

Fire Reaction Behaviour of Fibre Reinforced Composite Materials

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“Always walk through life as if you have something new to learn and you will”

Vernon Howard (1918-1992)

Resumo

Um conjunto de propriedades interessantes fazem com que os materiais compósitos sejam cada vez mais utilizados em detrimento de materiais mais convencionais, particularmente os metais. Características tais como elevadas resistência e rigidez específicas, resistência à corrosão, baixa condutividade eléctrica e boas propriedades de isolamento térmico, garantem um leque interessante de aplicações onde a utilização destes materiais apresenta claras vantagens. Nas últimas décadas, a indústria dos materiais compósitos tem crescido de forma sustentável, especialmente devido à sua utilização em mercados chave, tais como os sectores automóvel, construção civil, energias renováveis, aeronáutica e Espaço, entre outros.

Dependendo da aplicação, os materiais compósitos podem ser de base polimérica termoendurecível ou termoplástica, enquanto os reforços mais utilizados são as fibras de vidro ou carbono. Estas últimas são naturalmente utilizadas para aplicações de maior desempenho, tais como aeronáutica e Espaço. A grande vantagem dos compósitos de fibra de carbono nestes sectores é sem dúvida a razão entre baixo peso e elevadas propriedades mecânicas, nomeadamente resistência e rigidez. Genericamente, as fibras de carbono são 8 a 10 vezes mais resistentes do que o aço, apresentando a clara vantagem de não sofrerem corrosão.

No entanto, a utilização de materiais compósitos pode ficar comprometida em determinados sectores, nomeadamente no que diz respeito ao seu comportamento ao fogo. As fibras usadas como reforço são tipicamente compostas por materiais inertes, no entanto, as matrizes poliméricas, tais como resinas de epóxico e poliéster, são orgânicas e, portanto, altamente combustíveis. De facto, estas resinas constituem a principal fonte de carga combustível nos materiais compósitos. É, portanto, crucial o estudo de novas soluções que permitam obter compósitos com melhores propriedades de reacção à chama.

Uma das abordagens mais frequentemente utilizadas é, sem dúvida, a modificação da matriz através da adição de cargas denominadas retardantes de chama. Estas podem atuar de diferentes formas, desde química ou fisicamente, nas fases condensada ou gasosa. A escolha depende, em grande medida, da própria matriz, da compatibilidade entre os componentes e, em última instância, da aplicação do material compósito. Outra abordagem consiste na utilização de revestimentos superficiais, revestimentos estes que podem ter diferentes composições químicas, sendo comum a utilização de grafite ou de componentes intumescentes. A utilização destes revestimentos pode ser considerada uma opção mais atrativa, na medida em que não são necessárias alterações no processo de produção do compósito e, adicionalmente, as propriedades mecânicas do material não são alteradas.

Nos últimos anos, o uso de materiais à escala manométrica tem concentrado atenções dentro da comunidade científica. Devido à elevada área superficial específica das nanopartículas, teoricamente, apenas pequenas quantidades são necessárias para produzir o efeito desejado nas propriedades finais. Neste sentido, a eficácia de várias nanopartículas tem sido testada em diferentes matrizes poliméricas, sendo definitivamente as argilas e os nanotubos de carbono as mais reportadas.

Na literatura é possível encontrar diversos artigos científicos sobre o efeito de diferentes tipos de nanopartículas nas propriedades de reacção à chama, tanto de matrizes

termoplásticas como termoendurecíveis, no entanto, a quantidade de trabalhos publicados no compósito reforçado com fibras é ainda escassa.

Desta forma, esta tese pretende apresentar diferentes abordagens para melhoria das propriedades de reacção ao fogo, por um lado da resina, por outro do compósito reforçado com fibra. Desde retardantes de chama tradicionais, tais como o hidróxido de alumínio (ATH) e o polifosfato de amónia (APP), a nanoargilas e nanotubos de carbono, diferentes soluções foram testados e são apresentadas aqui. Por outro lado, foram também testados diferentes tipos de revestimentos superficiais.

Dois tipos de materiais compósitos foram usados como base no decorrer do trabalho experimental: compósitos de epóxico e fibra de carbono, produzidos no INEGI, e compósitos comerciais de fibra de vidro com poliéster insaturado. Diferentes soluções são propostas, de acordo com o material compósito. Além dos resultados de calorimetria de cone, também a estabilidade térmica dos materiais foi avaliada por análise termogravimétrica.

Apesar de o comportamento de reacção ao fogo ser o principal alvo de estudo desta tese de doutoramento, uma pequena parte é dedicada ao estudo da cinética de cura das resinas de epóxico utilizadas no decorrer do trabalho experimental. O processo de cura de uma resina termoendurecível é reconhecido como sendo crítico para as propriedades finais do material compósito, nomeadamente em termos das propriedades térmicas e mecânicas. A adição de cargas à matriz poderá afectar as reacções de cura, acelerando ou inibindo as mesmas, tornando eventualmente necessário ajustar as condições de tempo e temperatura durante a cura dos materiais. Desta forma, nesta tese analisou-se o efeito da adição de retardantes de chama tradicionais nos parâmetros de cinética de cura de duas resinas de epóxico com viscosidades diferentes. Para tal, foi usada a calorimetria diferencial de varrimento em modo dinâmico.

Relativamente à modificação da resina através da adição de nanopartículas, verificou-se que as argilas aniónicas e nanotubos de carbono modificados termicamente promoveram os melhores resultados em termos das propriedades de reacção à chama obtidas por calorimetria de cone. No entanto, nenhum dos sistemas testados permitiu obter melhorias significativas na reacção ao fogo de compósitos de fibra de carbono produzidos a partir das resinas modificadas. Por outro lado, a utilização de materiais cerâmicos como revestimentos superficiais de protecção ao fogo melhorou as propriedades de reacção ao fogo dos compósitos reforçados com fibra de carbono estudados durante esta tese. A presença de fibras de celulose numa das composições testadas resultou na formação de uma estrutura mais compacta, promovendo uma maior protecção da estrutura compósita, com redução significativa da quantidade de calor libertado.

Nos compósitos reforçados com fibra de vidro, nos quais foram aplicadas diferentes espessuras de tinta intumescente de base aquosa, resultaram melhorias significativas no comportamento de reacção ao fogo dos materiais em diversas propriedades tais como a libertação de calor e a toxicidade dos fumos libertados.

Abstract

Composite materials offer higher specific strength and stiffness than other conventional materials, in addition to a great number of attractive features such as corrosion resistance, low electrical conductivity and good insulation properties, among others. For three decades, the composites industry has witnessed a sustained growth, especially due to market penetration of these materials in key markets, such as the construction, wind energy, aeronautics and automobile sectors.

Depending on the application, composite materials can be made from a thermoset or thermoplastic polymeric base, while most common used fibre reinforcement are glass and carbon. These last ones are naturally used where higher mechanical requirements are necessary such as for aeronautics and space applications. The main advantage from the use of carbon fibre composites is in its high strength and stiffness properties due to the presence of the carbon fibre with a relatively low weight – carbon fibres are 8 to 10 times stronger than steel but 5 times lighter and do not corrode like aluminium and steel.

However, current fibre-reinforced polymer composites are typically compromised to varying degrees with respect to their fire performance. The reinforcing fibres (usually carbon or glass) are typically made of inert materials, however, the resin matrices are organic materials, therefore combustible to differing degrees. In fact, these resins constitute the primary fire fuel load for composite materials. Hence, it is pertinent to study new solutions for imparting flame retardant properties to FRP composites.

One of the most commonly used approaches is indeed the additivation of the resin matrix, by adding the so-called flame retardants. These can act in different forms, from chemical to physical actions, in the condensed or gas phases. The choice depends, to a large extent, on the matrix itself, the compatibility between the components and, ultimately, on the application of the composite material. Another approach consists in the use of surface coatings, which can also have different compositions, from graphite based to intumescent components. The use of surface coatings can be regarded as a more attractive option, as no modifications during manufacturing are necessary and, besides, the mechanical properties of the composite material are not altered.

In the last years, the use of nano-based solutions has gained increased attention within the scientific community. Due to the high specific area of the nanoparticles, theoretically, only small amounts are needed in order to provide enhanced properties. In this sense, the efficacy of several nanoparticles, like nanoclays and carbon nanotubes, have been tested in different polymeric matrices.

In the literature, one may find a considerable amount of work on the flame retardancy of different types of nanoparticles in both thermoplastic and thermoset matrices, however, not much work has been done on the fibre reinforced composite material.

It is intended with this thesis to study different approaches in order to provide flame retardant properties to both the resin and the fibre reinforced composite material. From traditional flame retardants such as aluminium trihydroxide (ATH) and ammonium polyphosphate (APP), to nanoclays and carbon nanotubes, different solutions were tested

and are presented here. On the other hand, different types of coatings were also tested. In this case, two core materials were used: carbon fibre epoxy composites, manufactured at INEGI, and commercial glass fibre unsaturated polyester composites. Different solutions are proposed for these materials. Besides cone calorimeter results, also the thermal stability of the materials was assessed by thermogravimetric analyses.

Although the focus of this thesis was to study the fire reaction behaviour of composite materials, a small part was dedicated to the cure kinetics study of the two epoxy resins used throughout the experimental work. The curing process of a thermoset resin is recognized as critical to the final composite materials properties, both thermal and mechanical. The addition of fillers to the resin matrix is likely to affect the cure reactions, by accelerating or inhibiting them, which can eventually lead to adjustments in the curing conditions of the material, namely time and temperature. Therefore, the effect of adding traditional flame retardants in the kinetic parameters of two different epoxy resins was also studied within this thesis. For that, differential scanning calorimetry in the dynamic mode was used.

Concerning the modification of the resin matrix with the addition of nanoparticles, the results showed that anionic clays and thermally modified carbon nanotubes resulted in the best results concerning the fire reaction properties obtained by cone calorimetry. However, none of the tested systems allowed significant improvements in the fire reaction behaviour of carbon fibre composites produced from these modified resins. On the other hand, the use of ceramic materials as surface fire protective coatings to fire significantly enhanced the fire properties of the selected carbon fibre reinforced composites. The presence of cellulose fibres in one of the tested formulations resulted in the formation of a compact structure, which promoted a greater fire protection of the composite structure, with significant reductions in the heat released.

In the case of glass fibre reinforced composites, in which a water-based intumescent paint was applied in different thicknesses, significant improvements were achieved in different fire reaction properties such as heat release and toxicity of the produced smoke.

Thesis Motivation and Structure

Fibre reinforced composite structures have become very competitive engineering materials in past years, successfully replacing conventional metallic and other polymeric materials in many important sectors of industry.

A clear example is the transport industry: instead of heavy steel and wood construction, lighter and more ergonomic plastics, composite materials and fire-safe foams and textiles have demonstrated great advantages to the manufacture of modern trains and planes, allowing the production of more comfortable seats as well as sleeker designs.

Fibre reinforced composite materials are also used in building and construction applications, providing significant advantages over traditional building materials. Application areas include structural components, cladding and facades, roofing, doors and windows, acoustics, rehabilitation and the fabrication of unique structures and components. In this thesis, a chapter is dedicated to the improvement of the fire reaction properties of glass fibre composites that have the potential to be used in the rehabilitation, repair and strengthening of reinforced concrete.

Other sectors, such as aviation and aerospace, demand higher performance products, lightweight and high-strength, and usually operate on the cutting-edge of advanced composite materials. In this thesis, also studies regarding the fire properties of higher performance materials are presented, by using a Space qualified resin and carbon fibres as reinforcement.

With the use of composite materials, the structure and weight of transport vehicles have become much lighter, helping to reduce the amount of fuel needed, therefore leading to improved energy and cost efficiency. These are crucial aspects in some transport sectors, namely aeronautics and Space, where each kilogram of weight reduction leads to very significant cost savings. Even a 1% saving on fuel worldwide can provide a massive contribution to making limited oil resources last longer.

The increased use of diverse plastics in different sectors can, however, contribute to the materials flammability, unless appropriate fire safety measurements are used. While polymeric based composites offer many benefits, they also create a new problem, tending to pose a greater fire risk than the materials they have replaced (namely metals). That is why flame retardants have become an essential component of many products and are often used to meet safety standards and regulations. Due to the flammability characteristics of composite materials, their use depends on making sure these materials are fire safe. In particular, when they are used in public transport, public authorities and private operators have a high degree of responsibility to guarantee the maximum possible level of safety for passengers. As an example, international aviation regulations dictate fire safety standards that are probably stricter than for any other mode of transport today. This is because of the impossibility to escape from an airplane in case of a fire.

Fire safety regulations are often different between nations, and sometimes the differences can be quite significant. For instance, regulations applied to the use of composite materials in rail carriages differ considerably between the United States, United Kingdom, Australia, Japan and many other countries. Therefore, it is not surprising that certain types of materials may fulfil the fire safety requirements in one or several countries, while failing in other ones. As expected, the fire standard regulations are highly dependent on the

composite material application. As an example, in the 90's, the Federal Aviation Administration (FAA) established regulations that required stringent flame-smoke-toxicity (FST) and low heat release in the event of a fire, while keeping aircraft weight as low as possible for maximum efficiency. Equivalent European regulations have been formulated by the European Aviation Safety Agency (EASA). Aircraft manufacturers Boeing and Airbus often require even more rigorous fire resistance to ensure that the entire interior will work in concert to meet the agency specifications. The ultimate goal of FAA's Fire Safety Branch is cabin interiors made with zero heat release materials, i.e., completely fire resistant.

In civil engineering applications, most countries have their own requirements for fire performance. The European Union has established fire safety regulations on composite materials used in construction products for buildings, including multi-occupancy dwellings, hospitals, schools, shops and clubs, among others. The evaluation include properties such as heat and smoke release, ignitability, production of flaming droplets and fire resistance.

In the 1970s, when the use of new polymers faced a serious growth, the need to reduce their combustibility for the protection of property, people and the environment also gained relevance. This is when most flame retardants appeared in the market. These chemicals have the ability of acting on several stages: they can delay ignition, slow down the combustion process, or even make the material self-extinguishing. An important characteristic of flame retardants is the potential reduction of fire spreading, leading to increased escape times. Increasing time to flashover from 2-3 minutes to 10-15 minutes can make the difference between escape or fatalities. The flashover can be defined as the stage when fire gases ignite and a room becomes a fireball with temperatures rapidly escalating to 800 – 1000°C, making escape or survival impossible.

INEGI has a long and prestigious tradition in composite materials. Composite materials and structures research unit is the largest of the institute, with a set of relevant laboratory equipment and means to provide support in several areas, from product design to manufacturing and testing. In this field, INEGI has a unique fire and smoke laboratory, accredited by IPAC for several tests. Therefore, it was relevant to bring these areas together in a PhD thesis aiming at studying the fire reaction behaviour of fibre reinforced composite materials.

INEGI has in fact facilities to perform several fire reaction and smoke tests, allowing materials certification or classification, according to specific standards. Product safety standards and national regulations usually require different types of fire testing, such as resistance to ignition by different heat sources, levels of heat release after ignition, smoke density, acidity and toxicity. Fire tests can be performed at different scales (small, medium or large scale) and can be performed on standardized specimens or on the final item (product testing). However, even standardized fire testing may not always reflect real-life fire scenarios. Fire testing may not accurately predict the hazards of a full-scale fire, nevertheless they are the best tool aiming to assess the fire safety of certain products, possibly contributing to prevent fire injuries and damages, including human lives.

In this thesis, the cone calorimeter was the equipment chosen for obtaining the fire reaction properties of the produced materials. This equipment is mainly used for materials research, as it does not allow any type of material classification. This thesis was not focused in achieving any particular fire requirement or standard, but rather in understanding the flame retardant mechanisms associated with the different methodologies used –

particularly with the addition of nanofillers to the resin matrix. Furthermore, the cone calorimeter allows a very complete materials fire reaction characterization, by obtaining data on ignition time, heat release, smoke toxicity (including carbon dioxide and monoxide) and mass loss. One very attractive characteristic of this device is the sample size requested, which is in fact much smaller when compared with other fire testing – 100 cm². When developing new materials formulations, sometimes the available raw materials amount is limited, and preparing large samples for testing is not really feasible.

This thesis presents a study focused on the fire reaction properties of different fibre reinforced composite materials – carbon fibre/epoxy and glass fibre/polyester. For each of these materials, different flame retardant approaches were tested, according to the intended target application: carbon/epoxy for aerospace and glass/polyester for civil engineering applications. In carbon/epoxy composites, both surface coatings and modification of the resin matrix were studied, as these materials were produced “in house” by liquid infusion techniques, i.e., at INEGI’s facilities. For glass/polyester composites, the used raw materials were commercially available and because of that, only surface coating approach was studied.

Nanoparticles have gained a considerable attention within the scientific community, as potential replacement of traditionally used micro fillers in different applications. In the case of flame retardancy, carbon based nanomaterials such as carbon nanotubes and graphene, or silicate layered nanomaterials such as nanoclays, have definitely been in the spotlight within the past 10 years. For the development of this thesis, it was also a matter of context within our research team, which was beginning to work – mostly – with different forms of carbon nanotubes for obtaining multifunctional carbon fibre epoxy composites. The motivation to use these carbon nanomaterials gained relevance throughout the ongoing ESA projects NACO and NACO2 (Non-conventional matrix-Carbon nanotube reinforced composites for applications in space) and COPE (Composite Materials for Payload and Platform Elements), where the interest in studying more in detail the properties of these new materials was raising in our team. The fire reaction properties were a set of characteristics not properly explored at that time. Furthermore, the project partners were already engaged in the materials characterization from the mechanical and electrical point of view, therefore, within the projects context, it made sense for us to focus mainly on the thermal properties.

The interest in using nanoclays - which was at that point limited to cationic clays such as montmorillonite – started with a collaboration work with the University of Salamanca (USAL), with the team had a consolidated experience in synthesizing anionic nanoclays (LDHs) with different organic treatments. At that point, there were very few studies regarding the flame retardant effects of these layered nanomaterials in thermoset resins and fibre reinforced composite materials. Similar to carbon nanotubes, the reported work was mainly focused on the enhancing the mechanical properties. This collaboration started from fruitful participations in different events inside the COST Action MP1107 - Composites with Novel Functional and Structural Properties by Nanoscale Materials (Nano Composite Materials-NCM) – where, once again, the flame retardancy of these nano materials was not fully understood. Still within this Action, I had the great opportunity to perform a short-term scientific mission at USAL, allowing me to learn how to synthesize and characterize anionic nanoclays with different organic treatments.

As the modification of the resin matrix is a well-developed approach for obtaining composite materials with proper fire behaviour, it made sense to compare the performance of well-established commercial flame retardants with these proposed alternative nanomaterials. Since it was the purpose to maintain the resin workability – especially in terms of the viscosity levels – for liquid resin processes, the traditional flame retardants amount added to the resin matrix was kept low (5-10 wt%), compared with the values that are usually found in the literature (up to 50 wt% or more).

As usual, the thesis began with a comprehensive state of the art review regarding the fire reaction behaviour of fibre reinforced composite materials, based on the addition of nanoclays or carbon nanotubes to the polymeric matrix, which is presented in chapter 1. This review study addressed only epoxy and unsaturated polyester resins. It was also intended to present an overview concerning the most relevant tests and material properties usually discussed in flame retardancy studies. The decomposition phenomena that takes place when composite materials are exposed to fire conditions were also discussed. This review was published in 2014, as a chapter of “Polymer Green Flame Retardants” (Elsevier).

The first experimental studies aiming at enhancing the fire reaction behaviour of a low viscosity, low curing temperature epoxy resin are explored in chapter 2. The aim of this work, published in *Solid State Phenomena* (volume 151) as part of a special issue on *Nanocomposite Material*, was to show the effect of the addition of low amounts of nano-magnesium hydroxide on the flammability and thermal properties of an epoxy resin. The performance of this nano flame retardant was compared with a traditional one (ammonium polyphosphate), also used in low amounts.

Continuing the studies on the effect of adding different types of particles in the fire reaction properties of an epoxy resin, a high viscosity, high curing temperature resin, neat and reinforced with carbon fibres was used. These materials were also being used by my research team at INEGI in several projects, therefore it made sense to assess their fire reaction behaviour properties. The selected resin has a high glass transition temperature and is qualified for Space applications. The effectiveness of distinct fillers, micro (ATH and APP) or nano-sized scaled (carbon nanotubes and nanoclays) on the fire reaction behaviour of both the epoxy resin and its fibre reinforced composite was assessed using cone calorimetry. In this chapter (3), also the thermal stability, glass transition temperature and microstructure of the manufactured materials were evaluated. Some of the methods used in this chapter, in terms of the materials preparation (such as mixing times and methodologies) were running in parallel with a Master thesis. The Master student performed several studies in order to determine the best mixing methods for these particular materials, taking into account the equipments that were available at that time.

A different approach in order to enhance the fire reaction behaviour of carbon fibre composites is presented and discussed in chapter 4. Eco-friendly water based ceramic tapes with different compositions were produced using tape casting technology and afterwards applied as top surface of an epoxy carbon fibre composite. The idea to use these ceramic materials started during our participation on two COST actions (MP0701 and MP1105), as one of the participants of these actions (IKTS, Fraunhofer Institute of Ceramics) was developing new water based ceramic tapes, and the application in composite materials was not explored at all. Ceramic materials are extremely resistant to high temperatures; hence, it made sense to test their ability to act as fire protective coatings.

The use of coatings is regarded as a viable alternative to the modification of the resin matrix because the non-modified, virgin materials, can be used to manufacture the composite. “Green”, non-sintered ceramic tapes were used in this work. The main advantage of non-sintered tapes is their high flexibility, allowing the proper positioning in any FRP structure, even a curved one.

Composite materials produced at INEGI were manufactured using hand lay-up, followed by curing in the autoclave, under the application of both vacuum and positive pressure. For modified resin composites, the resin containing micro or nanosized flame retardant was applied using a roller in the different carbon fibre layers. In the case of the surface coatings, the neat resin was used and the composite laminate ply arrangement was kept the same, but with the coating applied as top, surface layer. The autoclave is essentially a pressure vessels used to process parts and/or materials with the use of pressure, vacuum and temperature, pressure and temperature. High-performance advanced composites used for composite bonding in the aerospace, military, and other high performance applications, are normally cured in the autoclave. These materials are typically associated to high fibre/resin ratios and no air voids, which can be achieved by subjecting the material to elevated pressures and temperatures in the autoclave. Fibre volume fraction and laminate void content are two of the characteristics that greatly affect the mechanical performance of the composite materials.

Before going to the autoclave, the composite parts were vacuum bagged. This procedure allows the application of a compaction pressure that helps to consolidate the laminate plies, while guaranteeing a uniform material thickness. Further, by vacuum bagging the materials, the eventual moisture and solvents content, as well as volatiles formed during the resin curing, can be released. The autoclave applies a much higher compaction pressure than the vacuum bag alone, providing a composite material with good quality.

It was the purpose of the thesis to use a liquid resin process, therefore, as mentioned before, it was crucial to maintain the resin viscosity levels so that the hand lay-up processing was feasible. When processing thermoset resins, the viscosity levels are in fact crucial for guaranteeing a proper fibre wetting. In the case of filled resins, there is an increased risk of particles filtration in the fibre. That is why resins need to have acceptable viscosity levels to be workable by hand. Low filler levels were used throughout this thesis in order to maintain a resin viscosity suitable for liquid processes.

In chapter 5, as mentioned before, significantly different materials were used as baseline, namely commercial glass fibre polyester composites produced by pultrusion. These pultruded composite materials have a great interest for applications in the civil construction sector, namely for rehabilitation, repair and strengthening of reinforced concrete, steel or masonry. However, the poor fire performance of these materials determines the need to use fire protection systems. In this work, performed under a Portuguese nationally funded (FCT) project “Fire Protection Systems for GFRP Pultruded Profiles - FIRE-FRP”, a passive fire protection system was tested. A water based intumescent paint, typically used for the fire protection of metallic structures or wood ignifugation, was selected. Contrary to traditionally used solvent-based paints, this can be considered an environmentally friendly passive fire protection system, mainly due to the low levels of Volatile Organic Compounds (VOCs) released during application and usage (which is especially important for indoor

applications). Three different paint thicknesses were tested and the fire reaction properties of the materials were assessed using cone calorimeter tests.

When working with thermoset resins, one crucial issue that may definitely affect the properties of the resulting material are the applied curing cycles, namely the balance between curing times and temperatures. Curing is the transformation of a liquid thermoset to a glassy solid by means of chemical reactions. During the cure process, polymer chains of low molecular weight convert to a three-dimensional network of extremely large cross-linked chains. The resin three-dimensional network formed during these thermal cycles is the key parameter that allows obtaining optimized composite thermal and mechanical properties. Usually, the resin manufacturer advises an optimized cure cycle, however, the addition of fillers may have catalytic or inhibiting effects on the curing reactions. These effects may set the need to adjust the curing cycles of the materials, in order to obtain maximized properties. Non-uniform curing can lead to incomplete cure or formation of entrapped volatiles or voids, which may ultimately cause a reduction in the overall quality and in service performance of the composite material. Composite manufacturers are always seeking to achieve the best material properties, namely mechanical and thermal. A crucial contributor to these properties is definitely the cure schedule.

When performing a bibliographic review, it was noticed that, to the extent of our knowledge, there were no studies regarding the effect of traditional flame retardants on the cure kinetics of epoxy resins. On the other hand, the cure kinetic studies of nanoclay or CNT-modified epoxy resins is already extensively reported in the literature. In chapter 6, both epoxy resins used throughout this thesis were used as matrix materials and the effect of adding traditional flame retardants - either ATH or APP - in the curing kinetics was analyzed using differential scanning calorimetry. The kinetic parameters were determined using the Kissinger model applied to the results obtained in non-isothermal (dynamic) DSC tests at three different heating rates.

Table of Contents

1 FLAME RETARDANCY OF FIBRE REINFORCED POLYMER COMPOSITES BASED ON NANOCLOCKS AND CARBON NANOTUBES 24

1.1	INTRODUCTION	24
1.2	FIBRE REINFORCED POLYMER COMPOSITES.....	25
1.2.1	<i>Introduction</i>	25
1.2.2	<i>Applications</i>	27
1.2.3	<i>Main Concerns</i>	28
1.3	FIRE BEHAVIOUR, TEST METHODS AND FIRE REACTION PROPERTIES.....	29
1.3.1	<i>Fire Behaviour</i>	29
1.3.2	<i>Test Methods</i>	30
1.3.3	<i>Fire Reaction Properties</i>	32
1.4	FRP COMPOSITES IN FIRE.....	33
1.4.1	<i>Introduction</i>	33
1.4.2	<i>Thermal Decomposition</i>	34
1.4.3	<i>Fire Reaction Properties versus Composite Structure and Fire Intensity</i>	36
1.5	FLAME RETARDANCY	40
1.6	POLYMER/CLAY NANO AND MICROCOMPOSITES	42
1.6.1	<i>Nanoclays</i>	43
1.6.2	<i>Flame Retardant Polymer/Clay Nano and Microcomposites</i>	44
1.6.3	<i>Flame Retardancy Mechanisms of Nanoclays</i>	52
1.7	POLYMER/CNT NANO AND MICROCOMPOSITES	53
1.7.1	<i>Carbon Nanotubes</i>	53
1.7.2	<i>Flame Retardant Polymer/CNT Nano and Microcomposites</i>	54
1.7.3	<i>Flame Retardancy Mechanisms of Carbon Nanotubes</i>	58
1.8	CONCLUSIONS AND IDENTIFICATION OF MAIN RESEARCH NEEDS.....	58

2 EFFECT OF NANO-MAGNESIUM HYDROXIDE ON THE FLAMMABILITY OF EPOXY RESINS 67

2.1	INTRODUCTION	67
2.2	EXPERIMENTAL.....	68
2.2.1	<i>Materials</i>	68
2.2.2	<i>Sample Preparation</i>	68
2.2.3	<i>Sample Testing</i>	69
2.3	RESULTS AND DISCUSSION.....	69
2.3.1	<i>SEM Characterisation</i>	69
2.3.2	<i>DSC Tests</i>	70
2.3.3	<i>Cone Calorimeter Tests</i>	71
2.4	CONCLUSIONS.....	72

3 EFFECT OF TRADITIONAL FLAME RETARDANTS, NANOCLOCKS AND CARBON NANOTUBES IN THE FIRE PERFORMANCE OF EPOXY RESIN COMPOSITES 75

3.1	INTRODUCTION	75
3.2	EXPERIMENTAL.....	77
3.2.1	<i>Materials</i>	77
3.2.2	<i>Sample preparation</i>	78
3.2.3	<i>Sample Testing</i>	78
3.3	RESULTS AND DISCUSSION	80
3.3.1	<i>Resin Samples</i>	80
3.3.2	<i>CFRP Samples</i>	91

3.4	CONCLUSIONS	97
4	CERAMIC TAPES AS FIRE PROTECTIVE COATINGS FOR CFRP COMPOSITES	102
4.1	INTRODUCTION	102
4.2	EXPERIMENTAL	103
4.2.1	<i>Materials</i>	103
4.2.2	<i>Sample Preparation</i>	104
4.2.3	<i>Sample Testing</i>	107
4.3	RESULTS AND DISCUSSION	108
4.3.1	<i>Thermal Stability</i>	108
4.3.2	<i>SEM Characterisation</i>	109
4.3.3	<i>Fire Reaction Properties</i>	111
4.4	CONCLUSIONS	113
5	ENVIRONMENTALLY FRIENDLY PASSIVE FIRE PROTECTION SYSTEMS FOR GLASS FIBRE REINFORCED POLYMER PULTRUDED PROFILES.....	115
5.1	INTRODUCTION	115
5.2	EXPERIMENTAL	116
5.3	RESULTS AND DISCUSSION	118
5.3.1	<i>Visual Inspections of Samples Before Burning</i>	118
5.3.2	<i>Burning Behaviour and Fire Reaction Properties</i>	118
5.4	CONCLUSIONS	130
6	EFFECT OF RESIN VISCOSITY ON THE CURE KINETICS OF FLAME RETARDANT EPOXY FORMULATIONS	132
6.1	INTRODUCTION	132
6.2	EXPERIMENTAL PROCEDURE	133
6.2.1	<i>Materials</i>	133
6.2.2	<i>Sample Preparation and Testing</i>	134
6.3	RESULTS AND DISCUSSION	138
6.3.1	<i>Thermal Behaviour of Fillers</i>	138
6.3.2	<i>Effect of ATH and APP on the dynamic heat of reaction</i>	139
6.3.3	<i>Effect on the Reaction Rate and Fractional Conversion</i>	142
6.3.4	<i>Effect on the Kinetic Parameters</i>	143
6.4	CONCLUSIONS	145
7	MAIN CONCLUSIONS AND FUTURE WORK	149

List of Figures

FIGURE 1: USE OF FIBRE-REINFORCED POLYMER COMPOSITES IN AIRBUS A380 (SOURCE: [6])	27
FIGURE 2: UL94 TEST FOR FLAMMABILITY FOR V0, V1 AND V2 CLASSIFICATION (SOURCE:[15])	30
FIGURE 3: EXPERIMENTAL SET-UP FOR LOI MEASUREMENT (SOURCE:[17])	31
FIGURE 4: SCHEMATIC REPRESENTATION OF A CONE CALORIMETER (SOURCE: [19])	31
FIGURE 5: SCHEMATIC REPRESENTATION OF THE DIFFERENT PHASES, MECHANISMS AND REACTION PROCESSES INVOLVED DURING THE EXPOSURE TO FIRE OF A POLYMER COMPOSITE.....	34
FIGURE 6: THE EFFECT OF EXTERNAL HEAT FLUXES IN THE IGNITION TIMES FOR TWO DIFFERENT COMPOSITES (SOURCE: [5])	36
FIGURE 7: EFFECT OF HEAT FLUX ON THE PEAK HEAT RELEASE RATE FOR VARIOUS GLASS/POLYMER LAMINATES (SOURCE: [5])	37
FIGURE 8: SCHEMATIC REPRESENTATION OF THE DIFFERENT PHASES, MECHANISMS AND REACTION PROCESSES INVOLVED DURING THE EXPOSURE TO FIRE OF A POLYMER COMPOSITE (SOURCE: [5]).....	38
FIGURE 9: DIFFERENTIAL SCANNING CALORIMETER TEST SHOWING THE ENDOTHERMIC DECOMPOSITION BEHAVIOUR OF ATH	41
FIGURE 10: SCHEMATIC ILLUSTRATIONS OF (A) LDH (SOURCE [44]) AND (B) MMT (SOURCE: [16])	44
FIGURE 11: HEAT RELEASE RATE (LEFT) AND SPECIFIC EXTINCTION AREA (RIGHT) CURVES FOR ADIPATE LDH/UP NANOCOMPOSITES (SOURCE: [62])	50
FIGURE 12: STRUCTURE OF SINGLE AND MULTI-WALLED CARBON NANOTUBES (SOURCE: [79])	54
FIGURE 13: HEAT RELEASE RATE CURVES FOR EPOXY/CNT NANOCOMPOSITES (SOURCE: [88])	55
FIGURE 14: SEM MICROGRAPHS OF TWO MAGNIFICATIONS- 1000x(A) AND 100 000x (B) – FOR 1% AND 1000x MAGNIFICATION FOR 5% (C) AND 10% (D) OF NANO-Mg(OH) ₂ -EPOXY COMPOSITES.....	70
FIGURE 15: DSC CURVES FOR THE PURE EPOXY RESIN WITH NANO-Mg(OH) ₂ -EPOXY COMPOSITES APP-EPOXY COMPOSITES, MEASURED UNDER A NITROGEN ATMOSPHERE.....	70
FIGURE 16: HEAT RELEASE RATE (HRR) CURVES FOR THE EPOXY RESIN, NANO-Mg(OH) ₂ -EPOXY COMPOSITES AND APP-EPOXY COMPOSITES.....	72
FIGURE 17: MASS LOSS CURVES OF 5 WT% NANOCLAY FILLED EPOXY RESIN	81
FIGURE 18: MASS LOSS CURVES OF 1 WT% CNT FILLED EPOXY RESIN	82
FIGURE 19: MASS LOSS CURVES OF 5 WT% FR FILLED EPOXY RESIN.....	84
FIGURE 20: XRD SPECTRA OF NANOCLAYS AND NANOCLAY RESIN SAMPLES: R5-LD (TOP LEFT), R5-FR (TOP RIGHT), R5-N2 (BOTTOM LEFT), R5-N116 (BOTTOM RIGHT)	85
FIGURE 21: HEAT RELEASE RATE CURVES OF 5 WT% NANOCLAY FILLED EPOXY RESIN	85
FIGURE 22: RESIDUES OF 5% NANOCLAY-FILLED RESIN AFTER CONE CALORIMETER TESTS: A) 5 WT% ANIONIC MODIFIED CLAY, (B) 5 WT% ANIONIC NON-MODIFIED CLAY, (C) 5 WT% CATIONIC MODIFIED CLAY, (D) 5 WT% CATIONIC NON-MODIFIED CLAY.....	87
FIGURE 23: HEAT RELEASE RATE CURVES OF 1 WT% CNT FILLED EPOXY RESIN.....	88
FIGURE 24: RESIDUES OF 1% CNT FILLED RESIN AFTER CONE CALORIMETER TESTS (A) CNT NO TREATMENT (B) CNT COOH FUNCTION (C) CNT THERMALLY OXIDIZED	89

FIGURE 25: (A) HEAT RELEASE RATE CURVES OF 5 WT% FR FILLED EPOXY RESIN (B) RESIDUE OF 5% ATH FILLED RESIN (C) RESIDUE OF 5% APP FILLED RESIN.....	90
FIGURE 26: ELECTRON MICROSCOPY OBSERVATIONS OF NANOCLAY FILLED CARBON FIBRE COMPOSITE PLATES (A) ANIONIC NON-MODIFIED CLAY (5000x) (B) ANIONIC MODIFIED CLAY (5000x).....	92
FIGURE 27: ELECTRON MICROSCOPY OBSERVATIONS OF CNT FILLED CARBON FIBRE COMPOSITE PLATES (A) CNT NO TREATMENT (10000x) (B) CNT COOH FUNCTION (10000x) (C) CNT THERMALLY OXIDIZED (10000x).....	93
FIGURE 28: HEAT RELEASE RATE CURVES OF (A) 5 WT% NANOCLAY FILLED CFRP COMPOSITES (B) 1 WT% CNT FILLED CFRP COMPOSITES (C) 5 WT% FR FILLED CFRP COMPOSITES	95
FIGURE 29: TAPE CASTING PROCESS FLOWSHEET.....	106
FIGURE 30: ASPECT OF THE CERAMIC TAPE AFTER CASTING AND FLEXIBILITY IN THE GREEN STATE.....	107
FIGURE 31: THERMAL STABILITY OF THE CERAMIC TAPES AS A FUNCTION OF TEMPERATURE	108
FIGURE 32: SCANNING ELECTRONIC MICROSCOPY PICTURES OF COMPOSITE SAMPLE SURFACES AT DIFFERENT MAGNIFICATIONS: (A) CF-TA, 20000x (B) CF-TB, 20000x (C) CF-TC, 20000x (D) CF-TA, 500x (E) CF-TB, 5000x (F) CF-TC, 5000x.....	109
FIGURE 33: COMPOSITIONAL MAPPING OF TAPE B: (A) ALUMINIUM (B) CALCIUM (C) CARBON (D) OXYGEN (MAGNIFICATION 23000x).....	110
FIGURE 34: FIRE REACTION PROPERTIES OF COMPOSITE SAMPLES: (A) HEAT RELEASE RATE (B) SPECIFIC EXTINCTION AREA (C) TOTAL HEAT RELEASED (D) MASS %	111
FIGURE 35: PICTURES OF COMPOSITE SAMPLES WITH CERAMIC TAPES AS COATINGS (A) TAPE A (B) TAPE B (C) TAPE C	112
FIGURE 36: SAMPLE HOLDER WITH CALCIUM SILICATE BOARD USED IN CONE CALORIMETER TESTS WITH TEMPERATURE MEASUREMENT (LEFT) AND UNPROTECTED SAMPLE WITH THERMOCOUPLE WIRES (RIGHT)	117
FIGURE 37: (A) SAMPLE WITH 2 MM OF AQUEOUS PAINT BEFORE CONE CALORIMETER TEST (B)(C) DETAILED VIEW OF THE SAMPLE ACROSS THE THICKNESS, SHOWING GOOD ADHERENCE BETWEEN THE PAINT AND THE COMPOSITE MATERIAL.....	118
FIGURE 38: DIFFERENT STAGES OF UNPROTECTED SAMPLE BURNING BEHAVIOUR DURING CONE CALORIMETER TESTS: (A) SMOKE RELEASE BEFORE IGNITION (B) INTENSE FLAMES AFTER IGNITION (C) BURNING ONLY AT THE SIDES OF THE MATERIAL (D) SAMPLE AFTER EXTINGUISHING	118
FIGURE 39 : INTUMESCENCE FORMATION OF THE PAINT AFTER CONE CALORIMETER TESTS (A) 0.5 MM OF PAINT (B) 1.0 MM OF PAINT (C) 2.0 MM OF PAINT	119
FIGURE 40: DIFFERENT STAGES OF SAMPLES PROTECTED WITH INTUMESCENT WATER BASED PAINT BURNING BEHAVIOUR DURING CONE CALORIMETER TESTS (A) FORMATION OF INTUMESCENCE BEFORE IGNITION (B) FLAMES STARTING IN THE CORNERS OF THE SAMPLE (C) HIGHER FLAMES, LOCATED MAINLY IN THE CORNERS OF THE SAMPLE.....	119
FIGURE 41: (A) HEAT RELEASE RATE AS A FUNCTION OF TIME (B) PEAK AND AVERAGE HEAT RELEASE RATE AS A FUNCTION OF PAINT THICKNESS.....	121
FIGURE 42: (A) SPECIFIC EXTINCTION AREA AS A FUNCTION OF TIME (B) PEAK AND AVERAGE SPECIFIC EXTINCTION AREA AS A FUNCTION OF PAINT THICKNESS	122

FIGURE 43: (A) CARBON MONOXIDE YIELD AS A FUNCTION OF TIME (B) CARBON DIOXIDE YIELD AS A FUNCTION OF TIME (C) PEAK AND AVERAGE CARBON MONOXIDE YIELD AS A FUNCTION OF PAINT THICKNESS (D) PEAK AND AVERAGE CARBON DIOXIDE YIELD AS A FUNCTION OF PAINT THICKNESS	124
FIGURE 44: (A) REMAINING MASS AS A FUNCTION OF TIME (B) REMAINING MASS AS A FUNCTION OF PAINT THICKNESS	125
FIGURE 45: (A-C) UNPROTECTED SAMPLE (D-F) SAMPLE WITH 0.5MM AQUEOUS PAINT (G-I) SAMPLE WITH 1.0MM AQUEOUS PAINT (J-L) SAMPLE WITH 2.0MM AQUEOUS PAINT, ALL AFTER BEING TESTED	127
FIGURE 46: TEMPERATURE PROFILES OBTAINED AT DIFFERENT MATERIAL THICKNESSES (A) 2 MM (B) 4 MM (C) 6 MM (D) 7.5 MM	128
FIGURE 47: TEMPERATURE AND DERIVATIVE TEMPERATURE AS A FUNCTION OF TIME FOR UNPROTECTED SAMPLE	129
FIGURE 48: (A) MAXIMUM TEMPERATURES REACHED FOR ALL MATERIAL PAINT THICKNESSES (B) TIME TO REACH SPECIFIED TEMPERATURES AS A FUNCTION OF PAINT THICKNESS (AVERAGE VALUES FOR DIFFERENT MATERIAL DEPTHS).....	130
FIGURE 49: THERMAL DECOMPOSITION BEHAVIOUR OF ATH AND APP.....	138
FIGURE 50: CHEMICAL STRUCTURES OF APP: (A) APP FORM I (B) APP FORM II	139
FIGURE 51: CURE BEHAVIOUR OF HIGH (A, C) AND LOW (B, D) VISCOSITY EPOXY RESINS OBTAINED AT THREE DIFFERENT HEATING RATES AS A FUNCTION OF TEMPERATURE (A, B) OR TIME (C, D).....	140
FIGURE 52: INFLUENCE OF AMMONIUM POLYPHOSPHATE (A) AND ALUMINIUM TRIHYDRATE (B) FILLERS ON THE TOTAL HEAT OF REACTION OF HIGH VISCOSITY EPOXY RESIN.....	141
FIGURE 53: INFLUENCE OF AMMONIUM POLYPHOSPHATE (A) AND ALUMINIUM TRIHYDRATE (B) FILLERS ON THE TOTAL HEAT OF REACTION OF LOW VISCOSITY EPOXY RESIN.....	141
FIGURE 54: REACTION RATE AS A FUNCTION OF FRACTIONAL CONVERSION FOR HIGH (A) AND LOW (B) VISCOSITY EPOXY RESINS.....	142
FIGURE 55: FRACTIONAL CONVERSION AT SELECTED TEMPERATURES OBTAINED AT 5 °C/MIN FOR FILLED RESIN SAMPLES (A) HIGH AND (B) LOW VISCOSITY EPOXY RESIN	143
FIGURE 56: VARIATION OF MAXIMUM CURE TEMPERATURE AS A FUNCTION OF HEATING RATE FOR HIGH VISCOSITY RESIN (A) EFFECT OF APP (B) EFFECT OF ATH AND LOW VISCOSITY RESIN (C) EFFECT OF APP (D) EFFECT OF ATH.....	144

List of Tables

TABLE 1: RESUME OF PAPERS IN OPEN LITERATURE REPORTING THE USE OF NANOCCLAYS FOR FLAME RETARDANCY	45
TABLE 2: RESUME OF PAPERS IN OPEN LITERATURE REPORTING THE USE OF CARBON NANOTUBES FOR FLAME RETARDANCY.....	57
TABLE 3: GLASS TRANSITION TEMPERATURES AND THE ONSET TEMPERATURES OF DEGRADATION BY PYROLYSIS FOR PURE EPOXY RESIN AND COMPOSITE SAMPLES.....	71
TABLE 4: CHARACTERISTICS OF THE NANOCCLAYS USED.....	77
TABLE 5: COMPOSITION OF THE SAMPLES.....	79
TABLE 6: FIBRE CONTENT OF THE CFRP COMPOSITE PLATES.....	80
TABLE 7: TEMPERATURES AT 5% MASS LOSS, PEAK IN FIRST DERIVATIVE MASS LOSS CURVE AND FINAL RESIDUE OF 5 WT% NANOCCLAY FILLED EPOXY RESIN	81
TABLE 8: TEMPERATURES AT 5 AND 50% MASS LOSS AND FINAL RESIDUE OF 1 WT% CNT FILLED EPOXY RESIN ...	82
TABLE 9: TEMPERATURES AT 5 AND 50% MASS LOSS AND FINAL RESIDUE OF OF 5 WT% FR FILLED EPOXY RESIN.	84
TABLE 10: RESUME OF THE OBTAINED RESULTS FROM CONE CALORIMETER TESTS ON RESIN SAMPLES	91
TABLE 11: GLASS TRANSITION TEMPERATURES OF COMPOSITE SAMPLES.....	93
TABLE 12: RESUME OF THE OBTAINED RESULTS FROM CONE CALORIMETER TESTS ON COMPOSITE PLATE SAMPLES	96
TABLE 13: COMPONENTS REQUIRED FOR THE PRODUCTION OF A TAPE CASTING SLURRY FORMULATION [13][14]	104
TABLE 14: CERAMIC TAPES PRODUCED BY TAPE CASTING.....	106
TABLE 15: COMPOSITE MATERIALS PRODUCED.....	107
TABLE 16: RESUME OF THE MAIN FIRE REACTION PROPERTIES OF THE TESTED SAMPLES.....	120
TABLE 17: PROPERTIES OF THE TWO RESIN SYSTEMS TESTED IN CURE KINETICS STUDIES.....	134
TABLE 18: FORMULATIONS PREPARED AND TESTED FOR CURE KINETICS STUDIES	134
TABLE 19: ONSET AND PEAK DEGRADATION TEMPERATURES OF ATH AND APP.....	138
TABLE 20: AVERAGE HEAT OF REACTION OBTAINED FROM DYNAMIC SCANS FOR ALL RESIN SAMPLES.....	140
TABLE 21: ACTIVATION ENERGIES AND ARRHENIUS PRE-EXPONENTIAL FACTORS OBTAINED USING KISSINGER MODEL	145

List of Abbreviations

α	Degree of conversion (or extent of reaction)
A	Arrhenius pre-exponential factor
AHRR	Average Heat Release Rate
AMLR	Average Mass Loss Rate
APP	Ammonium polyphosphate
ASEA	Average Specific Extinction Area
ATH	Aluminium hydroxide
β	Heating rate (dT/dt) (°C/min)
B/D	Borchardt and Daniels
BET	Brunauer–Emmett–Teller Theory
CF	Carbon Fibre
CFRP	Carbon Fibre-Reinforced Polymer
CNF	Carbon nanofibres
CNT	Carbon Nanotubes
CP	Ceepree
$d\alpha/dt$	Reaction Rate
DSC	Differential Scanning Calorimetry
DGEBA	Diglycidyl Ether of Bisphenol-A
DMA	Dynamic Mechanical Analysis
DWCNT	Double-Walled Carbon Nanotubes
E_a	Activation Energy
EP	Epoxy
EVA	Ethylene-Vinyl Acetate
FR	Flame Retardant
FRP	Fibre Reinforced Polymer
FTIR	Fourier Transform Infrared Spectroscopy
HRR	Heat Release Rate
GFRP	Glass Fibre-Reinforced Polymer
k	Rate Constant
LCA	Life Cycle Assessment
LDH	Layered Double Hydroxide
LFT	Long Fibre-Reinforced Thermoplastic

LOI	Limiting Oxygen Index
MH	Magnesium Hydroxide
MLR	Mass Loss Rate
MMT	Montmorillonite
MWCNT	Multi-Walled Carbon Nanotubes
n	Reaction Order
NMH	Nano Magnesium Hydroxide
PAN	Polyacrylonitrile
PA6	Polyamide 6
PE	Polyethylene
PHRR	Peak Heat Release Rate
PMLR	Peak Mass Loss Rate
POSS	Polyhedral Oligomeric Silsesquioxane
PP	Polypropylene
R	Gas Constant
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RTM	Resin Transfer Moulding
SEA	Specific Extinction Area
SEM	Scanning Electron Microscopy
SWCNT	Single-Walled Carbon Nanotubes
t_{PHRR}	Time to peak heat release rate
TGA	Thermogravimetric Analysis
T_g	Glass Transition Temperature
TGDDM	Tetraglycidyl Diamino Diphenyl Methane
THR	Total Heat Released
THE	Total Heat Evolved
T_p	Peak Temperature
TSP	Total Smoke Produced
TSR	Total Smoke Released
TTI	Time to Ignition
TTT	Temperature–Time–Transformation
UL94	Underwriters' Laboratory UL94 Test
UP	Unsaturated Polyester

1 Flame Retardancy of Fibre Reinforced Polymer Composites based on Nanoclays and Carbon Nanotubes

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Abstract

An introduction to the most widely used fibre reinforced polymer composites, their applications, advantages and fire behaviour concerns is presented. The effects of fire intensity, structure (e.g. resin composition and content, fibre type and organization, fibre sizing agents) and specimen thickness on composites fire reaction properties are discussed. It is intended here to bring out the state of the art regarding the most recently approached flame retardant solutions for composite materials, namely through the use of nanoclays and carbon nanotubes. Despite the large number of polymers and fibres combinations used in these composites, only the properties of the most commonly used thermoset matrices - epoxy and unsaturated polyester resins - and reinforcing fibres - glass and carbon - will be addressed here.

