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Development of polymer composites based on agro-industrial and forest solid residues

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ABSTRACT

The current environmental situation has been a growing concern for the World population, as the extent of its damages are being increasingly felt. Plastics represent one of the major classes responsible for this scenario, given their petrochemical base, widespread usage, and inefficient and incorrect manners to deal with generated wastes. On the run to develop more sustainable and renewable materials, composites assembled with natural polymers as reinforcing phase, also called green composites, constitute a popular approach. The reuse of natural residues from forest and agro-industries, to be employed as reinforcing phase in these materials, holds increased interest given the reduced associated costs. Aiming the preparation of sustainable materials with properties capable of competing with currently leading solutions, green composites using polypropylene (PP) or polylactic acid (PLA) as matrix phase, and different contents of woof flour (WF) as reinforcing phase, were herein developed by twin-screw extrusion. To improve the adhesion of WF to the polymer matrix, a previous surface modification of the residue, with soybean oil solutions was also studied, by FTIR-ATR and TGA. The results showed that the treatment with a 5 wt.% soybean oil/ethanol solution was the most effective at promoting the intended hydrophobicity on the natural residue. WF treated by this method was also compounded with the two selected polymers, having the thermal, rheological, physical, and morphological properties of all developed compositions been assessed. The wood content showed to play major role on composites' properties, where higher moisture and water absorptions, lower thermal stabilities and lower melt flow indexes were generally obtained. However, these were in some cases compensated by the previous functionalisation of WF. In general, better results of these properties were achieved in compositions using PP and 15 wt.% and 20 wt.% of oil-treated WF. Furthermore, in these cases, indications of higher adhesions established between reinforcements and the matrix were also provided by SEM analysis, suggesting that materials with interesting features were achieved.

KEY-WORDS

Green composites | Wood flour | Reinforcement/matrix adhesion | Soybean oil treatment

RESUMO

A atual situação ambiental tem sido uma crescente preocupação para a população Mundial, à medida que a extensão dos danos é sentida de forma progressiva. Os plásticos constituem uma das principais classes responsáveis por este cenário, dada a sua base petroquímica, ampla utilização, e formas ineficientes e incorretas de lidar com os seus desperdícios. Na corrida para o desenvolvimento de materiais mais sustentáveis e renováveis, compósitos constituídos por polímeros naturais como fase de reforço, também reconhecidos como compósitos verdes, têm sido uma abordagem comum. A reutilização de resíduos de florestas e agroindústrias, para serem empregues como fase de reforço nestes materiais, possui ainda interesse acrescido, dado os reduzidos custos que lhes estão associados. Tendo como objetivo a preparação de materiais sustentáveis, com propriedades capazes de competir com as presentes principais soluções, neste projeto foram desenvolvidos vários compósitos verdes por extrusão de duplo fuso, utilizando polipropileno (PP) ou ácido polilático (PLA) como matriz polimérica, e diferentes teores de pó de madeira (WF) como fase de reforço. Para melhorar a adesão da madeira à matriz, foi previamente estudada a modificação da superfície do resíduo, com soluções de óleo de soja, por FTIR-ATR e TGA. Os resultados mostraram que o tratamento com a solução 5 wt.% óleo de soja/etanol foi o mais eficaz a induzir a hidrofobicidade pretendida no resíduo. Foi também feita composição com pó de madeira tratado por este método, e os dois polímeros selecionados, tendo sido estudadas as propriedades térmicas, reológicas, físicas e morfológicas de todas as composições. O teor em madeira mostrou ter um papel fulcral nas propriedades dos compósitos, tendo-se geralmente obtido maiores absorções de humidade e água e menores estabilidades térmicas e índices de fluidez. No entanto, estes resultados foram em alguns casos compensados pela prévia funcionalização da madeira. No geral, relativamente a estas propriedades, foram adquiridos melhores resultados nas composições com PP e 15 % ou 20 %, em massa, de pó de madeira tratado com óleo vegetal. Além disso, nestes casos, a análise SEM forneceu indicações de melhores adesões estabelecidas entre reforços e matriz, sugerindo que foram alcançados materiais com interesse acrescido.

PALAVRAS-CHAVE

Compósitos verdes | Pó de madeira | adesão reforço/matriz | tratamento com óleo de soja

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LIST OF SYMBOLS AND ABBREVIATIONS

α-cell, α-cellulose

ΔH_c, crystallisation enthalpy

ΔH_m, melting enthalpy

ΔH_m°, melting enthalpy of fully crystalline polypropylene

L/D, length/diameter ratio

T_c, crystallisation temperature

T_g, glass transition temperature

T_m, melting temperature

X_c, degree of crystallinity

w, weight fraction of wood on composites

Wd, dry weight

Ww, wet weight

A

A-Oil, soybean oil/acetone solution

APTES, (3-aminopropil)triethoxysilane

B

bio-PE, bio-Polyethylene

bio-PET, bio- Polyethylene terephthalate

bio-PU, bio-Polyurethane

C

C.A4, Citroflex A4

CA, Cellulose acetate

CF, Cellulose fibres

CP, Cork Powder

D

DTG, Derivative thermogravimetric curve

DSC, Differential scanning calorimetry

E

EDS, Energy-dispersive X-ray spectroscopy

EU, European Union

E-Oil, soybean oil/ethanol solution

E-NaOH + Oil, soybean oil/ethanol solution with catalyst

F

FTIR-ATR, Fourier transformed infrared spectroscopy, with attenuated total reflectance

H

HDPE, High-density polyethylene

L

LDPE, Low-density polyethylene

LLDPE, Linear low-density polyethylene

M

MA, Maleic anhydride

MAPE, Maleic anhydride grafted polyethylene

MAPP, Maleic anhydride grafted polypropylene

MC, Moisture content

MFI, Melt flow index

N

NaOH-αcell, alkaline pre-treated α-cellulose

NaOH-WF, alkaline pre-treated wood flour

O

Oil-αcell, α-cellulose pre-treated with soybean oil solution

Oil-WF, Wood flour pre-treated with soybean oil solution

P

PBAT, Polybutyrate adipate terephthalate

PBS, Polybutylene succinate

PBT, Poly (butylene terephthalate)

PCL, Polycaprolactone

PE, Polyethylene

PET, Poly (ethylene terephthalate)

PHAs, Polyhydroxyalkanoates

PLA, Polylactic acid

PP, Polypropylene

PPP, Peristaltic pump position

PU, Polyurethane

PVC, Poly (vinyl chloride)

S

SEM, Scanning electron microscope

T

TGA, Thermogravimetric analysis

TPS, Thermoplastic starch

U

U-αcell, Unmodified α-cellulose

U-WF, Unmodified wood flour

V

VFP, Volumetric feeder position

W

WA, water absorption

WCA, Water contact angle

WF, Wood flour

1. STATE OF THE ART

1.1 The environmental need for sustainable polymers

The polymer world has been continuously growing since its early days, aiming to keep up with the demands of the also growing population. Synthetic polymers are the main elements used in plastics' production, being therefore the essential constituents of the great majority of today's products, from food packages, construction or automotive materials, to biomedical applications [1]. The capacity to adapt the properties of these polymers according to the intended application, their ease of processing, low cost, and durability, are the main key features on the basis of their widespread usage, causing the tremendous increase in plastics production, and allowing them to replace many of the traditional materials like wood, ceramic or glass, ever since the first industrial production of synthetic polymers in 1940 [1],[2].

Despite all plastics' appealing features, they also hold some serious drawbacks, which have caught the attention of governments and industries, prompting the need for new and improved solutions. The great majority of synthetic polymers are derived from fossil fuels [3], which, given the economic problem associated with the depletion of these resources, constitutes a severe concern to plastics' applications. As plastics hold a petrochemical basis, these products also generate several environmental hazards along their life cycle [2]. Since their early stages, plastics threaten the environment by the release of high levels of greenhouse gases into the atmosphere during their manufacturing process, largely contributing to one of the top environmental concerns these days: global warming. Afterwards, the major threat stands on the waste management of these products, which, given their large durability mostly due to non-biodegradable nature, constitutes a massive problem [2].

Plastic wastes may be given a new end by recycling processes, being this the most valuable available solution to reduce the impact of discarded plastics and the dependence on petrochemical resources [3]. However, due to contamination or technical limitations, a great portion, after their useful life, cannot undergo these procedures [2]. In the European Union (EU), plastics occupy the major fraction of the generated amount of municipal waste, where from the total amount, only 28 % are recycled, whose percentage is reduced to 16 % in Portugal's particular case. Instead, they are favourably landfilled, despite the environmental hazards of this approach [4].

The landfilling of plastics, besides leading to soil impregnation with contaminants, also generates high levels of methane gas, produced from plastics' anaerobic degradation, this being a much more potent gas than carbon dioxide for the greenhouse effect [3]. From **Figure 1,** it is visible an intensification of the amount of recycled waste in EU over the years, mostly to detriment of landfilling, owing to constant advances in recycling technologies, systems for collection, sorting and reprocessing [3]. However, it can also be observed that the percentage of recycled wastes remain rather low comparatively to what is desired, forcing us to still rely on solutions with high negative impact to the environment.

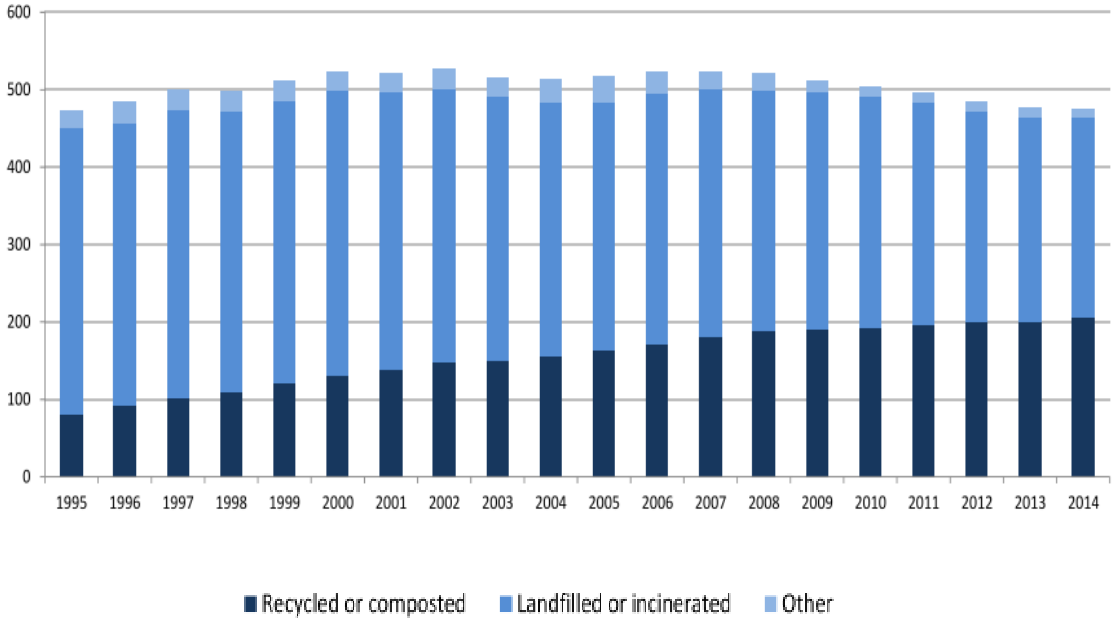


Figure 1 | Average amount of municipal waste generated and treated in the EU. The annual amounts of waste are presented in kg per person, from 1995 till 2014. Retrieved from [4].

