwanted chemical reactions. In battery systems, corrosion primarily affects the interface between the current collector and the electrode materials. When corrosion occurs at this interface, it compromises the electrical and mechanical contact between the cathode and the current collector. This leads to the formation of areas with high electrical resistance, which negatively impacts battery performance. As a result, the battery's capacity and power output decrease over time due to corrosion-induced degradation ([Gabryelczyk et al. \(2021\)](#); [Shi et al. \(2017\)](#)). Corrosion, defined as the chemical or electrochemical interaction between materials and their environments, plays a critical role in the performance and durability of materials, especially in battery applications. Although aluminum generally resists corrosion through the formation of a protective native oxide layer, certain electrochemical conditions can damage this barrier. Despite this vulnerability, the oxide film on aluminum exhibits strong self-healing properties, allowing it to quickly regenerate when compromised. However, while this layer provides some corrosion protection, it also functions as a semiconductor or insulator, which can be a disadvantage when aluminum is used as a current collector ([Hunter and Fowle \(1956\)](#); [Song et al. \(2023\)](#)). Carbonaceous coatings play multiple important roles in battery applications. First, they serve as protective barriers against corrosion, shielding current collectors from harmful substances within the battery environment by preventing direct contact with corrosive elements ([Jeong et al. \(2022\)](#)). Second, they offer excellent electrical conductivity, reducing interfacial resistance and overcoming the conductivity challenges of newer electrode materials. Additionally, carbonaceous coatings provide both physical and chemical stability, enhancing mechanical strength and flexibility to protect active materials from fracturing during battery operation. They also exhibit strong heat transfer properties, helping to prevent heat buildup and related safety risks. Their chemical stability and compatibility with active materials and electrolytes reduce irreversible side reactions, promoting stable interfacial interactions. Furthermore, carbon coatings are cost-effective and widely accessible due to the abundance of carbon sources and versatile coating methods, such as sintering organic precursors or chemical vapor deposition, making them a valuable solution for improving battery performance and durability ([Li et al. \(2018\)](#)).

Materials and method

In this study, three carbonaceous materials—reduced graphite oxide, superconductive carbon, and graphite—were selected as coatings for copper C110 H02 and aluminum 2024-T3 substrates. The coated samples were immersed in a 5% NaCl solution for two weeks. Performance was evaluated by comparing visual inspection results and electrical resistance measurements to assess the coatings' effectiveness under corrosive conditions. In this study, three distinct carbonaceous materials were used: reduced graphite oxide (rGO-V50-M1), superconductive carbon, and graphite. The substrates were copper C110 H02 and aluminum 2024-T3 alloy. Prior to coating, the substrates were carefully cleaned with acetone to remove dust, oils, and other contaminants from manufacturing. To improve adhesion and remove the native oxide layer, the surfaces were abraded with 800-grit sandpaper, followed by a second acetone cleaning and drying at room temperature. Each carbonaceous material was mixed with N-methyl-2-pyrrolidone (NMP) and stirred for approximately 3 hours at 50°C. The resulting suspensions were then applied as coatings onto the prepared metal surfaces. For aluminum substrates, the coated samples were dried at 80°C for 3 hours, then heat-treated at 300°C for 1 hour to enhance coating adhesion. After this, the coated aluminum samples were immersed in a 5% NaCl solution at room temperature (20°C) for 2 weeks to assess corrosion resistance. In contrast, coated copper substrates were dried at a lower temperature of approximately 40°C to minimize the formation of copper oxide, which acts as an insulating layer and impairs current collector performance (Gozar et al. (2008)). To further prevent oxidation, uncoated areas of the copper were covered with tape during drying and testing. The coating process for copper is illustrated in Figure 1. Both aluminum and copper substrates were separately immersed in the 5% NaCl solution at room temperature for two weeks, and the results were recorded and analyzed.