Keywords: flame retardancy, polymer nanocomposites, FRP, nanoclays, carbon nanotubes

1.1 Introduction

Fibre reinforced polymer (FRP) composites have been in a sustained growth use since the 1960s. Their advantages over other materials for high-performance and lightweight applications have increased their exploration and usage in many industries such as aerospace, automobile, civil infrastructures, sports and marine. It is expected that the use of composite materials continues to grow in coming years with emerging applications in large bridge structures, wind blades, offshore platforms, engine machinery, computer hardware and medical devices [5].

Key advantages of FRP composites over many metal alloys include low density, high specific stiffness and specific strength, good fatigue endurance, excellent corrosion resistance, outstanding thermal insulation and low thermal expansion.

However, composites have several disadvantages related to their anisotropic structure, low through-thickness mechanical properties, poor impact damage tolerance and poor performance in fire, mainly due to their polymeric or organic constitution. Polymers are in general highly flammable and produce large quantities of smoke and toxic gases.

With the increasing usage of composites, these polymers may be brought into fire situations at any time, adding urgency for the development of effective and environmental friendly flame retardant systems to reduce fire hazards.

Commercially available flame retardants for polymers matrices can be highly effective, but have some important disadvantages, such as a negative influence on the resin workability (e.g. viscosity, reactivity), the quality (physical and mechanical properties) of the final

product, in addition to being harmful (e.g. halogenated based flame retardants). The concept of nanoscale reinforcement and flame retardancy provides opportunity for synthesis of new polymer materials with unique properties. Several nanoparticles, like nanoclays and carbon nanotubes, can also represent a rational alternative to the conventionally filled polymers because they have distinct advantages over traditional flame retardants on its related problem areas.

An overview of the effects of different nano- and microscale materials (e.g. glass and carbon fibres) on the flammability of advanced fibre reinforced polymer composites will be detailed and discussed in this chapter. Its goal is to bring together the recent bibliographic reviews and experimental results obtained for different materials. The synergetic effect of inorganic based traditional flame retardants will also be mentioned.

1.2 Fibre Reinforced Polymer Composites

1.2.1 Introduction

A composite material can be defined as a heterogeneous mixture of two or more materials. The term composite was originally used in the engineering field when two or more distinct materials were combined into one with the intention of overcoming the individual limitations and favour individual advantages [1][2]. The final properties of a composite material depend on both the nature of the constituent materials, and on their physical or chemical affinity. In fibre reinforced polymer (FRP) composites, the major constituents are the polymer matrix and the reinforcing fibres. The role of the polymer matrix, which is also called the continuous phase of the composite, is to primarily bind the fibres together by keeping them in the desired location and orientation, to act as a load transfer medium between fibres and to protect the fibres from environmental damages [3]. The reinforcing fibres carry out the structural load, reduce thermal stresses and provide macroscopic stiffness and strength.

Composite materials can be classified into three types based on reinforcing filler organization: particulate, fibrous (short or long fibre) and laminate. Particulate composites consist of a matrix reinforced by a dispersed phase in form of particles, which can have a random or preferred orientation. Composite laminates consist of several layers of fibrous materials dispersed in a polymeric, ceramic or metallic matrix, which can be combined in different fibre orientations (multilayer composite). A sandwich structure is a special type of composite material, composed of two or more thin layered composite materials attached to a relatively thick core material.

The type of polymer matrix, thermoset or thermoplastic, plays an important role in FRP composites processing manufacturing. Thermoset materials have in general low viscosity, 50 to 500 times more than water, and can easily impregnate the empty spaces between the fibres. These type of resins require an additional processing step known as curing, which involves the exothermic chemical reaction of cross-linking between the polymer chains. The high density of cross-linking within the thermoset structure is responsible for the superior thermal stability and mechanical properties. Epoxies, polyesters, vinyl esters and phenolic resins are the thermoset polymers commonly used as matrix in continuous or long fibre-reinforced composites. Unsaturated polyester resins are mostly used as matrix for glass fibre reinforced composites, due to their lower costs and mechanical properties.

Epoxies, on the other hand, are more expensive than polyester resins but have superior mechanical properties and good resistance to alkaline conditions. Epoxies are by far the most widely used polymer matrix for carbon fibre composites. The vinyl ester resins have properties that are intermediate between polyesters and epoxies, are easier to process than epoxies, coupled with a better chemical resistance than polyester resins. Phenolic resins are relatively cheap, have good high temperature performance, excellent fire and smoke properties and good resistance to acids [4]. Phenolic resins are cured by a condensation reaction, creating voids in their structure, which makes their mechanical properties far below other thermoset resins.

On the other hand, thermoplastic polymer chains do not cross-link and are highly viscous. Their viscosity can be high as 106 times higher than that of water. They flow after being heated-up and with effort (e.g. under pressure) fill the empty spaces between the reinforcing fibres. After the cooling-down step, the thermoplastic polymer chains keep their initial size, however the repetitive molecules (monomers) can be re-organized in different ways. Thermoplastic polymers are more commonly used in short fibre-reinforced composites that are injection-moulded; however, the interest in continuous or long fibre-reinforced thermoplastic (LFT) matrix is growing. Polyamides and polycarbonates are examples of thermoplastic polymers used as matrix in injection-moulded composites.

Various types of fibres are used as reinforcements for polymer composites. The fibre type, length, orientation and volume fraction are extremely important, since they influence the density, the mechanical and fire reaction properties, the electrical and thermal conductivities, and the cost of the material. Several types of fibres are commercially available however the most commonly used are glass and carbon fibres. Glass fibres are the most widely used reinforcement in polymeric matrix composite. The principal advantages of glass fibres are their low cost, high tensile strength, high chemical resistance and excellent insulating properties [2]. The main disadvantages are their relatively low tensile modulus, fatigue resistance and high density. Glass fibres are chemically inert in fire and retain their chemical and physical stability even at high temperatures and heat fluxes [5]. Glass fibres remain unaffected by the fire until heated up to 830 and 1050 °C in the case of E-glass and S-glass fibre types, respectively. Carbon fibres are available in various types, depending on their production method. The two most common types are polyacrylonitrile-based (PAN) and pitch-derived carbon fibres. The main advantages of carbon fibres are their high specific tensile strength and modulus, very low coefficient of linear thermal expansion, high fatigue strength and high thermal conductivity. The disadvantages are their high cost, low strain-to-failure, low impact resistance and high electrical conductivity, which may cause undesirable electrical discharges in unprotected equipment. When exposed directly to fire, carbon fibre's surface can be oxidized and the onset degradation temperatures are about 350 and 450 °C, respectively, for PAN and pitch-based fibres.

A key ingredient in the successful production of a material or a component is a cost-effective and reliable manufacturing method [1]. Hand layup, compression moulding, pultrusion, resin transfer moulding (RTM) and filament winding are examples of manufacturing processes for thermoset FRP composites. For thermoplastic based composites, the two most commonly used manufacturing techniques are extrusion and injection moulding.

1.2.2 Applications

Commercial and industrial applications of fibre-reinforced polymer composites are diverse in both structural and non-structural application areas due to their many outstanding physical, thermal, chemical and mechanical properties. The major structural application areas include aircraft, space, automotive, sporting goods, marine, infrastructures and building construction (e.g., floor beams). In non-structural applications, fibre-reinforced polymer composites are also used in electronics (e.g., printed circuit boards), furniture (e.g., chair springs), power industry (e.g., transformer housing), oil industry (e.g. offshore oil platforms and oil sucker rods used in lifting underground oil), medical industry (e.g., bone plates for fracture fixation, implants, and prosthetics) and in many industrial products, such as step ladders, oxygen tanks, and power transmission shafts [1]. Their use requires careful design practice and appropriate process development based on the understanding of their unique characteristics.

Commercial aircrafts are one of the major applications for FRP composites. Airbus was the first commercial manufacturer to make an extensive use of composites in their A310 aircraft, introduced in 1987. Figure 1 shows the distribution of different composite materials used on Airbus A380, introduced in 2006. About 25% of its weight is made of composites, including 23% of carbon fibre-reinforced polymer. Some of the components in composites are the central torsion box, the tail, the flaps, spoilers and ailerons.

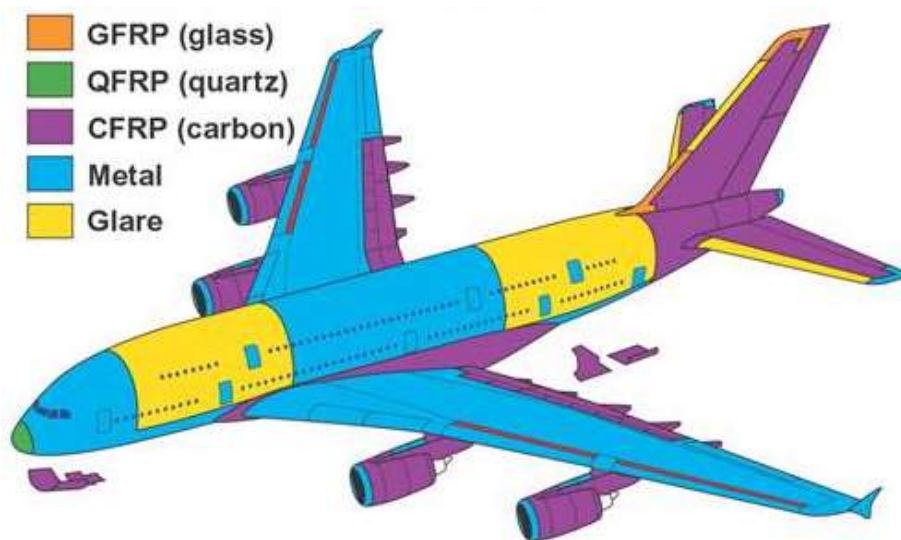


Figure 1: Use of fibre-reinforced polymer composites in airbus A380 (source: [6])

According to Airbus, the use of composite materials has increased the service intervals for the aircraft from six years to twelve, significantly reducing maintenance costs. The high percentage of composites also reduces the need for fatigue-related inspections, usually required on more traditional aluminium jetliners, and lessens the requirement for corrosion-related maintenance checks. Boeing has started the use of composites in 1995, with the incorporation of about 10% of carbon fibre-reinforced epoxy. The next line of airplanes, called Boeing 787 Dreamliner is pushing the envelope with a total composite of 50% by weight, including the integration of an all composite fuselage, wings and tail [6]. In aerospace industry, materials used in external structures are usually carbon fibre epoxy

composites, while glass/phenolic composites are mostly used in internal structures such as walls and ceilings. In all cases, mostly thin sections of composite laminates are used. The main reasons for using these materials in aerospace are: weight savings, with consequent fuel saving and payload increasing; reduction in the number of components and fasteners; higher fatigue and corrosion resistance; furthermore, FRP fabrication allows the possibility of aeroelasticity tailoring the stiffness of the airframe structure. The key limiting factors in using CFRP in aircraft structures are the high cost, relatively low impact damage tolerance, susceptibility to lightning damage and low fire resistance.

Applications in automotive industry can be classified in three groups of components: body, chassis and engine. Glass fibre reinforced polymer (GFRP) are the primary composite materials used in automobiles, however, it is recognized that the vehicle weight reduction for improved fuel efficiency can only be achieved with carbon fibre composites because of their higher specific strength and stiffness. Cars can start a fire in several ways, namely through mechanical failures, breakages, leaks and electrical faults. Fire tests have shown that a fire starting in the engine compartment of a modern car results in flames reaching the passenger cabin in 10 to 20 minutes. Plastics in the engine compartment and body panels represent a real fire hazard and are not (yet) subject to any particular performance test [7]. Fire safety requirements for cars are lower than for public transportations; however, legislation in this field of application is becoming more restrict.

Composites also find several applications in the railway industry. They are commonly used in passenger coaches due to their excellent structural properties and improved aesthetics. In this particular case, glass fibre reinforced with polyesters, epoxies and phenolic resins are the most commonly used materials. Weight savings in the order of 50% for structural and 75% for non-structural applications benefits a high-speed transportation, reduces power consumption and increases the ability to carry greater pay-loads. Composites also provide greater versatility in train design and optimization of train performance, such as lowering the center of gravity for enhanced stability. In transportation industries, glass fibres with unsaturated polyester or vinyl ester resins are the most commonly used FRP composites. These materials are also used in marine industries in the form of thick sections of composite laminates.

Although advanced polymer composite materials have been used mostly in transportation industries, in the last decades there has been a growing awareness amongst civil engineers of the importance of the unique mechanical and in-service properties of these materials, along with their customized fabrication technologies. FRP composites have been therefore employed not only in new construction of structures, but also as reinforcement materials in concrete, bridge decks, modular structures, formwork and external reinforcement for strengthening and seismic upgrade [8][9].

1.2.3 Main Concerns

Composites have several disadvantages and problems, such as low through-thickness mechanical properties, poor impact damage tolerance, anisotropic structure and significantly poor performance in fire, that have hindered their growth on some markets like such as aircrafts and naval applications. As example, aircraft fires are extremely hazardous due the difficulty to escape from the fire scenario. In addition, aircraft composites

must have excellent fire resistant properties to prevent structural failure during and after a fire [5].

Many polymer composites ignite when exposed to high heat fluxes, releasing heat that can, in some circumstances, contribute to the growth of the fire. Significant quantities of smoke and toxic fumes may also be released, limiting visibility and posing a serious health hazard. For these reasons, stringent fire regulations govern the use of composites in aircraft, ships, buildings, land transport, oil and gas facilities, and other applications. These regulations require that the fire reaction properties of these materials meet specified levels. The reaction properties that are often used to define the fire hazard include heat release rate, time-to-ignition and flame spread rate.

In spite of such unfavorable properties, FRP materials present other attributes that are advantageous in a fire situation. In contrast with other traditional materials, such as steel, composites are very good heat insulators, and this feature is important for slowing the spread of fire from room to room [10]. Also when compared to steel, composites present better burn-through resistance, providing an effective barrier against flame, heat, smoke and toxic fumes. Furthermore, several procedures can be applied to improve the fire performance of FRP materials [11].

1.3 Fire Behaviour, Test Methods and Fire Reaction Properties

1.3.1 Fire Behaviour

Fire is a complex event that can be developed in stages of increasing temperature and size before decaying. This event becomes even more complex when polymer composite materials are involved because they contribute (as a rich source of fuel) to temperature, size and spread of the flame. The initiation and growth of a fire is determined by several factors: type, load and area of the fuel, oxygen content, wind speed, and closed or open space [5]. The fire hazard increases in enclosed spaces, such as in aircraft cabins and railway compartments, due to the heat, smoke and toxic gases entrapment. Within a closed compartment and according to the respective conditions, a fire can be distributed in four main stages:

- Ignition: materials are exposed to an ignition source, good exposure to air, low temperatures;
- Developing fire: the fire will grow and the environment temperature will continue to rise, resulting in external heat fluxes in the range of 20-60 kW/m² and ventilated temperatures to 300-800 °C;
- Fully developed fire: this stage occurs when the heat release rate and temperature of a fire are at their maximum, resulting in high external heat fluxes, >40 kW/m², low ventilation and temperatures >800 °C;
- Decay: occurs after the consumption of all combustible materials.

Different fire properties are discernible in each of these stages. Materials ignitability and flammability is determined in an ignition scenario. Heat release and flame spread control the fire behaviour in a developing fire. Fire load and fire penetration are the critical aspects of fire behaviour in fully developed fires [12].

1.3.2 Test Methods

The fire behaviour of polymeric materials is primarily characterised by their ignitability, flame-spread rate and heat release. The appropriate tests needed for measuring the fire behaviour depend on the application of the target materials. Each experimental setup or test defines a specific fire scenario and differ in their heat and mass transport characteristics such as applied heat flux, temperature, horizontal/vertical position, length scale and ventilation [12][13][14]. Therefore, each fire test characterises the performance resulting from an interaction of material properties, specimen and defined fire scenario. The obtained results may have little relevance for other fire scenarios or fire tests.

There are numerous flammability tests used in industrial or academic laboratories, either for screening materials during product development or testing manufactured products. The three more commonly used laboratory test methods for studies of polymer flammability are: UL-94 vertical burning test, limiting oxygen index (LOI) and cone calorimeter.

Underwriters' laboratory UL94 test (Figure 2) is designed to assess the ignitability and flame spread of polymeric materials exposed to a small flame. It is accepted for standardization in many countries and provides three major classifications of materials flammability. The three categories, V-0, V-1 and V-2, depend on the performance of the material, regarding the burning duration of individual and all specimens and also on the presence or absence of burning drips.

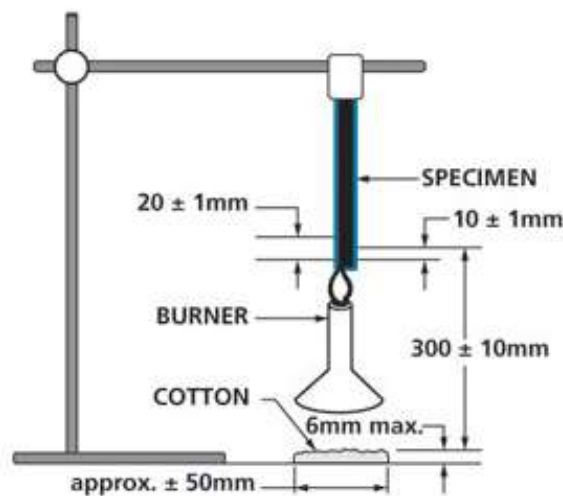


Figure 2: UL94 test for flammability for V0, V1 and V2 classification (source:[15])

The LOI test (Figure 3) is a screening tool and does not represent a real fire scenario. It is applied to quantify the resistance to ignition of material. The purpose of this test is to assess the minimum oxygen concentration in an oxygen/nitrogen mixture that is able to support the combustion of the material for at least 3 minutes or for the consumption of 5 cm of the same sample. The more the oxygen required, the more flame retarded the material is [16].

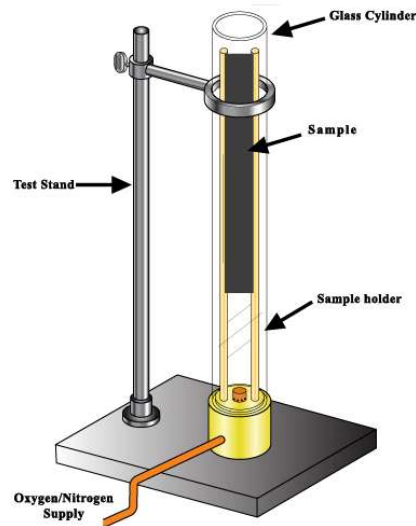


Figure 3: Experimental set-up for LOI measurement (source:[17])

Cone calorimeter has become one of the most important and widely used instruments for the research and development of fire retarded polymeric materials [13]. The popularity of this method is due to the fact that it allows the determination of several parameters in one single test, using samples with reduced dimensions, plates with 100x100 mm² in size [5]. The sample size is of the smallest order of magnitude discussed in fire engineering and of the largest used in polymer analysis. In addition, the cone setup was developed thoroughly to target the properties of materials rather than to correspond to a special full-scale scenario of a real fire [13]. Cone calorimeter investigations can be used as a universal approach to ranking and comparing the fire performance of different materials, pass or fail a material according to a certain fire criteria, assess the likely response of a material when exposed to a large fire and generate fire reaction data to validate fire models [5][13][18].

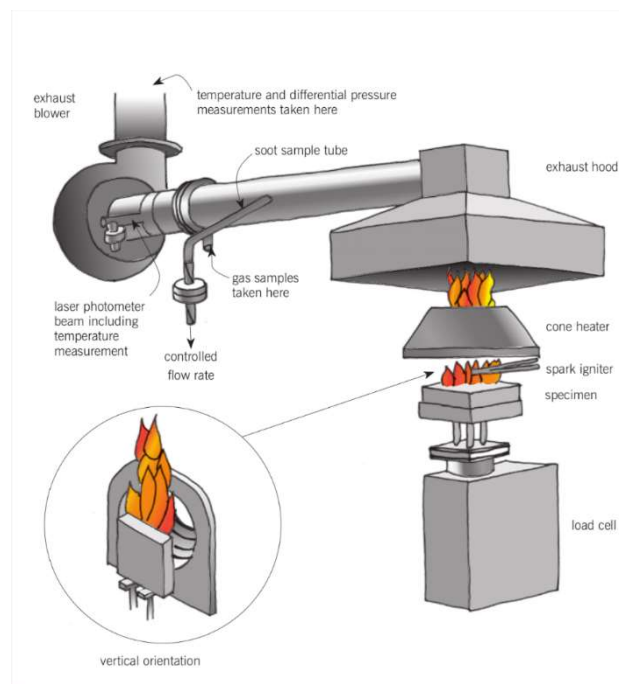


Figure 4: Schematic representation of a cone calorimeter (source: [19])

Fire tests using the cone calorimeter involve exposing a flat specimen to an incident heat flux generated by the cone shaped heater. It consists of an electric heater rod that is tightly wound into the shape of the truncated cone. Heating is controlled using a thermostatically controlled radiant heater that is capable of submitting a specimen to any heat flux usually up to 100kW/m^2 . Fire tests can be performed with the specimen in a horizontal or vertical direction. Tests are usually performed in the horizontal orientation because in this mode the convective component of heat transfer is almost negligible, although vertical tests may be preferred if the actual fire scenario involves a vertical face [5]. The combustion gases produced pass through the heating cone and are captured by means of an exhaust duct system with a centrifugal fan and a hood. The gas flow, oxygen, CO and CO₂ concentrations and smoke density are measured in the exhaust duct. The gas flow and oxygen concentration measurements are used to calculate the quantity of heat released per unit of time and surface area: the HRR (heat release rate), expressed in kW/m^2 . In addition, the cone calorimeter test also enables characterisation of time to ignition, mass loss and total smoke released [20].

1.3.3 Fire Reaction Properties

Of the many fire reaction properties, it is generally recognized that *heat release rate* (HRR) is the single most important parameter in controlling fire hazard. The amount of heat released from a polymer composite is controlled by the combustion of flammable gas products resulting from the decomposition of the organic components. The heat release rate is a complex property determined by the balance of the heat released by the flammable volatiles and the heat absorbed by the endothermic decomposition reactions occurring in the condensed phase or solid composite. Mouritz and co-authors [21] correlated smoke density, carbon monoxide and carbon dioxide yield, mass loss rate, total mass loss and flame spread with the heat release rate.

The *peak of heat release rate* (PHRR) is not only the cone calorimeter result probably most communicated to the polymer science community, but also a characteristic that displays a very strong and quite complex dependence on the fire scenario defined by the cone calorimeter setup. The PHRR represents the maximum amount of heat released by the material during the combustion process and frequently occurs shortly after the ignition. This is also considered a critical parameter as it controls the maximum temperature achieved during combustion and the rate of flame spread [5]. The peak heat release rate is strongly dependent not only on the properties of the material, but also on the geometry and the conditions of the fire test [13], as will be discussed afterwards.

From the curve of HRR versus time, the *total heat released* (THR) during a cone calorimeter test can also be determined. It is calculated as the integral of the HRR curve with respect to time, representing the total heat output up to that time. The THR depends strongly on the total mass loss, the effective heat of combustion of the volatiles and the combustion efficiency in the flame zone [14].

Time to ignition is defined as the time a combustible material can support, when exposed to a constant radiant heat flux, before initiating ignition and be subjected to combustion with continuous flame. It can be used as a simple measure of the material's resistance to fire [21]. The ignition time depends on several factors, namely the oxygen availability, the

temperature and the chemical and thermo-physical properties of the polymeric matrix and the reinforcement.

Mass loss is another important parameter when characterizing the fire reaction properties of a material, since it represents a quantitative measurement of the materials that decompose in a fire. The amount and rate of decomposition of the organic substances of a composite material can be determined by measuring the weight variation of the sample during cone calorimeter testing. The total mass loss is largely conditioned by the char yield of the organic constituents. Composites that yield a small amount of char experience a greater mass loss than materials with a high char yield. The mass loss rate is not constant, because it is controlled by diverse thermal processes that change with time, including ignition, combustion, char formation and the transition of the material's behaviour from thermally thick to thermally thin [5]. A sample is considered to be thermally thin when its thickness is below 1-2 mm.

Smoke is a combination of complete and incomplete combustions species, which can be composed of water, carbon dioxide and monoxide, acid gases and soot. Additionally, it can also contain small fibre fragments [22]. Depending on the ventilation and burning rate, smoke can be the main fire hazard; it can be extremely dense and consequently reduce visibility and cause disorientation during a fire. Furthermore, carbon monoxide is toxic and acid gases are irritating to eyes. In fact, it is known that most deaths in a fire are caused by inhalation of smoke and toxic combustion gases, carbon monoxide being the most common cause. Smoke formation during burning of a material is not an inherent property. The level of smoke actually measured in a test depends on the burning conditions (heat flux, oxidant supply, specimen geometry, presence or absence of flame) as well as the test conditions (ambient temperature, test chamber volume, ventilation) [1]. The *specific extinction area* (SEA) is the parameter measured during cone calorimeter tests, which characterises the density of the released smokes. It describes how effectively a given mass of volatiles generated by the combustible material is converted into smoke [5]. SEA is expressed in m^2/kg , representing the amount of smoke released per mass unit of sample.

1.4 FRP Composites in Fire

1.4.1 Introduction

Fire performance is one of the most significant factors affecting the wider use of composites. When heated to moderate temperatures (100–200 °C), FRP materials soften and creep, causing a considerable reduction of both strength and stiffness. Furthermore, when FRP materials are exposed to high temperatures (300–500 °C), their organic matrix decomposes, releasing heat smoke, soot and toxic volatiles [5]. The behaviour of FRP composite materials in fire is governed largely by the chemical processes involved in the thermal decomposition of the polymer matrix. When present, organic fibres such as aramid, polyethylene, flax, hemp, are also important contributors in the material fire response. A description of the main processes involved in the thermal decomposition is presented in section 1.4.2.

The effects of the fire intensity, composite structure (e.g. resin composition and content, fibre type and organization, fibre sizing agents) and specimen thickness on the most critical fire reaction properties of FRP composites are described in section 1.4.3. Despite the large

number of polymers and fibres combinations used in composites, only the properties of the most commonly used thermoset matrices - epoxy and unsaturated polyester resins – and reinforcing fibres - glass and carbon - will be addressed here. The thermal stability and fire response of combustible organic fibres are out of the scope of this revision paper, even if some of them are extensively used.

1.4.2 Thermal Decomposition

The events involved in the decomposition of a FRP composite exposed to fire conditions are represented in Figure 5. When the composite material is exposed to a sufficiently large source of heat radiated from a fire, the organic components will start to thermally decompose, releasing volatile gases and airborne soot particles (smoke) and yielding liquid products, tar and solid carbonaceous char [5]. The volatiles consist of a variety of vapors and gases, both flammable (eg. carbon monoxide, methane, low molecular weight molecules or polymer fragments) and non-flammable (carbon dioxide, water). The flammable volatiles diffuse from the decomposing composite into the air creating a combustible gaseous mixture. These volatiles will react with the oxygen from air, leading to ignition, at low temperature when submitted to an external source of intense energy (spark, flame, etc.) or when the auto-ignition temperature is reached. After ignition, the combustion products are carbon dioxide and monoxide, soot and heat. When the amount of heat liberated reaches a certain level new decomposition reactions are induced in the solid phase. The combustion cycle is thus maintained [20]. As it is represented in Figure 5, this global process is complex and involves several reactions and transport phenomena in the solid, gaseous and interfacial phases.

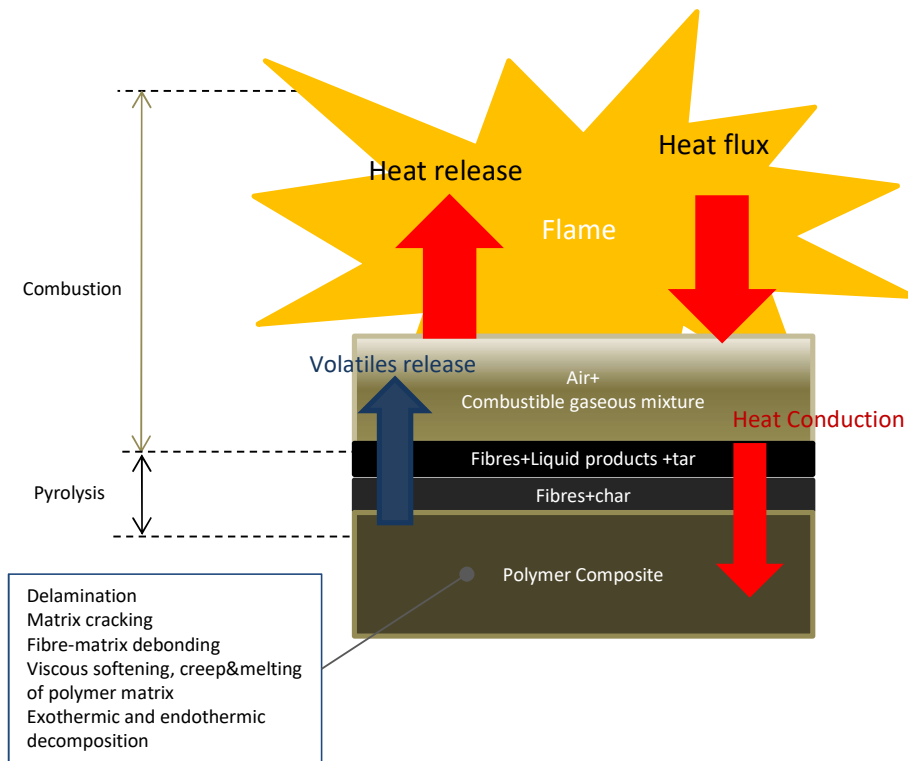


Figure 5: Schematic representation of the different phases, mechanisms and reaction processes involved during the exposure to fire of a polymer composite

Due to their chemical structure, made up mainly of carbon and hydrogen, polymers are the main source of flammable volatiles in a FRP composite. Thus, the amount of heat released is controlled by the combustion of flammable gas products resulting from the decomposition of the matrix when inorganic fibres are present.

The thermal decomposition of a polymer (i.e. covalent bond dissociation) is endothermic and therefore requires an input of energy. The amount of energy required to initiate combustion depends on the physical characteristics of the material. In the particular case of thermoset polymers, due to the absence of a melting point, the polymer immediately starts decomposing which occurs due to the dissociation of covalent bonds. Generally, thermal decomposition is the result of a combination of the effects of heat and oxygen where non-oxidizing and/or oxidizing thermal degradation take place. Polymers decompose through a series of chemical reaction mechanisms (mainly chain scissions) when heated to a sufficiently high temperature. The bonds requiring less energy are the first to break, with the liberation of volatile low molecular weight molecules (polymer fragments) that diffuse into the air. The thermal decomposition reactions of polymers may proceed by oxidative processes or simply by the action of heat (pyrolysis) [5]. The decomposition process is often accelerated by oxygen, but in thick composite sections it is generally only the surface region that decomposes in the presence of oxygen. The outgassing of volatiles from the decomposition zone obstructs the ability of oxygen to diffuse much beyond the surface layers of the composite. In oxidizing thermal conditions, the polymer reacts with oxygen in the air and generates a variety of low molecular weight products: carboxylic acids, alcohols, ketones, aldehydes, etc. Oxidation can lead to crosslinking through recombination reactions of the macromolecular radicals. However, bond scission usually remains the dominant reaction. In literature it is referred that at combustion temperatures below 300 °C, polymer degradation takes place via non-oxidizing thermal decomposition [20]. Under these conditions, the rate of pyrolysis is much faster than the diffusion of oxygen in the solid phase. Oxidation therefore only occurs in the gas phase due to the presence of low molecular weight compounds produced by thermal decomposition.

The processes occurring within a polymer laminate exposed to fire conditions and illustrated in Figure 5 are described by Mouritz and co-workers [18] and can be resumed as follows:

- Thermal processes: heat conduction from the fire into the composite; heat generated or absorbed from decomposition of the polymer matrix; convective heat transported by hot reaction gases and water vapours coming from the composite; heat generated through char or fibre oxidation; and heat generated by the ignition of flammable reaction gases at the composite/fire boundary.
- Chemical processes: this involves decomposition and volatilization of the polymer matrix; formation, growth and oxidation of char; oxidation of carbon fibres; and char/fibre reactions.
- Physical processes: this involves thermal expansion and contraction, viscous softening and melting of the matrix; thermally-induced strains; internal pressure build-up due to the formation of volatile gases and vaporization of water; formation of gas-filled pores; matrix cracking; fibre–matrix interfacial debonding; delamination damage; surface ablation; and softening, melting and fusion of fibres.

- **Failure processes:** the failure mode depends on the temperature, heat flux and duration of the fire; magnitude and type of load (e.g. tension, compression, bending, torsion); and geometry of the structure.

1.4.3 Fire Reaction Properties versus Composite Structure and Fire Intensity

Fire reaction properties of FRP composites used in aerospace, marine and infrastructure applications have received an increasing interest. As a result, the fire reaction behaviour of these materials have been extensively characterised, and a large data of information is available regarding their time-to-ignition, heat release rate, limiting oxygen index, flame spread, smoke density and smoke toxicity properties [5][21]. However, fire reaction behaviour of composite materials is greatly dependent on different parameters. In this section the effects of fire intensity, resin composition, resin content, fibre type and organization, fibre sizing agents and specimen thickness on the most critical fire reaction properties of FRP composites are described.

i. Fire Intensity

External heat flux or fire intensity is one of the fire conditions that greatly affect the fire reaction properties of a composite. Figure 6 shows the effect of heat flux on the ignition times of two different composite laminates. One can observe from the figure that the fire intensity shows a more pronounced effect on the flammability of carbon/epoxy composite, rather than for glass/polyester composite. The composites do not ignite below a threshold heat flux, even after exposure to fire for a very long time [5]. The onset heat flux is ~ 13 kW/m² for polyester and epoxy based composites, and ~ 25 kW/m² for phenolic based composites. An increase in heat flux (or environment temperature) increases rapidly the matrix pyrolysis with consequent production of volatiles that flows out of the composite, thereby promoting the ignition.

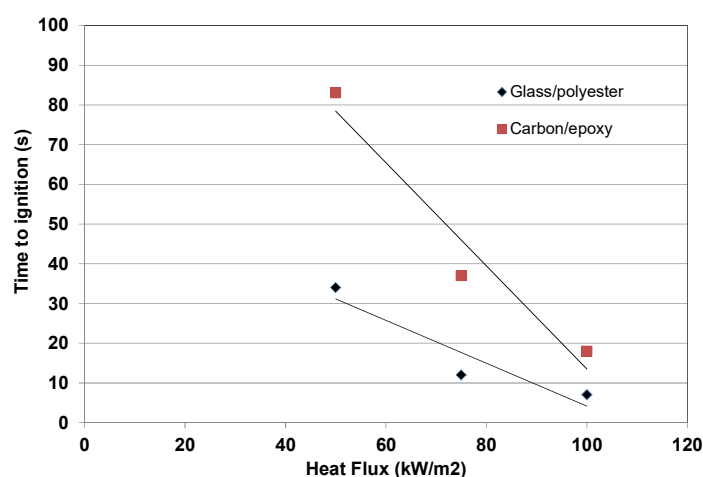


Figure 6: The effect of external heat fluxes in the ignition times for two different composites (source: [5])

The heat flux has also a significant influence on the heat release rate of a composite material. Figure 7 shows the effect of increasing heat flux on the PHRR values for a variety of glass/thermoset laminates. Glass/epoxy composite is the most flammable material and thus the heat released rises more rapidly with heat flux. The peak heat release rate of high-performance thermoset laminates is less sensitive to increases in the external heat flux.

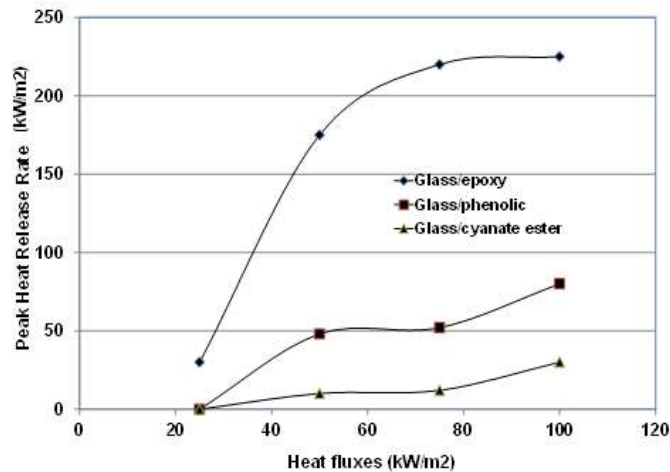


Figure 7: Effect of heat flux on the peak heat release rate for various glass/polymer laminates (source: [5])

Fire intensity also affects other fire reaction properties, namely the amount of smoke produced [5]. Smoke density may also be considered an indirect measure of the toxic potency of the fumes. While there is not necessarily a direct correlation between the density and the toxicity of smoke, the smoke density is still an indirect measure of the concentration of potentially hazardous gases and airborne particles [22].

ii. Resin Type

As previously mentioned, the behaviour of FRP composites is mainly governed by the thermal decomposition of the polymeric matrix and, as can be confirmed by the results reported in literature [5][23][24], the resin type has an important effect on the composite flammability. Cone calorimeter data reported by Brown and Mathys [23], particularly time to ignition, rate of heat release and smoke obscuration, clearly emphasize the superior combustion properties of phenolic composites when compared to epoxy or polyester resins.

Several authors [25][26][27] have reported the thermal decomposition of polyesters or the fire behaviour of polyester composites. The thermal decomposition process of all unsaturated polyesters is governed in the initial stages by scission of highly strained portions of the polystyrene cross-links, with the formation of free radicals that then go on to promote further decomposition, including some accompanying scission of the polyester backbone. This results in a variety of low molecular weight volatiles (CO, CO₂, methane, ethylene, propylene, butadiene, naphthalene, benzene and toluene). These styrene-based polymers have another important disadvantage: the tendency for smoke production due to the presence of styrene monomer. Additionally these resins tend, during decomposition, to form an important quantity of liquid products and tar, which can result in the loss of flaming droplets. These tendencies can be lightened to a certain extent through the use of composites with high inorganic content, by employing, where possible, a high glass or filler content [5].

Decomposition of most epoxies occurs via random chain scission reactions over the temperature range of about 380 to 450 °C [28]. In amine- or amide-cured epoxies, the nitrogen linkages have lower bond dissociation energies than the ether or ester linkages, and therefore chain scission occurs at the C-N bonds. The hydroxyl groups are also vulnerable to degradation at high temperature. The scission reactions decompose 80-90%

of the original polymer weight into almost 100 different volatile compounds, which are mainly various types of substituted alkylated phenols, aromatic ether derivations and other flammable organic species [29]. These compounds provide a fuel source for the decomposition reaction to continue until the epoxy is completely degraded. Between 10-20% of the original polymer weight is transformed into a highly porous char, and in the presence of air this will start to oxidize above 550 °C. As with polyester composites, the high yield of flammable volatiles produced in the decomposition reaction is the main reason for the relatively poor fire performance of epoxy matrix composites.

iii. Fibre Type, Content and Organization

The fibre reinforcement influences the composite fire reaction properties. Non-combustible fibres such as glass and carbon fibres show a diluting effect and have influence on the velocity of combustion through the formation of a protective layer [30]. Additionally, fibre reinforcement influences the combustion mechanism such as the radiation heat that penetrates into the material, the migration of the matrix degradation products, as well as the formation of char in the burning surface. Reinforcement acts as a barrier for these processes.

Glass fibres are inert to fire when the heat flux is below 100-125 kW/m² but affect the ignition process and the heat released by composite materials. On the other hand, carbon fibre's surface can be oxidized at 350 and 450 °C, respectively, for PAN and pitch-based, when exposed directly to fire. However, in most type of fires the extent of oxidation is small because only the fibres in the surface exposed to fire are also exposed to oxygen-rich environment. The majority of carbon fibres within a composite are protected by char [5].

One of the first works reporting that the amount of fibre changes the time to ignition and the amount of heat released by a burning composite was presented by Le Bras and co-workers [31]. They found that time-to-ignition increases with glass fibre content and heat released rate declines with glass fibre content, as it is shown in Figure 8. This behaviour occurs because less polymer matrix material is available to generate heat during thermal decomposition.

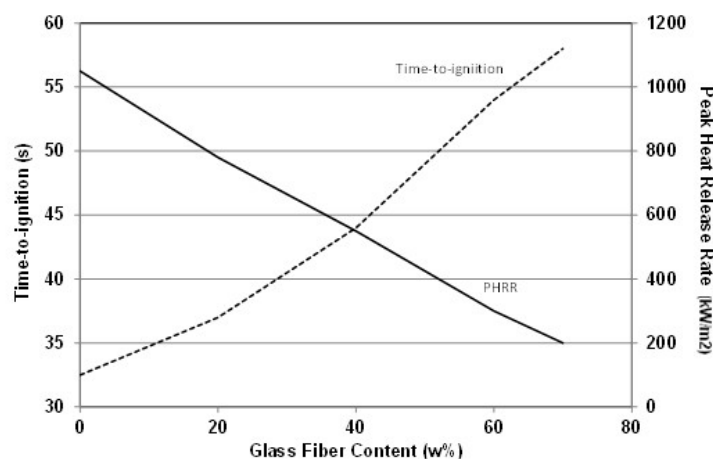


Figure 8: Schematic representation of the different phases, mechanisms and reaction processes involved during the exposure to fire of a polymer composite (source: [5])

Recently, Avila and co-workers [24] reported a study about the effect of resin type and glass content on the overall fire performance of composites. The resin type was found to affect the resultant fire performance; however, the effect of glass content was a little more subtle. PHRR and burning time decrease with glass fibre content, time-to-ignition increases with glass fibre content, but no significant difference in the average heat release was observed. These authors observed that the minimum heat flux for proper ignition increased with glass content, with exception for the polyester based composite.

