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Nature-based polymer composites with wood particles from industrial waste

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Thank you.

Daniela Oliveira

Abstract

The global production of plastics has witnessed significant growth, reaching 390.7 million tonnes in 2021, with bio-based plastics accounting for only a small fraction of that amount. Substituting plastic with bio-composite materials that incorporate wood byproducts can lead to environmental sustainability by reducing reliance on non-renewable fossil fuels.

This thesis centers around the development of a wood-polymer composite integrating a biodegradable polymeric matrix (blend of poly(butylene adipate-co-terephthalate) with 30% starch) and 10, 20, 30, 40 and 50 wt% of wood particle byproducts (poplar wood and bark) with two different sizes (250 to 500 μm (*t1*) and 500 μm to 2 mm (*t2*)), as the filler.

Thus, the chemical, morphological and mechanical performance of the neat polymer and the composites were studied to determine whether the incorporation of natural particles into the polymer would be feasible. From scanning electron microscopy analysis, it was possible to conclude that polymer and filler have good compatibility, since wood particles seem to be well distributed in the polymeric matrix, with a continuous interface and no void spaces.

Regarding the water contact angle analysis, the incorporation of filler in the polymer increased its polar component of surface energy, and so its hydrophilicity. Thus, 50 wt% wood composite demonstrated to be the most hydrophilic one, with a contact angle of 64.8º, which was expected due to wood's high amount of available hydroxyl groups.

After submitting the samples to mechanical tests, it was possible to conclude that Young's modulus (stiffness) increased with increasing filler load in the sample, as well as tensile strength. Therefore, with the incorporation of wood particles, these values increased 2980% and 84.4%, respectively, when comparing to the neat polymer. On other hand, bark composites did not present significant variation on the tensile strength parameter.

Contrarily, strain at break and area under the stress-strain curve, which indicates the toughness of the material and its resistance to impact, decreased with the incorporation of filler. This was the expected behavior since natural particles add brittleness to the material and less energy is needed to fracture the composites.

This thesis made it possible to conclude that the incorporation of up to 50 wt% poplar wood and bark filler into polymeric poly(butylene adipate-co-terephthalate)/starch blends can lead to the production of usable materials. However, future research is needed to improve some of the mechanical properties for further application.

Keywords: poly(butylene adipate-co-terephthalate), starch, wood-polymer-composite, biodegradability

Resumo

A produção global de plásticos registou um crescimento significativo, atingindo 390,7 milhões de toneladas em 2021, com os plásticos de base biológica a representarem apenas uma pequena fração dessa quantidade. A substituição do plástico por materiais biocompósitos que incorporam subprodutos da madeira pode contribuir para a sustentabilidade ambiental, reduzindo a dependência de combustíveis fósseis não renováveis.

Esta tese centra-se no desenvolvimento de um compósito de madeira que integra uma matriz polimérica biodegradável (mistura de poli(butileno adipato co-tereftalato) com 30% de amido) e 10, 20, 30, 40 e 50% de partículas de madeira e casca de choupo com dois tamanhos diferentes (250 a 500 µm (t1) e 500 µm a 2 mm (t2)), como carga.

Deste modo, o desempenho químico, morfológico e mecânico do polímero puro e dos compósitos foi estudado para determinar se a incorporação de partículas naturais no polímero seria viável. Da análise por microscopia eletrónica de varrimento, foi possível concluir que o polímero e a carga têm boa compatibilidade, uma vez que as partículas de madeira parecem estar bem distribuídas na matriz polimérica, com uma interface contínua e sem espaços vazios.

Relativamente à análise do ângulo de contacto com a água, a incorporação de carga no polímero aumentou a sua componente polar de energia de superfície, e assim a sua hidrofilicidade. Assim, o compósito com 50% de madeira demonstrou ser o mais hidrofílico, com um ângulo de contacto de 64,8º, o que era esperado devido à elevada quantidade de grupos hidroxilo da madeira.

Ensaios mecânicos permitiram concluir que o módulo de Young (rigidez) aumenta com o aumento da carga na amostra, bem como a resistência à tração. Assim, a incorporação de partículas de madeira, potenciou o aumento de 2980% e 84,4% destes parâmetros, respetivamente, em comparação com o polímero puro. Por outro lado, os compósitos de casca de choupo não apresentaram variação significativa da resistência à tração.

Contrariamente, a deformação de rotura e a área da curva tensão-deformação, que indicam a tenacidade do material e a sua resistência ao impacto, diminuíram com a incorporação de carga. Este era o comportamento esperado, uma vez que as fibras naturais acrescentam fragilidade ao material e é necessária menos energia para fraturar os compósitos.

Esta tese permitiu concluir que a incorporação de até 50% de carga neste polímero pode levar à produção de materiais mais sustentáveis. No entanto, é necessária investigação futura para melhorar algumas das propriedades mecânicas para posterior aplicação.

Palavras-chave: poli(butileno adipato co-tereftalato), amido, compósitos polímero-madeira, biodegradabilidade

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source

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Porto, July 2nd, 2023

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Notation and Glossary

Mt	Million tonnes	
T_m	Melting temperature	ºC
T_c	Crystallization temperature	ºC
T_g	Glass transition temperature	ºC
YM	Young's Modulus	MPa
TS	Ultimate Tensile strength	MPa
SB	Strain at Break	%
AUC	Area under the curve	MPa
θ	Contact angle	
σ_S	Total Surface energy	mJm^{-2}
σ_S^P	Polar component of Surface Energy	mJm^{-2}
σ_S^D	Dispersive component of Surface Energy	mJm^{-2}

List of Acronyms

P	Polymer
PW	Poplar wood
PB	Poplar bark
PPW	Composite Polymer/Poplar wood
PPB	Composite Polymer/Poplar bark
PBAT	Poly(butylene adipate-Co-terephthalate)
PBA	poly(butylene adipate)
PBT	poly(butylene terephthalate)
TPS	Thermoplastic starch
FTIR	Fourier Transform Infrared
TGA	Thermogravimetric Analysis
DTG	Differential Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
WCA	Water Contact Angle
SEM	Scanning electron microscopy
t1	Particles' smaller size (250 μm to 500 μm)
t2	Particles' larger size (500 μm to 2 mm)

1 Introduction

1.1 Scope and presentation of the work

In the past half-century, traditional petroleum-derived plastics have seamlessly integrated into our daily routines. Their widespread adoption can be attributed not only to their cost-effectiveness but also to a range of exceptional characteristics, such as their robustness, structural integrity, lightweight nature, electrical and thermal insulation, as well as their resistance to chemicals and corrosion.

The global production of plastics has surged significantly after a stagnation in 2021, due to the Covid-19 pandemic, increasing from 373.5 million tonnes (Mt) in 2018 to 390.7 Mt in 2021, being just 5.9 Mt bio-based plastics. Within this total, Europe alone accounted for the production of 57.2 Mt, which includes 1.3 Mt of bio-based plastics. According to Plastics-The Facts (2022), polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC) continue to be the principal type of plastic produced and the main application of plastic usage is packaging (PlasticsEurope 2022).

In addition to the visible issues, microplastics poses significant threats to terrestrial, marine, and freshwater ecosystems, resulting in severe consequences for living organisms and potentially endangering human health. Paradoxically, the long durability that makes plastics an appealing material becomes problematic, as their resistance to degradation in natural environments exacerbates the impact of their presence (Geyer, Jambeck, and Law 2017).

Bioplastics, encompassing both bio-based and biodegradable variants, hold great promise in tackling numerous environmental issues. Bio-based plastics are derived from biomass sources such as cellulose, starch, lignin, and others. Certain bio-based plastics have the ability to naturally degrade in the environment, transforming into harmless substances, while others may require specific conditions for degradation (EuropeanBioplastics 2022).

Recent market data, compiled by European Bioplastics in collaboration with the nova-Institute, projects a significant increase in global bioplastics production capacities from around 2.2 Mt in 2022 to approximately 6.3 Mt in 2027. In terms of regional capacity, Asia has solidified its position as a key production hub, accounting for over 41% of the current bioplastics production. Currently, slightly over a quarter of the production capacity is situated in Europe. However, both Europe's share and that of other global regions are expected to decrease notably within the next five years.

Conversely, Asia's production capacities are projected to rise significantly, reaching nearly 63% by 2027 (EuropeanBioplastics 2022).

As said before, substituting plastic with composite materials, incorporating natural materials such as wood byproducts, can yield numerous advantageous outcomes such as environmental sustainability since they are renewable resources with a lower ecological impact than plastic, which relies on non-renewable fossil fuels. By utilizing wood waste and residues, composite materials diminish reliance on plastic, thereby contributing to a more sustainable packaging solution.

Another advantage is the biodegradability given that these composites can be intentionally designed to exhibit biodegradable and compostable properties. Consequently, they undergo natural decomposition without leaving behind persistent plastic waste. These materials can be degraded to enrich soil health, rather than accumulating in landfills or polluting marine environments. In addition, utilizing wood-based composites holds the potential to reduce carbon footprints since wood is considered a carbon-neutral material. By incorporating wood byproducts, the emissions associated with plastic production and disposal can be mitigated (Asgher et al. 2020).

When it comes to the product image, modern consumers increasingly prioritize the environmental impact of the packaging. By adopting these types of renewable materials, companies can effectively demonstrate their commitment to sustainability, aligning with consumer preferences. This, in turn, can improve brand image and appeal to environmentally conscious customers.

Lastly, composite materials can be engineered to possess tailored properties suitable for specific packaging requirements. By adjusting the composition and employing appropriate processing techniques, the strength, durability, and barrier properties of wood-based composites can be optimized to meet diverse packaging needs. This versatility allows for a wide range of applications, encompassing rigid containers and flexible films.

This work was developed at ARCP CoLAB (Associação Rede de Competência em Polímeros), in the context of a broader ongoing project, with the aim of developing a sustainable biodegradable composite, able to incorporate the maximum percentage of wood byproducts in the polymeric matrix, in order to valorize them. Thus, the success of this research would involve the determination of the mechanical properties of the composite material for different amounts and types of wood waste particles. Due to

the project context, the particles chosen were from poplar wood and bark, provided by FWFI Company. These are wastes from their wood-based packaging manufacture process. The polymer matrix was a starch/PBAT blend provided by United Biopolymers.

1.2 Contribution of the author to the work

The respective academic and ARCP company advisors played a crucial role in conceptualizing a plan to follow for the development of this thesis.

By conducting an extensive and comprehensive literature review on the subject to be studied, the author was able to create moments of discussion with the advisors to clarify objectives and identify the most appropriate methodologies to obtain and process data.

The author took responsibility for acquiring data and analysing it in a credible and relevant manner. This included sample preparation (grinding, sieving, and drying), experimental procedures (mold design, chemical characterization, thermogravimetric and dynamic scanning calorimeter analysis, Fourier transform infrared spectroscopy, scanning electron microscopy and water angle analysis), testing of specimens' mechanical performance and, subsequently, data analysis. It should be noted that the input from the mentors and research coworkers facilitated the whole process.

When it came to writing this thesis and creating illustrations, the author was the main responsible, and the mentors' opinion was always taken into consideration.

1.3 Organization of the dissertation

This thesis is divided into six chapters.

Chapter 1 provides an overview of the plastic production environmental impact and usage and introduces the potential of bio-based and biodegradable composite materials as a sustainable alternative. Therefore, it presents the research problem and the motivation behind this investigation.

Chapter 2 defines the context and presents some previous studies conducted on the topic addressed in this thesis. It introduces the incorporation of wood byproducts into composite materials and explores methods for enhancing its' performance. Furthermore, it presents insights from other authors regarding composites' biodegradable nature and potential application in the packaging area.

Chapter 3 consists of the methodological framework, in which are presented all the steps and equipment needed to proceed the study, namely the preparation of the composites, its characterization and morphological and mechanical performance analysis.

Chapter 4 discusses the results and compares them with the ones obtained by previous researchers.

Chapter 5 summarizes the results and provides final considerations and suggestions for future research in the field.

2 Context and State of the art

This thesis investigates the possibility of reinforcing a biodegradable polymeric matrix, composed by starch and Poly(butylene adipate-Co-terephthalate) (PBAT), with wood byproducts, notably poplar wood and bark. Thus, the produced composites were characterized and analysed for its mechanical and morphological performance, throughout the study, to, possibly, produce biodegradable food packaging.

2.1 Wood-polymer composites

Wood is a renewable, bio-based, biodegradable and carbon-sink material with outstanding mechanical resistance and used in landscaping timbers , fencing, joining and craft industries, furniture and automotive products (Ramesh et al. 2022). However, the main disadvantage of this material is its vulnerability to degradation by the absorption of water and the contact with wood-degrading biological agents (fungi, insects, bacteria, marine borers, among others) (Espert, Vilaplana, and Karlsson 2004).