Plastic wastes may even have a third end, the least desired of them all, because of their long persistence: environmental accumulation. These wastes rise from discarded materials both from urban or industries litter, where a large part of it ends up in marine environments, affecting not only the landscape but also the fauna. It is estimated that the amount of plastic waste accumulated in the Atlantic and Pacific oceans is in the range of 80 million tonnes [2].

When exposed to UV radiation, plastics can be degraded and divided into smaller pieces, however, due to their non-biodegradable nature, their residues may remain in the environment for hundreds of years. As more plastics end up in the oceans, more and more is ingested by animals, which confuse the floating litter with their natural food [5]. The wildlife may even be affected by other means, directly related with plastics disposed in the environment. The great number of species who get entangled on old fishing nets that are dumped on the oceans, eventually suffering from strangulation or starvation, are a good example of such. On the other hand, the dumping of plastic litter on the environment, also affects several habitats, not only of marine species but also terrestrial, by filling up spaces that are normally occupied by those species [5].

Given the not so bright scenario for petrochemical based synthetic polymers and lack of effective strategies to manage their wastes, the interest of industries for renewable and biodegradable solutions has increased in the latest years, along with the growing concerns of consumers for environmental issues, and the emergent legislation for the reduction of the carbon footprint [1],[6]. Therefore, several strategies are currently being outlined aiming the achievement of materials which fulfil the existing gaps of conventional plastics, namely: minimize wastes and environmental pollution by being biodegradable and more easily recycled; minimize greenhouse gas emissions and toxicity; and reducing the demands for petrochemical resources, and consequently, costs [1],[6].

1.2 Synthetic plastic materials

The vast majority of plastic materials, as previously referred, are still composed of synthetic polymers which are often supplemented with different additives that enable the tailoring of plastics' properties, making them ideal for different applications. The physical and chemical properties of these materials depend greatly on the nature of the monomers that constitute them, being this the basis for the wide spread research and application on synthetic polymers, since they can be engineered according to the desired properties or applications [7].

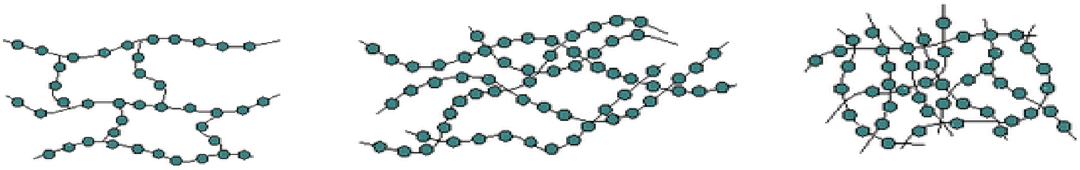
Synthetic polymers are man-made polymers deriving from fossil fuels with great responsibility on the environmental situation that we are currently crossing. The continuous demands of the growing population for new, improved, and cost-effective technologies, forced the progress of polymers engineering, being nowadays included in all kinds of items in our daily lives as versatile and low-cost materials with high performance. Considering their wide application, it becomes necessary to approach the most commonly used polymers/plastics, so a better understanding of their properties can be achieved, and on how other, more sustainable, materials can replace them.

Given the wide range of synthetic polymers, there is a need for their classification, which may be done in several different ways [7]. Considering the general physical properties, synthetic polymers can be grouped into three main clusters, whose typical structures are represented in **Figure 2**:

i) Elastomers, which are rubber-like materials with elastic properties and a slightly cross-linked structure;

ii) Thermoplastics, typically with linear or branched structures, that can be repeatedly melted by heating and solidified upon cooling, thus making them able to be reversibly moulded;

iii) Thermosets, presenting a three-dimensional network (i.e. highly cross-linked structure) that, unlike thermoplastics, solidifies irreversibly upon cooling, and thus cannot be re-melted and reprocessed by heating, without degradation of its structure.



Elastomers **Thermoplastics** **Thermosets**

Figure 2 | Arrangements of polymer chains on the three main classes of polymer materials.

Despite the existence of different possible forms of classification for synthetic polymers, their division according to their structure and the monomers that constitute them still stands as the most common and direct form of classification, and for this reason, in the next sections, the most common plastics approached are divided according to this.

1.2.1 Polyolefins

Polyolefins, or polyalkanes, are composed by unsaturated hydrocarbons as monomers, containing at least one carbon–carbon double bond. Thus, ethylene is the simplest monomer and polyethylene (PE), represented in **Figure 3**, one of the most resorted subclasses of polyolefins. A variety of PEs can be produced, differing in molecular weight, crystallinity, and branching, where the most common are the low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE).

LDPE is a material with low-crystallinity and high impact strength, possessing both long and short branches, which prevents the molecules from packing together and forming hard and stiff domains, and thus holding high flexibility. Properties like rigidity, tensile strength and chemical resistance increase with higher levels of density and crystallinity, therefore HDPE, given the low branching level compared to LDPE, has higher levels of these properties, holding lower permeability to liquids. LLDPE has less and shorter branches than LDPE, resulting in an also flexible material, but higher tensile strength due to higher crystallinity. In terms of application, PE is used in several areas and products, such as plastic bags and wraps, as films, or in pipes, toys, or bottles, as injection or blow moulds [8].

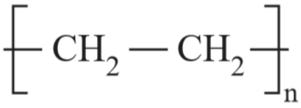
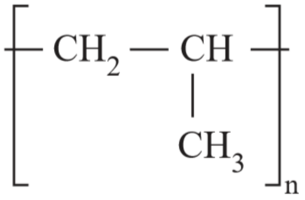


Figure 3 | Basic structure of polyethylene.

Propylene is another commonly used monomer, giving rise to the second major subclass of polyolefins, polypropylene (PP), represented in **Figure 4**. This polymer has high crystallinity, and therefore high tensile strength and stiffness, and also excellent electrical insulating properties, chemical inertness, and moisture resistance, typical features of nonpolar hydrocarbon polymers [8]. PP competes in many areas with HDPE, having, however, higher temperature resistance and generally higher tensile strength, reason why it is often a better choice. In terms of application, PP is commonly applied in the automotive industry for pedals or battery casings, but also for cups, plates, food containers or toys. It can also be used in its fibre form for application in carpets or upholstery [8].



$$\left[CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} \right]_n$$

Figure 4 | Basic structure of polypropylene.

1.2.2 Poly (vinyl chloride)

Poly (vinyl chloride) (PVC), represented in **Figure 5**, is produced from the vinyl chloride monomer, resulting in a predominantly non-crystalline polymer. It is an economic, chemically inert, remarkably durable, and versatile polymer, ranging from flexible to rigid material, whose properties can be modified through chemical modification, copolymerization, or blending. Rigid PVC finds application mainly in the manufacture of pipes or building construction products such as window frames and flooring.

Nevertheless, when plasticizers or copolymers like vinyl acetate are added, a more flexible PVC is obtained, suitable for wire and cable insulation or phonograph records. The temperature ranges of application of this material may also be extended by the adjustment of the chlorine content, otherwise it degrades rapidly upon heat exposure. The usage of PVC for packaging is controversial, because its degradation produces toxic compounds [8].

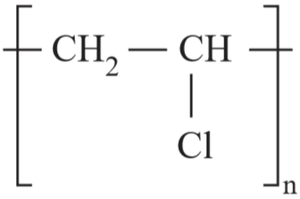


Figure 5 | Basic structure of poly (vinyl chloride).

1.2.3 Polyesters

Polyesters are polymers containing the functional group ester, where terephthalic acid stands as the most common building block, and poly (ethylene terephthalate) (PET), represented in **Figure 6**, and poly (butylene terephthalate) (PBT), as the most commercially produced polyesters. These polyesters possess an extensive range of appealing properties such as: high strength, rigidity, low creep at elevated temperatures, chemical and solvent resistance, low moisture absorption and excellent electrical properties. PET is frequently applied as a fibre in textile industry because of its outstanding work recovery, resulting in textiles with good wrinkle resistance. On the other hand, as a plastic, PET has been used for films production or blow-moulded bottles. The reinforcement of PET and PBT with glass fibres is a common approach which improves many of their properties, making them applicable for automotive purposes like rear-view mirror housings and hinges for PET, or window and door hardware, speedometer frames and ignition system components for PBT, among others [8].

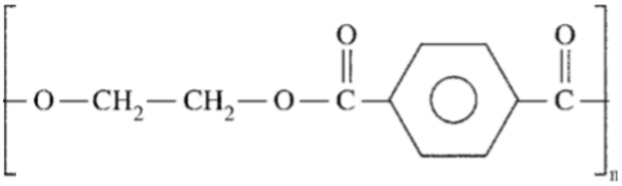


Figure 6 | Basic structure of poly (ethylene terephthalate).

1.2.4 Polyurethanes

Polyurethanes (PU) are polymers with the urethane linkage between its units, which are normally chains based on polyethers or polyesters. These products may appear in different forms, depending on the monomers used in the polymerization reaction. PUs are used extensively as highly durable and resilient foams, which may be flexible, semi-rigid or rigid. Generally, softer and more flexible products are achieved using polyethers in the manufacturing process, being commonly applied in upholstery. Semi-rigid foams are lightweight, shock absorbing, and resistant to abrasion, reason why they find extensive applicability in automobiles' head rests and dashboard covers or shoe soles. Rigid foams are regularly applied as insulators both in houses and automobiles, or refrigerator doors.