The presence of binder and the different physical constructions of chopped strand and woven roving reinforcements have significant effects on the combustion properties of their glass reinforced polymer composites. Chopped strand based composites having shorter ignition times, lower maximum heat release rates, lower and broader rate of heat release vs. time profiles and higher total heat release values than the corresponding woven roving based composites [23]. Eibl [30] observed from cone calorimetry and temperature distributions measurements through a laminate that the velocity and degree of combustion are dominated by fibre orientation for a given resin. They concluded that in general a quasi-isotropic fibre orientation leads to faster ignition, because of preferred delaminations, but delays combustion processes more effectively than a unidirectional lay-up. In general, a quasi-isotropic fibre orientation leads to faster ignition, because of preferred delaminations, but retards combustion processes more effectively than a unidirectional lay-up. The quasi-isotropic fibre lay-up causes a higher resistance for the migration of the pyrolysis zone because of occurring delaminations, whereas the resin in the UD specimen is continuously accessible to degradation.

iv. Specimen Thickness

Besides the chemical composition of a material, the dimensions of a component also influence its combustion properties. It is known that increasing specimen thickness retards ignition because of heat conduction into the bulk material. The total heat emitted during combustion rises with specimen thickness but can diminish when expressed as specific heat released per volume unit for thicker composite specimens [30]. The ignition time generally increases with thickness, as the thermal response changes from thermally thin to thermally thick behaviour. The total HRR decreases with laminate thickness as reported in literature by Mouritz and Gibson [5][14].

Despite their combustibility, organic matrix composites have considerable potential for use in structures that may be subject to fire. When used in sufficiently thick sections, typical polyester/glass systems are capable of withstanding severe temperatures and ablative effects by virtue of their low intrinsic thermal conductivity and the endothermic nature of the resin decomposition process [10].

Delamination is one of the main concerns of thick structural composite laminates induced by fire conditions. Delamination is defined as the mechanical separation of interlaminar layers or plies. Sources of delamination can be attributed to internal pressure build up resulting from expansion of hot gases. These gases consist of combustion gases, i.e. combustion byproducts, and evolution of absorbed water or other liquids (e.g. residual solvents or low molecular weight components in the matrix). Because of the rapid heating conditions of fires the hot gases are incapable of quickly diffusing through the matrix material, thus producing a pressure build up. Due to this fact initial moisture content is a major factor in the development of delaminations in thick composites exposed to fire.

1.5 Flame Retardancy

Flame retardant systems are intended to inhibit or stop polymer pyrolysis and combustion processes by interfering with the various mechanisms involved - heating, ignition and propagation of thermal degradation [20]. In this chapter, the most prevalent principles, mechanisms and modes of action in the field of flame retardancy of polymers are resumed.

Flame retardants can be divided in two main types: gas-phase-active and condensed-phase-active, and in function of their nature, they can either act physically or chemically. Gas-phase-active flame retardants disrupt the combustion in the flame and act either by:

- Physical mechanisms: some flame retardants generate large amounts of non-combustible gases (H_2O , CO_2 , NH_3 , etc.), which dilute flammable gases; additionally, sometimes they dissociate endothermically causing a decrease in temperature by absorbing heat.
- Chemical mechanisms: the free-radical mechanism of the combustion process can be stopped by the incorporation of flame retardant additives that preferentially release specific radicals (e.g. Cl^* , Br^* , P^*) in the gas phase [20]. These radicals can react with highly reactive species (such as H^* and OH^*) to form less reactive or even inert molecules.

Condensed-phase-active mechanisms of action (physical and chemical) are numerous, as listed below:

- Dilution of the amount of combustible organic material by addition of inert particles.
- Reduction of the temperature of the composite by the addition of filler that acts as heat sink by absorbing heat due to their high specific heat capacity.
- Reduction of the temperature by the addition of fillers that decompose endothermically (heat consumption) to yield water or other non-combustible products.
- Reduction of the heat release rate by using polymers that decompose via endothermic reactions.
- Increase the aromaticity of the polymer matrix in order that it decomposes into an insulating surface layer of carbonaceous char (charring) that slows conduction into composite and reduces flammable gas emissions. Charring is the most common mode of action in condensed-phase [32].

In addition, flame retardants can be classified in two categories: additive flame retardants (generally incorporated during the transformation process and do not react with the polymer at this stage) or reactive flame retardants (introduced into the polymer during synthesis or in a post-reaction process). Reactive flame retardants are mainly based on halogen (bromine and chlorine), phosphorus, inorganic and melamine compounds. These compounds act by liberating bromine and chlorine atoms into the flame where they disrupt the combustion reactions. However, these halogenated materials have severe health and environment concerns, mainly due to their high toxicity, and for that a new European regulation on chemical products (REACH) hinders their use. Traditional flame retardant additives for polymer composites include aluminium trihydroxide (ATH), magnesium hydroxide and phosphorous compounds such as ammonium polyphosphate (APP) or red phosphorous. Hydrated metal salts like

ATH act mainly by the absorption of heat from the polymer when it decomposes endothermically and by the dilution of the concentration of flammable gases due to the release of water vapor during decomposition. ATH suffers decomposition between 210 and 400 °C. The endothermic decomposition behaviour of ATH is shown in Figure 9.

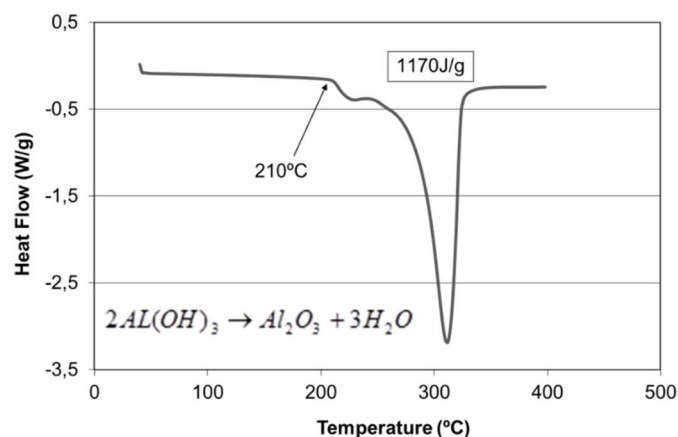
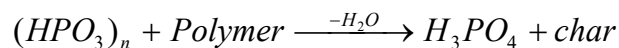
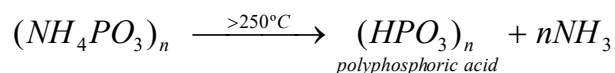


Figure 9: Differential scanning calorimeter test showing the endothermic decomposition behaviour of ATH

ATH is widely used in polymer and polymer composites mainly due to its notably low cost, good flame retardant properties and non-toxic smoke [5]. The efficacy of ATH as flame retardant in FRP composites is presented by several authors [5][33]. However, it is often necessary to add 50 wt% or more of ATH to many resin systems to achieve good flammability resistance and these high loadings affect negatively the polymer processability - which is particularly negative in the case of liquid infusion techniques for thermoset resins - and degrade the mechanical and durability properties of most types of polymer composites. ATH particles are usually 1 micron or bigger, and must be uniformly dispersed in the matrix in order to ensure even flame retardancy of the composite. This uniform distribution within the composite could be difficult to obtain mainly due to potential particles filtration in the fibres. As far as we know, this phenomenon is not reported in literature for flame retardants, but is referred several times in the case of processing FRP composites by using nano doped resins and liquid infusion techniques [34][35]. These phenomena must be also discarded and investigated in the case of micro-particulate flame retardants.

Phosphorous based flame retardants act in the gas phase by a radical mechanism that interrupts the exothermic processes and suppresses combustion. Additionally, they act in the condensed phase, promoting char formation, therefore creating a barrier to inhibit gaseous products from diffusing to the flame and shielding the polymer from heat and air. The efficacy of phosphorous based flame retardants depends on the chemical structure of the polymer; they are usually mostly effective in oxygen containing polymers such as epoxy resin [36]. Traditional flame retardant ammonium polyphosphate (APP), $(\text{NH}_4\text{P}_3\text{O}_{10})_n$ is a non-volatile, relatively water insoluble powder, with a phosphorous content of about 30%. When exposed to heat, ammonium polyphosphate is converted in phosphoric acid through thermal decomposition, as presented below. The degradation continues with the formation of polyphosphoric acid, which dehydrates the polymer in the pyrolysis stage, therefore creating unsaturated compounds that form a carbonaceous structure known as

intumescence. This protecting layer is resistant to high temperatures and protects the polymer from the attack of heat and flame.



Mouritz and Gibson [5] refer reductions in both the peak and average heat release rate of an epoxy/carbon fibre composite with increasing phosphorous contents. A study about the influence of the oxidation state of different phosphorous based hardeners on the fire behaviour of epoxy/carbon fibre composites was reported by Braun and co-workers [37]. Phosphine based composites showed significant reductions in PHRR, V-1 classification in UL94 tests and a LOI value of 39. However, these authors do not report about the possible delamination in the composite structure during the fire exposure. As explained in section 4, delamination can occur when the internal pressure builds up as a result of the formation of hot gases, such as NH_3 gas molecules when APP is present in the matrix.

1.6 Polymer/Clay Nano and Microcomposites

Over the past decade, clay based polymer nanocomposites have attracted considerable attention from scientific community. One of the first reviews describing the properties of polymer-clay nanocomposites was made by Alexandre and Dubois [38]. They presented a complete study on the methods of preparation of polymer/clay nanocomposites using different matrices, as well as their mechanical, thermal and flame retardant properties. This work, however, had a general focus, and flame retardancy was not exhaustively discussed. Furthermore, it has been more than 10 years since this review was published, and much work has been done since. In 2008, Paul and Robeson [39] presented a review study on clay based polymeric nanocomposites. Attention was given to the reinforcement potential of clays, while other properties such as thermal, barrier and flammability resistance were briefly mentioned. One of the first comprehensive overview of polymer nanocomposites for flame retardancy applications was presented by Morgan and Wilkie [32]. The book covered themes as nanocomposite fundamentals, design, synthesis, characterisation and flammability fundamentals, emphasizing the effects of nanocomposites on polymer flammability. They have focused their review mainly on thermoplastic based nanocomposites and slight references were made to epoxy flame retarded nanocomposites.

In the following years, a joint revision work from the teams of Lopez-Cuesta and Dubois [20] put- out the fundamentals of the polymer combustion theory, the main flame retardant properties and tests used to describe fire behaviour, together with the nature and modes of action of the most representative flame retardants (including nanometric materials such as nanoclays and other nanoparticles) and the synergistic effects that can be achieved by combining them. Again, they have focused their review on thermoplastic based nanocomposites and have shown that nanoparticles alone or in combination with other traditional flame retardants are very promising flame retardant solutions. However, it was demonstrated that the flammability of plastic materials remains a very complex scientific problem for which no single solution can be found, mainly due to the extensive diversity of polymers.

The team of Papaspyrides [16][40] reviewed extensively the recent advances in the field of polymer-layered silicate nanocomposites.

One of these papers [16] was focused on the flame retardancy enhancement. The combination of clays with halogenated and non-halogenated flame retardants was analyzed, either for thermoplastic and thermoset polymers. They concluded that nanoclays are not effective on ignition and in fully developed fires stages, however helpful in retarding flame spread in developing fires. The combination with traditional flame retardants is pointed out as solution for obtaining fully retarded materials. Interestingly is the fact that authors figure out several questions such as, what is the effect of reactive sites of silicates during fire; what is the correlation (theoretical fundamentals) between the dispersion degree and the reduction in PHRR; and how important is the lack of thermal stability of the clay's organic modifier (alkyl-ammoniums decompose above 200 °C) on the fire reaction properties (mainly earlier time to ignition) and (catalytic) degradation of the polymer matrix.

Although some promising works have recently emerged presenting nanoclays as promising flame retardants for FRP composites, no reference was done in all these reviews. The present work intends to overcome this gap and will present an overview of the current state of the art on these materials. Focus will be given to thermoset matrices (epoxy and UP) and their glass and carbon fibre reinforced composites.

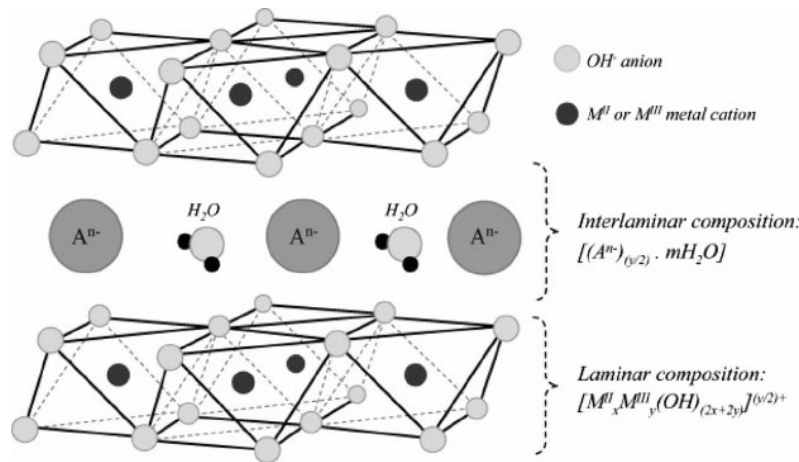
1.6.1 Nanoclays

Nanoclays are the most commonly used nanoparticles for flame retardancy; they can be natural or synthetic, cationic or anionic materials. While metal and metal oxide nanoparticles in use are typically spherical, nanoclays have flaky shapes with two of their dimensions within the range of 100-1000 nm. One of the main advantages of nanoclays is that the lamellas on their structure can be exfoliated, increasing the interfacial contact with the polymer matrix, and this is one of their major advantages. In this regard, montmorillonite (MMT) clays are being used in order to obtain polymeric nanocomposites with enhanced properties [38][39][40]. MMT clays are the most extensively studied [15]. MMT is a crystalline 2:1 layered cationic clay mineral with a hydrophilic surface in nature (see Figure 10), which can be organically modified to increase the compatibility with the organic polymer matrix. Alkylammonium cations type surfactants are the most widely used in the ion-exchange reaction to render the hydrophilic clay surface organophilic characteristics. The silicate layers are highly anisotropic, having a platelet thickness of 1 nm and a lateral size of about 30 nm. MMT is the basic mineral constituent of Bentonite clays.

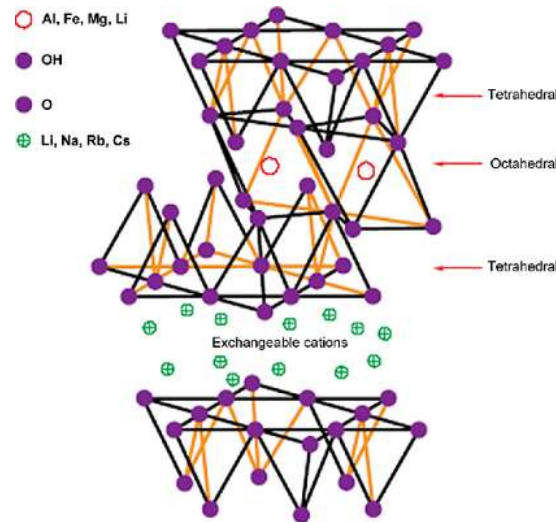
LDH, also known as hydrotalcite-like compounds or anionic clays, are brucite-like layered materials with anionic counterions in the gallery space [36], as schematically represented in Figure 10.

The positive layer charge is originated by the partial isomorphic substitution of the divalent cation for a trivalent one. In order to attain electroneutrality, an appropriate number of anions must be incorporated into the interlamellar domain. Their general chemical formula is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{m-})_{x/m} \cdot nH_2O$, where M^{2+} is a divalent cation, M^{3+} is a trivalent cation and A is an interlamellar anion with formal charge m-. The identities of M^{2+} , M^{3+} and the interlayer anion, along with the value of the stoichiometric coefficient (x) may vary over a wide range, giving rise to a large class of isostructural materials. This flexibility in composition allows LDHs with a large variety of properties to be prepared and this is one of

their most attractive features [42]. When LDHs are used as additives, the exchange for organic molecules leads to materials with improved interactions with the polymeric chain and increased interlayer spacing [43].



(a)



(b)

Figure 10: Schematic illustrations of (a) LDH (source [44]) and (b) MMT (source: [16])

1.6.2 Flame Retardant Polymer/Clay Nano and Microcomposites

By far, the most common applications of nanoclays as flame retardants report their use in thermoplastic matrices. Enhanced fire reaction behaviour properties have been observed in different types of thermoplastic polymers, namely on poly(methyl methacrylate (PMMA) [45], Ethylene Vinyl Acetate (EVA) [46], Polypropylene (PP) [47], Polyamide 6 (PA6) [48] and Polyethylene (PE) [49]. Nevertheless, it is intended with this review to focus on thermoset polymers.

The number of papers reporting the fire reaction improvements of thermoset polymers with the incorporation of nanoclays is already extensive, as we can see in Table 1. However, the number of those reporting the use of these clay/polymer systems as matrices of fibre reinforced composites is for now very limited.

Table 1: Resume of papers in open literature reporting the use of nanoclays for flame retardancy

Composite	Reinforcement fibres	Polymer matrix	Clay type and amount	Thermal Improvements	Paper
Nano	No	Epoxy	Bentonite (ammonium and phosphonium modified) 4.7 wt%	-35% PHRR (70 kW/m ²) -20% PHRR (30 kW/m ²) +TTI nanocomposites LOI≈20 nanocomposites LOI≈18 pure resin	[50]
		Epoxy (modified with phosphorous)	MMT 5-7.5 wt%	-40% PHRR (DGEBA, clay) -38% PHRR (modified DGEBA+clay) -17% PHRR (TGDDM, clay) -48% PHRR (modified TGDDM+clay) 50 kW/m ²	[53]
		Epoxy	LDH 5 wt%	self-extinguishing in UL94 test -51% PHRR (ABS) -40% PHRR (TS) 35 kW/m ²	[48]
			MMT 5 wt%	-27% PHRR 35 kW/m ²	
		Epoxy	MMT (different commercial solutions) 10 wt%	-68% PHRR (Cloisite 30B; 50 kW/m ²)	[51]
		Epoxy	Bentonite and Sepiolite (with/without organophosphorous amine) 1 wt%	LOI=21 pure resin LOI=25 (Bent) LOI=36 (Bent+phosphorous amine) LOI=34(Sep+phosphorous amine) V-0 classification (clay+phosphorous amine)	[55]

Composite	Reinforcement fibres	Polymer matrix	Clay type and amount	Thermal Improvements	Paper
		Epoxy	Bentonite (phosphonium modified) (with/without ATH and organophosphorous FR) 5 wt%	+ decomposition temperature (clays+ATH) LOI=21 pure resin LOI=23 (clays) LOI=31 (clays+phosphorous FR) LOI=22 (clays+ATH) -38% PHRR (clays, 70 kW/m ²) -61% PHRR (clays+ATH, 70 kW/m ²) -73% PHRR (clays+ phosphorous FR, 70 kW/m ²) -25% PHRR (clays, 35 kW/m ²) -50% PHRR (clays+ATH, 35 kW/m ²) -67% PHRR (clays+ phosphorous FR, 35 kW/m ²)	[56]
		Epoxy	Bentonite (phosphonium modified) (with/without APP and MB) 5 wt%	LOI=20.5 pure resin LOI=21.2 (clays) LOI=21.9 (clays+APP) LOI=23.5 (clays+MB) -54% PHRR (clays, 70 kW/m ²) -65% PHRR (clays+APP, 70 kW/m ²) -30% PHRR (clays, 35 kW/m ²) -45% PHRR (clays+APP, 35 kW/m ²)	[57]
	No	Epoxy	MMT (different organic treatments) 0.5; 1; 2; 3 wt%	LOI=20.9 pure resin LOI=23.2 (2% nanocomposite)	[52]
		Epoxy	Bentonite (phosphonium modified) (with/without low-melting silicate glass - Cepree) 5 wt%	LOI=21 pure resin LOI=25 nanocomposite -42% PHRR (clay, 70 kW/m ²) -36% PHRR (clay, 50 kW/m ²) -34% PHRR (clay, 35 kW/m ²)	[59]
		Epoxy	LDH (different organic solvents) 1, 3 and 5 wt%	Lower burning rate Polymers for Advanced Technologies 22 (2011) 1581-1592V-2 classification)	[51]
		Epoxy	Bentonite (phosphonium modified) (influence of drying method) 5 wt%	-55% PHRR (freeze-dried clays) -47% PHRR (spray dried clays) -26% PHRR (unmodified clays)	[58]

Composite	Reinforcement fibres	Polymer matrix	Clay type and amount	Thermal Improvements	Paper
		UP	MMT (different commercial solutions - Cloisite) (with/without traditional FR) 5; 7,5 and 10 wt%	-39% PHRR (10% Cloisite 25A) -27% PHRR (5% Cloisite 10A) -64% PHRR (5% Cloisite25A+20% APP) -70% PHRR (5% Cloisite10A+20% APP) -55% PHRR (5% Cloisite25A+20% ATH)	[26]
		UP	LDH 1 and 5 wt%	-47% PHRR (1% A-LDHs) -33% PHRR (5% S-LDHs)	[60]
FRP	Glass	Epoxy	MMT (with/without organic treatment) 1, 3, 6 and 10 wt%	+7% T _g (laminates, 6% organic treated MMT) -85% average time of burning decreased (10 wt% organo clay) -75% average extent of burning decreased (1 0wt% organoclay) [Determined by UL-94]	[65]
	Carbon	Epoxy (DGEBA and TGDDM)	MMT 5wt%	-19% PHRR -14% AHRR -24% smoke obscuration (TGDDM, 50 kW/m ²)	[28]
	Glass	UP	MMT (commercial Cloisite) 0,05 and 0,20 wt% (in clay-CNF sheets)	-60% PHRR of composite (0.2 0wt% clay in CNF sheets) -14% weight loss of clay-CNF sheet at 1000 °C (when adding clay)	[66]
	Glass	UP	MMT (commercial Cloisites) 5, 15 and 25 wt% (in clay/CNF sheets)	+17 °C decomposition temperature (25 wt% clay) +40% residue after TGA (25 wt% clay) -41% PHRR (5 wt% clay Na+) -51% PHRR (15 wt% clay Na+) -70% PHRR (25 wt% clay Na+)	[67]
	Glass	UP	MMT 25 wt% (in clay/CNF paper) (comparison with POSS)	-67% PHRR (50 kW/m ²) -52% THR (50 kW/m ²) -35% ASEA (50 kW/m ²) -26% AMLR(50 kW/m ²)	[68]

From the analysis of table, one may conclude that cationic clays are the most widely studied, while the use of LDHs clays has been slightly approached on both epoxy and unsaturated polyester resins.

i. Epoxy Resin

Concerning epoxy resins with LDHs, one of the first works was published in 2005 by Zammarano and co-workers [50]. They have reported the use of three different organo-modified LDHs and compared with alkylamine modified MMT and conventional flame retardants such as ATH and APP. All tested formulations had 5% in weight of additive. Cone calorimeter revealed intumescent and self-extinguishing behaviour for LDH nanocomposites and a higher reduction in the peak heat release rate compared to MMT nanocomposites. They observed that the level of dispersion of LDH clays have a positive effect on the fire reaction behaviour. Becker and co-workers [51] have very recently also reported a self-extinguishing behaviour for LHD/epoxy nanocomposites prepared by solvent dispersion methods.

Several works [52][53][54][55][56][57][59][60][61] report the flame retardant behaviour of cationic clays (Bentonite and Montmorillonite) in epoxy resins. Hartwig and colleagues [52] observed that the incorporation of 5 wt% organo-montmorillonite - ammonium or phosphonium modified - enhanced the LOI of epoxy resin from 18.3% to 19.7%. Nanocomposites showed higher ignition times and a considerable decrease in PHRR. The presence of layered silicates on the sample surface, causing a barrier effect, was indicated by the authors as the main mechanism of flame retardancy for these nanocomposites, therefore resulting in a reduction of the fire growth rate.

In 2005, Camino and co-workers [53] claimed, for the first time, that besides the physical effects (formation of a protective layer), there is also a chemical effect of MMT clays in the flame retardancy of epoxy resins. They observed that the higher improvements - 68% reduction in PHRR - did not correspond to the exfoliated structure (with just 38% of reduction). In addition, time to ignition remained unaltered with presence of nanoclays. From the presented results, it is important to note that we are not able to conclude that the clay system tested by Camino is more effective than the LDH clay tested by Zammarano [50] since the cone heat fluxes used were different and, as it is known, they have a great influence on the flammability and on PHRR reduction, as stated in section 1.4 of this work review.

A large number of works report the use of cationic nanoclays combined with phosphorous groups, either present in the epoxy pre-polymer structure [55], in the hardener structure [57] or in the nanoclays structure [56][57][59][60][61]. The combination with other conventional phosphorous flame retardants is also an approach presented by the team of Shartel [56][59].

Hussain and co-workers [55] synthesized organo-phosphorous modified epoxy resins (DGEBA and TGDDM) and studied the effect of the addition of a commercial montmorillonite in the fire reaction, degradation and thermal properties. The modified DGEBA epoxy resin and the resin incorporating nanoclays showed significant reductions in the PHRR, 50 and 40%, respectively. No synergistic effects were observed with the incorporation of nanoclays in modified DGEBA, PHRR just decreases in 38%. Similar results were found for the TGDDM

epoxy resin. The authors suggest that improvements are a result of the higher polymer charring in fire conditions due to the presence of phosphorous groups.

Toldy and co-workers [57] tested a phosphorous modified amine hardener and nanoclays in order to improve the flame retardancy of epoxy resin. A V-0 classification was observed when phosphorous based hardener (TEDAP) and 1% nanoclays were used. Concerning LOI results the best value, LOI=36, was obtained when Bentonite and TEDAP were used. The authors observed that Sepiolite is more effective alone (without phosphorous groups) when compared with the other clays. In other side, Bentonite is more effective in the presence of phosphorous groups (due to the presence of iron ions present on the surface of this clay).

An antagonism effect in flame retardancy was verified by ScharTEL and colleagues [56] when using organo-phosphorous with clays, where reductions in PHRR were of 67% (35 kW/m²) and 73% (70 kW/m²). Similar results were obtained when using of the phosphorous flame retardant alone. Further studies from this team [59] confirm the antagonism effect of another phosphorous system, namely APP, with clays. The strong antagonism was shown in properties such as HRR, THR and LOI, because of inhibiting intumescence caused by the presence of clays. The authors explained that the addition of clays increases the viscosity of the liquid products formed in the pyrolysis zone, hindering the formation of the intumescent layer.

Very recently, the same team [60] determined the influence of the phosphonium based clay's drying process on epoxy flame retardant nanocomposites. They have tested different drying processes and verified the formation of different surface areas that have promoted different flame retardancy effects. The BET (Brunauer-Emmett-Teller Theory) surface of clays increased with spray drying and freeze-drying processes resulting in their homogeneous distribution in the resin. These differences in the morphology resulted in different reductions in the PHRR, higher BET surfaces gives higher reductions in PHRR – about 55% at 50 kW/m². They have observed and concluded that a nanocomposite morphology indicates a promising flame retardant structure, however, this behaviour is very dependent of ablation and migration mechanisms that will occur at higher temperatures and are the key for protective barrier formation.

Another recent work on phosphonium modified clays (TPPMMT) was presented by Wu and his team [61]. They have studied the combination of these modified clays with low-melting silicate glass, Ceepree (CP), for epoxy flame retardancy. CP and TPPMMT together do not change the pyrolysis behaviour of the epoxy resin, but increase, as expected, the inorganic residue. The PHRR is reduced by around 32–42% when 5 wt% TPPMMT is added, and 51–63% when 10 wt% CP is added. CP is more effective than clays due to an important inorganic-carbonaceous surface protection layer formation. An antagonism effect was observed through the combination of these two additives.

The combination of ATH with phosphonium modified clays was also approached by ScharTEL [56] who has considered this combination as a promising flame retardant solution. They observed reductions in PHRR of 50% (heat flux of 35 kW/m²) and 61% (heat flux of 70 kW/m²) for the referred clay+ATH system in epoxy resin.

ii. Unsaturated Polyester Resin

Despite the interest on clay based polymer for flame retardancy, as previously shown for epoxy resins, a limited number of works studied the use of clays on UP resin [26][62].

Nazaré and colleagues [26] studied the effect of different organic modified nanoclays and their combinations with ATH and APP in the fire reaction properties of an unsaturated polyester resin. They observed that the addition of 10% of organoclay to the polyester matrix decreased PHRR in 39% and THR in 15%. The total smoke produced, however, was increased by 11%. These cone calorimetric results together with XRD analysis suggested to the authors that flammability improvements are not always dependent on the formation of nanocomposite structures. The authors found a nearly linear relationship between the PHRR and the clay content, stating that higher clay loadings result in the formation of thicker insulating layers on the surface of the polymer, therefore providing a barrier to mass and energy transport. They have also observed a synergetic effect between nanoclays and traditional flame retardants.

Anionic clays, namely modified adipate LDHs, have also provided significant decreases in the flammability of a polyester resin [62], with decreases in PHRR of 47% (1wt% clay) and 22% (5wt% clay). The HRR and smoke production (SEA) curves of UP/adipate LDH nanocomposites are shown in Figure 11.

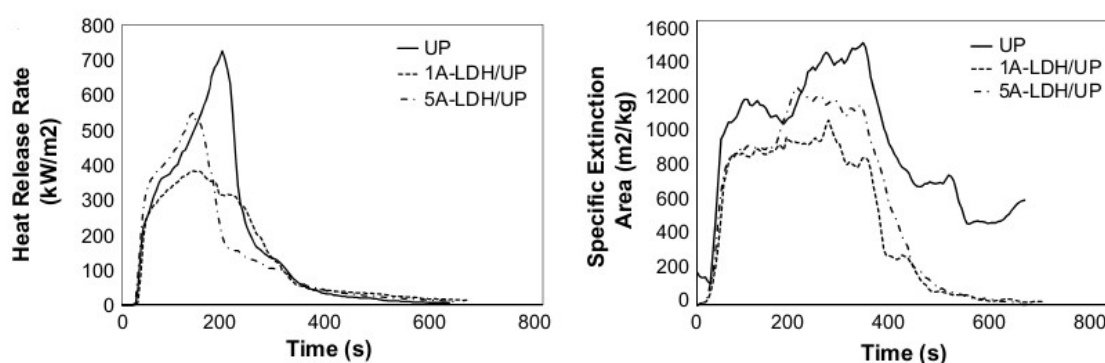


Figure 11: Heat Release Rate (left) and Specific Extinction Area (right) curves for Adipate LDH/UP nanocomposites (Source: [62])

When comparing with the results obtained by Nazaré et al and colleagues, these suggest that LDH clays can be more effective than conventional clays in generating a barrier structure which prevents the volatiles to escape. According to the authors, the process of barrier formation is composed of two steps: first, an intercalated char/metal oxide structure is formed, and then further oxidation of the residue is catalyzed by the metal oxides themselves. In addition, they decompose by an endothermic reaction, releasing water vapor, consequently promoting the dilution of the combustible gases and reducing the heat release of the nanocomposite. The authors concluded that the fire reaction behaviour of the prepared nanocomposites is not always dependent on the formation of well dispersed and exfoliated structures. This enhancement of properties can be related to the thermal and physical linkage of the clay platelets and the polymer chains or to the physico-chemical adsorption of the degradation volatiles on the LDH, which depends on their organic modification.

iii. Fibre Reinforced Polymer Composites

Several methods are currently used for providing flame retardant properties to fibre reinforced polymer composites, such as the use of mineral and ceramic wool, high performance fibres, surface coatings or modified polymer resins. In the aerospace industry, for instance, the use of surface coatings or the chemical or physical modification of the resin are seen as the most suitable solutions, as the retention of mechanical properties after heat exposure are fundamental requirements. On the other hand, the use of thermally insulative layers of mineral and ceramic wool is considered an appropriate solution for naval and transportation industries.

Surface coatings are passive fire protection systems that can be bonded onto the surface of fibre-reinforced composites in the form of paint, spray or mat. They are considered an efficient way to provide fire protection to composite materials without affecting physical and mechanical properties. They also have the advantage of being applied after composite's manufacturing, therefore not requiring changes during the processing.

The use of intumescent surface coatings in GFRP composites has been reported by Lungille [63] and Correia [64]. Kandola and co-workers reported the use of hybrid intumescent mats [65] and the simultaneous use of conventional fire-retardant additives added to the resin [66] as fire protection systems to UP/GFRP composites.

However, in this work, focus will be given on fire protection systems based on modified polymeric resins, namely through the addition of nanoparticles.

iv. FRP - Epoxy Resin

In a work from 2007, the fire performance of two different epoxy resins modified with nanoclay and phosphorous based curing agent and their corresponding laminates produced with carbon fibres were reported by Liu and co-workers [28]. The use of nanoclays, phosphorous curing agent or the combined use of both worsened the fire performance of the DGEBA (Diglycidyl Ether of Bisphenol A) resin composite. When using a TGDDM (Tetraglycidyl Diamino Diphenyl Methane) resin, there were slight improvements in the phosphorous containing sample, namely decreases of 19% in PHRR, 14% in the AHRR and 24% in the smoke obscuration. This work emphasized the close relationship between char yields obtained in TGA and cone calorimetry with the PHRR, highlighting the role of the condensed phase in minimizing combustion.

In the same year, Bozkurt and co-workers [67] published a work on the thermal and mechanical properties of glass fibre reinforced clay/epoxy nanocomposites by adding clays to the epoxy resin. Addition of clay significantly reduced the flammability of polymer composites. The average extend of burning and average time of burning were reduced by 75% and 85%, respectively due to the addition of 10 wt% organically modified MMT into epoxy. The improvements were higher with organo-modified clays due to enhanced dispersion in the polymeric matrix.

v. FRP - Unsaturated Polyester Resin

Gou and his teams have been one of the most active working in the flame retardancy of unsaturated polyester/glass fibre reinforced composites [68][69][70]. In their first published work in this area, they have studied the production and incorporation of

clay/carbon nanofibre hybrid sheets onto the surface of GFRP composites [68]. Significant improvements in the thermal stability of the carbon nanosheet with the addition of nanoclays were obtained. 0.20 wt% of nanoclay content in carbon nanosheet provided reductions in PHRR of 60%. Authors concluded that a combined effect of barrier/insulation from the nanoclays and re-emitting effect of carbon nanofibres acted on the combustion of the composites. A continuous barrier to oxygen supply to the composite was effectively produced by combining these two nanomaterials.

The same approach was used by Zhuge and colleagues [69] but comparing two different commercial clays (Cloisite Na⁺ and organically modified Cloisite 20A) in higher amounts. When unmodified MMT clay was incorporated into the CNF nanopaper, the PHRR decreased dramatically with the weight fraction of MMT and reductions in the PHRR of 70% were achieved with 25%wt of clay content in the nanopaper.

When this team have compared clays with POSS (Polyhedral Oligomeric Silsesquioxane) [70] they observed that clays were more effective in reducing not only the PHRR, but also the average mass loss, average smoke obscuration and total heat released. The PHRR of composite materials increased significantly with the addition of POSS-CNF nanopaper in the surface. On the contrary, for the CNF-clay nanopaper, significant decreases in PHRR (67%) were obtained. POSS particles were observed to migrate rapidly to the surface of polymer nanocomposites, leading the authors to believe that this could increase the HRR or even quickly ignite the polymer resin. Furthermore, clays have a layered structure, serving as a barrier to mass and heat transfer, while POSS has a cage-like structure with organic groups attaching to each corner of the cage, where no barrier effect can be attained.

1.6.3 Flame Retardancy Mechanisms of Nanoclays

Just as reference, the flame retardant effect of clay mineral particles and its mechanism in thermoplastic matrices is well described in the literature and they can be summarized as follows:

- i. migration of the clays to the surface of the polymer during combustion, leading to the formation of a rich silicate layer which acts as a physical barrier that slows mass and heat transfer during combustion [71][72][73];
- ii. the silicate layer protects the polymer from heat and also limits the oxygen flow and the escape of volatiles; these actions interfere with the combustion process reducing the amount of available combustible [74].

In the case of a thermosetting matrix, the mechanism is essentially different from that described in thermoplastic matrices, since the cross-linked structure hinders the migration of clay particles to the polymer surface and the formation of a protective layer there. However, the barrier effect provided by the clays during the combustion of thermoset polymers has been pointed out as the main responsible flame retardant mechanism [26][28][52][74].

A recent work by Scharrel [60], though, has stated that there is a migration of rich silicate bubbles to the surface of the polymer during combustion. Bubbling is therefore reported as a mechanism responsible for the improved flame retardancy of epoxy/layered silicate nanocomposite. The formation of the bubbles, which are covered by silicate agglomerates,

is important both in the creation of solid agglomerates and on its transportation process to the surface, thus contributing to the creation a protective barrier. The formation of bubbles, their migration, reorientation, agglomeration and ablation mechanisms have shown an effect on the development of a residue layer during the combustion of epoxy nanocomposites.

Clay minerals are also claimed to act as flame retardants due to their catalytic effect on charring and/ or reinforcement of the char structure. The formation of a carbonaceous layer changes the combustion products and promotes a reduction on the permeability of oxygen and mass transport [53][57][60].

In the case of anionic nanoclays, their main flame retardant mechanisms are: LDHs release aqueous vapour and carbon dioxide during decomposition, promoting dilution of combustible gases of pyrolysis, increasing the ignition time and reducing the heat release during the combustion; porous thermal-decomposed products of LDHs with large specific surface area, absorbing the smoke and gases produced in the course of combustion [62].

The thermal decomposition of LDHs depends on the nature of the layer cations and interlayer anions, and, as expected, on the experimental conditions during heating (oxidant, inert, or reducing conditions) [76][77]. Usually, decomposition takes place in four steps:

- i. loss of physically adsorbed water (50-200 °C);
- ii. loss of interlayer water and removal of hydroxyl groups from the layers as water vapour (250-500 °C);
- iii. loss of the interlayer anion, with the formation of metal oxides [e.g.: Al_2O_3 , MgO] and carbon dioxide (500-800 °C).

From this behaviour, it is expected that the metal oxides formed during the different decomposition stages increase the thermal stability of the yield char.

1.7 Polymer/CNT Nano and Microcomposites

1.7.1 Carbon Nanotubes

Carbon nanotubes (CNTs) are one dimensional carbon materials consisting of graphitic sheets rolled into seamless tubes. The properties of nanotubes depend on atomic arrangement (how the sheets of graphite are 'rolled'), the diameter and length of the tubes, and the morphology, or nano structure. They have diameters ranging from about a nanometer to tens of nanometers with lengths up to centimeters, therefore aspect ratios greater than 1000. Due to their symmetric structure, carbon nanotubes usually have excellent properties [78].

For the synthesis of CNTs, three main synthetic methods are used: arc-discharge, laser ablation and catalytic methods such as chemical vapor deposition. Depending on the process of fabrication, it is possible to obtain three types of CNTs: single-walled CNTs (SWCNTs), double-walled (DWCNTs) and multi- walled CNTs (MWCNTs). As the name implies, SWCNTs consist of a single graphene layer rolled up into a seamless cylinder, whereas DWCNTs and MWCNTs consist of two or more concentric cylindrical shells of graphene sheets. MWCNTs show a lower tensile strength and modulus, when compared to SWCNTs. SWCNTs have diameters in the range of 0.4 up to 5.6 nm and MWCNTs have much

higher diameters, which may vary from 20 to 100 nm. MWCNTs are also more rigid because their section is much larger compared to that of SWCNTs [79][80].

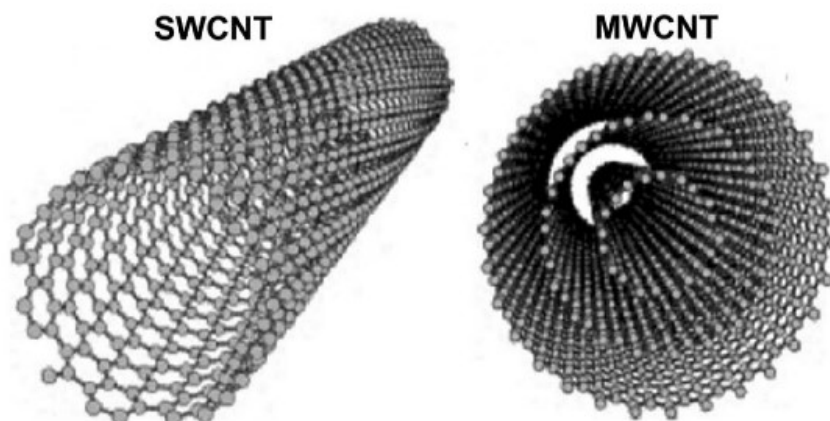


Figure 12: Structure of single and multi-walled carbon nanotubes (source: [81])

In recent years the potential of carbon nanotubes has been investigated for many highly demanding applications such as aerospace applications [82][83]. The combination of high mechanical performances with extraordinary high electrical and thermal conductivities of CNT, allied with their high aspect ratio and low density, makes them a very interesting solution for multifunctional polymeric composites reinforcement. The increasing utilization of multifunctional composites in a wide range of technical applications will eventually lead them to encounter events where extreme thermal resistance is required, thus motivating the need of understanding the thermal and fire reaction behaviour of these new composite systems. Furthermore, carbon nanotubes are interesting flame retardant candidates due to their elongated shape and thermal stability.

1.7.2 Flame Retardant Polymer/CNT Nano and Microcomposites

Despite the reports of the exceptional physical and mechanical properties of epoxy nanocomposites with CNTs [84][85][86][87] there are only a very limited number of studies on the epoxy/CNT composites flammability and the reported results are dependent of raw materials (nanotubes and epoxy resin types) and samples preparation processes.

To our knowledge, one of the first works reporting the flammability of epoxy resins filled with carbon nanotubes was made by our team [80]. The addition of 1% CNT to a low viscous epoxy resin promoted a small increase in time-to-ignition and a decrease (17%) in PHRR, as it is possible to see in Figure 13.

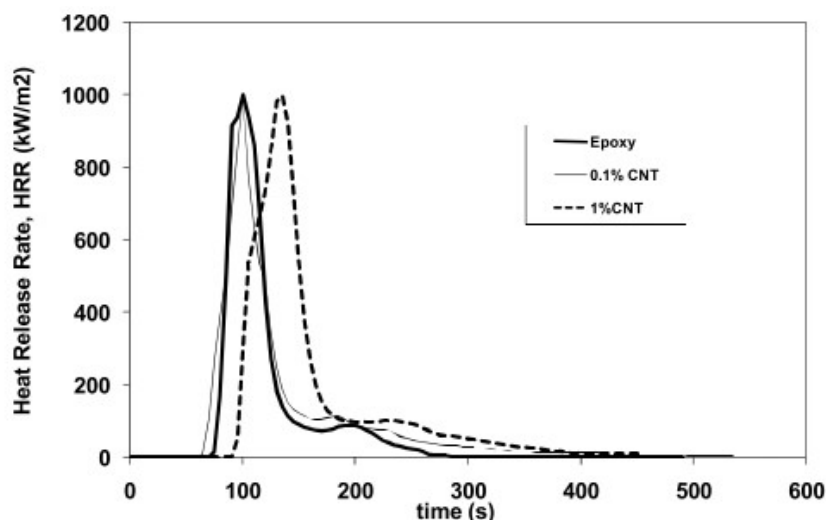


Figure 13: Heat Release Rate curves for epoxy/CNT nanocomposites (Source: [88])

Rahatekar and colleagues [89] reported reductions of almost 50% in peak of mass loss with a small addition (0.0025 wt%) of highly aligned MWCNTs to an epoxy resin. Tests were performed in a gasification apparatus, which measures the mass loss rate (MLR) of a sample exposed to a constant heat flux under an inert atmosphere. Comparison with a MMT/epoxy nanocomposite allowed the conclusion that it is necessary to use higher clay loading to obtain similar reductions. Authors claimed that these aligned nanotubes were easily exfoliated in the resin using high shear mixing, therefore contributing to enhanced properties. The combination of MMT and MWCNTs for improved flammability of an epoxy resin was approached by Lee et al. [90]. A significant increased LOI (33) was obtained with 10% MMT and 1% MWCNTs; the pure epoxy resin showed a LOI of 21. The same team [91] published a similar study, however using fluorinated MMT and MWCNTs in order to create hydrophobic functional groups for improved dispersion into the epoxy resin, once again resulting in increased LOI values and char yield when using nanotubes. However, LOI value obtained (31) was not as high as in the previous study, when using both MMT and MWCNTs. The use of 0.1wt% of carbon nanotubes alone increased LOI from 21 (pure resin) to 23. In both cases, authors concluded that the increased char yield formed in the presence of MWCNTs acts as both heat barrier and as thermal insulation, in addition to decreasing the degradation rate of epoxy resin. Increased LOI values and a flame retardant classification (V-0) were also obtained by Kuan and colleagues [92], although considerable higher amounts (up to 9%) of functionalized CNTs were added to a modified epoxy resin containing silicon to induce a sol-gel reaction. LOI increased up to 29 with increasing carbon nanotube content and V-0 classification was obtained for nanotube contents higher than 3%. Considerable increases in glass transition (42 °C) and char yields (47%) were also reported.

Hapuarachchi and co-workers also studied the combined effect of nanoclays (Sepiolite) and MWCNTs, but using unsaturated polyester resin as matrix [93]. Carbon nanotubes alone hindered the thermo-oxidation of the resin in the early stages of degradation, by increasing the onset degradation temperature in 20 °C. An even higher increase in the onset degradation temperature (36 °C) was obtained when adding Sepiolite clays to the UP/MWCNT nanocomposites. A synergetic behaviour was also found in terms of PHRR, with a decrease of 50% for Sepiolite/MWCNTs nanocomposites. The THR, however, did not

change substantially, suggesting to authors that the physical barrier formed during combustion prolongs the burning times without decreasing the total amount of combustible material.