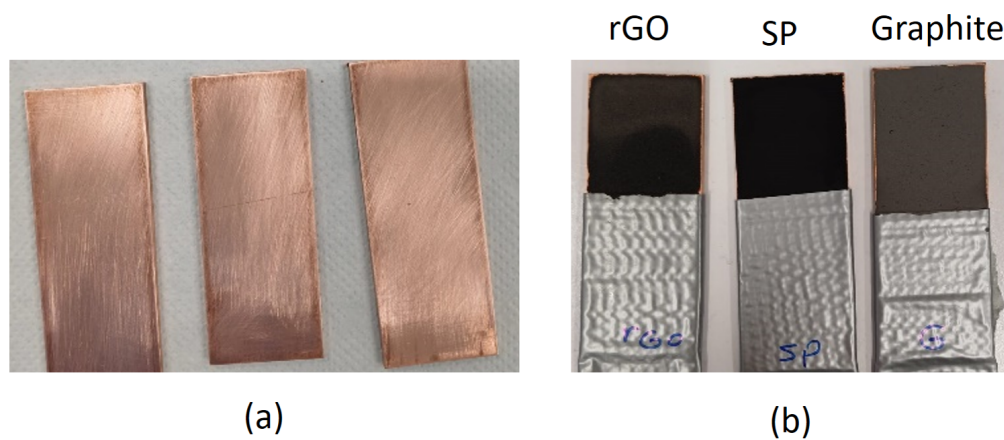


Figure A.1: Coating copper alloy with rGO, SP and graphite.

Results and discussion

The surface of each substrate was gently cleaned with acetone, as shown in Figure 1, which presents the condition of the substrates before and after cleaning. This figure also illustrates the corrosion effects observed after immersion in a 5% NaCl solution at room temperature for two weeks. It is clear that, using the applied coating method, both reduced graphite oxide (rGO) and graphite coatings failed to prevent corrosion, while the superconductive carbon coating effectively inhibited corrosion. Since corrosion increases electrical resistance in the affected areas—contributing to battery degradation and aging—this study also measured the electrical resistance of the coated regions. As shown in the subsequent figures, rGO exhibited high electrical resistance, whereas the superconductive carbon coating showed negligible resistance. The graphite coating displayed variable resistance, ranging from nearly zero to megaohm levels in different areas. The surface condition of coated aluminum substrates after immersion in 5% NaCl solution for two weeks are shown in Figure A.2.

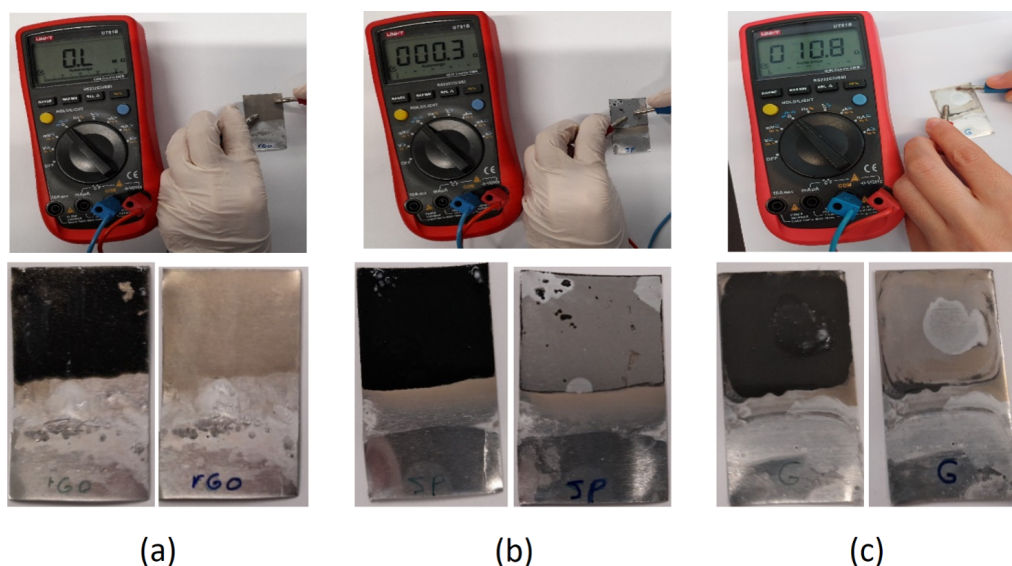


Figure A.2: Surface of aluminum substrate with different coatings after immersion in 5% NaCl solution for two weeks at room temperature, shown before (right) and after (left) cleaning of the coatings: (a) rGO, (b) SP, (c) Graphite.