Furthermore, the importance of wood comes with its availability, low weight, versatility (Khan, Srivastava, and Gupta 2020), possibility of being recycled and to recover stored energy (Plataform 2023), which is in line with the cascading utilization and resource efficiency principle (Teuber et al. 2016).

The chemical composition, anatomic structure, physical and mechanical characteristics, and thermal properties are different in various wood species (Khan, Srivastava, and Gupta 2020). Thus, basing on its anatomy and percentage of chemical compounds, wood can be classified into hardwood, obtained from deciduous trees as oak, beech and poplar (Bledzki, Sperber, and Faruk 2002), or softwood obtained from conifer trees, such as pine, spruce and fir (Lavine et al. 2001).

Some of the most common sources of wood, identified by the Chelsea Center for Recycling and Economic Development, include primary wood wastes (post-industrial wood wastes from sawmills), secondary wood wastes (generated during the manufacture of furniture, cabinets and doors), and post-consumer wood wastes (anything related with construction and demolition, debris to packaging, crates and pallets) (Optimat and MERL 2003). The most commonly used wood fillers are sawdust (SD) (Lette et al. 2018), wood flour (WF) (Zykova et al. 2021), wood feedstocks (Pokhrel, Gardner, and Han 2021) and other cellulose resources (Espert, Vilaplana, and Karlsson 2004).

The concept of a wood-polymer composite (WPC) emerged in Italy in the 1960s and became popular in the 1990s in North America. The first company in the world that invented and patented the WPC production process was *Covema* of Milan, founded by Terragni brothers (Raj 2019). Later, this idea spread to Asian countries in the 21st century (Ashori 2008).

Wood-polymer composites have been drawing more interest over the last few years because of the strict environmental legislation for using plastics, lack of petroleum resources and the deforestation due to the excessive use of wood (Xiao, Zhu, and Yu 2020, Wang, Chen, and Li 2021, Asim et al. 2020). It consists in an association of wood byproducts (Teuber et al. 2016), such as fibers or particles, with a polymer matrix and potentially some additives.

When it comes to the market opportunities, there are numerous possibilities such as decking, fencing and railing, building industries, and manufacture of pallets and exterior parts, in the automotive area (Ashori, Tabarsa, and Amosi 2012).

Its production can be made through various methods, such as thermoforming, extrusion, compression molding, hand lay-up, injection molding, and advanced manufacturing methods (e.g., 3D printing)) (Schwarzkopf and Burnard 2016, Gardner, Han, and Wang 2015).

The constitution of the wood component influences composites physical and mechanical performance. Fibers have a greater aspect ratio (length/width ratio) that enhance the tensile strength, while particles are easier to dose in the production process and to disperse in the polymeric matrix. Therefore, it results in a more homogeneous material (Teuber et al. 2016).

PVC, which has randomly orientated molecular chains, and polyolefin such as PE and PP, remain the principal resins used in commercial WPCs due to their cost-effectiveness, durability and good resistance to the moisture (Chan et al. 2018).

As mentioned before, wood is highly hydrophilic, which enhances the absorption of moisture and posterior swelling of the material. These properties reflect in the dimensional instability that wood offers, especially in exterior applications. One of the solutions to solve this problem is to associate this filler to a hydrophobic polymer matrix capable of reducing water absorption and sensitivity to fungal, or other potential microorganisms attack and subsequent degradation. At the same time, wood increases the stiffness, thermal stability and creep behavior of the polymer (Shahi et al. 2012).

One of the biggest limitations to the successful performance of these composites is the interfacial adhesion and compatibility between the filler and the polymer. This occurs due to the strong polarity of wood and non-polarity of some polymeric matrices (Michaud et al. 2009).

Another problem is the processing temperature that restricts the choice of the filler particles. These particles are composed of organic materials such as cellulose, lignin, and hemicellulose that are very sensitive to thermal variations, both physically and chemically. Thermal degradation may occur at temperatures above 200 ºC, altering its organoleptic properties such as odor and color. In addition, it may result in the release of gases and the subsequent creation of porous materials, with low density and reduced mechanical properties (Ashori 2008).

In order to overcome these drawbacks, composites have specific additives that enhance their performance, such as compatibilizers or coupling agents that interact with the hydroxyl groups (e.g. acid anhydrides, organosilanes, isocyanates); UV stabilizers (e.g. hindered amine light stabilizers); UV absorbers (e.g. benzophenone or benzotriazole); heat stabilizers (e.g. organotin); buffers; foaming agents (e.g. azidocarbonamide bicarbonate); flame retardants and lubricants (e.g. fatty acid salts, amide, oil, waxes, CaSt, ZnSt) (Optimat and MERL 2003).

Kajaks et al. (2018) investigated the behavior of high density polyethylene (HDPE) and birch wood plywood production residues (PSD) composites with 0,10, 20, 30, 40 and 50% of filler content. It was verified that when de percentage of wood increased, the impact strength diminished from 28.6 kJ m^{-2} (HDEP) to 6.88 kJ m^{-2} (HDPE + 50 wt% PSD). In addition, the tensile strength decreased from 33.13 MPa (HDPE) to 20.2 MPa for composites with 50% of PSD, but flexural strength increased from 22.2 up to 32 MPa, respectively. On the other hand, tensile and flexural modulus increased 2.5 to 3 times in both cases, from 163 up to 403 MPa (tensile modulus), and from 763 up to 2105 MPa (flexural modulus) (Kajaks, Kalnins, and Naburgs 2018).

In order to investigate the mechanical performance of WPCs made from both recycled wood filler and polymer matrices, Nukala et al. (2022) studied the behaviour of WPCs produced from sawdust waste, generated during wood product manufacturing, and recycled polypropylene (rPP), obtained from general waste, such as disposed PP plastic containers and caps. The authors concluded that sawdust (SD) was uniformily dispersed in the rPP matrix and the increase of SD content improved the thermal stability of rPPSD composites. In the same study, for 40% SD content, the tensile strength was 29% higher. When it comes to water absorption, it increased as the SD percentage was more

significant in the composite, due to its hidrophilicity. So, for 40% SD content, the water absorption rised from 1.2% to 19.9%. The results indicated that the performance of rPPSD was similar or comparable to composites made of virgin wood and plastic, and so this could be used as an alternative material to replace non-sustainable composites (Nukala et al. 2022).

Duan et al. (2023) studied the association of eucalyptus wood powder (149 μm diameter), as the filler, and PVC, as matrix. Due to the improvement of the mechanical properties and interfacial adhesion between reinforcement materials and matrix, it was used 2 μm silica powder (SiO_2) as toughening agent (Dongbao et al. 2021). The researchers concluded that when the silicon dioxide content was 3.0%, the tensile strength, flexural strength, and impact strength of WPC reached the maximum and improved the interfacial bonding ability, reducing the phenomenon of holes left after the wood fiber was pulled out. The strain at break value of 3.0% SiO_2 eucalyptus/PVC composite was 88.5% of the strain value without adding SiO_2 (Duan et al. 2023).

Dairi et al. (2017) showed that tensile and flexural properties of maleic anhydride-grafted polypropylene (MAPP) coupled pine WPs polypropylene/polyethylene-terephthalate composite (with 10, 20 and 30% of wood flour) improved significantly due to better interfacial bonding that smoothened the stress transfer from particles to the polymer matrix and vice-versa. Thus, it was shown that almost 50% of water absorption was reduced, which indicates that the incorporation of MAPP decreased the number of available hydroxyl groups and prevented the formation of voids in the composite surface (Dairi et al. 2017).

Yet, these type of materials are difficult to recycle and the encapsulation of the wood by the, essentially, non-biodegradable polyolefin means that these materials as a whole are nonbiodegradable (Chan et al. 2018). In order to replace the traditional polyolefins used in these composites, due to their environmental impacts, research has been carried out on the exclusive use of renewable and biodegradable materials (Gurunathan, Mohanty, and Nayak 2015).

2.2 Polymers from biological sources

In recent decades, natural biodegradable polymers have garnered significant attention for their uses in fields that promote environmental protection and support physical well-being. The appeal of natural polymers is largely due to their low cost, accessibility, versatility in terms of chemical modifications, and potential for

biodegradability and compatibility based on their natural origins (Deb, Das, and Das 2017).

Polysaccharides such as starch and cellulose represent the most abundant natural polymers in the biosphere, and therefore have a considerable market share. Starch has gained research focus in different areas, as mentioned before, due to its advantageous features such as low cost, good adhesive nature, availability and renewability (Zhao et al. 2018).

However, plant polysaccharides are highly hydrophilic and are not intrinsically thermoplastic, so they cannot be processed in the melt state without chemical modification and/or plasticization (Imre et al. 2019). In addition, starch presents poor deformability, low impact resistance, and high permeability to humidity (Zakuan, Jumaidin, and Selamat 2020).

Given these issues, according to Wang et al. (2020), starch's performance can be improved by replacing its hydroxyl groups with bulky hydrophobic groups, by acetyl, succinyl, carboxymethyl hydroxypropyl groups esterification and etherification processes (Wang et al. 2020). Other chemical modification options are cross-linking, grafting, and condensation reactions. This hydrophobicity is one of the conditions required for making starch-derived films or thermoplastic starch-derived films (TPS) less vulnerable to the effect of water or moisture (Bangar et al. 2021).

2.3 Biodegradable composites

Biodegradable polymers are polymers that, under the activity of water and new biomass by bacteria or other living organisms, can be converted in carbon dioxide due to biological activity, such as enzymatic action. The use of this type of polymers has been limited since they have a higher cost, slow crystallization rate, poor stability and narrow processing windows (Ludwiczak et al. 2019).

The most commonly studied biodegradable polymers have been either polysaccharides (e.g. starch) or aliphatic polyesters (e.g. polyhydroxyalkanoates (PHAs), polylactic acid (PLA) and polycaprolactone (PCL) (Chan et al. 2018). In particular, PHAs offer unique advantages over PLA in composites, such as having a higher melt flow index for easier processing and a faster biodegradation rate in soil under ambient conditions (Guo et al. 2012).

The typical mechanical and thermal properties of these biodegradable polymers are compared to the ones of PP and PE, which are non-biodegradable, in Table 1.

Table 1. List of typical properties of selected polymers (Chan et al. 2018).

Sample type	Density	Tensile strength (MPa)	Tensile Young's Modulus (GPa)	Elongation at break (%)
P(3HB)[1] (Laycock et al. 2013)	1.18 – 1.26	19 – 44	1.2 – 4.0	0.8 – 4.5
PLA (Pachekoski, Dalmolin, and Agnelli 2013)	1.21 – 1.25	21 – 60	0.35 - 3.5	2.5 – 6
PCL (Pachekoski, Dalmolin, and Agnelli 2013)	1.11 - 1.15	21 – 42	0.22 – 0.44	300 – 1000
Starch (Jiménez et al. 2012)	1.26 - 1.28	3.1 – 30	0.17 – 1.5	0.8 – 60
PP (Drobny 2012)	0.90 – 0.91	28 – 40	1.1 – 2.0	20 – 75
HDPE (Drobny 2012)	0.95 -0.97	20 – 40	0.70 – 1.4	100 – 1000
LDPE (Drobny 2012)	0.92 – 0.93	7 -17	0.14 – 0.30	200 – 900

[1] Poly(3-hydroxybutyrate) is a common PHA homopolymer.

As can be seen, starch presents lower tensile strength and elongation at break when compared to PP and PE, but, as mentioned before, the association of plasticizers can improve its properties, forming TPS (thermoplastic starch) (Jiménez et al. 2012).

Pushpadass et al. (2009) stated that the relative crystalline content of TPS samples increased from 3 % to 7%, 14%, and 17% after 3, 30, and 120 days of storage. As a result, tensile strength of TPS samples increased by 39.3 to 134.1% and elongation decreased by 81.1 to 48.0%. A lower elongation value means that TPS becomes stiffer, less flexible and more difficult to handle. Thus, crystallites may generate internal stresses of TPS, leading to the increase in tensile strength and decrease in elongation (Pushpadass and Hanna 2009).

When comparing the polar component of surface energy, Table 2, PHA, PLA and PCL have higher values (are more hydrophilic) than PP and PE, because of their ester groups. In addition, starch is the most hydrophilic of the biodegradable polymers, due to its hydroxyl groups that are available for hydrogen bonding.

Table 2. Surface free energy of selected polymers determined by contact angle measurement (Chan et al. 2018).

Polymer	Dispersive component of surface energy, σ_S^D (mJ/m^2)	Polar component of surface energy, σ_S^P (mJ/m^2)	Total surface energy, σ_S^T (mJ/m^2)
P(3HB)	29.8	11.3	41.1
PLA	30.3	11.0	41.3
PCL	25.4	9.7	35.1
Starch	5.4	65.2	70.6
PP	27.1	0.9	28.0
PE	28.4	0.4	28.8

Even though biodegradable polymers are more hydrophilic than PP and PE, they continue to be significantly more hydrophobic than starch, remaining the compatibility problem between the polymeric matrix and the filler. Since the cost of biodegradable composites is still quite high compared to conventional plastics, it becomes necessary to develop bio-composites with cheaper fillers.