Two other recent works, reported by Pereira [94] and Gérard teams [95] for imparting flame retardant properties to an epoxy resin, was the combination of traditional flame retardant APP with multi-walled carbon nanotubes. Pereira and co-workers report synergy in reducing PHRR and THR of an epoxy resin by using MWCNTs and APP. These authors refer that physical and chemical actions between CNT, APP and the polymer produce a “fire blocking” barrier that prevents the release of degradation volatiles. This barrier was perceptible during cone calorimeter tests where some smoke escaped by the sample holder bottom face. On the other hand, antagonism effects were found on properties such as ignition times and PHRR by Gérard and co-workers [95]. Authors stated that the presence of nanotubes increases the material thermal conductivity, therefore resulting in lower ignition times. Furthermore, another suggested phenomenon is that the sample containing CNT can absorb more quickly the radiant heat, leading to the accumulation of heat at the surface of the material, resulting in a faster ignition.

i. Fibre Reinforced Polymer Composites

The use of carbon nanotube buckypapers has very recently emerged as a solution for fire protection of fibre reinforced composites. Buckypapers are 3D structures consisting of sheets of entangled carbon nanotubes (CNTs) that can be produced by filtrating carbon nanotube suspensions. These sheets usually have thicknesses ranging between 30 and 500µm. Buckypaper structures represent a path towards the production of polymer composites with high and well dispersed nanotube content [96].

Recently, Zhang’s team published two works [97][98] regarding the use of carbon nanotube buckypapers as fire retardants in epoxy/carbon fibre composites. In their first work [97] they produced carbon nanotube buckypapers and incorporated them on the surface of carbon fibre epoxy composites for fire shielding. They have prepared carbon nanofibre, MWCNT and SWCNT papers, however, only MWCNT buckypaper acted as an effective flame-retardant. Important improvements on the ignition time, PHRR, THR and the smoke emission were reported, as resumed in Table 2. The authors discussed and demonstrated that buckypapers act as barriers, reducing the release of polymer fragments from matrix into the air, therefore delaying time to the critical point of the concentration of combustible gases, despite their high thermal conductivity. Due to their dense structures and small pore size, MWCNT buckypapers were able to provide low gas and mass permeabilities, acting therefore as a fire shield. In their second work [98], they compared the effectiveness of SWCNT and MWCNT buckypapers as fire shield for two different carbon fibre composites (based on epoxy and bismaleimide-BMI). They have demonstrated that the thermo-oxidation stability of buckypaper played a key role in improving flame retardant properties of composites. For the epoxy resin composites, the results were similar to the ones reported in their first paper. However, for BMI composites, they observed that both MWCNT and SWCNT buckypapers are effective, but acting differently. BMI resin has a higher thermo-oxidative stability than epoxy, and for that reason a more stable carbonaceous char is formed on the surface of SWCNT buckypaper, reducing their thermo-oxidative behaviour. In addition, SWCNTs are more exposed to oxidative damage during the fire when compared

with MWCNT, which can therefore destroy the protective network as the nanotubes are oxidized away through the walls of the tubes. In the case of MWCNT, as they have multiple layers for burning, the complete destruction of the tubes is more difficult.

This innovative method seems very promising for providing flame retardant properties to FRP composites. In a single manufacturing step a *flame retardant graded material* is produced.

Table 2: Resume of papers in open literature reporting the use of carbon nanotubes for flame retardancy

Composite	Reinforcement fibres	Polymer matrix	CNT type and amount	Thermal Improvements	Paper
Nano	No	Epoxy	CNT 0.1 and 1wt%	-17% PHRR Increase in TTI Decrease in smoke production (1wt% CNT)	[85]
		Epoxy	MWCNT 1wt% (combined effect with MMT)	LOI=21 pure resin LOI=33 (CNT+10% MMT) +10.5% Char yield (CNT+10% MMT)	[87]
		Epoxy	MWCNT 0.03, 0.25 and 0.5 wt% (comparison with MMT)	-50% PMLR (0.25 and 0.5 wt% CNT) -40% PMLR (0.03 wt% CNT) (determined in a gasification apparatus)	[86]
		Epoxy	Fluorinated MWCNT 0.1 wt% (with/without MMT)	LOI=21 pure resin LOI=23 (CNT) LOI=31 (CNT+MMT) + 2.5% Char yield (CNT) +6% Char yield (CNT+MMT)	[88]
		Epoxy	MWCNT 1, 3, 5, 7 and 9 wt%	+42 °C in T _g (7% CNT) +47 % char yield at 750 °C LOI=22 pure resin LOI=29 (9 wt% CNT) V-0 classification (3, 5, 7, 9 wt% CNT)	[89]
		Epoxy	MWCNT 0.5wt% (combined effect with APP)	-28% PHRR (APP+CNT) -4% THR (APP+CNT) +8% char yield (APP+CNT)	[92]

Composite	Reinforcement fibres	Polymer matrix	CNT type and amount	Thermal Improvements	Paper
				(determined in mass loss calorimeter)	
		UP	MWCNT 0.5, 1 and 2 wt% (combined effect with Sepiolite)	-50% PHRR (0.5% CNT+Sepiolite) +20 °C degradation temperature (CNT) +36 °C degradation temperature (CNT+Sepiolite)	[90]
FRP	Carbon	Epoxy	SWCNT or MWCNT buckypaper (2 layers on the surface) (comparison with CNF paper)	+40% TTI -55% PHRR -40% THR -50% TSR (improvements in epoxy composites)	[94]
	Carbon	Epoxy (comparison with Bismaleimide)	SWCNT or MWCNT buckypaper (2 layers on the surface)		[95]

1.7.3 Flame Retardancy Mechanisms of Carbon Nanotubes

CNTs are interesting candidates as flame retardant additives because they can form closed carbon char layers (either by chemical or physical actions), which protect the polymer surface; the large aspect ratio of nanotubes acts as a gas barrier; nanotubes increase the melt or resulting liquid products viscosity; nanotubes may also influence the fire behaviour of polymers by changing the energy absorption and heat conductivity. Some of those not obvious flame retardancy mechanisms were demonstrated by using multi-walled carbon nanotubes (MWNT) in polypropylene (PP) [99][100], in poly(ethylene vinyl acetate) [101] and, very recently, in epoxy [91]. Im and co-workers [91] referred that free radical scavenger effect of MWCNT is the main reason for the improvement in the thermal stability of epoxy resin.

The *in situ* formation of a continuous network structured protective layer from the tubes is critical to the significant reduction in heat release rate, because the layer thus acts as a thermal shield against energy and gases feedback from the flame [100]. Single walled nanotubes have also potential as flame retardants by the same mechanisms.

1.8 Conclusions and Identification of Main Research Needs

It was intended with this review to focus on the fire reaction properties of thermoset based fibre reinforced composites containing nanoparticles, namely clays and carbon nanotubes. These nanoparticles offer advantages over traditional flame retardants, as only a small amount of filler has the potential to dramatically change the final properties of the host

material. Regarding the use of halogenated additives, nano-based additives offer the great advantage of being environmental friendly. The use of nanoclays and carbon nanotubes may also be a strategic approach for producing new fibre reinforced polymeric composites with enhanced thermal and mechanical properties.

In terms of flame retardancy, nanoclays and carbon nanotubes have shown to be efficient in reducing the mass loss rate, therefore promoting significant reductions in the peak of heat release rate. However, time to ignition usually decreases and smoke production increases. This effect is far below that achieved when using traditional flame retardants such as ammonium polyphosphate or aluminium trihydrate. Therefore, the possible synergistic effect of combining nanoclays with traditional flame retardants has been of increasing attention.

The variety of available nanomaterials and the possibility to change the composition during their synthesis continues to make these very interesting candidates for producing materials with new features. One of the main drawbacks, however, is that most work done in this area shows that it becomes crucial to produce well dispersed polymer nanocomposites in order to achieve the best results. It becomes necessary to establish a dispersion procedures for each system used. An alternative solution to overcome the dispersion difficulties in FRP composites could be the use of preassembled stable nanomaterial structures such as buckypapers. This new approach must be investigated, as well as other several critical issues when using nanomaterials for flame retardancy as listed below:

- Health safety concerns: either during nanoparticles's handling and during fire scenario (effect on smoke toxicity or asbestos).
- Durability and aging: nanocomposites could suffer from hydrolytic, oxidative and photo-oxidative instability. A deep understanding about these effects on the composite durability is needed.
- Life cycle assessment (LCA): for example, the impact of introducing nanoparticles on the recyclability of composites must be evaluated.
- Processing parameters: when flame retardants and nanomaterials are incorporated into resins, knowledge about the rheology and cure kinetic is fundamental for process control and optimization.
- Mechanical properties: composite materials are mainly used due to their superior mechanical performance at lower weight. Assessing the effect of adding nanoparticles in the mechanical properties is therefore crucial.

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2 Effect of Nano-Magnesium Hydroxide on the Flammability of Epoxy Resins

Marta Martins, Celeste M.C. Pereira, "A study on the effect of nano-magnesium hydroxide on the flammability of epoxy resins", Solid State Phenomena 151 (2009) 72-78, DOI: 10.4028/www.scientific.net/SSP.151.72

Abstract

In this work the effect of nano-magnesium hydroxide (nano-Mg(OH)_2) on the flammability of epoxy composites is presented and compared with the traditional flame retardant used in just small amounts for epoxy resins, ammonium polyphosphate (APP). The fire reaction properties of epoxy composites were obtained by cone calorimeter tests. It was observed that the flammability of the unfilled resin is significantly changed with nano-Mg(OH)_2 addition and reductions of 33, 22 and 23% in the epoxy composite heat release rate peak (PHRR) by incorporating 10%, 5 % and 1% of nano-Mg(OH)_2 , respectively, were achieved. Cone calorimeter analyses confirm the better behaviour of APP composites compared with nano-Mg(OH)_2 composites. SEM micrographs show some agglomerations on the distribution of nano-Mg(OH)_2 in the epoxy matrix.

Keywords: flame retardancy, epoxy resin, nano-magnesium hydroxide

2.1 Introduction

An increasing number of structures are being made from fibre reinforced composites. For example, on aircraft, some crucial components are generally made from carbon fibre reinforced composites using an insulating epoxy matrix. Furthermore, standard epoxy resins are highly flammable and produce large quantities of smoke and toxic gases [1]. Their increasing commercial utilization may bring these polymers into fire situations at any time, adding urgency to the development of effective flame retardant systems to reduce fire hazards.

Halogen-containing compounds are commonly applied as flame retardants in epoxy resins, either by blending or chemical modification to improve their thermal and flame-retardant properties, but because of their toxic gas emissions are becoming much less favored [2]. In general, the addition of these types of fillers to epoxy resins can significantly influence their combustion behaviour, by increasing ignition time and decreasing heat release rate, but can also increase the amount of toxic and corrosive fumes during thermal decomposition, making their further usage limited. Consequently, nowadays environmental legislations have limited or prohibited the applications of these halogen-based flame retardants in polymers. Ammonium Polyphosphate (APP) and hydrated fillers like aluminium trihydroxide (ATH) and magnesium hydroxide (MH) have received increased interest as flame retardant for polymers [3]. As a halogen-free retardant, MH has attracted people's attention because of its smoke suppression property, flame retardancy and good thermal stability. Magnesium hydroxide is usually more suitable for thermoplastic matrices, since its degradation temperature is lower than most thermoplastics' degradation temperature. However, some thermoset matrices, such as several epoxies for high performance

composites, have high degradation temperatures and MH could be suitable for these resins. They are also particularly low viscous for being processed by infusion and, for that reason, viscosity is a critical parameter that must remain quite unchanged by the addition of flame retardants. Ammonium phosphate is particularly useful for this purpose because just a small amount of it leads to the formation of an important intumescent layer in the beginning of the burning process. Notwithstanding its advantages, ammonium polyphosphate suffers from the distinct disadvantage that it is water-soluble. Leaching of APP can lead to disastrous failure of the flame retardant effect.

In 2005, the concept of nanoscale flame retardants provides opportunity for synthesis of new polymer materials with unique properties. Nano-magnesium hydroxide, nano-Mg(OH)₂, could also represent a rational alternative to the conventionally filled epoxy because they could have distinct advantages over traditional flame retardants on its related problem areas. Very recently, a Japanese research team [4] studied the flame retardant effect of nano-Mg(OH)₂ in an epoxy resin. These authors have observed significant reductions in the resin flammability and the formation of a dense char layer with large quantities of filler, 40 wt% for 10nm and 70 wt% for 600 nm in size of Mg(OH)₂ particles. Hence very high loadings (about 60% or more) were proved to be needed to meet an adequate level of flame-retardant property. Another published work [5] reports the flame retardation of ethylene-vinyl acetate copolymer (EVA) using nano-Mg(OH)₂ and also presents significant reduction in the polymer flammability. Again very high loadings, 60wt% and more, were proved to be needed to meet the adequate level of flame retardancy.

The aim of the work presented here is to show the effect of the addition of low amounts of nano-Mg(OH)₂ on the flammability and thermal properties of a high performance and low viscosity epoxy resin. This nano flame retardant is also compared with a traditional one, also used in low amounts, ammonium polyphosphate.

2.2 Experimental

2.2.1 Materials

The epoxy resin used in this study was SR8100 (Sicomin) with a viscosity of about 700±100 mPa.s (at 25 °C); nano-Mg(OH)₂ used was supplied by the Portuguese company METOXID – Óxidos Metálicos, S.A. and was coated with inorganic carbon with a crystallite size lower than 20 nm; Ammonium Polyphosphate (APP) used was EXOLIT AP 422 (Clariant) with an average particle size (D50) of 15 µm.

2.2.2 Sample Preparation

Prior to curing and addition of hardener, epoxy resin was mixed by vigorous stirring with the desired amount (1%, 5% and 10% in resin weight) of nano-Mg(OH)₂ for 10 minutes at room temperature. Epoxy resin was mixed with an amount of 5% in resin weight of APP, following the process described before. Blanks of pure epoxy resin were also prepared through the same method for reference. All the samples were cured at room temperature during 24 hours and post-cured at 60 °C for 8 hours.

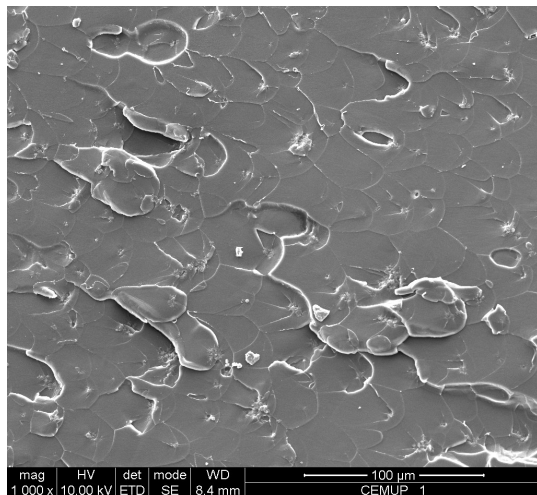
2.2.3 Sample Testing

Fractured surfaces of samples on liquid nitrogen were investigated with a JEOL JSM 6301F high resolution scanning electronic microscope (SEM). Dynamic Scanning Calorimetry (DSC) experiments were performed using a temperature program between 40 °C and 350 °C (ramp), with a heating rate of 10 °C/min, using a sample mass of approximately 10 mg and nitrogen at 50mL/min as purge gas. Cone calorimeter (FTT- Fire Testing Technology) tests were performed at a heat flux of 25 kW/m² using the cone shaped heater. Heat release rate and the time-to-ignition were obtained from the cone calorimeter experiment using on-line software. The cone data reported here are obtained by burning samples in the horizontal position with an exposed surface of 100×100 mm² and are the average of two or three replicated samples. The peak heat release rate is reproducible to within ±10% and the time to ignition data is reproducible to within ±15% [6].

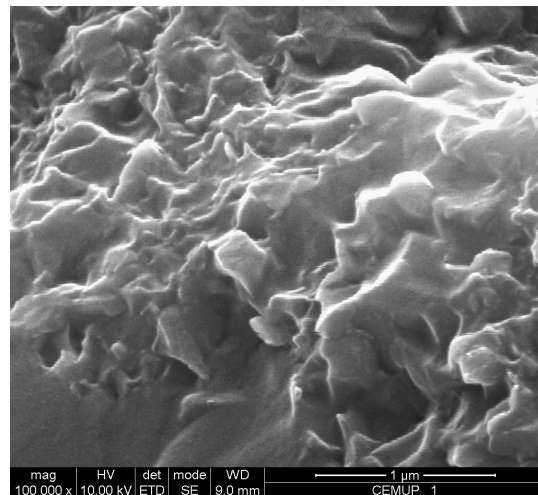
2.3 Results and discussion

2.3.1 SEM Characterisation

The presence of nano-Mg(OH)₂ agglomerates can be seen in all the SEM pictures (Figure 14), particularly in the low magnification images (a, c and d). When the percentage of flame retardant amount increases, the number of these agglomerates also increases. Moreover, it is possible to identify the needled structure of the Mg(OH)₂ particles in the higher magnification picture (b), 100 000x of 1% nano-Mg(OH)₂ sample, and see that the matrix does not cover the nano-filler. This behaviour might be an indication of poor interaction between the matrix and the nano-Mg(OH)₂ and a method for improving the dispersion of these particles in the matrix is under development.



(a)



(b)

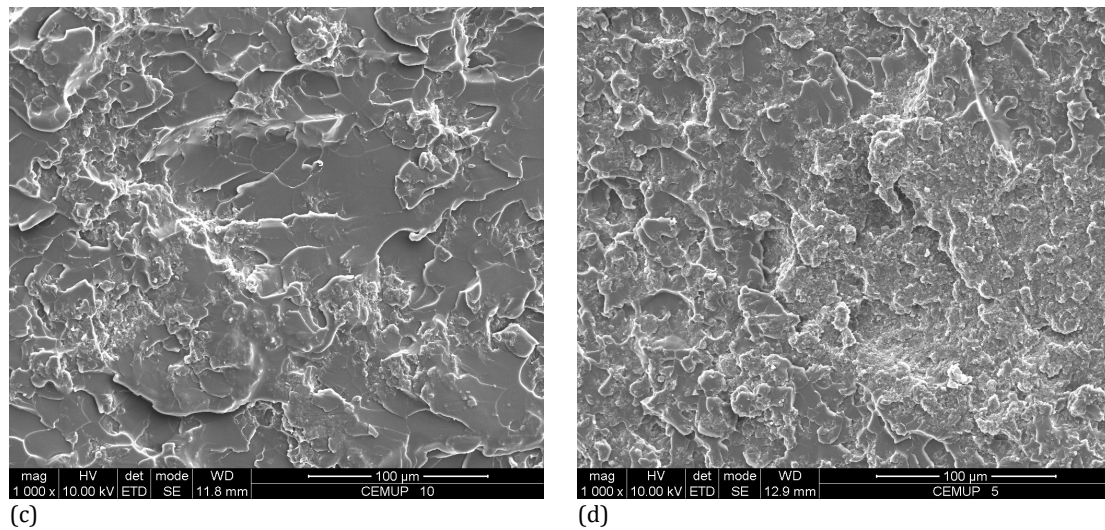


Figure 14: SEM micrographs of two magnifications- 1000x(a) and 100 000x (b) – for 1% and 1000x magnification for 5% (c) and 10% (d) of nano-Mg(OH)₂-epoxy composites

2.3.2 DSC Tests

In Figure 15 one can see the DSC curves obtained for the resin and the epoxy composites containing nano-magnesium hydroxide and APP. The glass transition temperature and the onset temperature of degradation of all samples were determined from these curves and are presented in Table 3. The glass transition temperature for the samples containing nano-Mg(OH)₂ are approximately 60 °C, very close to the value of the pure resin, 63 °C. Consequently, we can presume that the addition of small quantities of these nano particles has a slight effect on the chemical structure of the polymer. On the other hand, the addition of 5% of the traditional flame retardant APP raises the T_g in more than 5.5 °C.

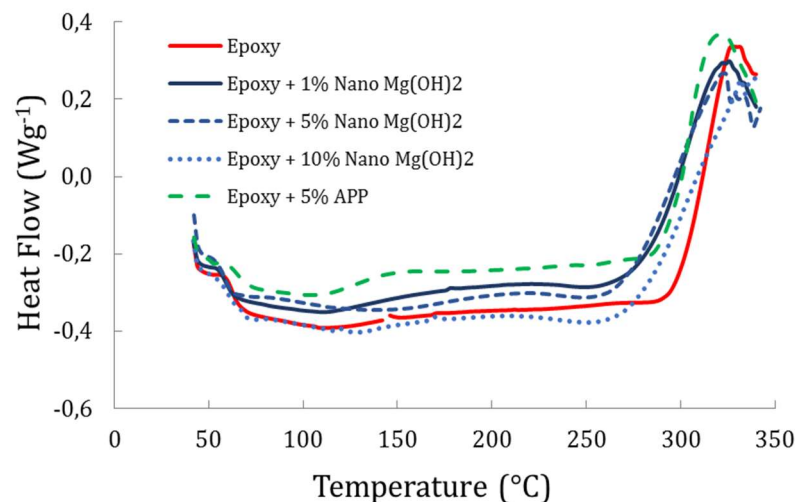


Figure 15: DSC curves for the pure epoxy resin with nano-Mg(OH)₂-epoxy composites APP-epoxy composites, measured under a nitrogen atmosphere

Analysing the values of the onset temperature of degradation, we can see that as the content of nano-Mg(OH)₂ in the composite increases, there is a reduction in the temperature of

degradation by pyrolysis, which indicates that the addition of these components accelerates the thermal decomposition of the nanocomposites. This reduction in the degradation temperature was not expected because $\text{Mg}(\text{OH})_2$ is thermally stable up to 330-340 °C [7], and will be explored by further experiments. The nano-MH used may have some impurities that are activating the composites degradation. In addition, the NMH used was coated with inorganic carbon, which may as well have some influence on the degradation. MH decomposition can be activated by some elements, including Fe, and through coating using certain organic surface treatments [8]. The sample containing APP has the lower loss in thermal stability. This consents with observations of other authors where APP starts degradation at 290 °C [7].

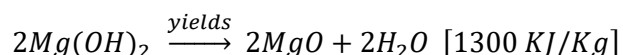
Table 3: Glass transition temperatures and the onset temperatures of degradation by pyrolysis for pure epoxy resin and composite samples

Sample	T _g (°C)	T _{degradation} (°C)
Epoxy Resin	63	300
Epoxy + 1% Nano-Mg(OH) ₂	60	284
Epoxy + 5% Nano-Mg(OH) ₂	59	274
Epoxy + 10% Nano-Mg(OH) ₂	60	277
Epoxy + 5% APP	69	295

2.3.3 Cone Calorimeter Tests

Cone calorimeter is one of the most effective bench-scale methods for studying the flammability properties of materials. Cone calorimeter investigations can be used as a universal approach to ranking and comparing the fire behaviour of materials. Heat release rate, in particular the peak, PHRR, has been found to be the most important parameter to evaluate fire safety [6]. When a material burns, it generates heat, heating up and igniting additional combustible material. The material decomposes with the evolution of a flammable gas mixture. Determination of the rate of heat release from a material in a fire situation is important because of its influence in the initiating fire.

Figure 16 shows the HRR curves evolution for pure resin, nano-Mg(OH)₂-epoxy and APP-epoxy composite samples. Comparing all the nanocomposites with pure epoxy resin, it is possible to see that there are important reductions in HRR for the whole amounts of nano-Mg(OH)₂ used. The reductions in PHRR were about 33% for 10% nano-Mg(OH)₂, 22% for 5% nano-Mg(OH)₂ and 23% for 1% nano-Mg(OH)₂. From these results one can suggest that NMH is acting as a flame retardant by the following mechanisms: energy absorption and *in situ* formation of a continuous network structured protective layer that behaves as a thermal shield and gas barrier to the oxygen diffusion and to the escape of degradation compounds. This barrier is effective due to nanoparticles needle form and size (large inorganic surface area). The energy absorption mechanism happens because magnesium compounds undergo a highly endothermic decomposition reaction that slows the heating rate of the host material in a fire.



In addition, the hydroxyl groups bonded to the magnesium are converted in the reaction into vapour water, which dilutes the concentration of flammable organic volatiles and $H/OH\cdot$ radicals in the flame. But the dilution effect is probably not relevant in this case because the polymer's degradation temperature is around 300 °C, about the same as the magnesium hydroxide one. We can also observe from the figure that the nanocomposite containing 1% amount of nano- $Mg(OH)_2$ starts to burn earlier, which means it has a shorter time-to-ignition, suggesting that this amount is not enough for the thermal protection effect needed in this early fire stage.

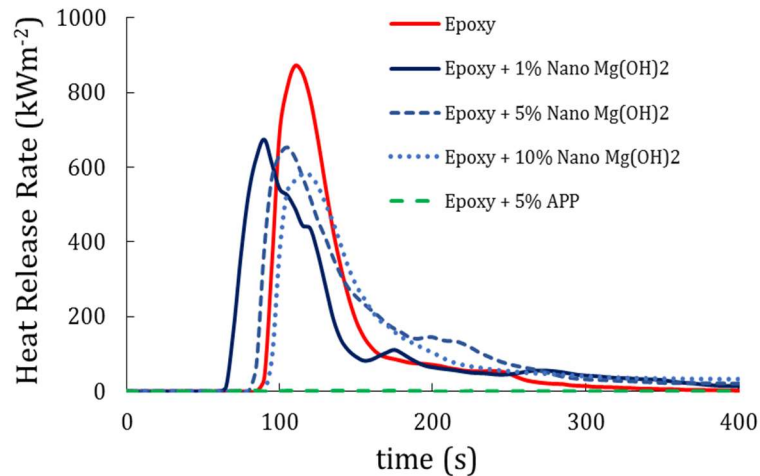


Figure 16: Heat release rate (HRR) curves for the epoxy resin, nano- $Mg(OH)_2$ -epoxy composites and APP-epoxy composites

Comparing with the traditional flame retardant, APP, used in this epoxy resin in a small amount, one can observe that it is more effective due to the formation of an important intumescent layer in the beginning of the burning test. The APP sample did not ignite. The concept of intumescence relies upon the formation of an expanded carbonized layer on the surface of the polymer during thermal degradation. This layer acts as an insulating barrier, reducing heat transfer between the heat source and the polymer surface. In general, the formulation of an intumescence system requires an acid source, a carbonizing agent and a blowing agent. The most widely used acid source is ammonium polyphosphate [7][9]. In future work the synergy between these flame retardants and their long-term stability will be studied headed for finding an appropriate fire retardant solution that does not affect the processability of the resin and mechanical properties and durability of the final composites.

2.4 Conclusions

The presence of nano- $Mg(OH)_2$ agglomerates can be seen in all SEM's pictures and by increasing the flame retardant amount the number of these agglomerates increases. Nano- $Mg(OH)_2$ particles have little effect on the thermal stability of epoxy composites at lower temperatures but decrease the thermal stability for higher temperatures (degradation by pyrolysis). These results are unexpected, and must be explored by further experiments, namely by chemical and TGA measurements. Comparing all the nanocomposites with pure epoxy resin, it is possible to see that there is a reduction in the flammability for all of the percentages of nano- $Mg(OH)_2$ used. These results are very promising regarding the use of epoxy resin as matrix of glass or carbon fibres composites where the PHRR is reduced by

the fibres, and further experiments are ongoing in order to evaluate and understand the flame retardant mechanism of these nanoparticles and fibres. Concerning APP/epoxy results, it was observed the formation of an important intumescent layer in the beginning of the burning test and the sample did not ignite. In future work the synergy between these flame retardants and their long-term stability will be studied headed for finding an appropriate fire retardant solution that doesn't affect the processability of the resin and mechanical properties and durability of the final composites.

A different approach for incorporating the nano-particles into the resin, in order to avoid agglomerations, which are probably reducing the flame retardant properties of the composite, will be studied in a future work. Another point that deserves some consideration is the consequence of using nano-magnesium hydroxide that is not coated with inorganic carbon.

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3 Effect of Traditional Flame Retardants, Nanoclays and Carbon Nanotubes in the Fire Performance of Epoxy Resin Composites

Marta S.S. Martins, B. Schartel, F.D. Magalhães, C.M.C. Pereira, “The effect of traditional flame retardants, nanoclays and carbon nanotubes in the fire performance of epoxy resin composites”, *Fire and Materials* (2016), DOI: 10.1002/fam.2370
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Abstract

The effectiveness of distinct fillers, from micro to nano-size scaled, on the fire behaviour of an epoxy resin and its carbon fibre reinforced composites was assessed by cone calorimetry. The performance was compared not only regarding the reaction to fire performance, but also in terms of thermal stability, glass transition temperature and microstructure. Regarding the fire reaction behaviour of nanofilled epoxy resin, anionic nanoclays and thermally oxidized carbon nanotubes showed the best results, in agreement with more compact chars formed on the surface of the burning polymer. For carbon fibre reinforced composite plates, the cone calorimeter results of modified resin samples did not show significant improvements on the heat release rate curves. Poorly dispersed fillers in the resin additionally caused reductions on the glass transition temperature of the composite materials.

Keywords: epoxy resin, carbon fibre reinforced composite, nanoclays, carbon nanotubes, flame retardants

3.1 Introduction

Due to their advantages regarding traditional metallic materials, namely low density, high specific stiffness and strength, good thermal insulation, corrosion resistance and improved fatigue properties, the use of polymer composites has been increasing in the past 50 years. Diverse applications in aircraft, spacecraft, boats, ships, automobiles, civil infrastructures, sporting goods and consumer products have been responsible for the continuous growth in the use of these materials [1]. Carbon fibre epoxy composites, in particular, because of their high strength, light weight and versatility, are being considered for use in the design of new advanced aircraft structural components [2][3]. Epoxy resins are the most commonly used polymeric matrix in advanced composite materials used for the fabrication of light structural panels for aircraft and other transport vehicles [4].

However, despite their remarkable combination of properties, composite materials are also known for their high flammability, which partly offsets their many advantages [5]. Consequently, improving the fire retardant behaviour of polymers and polymer composites is a major challenge for extending their use in a broader range of applications [6].

When these materials are exposed to high temperatures, the organic matrix decomposes with the release of heat, smoke, soot and toxic volatiles. Composites also soften, creep and distort when heated to moderate temperatures ($>100\text{ }^{\circ}\text{C}$), which can result in buckling and failure of composite structures [7]. For these reasons, stringent fire regulations have governed the use of polymer composites in many infrastructures and public transportation applications [1] [7].

Different methods can be used for imparting flame retardancy to polymer composites, one example being the modification of the polymeric resin through the addition of fillers. Alumina trihydrate (ATH) is currently the most commonly used flame retardant for polymeric matrices, due to a set of characteristics such as low cost, good flame retardant properties and low toxicity of the produced smoke [7]. Inorganic and organic phosphorous compounds are also effective flame retardants for many polymers. The flame-retardant mechanism depends on the type of phosphorus compound and the chemical structure of the polymer. One of the main issues regarding the use of traditional flame retardants, though, are the high loadings (sometimes 50 wt% or more) needed to achieve good flammability resistance. These high loadings affect negatively the polymer processability - which is particularly negative in the case of liquid infusion techniques for thermoset resins - and degrade the mechanical and durability properties of most types of polymer composites.

In the past years, however, the potential of nanomaterials such as carbon nanotubes or nanoclays as flame retardants for different polymeric matrices – both thermosets [8][9] and thermoplastics - has been of increasing interest. The reduction from micro to nano-scale significantly increases the filler's specific surface area, leading to a reduction in the amount of material necessary to promote changes in the host material's properties. To the best of our knowledge, however, there are only a limited number of works reporting the use of nanoclays for enhancement of fire reaction behaviour of reinforced composites. One of those works report that the use of nanoclays, a phosphorous-based curing agent or the combined use of both worsened the fire performance of the DGEBA (Diglycidyl Ether of Bisphenol A) resin composite [10]. The addition of an organically modified MMT (Montmorillonite) clay at 10 wt% loading to an epoxy glass fibre composite significantly reduced both the average extend and time of burning [11].

The potential of carbon nanotubes has been investigated for many highly demanding applications such as aerospace [12][13]. Despite the reports of the exceptional physical and mechanical properties of epoxy nanocomposites with CNTs [14][15][16][17] there are only a very limited number of studies on the epoxy/CNT composites flammability. Besides, the reported results are dependent on raw materials (nanotubes and epoxy resin types) and sample preparation. To our best knowledge, one of the first works reporting the flammability of epoxy resins filled with carbon nanotubes was made by our team [18]. The addition of 1% CNT to a low viscosity epoxy resin promoted a small increase in time-to-ignition and a decrease of 17% in PHRR (Peak Heat Release Rate).

In this study, the use of micro-sized flame retardants traditionally used in epoxy resins, namely APP (ammonium polyphosphate) and ATH (aluminium trihydroxide) were tested, both in the epoxy resin and in the carbon fibre reinforced composite. As an alternative to these conventional filled materials, nano-sized layered silicates, namely anionic and cationic clays, were also tested in amounts as low as 5%. Anionic clays have proven to be more effective in the selected epoxy resin, therefore carbon fibre composites were produced and

characterised selecting these nanofillers. Three different carbon nanotubes, non-treated, thermally or chemically treated, were also tested in low amounts (1 wt%), in both the resin and composite. The produced systems were characterised in terms of their reaction to fire behaviour, using cone calorimetry and also in terms of their thermal properties, using thermogravimetry. The microstructure and fillers dispersion was assessed by scanning electronic microscopy. Thermally oxidized carbon nanotubes promoted an increase in char formation, in agreement with the better results obtained, when compared to non-functionalized or chemically functionalized CNTs. None of the selected fillers was able to promote significant improvements of the fire reaction behaviour of their correspondent carbon fibre reinforced composite sample, probably a result of both low filler dispersion and amount, associated with limited sample thickness.

3.2 Experimental

3.2.1 Materials

The epoxy resin used was LY556 from Huntsman. This resin is a diglycidyl ether of bisphenol-A (DGEBA) with an epoxy content of 5.3-5.45 eq/kg and a viscosity of 10000-12000 mPa.s (at 25 °C). The curing agent used was an anhydride hardener and the catalyst an imidazole accelerator. The carbon fibre fabric used was Torayca T300, the baseline carbon fibre used in aerospace applications.

Two types of commercial nanoclays were used: Perkalite®, anionic (layered double hydroxide, LDH) from AkzoNobel (The Netherlands) and Nanofil®, cationic montmorillonite (MMT) clays from Süd Chemie Inc. (Germany). Table 4 presents the main characteristics of the clays used. The organic content was estimated by performing thermogravimetric analyses under nitrogen atmosphere.

Table 4: Characteristics of the nanoclays used

Nanoclay	Type	Organic Treatment	Organic Content (wt%)
Perkalite®	FR100	Hydrogenated fatty acid	68
	LD	No treatment	43
Nanofil®	116	No treatment	15
	2	Quaternary ammonium salt	32

Traditional flame retardants used as fillers in this study were micro sized ammonium polyphosphate (APP 422) from Clariant (Switzerland) and aluminium trihydroxide (ATH Martinal OL-104) from Albemarle (USA).

The carbon nanotubes were used in the form of a commercial masterbatch (from Future Carbon GmbH) and diluted to obtain the final desired concentration. A masterbatch is a product in which the additives are already optimally dispersed in a carrier material, i.e, in the resin. Three different types of treatment were tested: A – no treatment, CNTs “as

produced”; C – chemical treatment, CNTs with carboxylic acid functionalization; T – thermal treatment, thermally oxidized CNTs.

3.2.2 Sample preparation

i. Resin Samples

For CNT resin samples, the commercial masterbatches were diluted in LY556 resin to achieve the desired CNT mass concentration. The mixing conditions were the following: 10 minutes of manual stirring, 10 minutes of mechanical stirring at 1500-2000 rpm and 30 minutes of ultrasonication. For nanoclay and FR filled samples, the mixing procedure was the same. The hardener and catalyst were added in the proper amounts (95 wt% and 2 wt% regarding resin weight, respectively) and the resin plates were then cured (2 h, 120 °C) and post cured (2 h, 180 °C) using an electrical oven.

ii. CFRP Samples

For the preparation of Carbon Fibre Reinforced Polymer (CFRP) composite plates, the resins filled with nanoclays, carbon nanotubes (CNT) or flame retardants (FR) were prepared following the procedures described above. After observation of the cone calorimetry results for nanoclay composites, anionic clays were selected for CFRP composite manufacturing. The carbon fibre fabric was manually impregnated with the resin and then the materials were vacuum bagged and cured in the autoclave under the application of a positive pressure of 3 bar and a vacuum level of 150-250 mbar. The curing cycle was the same as the one used for resin samples. The compositions and abbreviations used for the different samples containing the various fillers are summarized in Table 5. All resin samples were identified starting with R, while CFRP samples were identified starting with CF (Carbon Fibre), followed by R (Resin).

The fibre content of the composite plates was determined by digestion of the resin matrix following standard ASTM D3171-76. The results are shown in Table 6.

3.2.3 Sample Testing

For assessing the fire behaviour of the materials, a cone calorimeter (Fire Testing Technology) was used at an incident heat flux of 50 kW/m² according to ISO 5660. Samples were conditioned at least during one week at constant temperature and humidity and wrapped in aluminium foil for the tests. Since tested samples (two of each formulation) had low thicknesses (2.5 mm), two metallic wires were used in order to maintain the material integrity during the tests, allowing the distance between the conical heater and the sample to be remain constant. First resin sample burning showed bending during the tests, therefore a special set-up was necessary. All samples were measured in a horizontal sample position using a sample holder with a retainer frame.

For assessing the dispersion level, XRD analysis were performed on both nanoclays alone and nanoclay filled resin samples using a Philips X’Pert MPD with a cobalt anticathode.

The morphology of composite plates was examined using a scanning electronic microscope (SEM) FEI Quanta 400 FEG_ESEM. Before observation, samples were fractured in liquid

nitrogen and covered with a thin layer of gold/palladium for increasing the surface conductivity.

For determining the glass transition temperature of the produced materials, a DMA Q800 from TA Instruments was used. Samples were tested at a frequency of 1Hz using a heating ramp of 5 °C/min from room temperature to 250 °C. The glass transition temperature (T_g) was taken at the maximum of the $\tan \delta$ curve. CCC

The thermal stability of the materials was assessed with a STA Q600 from TA Instruments. Samples of about 15 mg were tested at a heating rate of 10 °C/min under a flowing nitrogen atmosphere.

Table 5: Composition of the samples

Sample	Description	Filler	
		Type	Amount (wt%)*
R	Epoxy resin	---	---
R5-LD	Resin with nanoclays	Anionic, non-modified clay (Perkalite LD)	5
R5-FR		Anionic, modified clay (Perkalite FR100)	
R5-N2		Cationic, modified clay (Nanofil 2)	
R5-N116		Cationic, non-modified clay (Nanofil 116)	
R5-A	Resin with traditional FR	ATH	
R5-P		APP	
R1-CA	Resin with CNTs	CNTs no treatment	1
R1-CC		CNTs chemical treatment	
R1-CT		CNTs thermal treatment	
CFR	Carbon Fibre Epoxy Composite	---	---
CFR5-LD	Carbon Fibre Epoxy Composite with nanoclays	Anionic, non-modified clay (Perkalite LD)	5
CFR5-FR		Anionic, modified clay (Perkalite FR100)	
CFR5-A	Carbon Fibre Epoxy Composite with traditional FR	ATH	
CFR5-P		APP	
CFR1-CA	Carbon Fibre Epoxy Composite with CNTs	CNT no treatment	1
CFR1-CC		CNTs chemical treatment	
CFR1-CT		CNTs thermal treatment	

Table 6: Fibre content of the CFRP composite plates

Sample	Description	Fibre content vol %
CFR	CFRP	44.1
CFR5-LD	CFRP with nanoclays	43.0
CFR5-FR		47.0
CFR5-A	CFRP with traditional FR	45.0
CFR5-P		44.7
CFR1-CA	CFRP with CNTs	46.0
CFR1-CC		44.4
CFR1-CT		47.6

3.3 Results and Discussion

3.3.1 Resin Samples

i. Thermal Stability

Nanoclay Filled Resin Samples

For assessing the thermal stability of the samples, the decomposition stages, temperature peaks and mass losses are usually determined using thermogravimetric analysis (TGA). The beginning of decomposition can be characterised by the temperature at which samples lose 5% of their original weight, $T_{5\%}$ (°C). The most suitable temperature for characterizing the thermal decomposition is the maximum in first derivative mass loss curve, $T_{\text{máx}}$ (°C), indicating the temperature at which the rate of weight loss is maximum. The total weight loss, W (wt %), and the char content (or residue), $100 - W$ (wt %), characterise the decomposition level and may indicate a reduced flammability [19]. These results are depicted in Table 7 and the mass loss curves of nanoclay-filled resin samples, as well as resin alone, are depicted in Figure 17.

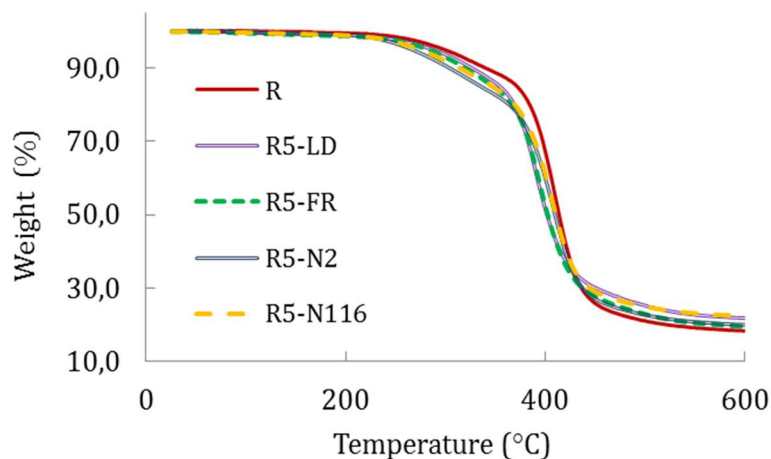


Figure 17: Mass loss curves of 5 wt% nanoclay filled epoxy resin

Table 7: Temperatures at 5% mass loss, peak in first derivative mass loss curve and final residue of 5 wt% nanoclay filled epoxy resin

Sample	T _{5%} (°C) Thermal stability	T _{máx} (°C) Thermal decomposition	Residue (%)
R	304	412	17.8
R5-LD	288	392	21.4
R5-FR	284	396	19.0
R5-N2	266	402	19.0
R5-N116	275	410	21.6

All samples start losing weight at about 270-300 °C and at 600 °C the decomposition is terminated, as shown by the stabilization of the residue content. Two decomposition steps occur: the first one, until about 380 °C, is attributed to the water elimination through dehydration of secondary alcohol groups and the formation of unsaturated structures. The second and most significant one (where mass losses of 45% were achieved) is due to the breakdown of the chemical bonds of the epoxy network, leading to complete volatilisation. For the neat epoxy resin, about 18% of the original polymer weight was transformed into a highly porous char. The residues typically obtained for epoxy resins in nitrogen atmosphere are in the range of 4 to 30% and depend on the functionality of the resin and choice of the hardener, which in turn affects the crosslink density [20][21].

The nanoclay-filled samples show the same thermal decomposition behaviour as the neat resin, with two main weight loss steps occurring. In both of these decomposition steps, the resin is more thermally stable than the nanocomposites. At higher temperatures, the non-modified clays (both anionic and cationic) show an increase in the residue yield from 18% to 21%. In both anionic and cationic clays, non-modified fillers show higher residue amounts, which is related to their higher inorganic contents, as shown in Table 4.

In the first decomposition step, anionic clays seem to provide a higher thermal stability than MMT ones. However, the situation is quite the opposite in the second decomposition step (i.e., from 380 °C forward). The first decomposition step of anionic clays is due to the loss of interlayer water and usually occurs between 100 and 300 °C.

In table 4 one may see that the temperatures required to 5% of mass loss and the peak temperature of the first derivative mass loss curve, referring to the thermal stability and thermal decomposition behaviours, respectively, decrease with the addition of layered silicate nanoparticles to the epoxy resin. These observations confirm the negative impact of the addition of nanoclays, both anionic and cationic, in the thermal stability of the epoxy resin under non-oxidative conditions. It is known that the addition of nanoclays can show deleterious effects on the thermal behaviour of epoxy resins as these fillers have the ability to decrease the curing reactivity of the resin, therefore resulting in lower crosslink density. This means that the resulting epoxy network is formed by polymeric chains which are not chemically bonded, i.e., crosslinked with each other. These are less thermally stable and therefore easier to degrade than highly crosslinked structures. The presence of the nanoclay layers, which possess a high aspect ratio and high surface area, may act as physical barriers to the crosslinking reactions between polymer chains. In fact, several authors [22][23][24][25][26] have reported decreased thermal stability of epoxy resins with the addition of different types of layered silicate nanoclays.

CNT Filled Resin Samples

The mass loss curves of CNT-filled resin samples, as well as resin alone are depicted in Figure 18 and the corresponding main results are summarized in Table 8.