Polyurethanes are also produced in the form of elastic fibres and thermoplastics. The fibres are widely used in apparel to improve fit, being commonly known as the materials Spandex or Lycra®. The produced thermoplastics are regularly based on polyester due to its higher tensile strength compared to polyether, becoming elastic and resilient materials with vibration damping, and abrasion and oil resistance [9].

1.3 Bioplastics

Long before the first appearance of synthetic polymers, natural ones had already been acknowledged and exploited. These natural materials consist of polymers which are present in, or created by, living organisms, including polysaccharides, polypeptides, and polynucleotides [10]. Materials such as wool, cotton, silk, and rubber (latex) are included in this category, being widely used by man for a long time. However, natural polymers have more recently held the World's attention due to their characteristic biocompatibility and biodegradability, reason why there have already been several attempts to take advantage of them in different fields, like biomedicine, packaging, or agriculture, for various purposes. These natural polymers are, thus, key renewable resources being used in the up-to-date studies on sustainable plastics, namely as raw materials for the production of bioplastics, targeting the achievement of more easily biodegraded, recycled or composted materials [10].

Since the acknowledgment of the necessity for more sustainable plastic alternatives, several advances have been made on the bioplastics field, both at academic and industrial levels. Today, for almost every conventional plastic, there is a "bio" homologous, where the same processing methods are used, and very similar properties are achieved, with additional advantages, such as reduction on the carbon footprint, or enhancing the possibility to handle the generated wastes [11].

Bioplastics are a class of materials that embrace a large variety of materials, where two major concepts are covered: biodegradation and bio-based [11]. This sometimes generates confusion, because not every renewable-based plastic can be biodegraded, and yet, some fossil-based plastics can be biodegraded. Taken this into account, in this class, three types of plastics are included:

(i) Plastics having a renewable resource (bio-based) which are biodegradable;
(ii) Bio-based or partially bio-based plastics which cannot be biodegraded;
(iii) Plastics from petrochemical resources which can be biodegraded.

Biodegradable plastics are defined as plastics capable to be degraded either by enzymatic activity, microorganisms, or chemical hydrolysis, breaking down their chains and converting them into carbon dioxide, methane, water, biomass, and other natural substances. This property of degradability is not dependent on the type of resource used for manufacturing the material, instead, it is mainly due to the chemical structure of polymers, and the type of linkages present. For this reason, even some plastics derived from fossil fuels can be biodegraded, as is the case of polycaprolactone (PCL), a polyester used, among other applications, in bio-absorbable medical items [12], and polybutyrate adipate terephthalate (PBAT), a fully biodegradable alternative to LDPE, applied in similar purposes like plastic bags [12].

Bio-based plastics, on the other hand, are defined as materials derived from renewable carbon resources. These resources are generally natural polymers or other natural components extracted from agricultural and forest biomass, which are further chemically modified and/or polymerised into several different materials. Besides reducing the dependence on fossil fuels, the plastics achieved by such resources are known as eco-friendly or green plastics, among other reasons, for promoting a “carbon neutral” cycle, that is: the carbon dioxide that is generated by burning of these plastics during manufacture or disposal, will be further uptaken by biomass during photosynthesis events, which in turn will serve as feedstock for the next cycle of bioplastics production.

There are two general approaches for the preparation of bio-based plastics, being these schematized in **Figure 7**. The first approach is based on the use of renewable resources to obtain already commonly used monomers, leading to the above stated “bio” counterparts from the common petrochemical polymers, such as bio- Polyethylene terephthalate (bio-PET) or bio-Polyethylene (bio-PE).

The second approach, is based on the use of the biological resources for the preparation of new monomers, resulting in novel and innovative materials like polylactic acid (PLA) [13].

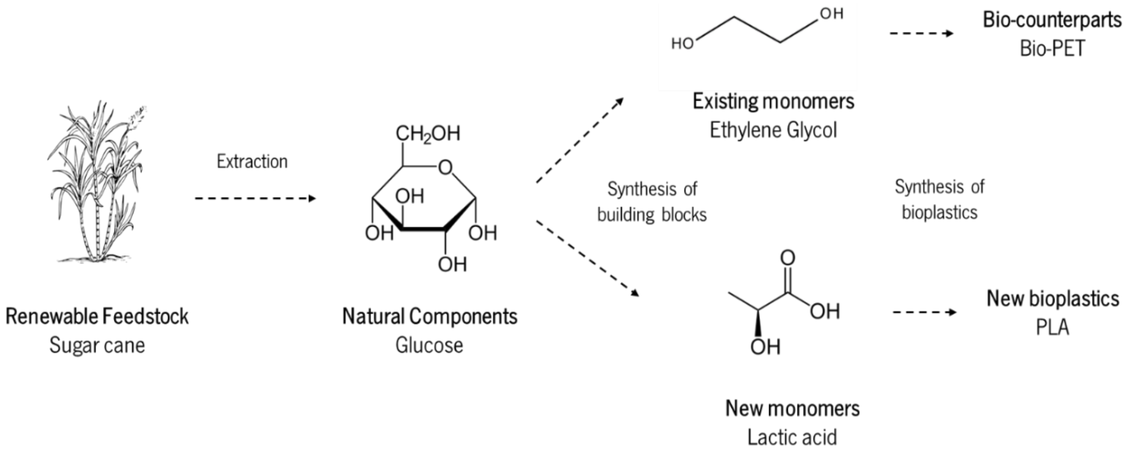


Figure 7 | Scheme of the two main routes used to produce bio-based bioplastics.

Plant's carbohydrates cellulose and starch are the major natural and biodegradable polymers, leading the run as the most used resources, and often the least expensive alternative, to produce bioplastics. Materials like cellulose acetate (CA), finding application for a long time in films, such as photographic films or coatings, or as fibres for cigarette filters [14], or like thermoplastic starch (TPS), used mainly for composting bags due to its moisture sensitivity, are the most acknowledged bioplastics achieved by these resources, being produced long ago.

Sugars, which can also be obtained by depolymerisation of starch, have been revealed as appreciated raw materials as well. From the monomer glucose, valuable bioplastics arise, as is the case of bio-PET and Polyhydroxyalkanoates (PHAs), being this latter group mostly applied in the medical field, especially for drug delivery systems [13],[14]. Polybutylene succinate (PBS) is also obtained from sugars, being an interesting material for its ease of processing, and chemical and thermal stability, having however low biodegradation rate and low biocompatibility [13].

Despite the preference for cellulose, starch, and sugars as resources, other raw materials find application in the bioplastics field as well, such as proteins, achieving materials used for edible coatings or food active packaging [15], or vegetable oils, used to produce polyols involved in the formulations of bio-derived polyurethanes (bio-PU) [16], among others, although with less extent and efficacy. **Figure 8** resumes the currently leading alternatives on the bioplastic field, being the materials separated accordingly to the type of bioplastic they constitute, as earlier defined.

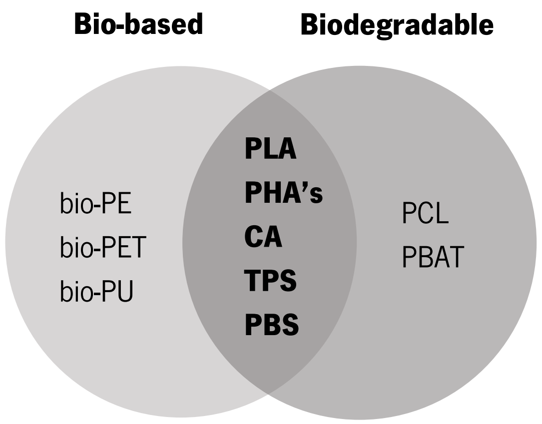


Figure 8 | Most common bioplastics. The represented materials are divided into the two concepts that define this class of plastics, where those appearing in the common area possess both the characteristics.

1.3.1 Polylactic acid

Polylactic acid, or polylactide, is an aliphatic polyester and one of the most valuable bioplastics being currently commercialized, therefore deserving a more thorough assessment. As the name of the material suggests, lactic acid is the monomer of this polymer, generally resulting from the bacterial fermentation of glucose from starch. The most common route followed for the synthesis of the bioplastic is by ring opening of lactic acid dimer, lactide, which is then polymerised resulting in a high molecular weight PLA (**Figure 9**) [17].

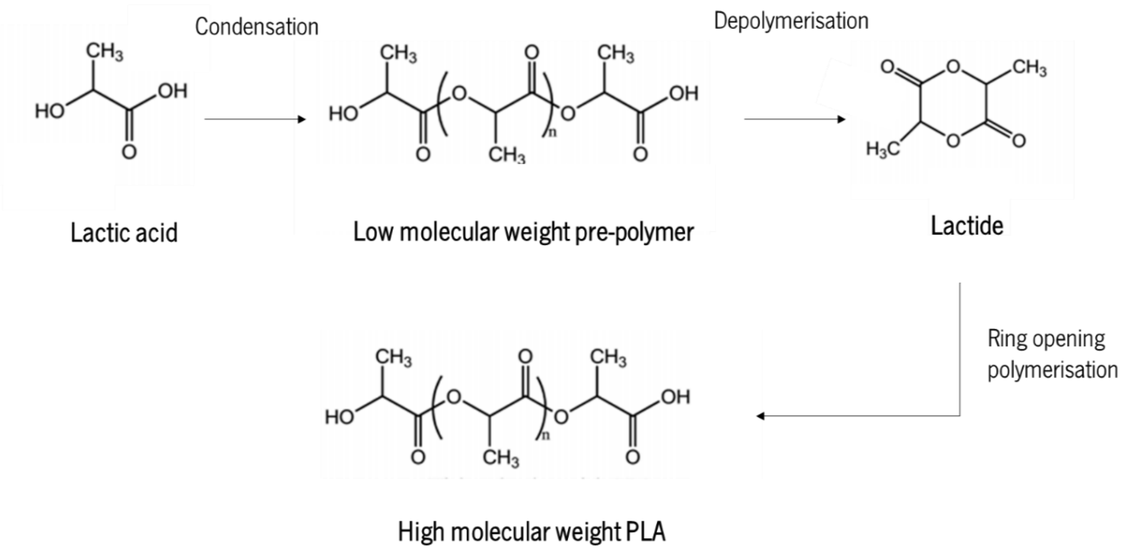


Figure 9 | Synthesis of polylactic acid. Adapted from [17].