The production of bio-composites with re-used or recycled post-consumer wood can be an environmentally friendly solution to minimize and utilize the amount of solid waste produced (Musiol et al. 2020).

Cintra et al. (2022) studied the development of environmentally friendly polycaprolactone matrix (PCL) composites with the addition of 5 and 15 wt% of wood flour (WF) (without any treatment and granulometric separation), in order to obtain a new material with thermal, mechanical, physical and morphological properties similar to neat PCL. In the same work, it was observed that the 5 wt% WF and PCL matrix had good distribution, interaction, and adhesion. When the content of natural filler was higher, the composite absorbed a higher humidity (due to its hydrophilicity and generation of hydrogen bounds by the hydroxyl groups), which contributed to the reduction of the Izod impact strength values. However, it was observed that the tensile strength and Young's modulus values for the composites with higher content were better than the ones observed for neat PCL. This confirms that the WF particles are dispersed and adhered to the PCL matrix, acting as reinforcement of the PCL matrix (Cintra et al. 2022).

Ludwiczak et al. (2019) investigated the behavior of PLA/PBS (polybutylene succinate) matrix associated with 10, 20 and 30 wt% of 70 to 150 μm diameter WF natural filler, and additionally modified with a chain extender (CE). Observing the results, it was proven that WF increased the Young's Modulus of the composite and the presence of an extended chain did not significantly affect this parameter. In the case of stress at break, the addition of CE and WF increased the stress at break value as compared to the neat PLA/PBS blend, causing, almost, immediate break of the composite under the applied load. Yet, the addition of CE decreases the negative impact of WF on the material's mechanical properties. Finally, it was also observed that PBS had the highest impact strength and the addition of WF caused deterioration of this parameter, while CE had the exact opposite effect. The amount of the water uptake increased as the amount of WF in the blend increased, due to its affinity to water (Ludwiczak et al. 2019).

Musiol et al. (2020) reported the behavior of poly[(R)-3-hydroxybutyrate-co-4-hydroxybutyrate (P(3HB-co-16 mol%-4HB)) composites with 10, 20 and 30 wt% of WF (diameter particle size of 96% < 75 μm and average width of 25 μm). Composites with wood flour as filler exhibit decreased tensile strength value when compared to the neat matrix, because of the weak adhesion between polymer matrix and filler (the WF used was obtained from coniferous trees which are a softer filler). Also, the distribution of particle size and width are factors that influence the mechanical properties. The increase of filler content in the composite led to higher values of Young's modulus and reduction of the flexural strength due to its lower elasticity. When it comes to degradation due to environmental exposure, under abiotic conditions, they observed pinholes formation, indicating water penetration, since wood flour is a porous and hydrophilic material and has poor adhesion to the hydrophobic polymer matrix (Musiol et al. 2020).

Bulanda et al. (2020) studied the mechanical and morphological response of PLA and powdered natural ground fillers (bamboo dust (PB) with 2.0 to 4.5 mm diameter, cork dust (PK) with 0.2 to 0.5 mm diameter, and wood dust (PD) with 2 to 5.5 mm diameter). It was found that the addition of natural fillers increased the fluidity of the obtained polymeric materials in the case of PLA/48.73% PK composite, when compared to unfilled PLA. Also, it was observed that the obtained composites had lower Charpy impact strength, Rockwell hardness and tensile strength. In addition, the results of SEM microscopy (scanning electron microscope) indicated that the microstructure of the natural fillers was evenly distributed in the polymer matrix. Finally, it was observed that the samples obtained by injection molding had better mechanical

performance and functional properties, compared to the samples obtained by a MEP printer (Bulanda et al. 2020).

2.4 PBAT/starch blends

Polybutylene adipate terephthalate (PBAT) is a ternary copolyester synthesized from adipic acid, terephthalic acid, and 1,4-butanediol through direct esterification or ester exchange polymerization (Yi et al. 2020). PBAT is a biodegradable aromatic/aliphatic copolyester extensively utilized in the production of biodegradable films due to its exceptional processability properties, excellent flexibility, and high elongation properties (Xing et al. 2019, Phetwarotai, Phusunti, and Aht-Ong 2019, Li et al. 2018). It has been widely used in various fields such as daily plastic bags, food packaging bags, garbage bags, agricultural films, greenhouse insulation films, and other fields (Yi et al. 2020).

As can be seen from Figure 1, PBAT is a copolyester that can be divided into two segments. The rigid segment is characterized by the benzene ring and the methyl groups and esters identify the soft segment.

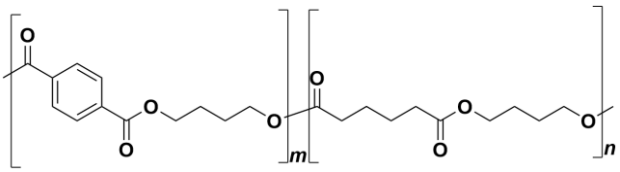

Figure 1. Chemical structure of PBAT.

PBAT's biodegradation consists in the polymer hydrolysis under the effect of microbial enzymes. This process, Figure 25, Anex A, occurs due to the cleavage of ester linkages and the reaction between water and the carbonyl groups located in the proximity of the benzene rings (Fu et al. 2020).

However, this polymer has an high cost when compared to polyethylene, for example, being approximately double or even triple the price of the traditional plastics. In addition, due to the presence of ester groups, its degradation rate is very slow. These are factors that limit its wide application in the market (Fialho e Moraes et al. 2017).

Several studies have recently explored blending PBAT with starch, significantly reducing the costs associated with the production of PBAT films without decreasing product quality, and maintaining its high biobased carbon content (Bai et al. 2021).

Starch is characterized by its high availability of hydroxyl groups that justify its strong hydrophilic character, Figure 2.

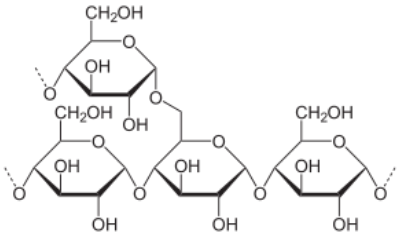

Figure 2. Chemical structure of starch.

However, hydrophilic starch and hydrophobic PBAT have poor compatibility issues, therefore, the mechanical performance of simple blends produced are weak (Park et al. 2012).

Garalde et al. (2019) verified that the higher the percentage of TPS incorporated in the PBAT/TPS blend, the lower the tensile strength, elongation at break and Young's Modulus. In the specific case of increasing the TPS/PBAT ratio from 20/80 to 40/60, tensile strength decreased from 8.3 to 6.8 MPa, elongation at break decreased from 819% to 551%, and finally secant modulus at 2% strain decreased from 33.0 to 24 MPa (Garalde et al. 2019).

Several reactive coupling agents have been reported to improve these results, including maleic anhydride and citric acid, maleated TPS, maleated PBAT epoxy additive, maleic acid and tartaric acid. In all of these compatibilizers, apparently, the anhydride group of maleic anhydride, the carboxyl group of acrylic acid and citric acid are efficient to improve the mechanical properties of PBAT/TPS blends by enhancing the interfacial adhesion between the two phases (Dammak et al. 2020).

Moreover, also Ivanič et al. (2019) verified that the incorporation of TPS into PBAT significantly reduced tensile strength and elongation at break and reported that the addition of plasticizers, urea and glycerol improved the mechanical performance of this composite. Innitially, neat PBAT showed a tensile strength of 19.1 MPa and when mixtured with TPS these values decreased significantlly. However, when the wt% of TPS was 50%, and the ratio TPS/urea was 1/0.6, the value of the tensile strength significantly increased to 13.4 MPa. This result is noteworthy as it suggests the potential for incorporating a relatively high quantity of TPS into a polymer mixture without experiencing a significant decline in mechanical properties, particularly tensile strength. As for the elongation at break, the materials exhibit contrasting behavior in terms of tensile strength, where the elongation is higher for PBAT with TPS

plasticized by glycerol compared to PBAT with TPS plasticized by urea, in general. In all of the cases, elongation at break decreased significantly by a unit, from 985% to around 76% (which was the highest value obtained), for 20 wt% TPS with TPS/urea ratio of 1/0.6. Finally, The Young's modulus of the blends with urea–plasticized starch were found to be, by one order of magnitude, higher compared to blends with glycerol–plasticized starch (Ivanič, Kováčová, and Chodák 2019).

Also, Dammack et al. (2020) investigated the behaviour of PBAT/TPS blends for packaging applications with the presence of maleated PBAT and maleic anhydride coupling agents. They concluded that at a given content of TPS, between 40 to 60%, the tensile strength and elongation at break were the highest in the presence of PBATg-MA compatibilizer. For instance, in the case of the blend comprising 50% TPS, the absence of any additive yielded a tensile strength of 12.8 MPa and an elongation at break of 205%. However, the incorporation of PBATg-MA as a compatibilizer led to an increase in tensile strength to 15.1 MPa, as well as the notable enhancement in elongation at break to 614%. In contrast, when the blend was processed in the presence of 2% MA, the values for tensile strength (6.5 MPa) and elongation at break (36%) significantly declined, indicating a limited efficacy of MA as a compatibilizer. It was concluded that the utilization of PBATg-MA as a reactive compatibilizer demonstrated its remarkable capacity to enhance both tensile strength and elongation at break, thereby affirming its effectiveness in promoting favorable interfacial adhesion between the PBAT and TPS phases (Dammak et al. 2020).

2.5 Potential application of bio-composites in the food packaging market

Bioactive materials, which possess small amounts of antimicrobial additives, belong to a very attractive packaging industry solution. The use of polymeric materials for the sustainable packaging sector is constantly improving due to meet the required properties for the application (Cintra et al. 2022).

The food packaging containers require suitable and mechanical properties from the used bio-composites. Its primary function is to protect and preserve the food, reduce food waste, and maintain its quality and safety, by considering the changes in the characteristics of bio-composites and the food itself, during their interaction (Jariyasakoolroj, Leelaphiwat, and Harnkarnsujarit 2020).

Starch-based polymers are odorless, semipermeable to moisture, O_2, CO_2, and non-toxic (Shah et al. 2016). To expand its functionality, starches can be chemically modified into more hydrophobic, thermally stable and to enhance its mechanical characteristics.

The mechanical performance of these bio-composites depends on the shape, quantity, alignment of nanoparticles, and potential of the polymer matrix to transfer stress. Tensile strength (TS) and strain at break (SB) indicate the food packaging breaking resistance potential and capacity of maintaining its integrity under stress and storage. Thus, polymers used for packaging need high TS, SB, and flexibility (Salmieri et al. 2014).

Yang et al. (2015) and Zhou et al. (2015) investigated the production of TPS from modified starch, i.e., epoxidized cardanol grafted starch and acetylated starch, respectively, and concluded that this modification reduced TPS hydrophilicity resulting in enhanced compatibility with PLA polymer (Bangar and Whiteside 2021). Thus, this bio-composite can lead to potential application in the food packaging area (Yang et al. 2015, Zhou et al. 2015).

Recently, Romainor et al. (2022) investigated the association of 1 to 7 wt% of starch (average diameter of 20 to 40 μm) with citric acid (antimicrobial agent) and polyvinyl alcohol (PVA), as plasticizer, to prevent food spoilage and to prolong its shelf life. It was concluded that this antimicrobial agent is capable of suppressing 98 to 99% of food borne bacteria growth, and 87 to 99% of fungal growth (Ramírez-Hernández et al. 2017). In addition, when allied with 5 wt% starch and PVA, it can extend the shelf-life of the food products for 10 days, for cake, and 40 days, for bread (Romainor, Chin, and Lihan 2022).

Ge et al. (2021) investigated the performance of multi-layered films from TPS/PVOH blends sandwiched between LDPE (low density PE) outer layers in a co-extruded blown film line, and concluded that blends containing TPS might serve as alternative barrier layers because of reduced material cost, oxygen barrier, and good material properties (Ge, Lansing, and Lewis 2021). Although this is not an absolute biodegradable composite, due to PE utilization, it can also be a more environmentally friendly solution to the food packaging market.

Zhou et al. (2021) studied the effects of AgNPs@SiO_2 at various loadings (0, 1, 2, 3, and 4 wt%) on the physicochemical properties and antibacterial activities of starch/PBAT composite films. It was concluded that the compatibility between the two phases was

low, by the presence of holes in SEM microscopy analysis. The preferential partitioning of AgNPs@SiO_2 within the starch phase could be attributed to their similar polarity and compatibility, and so the higher the wt% of AgNPs@SiO_2, the bigger the agglomeration of these particles in the starch phase. When it comes to mechanical properties, TS and elongation at break values increased and then decreased with increasing the wt% of AgNPs@SiO_2. Thus, the maximum values corresponded to 2 wt% of AgNPs@SiO_2, in which TS was 11.29 MPa and elongation at break was 774.40%, compared to the ones obtained for neat PBAT/starch, 10.27 MPa and 656.63%, respectively. They also concluded that the film loaded with 1 wt% AgNPs@SiO_2 produced nearly 90% inhibition efficiency against both S. aureus and E. coli within 3h, and the dispersion of AgNPs@SiO_2 particles in starch/PBAT films was a promising approach to develop antibacterial films for commercial food packaging (Zhou et al. 2021).