After immersing the copper alloy in a 5% NaCl solution for one week, distinct outcomes were observed for each coating. The reduced graphite oxide coating exhibited significant corrosion depth in certain areas, accompanied by elevated electrical resistance on the metal surface. In contrast, the superconductive carbon coating showed minimal visible corrosion on the copper. Notably, carbon infiltration into the copper was observed in specific regions. Additionally, the coating, as shown in the pre-cleaning image, demonstrated remarkable resilience, indicating strong adhesion between the coating and the metal due to the applied procedures. Impressively, the electrical resistance in this region reached zero ohms. Regarding the graphite coating, certain areas were compromised during the immersion test. Varied levels of surface corrosion on the cop-

per were observed, leading to a wide range of electrical resistances, from zero ohms to several megaohms. These outcomes highlight the susceptibility of the graphite coating to degradation under the given test conditions. The surface condition of coated aluminum substrates after immersion in 5% NaCl solution for two weeks are shown in Figure A.3.

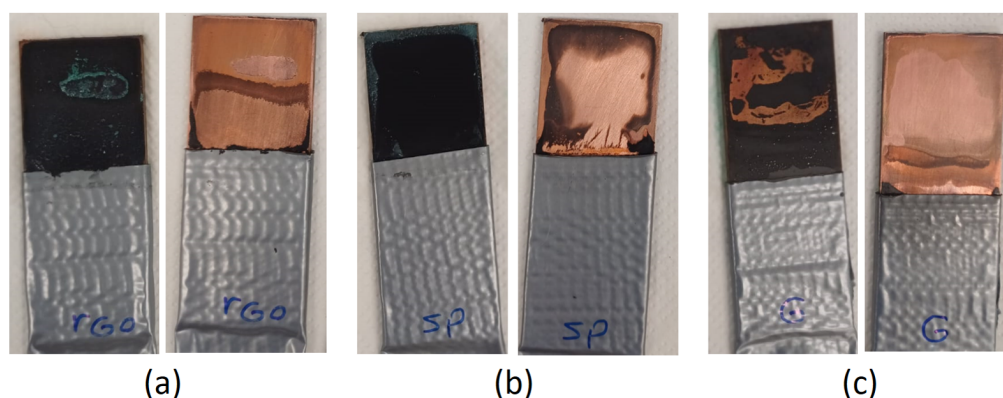


Figure A.3: Surface of copper substrate with different coatings after immersion in 5% NaCl solution for two weeks at room temperature, shown before (right) and after (left) cleaning of the coatings: (a) rGO, (b) SP, (c) Graphite.

The Nyquist plots in Figure A.4 illustrate the aging behavior of aluminum and copper alloy current collectors in full cells composed of an LFP cathode, graphite anode, and a PVA-based solid polymer electrolyte containing 40% LiTFSI and 20% trapped water, without any additional precoating on current collectors. This configuration simulates a harsh environment for solid-state batteries, as the presence of water with salts is known to promote corrosion and accelerate degradation, particularly at the current collector–electrolyte interfaces. The electrolyte had a thickness of 0.07 mm, and the current collectors were in contact with the active material and electrolyte over an area of 20 mm × 20 mm.

The results show a progressive increase in impedance over time when no coating is applied between the active materials (cathode and anode) and the current collectors (aluminum and copper alloy). The growing semicircle size in the Nyquist plots, particularly noticeable after 90 days, indicates a significant rise in charge transfer resistance due to interfacial degradation and corrosion of both the aluminum and copper substrates.

Figure A.5 shows the Nyquist plots for cells using the same setup, but with a Super P (SP carbon) precoating applied on aluminum and copper current collectors (between current collectors and the active materials). This precoating helped reduce the extent of aging. Although some impedance increase was still observed over time, it was substantially lower than in the uncoated case. This suggests that the SP layer provides partial protection by stabilizing the interface and limiting direct interaction between the electrolyte and the current collectors. Interestingly, after 90 days, the impedance even decreased slightly, indicating no observable aging. This could be partially attributed to slightly higher ambient temperatures during testing (mid-July), which may have enhanced ionic conductivity.