When comparing PLA with other common thermoplastics, there are several appealing features that highlight and justify the selection of this material on the run to sustainable plastics. Features such as very low-toxicity; biodegradability; recyclability; lower energy consumption and CO_2 emissions (relatively to PET and PE, it reduces the greenhouse gas emissions up to 40 % and up to 25 % in non-renewable energy usage) [13], and presenting high mechanical performance, are fine examples of its capacity to effectively compete with current widespread materials. In turn, when compared to other presently available bioplastics, its lower production costs, which are increasingly closer than those of common petro-based plastics, along with its capacity to be processed by the most frequently used techniques, like injection moulding, film extrusion, blow moulding, thermoforming, fibre spinning, and film forming, are also examples that justify the preference for PLA and its strong expansion on different market applications [18]. The medical field has been taking advantage of PLA's good mechanical performance and capacity to degrade into non-toxic substances, being used in implants conferring support, like bone internal fixation devices, or in its fibre form for sutures. Packaging is another common application for PLA, serving as base material for cups, bottles, disposable tableware, or compostable plastic bags. However, its brittleness, lower ability to absorb shock without breaking (low impact strength) and low heat resistance, limits PLA's application in more demanding requests [14].

1.4 Green composites

In certain applications, polymers by themselves are not sufficient and there is need to reinforce them with specific additives, according to the final intended properties. The materials resulting from the combination of a polymer matrix with a reinforcing additive, depending on the type of product that is used as reinforcement, is called a composite. Composites are, thus, materials consisting of two or more phases, having an interface between them that allows their differentiation, caused by the different chemical and physical properties of each of the components [19], [20]. The major advantage associated to composites is thus related to the properties held by the resulting materials, which encompasses the individual properties of the different components, leading to a final product that benefits from the characteristics of both, achieving structural and functional properties that none of the constituents reaches by their own, as exemplified in **Figure 10** [19], [20]. This improved mechanical performance, conferred by the addition of the reinforcement, thus differentiates this type of materials, for example, from polymer blends.

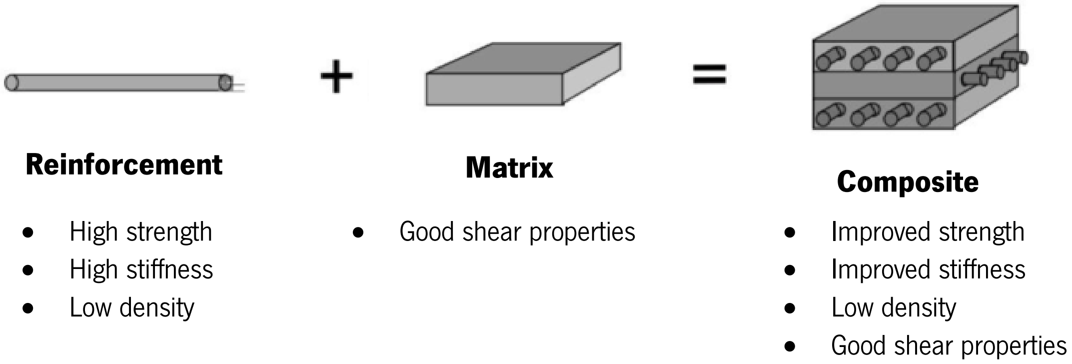


Figure 10 | Illustration of composites components and resulting structure. An example of the properties held by the composite, achieved by the cooperation of its components, is also given.

Different types of polymers can be used as matrix, and similarly, different reinforcements can be used in composites' manufacture, which will consequently have a different impact on the properties of the material depending on their type and quantity. Additionally, in the particular case of reinforcements, their form and size, and how they're orientated and dispersed in the matrix, also plays major role in the final result [19].

Among the wide-ranging category of polymer composites, a group of valuable materials has been emerging and continuously being expanded and recognized as feasible sustainable options. Green composites, or biocomposites, are classified as bio-based materials, presenting, in general, environmental advantages over conventional composites and polymers. These materials may appear in two different forms (**Figure 11**), where composites made of a synthetic matrix with a bio-based reinforcing phase were the first to be developed. In these type of composites, natural renewable resources generally in the form of fibres, like sisal or wood fibres, are added to the common petrochemical based polymers like PP [21] or PE [22], lowering the petro-based content of the materials, and therefore, contributing to the intended reduction of dependency on fossil resources, environmental accumulation of plastic wastes, and high levels of greenhouse gas emissions. The same is true for the second type of biocomposites, also called fully-green composites, where, usually, natural polymers are used both for reinforcing and matrix phases, as is the case of composites using PLA as base polymer [23]. This reinforcement of biodegradable bioplastics with a second bio-based constituent is a very valuable strategy for the enhancement of their mechanical properties, without compromising biodegradability, increasing their chances to compete with traditional polymers [23]. This concept is gaining considerable approval day by day, being presently one of the major fronts of studies on sustainable plastics.

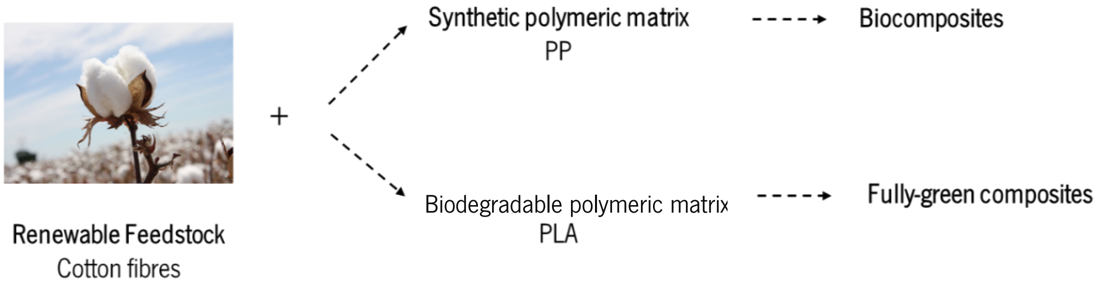


Figure 11 | Illustration of two possible compositions of green composites.

Besides having a positive impact on the environment, the properties held by green composites may also have additional advantages, allowing the development of products that suit best the demands of certain applications. Firstly, one of the major drivers in biocomposites production is related with the lower manufacturing costs of these materials. The high abundance and availability of the natural components used as reinforcements is favourable compared to the expensive commonly used synthetic additives, like carbon fibre [23], [24]. Besides, features like reduction on materials' weight, which has long been taken advantage by the automotive industry [23], or improvement in biocompatibility and reduced toxicity, are frequently reported characteristics that strengthens their application. Some reports have even proved that the reinforcement of plastics with bio-based components can achieve materials with interesting mechanical, acoustic and thermal insulating properties [24].

Nevertheless, some drawbacks also appear associated with these type of materials, namely related to the limited processing temperature range, because natural reinforcements often degrade at temperatures near 200 ˚C [21], or the existent variability on the composition of natural components, among: different varieties, geographical locations, and/or climate conditions [25]. However, the poor interaction between the hydrophilic reinforcement and the hydrophobic matrix, and the increased capacity for moisture absorption and swelling constitutes the major obstacle in green composites' performance [22], [26], [27]. To overcome this, and to broaden the applicability of green composites, the reinforcements generally undergo physical or chemical surface treatments, which will be later discussed in the present work, that change their chemical structure and reduce the number of hydrophilic functional groups, having a positive effect on general mechanical properties of the materials [26], [27]. The degree of interaction between the two phases can additionally be affected by the processing strategy used to prepare the composite, since it can greatly influence the dispersion of the reinforcement on the matrix.

To better understand the pros and cons associated to these materials, as well as how we can take the most advantage of them, **Table 1** summarizes the most important info.

Table 1 | Green composites’ advantages, disadvantages, and potential applications.

Composites’ characteristic properties		**Possible application**
Advantages	Low density High stiffness High strength	Automobile Sport equipment
	Low cost Less abrasive	Competitive substitution of glass fibre products
	Renewable resources CO_2 absorption Biodegradability/ low durability	Disposable and short-life products: packaging
	Lower toxicity Biocompatible	Children’s toys Medical applications
Disadvantages	Variable fibre properties Poor interface interaction	Products where mechanical performance is not fundamental
	High water absorption/ swelling	Products intended for dry uses
	Lower processing temperatures	Products where the utilization of matrices that can be processed in the same temperature range is possible

Several combinations of matrix/reinforcement can be arranged for green composites, regarding both the type of polymers used in each phase and the proportion in which they are combined. Natural fibres and wood derived components are the leading bio-derived reinforcements in this field, where several valuable mixtures have been achieved and continuously being improved and used for different applications.

1.4.1 Natural fibre derived composites

From textiles to paper, natural fibres have long been exploited by man, and their application in the field of green composites as reinforcing materials has more recently been recognized as valuable and advantageous for the replacement of synthetic fibres, like glass fibres, becoming one of the fastest growing additives in composites industry [28]. They can have an animal or vegetable source, being the latter the most resorted. Natural fibres commonly used as reinforcement mainly arise from plants’ basts, leaves, seeds, or canes, where flax, jute, hemp, sisal and kenaf are the most popular resorted species [25].

The performance of composites reinforced with these natural components greatly depends on fibre content, length, chemical composition, crystallinity, own mechanical properties, and orientation in the matrix, thus being necessary to take these aspects into account before further application so that the maximum potential can be reached [28]. In comparison with common synthetic reinforcements, the use of natural fibres generally results in materials with weaker mechanical properties, which is experienced in more extent when higher loads of these reinforcements are used. However, several publications report the achievement of green composites often with increased stiffness and fairly good mechanical properties [23].

The automotive sector rises as the main application sector for such materials driven by the intention of vehicles' weight reduction, and increase of the weight that can undergo reuse or recycling processes, demanded by governmental regulations [23]. Accordingly, these composites are particularly applied in the manufacture of interior structures, such as door and floor panels, which also take advantage of the insulating properties of the materials, dashboards, roof upholstery, arm rests or head restraints [25]. Other application fields have been attempted for these green composites, mostly when high load-bearing capacities are not required, namely for electronic applications or sport equipment.

1.4.2 Wood derived composites

Wood is a fantastic structural material to achieve multiple kinds of ends. Thus, the use of wood derivatives as reinforcing additives for the manufacture of green composites may well constitute an effective strategy, to achieve interesting materials, while diminishing the use of petro-based compounds, with all the environmental benefits that result from that.