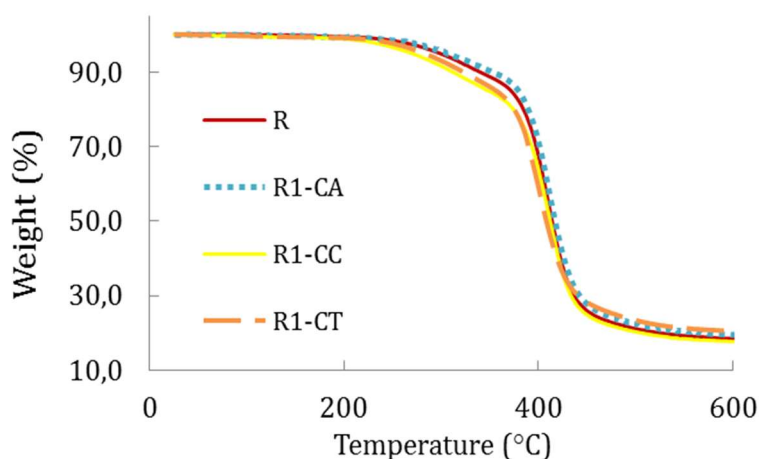


Figure 18: Mass loss curves of 1 wt% CNT filled epoxy resin

Table 8: Temperatures at 5 and 50% mass loss and final residue of 1 wt% CNT filled epoxy resin

Sample	T _{5%} (°C) Thermal stability	T _{máx} (°C) Thermal decomposition	Residue (%)
R	304	412	17.8
R1-CA	306	414	18.5
R1-CC	270	410	16.9
R1-CT	283	395	19.6

Similar to the results obtained for nanoclay filled resin samples, the thermal decomposition of carbon nanotube filled samples is characterised by two main decomposition steps. One can see that the pristine non-modified “as produced” carbon nanotubes are the only ones

providing an increase (although not considerable) in the thermal stability ($T_{5\%}$) and thermal decomposition ($T_{\text{máx}}$) of the DGEBA epoxy resin throughout the whole temperature range. Hammed [27] has recently reported that pristine CNTs are more thermally stable than functionalized ones due to their defect-free, crystalline structure. Additionally, Chen *et al.* [28] have shown that CNTs chemically functionalized with COOH are not dispersible in DGEBA epoxy resin, settle in the bottom and form agglomerates. SEM observations presented in the same study exhibited isolated regions of agglomerated CNTs and devoid of nanotubes in other regions. This low dispersion may explain the thermal destabilization of the epoxy resin, especially in the first degradation step. Furthermore, the chemically treated carbon nanotubes possess a higher organic content in their composition than pristine or thermally treated ones. Uzunpınar [29] has shown that COOH functionalized nanotubes suffer a fast weight loss process ending at about 300 °C, followed by a slowly and continuous weight loss process, active in the whole temperature range (until 800 °C). He reported that most of the graft COOH groups in the nanotubes were lost at about 300 °C. The thermally treated CNTs provide a slight increase of 1.8 % in the final residue, while the untreated CNTs promote a residue increase of 0.7 % comparing with the neat resin. The impact of carbon nanotubes in the thermal stability of the resin appears to be lower than nanoclays. However, a direct comparison cannot be made as the filler loading is different for both types of samples (5 wt% for nanoclay filled and 1 wt% for CNT filled resin).

FR Filled Resin Samples

The thermal stability of epoxy resin filled with 5 % of either ATH or APP is graphically depicted in Figure 19 and summarized in Table 9. The presence of ATH does not change the thermal decomposition behaviour of the resin, but there is a more rapid mass loss between 220 and 400 °C (in the first decomposition step) in the presence of this flame retardant. This is consistent with the well-known decomposition behaviour of aluminium trihydroxide, occurring in the same temperature range due to formation of aluminium oxide and water. Similar results have been reported by Mahrholz and co-workers [30] who have additionally observed that as the ATH content increases from 5 to 20%, the decrease in mass loss of an epoxy resin occurs earlier and is simultaneously more pronounced.

The mass loss of ammonium polyphosphate filled epoxy resin is even more pronounced, especially in the temperature range between 320 °C and 400 °C, until a stable char residue is formed (at about 415 °C). This increased mass loss is due to the decomposition of the filler itself - APP starts decomposing around 280 °C with the elimination of ammonia and water. Wang and co-workers [31][32] stated that the addition of ammonium polyphosphate to an epoxy resin leads to a decrease in the thermal stability during the first decomposition stage, but increases the thermal stability of the second stage. The phosphoric acid derived from APP decomposition catalyzes the dehydration reaction of polymer end chains, causing char formation. This char protects the polymer from further decomposition during the second stage and acts as a barrier to the release of fuel gases from the surface. Kandola *et al.* [33] reported a reduction of 47 °C in the onset temperature of thermal decomposition (temperature at which 10% of the original mass of the sample has been lost) of an epoxy resin, as well as an increase in char formation at temperatures above 500 °C with the addition of 15 wt% ammonium polyphosphate.

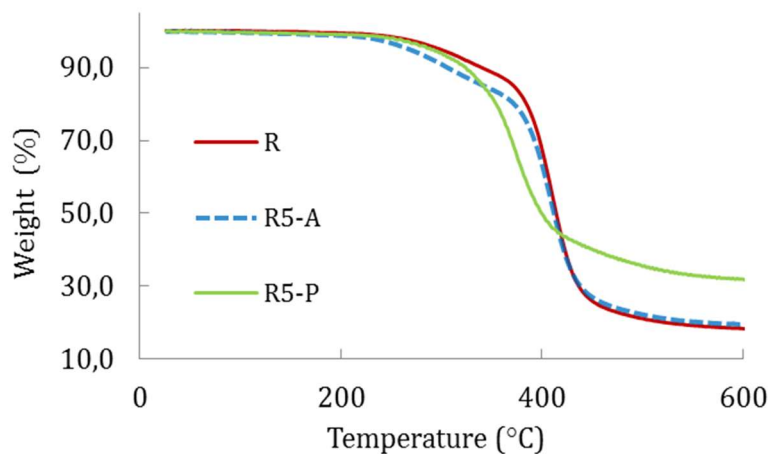


Figure 19: Mass loss curves of 5 wt% FR filled epoxy resin

Table 9: Temperatures at 5 and 50% mass loss and final residue of of 5 wt% FR filled epoxy resin

Sample	T _{5%} (°C) Thermal stability	T _{máx} (°C) Thermal decomposition	Residue (%)
R	304	412	17.8
R5-A	269	410	18.6
R5-P	290	376	30.7

ii. Dispersion of Nanofillers

Nanoclay Filled Resin Samples

The XRD spectra obtained for all nanoclay filled resin samples, as well as the corresponding nanoclay alone, are depicted in Figure 20.

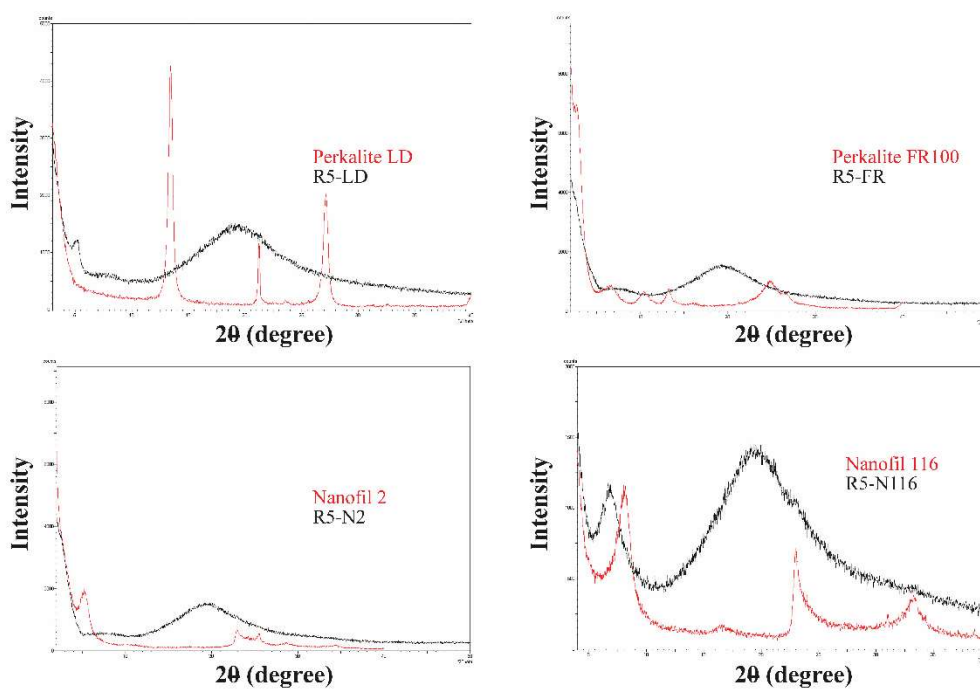


Figure 20: XRD spectra of nanoclays and nanoclay resin samples: R5-LD (top left), R5-FR (top right), R5-N2 (bottom left), R5-N116 (bottom right)

One may see that in non-modified clays (N116 and Perkalite LD), there is a shift in the first peak to a lower angle, which can be attributed to an expansion of the basal spacing (anticipating the formation of an intercalated structure). Although the layer spacing increases, there still exists an attractive force between the silicate layers leading to stacking in an ordered structure. By Bragg's Law, this is visible by higher spacing: nanoclay N116 (cationic) spacing increases from 12.6Å to 15Å, while Perkalite LD (anionic) spacing increases from 7.7Å to 18.9Å.

In modified clays (N2 and Perkalite FR), the first peak disappears in the XRD spectra, which can be indicative that the spacing between clay lamellas is high enough not to be able to be measured by the diffractometer. If no peaks are observed in the XRD pattern, this is due to the loss of the structural ordering of the layers. The absence of Bragg diffraction peaks in the nanocomposites may indicate that the clay has been completely exfoliated. This means that the clay modification with organic compounds can be effective towards obtaining homogenous epoxy nanocomposites.

If no peaks are observed in the XRD pattern, usually this is due to the loss of the structural ordering of the layers. In that case, the absence of Bragg diffraction peaks in the nanocomposites may indicate that the clay has been completely exfoliated. However, Morgan and Gilman [34] have shown that, for polymer layered silicate nanocomposites, the absence of a peak can be related to many factors besides exfoliation, such as low clay concentration, orientation, and poor calibration of the XRD instruments at very low angles. The hypothesis of effective exfoliation must therefore be assumed with some caution.

iii. Fire Reaction Behaviour

Nanoclay Filled Resin Samples

Figure 21 shows the heat release rate curves of the pristine resin sample, as well as nanoclay filled samples obtained during cone calorimeter testing at 50 kW m^{-2} .

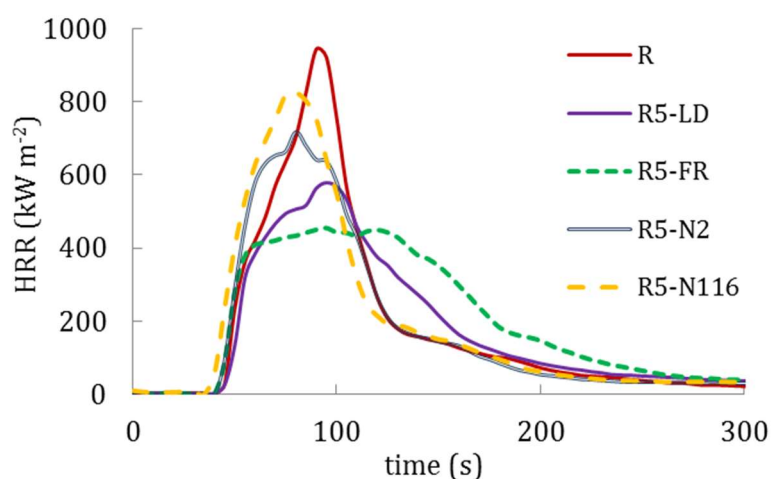


Figure 21: Heat release rate curves of 5 wt% nanoclay filled epoxy resin

Depending on the characteristics of the burning material, different shapes of heat release rate curves can be obtained. Usually the classification of the burning behaviour typically

results in a) thermally thick non-charring, b) thermally thick charring or c) intermediate thickness non-charring material. Despite the fact that the tested resin based samples have low thicknesses (around 2.5 mm), they show a burning behaviour closer to intermediate thick non-charring materials, rather than a thermally thin ones. Intermediate thick non-charring polymers show an initial, strong increase in the HRR after ignition up to a value identified as the averaged steady HRR which can be seen as a shoulder followed by a peak behaviour closer to the end of the test [35]. Scharrel and co-authors [36] attributed this peak near the end of the thermal feedback that occurs when the pyrolysis zone reaches the back of the sample. This epoxy resin shows an additional small shoulder on the heat release rate curve.

On the other hand, especially for anionic clay filled samples, the burning behaviour changes to a typical pattern of charring, residue-forming materials [37]. Char forming materials tend to burn slowly due to the formation of an effective char layer at the surface of the polymer; therefore the shape of the heat release rate does not show sharp peaks.

In fact, it has been reported that nanocomposite materials change the burning behaviour of the polymer from non-charring to charring or residue-forming. Charring materials show an initial increase to the averaged steady HRR, followed by a decrease in HRR until flame-out. The initial increase in HRR happens until an efficient char layer is formed. The HRR decreases as a result of char layer thickness increase [37][38]. Non-charring materials burn away completely, but charring materials leave relatively significant amounts of residue. The influence of sample thickness on the peak and average heat release rate is less significant in charring polymers than in non-charring ones. For charring polymers, the char layer will block the penetration of heat, resulting in small changes on the peak heat release rate under high irradiance [35].

The heat release rate curves of samples filled with 5 % of nanoclays show that anionic (layered double hydroxide) clays have a superior performance when compared to cationic ones. Considerable reductions in the PHRR are observed for LDH-filled samples, namely 39 and 52% for non-modified and modified clays, respectively.

Other authors [39] have already reported that LDH are more effective flame retardants than MMT for epoxy resins. The difference in performance has been justified with a more compact and intumescent char obtained with LDH/epoxy as compared with fragmented residues in the case of the montmorillonite/epoxy system. Analyzing the residues formed after cone calorimeter tests (Figure 22), one may observe that in fact anionic clay filled samples show a more stable char with clay platelets being visible, while MMT filled resin samples show a lower residue amount, which seems to be in a carbonized stage. It is reported in the literature [20] that the reduction in the (peak) heat release rate of nanocomposites is a consequence of a lower fuel feed rate caused by a physical barrier built by the inorganic clay nanoparticles. These act as a mass transfer barrier, lowering the release of generated gas fuel and, additionally, having the ability of re-radiating the heat flux, acting as a heat shield [40][41].

Anionic nanoclays, namely LDHs, act additionally by releasing aqueous vapour and carbon dioxide during decomposition, promoting dilution of combustible gases of pyrolysis, and reducing the heat release during the combustion [42]. It is also expected that the formation of metal oxides [e.g.: Al_2O_3 , MgO] during LDH decomposition increase the thermal stability of the yield char. The compactness of the residue during burning is generally related to the

efficiency in HRR reduction; the higher the compactness, the lower the heat release rate [20].

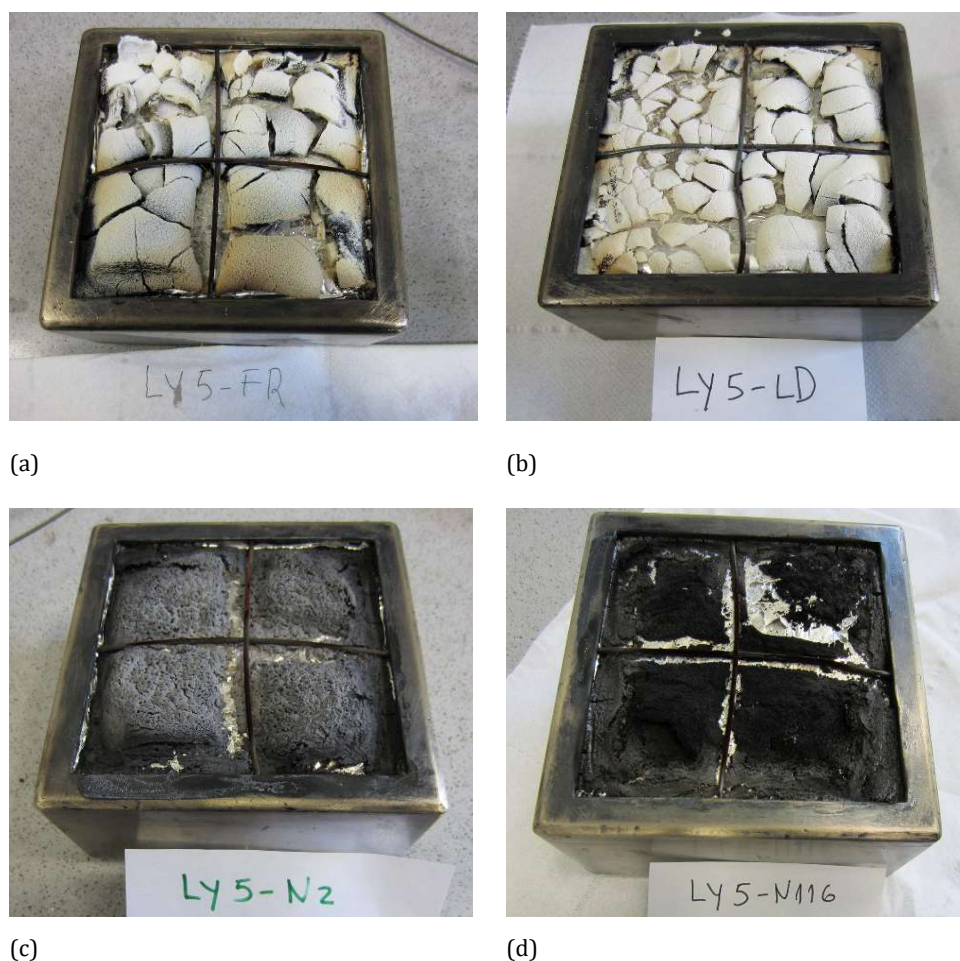


Figure 22: Residues of 5% nanoclay-filled resin after cone calorimeter tests: (a) 5 wt% anionic modified clay, (b) 5 wt% anionic non-modified clay, (c) 5 wt% cationic modified clay, (d) 5 wt% cationic non-modified clay

The total heat release values obtained for resin and nanocomposite samples are quite similar. This is considered a major disadvantage of these materials in a fully developed fire, as the nanocomposites do not extinguish until most of the fuel has been burned, as they burn slowly but burn nearly completely [43]. The obtained residue is formed primarily by the inorganic portions of resin and nanoclay. Especially for the sample filled with 5 wt% of modified LDH, there is a clear change in the fire behaviour of the resin, as no sharp peak is observed in HRR vs. time curve, with a smoother, broader heat release with time, once again confirming the barrier effect that the clay particles promote.

CNT Filled Resin Samples

Figure 23 shows the heat release rate curves for carbon nanotube modified resin samples. These samples show a decrease in the ignition time at a loading of 1 wt% for all CNT treatments. A major effect influencing the ignition properties of polymeric materials is thermal inertia, which is a function of the product of specific heat capacity, material density and thermal conductivity [44][45].

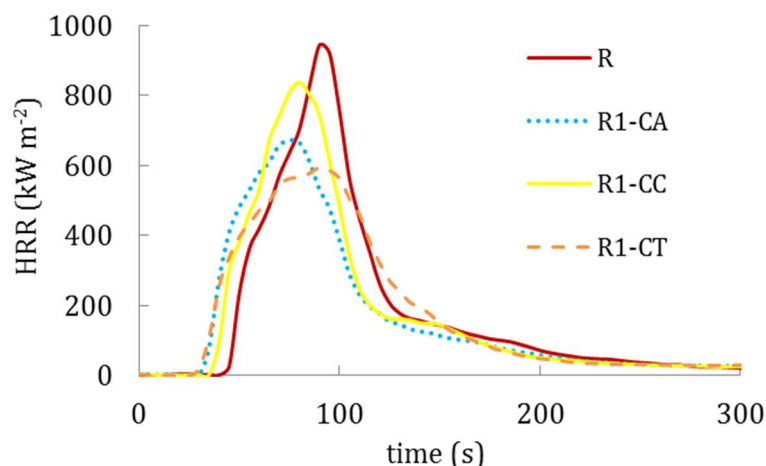


Figure 23: Heat release rate curves of 1 wt% CNT filled epoxy resin

As already reported by Dittrich *et al.* [44], there are mainly three parameters that affect the ignition properties of polymer materials – specific heat, density and thermal conductivity. Carbon nanomaterials are supposed to significantly increase thermal conductivity as has already been reported for PP/MWCNT [46] and epoxy/CNT nanocomposites [38]. More thermally conductive materials promote heat conduction from surface to sample interior, delaying ignition [46].

However, Dittrich *et al.* [44] showed that an increase in heat absorption, induced by the carbon nanofillers, can offset the effect of thermal conductivity, and become the main parameter controlling ignition. In their study, through experimental measurements of the in-depth heat absorption during cone calorimeter tests, those authors were able to conclude that radiative heat flux was completely absorbed at low material thicknesses (0.6 mm) when in the presence of carbon nanofillers. The absorbed heat yields a more rapid temperature increase at the surface and triggers earlier polymer ignition. Heat absorption coefficient was observed to increase with nanoparticles loading, leading to lower ignition times, even if this effect is partly counterbalanced by an increase in thermal conductivity.

The thermally oxidized CNT promote higher reductions in the peak heat release rate of this DGEBA resin, and a broader heat release rate curve along time, indicating that resin burning is slower in the presence of thermally oxidized carbon nanotubes. The reduction in PHRR for thermally treated CNT filled sample is of about 38 %.

The less thermally stable CNT in thermogravimetric analyses are the ones providing less improvements in the heat release rate behaviour; in fact, the burning behaviour of 1 % chemically modified CNT filled sample is the same as the neat resin, but with an accelerating effect, in agreement with the observed in TGA tests. This behaviour is most likely to be attributed to the loss of carboxyl groups from CNT surface, followed by the elimination of hydroxyl groups. As previously mentioned, COOH functionalized nanotubes suffer a fast weight loss process ending at about 300 °C. Covalent functionalization of CNTs is usually achieved by introducing functional groups on defect sites of CNTs by using oxidizing agents such as strong acids, which results in the formation of carboxylic or hydroxyl groups (-COOH, -OH) on the surface of nanotubes. This type of functionalization is known as defect group functionalization [21].

The thermal oxidation of carbon nanotubes creates bonding sites on the tube walls by breaking the C–C bonds, leading to narrower diameter distribution, free of amorphous carbon. Additionally, they have more bonding sites for better functionalization. According to Gogotsi and co-workers [47], individual nanotubes seem to be more graphitic after high temperature annealing treatment. Unlike in the case of acid treatment, thermal treatments do not promote damages in the walls of the tubes. Furthermore, thermal oxidation eliminates initial defects in tube walls, providing a potential enhancement of electrical and thermal properties in comparison to tubes that have been acid etched or otherwise damaged in a chemical treatment.

Figure 24 shows the aspect of the residues obtained after cone calorimeter tests of the carbon nanotube filled epoxy samples. It is clearly seen that thermally oxidized nanotubes promoted an increase in char formation, which can help explain the better results obtained, when compared to non-functionalized or chemically functionalized CNTs. Dittrich *et al.* [44] reported that in order to achieve effective protection, the structure and surface of the residue layers have to be dense and closed. Good and effective nanoparticle dispersion is fundamental for fire retardancy improvements.

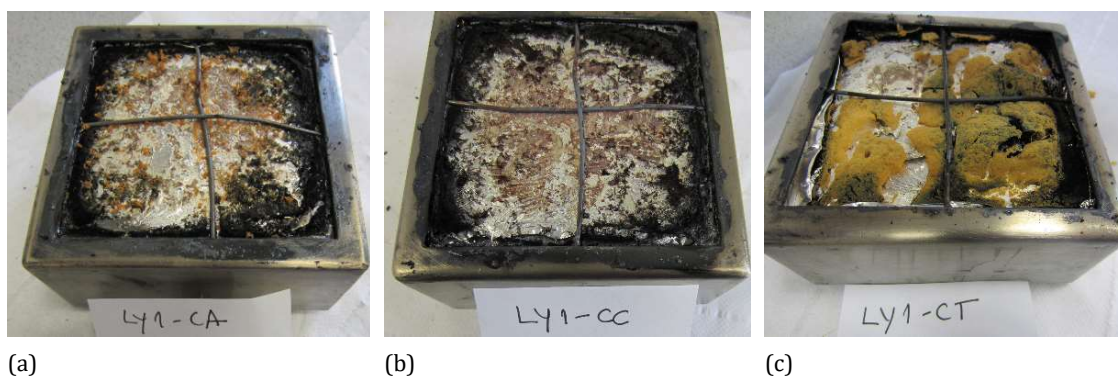


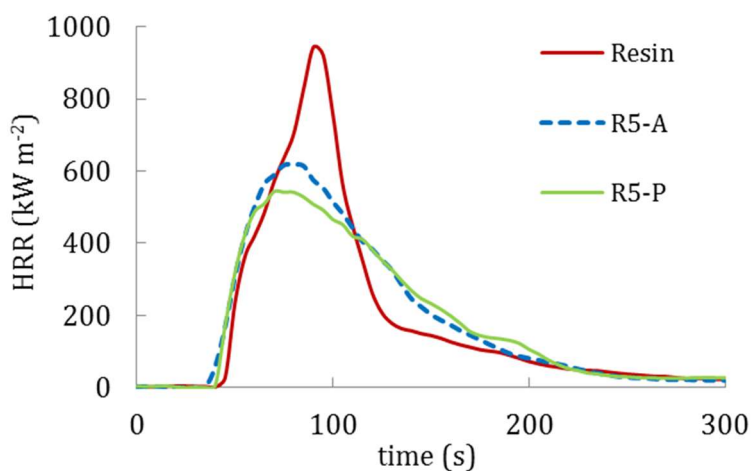
Figure 24: Residues of 1% CNT filled resin after cone calorimeter tests (a) CNT no treatment (b) CNT COOH function (c) CNT thermally oxidized

FR Filled Resin Samples

The addition of different types of inorganic fillers such as magnesium or aluminium hydroxide, influence the fire behaviour of polymeric materials because the content of combustible material is reduced, the thermal conductivity of the material is altered and the melt viscosity is changed (in the case of thermoplastics). However, due to severe fire regulations, very few inorganic fillers have achieved market acceptance for commercial uses [20]. The application of ATH is further limited due to its relatively low decomposition temperature; therefore it shall be used only in polymers requiring processing temperatures below its decomposition temperature.

The fire reaction behaviour of 5 wt% flame retardant filled epoxy resin is shown in Figure 25. Both traditional FR – ATH and APP – are able to significantly reduce the burning rate of the pristine resin, with reductions of 35 and 42% in PHRR, respectively. The behaviour of both filled resin samples is quite similar, although APP is slightly more effective than ATH. The shape of the heat release rate curves changed towards the behaviour associated with the formation of a resistant char barrier layer on the surface of the burning polymer. Photographs of the residues clearly show the formation of a vitreous intumescent char

formed at the surface of APP filled resin, which clearly protects the polymer and slows down the combustion mechanism. The total heat released during cone calorimeter tests is similar for all samples, i.e., around 60 MJ.m^{-2} , indicating that the resin burns completely but at a slower rate.



(a)



(b)



(c)

Figure 25: (a) Heat release rate curves of 5 wt% FR filled epoxy resin (b) residue of 5% ATH filled resin (c) residue of 5% APP filled resin

A summary of the main reaction to fire parameters obtained in all resin systems tested is presented in Table 10. All of the tested fillers were able to reduce the peak heat release rate of the selected epoxy resin. Anionic nanoclays showed the higher reductions in this parameter. Comparison with the same loading of traditional flame retardants ATH or APP shows better performance of the nanoclays. Non-modified anionic clays show additional, albeit very slight, improvements in the total heat released and the smoke production parameters. Thermally oxidized carbon nanotubes at a loading of 1 wt% provided decreases of 38, 10 and 6% on peak heat release rate, total smoke production and total heat released, respectively.

Table 10: Resume of the obtained results from cone calorimeter tests on resin samples

Sample	TTI (s)	PHRR (kWm ⁻²)	t _{PHRR} (s)	THR (MJm ⁻²)	TSP (m ²)
R	38	943	90	60.3	21.5
R5-LD	35	578	95	58.4	18.2
R5-FR	38	453	95	66.5	20.8
R5-N2	33	823	80	61.7	18.8
R5-N116	38	717	80	58.6	18.3
R1-CA	26	673	75	53.8	19.4
R1-CC	32	837	80	57.4	20.9
R1-CT	25	585	95	56.6	19.3
R5-A	35	617	80	59.2	22.1
R5-P	36	543	70	58.8	20.1

3.3.2 CFRP Samples

i. Morphology

Scanning electronic microscopy observations were performed on fractured samples, in order to observe the filler distribution along the thickness. CFRP composite plates were produced from modified resin samples prepared using the same methodology as the resin ones. Figure 26 shows the distribution of the anionic nanoclays, modified or unmodified, on the composite plates. Nanoclay agglomerates can be seen in both samples, although the size of the aggregates seems to be slightly larger on the modified clay. The agglomerates seem to be dispersed throughout the matrix, therefore one may conclude that there is no sedimentation or filtration of the nanoparticles in the fibre. To be noted that for these observations, resin layers between the carbon fibre fabrics were selected. Other images taken with different magnifications do not show significant differences between the unmodified and organically modified LDH based samples. These microscopic visualization of agglomerates could lead to the assumption that the nanoclays are not fully dispersed within the epoxy matrix. In XRD analysis, spectra of non-modified clay epoxy samples showed evidence of intercalated structure, while in modified clay samples no peaks are observed in the XRD pattern.

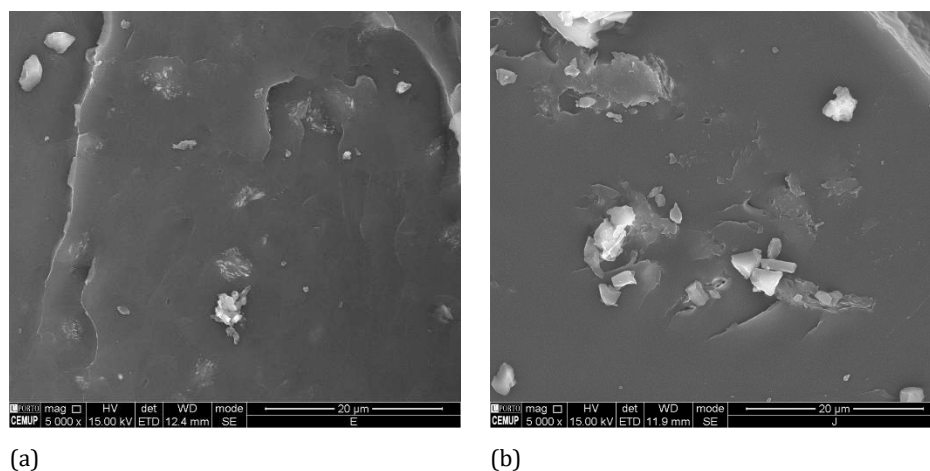


Figure 26: Electron microscopy observations of nanoclay filled carbon fibre composite plates (a) anionic non-modified clay (5000x) (b) anionic modified clay (5000x)

Figure 27 shows the differences between the dispersion of the different carbon nanotubes in the resin at a magnification of 10000x. Significant differences can be seen for thermally oxidized CNTs, which are better dispersed than chemically functionalized or non-treated ones. Although some agglomerates are visible, the nanotubes are clearly distributed throughout the resin matrix. Chemically (COOH) functionalized CNTs seem to be poorly dispersed, with large aggregates visible and few nanotubes outside these agglomerated areas. These SEM observations correlate well with the fire reaction results observed during cone calorimeter tests. It was already reported in the literature that nanoparticle dispersion is fundamental for achieving good flame retardant properties and, in the case of the tested nanotubes, it is clear that the functionalization affects the dispersion in the host matrix, which in turn affects the heat release rate behaviour. Thermally oxidized CNTs promoted better dispersion in the epoxy resin and higher reductions in the heat release rate. It is interesting to note, however, that despite the fact that chemical treatments are usually intended to increase the compatibility with the matrix [48][49][50], in this case, turned out to be the most poorly dispersed nanotubes in the resin, promoting less improvements in the fire reaction behaviour of the resin.

In this field, contradictory results have been reported in the literature. As mentioned before, Chen *et al.* [28] shown that carboxylic functionalized carbon nanotubes are not dispersible in DGEBA epoxy resin, forming agglomerates. On the other hand, other authors [51][52][53] reported that the presence of carboxylic acid groups on the surface of CNTs enables a better dispersion in the epoxy resin. According to these authors, the introduction of tailored chemical groups such as amino or carboxyl, enables covalent bonding between CNTs and epoxy, improving the interfacial stress transfer and positively affecting the dispersibility of the nanofiller.

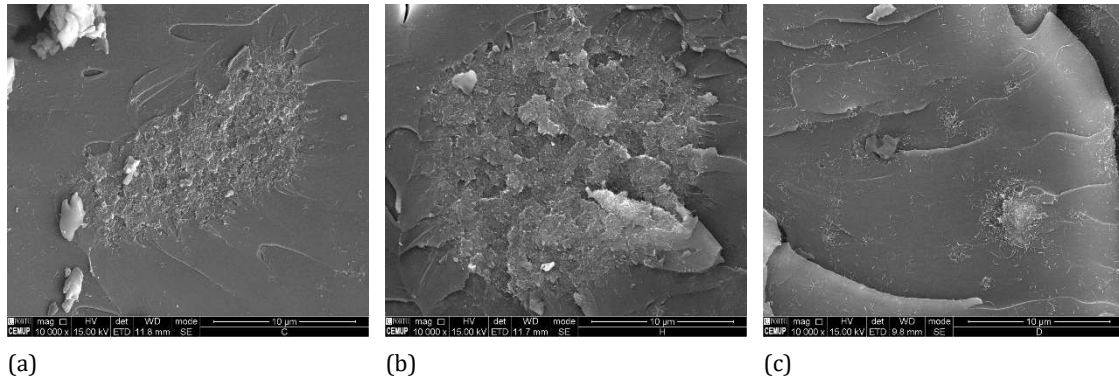


Figure 27: Electron microscopy observations of CNT filled carbon fibre composite plates (a) CNT no treatment (10000x) (b) CNT COOH function (10000x) (c) CNT thermally oxidized (10000x)

A work by Dittrich *et al.* [44] on the effect of different carbon nanofillers on the properties of polypropylene showed that the degree of exfoliation of graphene layers significantly affected the burning behaviour of the host polymer. While poorly dispersed systems led to reductions on PHRR in the order of 45%, highly dispersed systems were able to reduce this parameter in about 75%. Although reductions in PHRR are effectively achieved, well dispersed nanomaterials have the potential to dramatically decrease peak heat release rate of the host polymeric material. Another work from Katsoulis *et al.* [22] reported similar results: poorly dispersed double walled nanotubes were still able to promote a 12% reduction in the PHRR a high viscous, high temperature epoxy resin and an 11% reduction for THR of a low-viscosity and room temperature curing epoxy resin, while showing no significant effect on all other parameters.

ii. Glass Transition Temperature

As mentioned in the experimental section, the glass transition temperature (T_g) of all samples were measured using a dynamic mechanical analyses equipment and taken as the maximum point of the tan delta curves. The results obtained for all composite plate samples are summarized in Table 11.

Table 11: Glass transition temperatures of composite samples

Sample	Description	T_g (°C)
CFR	CFRP	158
CFR5-LD	CFRP with nanoclays	137
CFR5-FR		138
CFR1-CA	CFRP with CNTs	151
CFR1-CC		153
CFR1-CT		157
CFR5-A	CFRP with traditional FR	140
CFR5-P		144

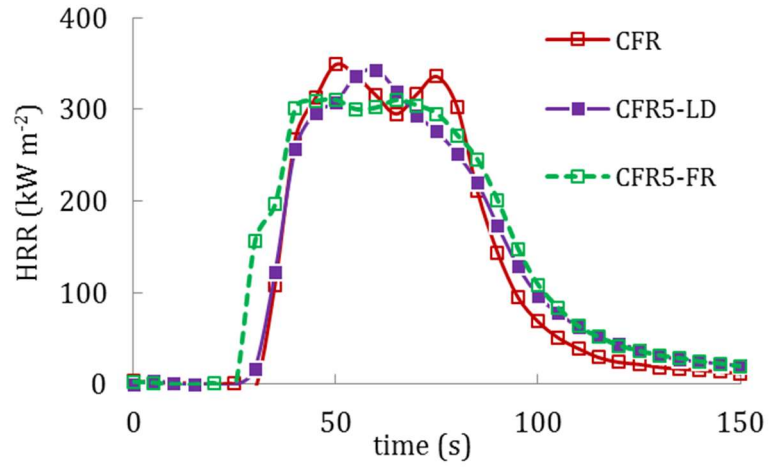
The pure composite sample shows a glass transition temperature of about 158 °C and the addition of fillers, nano or micro-sized, lead to reductions of this value. Thermally oxidized nanotubes are able to maintain the glass transition temperature of the composite plate. Non-modified and chemically modified carbon nanotubes reduce the T_g in about 5 to 7 °C. These results are again linked with the SEM observations which revealed better dispersion of thermally treated CNTs when compared with other carbon nanomaterials. One could therefore assume that the properties of the CFRP materials could be enhanced if good dispersions were obtained. Property enhancement is limited by low particle dispersion. The addition of nanoclays promoted decreases in the glass transition temperature of about 20 °C, and traditional flame retardants also show negative impacts on this property.

The glass transition of a polymeric system can be affected by many different factors, but in this case, as the resin system and curing conditions used were always the same, the differences in T_g must be mainly due to the presence of the fillers. A significant decrease in the glass transition temperature of nanoclay filled epoxy composites could be caused by the complex interaction between the polymer matrix and layered silicates in which the formation of chemical bonding at the interface can restrict the motion and mobility of the polymer segments. As a consequence, there is a decrease in the crosslink density of the epoxy network, leading to a drop in T_g . As reported by Wang *et al* [54], these effects may be enhanced at high clay concentration. These authors reported increased T_g with incorporation of 1 wt% of clay, but reductions after further addition. As a result, they were able to conclude that the effect of adding nanoclay in the glass transition of a polymer can promote opposite effects and, due to the complexity in epoxy/clay systems, it is hard to identify the dominant mechanisms unless precise characterisation of the polymer/clay interface is achieved. Chemical bonding at the interface of the silicate and epoxy matrix could lead to hindered relaxational mobility in the polymer segments near the interface, which leads to increase of T_g . But, as mentioned before, reduced crosslink density at the interface can be dominant, causing decreases in the glass transition temperature. Probably the effect is not so visible with CNTs because the filler mass added was lower (1 wt% versus 5 wt% for the nanoclays).

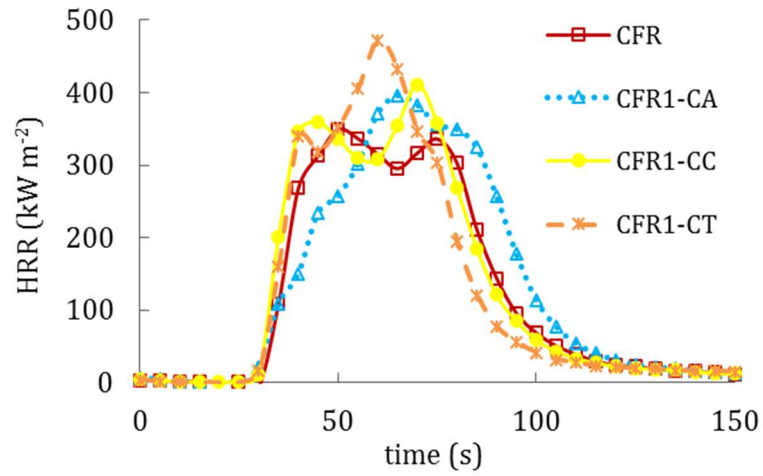
The most unexpected values were the ones obtained with the addition of traditional flame retardants ATH and APP, which lead to considerable reductions in the T_g of the composites. In a previous work [55] we have reported a slight increase in the T_g of a low viscosity epoxy resin with the addition of 5 wt% of APP. Similar results [56][57] were also published, showing that usually these fillers do not impact or even improve the T_g of the epoxy resin system. This means that further measurements shall be conducted in order to understand this behaviour.

iii. Fire Reaction Behaviour

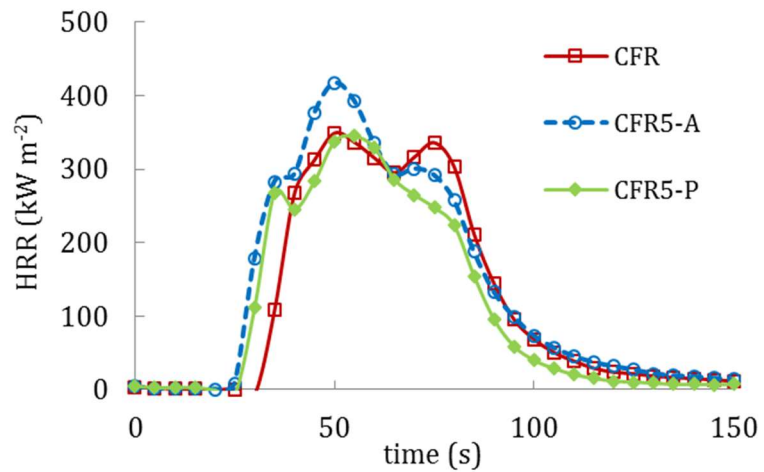
The heat release rate versus time curves obtained for all composite plates are shown in Figure 28 and the results summarized in Table 12. As previously mentioned, from the analyses to the nanoclay filled resin plates fire reaction behaviour, only anionic clays (LDH) were selected for manufacturing and testing of carbon fibre reinforced composite samples.



(a)



(b)



(c)

Figure 28: Heat Release Rate curves of (a) 5 wt% nanoclay filled CFRP composites (b) 1 wt% CNT filled CFRP composites (c) 5 wt% FR filled CFRP composites

The earlier ignition of flame retardant/nanoclay/CNT filled CFRP samples is probably due to the lower thermal stability of the resin matrix with the addition of these fillers, as observed in thermogravimetric analyses presented and discussed earlier.

Apart from ATH and thermally oxidized carbon nanotubes, which clearly degrade the fire reaction behaviour of the composite material, there is no significant change with the addition of micro or nanosized fillers to the resin matrix. This can be attributed to the fact that the tested materials have low thicknesses (between 2 and 2.5 mm), therefore possessing very low resin amounts (about 45% of composite mass). The amount of filler is thus very small when compared with the total composite plate mass, which means that probably higher amounts are necessary for obtaining flame retardant effects.

Furthermore, direct comparison of the performance between resin and fibre reinforced composites is not feasible. The fibre reinforcement influences the combustion mechanism. In fact, non-combustible fibres such as glass and carbon fibres show a diluting effect and have influence on the velocity of combustion. Furthermore, they act as barriers in the combustion mechanism [58]. Other authors have reported similar results. S.V. Levchik *et al.* [58] reported that carbon fibres mostly act as inert diluent of the combustible epoxy matrix and suppress the intumescent behaviour of fire retardant epoxy resins. More recently [59], Toldy and co-workers observed that the flame retardant performance achieved by the introduction of a phosphorus-containing reactive amine is less than expected from the additivity of effects of the amine and carbon fibres. Authors suggested that the reinforcing carbon fibre fabric plies in the composite systems hinder the solid phase intumescent flame retardant effect of phosphorous amine. Therefore, instead of forming a well-developed char, only thin char layers are formed between the carbon fibre plies, causing its delamination.

Table 12: Resume of the obtained results from cone calorimeter tests on composite plate samples

Sample	TTI (s)	PHRR (kWm ⁻²)	t _{PHRR} (s)	THR (MJm ⁻²)	TSP (m ²)
CFR	28	349	50	20.4	7.4
CFR5-LD	22	343	60	21.9	6.7
CFR5-FR	21	310	65	23.0	6.7
CFR1-CA	27	396	65	22.7	8.5
CFR1-CC	26	411	70	21.7	7.4
CRY1-CT	27	471	60	22.2	6.9
CFR5-A	22	417	50	22.6	7.1
CFR5-P	24	345	55	18.6	6.0

Carbon nanotube filled CFRP plates are the ones showing worse properties, particularly thermally oxidized CNTs, which lead to increases in peak heat release rate and total heat release. In this case, the balance between the chemical and physical effects is taking place. While thermally oxidized CNTs showed better dispersion (physical effects), the non-modified (chemical effects) carbon nanotubes did not affect as negatively the thermal decomposition of the resin. Nevertheless, none of the tested systems, whether nano or

microsized scaled, were able to enhance the fire reaction properties of a thin carbon fibre epoxy composite sample.

3.4 Conclusions

Anionic, layered double hydroxide clays, showed better performance than cationic (MMT) ones on the fire reaction behaviour of an epoxy resin obtained by cone calorimetry. The burning behaviour of the resin changed to a typical char forming material with the addition of 5 % of LDH, as also confirmed by the formation of a more stable char in the surface of the burning polymer. For carbon nanotube modified resin samples, thermally oxidized CNT promote higher reductions in the peak heat release rate. Chemically modified nanotubes are less thermally stable and lead to a lower reduction in peak heat release rate, most likely due to detachment of carboxyl groups from CNT surface.

Regarding the fire behaviour of thin carbon fibre epoxy composite samples, none of the tested systems - nano or microsized - were able to enhance its fire reaction properties. The thickness of the produced composite plates were low (in the range of 2 mm), therefore the filler amount added to the resin matrix can be lower than the necessary for achieving enhanced fire reaction properties. The presence of several carbon fibre layers in the burning material can also be hindering the activity of condensed phase flame retardant mechanisms such as the formation of stable chars or intumescence. Further research work shall be done in order to understand the limitations of the use of different fillers on the fire reaction behaviour of fibre reinforced composite materials.

XRD analyses of modified clay resin samples were not conclusive and the absence of Bragg diffraction peaks could not necessarily conclude about the exfoliation of the clay particles. Furthermore, microscopic observations showed the presence of some clay agglomerates. We believe that effort shall be put in order to obtain good dispersion levels of the nanofillers within the resin matrix. As already shown by other authors, proper filler dispersion is crucial for obtaining appropriate flame retardant effects.

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4 Ceramic Tapes as Fire Protective Coatings for CFRP Composites

Abstract

Ceramic tapes with different compositions were produced using tape casting technology. They were afterwards applied on the surface of carbon fibre reinforced epoxy composites during manufacturing and used in the green state as fire protective coatings. The thermal decomposition behaviour of the tapes was assessed using thermogravimetry and the fire reaction behaviour of the composite materials tested in the cone calorimeter.