Figure A.6 presents the Nyquist plots for cells with an rGO-coated interface. These results show higher impedance values and more pronounced aging compared to both the uncoated and SP-coated cases. This suggests that the rGO coating may hinder electron flow and fails to provide effective protection against interfacial degradation. Thus, rGO appears to be less effective in both maintaining low resistance and preventing aging.

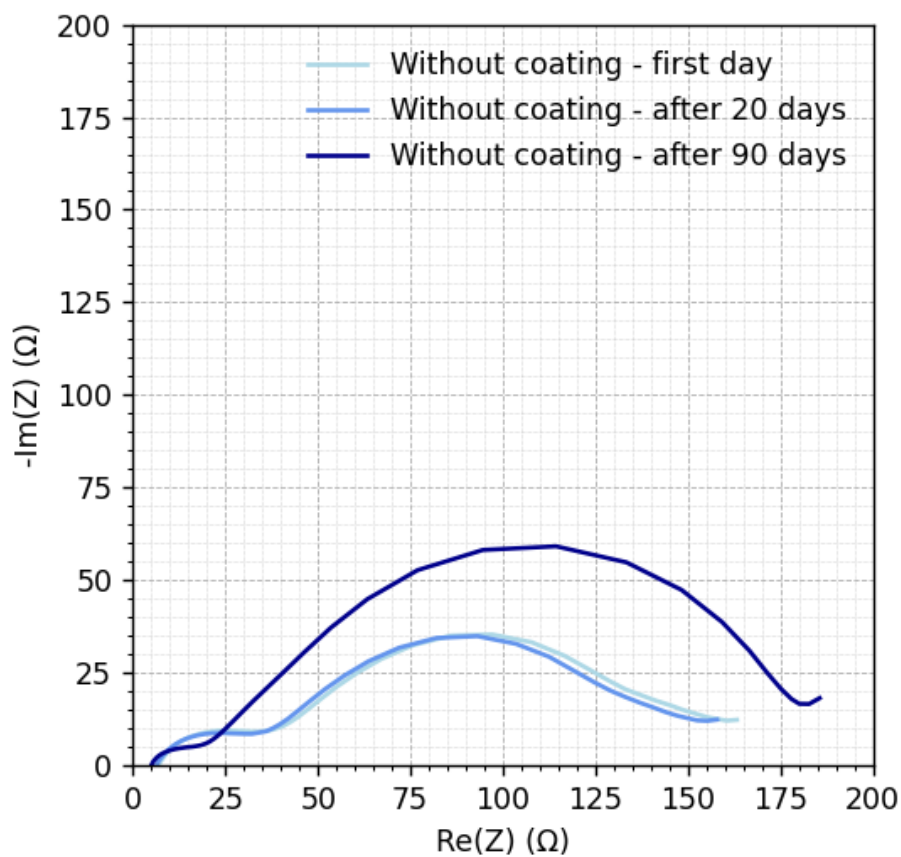


Figure A.4: Nyquist plot of the cell without coating on the current collectors on the first day, after 20 days, and after 90 days.