Bumbudsanpharoke et al. (2023) who studied the enhancement of PBAT/TPS biopolymer blend with CuO NPs for active packaging, determined that this blend was successfully compounded with various CuONP concentrations (0.05-2 wt%). Therefore, at the highest concentration of CuONP, tensile strength increased 29.1% and elongation at break increased 67% over PBAT/TPS film. When it comes to antimicrobial activity, PBAT/TPS-CuO 2% showed a 99.7% reduction of E.coli bacteria in the samples, which confirms its potential of being incorporated in the food packaging area (Bumbudsanpharoke et al. 2023).

3 Materials and Methods

Initially the wood by-product particles were dried in order to reduce the amount of water present in the sample and facilitate their feeding into the extruder, where they would later be mixed with the polymer matrix. Then, this mixture was directed to an injection molding machine in order to be molded for future characterization.

Firstly, the thermal behavior of the polymer and fillers was studied (DSC and TGA analysis) to, subsequently, define the processing conditions. Then, the morphological properties (SEM microscopy) of the polymer and the composites produced were analysed, as well as their mechanical behavior (tensile testing) with the increase of filler incorporated in the polymer matrix.

3.1 Materials

Polymer *Unik Biopar® FG1021-15* (PBAT/30 wt% starch) was provided by United Biopolymers, S.A., Figueira da Foz, Portugal. Polymers's data and its physical and mechanical parameters are represented in Table 3.

Table 3. PBAT/starch polymer parameters.

Parameter	Value
Density / gcm^{-3}	1.271
Melt flow rate / $g(10min)^{-1}$	2.1
Residual moisture / %L	2.0
Tensile strength (machine direction) /MPa	24.7
Tensile strength (transversal direction) /MPa	20.0
Elongation (machine direction) / %	284.7
Elongation (transversal direction) / %	627.1

Veneer cuts and bark of hybrid poplar (*Populus x canadensis* Moench) were provided by Freshwood – Forms Industry, Lda.

3.2 Preparation of polymer and poplar wood and bark composites

3.2.1 Preparation of the filler

Initially, wood byproducts were prepared following a shredding and sieving process at Polytechnic Institute of Viseu. Thus, shredding sieves of 10, 4, and 1 mm were used,

according to the standard *Retsch cutting mill SM 300*, to obtain the smallest possible particle size. Next, the filler was sieved according to the *Retsch vibrating sieve AS 200* to separate the particles by sizes from 45 micrometers to 2 millimeters.

Finally, in order to reduce the amount of water present in the sample, wood byproducts were dried in the oven at 105 ºC for 2 days and then, 12 h each day.

3.2.2 Preparation of Polymer, PPW and PPB Composites

The equipment used in the preparation process of polymer (P), polymer/poplar wood (PPW) and polymer/poplar bark (PPB) composites is illustrated in Figure 3.

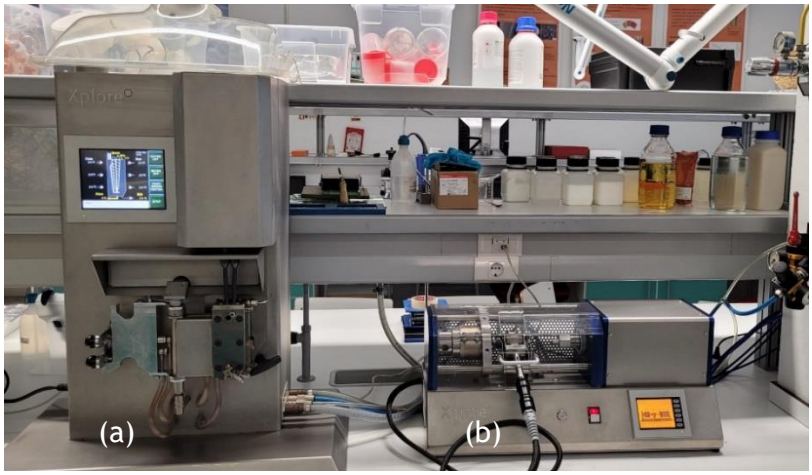

Figure 3. Laboratory equipment (a) micro extruder with twin screw mixer (b) injection moulding machine.

Initially, polymer was processed at different temperatures, as mentioned in Table 4. Then, wood and bark particles' moisture content was measured in a humidity balance (*Radwag MA 50.R Moisture Analyzer*) and mixed with the polymer in a laboratory micro extruder (*Xplore Micro Compounder IM 5*), according to the weight ratios shown in Table 5.

This equipment has a batch volume capacity of 5 mL and a twin screw, which rotation speed was kept between 80 and 200 rpm and the mixing temperature was varying between 140 ºC and 185 ºC throughout the mixing process. The mixing time was 3 minutes in all trials.

Table 4. Processing temperatures of the polymer specimens.

Sample	Processing temperature (ºC)
P_140	140
P_160	160
P_175	175
P_185	185

Table 5. Composition of PPW and PPB composites.

Sample	Polymer (wt%)	Poplar wood (wt%)	Poplar bark (wt%)
P	100	0	0
PPW10	90	10	0
PPW20	80	20	0
PPW30	70	30	0
PPW40	60	40	0
PPW50	50	50	0
PPB10	90	0	10
PPB20	80	0	20
PPB30	70	0	30
PPB40	60	0	40
PPB50	50	0	50

It should be noted that the mixing of the polymeric matrix with the filler was performed at different extrusion temperatures for different percentages of wood, so as not to reach the maximum operating force of the micro extruder, Table 7, Anex A. That is, in order to reduce the viscosity and facilitate the mixing process, the higher the percentage of filler added, the higher the temperature used.

Finally, the obtained composite mixture was directed into an injection moulding equipment (*Xplore Injection Moulding IM 5.5*) at the respective mixing temperature and with a pressure of 8 N/mm^2 to produce bone-shaped specimens for further characterization, Figure 4.

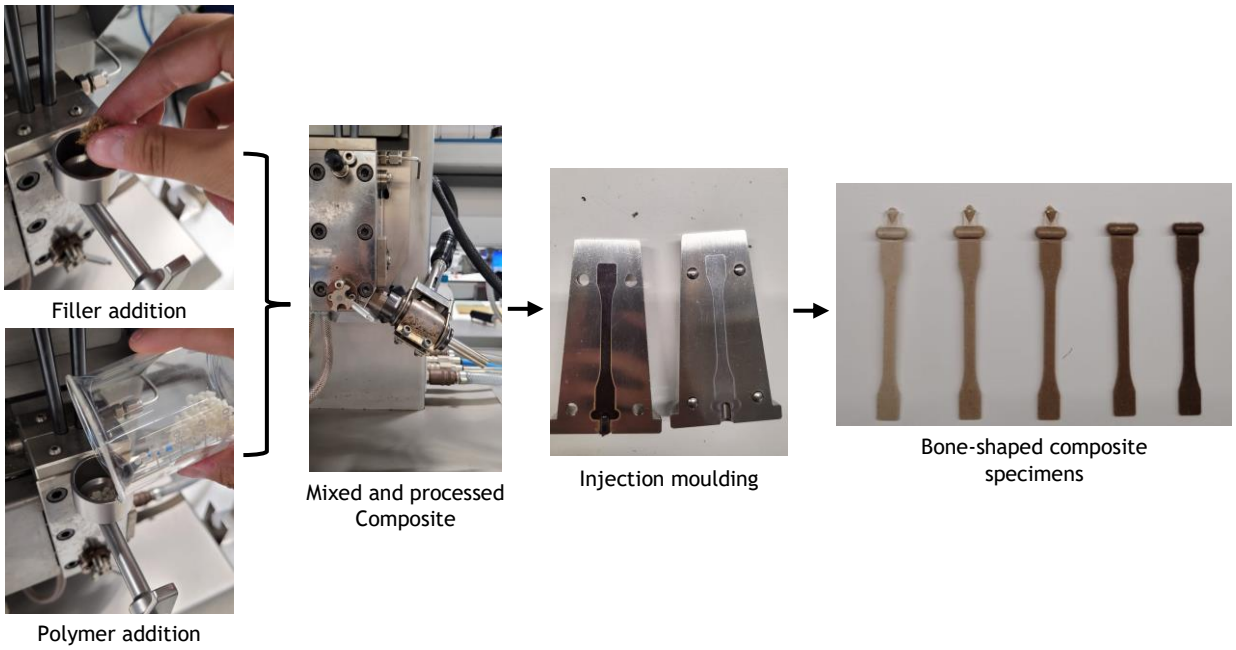

Figure 4. Production process of WPC's.

3.3 Fourier Transform Infrared spectroscopy

FTIR spectra of virgin PBAT/starch blend polymer was recorded on a *VERTEX 70v FTIR* spectrometer. Each spectrum was obtained by co-adding 64 consecutive scans with a resolution of 4 cm^{-1} within the range of 4000-500 cm^{-1}.

3.4 Thermal properties

3.4.1 Thermogravimetric Analysis

The thermal properties of the samples were analysed using a thermogravimetric analyser (*NETZSCH STA 449 F3 Jupiter*). The thermographs were obtained at thermal scan temperatures from 30 ºC to 900 ºC at 10 ºC/min under a nitrogen atmosphere.

3.4.2 Differential Scanning Calorimeter Analysis

Differential scanning calorimeter (*NETZSCH DSC 214 Polyma*) was used to determine the heat flow (in or out) of the samples. Firstly, the samples were heated from 20 ºC to 450 ºC, at 10 ºC/min. To avoid oxidation in the samples, all heating and cooling runs were conducted under a nitrogen atmosphere.

3.5 Water Contact Angle analysis

Contact angle analyses were carried out using a *Dataphysics Contact Angle System OCA* goniometer coupled with image analysis software (*SCA20*), in order to study the hydrophobicity of the polymer and the composites. The contact angle measurement

was done via sessile drop technique. The droplet was placed on the surface of the samples using a micrometer syringe, and the contact angle was measured by scanning the droplet profile for 120 seconds, every 1 second. To avoid the effects of weight, the size of the ultrapure water droplet was maintained at 4 µL.

3.6 Scanning Electron Microscopy

Scanning electron microscopy (SEM) analysis allowed observing the microstructure of the samples, but firstly the samples were fractured in liquid nitrogen to create straight cross-sectional surfaces, Figure 5.

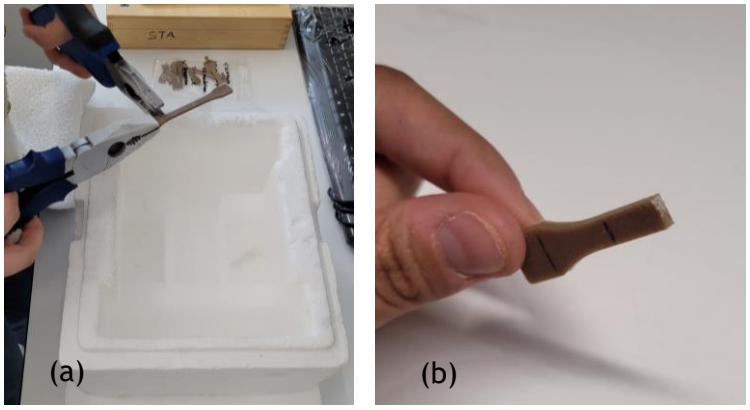

Figure 5. (a) Sample fracture process in liquid nitrogen (b) Sample cross-section surface.

The cross-section of the sample was mounted on a SEM specimen holder and coated with an Au/Pd thin film, by sputtering, using the *SPI Module Sputter Coater* equipment and with a 15 mA current.

Then, they were analysed using a High resolution (Schottky) Environmental Scanning Electron Microscope with X-Ray Microanalysis and Electron Backscattered Diffraction analysis: *FEI Quanta 400 FEG ESEM / EDAX Genesis X4M*.

3.7 Tensile testing

In this test, it was used a *Tinius Olsen H50KT* at a crosshead speed of 2 mm/min with a load cell of 10 kN, Figure 6, to determine mechanical properties such as, Young's Modulus (*YM*), Ultimate Tensile Strength (*TS*), Strain at Break (*SB*), and Area Under the Stress-Strain Curve (*AUC*).

Figure 6. Tensile testing equipment.