Wood flakes, flours, or fibres obtained from pulps, are the most resorted materials to be employed in wood-based green composites. Generally, the properties' profile of these composites is similar to those obtained when using natural fibres as reinforcement, that is: both types of composites behave similarly, when resultant from the same processing conditions, and/or when exposed to the same situations. The size of the reinforcements has great impact on the properties of composites [29], being therefore one of the major features that leads to different performances between wood-based and natural fibre composites. Fibres with higher lengths and lower diameters (higher L/D ratios) can lead to better mechanical properties, whereas reinforcements like wood flour generally lead to lower performances, due to the shorter length of the fibres, resulting in incomplete stress transfer from the matrix to the reinforcement [30]. Bledzki et. al [22], using softwood flour of approximately 75-180 μm and different natural fibres of

2 mm, observed this different mechanical behaviour. In this study, the composites reinforced with wood flour achieved lower flexural and impact strengths, having those, even so, been slightly higher than those obtained without any reinforcement. Faludi et. al [29] also compared different composites using wood flours with different L/D ratios, having obtained better strengths for those with higher ratio. Furthermore, in this study the importance of fibres orientation in the matrix was also studied, having observed that wood fibres achieve higher tensile strengths when pulled parallel to their axis. In fact, fibres orientation in the matrix, as already referred, plays major role on the performance of composites. These may be arranged in three main forms, represented in **Figure 12**, and organized accordingly to their positive impact on composites' performance. Generally, as the direction of fibres becomes more statistically distributed throughout the composite, the ultimate strength decreases, but the properties are more uniform in all loading directions. On the other hand, if oriented in a single direction, the strength of the materials is higher. Nevertheless, different results are achieved depending on the direction of the applied force [30].

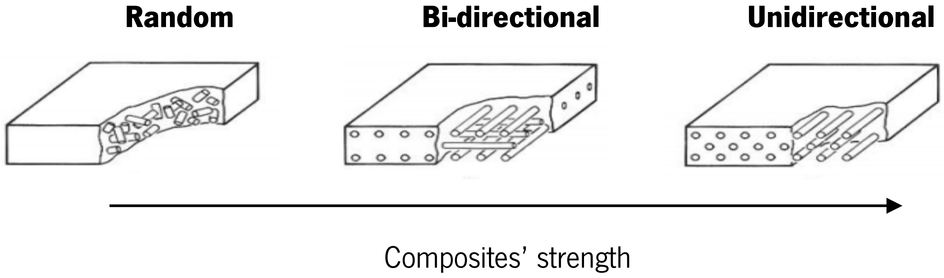


Figure 12 | Different types of fibres orientation in composites.

From trees, other wood derived reinforcements may arise, as is the case of cork, a remarkable material obtained from the bark of cork oaks, which is increasingly gaining attention for its impressive properties. Cork generally confers low permeability to liquids, good thermal and acoustic insulation properties, high energy absorption, and even improved fire resistance, that makes it an adequate material for a variety of applications [31]. Although the cellulose content of cork is lower than other wood based reinforcements, leading to lower mechanical performances, cork possesses one additional component, suberin, which qualifies composites with supplementary properties, namely improved flexibility. Suberin also confers lower hydrophilicity to cork materials, being thus also responsible for the lower water absorption of these composites. Even though, the surface treatment of cork, is still a necessity for improved adhesion to the polymeric matrices. Comparing cork composites, at 50 % reinforcement/matrix ratio, with commercially available wood fibreboards, Fernandes et. al [31] observed these characteristics, in which composites, despite the lower mechanical strength, exhibited improved flexibility and impact resistance and lower moisture absorption.

Wood composites find most application on building and construction industries, being mostly used in manufacture of non-load bearing indoor components, given their overall inferior properties than other structural materials, like wood itself, as well as their vulnerability to environmental attacks. Accordingly, window and door frames and panels, are among the products derived from the application of wood composites. Even so, more demanding applications, like furniture or outdoor decking, may also be accomplished by resorting to this class of materials [24]. Wood composites, along with natural fibre composites, may be also applied for broader fields, like toy's, packaging, musical instruments, or cases for electronic devices, where each different application may take advantage of different properties related to these materials.

1.5 Agro-industrial and forest residues as strategical biological resources

Annually, industries based on agricultural or forestry sources, like brewing, food or timber industries, produce large quantities of wastes, which, if not possessing any other application, are normally disposed by burning [32]. The residues generated by these industries have therefore been subject to a great amount of research over the years, aiming to combine their need for a better disposal end with their eco-friendly nature and highly economic value as resource (given their availability in abundance and low-cost).

Several of these industrial wastes are worth of attention, holding already an extensive history of research and application associated, as is the case of timber industry residues, composed mainly of bark, sawdust, or board ends. Frequently, such residues are compacted to produce highly energetic materials for the generation of thermal energy, named briquettes [33]. Wastes from cereal and beer industries, mainly composed by cereals' straws and husks, and wastes from other beverage and juice industries, generally sugar cane bagasse or peels from different fruits [34], are commonly applied for the production of different types of energy as well, namely bioethanol, or hydrogen [32]. Some of the residues have yet been used as substrates for the production of hydrolytic enzymes and other metabolites of industrial interest such as organic acids, pigments, and flavour and aroma compounds [34]. Other attempts have been developed in order to take the most advantage possible of biological wastes, one of them being the use of the residues as adsorbents for heavy metals [35], or dyes removal [36].

The use of renewable resources for the success of sustainable plastics' sector is undoubtedly crucial, even though, a noteworthy concern has been rising in this matter. The use of raw materials like corn or soy might possibly constitute a hindrance on the progress of sustainable plastics' market, since there is an inherent need to deviate these resources from their normally intended application: food or pasture requests. For this reason, aiming to reduce the use of edible resources for other purposes than those primarily intended, the bioplastics and green composites market has also been trying to take advantage of natural residues disposed by industries. This economically valuable strategy has been gaining increasing significance, where several different combinations have been attempted, being sawdust, or wood flour, the most effectively explored residue for composites' reinforcement.

1.5.1 Most common residues

Worldwide, the residues obtained from the different sources differ according to the agricultural practice, industrial activity, and the autochthonous species of the region. Relatively to crop residues, taking into account the total cultivated area, the World's most common residues derive from corn, wheat, rice and barley crops [37], and accordingly to the National Statistics Institute [38], Portugal follows the same pattern. On the other hand, with regard to forest occupation, eucalyptus, cork oak and pine trees are the most populated species [38], being therefore the main ones used by timber industry, and consequently, the major components of the resultant residues.

Portugal holds 34 % of the global area of cork oak (*Quercus suber*) forests, being the exporter leader of the tree's bark, designated as cork. The material finds application in a wide range of sectors such as construction, decoration or fashion, but mainly in the winery industry for stoppers production [39]. Being the only renewable tree bark, the cork industry generates high amounts of valuable wastes, essentially in the form of granules and powder, which are therefore also worth of attention.

The brewery industry is a well-developed sector in Portugal, ranked as the ninth European exporter country, accordingly to the Portuguese association of beer producers (APCV) [40]. Once the beer making process involves the cereal barley as substrate, this industry is also revealed as an important source for residues, namely barley straw and barley bagasse.

1.5.2 Residues' main components and properties

Agro-industrial and forest residues, most of which are frequently called lignocellulosic residues, often present similar properties due to their also similar chemical composition. They are fibrous materials whose composition is based on three main elements: cellulose, hemicellulose and lignin. Other components like starch, pectin, proteins, and lipids are often present, however in lower amounts [41]. The percentage of each component deeply differs, depending on several aspects previously referred, but typically, most of the residues possess about 30 to 50 % of cellulose, 20 to 35 % of hemicellulose and 10 to 25 % of lignin [41]. **Table 2** exhibits this variability, where the composition of the three main components in different residues is presented.

Table 2 | Percent composition of lignocellulosic components in various residues.

Residue	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Suberin (%)	References
Sugar cane bagasse	32-55	27-32	19-25	-	[42]
Corn straw	38-40	28	7-21	-	[42],[43]
Corn Husk	31-39	34-41	2-14	-	[42]
Wheat straw	29-38	26-32	16-21	-	[43]
Rice straw	28-36	23-28	12-18	-	[43]
Barley straw	31-45	27-38	14-19	-	[43]
Softwood	45-50	15-20	25-30	-	[21]
Cork	12-13		21-27	45	[44]

Cellulose, the most abundant natural polymer on earth, consists of repeated units of D-glucose held together in a linear chain, of variable length, by β-(1-4)-glycosidic linkages. It is the major component of plant cell walls, insoluble in water and difficult to hydrolyse. It is the responsible for the mechanical strength and chemical stability, due to the hydrogen bonds established between the oxygen atom of one glucose residue and the hydrogen atom of an hydroxyl group from a different cellulose chain. The hydrogen bonds lead therefore to the grouping of different chains, forming the cellulose microfibrils, that are composed of parallel structures both with crystalline and amorphous sections, as represented in **Figure 13**, being the latter more easily degraded [45].

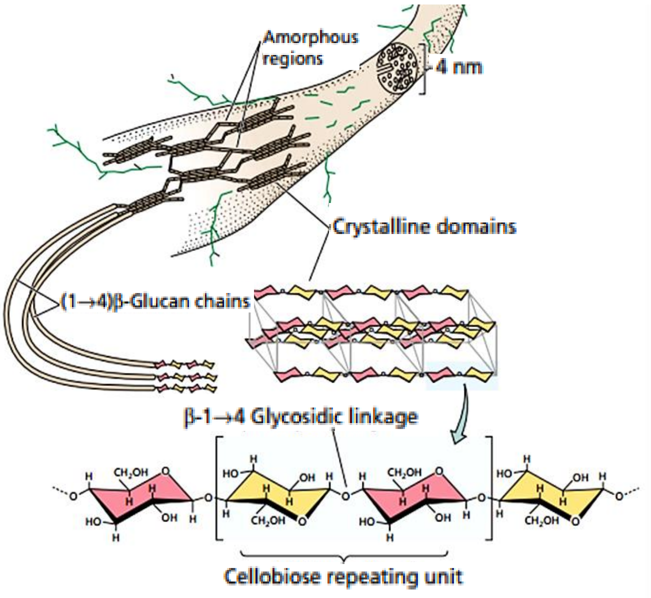


Figure 13 | Structural model of a cellulose microfibril. Retrieved from [45].