Keywords: FRP composites, fire reaction, tape casting, ceramic tapes

4.1 Introduction

The composites industry has experienced over the past three decades a long-term growth based on global economic development and higher penetration into key markets such as building and construction, wind energy, aerospace and automotive. Commercial and industrial applications of fibre-reinforced polymer (FRP) composites are diverse in both structural and non-structural application areas due to their many outstanding physical, thermal, chemical and mechanical properties.

Key advantages of fibre-reinforced composites over many traditional metal alloys include low density, high specific stiffness and specific strength, good fatigue endurance, excellent corrosion resistance, outstanding thermal insulation and low thermal expansion.

However, composite materials present several disadvantages and challenges, such as gradients in through-thickness mechanical properties, poor impact damage tolerance, anisotropic structure and significantly poor performance under fire. These have hindered their growth on specific markets such as aircrafts and naval applications. Aircraft fires, for example, are extremely hazardous due the difficulty in escape from the fire scenario. In addition, besides excellent fire resistant properties, aircraft composites must prove appropriate properties in order to prevent structural failure during and after a fire [1].

Many polymer composites ignite when exposed to high heat fluxes, releasing heat that can, in some circumstances, contribute to the growth of the fire. Significant quantities of smoke and toxic fumes may also be released, limiting visibility and posing serious health hazards. For these reasons, more and more stringent fire regulations govern the use of composites in aircraft, ships, buildings and land transport. The regulations require that the fire reaction properties of these materials meet specified levels. The reaction properties that are often used to define the fire hazard include heat release rate, time-to-ignition and flame spread rate.

Several methods are currently used for providing flame retardant properties to fibre reinforced polymer composites. Some of the approached methods are the use of mineral and ceramic wool, high performance fibres or inherently flame retardant resins and the chemical modification of the resin [2].

In the already manufactured FRP composite materials, the use of surface coatings is very attractive because these materials act in the solid phase and, as a result, the intrinsic

properties of the virgin material (such as the mechanical properties) are not modified. Furthermore, surface coatings can be easily applied by means of spray, brush, or roller to a large number of materials, such as metals, polymers, textiles and wood [3]. In fact, the use of fire retardant coatings is one of the easiest, oldest and most efficient ways to protect materials against fire. Moreover, since ignition occurs usually on the surface of a material, it is important to concentrate the protective action at this place [4]. In the aerospace industry, for instance, the use of surface coatings or the chemical or physical modification of the resin are seen as the most suitable fire retardant solutions, as the retention of mechanical properties after heat exposure are fundamental requirements. On the other hand, the use of thermally insulative layers of mineral and ceramic wool is considered an appropriate solution for naval and transportation industries.

Coatings can be classified as passive (e.g., inorganic fibre coatings, ceramic films) or active (e.g., intumescent) systems. These are mainly used to slow heat conduction from the fire into the composite, and thereby improve the fire endurance and survivability. Coatings are also used to minimize the spread of flame and extend the time to flashover by slowing the heat-up rate and decomposition rate of the composite material. Different types of coatings have already shown improvements on the fire reaction behaviour of composites [5][6][7][8][9]. The post-fire mechanical properties of glass fibre composites remain unchanged or even increase [10] when using a thermal barrier coating. Significant improvements in the post-heat flexural moduli retention in glass/epoxy laminates protected with surface coatings were also observed by E. Kandare *et al.* [11].

In this work, however, we propose the use of thin ceramic films as alternative coatings for obtaining flame retardant FRP composites. Ceramics are inorganic and nonmetallic materials that, in comparison with metals and polymers, possess features such as high-thermal stability, superior wear resistance, high hardness, low thermal and electrical conductivity and chemical stability. Retention of mechanical properties at high temperatures turns these materials into unique solutions to several engineering application problems. Ceramics can be used in many different applications such as cutting tools (Si_3N_4), medical implants (Al_2O_3 , ZrO_2), heat engines and gas turbines (ZrO_2 , SiC , Si_3N_4) [12]. The flexibility in composition, thickness and handleability makes these materials interesting to be used as fire shields for FRP composites. These ceramic tapes are used, for instance, as circuit boards in integrated multi-layer circuits, e.g. for so-called LTCC (low-temperature co-fired ceramics) circuits. In this work, ceramic tapes were produced using tape casting technology and applied on the surface of epoxy carbon fibre composite materials before curing. The thermal stability of the produced tapes was assessed using thermogravimetry and the composite plates were characterised in terms of their fire reaction behaviour using a cone calorimeter with an incident heat flux of 50 kW/m^2 .

4.2 Experimental

4.2.1 Materials

The epoxy resin used was LY555 from Huntsman. This resin is a diglycidyl ether of bisphenol-A (DGEBA) with an epoxy content of 5.3-5.45 eq/kg and a viscosity of 10000-12000 mPa.s (at 25°C). The curing agent used was an anhydride hardener and the catalyst an imidazole accelerator, also supplied by Huntsman. The carbon fibre fabric used was

Torayca T300, the baseline carbon fibre used in aerospace applications. For the production of the ceramic tapes, the powders used were aluminium oxide and calcium carbonate.

4.2.2 Sample Preparation

i. Preparation of Ceramic Tapes

For the production of the ceramic films or tapes, the tape casting technology was used. Tape casting is also known as *doctor blading* or *knife coating*, and this is a well-known technology in many industries, including paper, plastic and paint manufacturing. A scraping blade is used to spread the material and remove the excess substance from the surface being coated. The gap between the doctor blade and the carrier defines the wet thickness of the tape being cast. [13]. The main advantage of tape casting process is that it is the best way to form large area, thin and flat ceramic parts [13].

Tape casting is usually based upon a non-aqueous solvent as liquid system, as these solvents are easier to dry, especially in industrial processes. However, in this work, we produced ceramic tapes by tape casting using aqueous systems. In recent years, the environmental and health aspects of the tape casting process have received special attention, therefore, efforts to industrialize slurry formulations using water as the liquid medium, instead of organic solvents, are being made. Non-aqueous liquids have lower boiling points and avoid hydration of the ceramic powder, but require special precautions concerning toxicity and flammability. Typically, organic solvent recovery systems are needed to control emissions of compounds into the atmosphere. On the other hand, an aqueous system has advantages of incombustibility, non-toxicity and low cost, associated with the large amount of experience with the use of water in similar ceramic powder processes, such as slip casting [14]. For the production of ceramic tapes by knife coating, several chemical components need to be added in order to obtain a proper slurry. Table 13 summarizes the function of each of those components. As requested by Fraunhofer Institute for Ceramic Technologies and Systems IKTS, where these ceramic tapes were produced, the detailed composition of the materials will not be provided here.

Table 13: Components required for the production of a tape casting slurry formulation [13][14]

Component	Function	Examples
Solvent	The solvent dissolves the organic materials and distributes them uniformly throughout the slurry. It is the vehicle that carries the ceramic particles in a dispersion until it evaporates and leaves a dense tape on the carrier.	Depending on the composition of the ceramic powder and on the thickness of the tape, a variety of non-aqueous organic solvents such as alcohols, ketones or hydrocarbons are commonly used to prepare highly concentrated suspensions with reproducible rheological properties and drying behaviour. Ethyl alcohol, Xylene, Acetone, Ethyl Acetate, Ethylene Glycol

Component	Function	Examples
Powder	The most important ingredient in batch formulation is the ceramic, metallic or composite powder. After binder removal and final consolidation, the powder is the only portion of the batch left.	Al_2O_3 (aluminium oxide), ZrO_2 (zirconium dioxide), MgO (magnesium oxide), ZnO (zinc oxide), ZrB_2 (zirconium diboride)
Binder	The binder is probably the most important processing additive of the system. It supplies the network that holds the entire chemical system together for further processing. Being the only continuous phase in the green tape, the binder has the greatest effect on such green tape properties as strength, flexibility, plasticity, laminatability, durability, toughness, printability and smoothness.	The majority fall into two main families: polyvinyls (vinyl) and polyacrylates (acrylic). PVA [poly(vinyl alcohol)], PAA [poly(acrylic acid)], PEA (phenyl ethyl alcohol), PVB (Poly vinyl Butyral)
Plasticizer	Plasticizers are additives that soften the binder in the dry or semidry state. The purpose of the plasticizer in a green tape is to enable the tape to be bent without cracking. The plasticizer breaks the close alignment and bonding of the binder molecules, thereby increasing the flexibility and workability of the tape.	Organic substances with low molecular weight Glycerol, BBP (benzyl butyl phthalate), PPG (dibutyl phthalate), PEG (polyethylene glycol)
Surfactant	Additive that actively modifies (or coats) the particle surface to impart a desired characteristic such as lower surface charge, higher surface charge, high or low surface energy or specific surface chemistry.	Dodecylbenzene sulfonic acid, sodium salt, tributyl phosphate
Dispersant	The purpose of a dispersant is to disperse primary particles and to hold them in a homogeneous suspension	Acrylic dispersants, NH_4PA (Ammonium polyacrylate), NH_4PMA [Ammonium polymethacrylate], PAA [poly(acrylic acid)]

The tape casting process can be summarized as shown in Figure 29. In the case of this work, however, the sintering process was not performed, as it was intended to use the tapes in their “green” state, therefore the final tape was obtained after casting and solvent drying processes, as shown by the red alternative arrow.

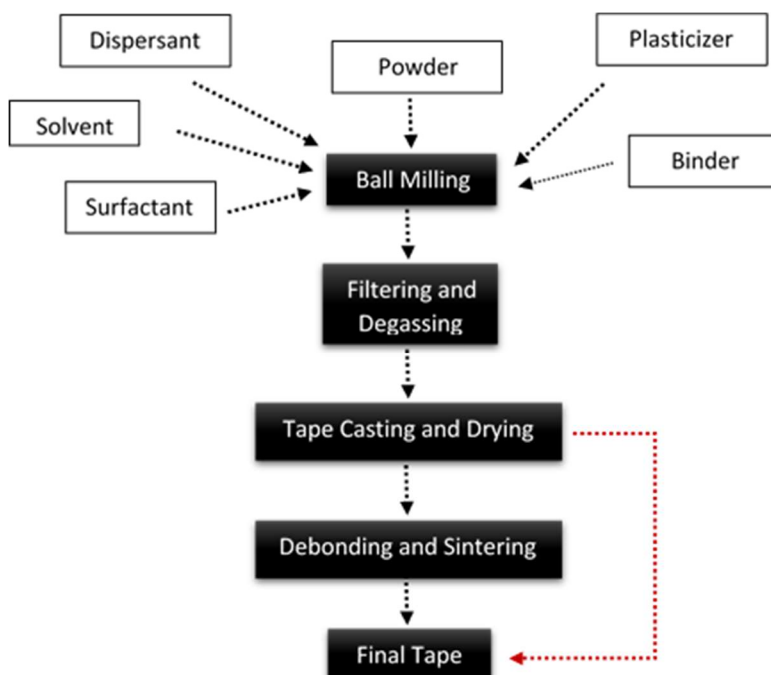


Figure 29: Tape casting process flowsheet

Two different inorganic powders were used: aluminium oxide and calcium carbonate. For tape A, only aluminium oxide was used. Tape B was formulated using both powders, while in tape C some cellulose fibres were added to the aluminium oxide slurry. These were intended to add some compactness to the tape. The characteristics of the ceramic tapes produced are shown in Table 14 and some pictures of the materials are shown in Figure 30.

Table 14: Ceramic tapes produced by tape casting

Ceramic Coating	Composition	Average wet thickness (mm)	Average dry thickness (mm)	Sintered
A	Al ₂ O ₃	1.2	0.3 – 0.4	No
B	Al ₂ O ₃ +CaCO ₃			
C	Al ₂ O ₃ +cellulose fibres			

In this work we have used “green”, non-sintered ceramic tapes as coatings for FRP composites. The main advantage of the non-sintered tapes is that they are very flexible, allowing their proper positioning in any FRP structure. They are also very easy to cut.



Figure 30: Aspect of the ceramic tape after casting and flexibility in the green state

ii. Preparation of CFRP Composites

The carbon fibre laminates were prepared by hand lay-up followed by autoclave curing (2h 120 °C) and post-curing cycles (2h 180 °C) under vacuum and positive pressure. Six layers of carbon fabric were used and the ceramic tape in the green state was applied as top layer. The details of the produced composite materials are depicted in Table 15. Reference carbon fibre composite was labeled as CF, while composite plates coated with ceramic tapes were labeled as CF followed by T (from tape), and A, B or C, depending on the composition of the ceramic tape used.

Table 15: Composite materials produced

Reference	Carbon Fibre	Coating	Thickness (mm)
CF	6 layers	---	1.6
CF-TA		Al ₂ O ₃	1.9
CF-TB		Al ₂ O ₃ +CaCO ₃	1.9
CF-TC		Al ₂ O ₃ +cellulose fibres	2.0

4.2.3 Sample Testing

The thermal stability of the produced ceramic tapes was assessed with a STA Q600 from TA Instruments. Samples of about 10 mg were tested at a heating rate of 10 °C /min under a flowing nitrogen atmosphere.

The surface morphology of composite plates was examined using a scanning electronic microscope (SEM) FEI Quanta 400 FEG_ESEM. Before observation, samples were covered with a thin layer of gold/palladium for increasing the surface conductivity. Additional analyses were made using the EDS (Energy dispersive x-ray detector mode), which allows mapping the distribution of chemical elements within the analyzed surface.

For assessing the fire behaviour of the materials, a cone calorimeter (Fire Testing Technology) was used at an incident heat flux of 50 kW/m² according to ISO 5660. Samples were conditioned at least during one week at constant temperature and humidity and wrapped in aluminium foil during the tests. Since tested samples had low thicknesses, two metallic wires were used in order to maintain the material integrity during the tests,

allowing the distance between the conical heater and the sample to be remain constant. All samples were measured in the horizontal position using a sample holder with a retainer frame.

4.3 Results and Discussion

4.3.1 Thermal Stability

The mass loss curves of the ceramic tapes as a function of temperature, as well as the corresponding first derivative curves, are shown in Figure 31.

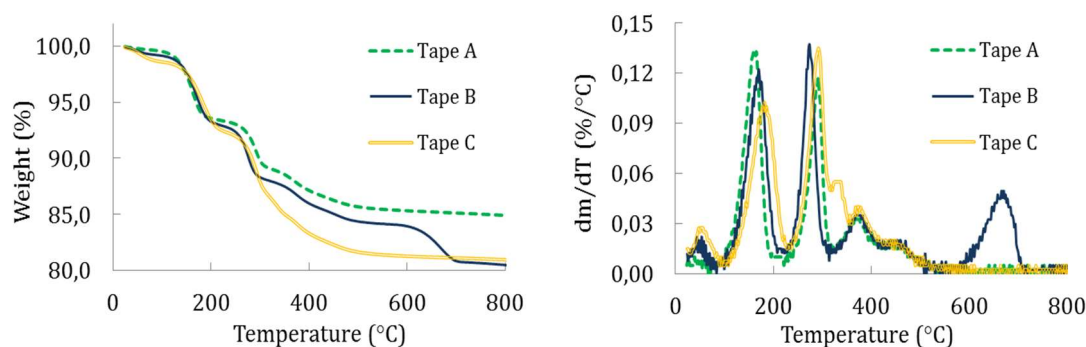


Figure 31: Thermal stability of the ceramic tapes as a function of temperature

The thermal decomposition behaviour of the tapes is similar until about 300 °C, after which significant differences are observed. Several mass loss steps can be identified:

- The first mass loss step occurs until 100 °C, which is caused by the loss of moisture content. Most water is lost during the drying process. However, since this was performed at room temperature, a small amount can still be present in the final tape composition. This loss is, however, very small in all materials (less than 2%) and is negligible comparing with the other decomposition steps.
- The second mass loss occurs between 100 and 210 °C and is due to the decomposition of the plasticizer. A total mass loss of about 6% is observed in all green tapes.
- The third mass loss step occurs between 210 and 310 °C.
- The fourth and smaller mass loss step occurs until about 500 °C. In steps 3 and 4, tape C loses more weight than tapes A and B, about 11%. For tapes A and B, a clear difference between steps 3 and 4 is visible and the total mass loss is about 7 to 8%. These two consecutive steps are due to the decomposition of the binders used in the tape casting slurry formulations. The decomposition of the first binder (which is a polyvinyl) occurs between 250 and 450 °C, while the second binder (which is an acrylic emulsion polymer) usually decomposes between 300 and 400 °C.

After these common decomposition steps, the thermal behaviour of the ceramic tapes differ from one another:

- The final residue of tape A is attained at about 550 °C. From the produced tapes, this is the one that shows a higher inorganic content: about 85% in mass.

- Tape B shows one additional mass loss step, with the maximum mass loss rate at 670 °C. In this last step, a mass loss of 3% occurs. For this material, the final inorganic content is about 81%. This mass loss is due to the decomposition of the calcium carbonate, only present in tape B. CaCO_3 starts decomposing at around 635 °C [15].

In fact, all of the ceramic tapes show high thermal stabilities, with low mass loss and high inorganic contents. Tape A seems to be the most thermally stable throughout the tested temperature range.

4.3.2 SEM Characterisation

As previously mentioned, the composite plates were produced with the different ceramic tapes as coating layers. The top surface layer, i.e, the ceramic tape, was applied before resin curing and post-curing temperature cycles. Scanning electronic microscopic pictures of the composite surface of the three coated composite samples at different magnifications are depicted in Figure 32.

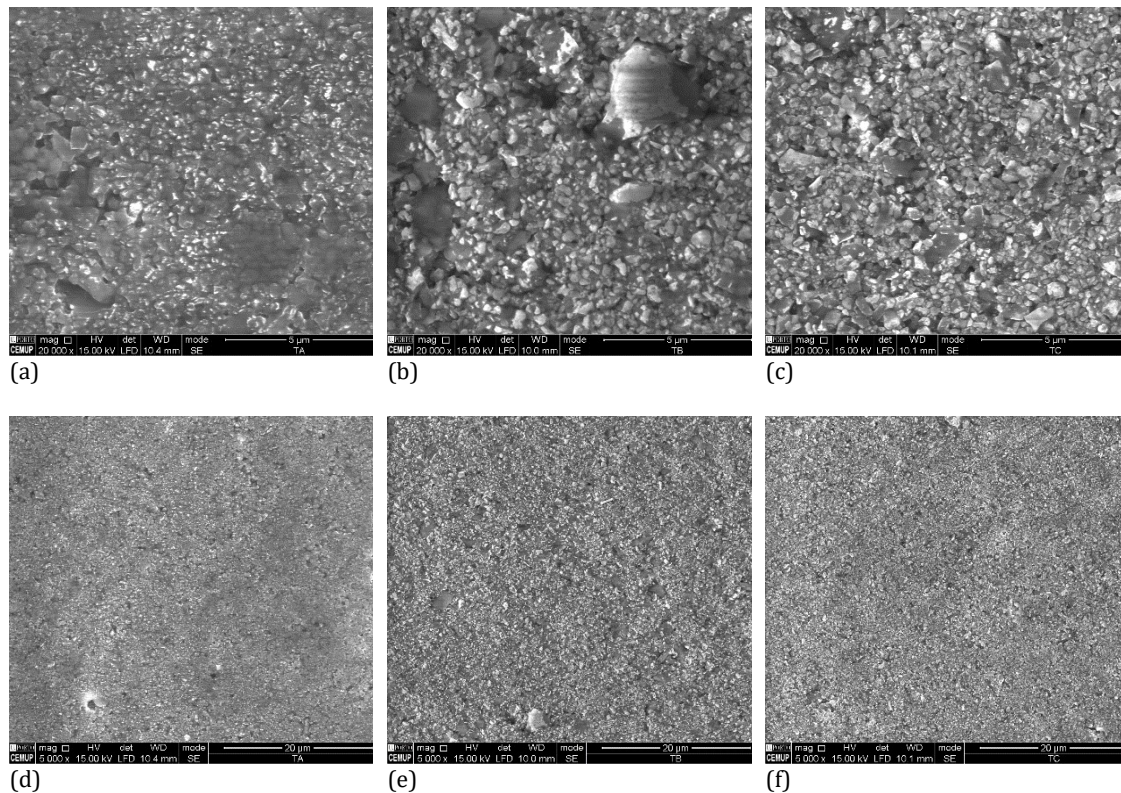


Figure 32: Scanning electronic microscopy pictures of composite sample surfaces at different magnifications: (a) CF-TA, 20000x (b) CF-TB, 20000x (c) CF-TC, 20000x (d) CF-TA, 5000x (e) CF-TB, 5000x (f) CF-TC, 5000x

Comparing the images at the magnification of 20000x (upper row), it seems that tape B is the one that shows a somewhat different structure. Particles with different sizes are visible, which is in agreement with the chemical composition of this material, composed of two ceramic powders. At a lower magnification (figure 32e), some resin points are visible, however, there are also small areas (similar to grains) that are not fully covered with resin (some of the brighter points of the picture). Tape A (figures 32 a and 32 c) seems to be more

impregnated with resin, when comparing with tape C (figures 32 c and 32 f). The presence of cellulose fibres in tape C slurry may be hindering the resin impregnation. It seems that tape C shows, however, a more compact and closed structure, which was precisely intended with the addition of the fibres. Tape C also appears to have a more homogeneous distribution in terms of particle size. The chemical composition of this tape, as assessed by SEM/EDS, is composed only by Carbon (C), Oxygen (O) and Aluminium (Al) (note that hydrogen is not detected in this mode). The same chemical composition is seen for tape A, while in Tape B additionally Calcium (Ca) is detected.

A map of chemical elements distribution was performed only in tape B. The selected elements for observation were Aluminium (in blue), Calcium (in yellow), Carbon (in red) and Oxygen (in green). Based on picture 29b, the obtained map for each of these elements is shown in Figure 33. This is an interesting analyses in the sense that it can provide not only a detailed mapping of the chemical elements present, but it also provides insight regarding the distribution/dispersion of the different components within the material.

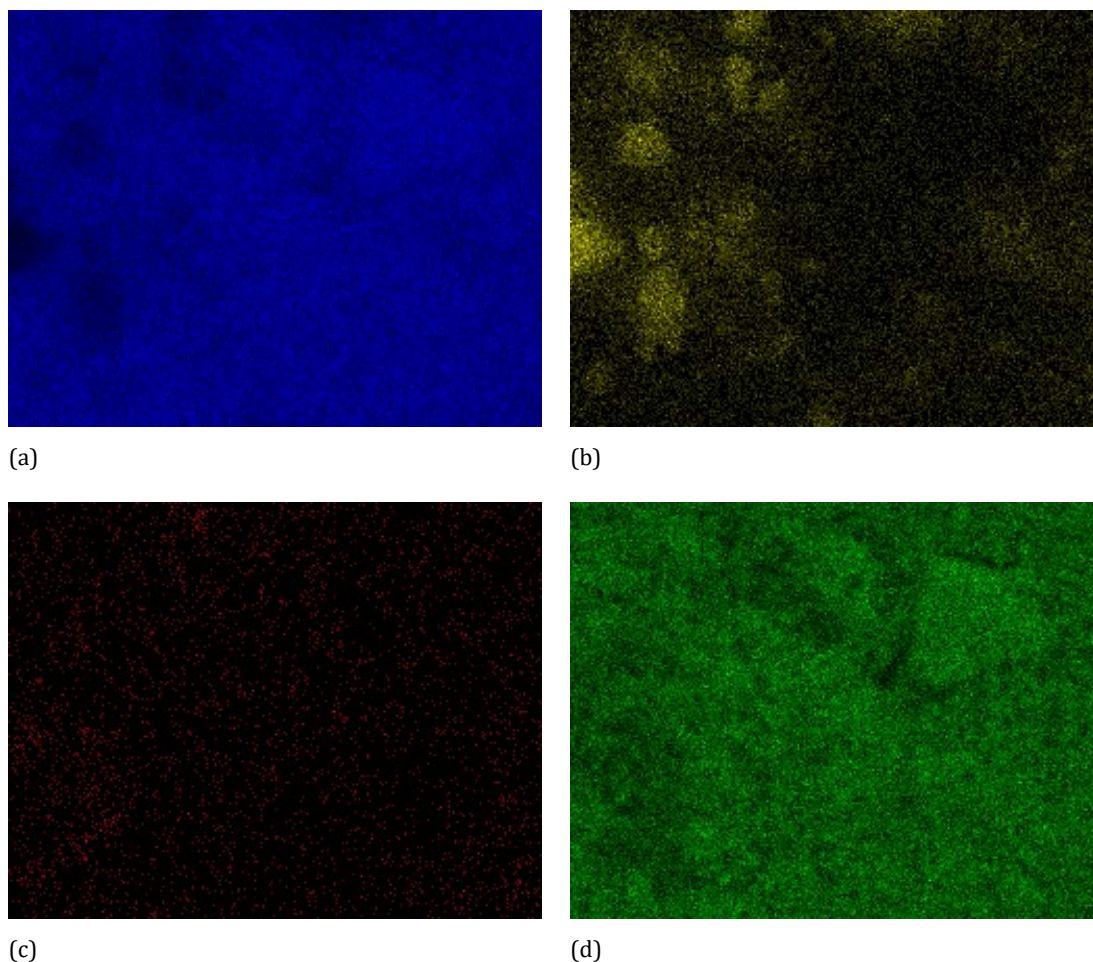


Figure 33: Compositional mapping of tape B: (a) aluminium (b) calcium (c) carbon (d) oxygen (magnification 23000x)

4.3.3 Fire Reaction Properties

The main fire reaction properties of the produced composite plates, obtained by cone calorimetry at an incident heat flux of 50 kW/m² are shown in Figure 34.

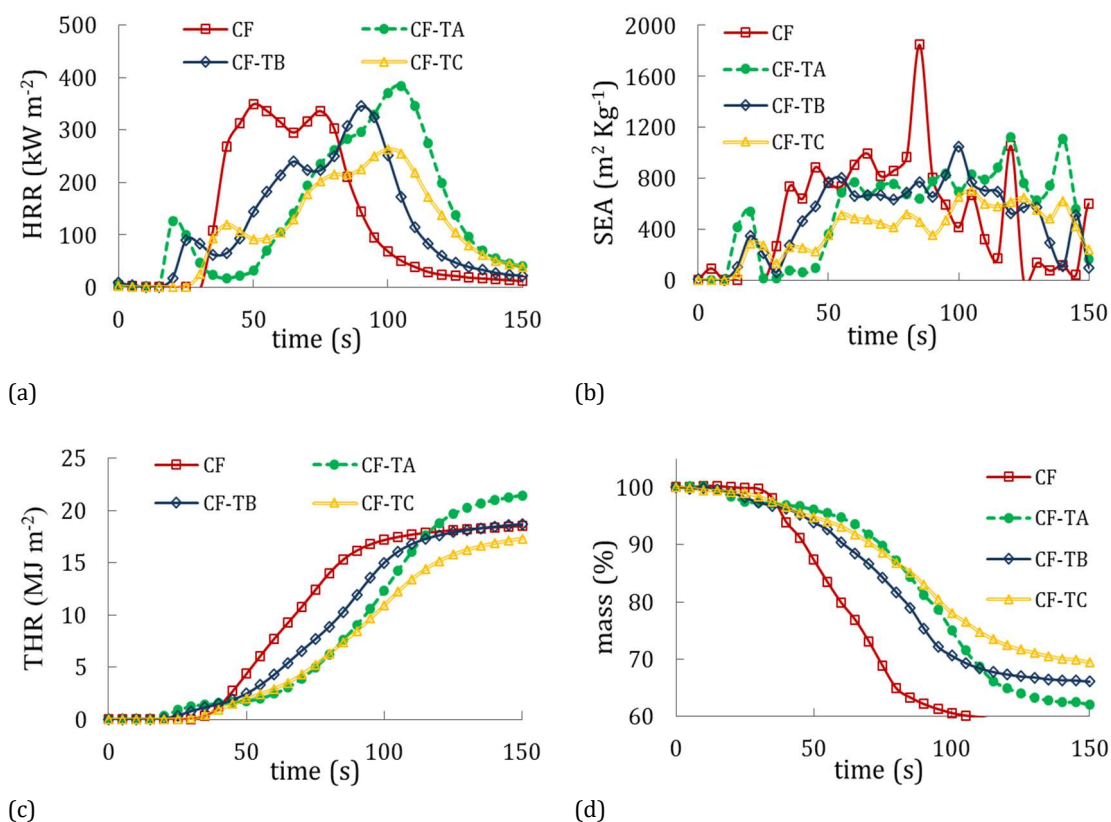


Figure 34: Fire Reaction Properties of Composite Samples: (a) heat release rate (b) specific extinction area (c) total heat released (d) mass %

The heat release rate versus time curves of neat and coated carbon fibre composites is quite different. Composite samples coated with ceramic tapes show a first, small peak, followed by the main exothermic peak, which happens later in time for all samples when compared with the pristine CFRP. The first peak occurs due to release of the organic volatile compounds that are present in the ceramic tapes, i.e, the binder and the plasticizer. However, this is not enough to maintain combustion and full composite ignition and burning are triggered later, when the resin starts to decompose and release volatiles. In fact, the first exothermic peak is related only with the burning of the ceramic tape and not the composite itself. It is clear that ceramic tape C is performing better than tapes A and B, as it shows a very positive effect on the heat release rate of the composite sample, by providing a significant decrease in the peak heat release rate. This is a key result, since heat release rate is considered a critical fire reaction property because it is the driving force for fire spread. Tape A, however, is only effective in delaying composite combustion, as the peak heat release rate happens later, but attains more or less the same values. The PHRR of neat CFRP happens at 50 seconds and attains a value of about 350 kW/m², while for sample coated with tape C, the peak heat release rate is delayed to a testing time of 100 seconds, attaining a maximum value of 265 kW/m², representing a reduction of 24%. In this case, there can be two effects taking place: on one hand, the presence of cellulose fibres in tape C allows a more compact structure, which can be acting as a more effective physical barrier to the passage

of heat to the material underneath the coating. On the other hand, as already stated, tape C seems to be less impregnated with resin and, as it is known, the resin is the organic part that releases heat during composite burning. Figure 35 shows pictures of the samples before cone calorimeter tests.

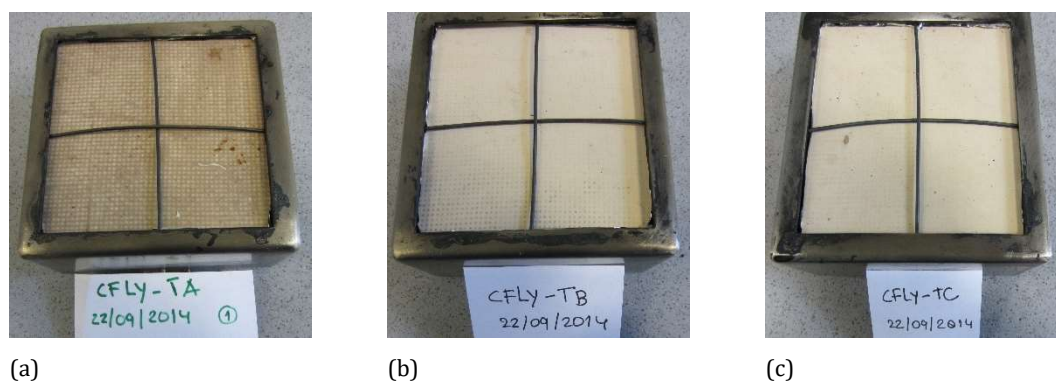


Figure 35: Pictures of composite samples with ceramic tapes as coatings (a) Tape A (b) Tape B (c) Tape C

One trend that is usually reported in fire reaction behaviour of thermoset-based materials is, in fact, the reduction of peak heat release rate. However, most of the times what happens is that the modified material burns at a slower rate than the original one, leading flatter heat release rate curves with time, instead of more abrupt and defined peaks. In this case, the integration under HRR curves, yielding the total heat released (THR) during burning time, is usually the same. The THR can be a useful parameter to measure how effective a modified material (coating, nanomaterial, etc) really is. In this case, the curves shown above show, once again, that tape C is effective in enhancing the burning behaviour of the epoxy carbon fibre composite. Throughout the testing time, this ceramic coating was able to reduce the heat released at each instant and the total heat released during the test, in agreement with the results observed for heat release rate. CFRP modified with tape A leads to a higher release of heat at the end of the test.

A crucial parameter when discussing flame retardancy is specific extinction area (SEA). As mentioned in section 1, the SEA is the parameter measured during cone calorimeter tests that characterises the density of the released smokes. Smoke optical properties are important when fire safety is concerned: by reducing visibility, smoke can present great threat to persons [16]. In the case of SEA, clearly all ceramic coated samples show better behaviour than the unmodified CFRP material, with reductions of this parameter throughout the entire test. This is important because when using the tapes in their green state, i.e., before sintering, they have in their chemical composition about 20% of organic materials (binder, plasticizer, etc) which could cause additional smoke release upon decomposition. As can be seen from Figure 34, it is not the case. Apart from small peaks that appear in the beginning of the test, in agreement with the observed behaviour of the heat release rate curves, during the full developed fire, the coatings are able to significantly reduce the opacity of the produced smoke. Again, tape C has proven to be more effective than tapes A and B, with much lower SEA values than the virgin composite material throughout the entire testing time.

The last parameter (d) in Figure 34 is the sample mass variation with time. It can be seen that after ignition, the neat composite suffers a very rapid mass loss due to resin burning. About 60% remains at the end of the test, which corresponds to the fibre content of the

material. Tape A slows down the mass loss of the composite, however, the residue is more or less the same at the end of the test. To note that the ceramic tapes, being very thin, and after losing its organic content during the tests, are very light and shall not be interfering significantly with the total mass of the material. Tape C, however, shows promising results also regarding the mass loss. Not only the rate at which the resin mass is being consumed during burning is significantly reduced, but also the final residue is higher by about 10%. These results are interesting in the sense that tape C is effectively protecting the integrity of the underneath material, helping the structure to remain safe during a longer time period.

4.4 Conclusions

In this work, we have produced ceramic tapes with different chemical compositions by tape casting technology. Unlike the traditional solvent-based slurries, we have used eco-friendly water based formulations. These thin coatings were afterwards used as top layer on 6-layered carbon fibre epoxy composites as intended fire protective coatings. The materials were co-cured and produced all in one row in order to make sure the conditions used were exactly the same. SEM observations allowed concluding that a more compact and closed structure is presented in tape C. To the ceramic bases slurry, cellulose fibres were added for formulation of tape C. Regarding the main fire reaction properties of the composite samples, tape C has demonstrated to be the most effective coating. Reductions in peak heat release rate, total heat released, smoke opacity and mass loss rate were observed. These results are very promising and shall be explored more in detail, namely by using other coating thicknesses and by combining different ceramic powders with the cellulose fibres.

Acknowledgements

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5 Environmentally Friendly Passive Fire Protection Systems for Glass Fibre Reinforced Polymer Pultruded Profiles

Submitted to:

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Abstract

Fire reaction experiments were performed in order to determine the effectiveness of an environmentally friendly water based intumescent paint used as a passive fire protection system for pultruded glass fibre unsaturated polyester reinforced polymer (GFRP) composites. Three different paint thicknesses were applied on GFRP laminates which were tested in a cone calorimeter. Results obtained show that, as expected, higher paint thicknesses result in higher fire protection, with reductions in peak of heat release rate (PHRR), total heat released (THR) and peak of smoke released (PSEA) of about 74%, 65% and 53% respectively, for samples protected with 2.0 mm of paint. Important reduction in the smoke toxicity were also observed. These are promising results regarding the fire protection of composite materials using a passive fire protection system that can be considered environmentally friendly due to the low levels of Volatile Organic Compounds (VOCs) released during application and use, which are extremely important, especially in indoor environments.

Keywords: flame retardancy, glass fibre composites, intumescent, aqueous paint

5.1 Introduction

Pultruded Glass Fibre Reinforced Polymer (GFRP) profiles are advanced composite materials consisting of glass fibres embedded in a polymeric matrix. Composite materials are often called "advanced" if they possess a combination of high strength and modulus substantially superior to structural metals and alloys on an equal weight basis. In recent years, they are finding increasing attention by the structural engineering research community as interesting materials for applications in civil construction (e.g. rehabilitation, repair and strengthening of reinforced concrete, steel or masonry, or new fully composite structural components). These materials have good mechanical properties, low density and durability, but their poor fire performance determines the need to use fire protection systems, in order to enable their use as structural materials in buildings. When heated to moderate temperatures (100–200 °C), FRP materials based on thermoset resins soften and creep, causing a considerable reduction of both strength and stiffness [1]. Furthermore, when FRP materials are exposed to high temperatures (300–500 °C), their organic matrix decomposes, releasing large quantities of smoke, soot and toxic gases. The behaviour of FRP composite materials in fire is largely governed by the chemical processes involved in the thermal decomposition of the polymer matrix. In fact, problems associated with the fire

resistance of FRP composites are seen by many civil engineers as the single most critical technical barrier to the widespread use of structural engineering applications in the civil infrastructure [2].

Several methods are currently used for providing flame retardant properties to FRP composites. One of the most commonly used methods is the addition of flame retardant systems to the polymeric matrix. Thermally active fillers, such as aluminium or magnesium hydroxides are just some of the examples [3]. Other tested methods comprise the use of high performance fibres (e.g. aramid) or inherently flame retardant resins and the chemical modification of the base resin. Presently, the commercially available flame retardant resins (e.g. phenolic) and flame retardants fulfil most of the flammability requirements; however, these solutions usually cause reductions in the mechanical performance of GFRP structural elements. Fire protection systems mostly used in the already manufactured FRP material can be classified, according to their mode of action, in passive or active fire protection systems. These fire protection systems are widely used in the protection of metallic structures, however, they are still not fully developed for composite materials.

Active fire protection systems are designed to come into play only when a fire is present and require activation through a combination of sensors or mechanical means. Active protection methods normally incorporate an automated detection of fire in its early stage and then suppress the fire and/or dissipate heat. Examples of active fire protection systems include the use of sprinklers or liquid-cooling systems [4]. Passive fire protection refers to fire control systems integrated in the structure of the material that do not require activation by automatic devices or any type of operation by people. Passive fire protection systems are typically used in the form of surface coatings (intumescent or ceramic) or insulative fabrics. An attractive advantage of surface coatings is that they act in the solid phase, and as a result, the intrinsic properties of the virgin material (such as the mechanical properties) are not modified. Furthermore, surface coatings can be easily applied by means of spray, brush, or roller to a large number of materials, such as metallic materials, polymers, textiles and wood [5]. They also have the advantage of being applied after composite's manufacturing, therefore not requiring changes during the processing. Intumescent coatings act as a heat-resistant barrier to the protected substrate under fire because when exposed to heat, the coating expands several times creating a foam like structure.

The main purpose of this work was therefore to study the fire reaction behaviour of pultruded GFRP profiles, unprotected and protected with a passive fire protection solution. A water based intumescent paint, typically used in the fire protection of metallic structures or in wood ignifugation, was selected to be used in this work. Opposite to traditional solvent-based paints, this can be considered an environmentally friendly passive fire protection system, mainly due to the low levels of Volatile Organic Compounds (VOCs) released during application and usage (very important in indoor applications). Three different paint thicknesses were tested and the fire reaction properties of the materials were assessed using cone calorimeter tests. Furthermore, the temperature profiles at four different material thicknesses were also obtained using very thin insulated thermocouples connected to a data acquisition system.

5.2 Experimental

The GFRP material used in the fire reaction experiments was produced and supplied by Fiberline, Denmark. It consisted of rectangular profiles (6 m × 0.5 m × 10 mm thick),

produced by pultrusion. The fibre content of the material is of about 69.4% in mass, as determined by calcination according to standard TL 52342. The aqueous paint (AQ) used in the fire experiments is an intumescent paint used primarily for fire protection of steel structures and wood ignifugation that under the action of heat, produces a foam with very low thermal conductivity, therefore protecting the material from the action of fire. It can be applied with brush, roller, conventional spray or airless. The following material properties are reported in the manufacturer technical datasheet: density $\rho=1.410\text{g/cm}^3$; solids volume content of 60%; $\text{VOC}<20\text{g/L}$.

Three different paint thicknesses were tested, namely 0.5 mm (sample AQ0), 1.0 mm (sample AQ1) and 2.0 mm (sample AQ2). Samples were prepared using manual brushing and were allowed to dry at least during three weeks before being tested. Small-scale tests were conducted in a cone calorimeter on protected and unprotected samples. Three tests were performed for each material and coating, one of them including temperature measurements, as described below. The heat flux used in the cone calorimeter tests was 75kW/m^2 , corresponding to an average temperature of $902\text{ }^\circ\text{C}$. Before being tested, samples were conditioned in an environment of $50\pm5\%$ of relative humidity and $23\pm3\text{ }^\circ\text{C}$ of temperature, at least during one week. All samples were insulated with aluminium foil, ensuring that only the top surface of the samples was exposed to incident heat flux. The test procedure was performed according to ISO 5660 standard. All samples were tested in horizontal position with the exhaust duct flow rate set at $0.025\text{ m}^3/\text{s}$.

As mentioned before, two tests of each experimental series were characterised in terms of temperature evolution inside the sample during the cone calorimeter tests. Temperature measurements were performed at material thicknesses of 2.0 mm (T1), 4.0 mm (T2), 6.0 mm (T3) and 7.5 mm (T4) from the cold surface (not submitted to heating during the cone calorimeter tests). Glass fibre insulated thermocouple wires with a tip diameter of about 1.5 mm were inserted in the sample at the above mentioned depths and connected to a TC08 Pico Technology data logger. Temperature was monitored every second during 30 minutes (time established for the cone calorimeter tests). A special sample holder allowing the proper position of the thermocouple wires (see Figure 36) was used in the cone calorimeter tests. The tests without thermocouples were performed with mineral wool as thermal insulator. In the tests where temperature measurements were performed, calcium silicate boards were used as heat insulators, positioned between the sample and the sample holder, insuring good positioning of the thermocouple wires. In Figure 36 it is possible to see the sample holder with calcium silicate board and thermocouple wires after being inserted in the unprotected GFRP pultruded laminate.

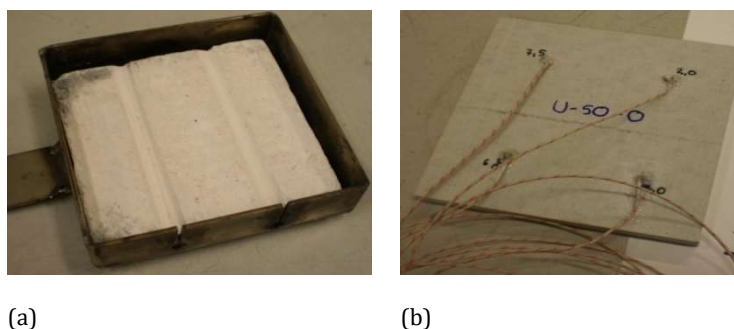


Figure 36: Sample holder with calcium silicate board used in cone calorimeter tests with temperature measurement (left) and unprotected sample with thermocouple wires (right)

5.3 Results and Discussion

5.3.1 Visual Inspections of Samples Before Burning

As previously mentioned, the water based paint tested in the experiments is traditionally used in the fire protection of metallic structures or wood ignifugation. In both cases, a primer and an intermediate coat are necessary for proper adhesion between the materials. In the case of the pultruded glass fibre composites, there is no need to use primer since the adhesion of the paint to the composite material is very good. Figure 37 shows the aspect of a sample protected with paint before the cone calorimeter tests (a) and detailed views of the same sample along the thickness, which shows good adherence between the materials ((b) and (c)).

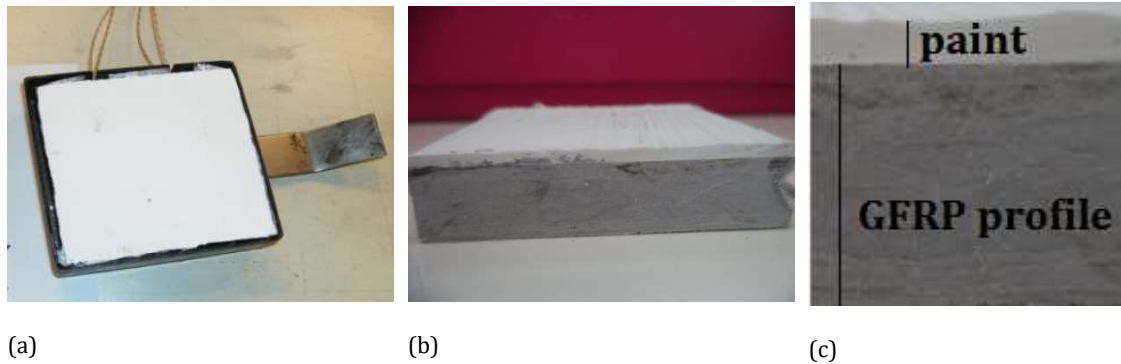


Figure 37: (a) Sample with 2 mm of aqueous paint before cone calorimeter test (b)(c) detailed view of the sample across the thickness, showing good adherence between the paint and the composite material

5.3.2 Burning Behaviour and Fire Reaction Properties

After few seconds of exposure to radiant heat, unprotected samples started to release smoke and their surface became darker, despite showing full integrity at this stage. After this initial stage, samples ignited in a few seconds. The time-to-ignition of the unprotected samples was of about 24 seconds. After a period of intense flaming, flames in the center of the sample disappeared and were only visible at the sides of the material, after which extinguishment occurred at about 25 minutes since the beginning of heat exposure. The different stages of the burning of unprotected samples are shown in Figure 38.