4 Results and discussion

4.1 Fourier Transform Infrared spectroscopy

Since the polymer specimens processed at higher temperatures presented a darker color, Figure 7, FTIR analysis was performed to detect any possible chemical change in the polymer blend, possibly associated with oxidative degradation.

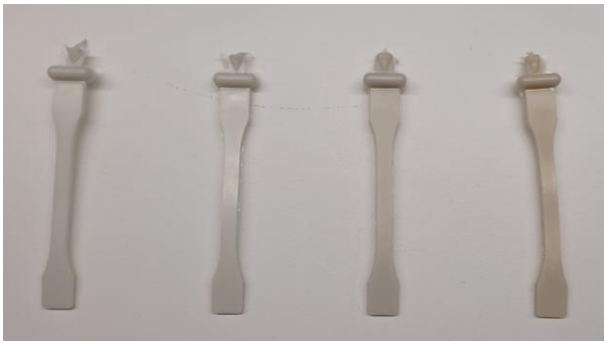

Figure 7. Polymer specimens processed at 140, 160, 175 and 185 °C, respectively.

Figure 8 represents the FTIR spectra of PBAT/starch polymer, processed at different temperatures.

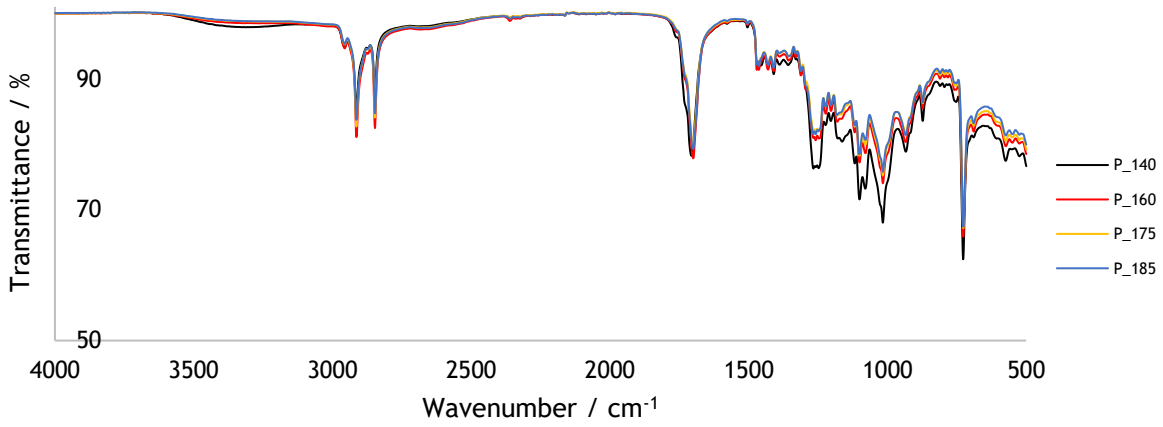

Figure 8. FTIR spectra of PBAT/starch polymer.

The blend verifies a wide peak around 3300 cm^{-1}, which corresponds to the stretching vibration of –OH groups of starch (Bumbudsanpharoke et al. 2023). Additionally, it demonstrates two peaks ranging from 2914 cm^{-1} to 2847 cm^{-1}, which are associated with the asymmetric and symmetric stretching of C–H bonds in the methyl group ($-CH_2$), respectively. The peaks at 1706 cm^{-1} and 1266 cm^{-1} are assigned to the stretching vibration of carbonyl (C=O) and C–O bonds in the ester group of PBAT, respectively. In addition, the peak at 1100 cm^{-1} corresponds to left-right symmetric

stretching vibration of C-O-C group, and the one at 1016 cm^{-1} relates to the vibration of the hydrogen atom of PBAT aromatic ring. Finally, the peak at 726 cm^{-1} signifies the CH-plane of the benzene ring (Zhou et al. 2021).

After submitting the samples to successively higher temperatures, PBAT transmittance bands suffered some alterations, e.g., 3000-2650 cm^{-1}, which includes C−H vibration peaks from the methyl group, Figure 9. This might be explained by the increased degree of polymerization, potentiated by higher temperatures (Siyamak et al. 2012).

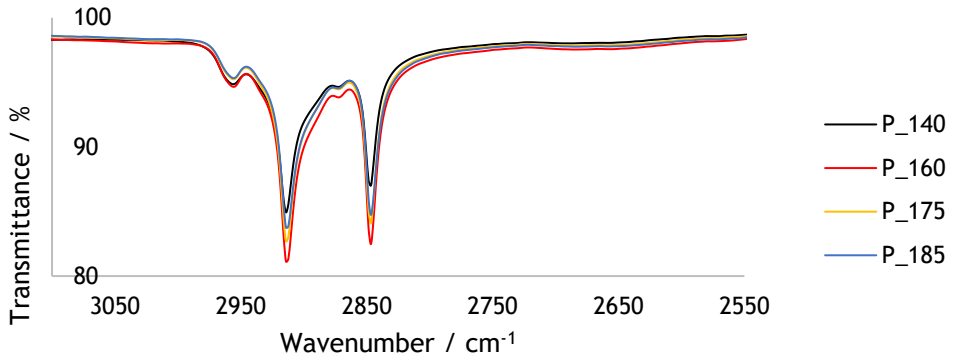

Figure 9. FTIR spectra of polymer's methyl group.

Another example is the decrease of the transmittance peak's amplitude and position at 1706 cm^{-1}, corresponding to carbonyl group, that changed to 1700 cm^{-1}, Figure 10.

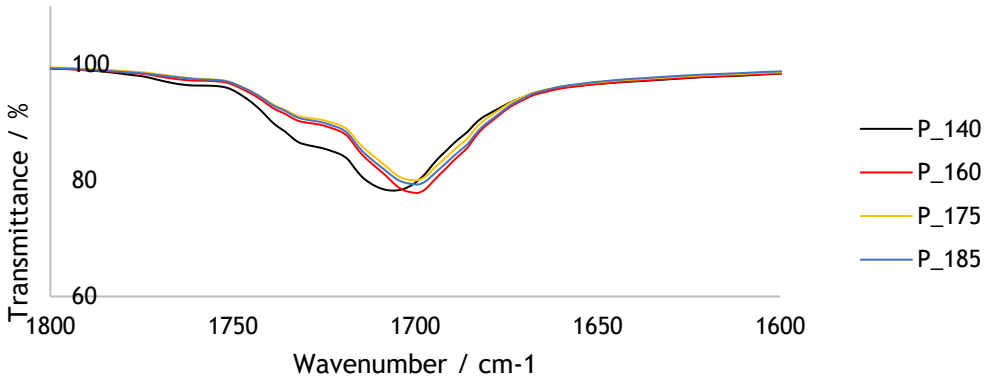

Figure 10. FTIR spectra of polymer's carbonyl group.

The reduction and shifting of carbonyl vibration peak might be occurring due to the extent of esterification reaction (Siyamak et al. 2012). The same behavior was also verified for the peak's amplitude, at the wavenumber range of 690-760 cm^{-1}, in relation CH-plane of the benzene ring, Figure 11.

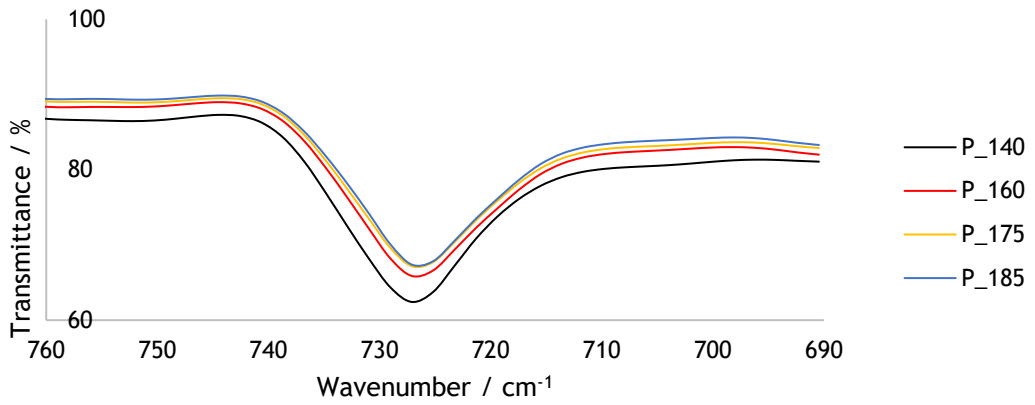

Figure 11. FTIR spectra of benzene ring's CH-plane.

4.2 Thermal properties

4.2.1 Thermogravimetric Analysis

4.2.1.1 PBAT/starch polymer

Figure 12 displays the mass loss (TGA) and differential mass loss (DTG) curves of the polymer. Notably, there are discernible mass losses occurring between the temperature range of 200 ºC to 450 ºC.

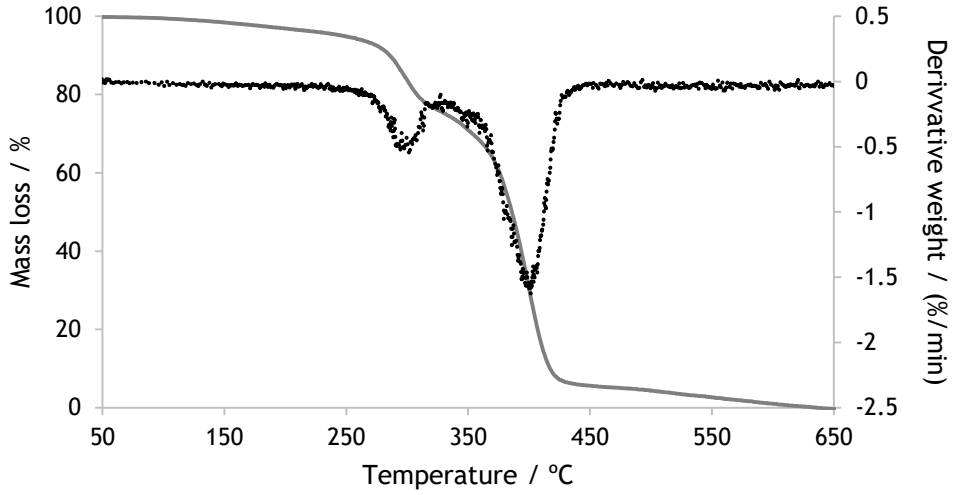

Figure 12. TGA and DTG curves of the polymer.

As can be seen, two stages stand out. The first occurs around 280 ºC, and the last at 400 ºC.

The step at 280 ºC, is associated to the starch decomposition (approximately 30% of mass loss) and the last one, at around 400 ºC, represents the decomposition of PBAT matrix and final degradation of partially decomposed starch (major mass loss of 70%) (Mohanty and Nayak 2009).

4.2.1.2 Poplar Wood

TGA and DTG curves of poplar wood are represented in Figure 13 and, initially, TGA presents a mass loss of 8% to 10% at 100 ºC that corresponds to evaporation of water.

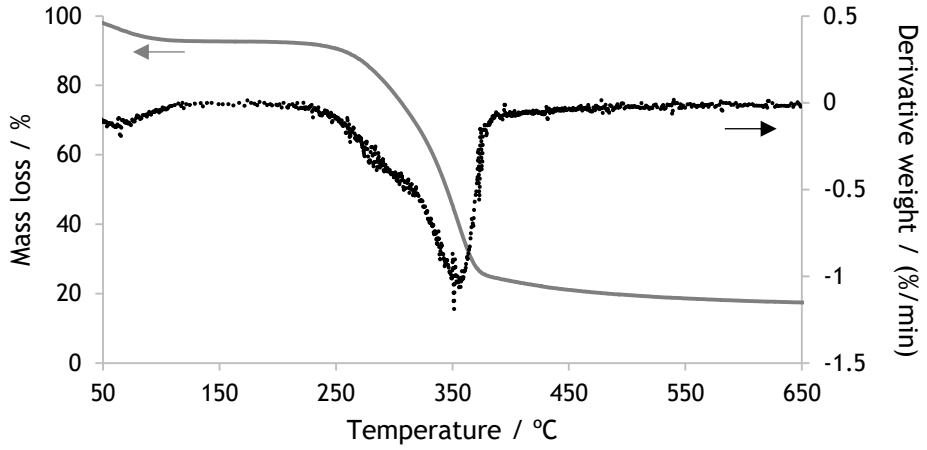

Figure 13. TGA and DTG curves of poplar wood.

Between 200 °C and 380 °C, significant weight loss (70–72%) appeared on, which is the decomposition of the wood fibers, namely hemicellulose, cellulose and lignin (Zhang et al. 2020).

4.2.1.3 Poplar Bark

Poplar bark seems to have the same thermal behavior, since, at 100 ºC, there is a mass loss (approximately 10%) due to water evaporation, and between 200 ºC and 400 ºC the most significant mass loss occurs (around 60%), Figure 14.