On the other hand, hemicelluloses are branched and shorter polymers, composed of different monosaccharides units such as arabinose, glucose, galactose, mannose and, the most important, xylose, also linked by β-(1-4)-glycosidic bonds (**Figure 14**). Contrary to cellulose, hemicelluloses are amorphous structures, partially soluble in water and highly soluble in alkali, being easily hydrolysed and therefore responsible for residues' moisture absorption, biodegradation, and earlier thermal degradation [41]. Hemicelluloses also bind cellulose microfibrils together, acting as matrix to form a cohesive network that provide structural strength of the plant [45].

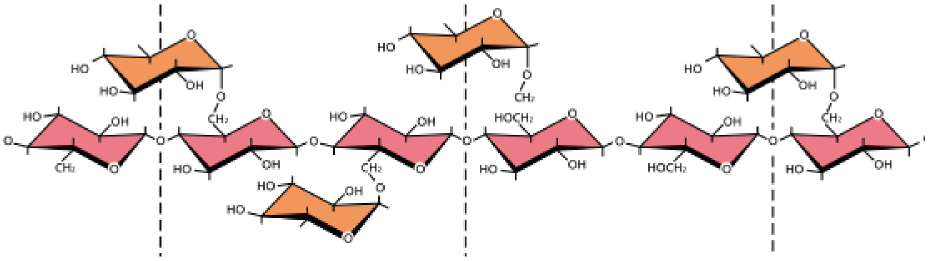


Figure 14 | Representative structure of a hemicellulose: xyloglucan. The presented backbone is composed of linked glucose residues and branched xylose residues. Retrieved from [45].

Lignin, the remaining major component, is a highly branched hydrophobic polymer of aromatic compounds, acting like bonding agent by surrounding and cross-linking the cellulose and hemicellulose fibres. Lignin thus provides structural strength to cell walls, protects from degradation and also serves as a barrier against water penetration [41], [45]. It consists of three phenylpropane units derived from *p*-coumaryl alcohol, sinapyl alcohol, and coniferyl alcohol, whose structures are represented in **Figure 15**. These units may have attached various functional groups, which are bound together through a set of linkages, forming a very complex structure that branches in three dimensions [45].

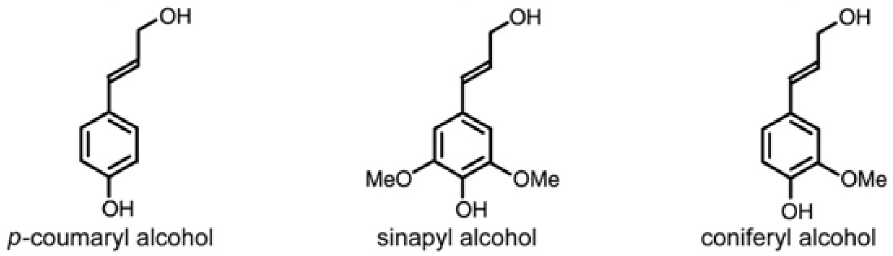


Figure 15 | Building units of lignin.

Besides these three components, an additional element appears in cork cell walls, which plays a central role in its properties. Suberin is a lipid polyester composed of long chain fatty acids, hydroxy fatty and phenolic acids, linked by ester groups. The high cellular content in suberin is thought to be the major responsible for cork's appealing properties, namely its characteristic elasticity, compressibility, low permeability to liquids, and thermal and acoustic insulation capacity, adding therefore tremendous value to this feedstock [44].

In short, the behaviour and consequent application of the residues, are greatly influenced by their chemical composition. In general, residues with higher content in cellulose and higher level of polymerization often hold better mechanical properties.

1.6 Improvement of materials properties

When intending to replace conventional materials for more sustainable ones, it is of major importance that those newly developed hold attractive properties, capable of practising the same functions with similar or improved performance, otherwise the replacement will not be effective nor advantageous. When dealing with green composites, using natural components like lignocellulosic residues as reinforcements, the properties of the resulting materials are, as referred, influenced by the individual properties of the reinforcements themselves, and consequently for their chemical composition. With this, one particular characteristic stands as the major drawback, limiting the performance and the wider application of these reinforcements. Given their higher content on cellulose and hemicelluloses, and consequently high content on hydroxyl functional groups, these often possess a great capability for water uptake. As pointed out in previous sections, this hydrophilicity of the reinforcements has proved to be a major disadvantage because poor interactions with the polymeric matrices are observed, which is normally translated into weaker mechanical properties.

Aiming to amend this situation, several strategies have been attempted to improve the interactions between the different phases, either by addition of coupling agents to the composition or by surface treatment of the reinforcements. These generally enable a better stress transfer from the matrix to the reinforcement and consequently a better performance by green composites, thus enhancing the possibilities for their efficient substitution and thrive.

1.6.1 Maleated Polyolefins

The reaction of maleic anhydride with polyolefins gives rise to powerful compounds, commonly called as maleic anhydride grafted polypropylene (MAPP) or polyethylene (MAPE), depending on the polyolefin used for the reaction. These compounds have proved, several times, to be effective coupling agents when used in green composites manufacture during melting processes, improving their mechanical performance and water absorption [26], [46]. For holding both a polar and non-polar end, these components are able to interact with both phases of the composites, promoting a better connection between them and consequently achieving better adhesions. The anhydride polar ends of maleated polyolefins generally react with hydroxyl groups present in the surface of natural reinforcements, forming ester or hydrogen bonds (**Figure 16**), reducing the hydrophilicity of the reinforcements, whereas the remaining non-polar ends are naturally compatible with the PP or PE matrices, thus promoting grafting [26], [46], [47].

Maleated polyolefins are classified as cost-wise products for the improvement of the interfacial adhesion between composites' phases, since good improvements are achieved at relatively low cost and ease, given that the coupling agents can be directly added during manufacturing without any previous processing step [26]. Despite the observed improved properties, in some cases, the increase in content of the coupling agent does not have a positive effect on the performance of composites [27]. For this reason, an optimization regarding the content in coupling agent for the enhancement of different properties of composites, and for different reinforcements, might be advantageous [26].

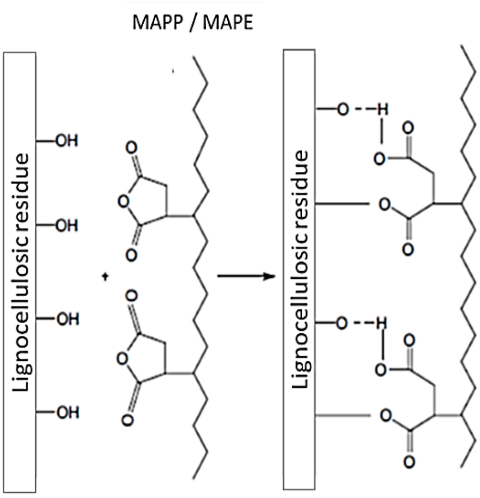


Figure 16 | Interface reaction between lignocellulosic reinforcements and maleated polyolefins. Adapted from [47].

1.6.2 Alkaline treatment

Before being applied in manufacturing processes, the bio-based reinforcements are sometimes soaked in an alkaline solution, such as sodium hydroxide approximately at 5 %. As hemicelluloses are soluble in alkaline solutions, when the reinforcements are previously subjected to this treatment, weigh losses are observed mainly due to removal of these components, but also of waxes, impurities, and even of lignin that may also be soluble in alkali [26], [48]. The removal of such components makes the surface of the reinforcements cleaner and rougher, which may positively influence the interaction with the polymeric matrices, leading to better performances as experienced by Nomai et al. [49]. However, as this treatment increments the amount of exposed cellulose, since the components that surround it are removed, and consequently increases the number of hydroxyl groups exposed, lower interactions with the polymeric matrices and weaker performances are more often observed [26], [48]. Even so, this better exposure might be advantageous when further treatments are to be performed on the reinforcements, thus functioning as a pre-treatment. Therefore, more reaction sites are available, possibly improving the yield of this second treatment and therefore the further reinforcement-matrix adhesion [26].

1.6.3 Silane treatment

Different silane compounds can also be used for improvement of green composites' performance. The normal procedure, represented in **Figure 17,** initially involves the hydrolysis of the silane compounds, with formation of silanol groups, which will afterwards react with the hydroxyl groups of the reinforcements to be used, and forming ester linkages during soaking of reinforcements in the silane solution. This treatment effectively conveys hydrophobicity to the bio-based reinforcements provided by the hydrocarbon chain present in the R group of the silane compound, which will in turn allow a better communication with the polymeric hydrophobic matrix. Through this method, several improvements on composites performance are reported, caused by the improved adhesion between the components that is clearly observed [48].

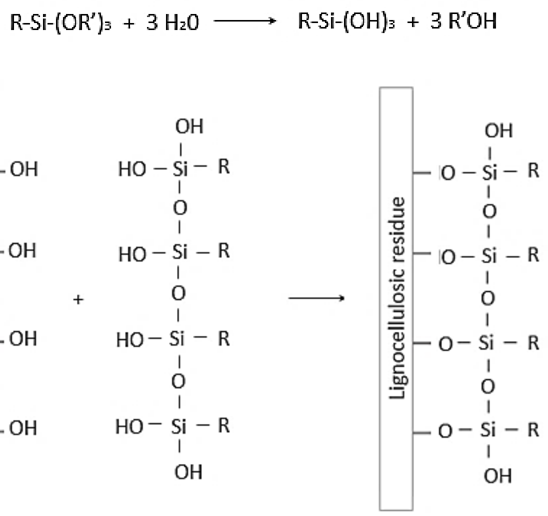


Figure 17 | Interface reaction between lignocellulosic reinforcements and condensed silane compounds. Adapted from [48].

1.6.4 Esterification

Several routes may be followed directing at the formation of ester bonds between the natural reinforcements and the resorted agents. The ester linkages are generally accomplished when carboxylic acids are used, which will once again react with the hydroxyl groups present mainly in cellulose and hemicelluloses, thus reducing the hydrophilicity of the reinforcements with all the benefits attached to the feat. In fact, this is the strategy applied for the manufacture of one of the first bioplastics to be developed: cellulose acetate [50].

The use of esters as reagents is also a suitable approach to obtain hydrophobic reinforcements, being, in this particular case, the chemical modification termed transesterification. The employment of vegetable oils for transesterification reactions is gaining considerable interest, given the fact that these oils, mostly used for food applications, are environmentally friendly compounds, composed of fatty acids of variable length and degrees of saturation, esterified with a glycerol backbone (triglycerides). The transesterification reaction between triglycerides and hydroxyl groups of the reinforcements, accomplished at temperatures over 100 °C, covalently bonds the hydrophobic long acyl chains of vegetable oils to reinforcements' surfaces (**Figure 18**). Furthermore, the use of vegetable oils with higher content on unsaturated fatty acids might be even more advantageous, due to the possible formation of a covalent bonded network by crosslinking reactions between chains [50].