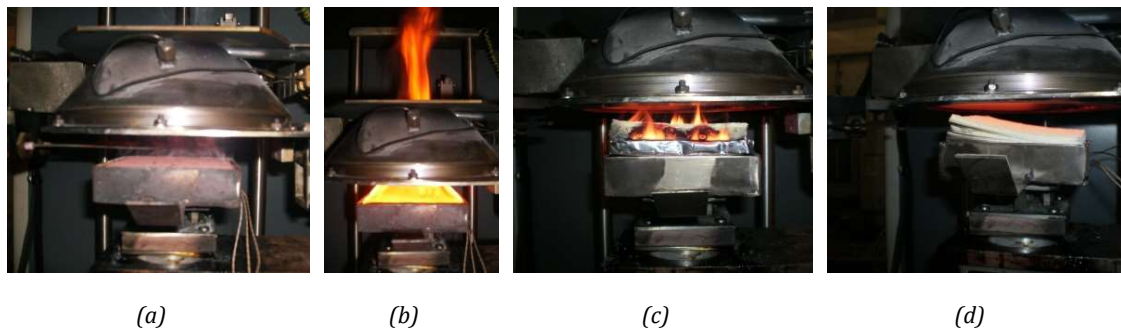


Figure 38: Different stages of unprotected sample burning behaviour during cone calorimeter tests: (a) smoke release before ignition (b) intense flames after ignition (c) burning only at the sides of the material (d) sample after extinguishing

Regarding the use of water-based intumescent paint, the initial behaviour of all samples was quite similar, as the paint became dark and samples started to release smoke immediately after exposure to radiant heat. Then, approximately 15 seconds after the beginning of heat exposure, transient flames were visible and samples ignited during 5 to 10 seconds and then extinguished. The thickness of the intumesced paint increased with heating exposure and higher paint thicknesses led to higher intumescence formation, as can be noticed comparing the images in figure 4. The average thicknesses of the paint at the end of the cone calorimeter tests were, respectively, 1.2-1.5 cm, 1.8-2.1 cm and 2.2-2.5 cm for samples with 0.5 mm, 1.0 mm and 2.0 mm. Figure 39 shows the aspect of the paint protected samples after cone calorimeter testing, evidencing the intumescence formation for the different paint thicknesses.

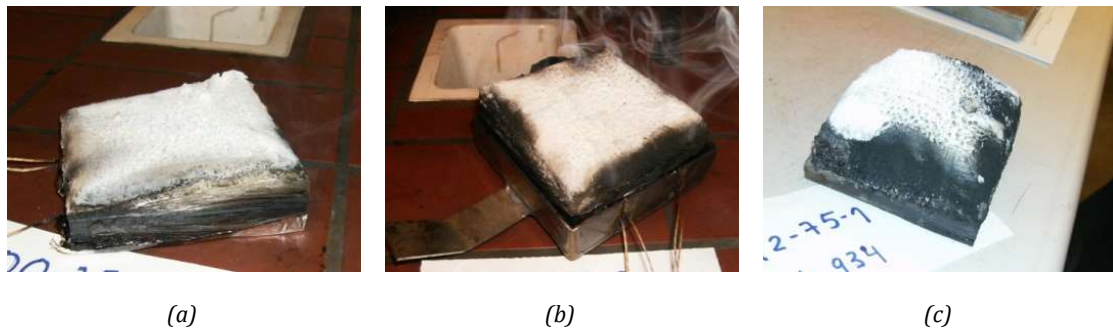


Figure 39 : Intumescence formation of the paint after cone calorimeter tests (a) 0.5 mm of paint (b) 1.0 mm of paint (c) 2.0 mm of paint

The sample with lower paint thickness ignited again at approximately 350 seconds, although the flames were only visible at the sides of the sample, as shown in Figure 40b. The intumescent behaviour became even more pronounced after this second ignition. At the end of the test, some of the fibres in the pultruded profile were visible, and the sides of the samples were dark due to resin degradation. The sample protected with 1.0 mm of aqueous paint ignited again at around 410 seconds, first in one of the corners, with flames then reaching all sides of the sample. The sample with higher paint thickness (2.0 mm) ignited again at about 880 seconds.

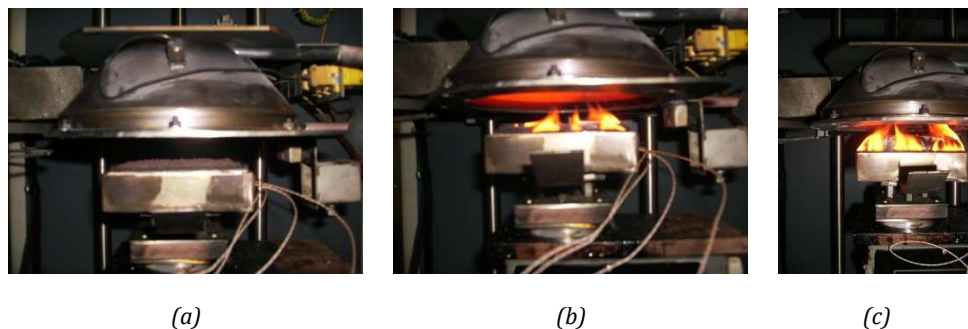


Figure 40: Different stages of samples protected with intumescent water based paint burning behaviour during cone calorimeter tests (a) formation of intumescence before ignition (b) flames starting in the corners of the sample (c) higher flames, located mainly in the corners of the sample

Tests performed on the cone calorimeter allowed measuring the following fire reaction properties: (a) time to ignition, (b) heat release rate (HRR), (c) specific extinction area (SEA), (d) carbon monoxide yield (CO), (e) carbon dioxide yield (CO₂) and (f) remaining mass (RM). Table 16 shows the following statistics for the different parameters: (i) the peak

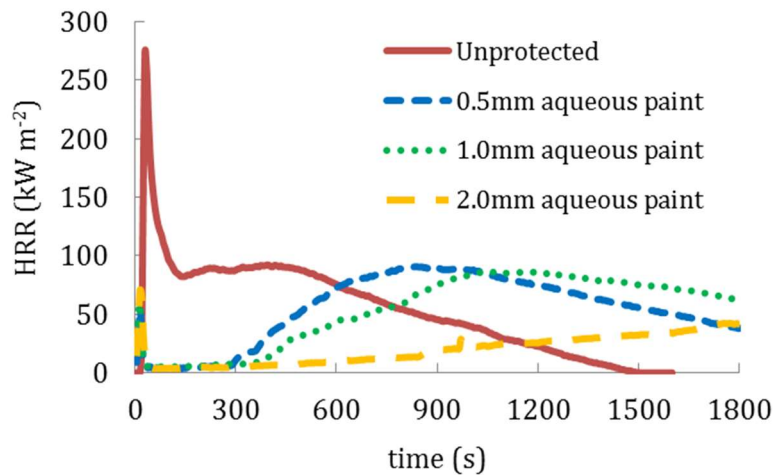
values (Peak) and (ii) the average values during the 30 minutes of exposure (Avg_{1800}). The time to ignition 1 represents, in the case of paint protected samples, the time for unsustained flames to appear. The time for sustained flaming combustion is reported in Table 16 by time to ignition 2.

Table 16: Resume of the main fire reaction properties of the tested samples

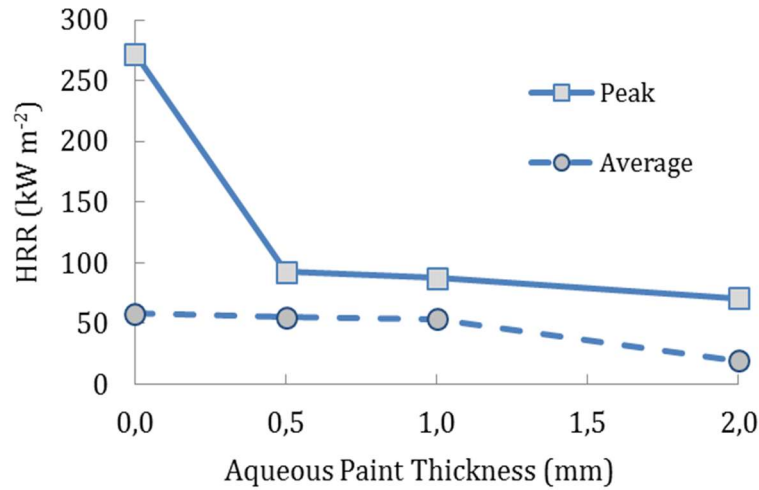
Material		Unprotected	AQ0	AQ1	AQ2
Heat Flux (kW/m ²)		75			
Time to ignition 1 (s)		24	17	14	14
Time to ignition 2 (s)		---	332	414	880
THR (KJ)		980.8	977.6	954.8	344.2
HRR (kW/m ²)	Peak	272.2	92.2	87.3	70.9
	Avg_{1800}	58.2	54.9	53.6	19.4
SEA (m ² /Kg)	Peak	1397.9	1306.7	1205.8	657.1
	Avg_{1800}	331.1	434.6	418.9	216.7
CO ₂ (Kg/Kg)	Peak	1.161	1.203	1.277	0.289
	Avg_{1800}	0.627	0.554	0.519	0.031
CO (Kg/Kg)	Peak	0.158	0.091	0.073	0.118
	Avg_{1800}	0.070	0.041	0.038	0.055
Remaining mass (%)		68.3	72.6	70.6	82.6

i. Heat Release Rate

The evolution of heat release rate with time for all samples during the cone calorimeter tests is shown in Figure 41. The dependence of both the peak (PHRR) and the average HRR with the paint thickness applied in the GFRP pultruded profiles is also shown.



(a)



(b)

Figure 41: (a) Heat release rate as a function of time (b) Peak and average heat release rate as a function of paint thickness

The heat release rate curve of the unprotected sample shows that the maximum heat released rate (PHRR – peak heat release rate) was achieved few seconds after ignition - a sharp peak can be observed at this instant. This heat release rate curve shows the typical behaviour of thermally thick charring (residue forming) samples, which have an initial increase in HRR until an efficient char layer is formed. According to Schartel and Hull [6], as the char layer thickens, a decrease in heat release rate is observed. This sample extinguished at approximately 25 minutes and at the end of the test it was completely degraded, especially in the upper layers, with the fibres visible and totally separated (showing full resin depletion).

The HRR curves of aqueous paint protected GFRP profiles show that higher paint thicknesses result in better fire protection, as both the peak heat release rate and the total heat released are considerably decreased in the sample protected with 2 mm of intumescent coating. In fact, it can be seen that although PHRR is significantly decreased for all paint thicknesses (figure 6b), only 2.0 mm of paint is truly effective as it also provides a decrease in the total heat released (determined as the area below the HRR vs. time curves). The decreases in PHRR and THR compared to the unprotected specimen were, respectively, of 74 and 65%. The average value of the heat released during the 30 minutes of heat exposure is also significantly decreased: from 58.2 to 19.4 kW/m², representing 67% of decrease. The behaviour of the protected samples is also different, when comparing with the unprotected GFRP, as no sharp peaks are observed, which means that the decomposition of the resin occurs at much slower speed.

ii. Specific Extinction Area

The density and toxicity of the produced smokes during combustion is one of the main concerns regarding fire reaction behaviour of composite materials. The produced smoke during burning of composite materials is a mixture of small fibre fragments and fine carbon particles (soot). These can be extremely dense and consequently reduce visibility, causing disorientation during a fire. Specific extinction area (SEA) is the smoke parameter measured by cone calorimeter. SEA is a measure of how effectively a given mass of flammable volatiles

released by a combustible material is converted into smoke, and is often used to quantitatively define the smoke density [3]. SEA units are m^2/kg , representing the amount of smoke released per unit of sample mass.

The evolution with time of the specific extinction area of all samples during the cone calorimeter tests is shown in Figure 42, where the dependence of both the peak and average SEA with paint thickness applied is also shown.

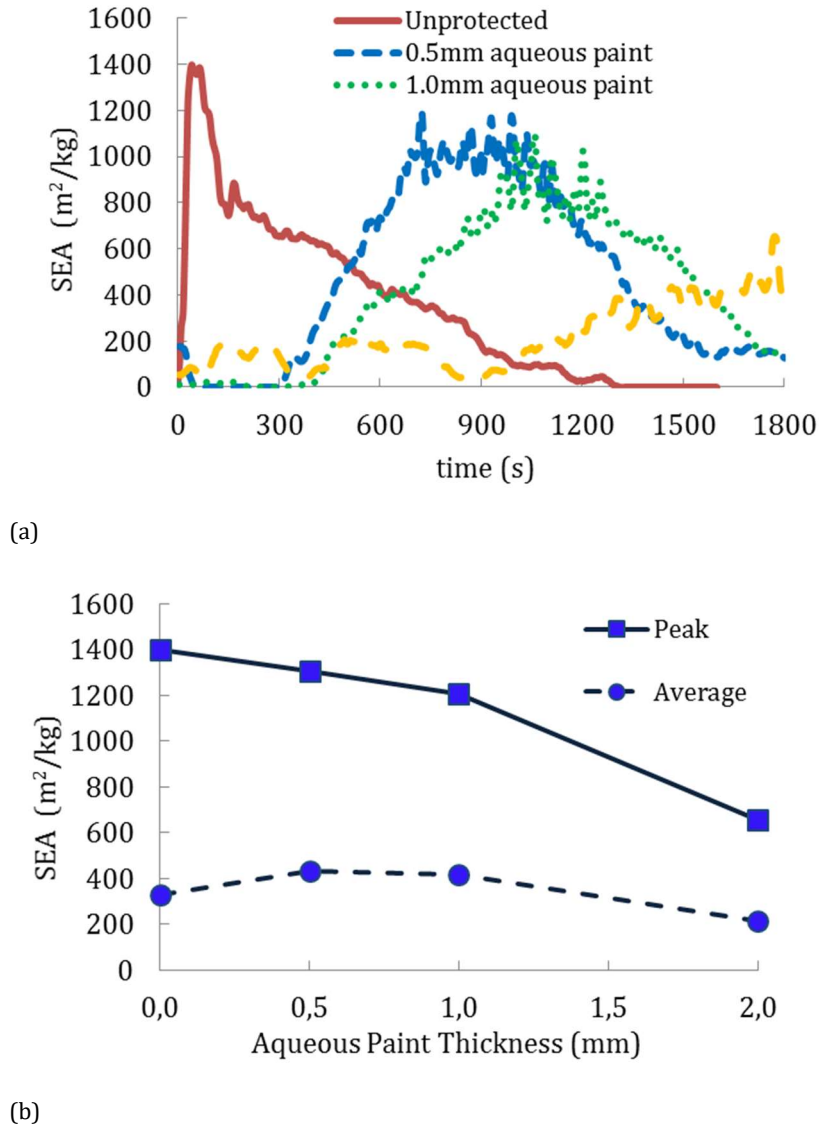


Figure 42: (a) Specific Extinction Area as a function of time (b) Peak and average Specific Extinction Area as a function of paint thickness

The SEA curves follow the same tendency as the heat release rate ones, as for the unprotected the density of the produced smoke shows a sharp peak a few seconds after the ignition (Figure 42 a). The maximum heat release rate value ($274 \text{ kW}/\text{m}^2$) was obtained after 30 seconds, while the maximum rate of smoke production ($1400 \text{ m}^2/\text{kg}$) was achieved after 50 seconds of heat exposure. The application of the aqueous paint was effective in delaying the production of smoke, however, once again lower paint thicknesses were not able to significantly reduce the maximum, average and total smoke density values, as can be seen in Figure 42 b. Higher paint thickness, however, was highly effective in reducing the smoke opacity produced during the combustion of GFRP pultruded profiles. Considerable

reductions in both the peak (53%) and average (35%) SEA values were obtained for the 2 mm paint protected sample.

For paint protected samples, no linear relationship was found between the SEA values and the heat release rate. These observations are not, therefore, in agreement with the behaviour observed by Mouritz *et al.* [7], who stated that for composite materials, the SEA values generally show a linear increase with the heat release rate, because the endothermic decomposition of the polymer matrix and organic fibres determines both the heat release rate and the amount of smoke released.

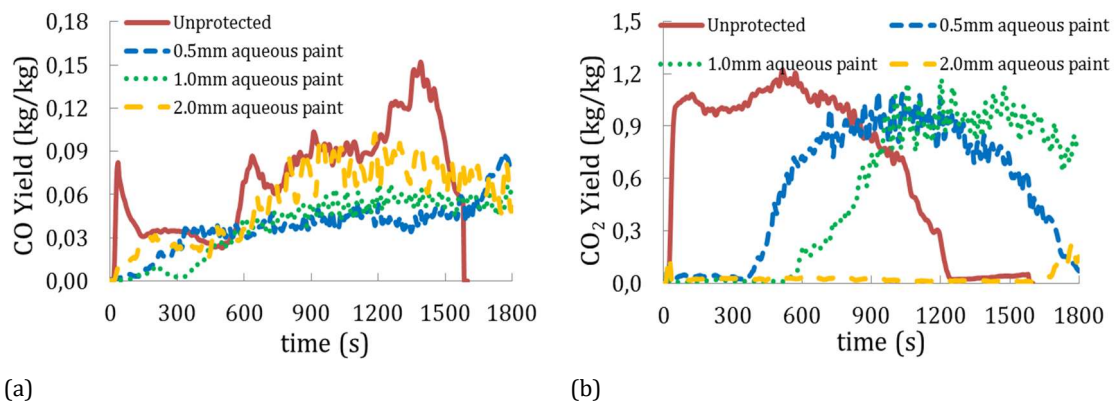
In fact, the sample with lower paint thickness (0.5 mm) shows a much lower PHRR than the unprotected sample and the peak of smoke production is quite the same, although delayed in time. The sample protected with 2.0 mm of paint thickness, however, shows a considerable reduction of the maximum and total smoke released, but only a slight reduction in the average smoke during the cone calorimeter test. The behaviour of the protected material is determined not only by the behaviour of the composite material, but also by the presence of the intumescent paint.

Interesting to note is the fact that unprotected and protected (0.5 and 1.0 mm of paint) samples start to release considerable amounts of smoke after ignition, while the 2.0 mm paint-protected material releases smoke since the beginning of the test, although almost no heat is released during the first 10 minutes of heat exposure. This initial release of smoke must be mainly due to the release of water vapour.

iii. Carbon Monoxide and Dioxide Yields

It is well recognized that the main cause of death in fires is the toxicity of combustion products, and the gas that generally has the greatest individual hazard is carbon monoxide. CO is a major safety concern because it is lethal at a relatively low concentration, with human death occurring within one hour at a concentration of about 1500 ppm [3]. Therefore, it is crucial to determine carbon dioxide and monoxide release during combustion of composite materials. In cone calorimeter measurements, usually CO and CO₂ production are expressed in mass per sample mass (kg/kg).

The evolution with time of the carbon monoxide and dioxide yields of all samples during the cone calorimeter tests are shown in Figure 43 where the dependence of both the peak and average CO and CO₂ release with paint thickness applied is shown.



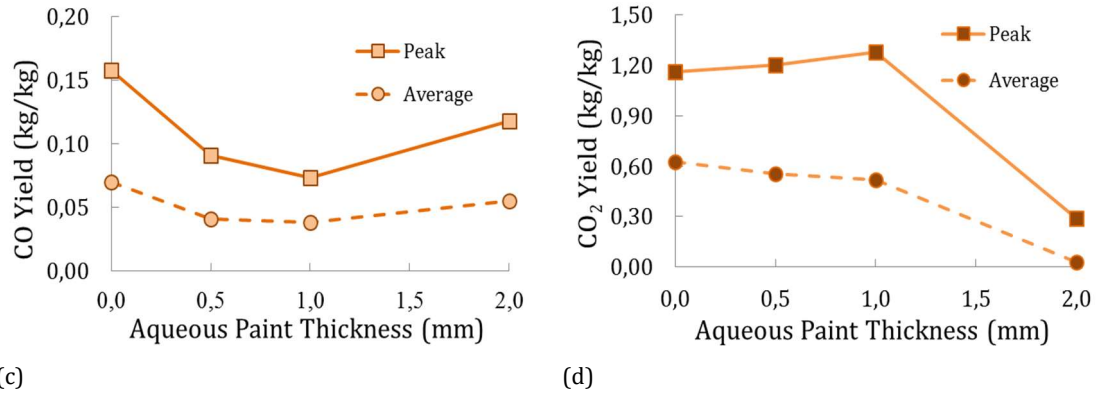


Figure 43: (a) Carbon monoxide yield as a function of time (b) Carbon dioxide yield as a function of time (c) Peak and average carbon monoxide yield as a function of paint thickness (d) Peak and average carbon dioxide yield as a function of paint thickness

For the unprotected sample, during an initial stage, the carbon monoxide curve also follows the same tendency as heat release rate and specific extinction area, with the CO production significantly increasing after ignition. After 20 minutes of test, the carbon monoxide production increased again, presenting a second and more significant increase and therefore attaining its maximum value. Carbon monoxide is a reaction product of the incomplete combustion of volatiles at the fire/composite boundary and can also be a product of the chemical decomposition of certain polymers. This means that the incomplete combustion of the material occurs both in the initial burning stage – when the polymer thermally decomposes with the release of volatile gases and airborne soot particles (smoke) – and during the decay fire stage – when the decomposition of the matrix nearby the bottom surface occurs largely in non-oxidative conditions.

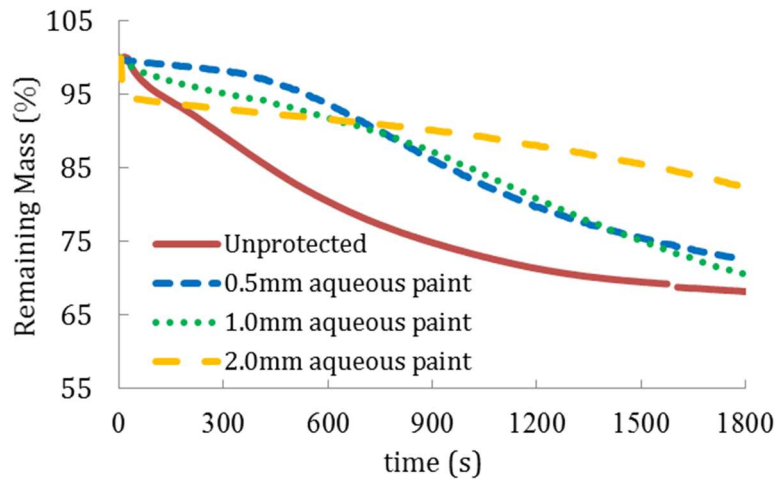
The curves of all protected samples were similar in behaviour, with increasing CO production at increasing exposure time, meaning that the incomplete combustion of the material tends to increase with burning time. The incomplete combustion occurs in these cases because there is an effective barrier to the passage of oxygen without preventing the GFRP composite heating up. As expected, higher paint thickness leads to higher CO production due to a more effective barrier formation. However, the maximum and total carbon monoxide released were reduced for all protected samples.

For unprotected samples, the CO₂ production stops 20 minutes after the beginning of the test, while at the same time the CO yield suffers a significant increase. This means that complete combustion stops at this moment, accompanying the heat release rate decay. Carbon dioxide curves of unprotected GFRP profiles also show the same behaviour observed for HRR and SEA, with maximum values achieved shortly after ignition. After 20 minutes, there was no carbon dioxide release and samples extinguished. This is associated with the fact that the CO₂ yield is intimately related to the complete combustion of the organic matrix.

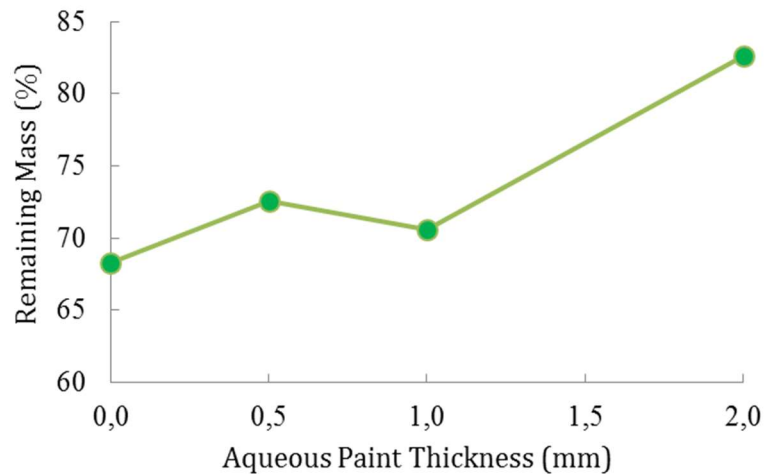
Significant reductions in CO₂ production were observed with the application of 2.0 mm of intumescent paint – 75% in the peak and 95% in the average values. Therefore, 2.0 mm provides a more effective barrier to oxygen and heat transfer than 0.5 or 1.0 mm thickness of paint. The complete degradation reaction (combustion) is almost inexistent throughout the entire burning test for the 2.0 mm protected sample.

iv. Remaining Mass

Pictures in Figure 44 show the mass loss behaviour of all samples during the test time (a-b), as well as the remaining mass as a function of the applied paint (c).



(a)



(b)

Figure 44: (a) remaining mass as a function of time (b) remaining mass as a function of paint thickness

The unprotected sample shows an initial delay period, during which mass loss was negligible. When samples ignited, mass started to decay constantly. After 20 minutes, the mass of the composite material is very close to the final residue, as only a small amount of resin is located in the lower layers and only incomplete combustion is occurring, as supported by CO/CO₂ curves. Samples lost all the resin, since the Remaining Resin Content at the end of the cone calorimeter test is equivalent to the fibre content ($\approx 69\%$). A significant increase in the remaining mass at the end of the test of about 14% was obtained for 2 mm paint protected sample, compared to the unprotected specimen. The paint content of this sample before the cone calorimeter test was of 18 wt%.

Samples protected with higher paint thicknesses (1.0 and 2.0 mm) show considerable decreases in the mass in the initial stages of the fire test, which could be caused mainly by

the release of water content still « trapped » inside the paint layers. This is also supported by the observations regarding smoke release for 2.0 mm paint protected sample. The total liquid content of the paint before application is of about 40%, which means that the drying process may have been insufficient to eliminate all the water, which could then be released during heat exposure. Therefore the drying procedure of this water based paint needs to be adjusted to the paint thickness applied.

After the initial seconds, the mass loss rate of 2.0 mm paint protected sample is more or less stable, until around 15 minutes, where it starts to loose mass more rapidly again due to ignition and consequent combustion of the polymer matrix.

v. *Visual Inspections of Residues*

At the end of the test, the unprotected sample showed complete degradation, especially in the upper layers, with the fibres visible and totally separated (showing full resin depletion). Figure 45 (a) to (c) show the residue of the unprotected sample after the cone calorimeter test. In Figure 45 (b) and (c), it is visible the disappearance of resin in the upper layers of the profile and a dark colour indicative of degradation in the lower section of the material (not directly subjected to radiant heat).

Figure 45 (d) to (f) show the aspect of 0.5 mm paint protected sample at the end of the test. Some of the paint is still visible on the surface of the composite. Figure 45 (e) and (f) show the degradation of the material along the thickness, however, slight improvements regarding the unprotected material can be seen, as no disaggregation of the fibre layers is seen and some resin, although degraded, is still present. The main difference of sample with 1.0mm of aqueous paint is the fact that the sample is able to maintain more or less its integrity and no separation layer is visible. In Figure 45 (j) to (l) residues of the sample with the highest paint thickness of 2.0 mm are shown. Despite showing some degradation and after losing almost 18% of their original content GFRP composites were able to maintain their integrity in the bottom layers.



(a)



(b)



(c)



(d)

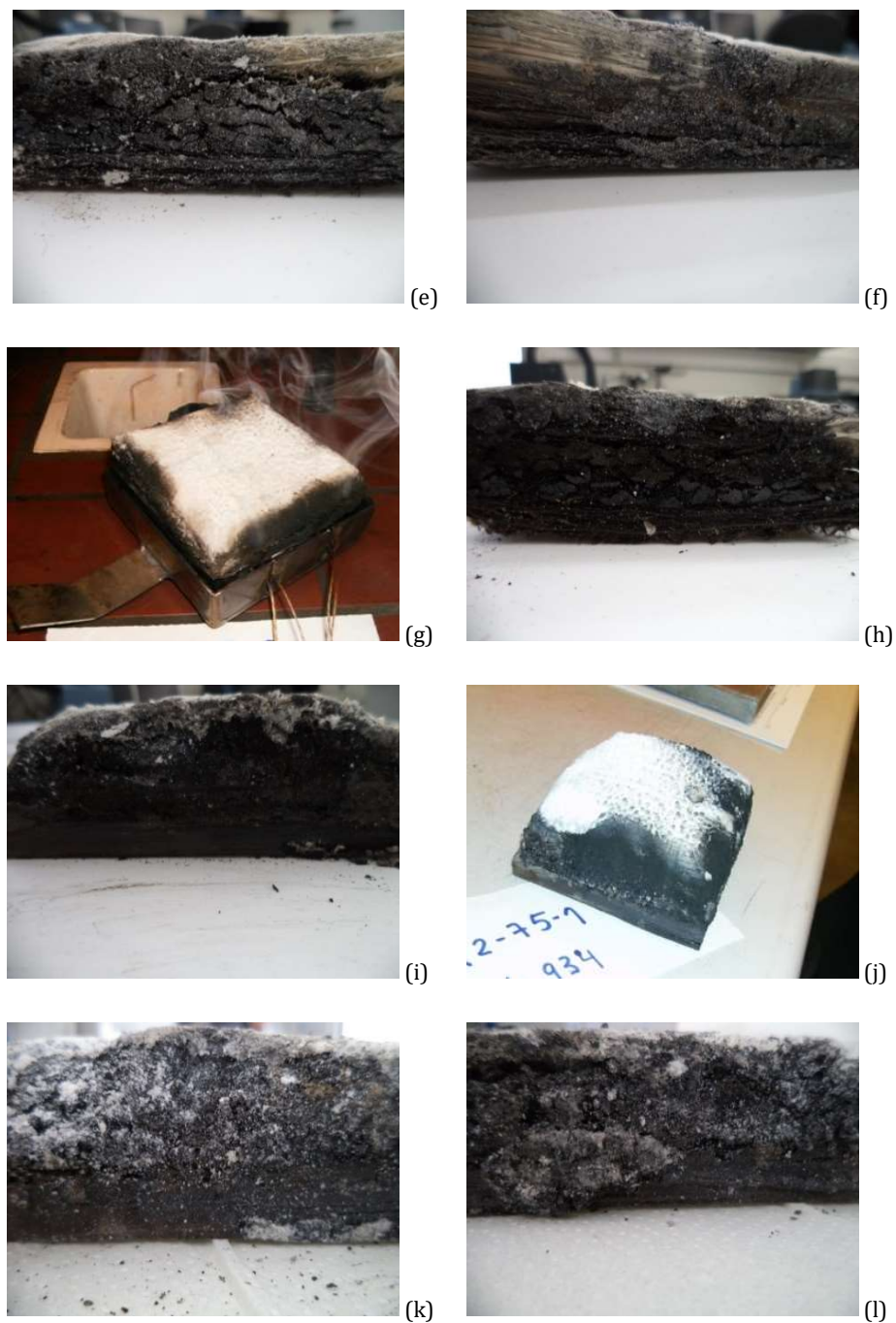


Figure 45: (a-c) Unprotected sample (d-f) sample with 0.5mm aqueous paint (g-i) sample with 1.0mm aqueous paint (j-l) sample with 2.0mm aqueous paint, all after being tested

vi. Temperature Profiles

Figure 46 shows the temperature profiles obtained for unprotected and aqueous paint protected samples at different material thicknesses.

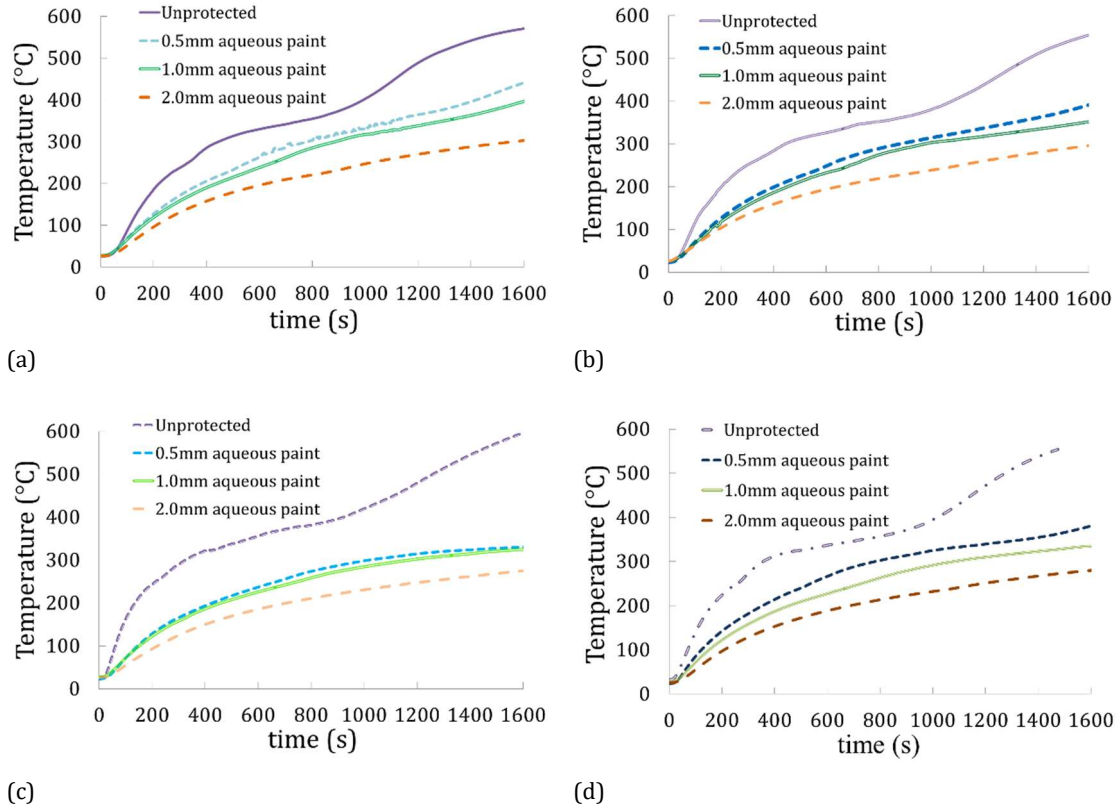


Figure 46: Temperature profiles obtained at different material thicknesses (a) 2 mm (b) 4 mm (c) 6 mm (d) 7.5 mm

As expected and in agreement with the main fire reaction properties, samples protected with lower paint thickness (0.5 mm) were the less effective in protecting temperature increase. For all material depths, the highest paint thickness was always the most effective in reducing the temperature inside the GFRP material.

The temperature profiles of the unprotected samples show a similar tendency, with three increasing temperature steps being detected. This behaviour, however, is not the same as for the passive fire protected samples, as in most cases a single and less pronounced temperature increase step is visible. This behaviour is due to the:

- overall temperature reduction provided by the intumescent paint and
- limited duration of the tests: in the protected specimens, a second step of temperature increase is not triggered

Figure 47 shows the derivative temperature curves as a function of test time for the GFRP composite material, where the three temperature steps can clearly be seen.

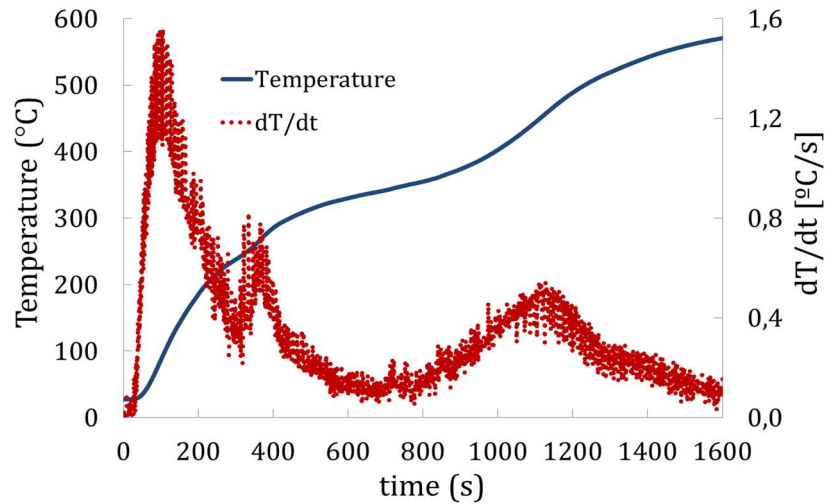


Figure 47: Temperature and derivative temperature as a function of time for unprotected sample

The first temperature step is the most pronounced one, where the temperature increase is faster. In this step, the temperature ranges between room temperature and 250 °C, the peak occurring at 90-100 °C, followed by a slowing down in the temperature increase due to the water vaporization. A second, less pronounced temperature step then occurs between 250 °C and 350 °C, when the degradation temperature of the glass fibre reinforced material is attained. At this stage, the scission of the polystyrene bonds and the oxidation and the breakage of the secondary bonds - accompanied by the release of smoke, CO and CO₂ - can occur [8][9]. The decrease of temperature slope and the burning slowing down for the above mentioned temperatures stems from the endothermic nature of these decomposition reactions. When the decomposition process progresses, the temperature slope increases again, since only a very small amount of resin is still present and a very low amount of energy is consumed during its decomposition.

The maximum temperatures achieved during the 30 minutes of cone calorimetry tests ranged from 620 °C (unprotected) to about 300 °C (2 mm paint protected sample), as shown in Figure 48 a.

Figure 48 b shows the time needed for all the samples to achieve specified temperature levels, namely 100, 200 and 300 °C (degradation temperature), as well as the glass transition temperature (T_g ≈ 150 °C). Once again, it is possible to conclude that 2.0 mm paint is highly effective in protecting the GFRP material against temperature increase. The average time to achieve the glass transition temperature (T_g) increases from 2 min (0.0 mm) to 6 min (2.0 mm). Thus, the GFRP material will keep its structural integrity for a longer period of time. The average time to achieve 300 °C, roughly the decomposition temperature of the resin, increases from 5 min (0.0 mm) to more than 26 min (2.0 mm).

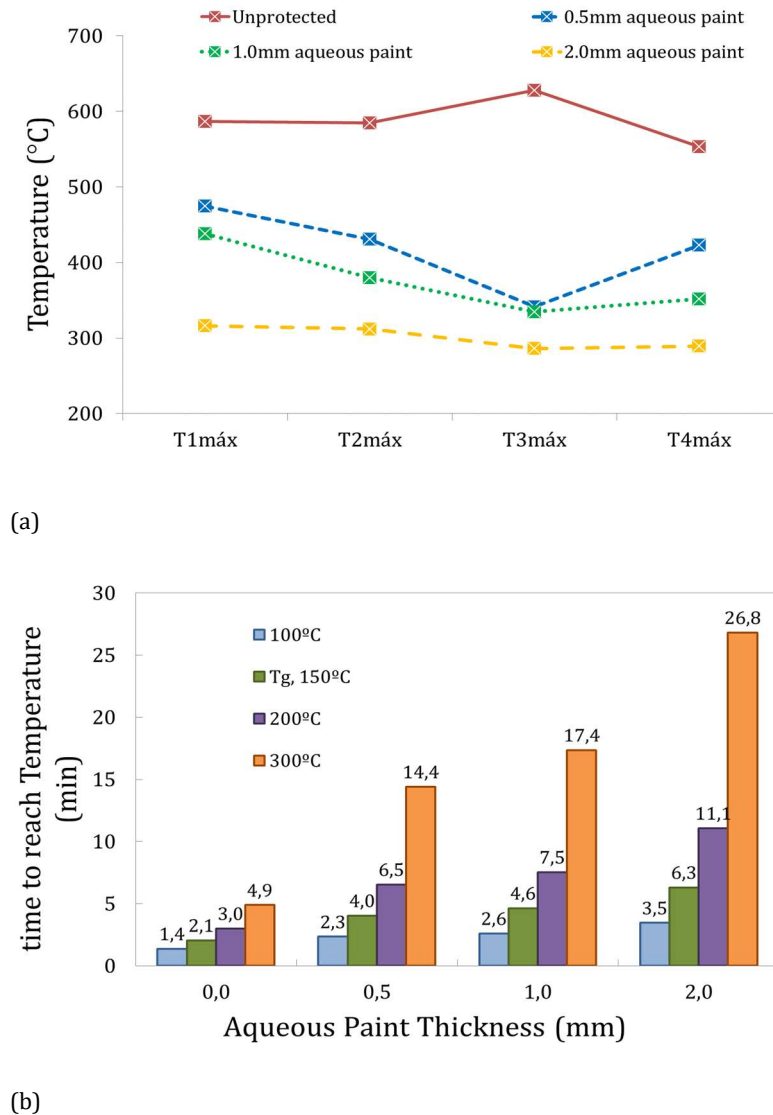


Figure 48: (a) Maximum temperatures reached for all material paint thicknesses (b) time to reach specified temperatures as a function of paint thickness (average values for different material depths)

5.4 Conclusions

This work focused on the fire behaviour of glass fibre composite materials produced by pultrusion and protected with an aqueous-based intumescent paint typically used in the fire protection of metallic structures. The improvements in the fire reaction behaviour were largely dependent on the thickness of the applied paint. As previously mentioned, and despite the drying process of these samples followed the paint manufacturer's recommendations, in the beginning of the tests, samples ignited and burned during some seconds. However, it is believed that the presence of retained substances were responsible for this early ignition. Further studies shall be conducted in order to determine the suitable drying method for each paint thickness applied.

Tests using the cone calorimeter at 75 kW/m² showed that a paint thickness of 2.0 mm provides a delay in ignition time of 850 seconds and improvements in overall fire reaction properties, namely in PHRR, THR and PSEA with reductions of 74%, 65% and 53%, respectively.

Furthermore, with 2 mm of paint the glass transition temperature of the structure was achieved after 6 min of heat exposure instead of 2 min (unprotected). In addition, with such protection, the GFRP composite starts to decompose after 26 min instead of 5 min (unprotected material).

These results are promising regarding the fire protection of composite materials using a passive fire protection system. The system applied can be considered an environmental-friendly paint due to the low levels of Volatile Organic Compounds (VOCs) released during application and usage. This is extremely important not only regarding the application process itself, but also concerning usage in indoor applications. In addition, important reductions in smoke toxicity can also be expected as shown here.

Acknowledgements

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6 Effect of Resin Viscosity on the Cure Kinetics of Flame Retardant Epoxy Formulations

Abstract

Key advantages of fibre reinforced polymer (FRP) composites over many traditional metal alloys have led to a continuous growth in the use of these materials on different areas such as automotive, aerospace and civil engineering. However, due to the presence of an organic polymeric matrix and its inherent flammability, more restrict legislation has constrained the wider use of FRP composite materials in critical areas such as public transports. It is therefore common practice to fill the resin with flame retardant additives to promote impart adequate fire reaction properties to these materials. Aluminium trihydroxide (ATH) and ammonium polyphosphate (APP) are the most commonly used flame retardants in epoxy resins. It is widely known that the kinetic behaviour of epoxy resins is one of the most important phenomena driving the morphological changes in the material structure during processing. Adding fillers to the matrix can therefore lead to changes in the kinetic behaviour, which can consequently promote different material properties. Therefore, it is the purpose of this study to present the cure kinetics of two different epoxy resins (of high and low viscosity) filled with ATH and APP by means of dynamic DSC scans at various heating rates.

Keywords: cure kinetics, epoxy resin, differential scanning calorimetry, flame retardants

6.1 Introduction

Fibre reinforced polymer (FRP) composites have been facing a sustained growth use since the 1960s. Their advantages over other materials for high-performance and lightweight applications have increased their exploration and usage in many industries such as aerospace, automobile, civil infrastructures, sports and marine. However, composite materials have several important disadvantages, one of the main issues being their poor performance in fire, mainly due to the polymeric or organic constitution. Polymers are in general highly flammable and produce large quantities of smoke and toxic gases during burning. It was in the 1970s, when new and more refined polymers and advanced materials appeared that the development of flame retardants was needed in order to reduce the combustibility of these materials for the protection of property, people and the environment. The European Commission has estimated a reduction of 20% in fire deaths as a direct result of the use of flame retardants over the past 10 years. In fact, flame retardants have become an essential component of many products and are often used to meet European safety standards and laws [1]. ATH (aluminium trihydroxide) and APP (ammonium polyphosphate) are the most widely used flame retardants in thermoset resins such as epoxy.

The properties of a FRP material are driven mainly by the quality of the fibre reinforcement but are also highly dependent on the quality of the matrix obtained at the end of the curing cycle. However, although the properties of the fibres do not usually change during a cure cycle, the kinetics of cure and the thermo-rheological properties of the resin matrix are

strongly influenced by the transients of the degree of cure and temperature cycle [2]. This is especially valid for epoxy resins, where a coupling between chemical and thermal effects takes place during the cure process. Inappropriate cure schedules can therefore cause thermal gradients leading to damages inside the FRP structure such as cracks and bubbles [3]. The kinetic behaviour of epoxy resins is one of the most important phenomena driving the morphological changes in the material structure during processing. The cure kinetics refers to the study and modelling of the effects of temperature and time upon the completion of cure of the resin. Modelling of cure kinetics provides the engineer with valuable information that can be used to optimize processing conditions. In fact, composite manufacturing requires knowledge of different areas such as chemistry, polymer and material science, rheology, kinetics, transport phenomena, mechanics, and control systems [4]. Understanding the mechanisms and kinetics of cure are also fundamental as they are the basis of the three-dimensional network morphology, which in turn will influence the physical and mechanical properties of the cured resin [5][6][7][8]. Therefore, understanding the cure kinetics of epoxy resins is critical for process development and quality control.

Several parameters can influence the curing reactions of epoxy resins. For instance, the curing conditions, namely time and temperature [5], the choice of hardener type and amount [9][10], as well as the presence of different types of fillers [11][12][13]. To our knowledge, however, the effect of traditional flame retardants on the kinetics of cure of epoxy resins is not yet studied. Therefore, it is intended here to present a study concerning the cure kinetics of flame retarded epoxy resin by means of dynamic differential scanning calorimeter tests.

The use of differential scanning calorimetry (DSC) as a reliable tool for the measurement of exothermic heats of reaction and glass transition temperatures – frequently associated with the degree of cure of epoxy resins – has been widely accepted within the scientific community. Differential scanning calorimetry, both in the isothermal and dynamic modes, has been extensively used [7][9][13][14][15][16][17][18][19][20] in the determination of the cure kinetic parameters, assuming a proportionality between the heat evolved during the cure and the extent of reaction.