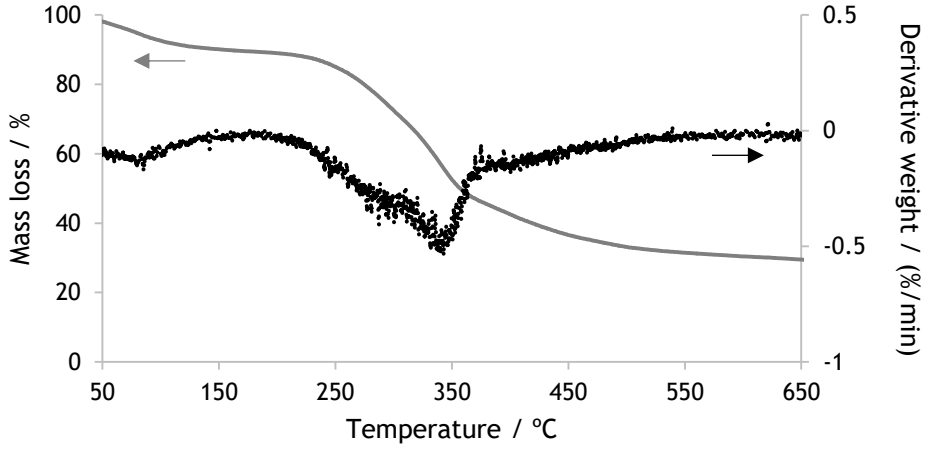

Figure 14. TGA and DTG curves of poplar bark.

However, it can be observed, in Figure 14, that bark´s major mass loss (60%) is lower than the one verified for wood (70%), Figure 13, when submitted to the same thermal conditions.

Comparing the DTG curves of both samples, Figure 15, there are two obvious peaks in the temperature range of 250 ºC to 400 ºC and it can be noticed that the peaks for bark sample are more separated than the ones observed for wood. Another visible difference is the intensity of the peaks, which relates to the rate of decomposition.

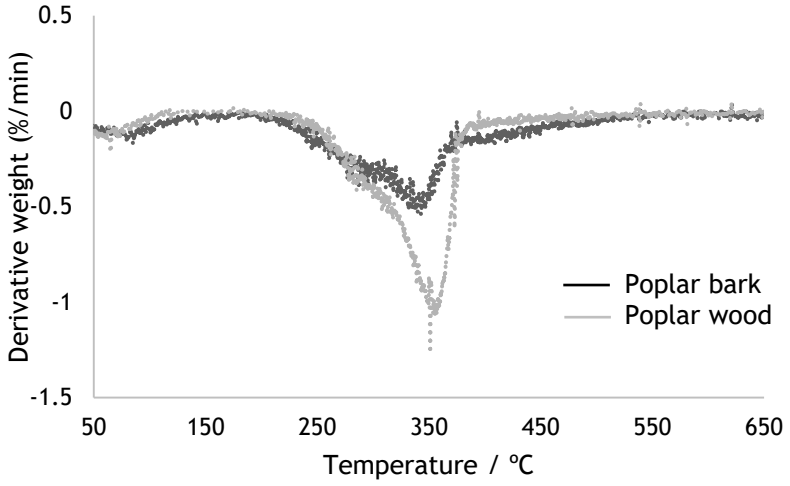

Figure 15. Poplar wood and bark DTG curves.

Poplar wood and bark DTG curves present three degradation peaks corresponding to hemicellulose at 280 ºC, cellulose at 320 ºC (the decomposition of amorphous cellulose occurs at lower temperature than crystalline cellulose), and lignin around 400 ºC, which was also verified by Raveendran et al. (1996) that studied the pyrolysis characteristics of biomass and biomass components, namely yellow poplar (Raveendran, Ganesh, and Khilar 1996).

In addition, the differences in peak separation could be explained by cellulose-to-hemicellulose ratios (2.1 for wood and 1.9 for bark). That is, a lower cellulose-to-hemicellulose ratio produced a clear separation of these peaks, which is verified in Figure 14. Furthermore, Raveendran et al. (1996) also affirmed that the higher peak in wood's DTG, comparing with barks' one, was caused by the higher amount of cellulose and hemicellulose content in biomass (Raveendran, Ganesh, and Khilar 1996).

4.2.2 Differential Scanning Calorimetric Analysis

DSC analysis gives information about thermal transitions events of the polymer, Figure 16, poplar wood, Figure 17, and poplar bark, Figure 18.

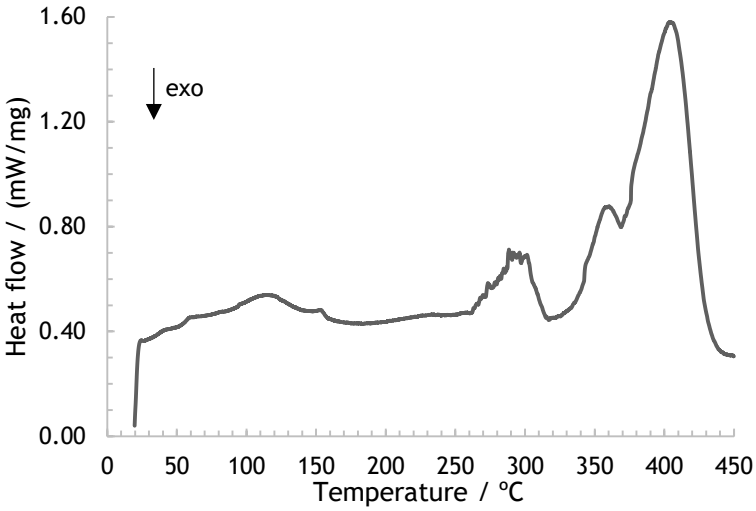

Figure 16. Polymer DSC.

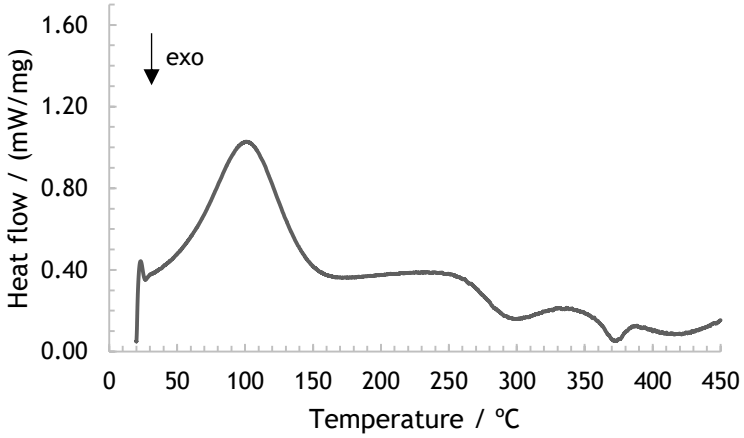

Figure 17. Poplar wood DSC.

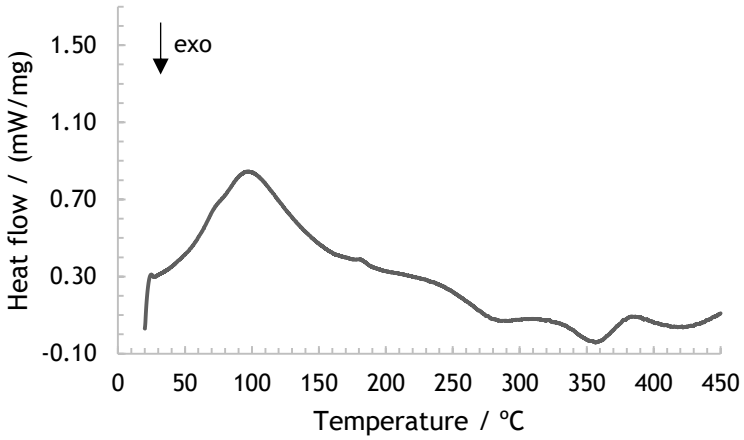

Figure 18. Poplar bark DSC.

Figure 16 verifies the presence of two endothermic peaks at 43 ºC and 109 ºC, corresponding to the melting point of the small crystal domain of poly(butylene

adipate) (PBA) soft segment and the crystalline poly(butylene terephthalate) (PBT) rigid segment, respectively. At 156 ºC, the melting temperature of starch was noticeable (Garalde et al. 2019). The glass transition temperature was not identified in the graphs due to the selected range, however Mohanty et al. (2009) determined that neat PBAT had a glass transition temperature (T_g) of -39.01 ºC (Mohanty and Nayak 2009).

When it comes to degradation, PBAT presents its degradation temperature onset at 362 ºC and reaches its maximum at 407 ºC. Regarding starch, it starts its degradation at 260 ºC (temperature onset) and reaches its maximum at 306 ºC (de Campos et al. 2019).

Poplar wood, Figure 17, and bark, Figure 18, have a major endothermic event occurring at approximately 110 º C, corresponding to water evaporation. The last three peaks in both wood and bark's DSC curves correspond to the degradation of hemicellulose (280 ºC), cellulose (320 ºC) and lignin (387 ºC) (Zhao et al. 2019).

However, there is a difference in the amplitude of the peaks. According to Tingi et al. (2013), who investigated the thermal behavior of yellow poplar, bark has less percentage of cellulose and hemicellulose (31.54% and 16.73%) than wood (55.07% and 26.46%, respectively), which can justify this difference. When it comes to lignin, bark has a higher percentage (17.98%) compared to wood (10.17%) (Tingi 2013), which translates in the height of the peak shown by Figure 17 and Figure 18.

Since bark has a higher percentage of extractives (such as tannins and waxes), it is possible to verify, Figure 18, a slight peak at 186 ºC, which is not noticeable in the case of wood, Figure 17.

Since TGA relates mass loss with temperature variation and DSC analysis provides information about the energy changes during different thermal phenomena, the results of these two methods can be related as presented above. That is, an energy variation event is directly related to a mass loss, such as water evaporation, PBAT degradation, and polysaccharide degradation.

4.3 Water Contact Angle Analysis

In order to evaluate the hydrophobicity of the composites, the contact angle (θ) between a drop of ultrapure water and the surface of each specimen was tested, Figure 19. Subsequently, the composites' total (equation 1), dispersive (equation 2) and polar (equation 3) components of the surface energy were calculated, according to Fowkes Model (Fowkes 1964), and, as observed in Table 6, these values tended to increase with greater wt% of filler.

$$\sigma_S = \sigma_S^D + \sigma_S^P \quad (1)$$

$$\sigma_S^D = \frac{\sigma_l\,(1+cos\theta)^2}{4} \quad (2)$$

$$\sigma_S^P = \frac{\left(\frac{\sigma_l\,(1+cos\theta)}{2} - \sqrt{\sigma_l^D.\sigma_l^P}\right)^2}{\sigma_l^D} \quad (3)$$

Being σ_l = 72,8 mJm^{-2}, σ_l^D = 21.80 mJm^{-2} and σ_l^P = 51 mJm^{-2} for water (Jańczuk and Białłopiotrowicz 1989).

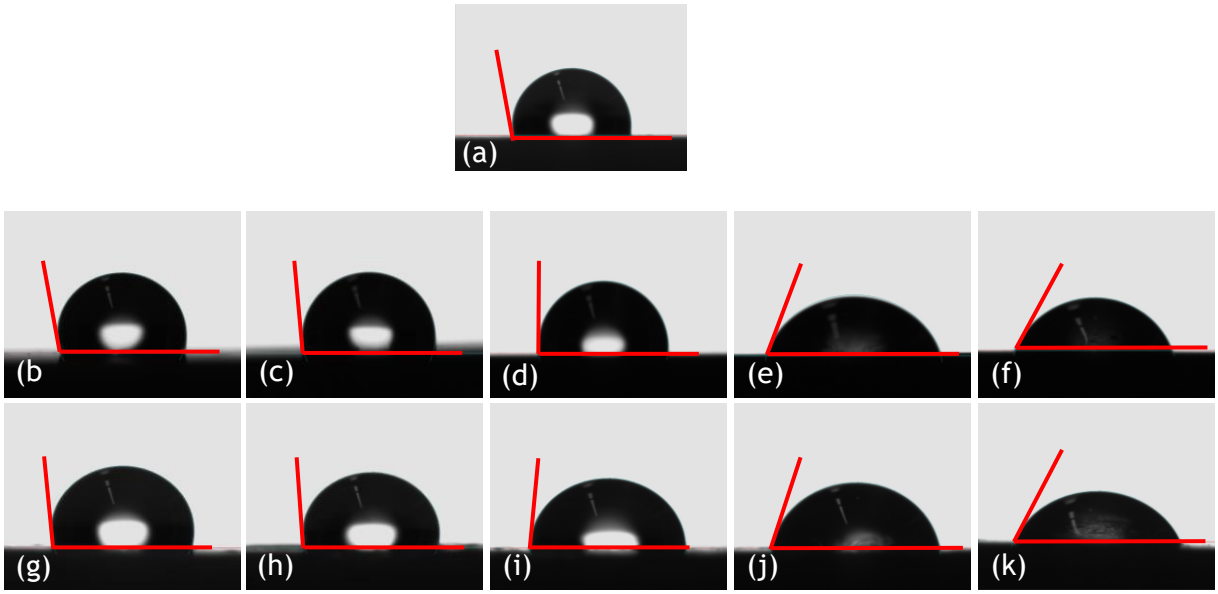

Figure 19. Contact angle of (a) P_140 (b) PPB10_t1 (c) PPB20_t1 (d) PPB30_t1 (e) PPB40_t1 (f) PPB50_t1 (g) PPW10_t1 (h) PPW20_t1 (i) PPW30_t1 (j) PPW40_t1 (k) PPW50_t1.