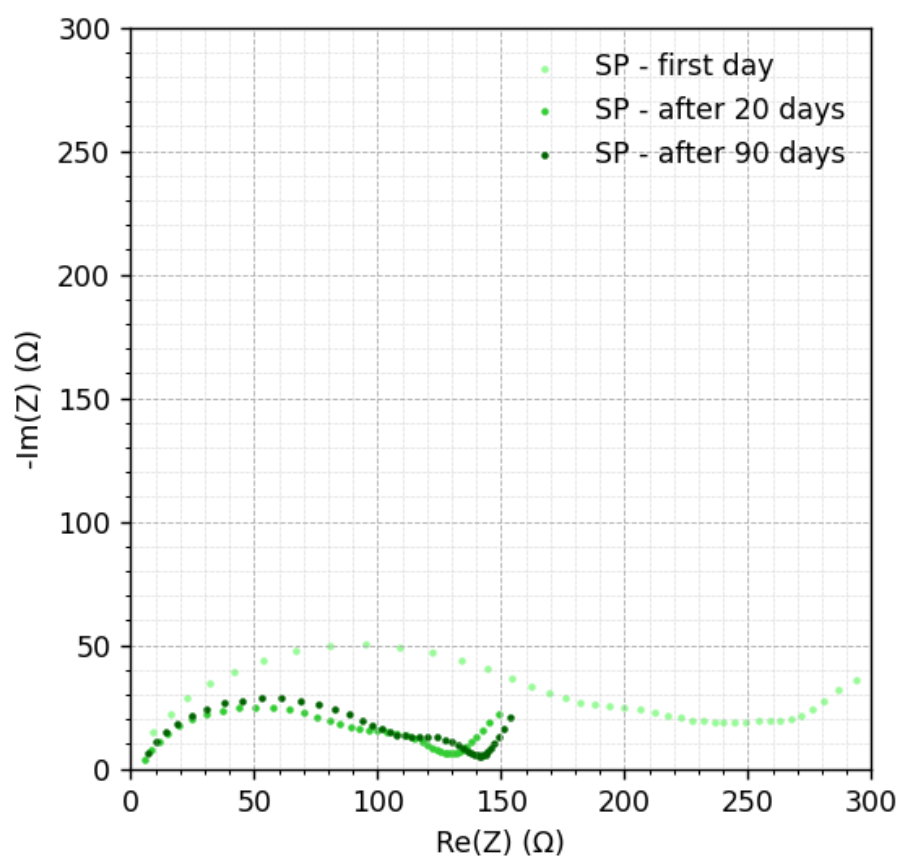


Figure A.5: Nyquist plot of the cell with SP coating on the current collectors on the first day, after 20 days, and after 90 days.

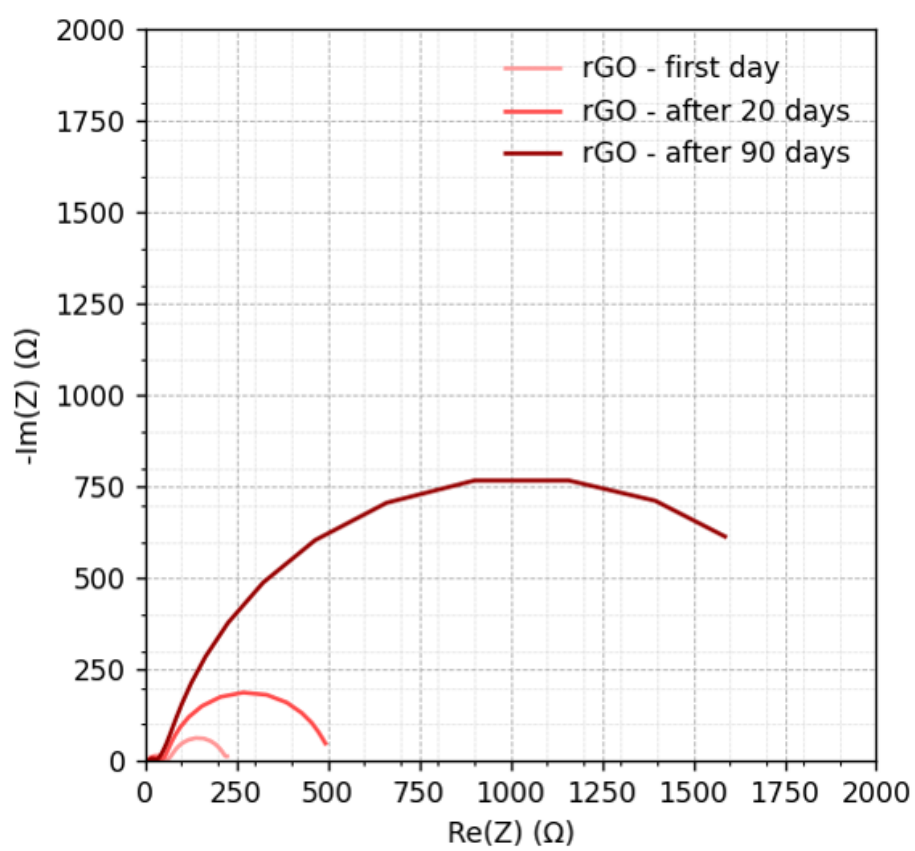


Figure A.6: Nyquist plot of the cell with rGO coating on the current collectors on the first day, after 20 days, and after 90 days.