6.2 Experimental Procedure

6.2.1 Materials

Two epoxy resin systems were tested. Resin 1 is a high viscosity space qualified DGEBA epoxy resin cured with an anhydride hardener and an imidazole accelerator. Resin 2 is a low viscosity infusion DGEBA epoxy resin cured with a diamine hardener. Table 17 presents the main properties of both resin systems tested.

Traditional flame retardants used as fillers in this study were micro sized ammonium polyphosphate (APP 422) from Clariant and aluminium trihydroxide (ATH Martinal OL-104) from Albemarle.

Table 17: Properties of the two resin systems tested in cure kinetics studies

Resin	Commercial name	Type	Hardener (type and amount)	Catalyst (type and amount)	Viscosity at 25 °C (mPa.s)	Typical Cure Cycle
1	LY556	DGEBA	Anhydride, 95 wt%	Imidazole, 2 wt%	10000-12000	2 h @ 120 °C + 2 h @ 180 °C
2	SR8100	DGEBA	Diamine, 22 wt%	---	110	24 h @ RT + 8 h @ 60 °C

6.2.2 Sample Preparation and Testing

The resin was mixed with the desired amount of additive at the weight ratios shown in Table 18. A stoichiometric amount of curing agent and accelerator was added just before the dynamic cure was initiated. A TA Instruments Q20 Differential Scanning Calorimeter was used for measuring heat flow and energy change during the cure reaction of the epoxy resins. The mass of resin used was about 8 to 10 mg. All experiments were conducted under a nitrogen flow of 50 mL/min using standard aluminium pans. Pure indium was used as a standard for calorimetric calibration and all runs were carried out using an empty cell as a reference. The dynamic cure DSC experiments were conducted between 0 and 200 °C at the heating rates of 1.0, 3.0 and 5.0 °C /min. After the cure, two ramps at 10 °C/min were performed for assessing the residual heat and the glass transition temperature, respectively. The reaction was considered complete when the signal levelled off to a baseline. The total area under the exothermic curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the heat of cure at a given heating rate. The results presented are the average of three replicates.

The thermal behaviour of both fillers – ATH and APP, were also assessed by performing ramps between room temperature and 500 °C at 10 °C/min.

Table 18: Formulations prepared and tested for cure kinetics studies

Resin	Sample	Flame retardant	Weight (%)
LY556, high viscosity	LY	-	-
	LY1P	Ammonium polyphosphate	1
	LY5P		5
	LY1A	Aluminium trihydroxide	1
	LY5A		5
SR8100, low viscosity	SR	-	-
	SR1P	Ammonium polyphosphate	1
	SR5P		5
SR8100, low viscosity	SR1A	Aluminium trihydroxide	1
	SR5A		5

*the percentage of flame retardant is related to the pre-polymer mass

With DSC, the cure kinetics of a thermosetting resin such as epoxy can be determined using three different approaches:

- Single dynamic heating experiment
- Multiple dynamic heating experiments (at 3 or more different heating rates)
- Isothermal experiments (at 3 or more different temperatures)

The isothermal approach provides the highest degree of accuracy of the cure kinetics of a thermosetting material, such as an epoxy resin. This is because the maintenance of isothermal conditions eliminates potential problems such as the occurrence of thermal gradients. The major assumptions in isothermal tests are that the total heat of reaction can be determined accurately, and that all reactions contributing to the overall reaction have the same enthalpy [21]. In order to perform isothermal experiments, the sample is usually put in the DSC cell previously heated to the desired temperature; small samples are required in order to insure minimal temperature gradients inside the pan. At higher temperatures, however, this procedure can be quite difficult to perform since a significant amount of exothermal heat of reaction from the sample may not be detected by the instrument during temperature stabilization. Other clear disadvantage of performing isothermal tests is the limited temperature range. While at high temperatures, as already mentioned, the heating time can be comparable to the characteristic time of the process, which means that a significant conversion can be attained even before the desired temperature is achieved. At lower temperatures it can be quite difficult or even impossible to attain full conversion of the resin system. A common feature when performing isothermal DSC tests is that at higher conversion degrees it becomes difficult to fit kinetic models into experimental data due to the vitrification of the resin [5][14][15]. During cure, the vitrification of epoxy resins occurs when the glass transition temperature of the reacting system reaches the cure temperature. It is more commonly observed in isothermal cure, when the cure temperature is lower than the glass transition temperature of the fully cured system. Due to reduced chain mobility, the reaction rate slows down and, as a result, eventually stops when the resin is only partially cured [22].

In non-isothermal scanning tests, the heat of reaction is monitored over a linearly increasing temperature scan and kinetic data is obtained with various analyses of the DSC curve produced. The biggest disadvantage of performing constant heating tests is the difficulty in identifying acceleratory and sigmoidal models and the induction periods associated with these types of models. The major assumptions included in performing dynamic experiments is that there is only one reaction mechanism over the temperature range scanned and that diffusion effects on kinetics are negligible [21].

The majority of the kinetic models consider the reaction rate to be a function of only two variables: temperature and conversion. If a single-step reaction is considered, then the reaction rate can be represented in terms of the rate constant $k(T)$ and the reaction model $f(\alpha)$. If a process is found to follow a single-step equation (Equation 1), however, it shall not be concluded that the process mechanism involves one single step. Usually the mechanism involves several different steps but one of them is determinant to the overall kinetics [23].

$$\frac{d\alpha}{dt} = k(T) \times f(\alpha)$$

Equation 1

If a reaction process is characterised by release or absorption of heat, the extent of conversion α is determined as a fraction of the total heat released or absorbed during the process. During dynamic DSC scans, a continuous heating rate of the reacting system provides enough energy to reach the fully cured state of the system ($\alpha=1$). The total heat of reaction (H_T) can therefore be determined as the heat generated during dynamic scanning. This heat is independent of the heating rate used in the experiments and can be calculated as follows:

$$H_T = \int_0^{t_f} \left(\frac{dH}{dt} \right) dt \quad \text{Equation 2}$$

Where dH/dt represents the instantaneous amount of heat generated and t_f is the amount of time required to complete the reaction during the dynamic scan.

This enables the determination of the degree of conversion α , due to the assumption that the heat generated is proportional to the degree of conversion. According to this definition, the resin is considered to be uncured when $\alpha=0$ and completely cured when $\alpha=1$.

$$\alpha(t) = \frac{H(t)}{H_T} = \frac{1}{H_T} \int_0^t \left(\frac{dH}{dt} \right) dt \quad \text{Equation 3}$$

For thermosets following a simple n^{th} order reaction, the reaction rate is proportional to the concentration of unreacted material, that is:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad \text{Equation 4}$$

However, different kinetic behaviours are often observed during the curing of thermoset resins. These can be classified according to three types: accelerating, decelerating or autocatalytic. The associated kinetic profiles can be identified by the shape of the α or $d\alpha/dt$ versus t or T curves. In accelerating processes, the reaction rate increases continuously with increasing conversion and attains its maximum value at the end of the reaction process. On the other hand, decelerating chemical processes show a maximum rate at the beginning of the reaction, followed by a continuous decrease. Autocatalytic models are the most commonly used to describe the kinetic behaviour of epoxy resins. They are characterised by a reaction rate maximum at conversion values between 20 and 40% [16][18]. Because the reaction occurs in a condensed phase, the rate of the cure reaction is controlled by the activity of the functional groups and additionally by their mobility. During the first stages, when the rate of movement of the groups is much faster than the rate of molecular collisions, the reaction is controlled by the chemical reactivity of these groups. As the reaction continues, there is an increase in chain branching until the system reaches the gelation stage; further polymerisation causes an increase of the crosslinking until the mobility of the reactive centres is progressively restricted and the reaction rate is lowered [24]. Kamal and Sourour [25] were the first to report that the n^{th} order model does not describe accurately the behaviour of thermoset resins because it does not satisfy the zero initial rate of reaction. Therefore, they proposed the following model:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1-\alpha)^n \quad \text{Equation 5}$$

Where k_1 and k_2 are the kinetic rate constants and m and n the reaction orders. The rate constants are temperature dependent and follow Arrhenius behaviour, as depicted in Equation 6.

$$k = A \exp\left(\frac{E_a}{RT}\right) \quad \text{Equation 6}$$

Where A is the Arrhenius parameter or pre-exponential factor, E_a is the activation energy and R is the gas constant.

It is frequently observed that the cure reaction stops before achieving full conversion because vitrification occurs. As the cure reaction reaches higher conversion values, the reaction becomes diffusion controlled, i.e, when the formed network reaches an infinite molecular weight, the viscosity is significantly higher and the resin behaviour is transformed from liquid to rubbery to glassy (vitrification). At this point, the advance of the reaction is limited by the lower motion of the molecules and is therefore diffusion-controlled [16][18]. Fournier and co-workers [26] proposed a modification to the Kamal's model by introduction of a diffusion factor f_d .

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1-\alpha)^n f_d(\alpha) \quad \text{Equation 7}$$

$$f_d(\alpha) = \frac{2}{1 + \exp\left(\frac{\alpha - \alpha_f}{b}\right)} - 1 \quad \text{Equation 8}$$

Where α_f is the final conversion obtained and b an empirical diffusion constant. For estimation of the activation energy E_a , isoconversion methods are traditionally used. These methods are based on the isoconversional principle that states that the reaction rate at a fixed extent of conversion is only a function of temperature [23]. The temperature dependence of the isoconversional rate can be used to determine the activation energy without assuming any particular form of the reaction model $f(\alpha)$. The Kissinger method is one of the most popular approaches for determining kinetic parameters by thermal analysis. It is based upon a series of experiments in which small quantities of the reacting material are heated at several heating rates β while the reaction exothermic peak temperature (T_p) is recorded. A representation of $\ln[\beta/T_p^2]$ versus $1/T_p$ is fitted to a straight line, where the slope equals $-E_a/R$ and the intercept yields $\ln[AR/E_a]$ where E_a is the activation energy, A is the Arrhenius pre-exponential factor and R is the gas constant. A first order reaction ($n=1$) reaction order is usually assumed [27].

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad \text{Equation 9}$$

This method is based on the assumption that the conversion corresponding to the maximum rate of reaction during dynamic cure remains constant and is, therefore, independent of the heating rate [2].

6.3 Results and Discussion

6.3.1 Thermal Behaviour of Fillers

In order to guarantee there was no filler degradation during the cure kinetic studies, differential scanning calorimetry scans were performed on both fillers using a heating rate of 10 °C/min. the results shown in Figure 49 and Table 19 show that both fillers start their endothermic decomposition above 200 °C, which excludes any thermal degradation and energy consumption in the temperature range of the kinetic analyses.

ATH starts decomposing at about 215 °C with the release of water and the formation of aluminium oxide Al_2O_3 . The first small endothermic peak is due to the decomposition of ATH to $\text{AlO}(\text{OH})$, also known as boehmite, while the major endothermic peak observed concerns the decomposition of ATH to Al_2O_3 . Studies have shown that the formation of boehmite is favoured by higher particle size ATH [28]. The dehydration and the formation of the ceramic aluminium oxide layer are both responsible for the flame retardant mechanisms of ATH.

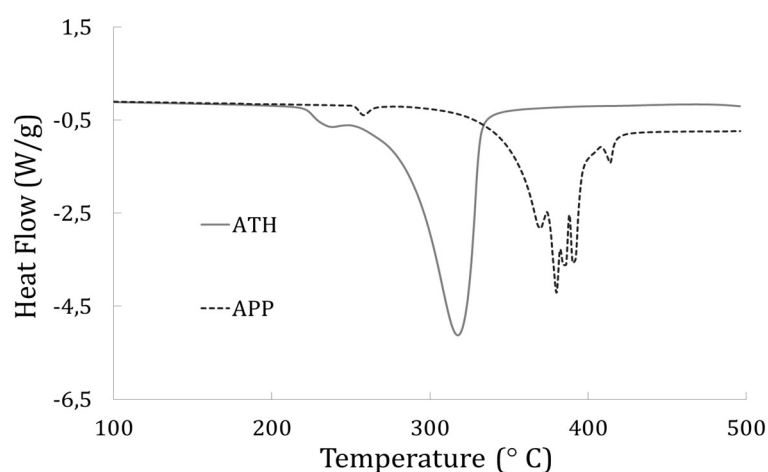


Figure 49: Thermal decomposition behaviour of ATH and APP

Table 19: Onset and peak degradation temperatures of ATH and APP

Filler	Onset Temperature of Degradation (°C)	Peak Temperature of Degradation (°C)
ATH	216.6	317.6
APP	250.3	380.9

The degradation of ammonium polyphosphate in the temperature range studied (up to 500 °C) is due to the endothermic release of ammonia and water. The degradation products crosslink with the resulting formation of polyphosphoric acid [29]. The first small endothermic transition can be attributed to polymorphic transitions of residual APP crystal structure from APP I to APP form II [30]. APP crystal structure I has a high water solubility and is mainly used in coatings and fertilizers; it is characterised by a variable linear chain length, showing a lower decomposition temperature. APP-II is the traditional water insoluble flame retardant with a crosslinked/branched structure [31]. The structures of APP-I and APP-II are shown in Figure 50. In APP I, “n” (number of phosphate units) is

generally lower than 100. The molecular weight of APP-II is much higher than APP I with an "n" value higher than 1000.

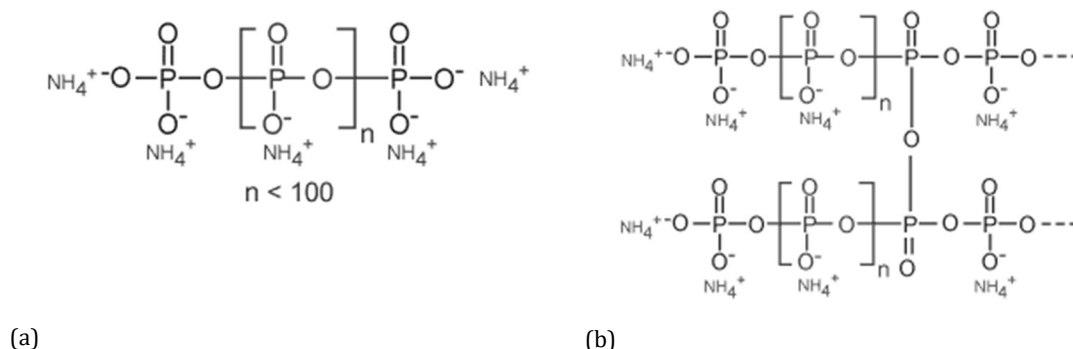
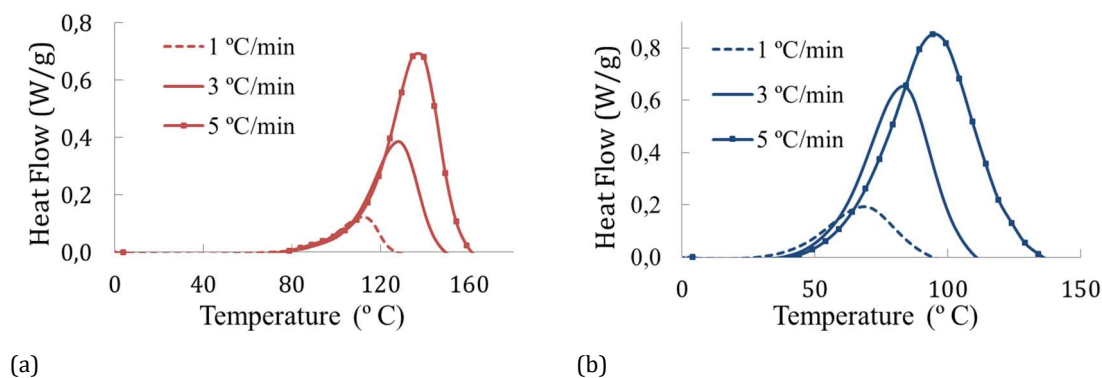


Figure 50: Chemical Structures of APP: (a) APP form I (b) APP form II

6.3.2 Effect of ATH and APP on the dynamic heat of reaction

As mentioned before, the DSC kinetic studies were performed at three different heating rates: 1.0, 3.0 and 5.0 °C/min. Figure 51 presents the cure behaviour of both resin systems without fillers at the three heating rates tested. As expected, higher heating rates lead to higher peak temperatures achieved during the cure reaction and a more pronounced exothermal effect (with the presence of sharp peaks). When the resin is cured at slower heating rates, the reaction starts earlier and is considerably slower. The low viscosity epoxy resin, as mentioned before, is cured at lower temperatures (see Table 17), which is in agreement with the experimental observations depicted in the figure. This curing reaction of the low viscosity resin is also considerably more exothermic; this behaviour has also been previously reported [32]. The peak temperatures achieved are between 110 and 140 °C for high viscosity resin and between 60 and 100 °C for the low viscosity resin.



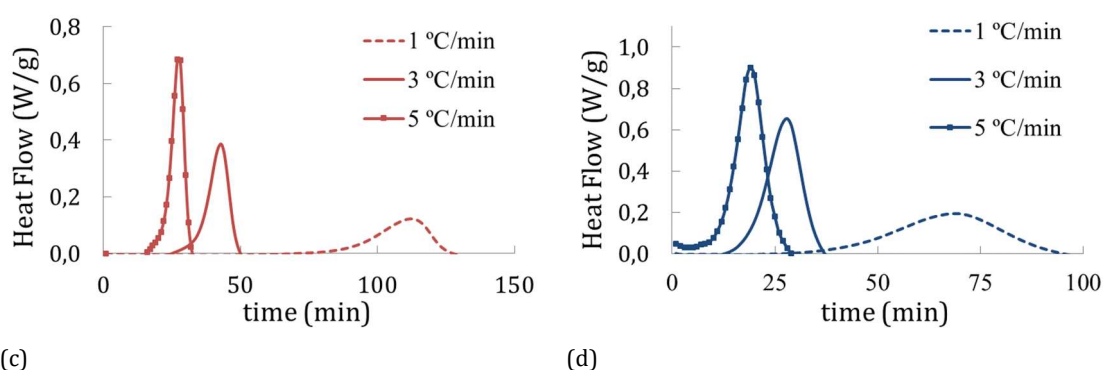


Figure 51: Cure behaviour of high (a, c) and low (b, d) viscosity epoxy resins obtained at three different heating rates as a function of temperature (a, b) or time (c, d)

The total heat of reaction for all systems was estimated using Equation 1. The values obtained are summarized in Table 20. The average heat presented is the result of the average values obtained from three different dynamic scans. For the filled samples, the heat of reaction presented in the table refers to the heat per mass of reactive system (i.e., mass of resin without filler). For each resin system, the total heat of reaction is independent of the heating rate used, as already verified by several authors [3][33][34].

Table 20: Average heat of reaction obtained from dynamic scans for all resin samples

Resin	Sample	Average Heat of Reaction (J/g)	Standard Deviation (J/g)
High Viscosity	LY	256.7	6.7
	LY1P	247.9	8.5
	LY5P	224.8	10.8
	LY1A	210.3	11.3
	LY5A	191.2	1.8
Low Viscosity	SR	454.8	6.1
	SR1P	515.7	10.6
	SR5P	524.7	5.8
	SR1A	461.8	7.2
	SR5A	471.4	9.1

i. High Viscosity Resin

The high viscosity resin system shows an average heat of reaction of 257 J/g, a value lower than the one obtained by N. Rabearison *et al.* [3]. These authors have studied the kinetics of the same pre-polymer epoxy resin, however, a different type and amount of hardener was tested. The heat of reaction reported was of 355 J/g with an uncertainty of ± 25 J/g.

The addition of both flame retardants influences the heat released during the cure reaction of high viscosity epoxy resin, as can be seen in Figure 52.

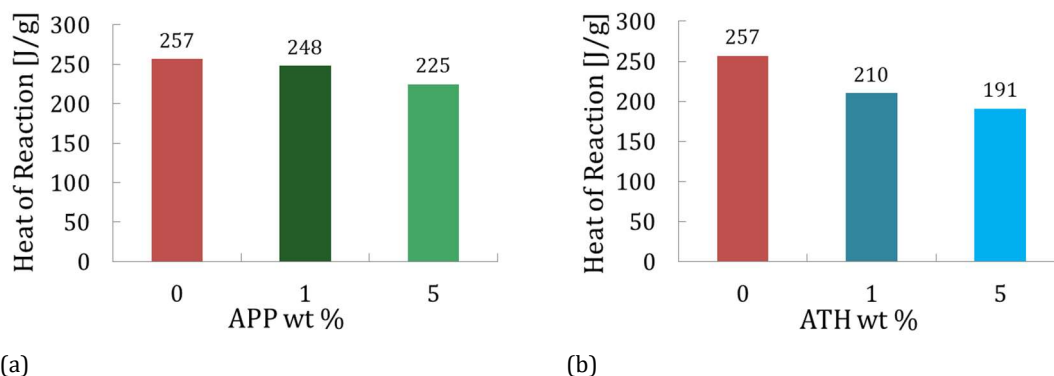


Figure 52: Influence of ammonium polyphosphate (a) and aluminium trihydrate (b) fillers on the total heat of reaction of high viscosity epoxy resin

Both APP and ATH reduce the amount of heat released by unit mass of epoxy resin during the cure reaction, although the effect of aluminium trihydrate is more pronounced. This could be due to the increased viscosity of the systems, which then restricts the mobility of the reactive molecules and therefore reduces the extent of crosslinking. The same behaviour was reported by M. Harsch *et al.* [35] with the addition of SiO₂ particles to an anhydride cured epoxy resin, and by T. Zhou [36] when adding multi-walled carbon nanotubes to an epoxy-imidazole system.

ii. Low Viscosity Resin

The low viscosity resin system shows an average heat of reaction of 455 J/g, as shown in Figure 53, which means that the cure reaction of this resin system is considerably more exothermic than the high viscosity resin. Similarly, a change in the resin's dynamic heat of reaction with the addition of either APP or ATH is also observed, as can be seen in Figure 53. In both cases, an increase in the heat released per mass of resin is observed. The increase is higher with APP though. This may suggest that the extent of resin cure filled with flame retardants, either ATH or APP, is higher than for neat epoxy samples, which may have a positive effect on the formed network and glass transition temperature.

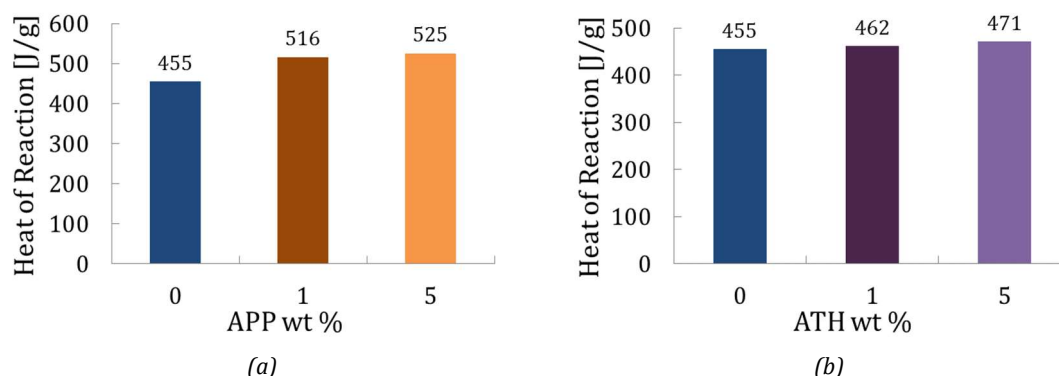


Figure 53: Influence of ammonium polyphosphate (a) and aluminium trihydrate (b) fillers on the total heat of reaction of low viscosity epoxy resin

D.D.L Chung and J. Wu [37] performed a study on the effect of carbon fillers on the kinetics of an epoxy resin, also cured with an amine curing agent. The presence of fillers promoted

increases in the total heat of curing reaction; particularly in the case of an ozone-treated carbon fibre, the increase was the highest. The authors stated that ozone treatments generate oxygen-containing groups on the surface of the fibre and these may eventually participate in the curing reaction, therefore increasing the heat during the reaction. This is in agreement with the results shown in Figure 53, where increasing APP shows a more pronounced increase in the heat, consistent with the fact that the amount of oxygen present is higher than in aluminium hydroxide. L. Torre and co-workers [17] studied the cure kinetics of an epoxy resin with a MMT nanofiller and/or a phosphorous bases flame retardant and concluded that neither of the fillers changed the mechanism of crosslinking of the resin. However, both were able to exert an evident catalytic action on the cure reactions, as seen by the increase in the total heat of reaction.

6.3.3 Effect on the Reaction Rate and Fractional Conversion

The basic kinetic parameter that dictates the state of the material is the chemical conversion. Proper determination of the reaction rate and its variation with temperature enables the determination of the chemical conversion achieved after a curing schedule.

The reaction rate depends on both the temperature and the conversion, as stated by Equation 1. The temperatures at which the curing reaction occurs depend on the heating rate (Figure 51). Figure 54 illustrates the variation of the reaction rate, i.e., the speed at which the curing reaction happens as a function of the fractional conversion for high and room temperature curing epoxy resins.

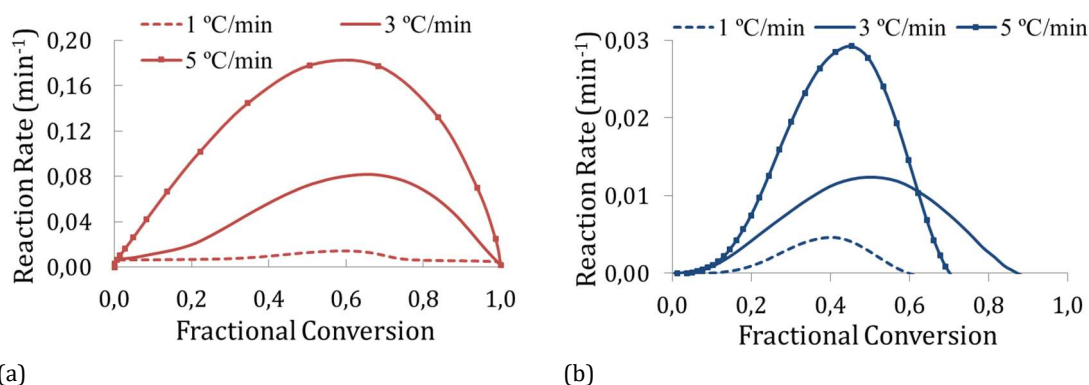


Figure 54: Reaction rate as a function of fractional conversion for high (a) and low (b) viscosity epoxy resins

The cure behaviour of both epoxy resins is different, especially at higher heating rates. High viscosity resin (left curves) starts curing with very high reaction rates, while for the low viscous epoxy resin, there is a slight plateau until conversion reaches about 10% and only then the chemical reaction starts increasing its speed. When the conversion reaches about 70%, the reaction rate is very low until full cure is attained. The high viscosity resin (LY556) curing reaction is faster than the low viscosity (SR8100), which is in fact in agreement with the curing cycles recommended by the manufacturer: a total of 4 hours at high temperature for LY556 resin and a total of 32 hours at low temperature for SR8100 epoxy resin. The curing reaction of the low viscous resin is quite slow, especially at low temperatures – the recommended manufacturer curing schedule is of 24 hours at room temperature – demonstrating that this resin has a slow curing reaction, which is in agreement with the curing profiles obtained and shown above.

The presence of diffusion effects are usually visible in the reaction rate versus conversion graphics. In both resins, the reaction rate peaks occur at intermediate conversions, which is typically indicative of autocatalytic curing reactions [2].

The effect of both fillers on the fractional conversion obtained at selected temperatures – 50, 100, 150 and 200 °C) is shown in Figure 55. For simplification, only the results of the dynamic heating at the higher heating rate (5 °C/min) are depicted here.

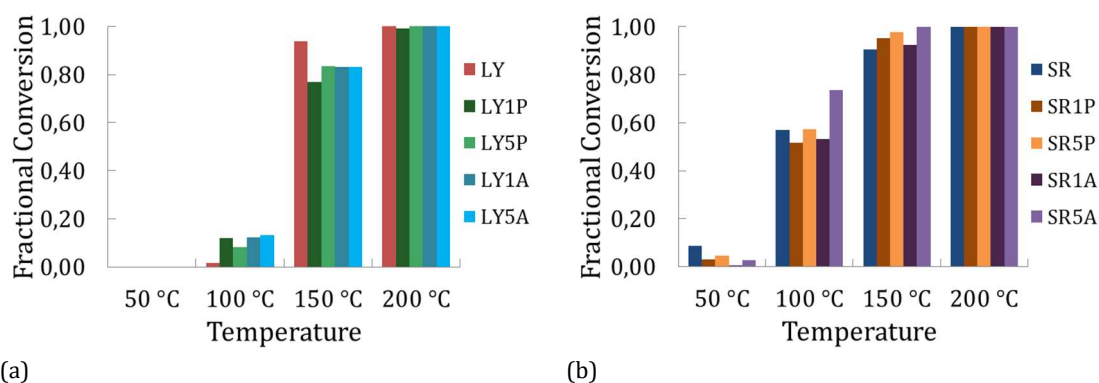


Figure 55: Fractional conversion at selected temperatures obtained at 5 °C/min for filled resin samples (a) high and (b) low viscosity epoxy resin

From the results depicted above, one can see that at 50 °C, the curing reaction of LY556 resin (left curves) is not yet started, while for low viscosity resin the conversions achieved at this temperature are in the range of 7 to 15%. This is once again in agreement with the data known for the resin systems: high viscosity resin cures at high temperatures while the low viscosity resin cures at room temperature. At 200 °C, both resins, with and without fillers, have achieved complete cure. These results were also observed for the other heating rates tested and for all fillers used. As already verified by the results of the total heat, the addition of fillers shows effects on the fractional conversion obtained during the cure reaction of both resins. At 100 and 150 °C, both APP and ATH decrease the fractional conversion of the high viscosity resin. On the other hand, fillers tend to increase the conversion of the SR8100 resin. These are important observations that should be taken into account when producing composite materials using filler-modified resins. The use of additives can likely change the resin cure behaviour and proper curing schedules shall be performed. Adjustments may be needed in both curing temperatures and times. In the case of the total heat released, additional problems can be encountered if the manufactured parts are produced in closed moulds and a higher heat of reaction is expected.

6.3.4 Effect on the Kinetic Parameters

For the determination of the kinetic parameters, the Kissinger method (equation 9), based on the variation of the curing peak temperature with the heating rate used, was used. In that sense, it is important to start by analyzing the influence of the fillers ATH and APP in the maximum temperatures achieved during the cure of both epoxy resins selected for this study. Figure 56 shows the results obtained.

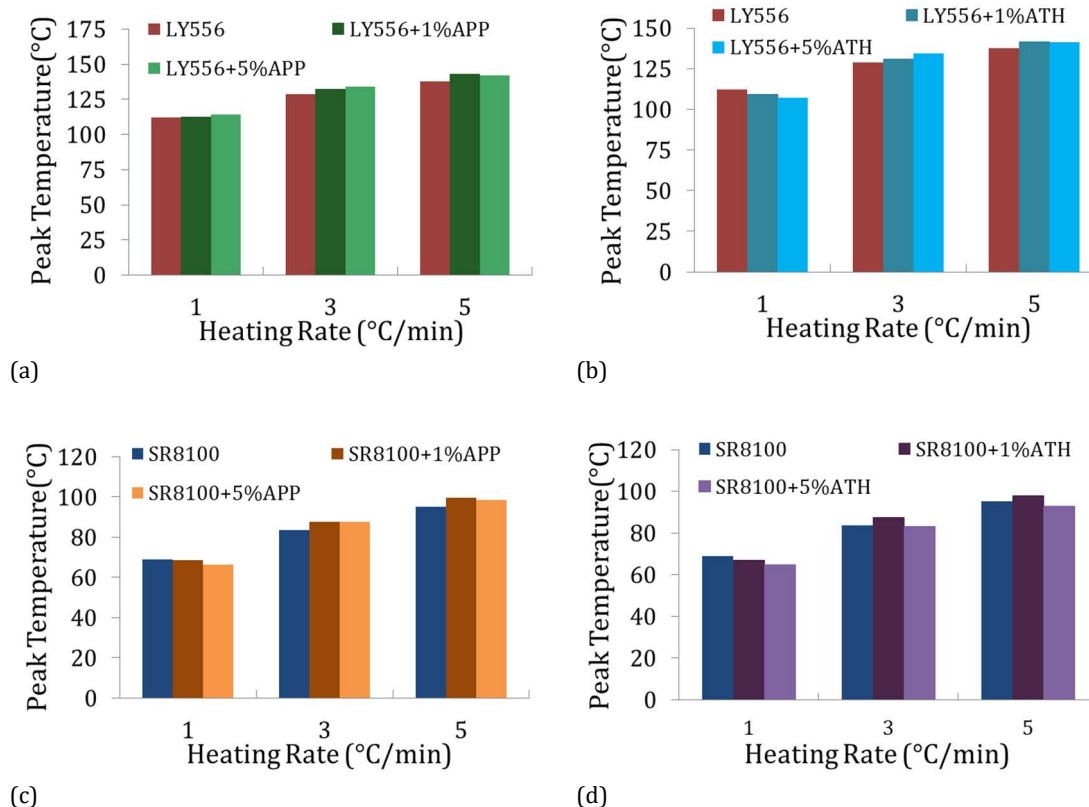


Figure 56: Variation of maximum cure temperature as a function of heating rate for high viscosity resin (a) effect of APP (b) effect of ATH and low viscosity resin (c) effect of APP (d) effect of ATH

It can be seen that, with exception of the lower heating rate for aluminium trihydroxide, the addition of fillers leads to higher temperatures achieved during the cure reaction in both epoxy resins. Although in the case of high temperature curing resin (LY556), the total heat released per mass of reactive resin is reduced, the peak temperature is higher with the addition of traditional flame retardants. The increase is in the range of 4 to 6 °C, for both resins and fillers.

These results are not consistent with what is usually reported in the literature. M. Ivankovic and co-authors [38] studied the effect of modified montmorillonite clays on the cure kinetics of an epoxy resin. They reported reductions on the maximum cure temperatures with clay loading for non-isothermal measurements performed at 3, 5 and 10 °C/min. Chung and Wu [37] had, in a previous work, also reported reductions in the peak temperature with different carbon based fillers, additionally stating that increases in the specific surface of the fillers lead to higher reductions in the temperature. A more recent work [39] also reports reductions in the peak temperature attained during epoxy cure by increasing the content of a commercial montmotilonnite clay (Cloisite). Authors concluded that, especially at higher heating rates, the organoclay enhances the cure reactions so that lower temperatures are needed in order to initiate the chemical reaction.

As mentioned before, the Kissinger model was applied to the results obtained in the non-isothermal tests, namely the heating rate and peak temperatures associated with each resin formulation. The apparent activation energy E_a of the curing reactions, the pre-exponential factors and coefficient of linear regression are summarized in Table 21.

Table 21: Activation Energies and Arrhenius pre-exponential factors obtained using Kissinger Model

Sample	Kissinger Model		
	Ea (KJ/mol)	ln A	r ²
LY	62.5	2.02	0.9991
+1 wt% APP	49.2	1.78	0.9996
+5 wt% APP	54.4	1.88	0.9960
+1 wt% ATH	45.1	1.69	0.9997
+5 wt% ATH	37.8	1.52	0.9605
SR	38.9	1.54	0.9649
+1 wt% APP	29.7	1.27	0.9925
+5 wt% APP	26.6	1.16	1.0000
+1 wt% ATH	28.1	1.22	0.9999
+5 wt% ATH	33.0	1.28	1.0000

The activation energy of the neat high temperature curing epoxy resin is in the order of 60 KJ mol⁻¹; these results are in the same order of magnitude as reported by other authors [3] [33]. The activation energy of resin system SR8100 is lower, in the range of 40 KJ mol⁻¹, indicative that less energy is needed in order for the components to trigger chemical reaction.

A decrease in the activation energy with the addition of fillers is obtained for both resin systems. In fact, it is known that the activation energy is related to the rate of the chemical reaction, rather than to a mechanism. The activation energy of a chemical reaction can be seen as an energy barrier that needs to be overcome for that reaction to occur. This means that, when adding ATH or APP, less energy is needed – creating therefore an accelerating effect. This is important when adjusting resin/composite curing cycles, as curing temperature and time shall be optimized in order to obtain maximized properties. The trend with increasing filler amount is not, however, clear. This can be caused by poor filler dispersion within the resin matrix.

6.4 Conclusions

It was intended with this work to study the effect of adding two traditionally used flame retardants (ATH, aluminium hydroxide and APP, ammonium polyphosphate) on the curing kinetics of two different epoxy resins. Non-isothermal tests at three different heating rates were performed using a DSC in order to obtain the kinetic parameters.

The high viscosity, high temperature curing resin LY556 showed a less exothermic cure reaction than the low viscosity epoxy resin. The average values obtained were of 255 and 455 J/g, respectively. Addition of both fillers influenced the heat released during the cure, but opposite effects were observed. For LY556 resin, fillers reduced the total heat of cure,

with ATH showing a more pronounced effect. On the other hand, for SR8100 resin it was concluded that the presence of fillers increased the heat of cure, and APP has a higher impact.

In the case of the kinetic parameters, an accelerating effect is created by the presence of flame retardants, as the activation energy obtained by modelling the results following the Kissinger model is diminished for both resin systems.

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7 Main Conclusions and Future Work

It is a fact that composite materials continue to find new applications and replace other materials, even in highly demanding applications such as in the Space sector. Carbon fibre composites, especially, are of great interest when high mechanical properties, stiffness and lightweight properties are required. The highly organic composition of the resins used as matrix in composite materials can put at risk the use of these materials when fire situations occur. The use of flame retardants, added to the resin matrix, usually leads to acceptable fire reaction properties. As an example, with the use of flame retarded materials, aircraft manufacturers are increasingly able to use plastics, polymers and composites in aircraft fittings, equipment, seats and even structures, while guaranteeing a proper fire behaviour. These flame retardants can act in one or more ways in order to slow or even stop the burning process, such as physical or chemical actions. Traditional flame retardants typically used are effective but require high loadings, which can have negative effects not only on the resin final workability (such as gel time and viscosity), but also on the properties, namely the mechanical ones. In more recent years, however, with clear benefits verified by the use of nanoparticles, different nano-solutions have been tested in order to replace conventionally used flame retardants. In this sense, nanoparticles can be a viable alternative due to their high specific surface area, theoretically leading to lower amounts needed to enhance the material properties.

This work presents different approaches aiming at enhancing the fire reaction behaviour of fibre reinforced composite materials. Throughout this theses, three main materials were studied, namely:

- (a) The base resin: in this case, two epoxy resins were used. A low curing, low glass transition and low viscous epoxy resin and a high performance, high viscosity epoxy typically used in aerospace applications. For both resins, the efficacy of traditional flame retardants and nano-based solutions were assessed using the cone calorimeter.
- (b) Carbon fibre epoxy composites manufactured at INEGI and typically used in aerospace applications, where the high viscosity epoxy was used as matrix. As for the resin alone, the efficacy of traditional flame retardants and nano-based solutions were assessed using the cone calorimeter. An innovative approach used in these materials was also the use of ceramic tapes as intended fire protective coatings.
- (c) Commercially available glass fibre composites that can be used, for instance, in civil engineering applications. For fire protection, an intumescent water based paint was used as coating.

The assessment of the state of the art on fire reaction of carbon fibre composite materials showed that, even though there are several works about the fire properties of resin matrixes (thermoset and thermoplastic), there is a considerably lower amount of work on fibre-reinforced composites. In this sense, chapter 2 presents a preliminary study about the effect of nanosized traditional flame retardant magnesium hydroxide on the flammability of a low viscosity epoxy resin. Chapter 3 compares the effectiveness of different nanofillers and compares their performance with traditional flame retardants, regarding the fire reaction properties of both epoxy and carbon fibre reinforced epoxy composites. Nanofillers used

included nanoclays and carbon nanotubes. Regarding the fire reaction behaviour of the epoxy resin, anionic nanoclays and thermally oxidized carbon nanotubes showed the best results, in agreement with visual observations during and after cone calorimeter tests, where more compact chars were formed on the surface of the burning polymer. For carbon fibre reinforced composite samples, the addition of fillers to the resin matrix did not show significant improvements on the heat release rate curves. These are interesting observations but also concerning results, in the sense that one may infer that the presence of reinforcing fibres may be inhibiting the flame retardant action of the tested fillers.

Regarding the use of modified resin systems for obtaining flame retardant composite materials, further work could include the use of other nanoparticles – especially carbon based such as graphite or graphene. Another approach that could be interest to test is the use of a surface resin layer in which the nanofiller loading would be concentrated. In this way, the nanoparticles could act as a barrier to the heat penetration throughout the composite structure. Another possible approach would definitely be the study of possible synergistic effects of traditional flame retardants such as ammonium polyphosphate or aluminium hydroxide, partially replaced with nanoparticles.

One critical issue, verified and discussed throughout this work, is the dispersion of nanofillers in the resin matrix. Usually, the nanoparticles show a great tendency for agglomeration, hindering proper dispersion. New solutions must be proposed for this purpose, such as the modification/compatibilization of the nanoparticles according to the resin matrix. Viscosity could also be a concern, especially if the resin matrix is a thermoset such as epoxy or polyester, as this parameter could limit the processing of the composite material. High resin viscosities are not suitable for infusion or pre-impregnation processes, for instance.

A different approach was also tested in this thesis – the use of ceramic materials or an intumescent paint as fire protective coatings. A clear advantage, when comparing with the addition of fillers to the resin, is that no modifications were introduced during the processing of the materials. The coatings were applied after (paint) or in the final stage (i.e., before curing) (ceramic) of the composites manufacturing process. Furthermore, both fire protective coatings used can be considered eco-friendly alternatives. The intumescent paint was water-based and the ceramic tapes were produced using water and not traditional solvents. In the case of the intumescent paint, the materials tested are commercially available and therefore easily accessible. It is recommended for metallic structures but has proven to be quite effective in glass fibre composite materials. It is simple to apply, the adherence to the composite surface is good, and the structure can afterwards be used in typical civil engineering applications, as esthetically speaking it shows the appearance of a regular painted wall/structure. The improvements in the fire reaction behaviour of the glass fibre composite material were largely dependent on the thickness of the applied paint. As expected, higher paint thicknesses resulted in higher fire protection. A thickness of 2 mm of water based paint was able to considerably reduce not only the heat released during burning, but also the amount and toxicity of smoke, as assessed by cone calorimetry.

For the ceramic tapes, three chemical compositions were tested: aluminium oxide alone, combined with calcium carbonate or with cellulose fibres. After manufacturing, the structure of the materials was observed with a scanning electron microscope, where a more compact and closed structure was observed in the presence of cellulose fibres. Furthermore,

this coating showed the best performance in the cone calorimeter tests, with higher reductions in the heat released, when compared with the neat carbon fibre composite. This ceramic coating was also effective on reducing the smoke opacity, which is critical in the sense that most deaths by fire are caused by smoke inhalation, rather than by burning. An additional feature that can be attractive regarding the use of the ceramic tapes is that they can be more or less tailored to the specific target applications. In the case of this thesis, traditional ceramic powders such as aluminium oxide and calcium carbonate were used. However, there is great interest in continuing this research work by combining different particles, such as nano-sized ceramic powders, among other possibly interesting nanosolutions such as nanoclays, carbon nanotubes or halloysites.

The cure kinetics study is essential when developing modified thermoset resin systems. This is because cure kinetics deals with several aspects of resin curing such as the effect of time and temperature on the kinetic profiles of the resin. In the case of thermoset composite materials processing, knowledge about the proper curing time is essential in order to obtain materials with optimized properties. Mechanical and thermal properties of composite materials are highly reliant on proper curing conditions. There are several studies published on the curing kinetics of epoxy resins with the addition of nanoclays or carbon nanotubes. However, to the best of knowledge, there were no studies regarding the effects of the addition of traditional flame retardants. In that sense, the materials prepared and tested in chapter 3 for fire reaction behaviour were also studied using differential scanning calorimetry in order to understand the effects of both fillers in the curing kinetics of an epoxy resin. In this case, non-isothermal testing was used, but in further studies the isothermal approach shall also be considered in the sense that it may provide more accurate results. The purpose was to study the cure kinetics of the two different epoxy resins used in this thesis (high and low viscosity), filled with ATH and APP, by means of dynamic DSC scans at various heating rates. Addition of both fillers influenced the heat released during the cure, but opposite effects were observed. For the high viscosity resin, fillers reduced the total heat of cure, with ATH showing a more pronounced effect. On the other hand, for the low viscosity resin, it was concluded that the presence of fillers increased the heat of cure and APP has a higher impact. These results must be explored in more detail, with the use of the isothermal approach during DSC tests. When the reported tests were performed, the equipment used was operating between 40 and 550 °C. Recently, with the acquisition of a cooling system, it is possible to lower the minimum temperature for -90 °C. It should also be interesting to test the kinetics starting at lower temperatures in order to see if there are effects on the curing profiles. As a complementary technique, FTIR studies could also be used to monitor the evolution of the epoxide group during the cure reactions. Infrared spectroscopy allows a very accurate determination of chemical conversions by band integration of the corresponding IR signals (epoxide and amino groups), allowing more accurate values at high conversions. The possibility of chemical reactions happening between the curing agents and the added flame retardants could also be explored as future work. This may also be affecting the obtained curing heats of reaction, causing either increases or decreases in that value.

The high mechanical performance associated to fibre reinforced composite materials, obtained at low material weights is considered the main advantage of these materials regarding traditionally used metallic ones. These properties were not studied in this thesis, as it was mostly focused on the fire reaction properties. It is recognized that the addition of

fillers can have impacts on the overall mechanical performance of the host material, thus, it is critical to mechanically characterize the obtained materials, especially if high performance applications are being targeted.