Table 6. Contact angle of processed WPCs with water.

Sample	Contact Angle (θ)	Dispersive component of surface energy (σ_S^D) / mJm^{-2}	Polar component of surface energy (σ_S^P) / mJm^{-2}	Total surface energy (σ_S) / mJm^{-2}
P_140	100.8	12.02	8.23	20.25
PPB10_t1	109.5	8.08	5.53	13.61
PPB20_t1	106.6	9.29	6.36	15.64
PPB30_t1	97.5	13.76	9.42	23.18
PPB40_t1	76.3	27.84	19.06	46.90
PPB50_t1	64.8	37.00	25.33	62.33
PPW10_t1	106.5	9.33	6.38	15.72
PPW20_t1	105.2	9.91	6.78	16.69
PPW30_t1	91.3	17.39	11.90	29.28
PPW40_t1	81.6	23.91	16.37	40.27
PPW50_t1	66.2	35.85	24.55	60.40

Given that the surface is considered hydrophilic when the contact angle is <90° and hydrophobic when it is >90°, by incorporating filler into the polymeric matrix, the composite becomes hydrophilic (Law 2015). That is, the increase of the wood/bark wt% in the composite leads to the decrease of the contact angle between the water droplet and the sample. This was the expected result, since natural particles, as wood and other natural particles, have higher hydrophilicity owing to their strongly polarized groups (such as hydroxyl group) (González Seligra et al. 2016, Cintra et al. 2022). Since surface energy increases with increasing hydrophilicity (contact angle decrease), this was the expected result.

4.4 Scanning Electron Microscopy

The properties of the PPW and PPB composites rely on the dispersion of PW and PB within the matrix and their interaction with the polymer matrix. Hence, the morphology examination of the neat polymer and PPW and PPB composites offered additional understanding of the microstructures involved.

Figure 20a shows P_140 polymeric matrix. Figure 20b, c, d and e show the cross-sectional SEM image of the PPW composites. As can be seen from the figures, wood

particles have an elongated shape and different sizes. Their interface with polymer seems to indicate favorable adhesion between the two, since there is a continuous interface, with no void spaces. In addition, filler is well distributed in the polymer matrix and verifies some areas with higher concentration, as shown in Figure 20e, which represents the composite with the greater percentage of added load.

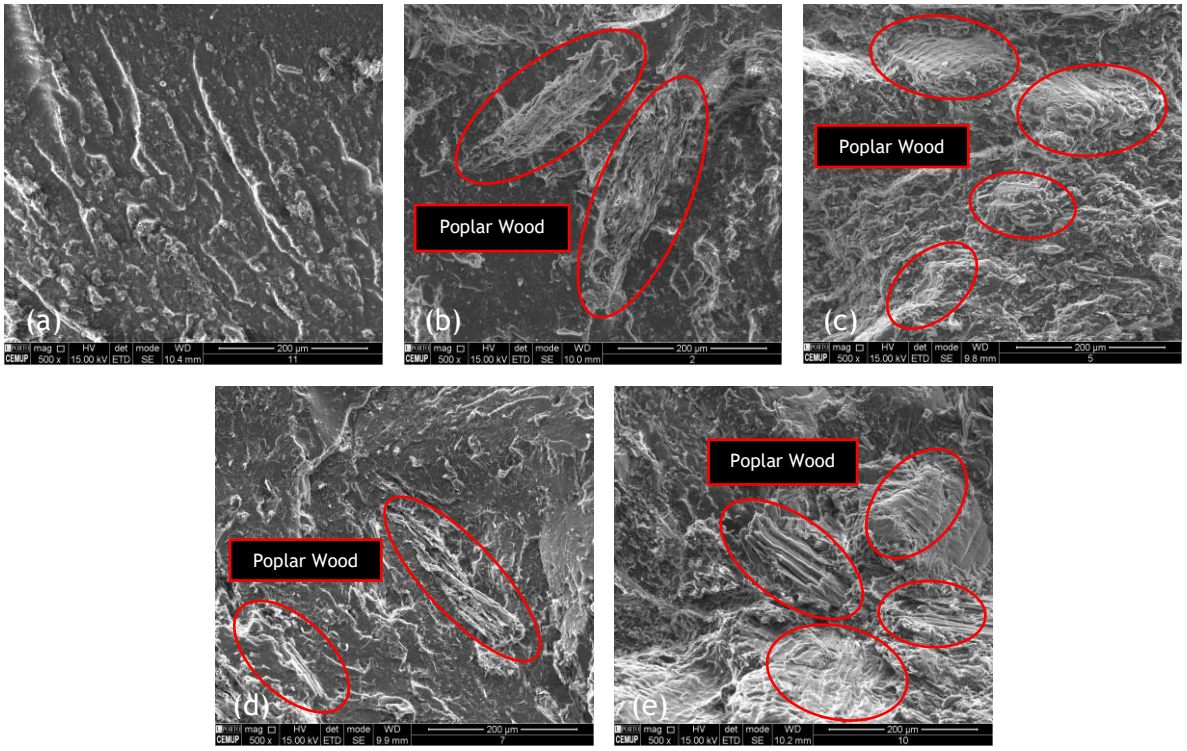

Figure 20. SEM Micrographs of a) PBAT/starch polymer; b) PPW20_t1; c) PPW50_t1; d) PPW20_t2; e) PPW50_t2.

4.5 Tensile properties

The specimens of neat polymer were mechanically analysed at different temperatures, namely 140, 160, 175 and 185 ºC, in order to verify if the temperature change would have an impact on the polymer's mechanical properties. This issue was raised by the observed change in the samples' color discussed above.

The evaluated properties included *YM*, *TS*, *SB* and *AUC* according to the ISO 527-2 international standard and the results are shown in Figure 21. It should be noted that samples of neat polymer were not tested until break, since the tests were stopped at 30 min, corresponding to strain about 256%. Therefore, the values of *SB* and *AUC* are

not sown for the neat polymer. A higher crosshead speed should have been used in order to make these measurements feasible for the polymer samples.

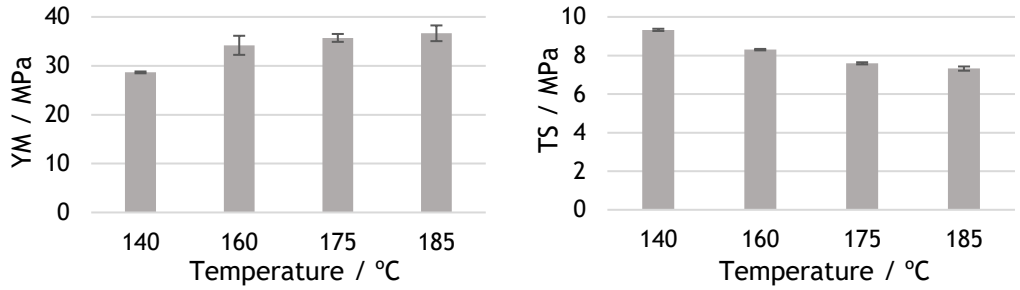

Figure 21. Temperature influence on *YM* and *TS* of the polymer.

As can be seen from the results represented in Figure 21, *YM* increases (from 28.7 MPa to 36.7 MPa) and *TS* decreases (from 9.3 MPa to 7.3 MPa) with higher temperature. This mechanical behavior was also verified in Nunes et al. (2018) study that investigated the rheological, mechanical and morphological properties of poly(butylene adipate-co-terephthalate)/thermoplastic starch blends, in the temperature range of 140-190ºC, and its bio-composite with babassu mesocarp (Nunes et al. 2018).

The mechanical tests were performed on the samples corresponding to the composites, PPW10, PPW20, PPW30, PPW40, PPW50, PPB10, PPB20, PPB30, PPB40 and PPB50, for both particle sizes, 250 µm to 500 µm (*t1*) and 500 µm to 2 mm (*t2*). Since temperature has been found to slightly influence the mechanical performance of the polymer, the comparison between P_140, P_160, P_175 and P_185 with the rest of the composites should be cautious.

Example stress-strain curves obtained for P_140, PPW10_t2 and PPW50_t2 are represented in Figure 22.

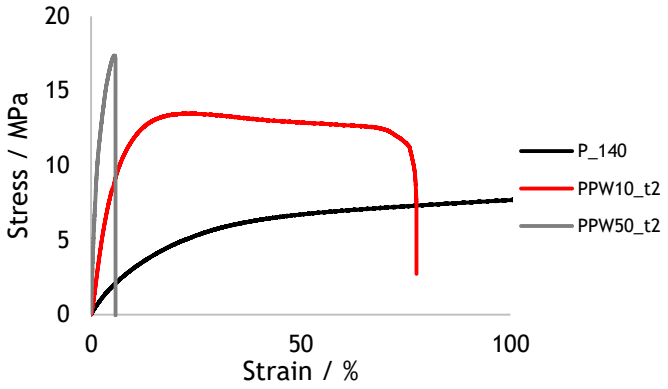

Figure 22. Stress-strain curves of neat polymer P_140 and PPW10_t2 and PPW50_t2 composites.

It is immediately clear that wood addition significantly increases the stiffness (*YM*) and the strength (*TS*) and decreases the toughness (*AUC*) of the material. A yield point (local stress maximum in the stress-strain curve) becomes evident when filler is present, probably associated with the realignment of the filler particles within the polymer matrix.

In addition, with the incorporation of higher percentages of load in the polymeric matrix, it was verified that the fracture went from ductile in the plastic zone of the stress-strain curves, to brittle in the elastic zone.

The tensile properties of the composites containing wood and bark fillers are represented in Figure 23 and Figure 24, respectively.

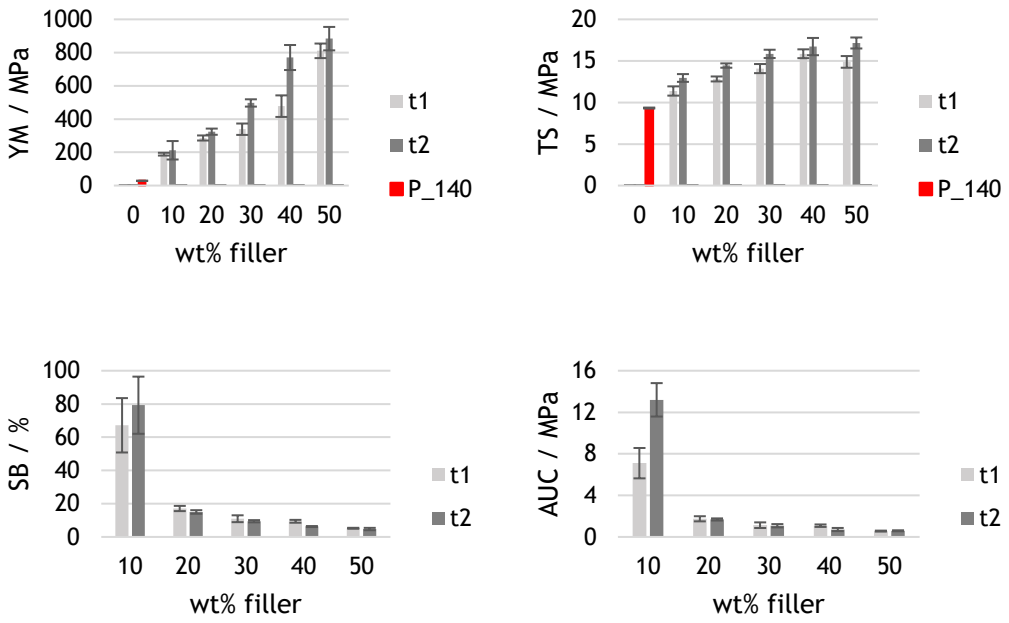

Figure 23. Influence of wood filler wt% and particle size on *YM*, *TS*, *SB* and *AUC* of the composites.