The use of vegetable oils for hydrophobization of lignocellulosic components has been proved efficient, where lower water absorption levels were registered [50], along with better mechanical performances such as higher impact and tensile strengths [51], proving the enhancement of interaction in composites' interface. Jang and Kim [51] could also observe that, with this transesterification reaction, the resulting composites presented higher values of elongation at break than those prepared with untreated reinforcements. This observation was attributed to the plasticization effect caused by the acyl chains introduced in the reinforcements' surface, detail which can amplify the possible application of green composites prepared by such method.

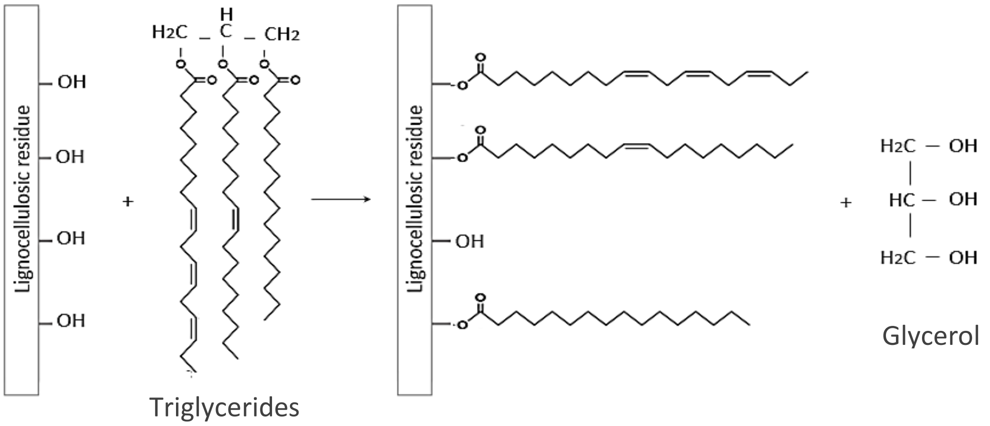


Figure 18 | Interface reaction between lignocellulosic reinforcements and triglycerides from vegetable oils. Adapted from [50].

Several other strategies have been attempted in green composites manufacture, aiming the best possible interaction between the two different phases, or also directed for the improvement of other properties aside from mechanical performance, such as thermal stability or weathering behaviour. Besides, different new strategies are being developed each day, enabling significant advances in the sustainable materials field at a speedy pace, thus contributing to their prosperity and consequent contribution to a greener and more sustainable world.

1.7 Global production and waste management

With the increase in polymer prices, governmental legislations are demanding more sustainable solutions. In parallel, with the available increasing incentives for adjustment of the current leading solutions to bio-based ones, in the latest years, the green composites market has been undergoing a substantial growth. During 2012, the share of green composites in the total European composites' market was already at 15 %, being wood composites the major responsible for that percentage [52]. On the other hand, the bioplastics sector itself is also growing, although at a slower rate. From the 300 million tonnes of plastic produced annually, during 2016, bioplastics' production only accounted for 1 % of that amount. The bio-derived and non-degradable plastics that replicate the commonly exploited synthetic plastics are among the more massively produced [53]. This seems reasonable, considering that the same manufacture equipment and similar properties are achieved.

When approaching sustainable plastics, it becomes essential to discuss the options available for their disposal after useful life, and whereas they are more beneficial and advantageous than the available for traditional plastics. Depending on the type of material, after serving their purpose, they may generally follow at least one of three possible recovery processes: mechanical recycling; organic recycling; or energy recovery [54].

Mechanical recycling is the most resorted strategy for the overall volume of discarded bioplastics. Bioplastics like bio-PET and bio-PE, being among those produced in greater number, are able to enter the recycling streams of their petro-based counterparts. However, a different scenario is observed when dealing with other sustainable materials [55].

Organic recycling, or composting, is the major strategy adopted by the remaining bioplastics and also by fully-green composites, which can be biodegraded without releasing toxic substances. Here, the post-consumer products, along with different bio-waste such as food or agricultural wastes, are degraded in aerobic conditions in industrial composting plants. The composting process, which lasts about 6-12 weeks, involves the degradation of large amounts of organic wastes, used as nutrients by microorganisms like bacteria or fungi and their enzymes, which break it down to the compost, CO_2, water, and energy that is released into the surrounding environment in the form of heat. The compost generated by this strategy, for being nutrient-rich, has great potential to be used in soils as fertilizer, promoting the growth of new plant species which may be further used as renewable feedstock to produce new bioplastics, and therefore contributing to the initiation of a new cyclic course [56].

When none of the above processes can be applied, the discarded sustainable materials can be used for the generation of bio-energy through incineration processes, where wastes volume is significantly reduced by burning and energy is produced, generally in the form of heat or electricity. Ideally, this generated energy is used in the manufacturing process of bioplastics' products, therefore contributing for the closure of a sustainable cycle, as illustrated in **Figure 19** [54]. This is the solution more regularly adopted to the disposal of wastes from green composites possessing synthetic polymers as matrix since, as they are assembled by different components, which cannot be separated and treated individually, they cannot either pass through mechanical recycling nor composting given their polymeric basis having non-biodegradable nature.

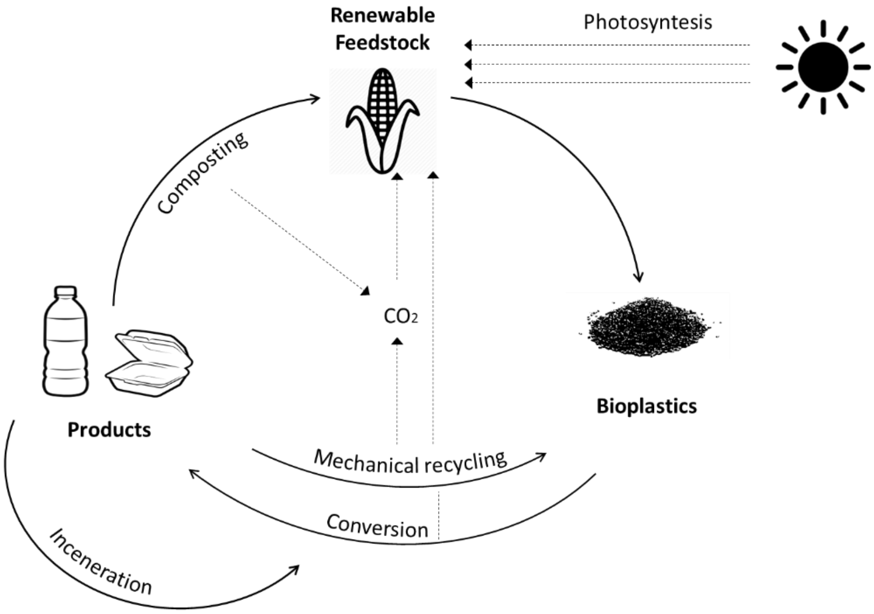


Figure 19 | Bioplastics production and disposal strategies contributing to a closed and carbon neutral cycle. Adapted from [54].

2. AIMS

As discussed in the state of the art section, plastics are one of the main classes of materials responsible for the adverse environmental scenario that we currently across, existing a great necessity of their substitution for more sustainable alternatives. Green composites are considered a valuable front of action to this matter, in which several advances have been reached over the last years. Following this, the major focus of the present work was the development of this type of materials, using agro-industrial and forest residues as reinforcements, and study their ability to substitute the currently leading alternatives. Considering the numerous possibilities of green composites' compositions, and the acknowledged need to improve the adhesion between the components, our main goals were:

(i) Evaluate the impact of the different conditions, such as type and amount of polymer basis and reinforcement, additives, and residues' surface modification, on materials' properties;
(ii) Evaluate the efficiency of vegetable oil treatments on residues hydrophobization to increase the polymer/reinforcement interaction;
(iii) Evaluate the efficiency of oil-treated wood flour as reinforcement for green composites.

To fulfil the outlined goals and reveal the achieved results, the present work is organized in six chapters.

In Chapter 1 an introduction to the work is given. In this, the importance of the portrayed theme is discussed, as well as the available sustainable alternatives for plastic materials. To better understand how these more ecological solutions can replace the currently leading plastic materials, the advantageous and disadvantageous properties of each are also discussed. Lastly, popular approaches reported to improve green composites performances are also presented.

The main aims and the structure of the thesis are introduced in the present chapter (Chapter 2).

In Chapter 3, the materials and methods used in the different stages of the work are presented, namely: the functionalization of residues, the laboratorial scale and twin-screw extrusion processes, and the thermal, chemical, rheological and physical characterizations performed.

The results obtained are presented and discussed in Chapter 4, being divided into three main categories: characterization of mixtures obtained from laboratorial scale extrusion; characterization of residues' functionalization through soybean oil solutions; and characterization of composites developed by twin screw extrusion.

In Chapter 5 the major conclusions obtained from the three stages of the developed work are resumed, as well as some recommendations for future works.

Finally, in Chapter 6, the bibliography consulted is presented.

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Natural solid residues

Throughout the experimental section, three different industrial forest residues available at CeNTI were used for the preparation of green composites, to function as the bio-based reinforcing phase (**Figure 20**): wood flour (WF), cork powder (CP), and cellulose (fibres (CF), and commercial α-cellulose (α-cell), this latter used as control). Despite not being a residue *per se*, CF were used in the preliminary stages given their possibility to be obtained from wastes derived, for example, from the paper industry. We also intended to use residues from agro-industries, namely rice husk, but these could not be effectively grinded so this possibility was discarded. To further study the soybean oil functionalization, α-cell supplied by Sigma Aldrich (USA), was used as the solid substrate.