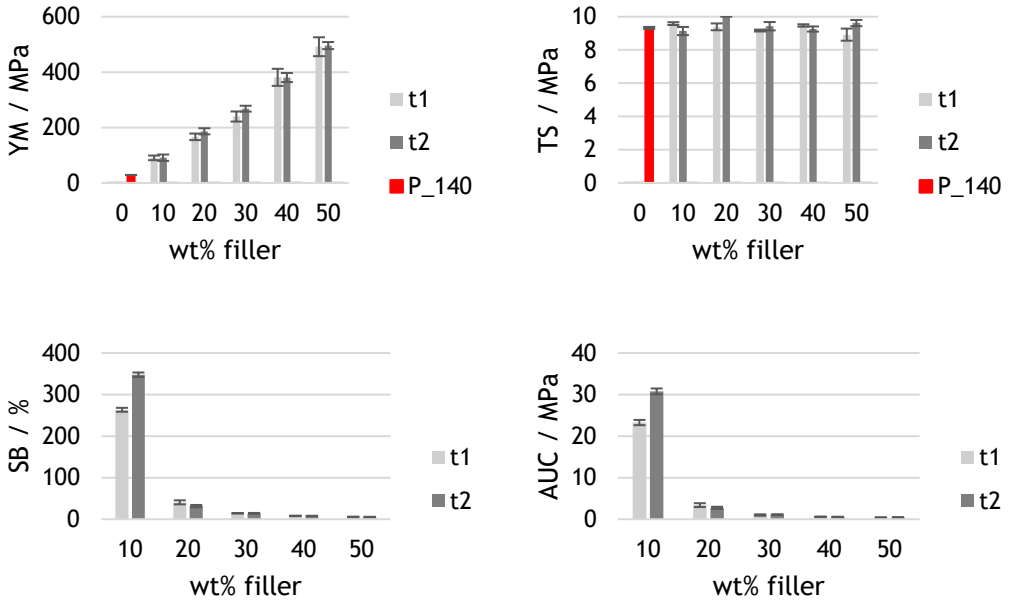

Figure 24. Influence of bark filler wt% and particle size on *YM*, *TS*, *SB* and *AUC* of the composites.

From the results in Figure 23 and Figure 24, since wood is a stiffer material due to higher percentage of cellulosic components, it contributes more to the composite stiffness than bark. Wood also significantly increases *TS*, at least until 40 wt%, showing good reinforcement performance due to effective stress transfer from the polymer to the filler particles. Thus, the *YM* maximum values correspond to 884 MPa for PPW50_t2 and 496 MPa for PPB50_t2. The greater *TS* was obtained for PPW50_t2, 17.2 MPa.

Bark composites show a different behavior, where stiffness increases but strength stays constant. This somehow inferior performance of poplar bark composites compared to poplar wood composites, in terms of tensile strength, can be attributed to several factors. Safdari et al. (2011) suggested that differences in chemical composition, poor dispersion and lower intrinsic strength of bark fibers compared to wood are the main reasons for this demarcation (Safdari et al. 2011).

Size *t2* leads to higher values of *YM* and *TS*. This may be associated with longer particles providing more effective reinforcement of the matrix, resulting in improved load transfer between the filler and the matrix and promoting a more effective reinforcement of the matrix. These results confirm the good compatibility between the filler and the polymeric matrix, since the stress-strain modulus and tensile strength increased with the increasing load, proving the consistency of morphological analysis (good adhesion between the polymer and the polymeric matrix).

However, when it comes to *SB* and *AUC*, bark seems to provide a better mechanical performance to the composites. Hence, higher *AUC* values translate into greater impact resistance, therefore greater capacity of absorbing more energy until the fracture of the samples.

SB and *AUC* seem to decrease exponentially with filler addition. This means that the composites filler contents of 20 wt% or higher, both for wood and bark, have a significantly more brittle behavior than the neat polymer, or even the 10 wt% composites. Even though *SB* and *AUC* are expected to become lower as filler content increases, the steep decrease observed may be due to the relatively large particle size of these fillers. As the particle content increases, particle realignment along the stress direction creates large void spaces, and fracture occurs at increasingly lower strains. Composites with bark filler show higher *SB*, which correlated with the lower stiffness (*YM*) observed for these composites.

The negative correlation between the impact strength and strain at break with higher percentages of filler occurs due to polymers' reinforcement with PW and PB, which have a similar behavior to other lignocellulosic material. Therefore, these fillers add brittleness to the polymer and less energy is needed to fracture the samples (Safdari et al. 2011). The presence of filler provides stress concentrators and weakens the samples, since the polymer chains lose their mobility due to the addition of a reinforcement agent, therefore reducing their capacity to absorb energy until rupture (Poletto, Zeni, and Zattera 2011).

5 Conclusion

This thesis focused on the development of a wood-polymer composite that incorporates a biodegradable polymeric matrix (with 30% of starch) and wood byproducts as a potential filler. The research showed that it is possible to incorporate up to 50 wt% of filler into the polymer to produce a usable material, as an alternative to plastic.

Since a micro extruder was used, it is likely that the possible percentage of filler added to the composite could be higher in the case of an industrial extruder. Thus, it would be interesting to compare the obtained results with others collected under the conditions mentioned above.

The thermal characterization of the polymer and natural particles allowed the determination of the melting and degradation temperatures of these materials. Thus, the soft segment of PBAT (PBA) started to melt at 43 ºC and PBT at 109 ºC. When it comes to its degradation, PBAT reached its maximum at around 400 ºC. Starch's melting and degradation temperatures were 156 ºC and 300 ºC, respectively. On the other hand, both bark and wood showed a large loss of mass around 100 ºC, corresponding to the evaporation of water and between 250 ºC and 450 ºC the degradation of cellulosic compounds, namely hemicellulose, cellulose and lignin, occurred.

The chemical, morphological, and mechanical analyses carried out on the composites provided valuable insights. FTIR analysis revealed the impact of temperature on the transmittance peaks and appearance of the polymer, emphasizing the importance of optimizing processing conditions. The SEM analysis confirmed the well-distributed filler within the polymer matrix, with a continuous interface and no void spaces, suggesting good compatibility between the components.

Additionally, WCA analysis demonstrated increased hydrophilicity in the composites since the contact angle value went from 100.8º for the neat polymer to 64.8º and 66.2º, respectively, for PPB50_t1 and PPW50_t1.

The tensile tests provided valuable mechanical property data, indicating an increase in *YM* and *TS* with more filler loaded into the samples. Thus, the neat polymer stiffness increased from 28.65 MPa to 884 MPa for PPW50_t2 composite. In addition, the ultimate tensile strength improved from 9.33, corresponding to the neat polymer, to 17.16 MPa, for PPW50_t2. This behavior was not verified for the composites integrating

bark filler, which did not show any significant variation in *TS* parameter. This could be occurring due to bark particles' lower intrinsic strength when compared to wood.

This suggests that the composites possess structural integrity and could potentially withstand real-world applications. However, the brittleness observed in some composites highlights the need for further research on improving the impact resistance and toughness through the addition of toughening agents or alternative processing techniques.

With regard to the application of the composite materials in the food packaging area, it would be necessary to carry out more tests, such as the inhibition of bacterial growth, to verify whether there really was a possibility of their integration in this industry.

Future research could explore the optimization of wood-polymer composite formulations by investigating another filler content options and compatibilizers. Additionally, the long-term degradation behavior, biodegradability, and environmental impact of these composites should be thoroughly evaluated to ensure their sustainability through life cycle assessment (LCA).

Finally, this study provides a valuable contribution to the development of more sustainable alternatives to traditional plastics. The findings highlight the potential of wood-polymer composites as a promising solution, while also suggesting areas for further research to improve their performance and expand their applications.

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Anex A

Table 7. Composites' mechanical performance.

Composite	Processing temperature (ºC)	Ultimate Tensile Strength (MPa)	Young's Modulus (MPa)	Strain at break (%)	Area under curve (MPa)
P_140	140	9.33	28.65	-	-
P_160	160	8.30	34.19	-	-
P_175	175	7.59	35.70	-	-
P_185	185	7.32	36.65	-	-
PPW10_t2	140	12.95	212.28	79.25	13.19
PPW20_t2	140	14.44	324.21	15.02	1.68
PPW30_t2	160	15.85	496.98	9.45	1.08
PPW40_t2	160	16.72	770.29	6.26	0.71
PPW50_t2	185	17.16	883.99	4.76	0.59
PPB10_t2	140	9.14	91.05	347.7	30.75
PPB20_t2	140	10.11	186.36	31.61	2.75
PPB30_t2	160	9.43	268.06	14.20	1.11
PPB40_t2	160	9.26	380.45	7.99	0.57
PPB50_t2	185	9.62	495.81	5.62	0.41
PPW10_t1	140	11.38	188.89	67.18	7.10
PPW20_t1	140	12.83	286.27	17.12	1.74
PPW30_t1	160	14.08	339.00	10.96	1.13
PPW40_t1	160	15.86	477.73	9.41	1.08
PPW50_t1	175	14.88	810.63	5.21	0.56
PPB10_t1	140	9.58	90.54	263.33	23.27
PPB20_t1	140	9.39	166.54	40.67	3.40
PPB30_t1	160	9.17	239.73	14.31	1.01
PPB40_t1	160	9.47	381.13	8.08	0.59
PPB50_t1	175	8.92	491.69	5.54	0.39

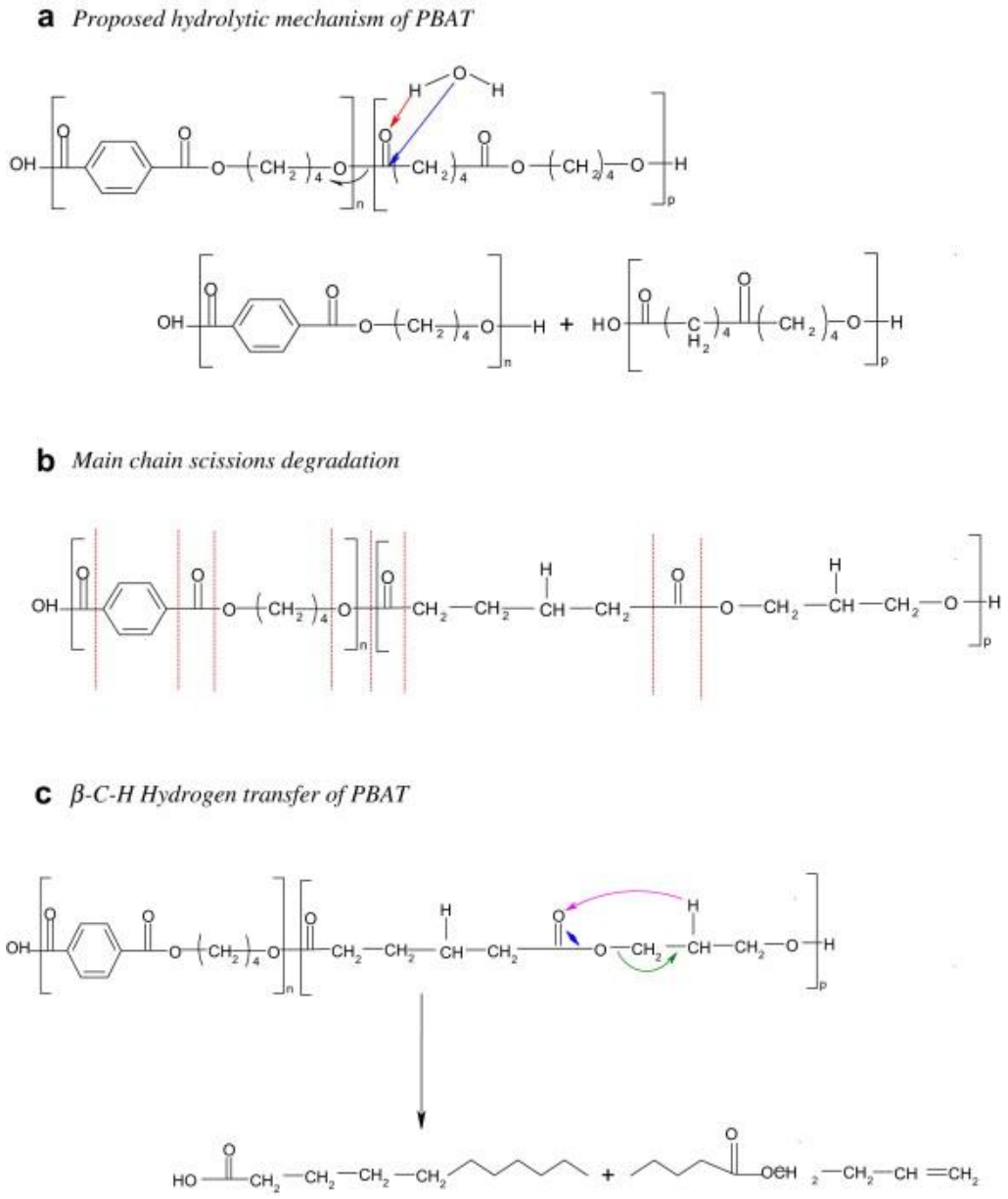

Figure 25. Proposed degradation mechanisms of PBAT (Al-Itry, Lamnawar, and Maazouz 2012).