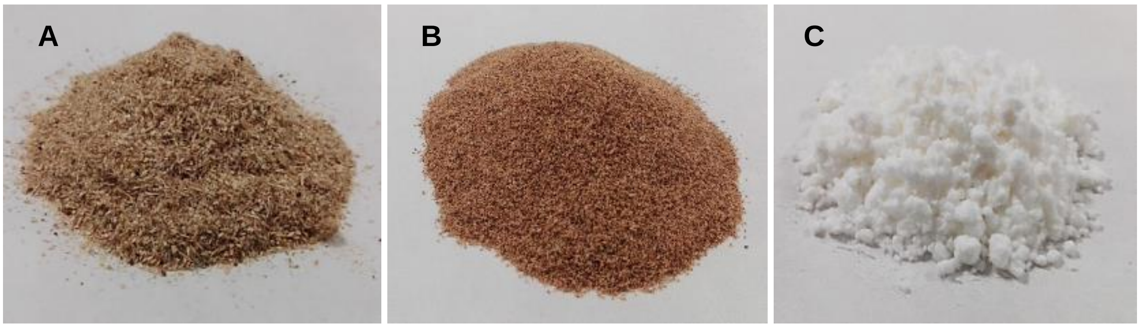


Figure 20 | Industrial forest residues used as bio-based reinforcing phases in the preparation of composites: Wood flour **(A)**, cork powder **(B)**, and cellulose fibres **(C)**.

3.1.2 Polymer materials, coupling agents and plasticizers

Three types of polymers were used as matrix phase for the preparation of composites through the experimental work. During processing at laboratorial scale, a PP homopolymer (ISPLEN® PP 086 Y1E), with a melt flow index (MFI) of 25 g 10 min^{-1} (230 °C, 2.16 kg), and a HDPE (HDPE R4805 D1), with a MFI of 0.55 g 10 min^{-1} (190 °C, 2.16 kg), both supplied by REPSOL (Spain) were used. For this same and subsequent processing stage, a PLA supplied by NatureWorks LLC, USA (PLA 4060D) was used, exhibiting a MFI of 10 g 10 min^{-1} (210 °C, 2.16 kg). ISPLEN® PP 088 Y1E, also supplied by REPSOL, was the PP grade used for twin-screw extrusion, holding a MFI of 31 g 10 min^{-1} (230 °C, 2.16 kg).

When testing laboratorial scale compositions using PP as polymeric matrix, a MAPP (PRIEX 20093), supplied by Addcomp (Netherlands), was in some cases added as coupling agent, having a MFI of 9-13 g 10 min^{-1} (190 °C, 0.325 kg), and a grafted MA content of 0.17-0.21 %.

To achieve better dispersions of the reinforcements on the matrices, two different plasticizers were used: Durasyn 180, supplied by INEOS Oligomers (England), and Citroflex A-4, a biodegradable plasticizer supplied by Vertellus LLC (Belgium), for the formulations using the polyolefins and PLA, respectively, as polymeric matrices.

3.1.3 Reagents

Aiming to improve composites' properties, different surface modifications of residues were attempted. For that purpose, a (3-aminopropil)triethoxysilane (APTES), purchased from Sigma-Aldrich (China), and a commercially available refined soybean oil (OliSoja, Portugal) were used, for silane and transesterification methods, respectively.

3.2 Methods

3.2.1 Residues' surface modification

3.2.1.1 Silane treatment

To reduce the characteristic hydrophilicity of the natural residues, and possibly, afterwards improve their adhesion to polymers, a silane treatment was attempted. For such purpose, silane was added at 1 or 4 wt.%, relatively to residue content, to an ethanol/water solution (70/30 vol.%), and the pH of the resultant solution was then adjusted with acetic acid to 4 in order to promote the hydrolysis of silane. After continuous agitation of the silane solution for approximately 30 min, the natural residues (WF or CP) were added individually and soaked for 3 h, under continuous stirring. After this time, the solution was filtered and washed 3 times with distilled water.

3.2.1.2 Alkaline treatment

An alkaline treatment was also tested, in which the residues (WF or CP) were added to a 5 % (w/v) NaOH solution and left under continuous stirring for 24 h. Afterwards, the residues were filtered and washed with distilled water, followed by washing with a 1 % (v/v) acetic acid solution, and washed again with distilled water to remove unreacted NaOH solution from the residues.

3.2.1.3 Transesterification with soybean oil

To improve hydrophobization of natural residues with vegetable oil, and test its posterior use for composites processing, two methods were evaluated, differing on the solvent used to promote transesterification. A solution of soybean oil/ethanol at 5 wt.%, and a solution of soybean oil/acetone at 1 wt.%, both related to oil content, were prepared. The solution using ethanol as solvent was heated under stirring at 70 °C to improve oil mixing. The natural residues (WF or CF), previously dried in an oven at 70 °C for approximately 24 h, were added to the solutions, ensuring that the oil solutions were just enough to completely cover them. After this, the suspensions were stirred for 5 min and air dried till most of the covering solution evaporated, and then reacted in an oven at 110 °C for approximately 1 h. To remove unreacted oil content, the dried residues were lastly washed with ethanol or acetone, depending on the solvent used, followed by washing with distilled water and once again with the respective solvent.

For a more comprehensive study of this functionalization strategy, small quantities of WF or α- cell, unmodified (U-) or previously treated with alkaline solution (NaOH-), were further treated with different oil solutions, as described in **Table 3**, following the above described method. In this study, α-cell was the used substrate. In this case, the use of catalyst (NaOH), and the reaction time of the oil solutions were also studied. For the solutions using NaOH, this compound was previously added to ethanol, at 1 wt.% relative to solvent content, and heated at 70 °C till dissolved. The oil was then added to these solutions. For the reaction time study, the oil solutions were kept in agitation, at 70 °C, for 1 h, before proceeding to the addition of the solid residues.

Table 3 | Composition of the different solutions prepared to study residues hydrophobization with soybean oil, and respective reaction conditions. Both oil and catalyst percentages are relatively to solvent content.

Code	Composition			Conditions	
	Solvent	*Oil content (wt.%)*	*NaOH (wt.%)*	*Reaction time (h)*	*Residues pre-treatment*
WF/α- cell + E	Ethanol	-	-	-	-
WF/α- cell + E-Oil (5 %)	Ethanol	5 %	-	-	-
WF/α- cell + E-Oil (10 %)	Ethanol	10 %	-	-	-
WF/α- cell + E-Oil 1h	Ethanol	5 %	-	1	-
WF/α- cell + E-NaOH + Oil	Ethanol	5 %	1 %	-	-
WF/α- cell + E-NaOH + Oil 1h	Ethanol	5 %	1 %	1	-
NaOH-WF/α- cell + E-NaOH + Oil	Ethanol	5 %	1 %	-	Alkaline
NaOH-WF/α- cell + E-NaOH + Oil 1h	Ethanol	5 %	1 %	1	Alkaline
WF/α- cell + A	Acetone	-	-	-	-
WF/α- cell + A-Oil (2.5 %)	Acetone	2.5 %	-	-	-
WF/α- cell + A-Oil (5 %)	Acetone	5 %	-	-	-

3.2.2 Composites processing

3.2.2.1 Extrusion at laboratorial scale and mixtures' characterization

Given the wide range of possibilities to combine composites' components, before going to the regular processing techniques, different compositions were pre-tested at laboratorial scale, aiming to reduce the possibilities for further processes by choosing beforehand the most interesting ones. Having this in perspective, in this previous stage, different compositions were tested regarding: the type of polymer and reinforcement in use; functionalization of the natural reinforcements; use of additives like plasticizers or coupling agents; the content of each components; and the processing conditions. To avoid confusion with the composite materials resultant from posterior phases, the materials obtained in this first stage are from now on referred to as mixtures.

In the tested mixtures, three different polymers (PP, PE, and PLA) were used as matrix. Besides being the most reported polymeric matrices when addressing green composites, the polyolefins PP and PE were mainly used due to their widespread application, low cost, ease of process, and extensive manufacture practice in our laboratory. In turn, PLA was used for its natural basis and capacity to biodegrade, enabling therefore the achievement of fully-green biocomposites.

Before processing, PLA granules and all the natural residues (WF, CP, or CF) used were dried in oven at 45 and 70 ˚C, during 5 and 24 h, respectively, to minimize moisture content. The natural residue content of the attempted mixtures was varied between 0-30 wt.%, where more emphasis was given to mixtures with 10 and 20 wt.% of the reinforcing phase. Whenever required, the adequate plasticizer with respect to the polymeric matrix used, was added in quantities between 5-30 wt.%, having been given major focus to contents of 5 and 10 wt.%. For PP mixtures, MAPP was in some cases also added, mostly at 5 or 10 wt.% in content. All components were manually pre-mixed to promote better dispersions and safeguard that the proportions between them are maintained, being posteriorly added to a LME laboratory mixing extruder (QualatiTest™) (**Figure 21**). The processing temperatures were tested between 170-200 °C and the screw was kept at maximum speed for all tests, to promote better dispersions. The specific percent composition of all tested mixtures are more extensively presented in **Appendix A**.

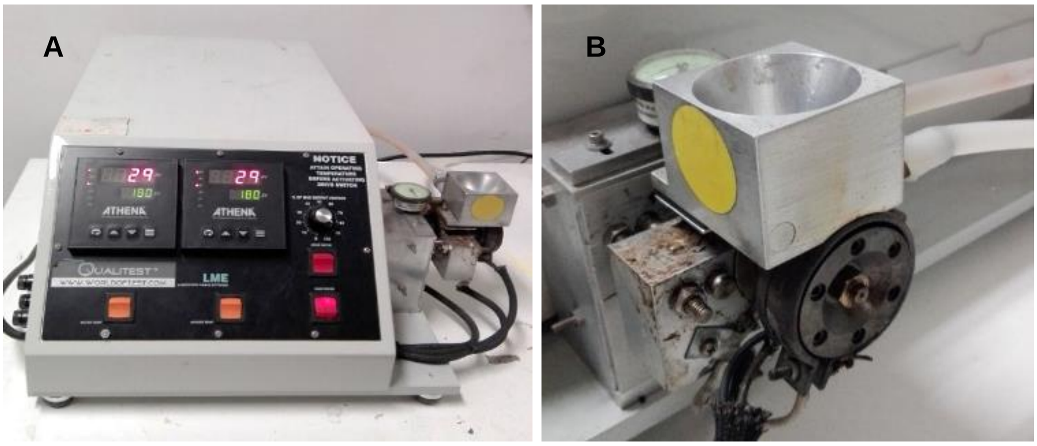


Figure 21 | LME laboratory mixing extruder **(A).** Feeder and die are presented in detail **(B)**.

The resultant mixtures were characterized, although in a qualitative manner, by observing their ease of processing (ease of flow) and surface roughness, as well as by exploring their mechanical behaviour when manually stretched or bended, therefore analysing their resistance to break and flexibility. To accomplish a more standardized evaluation, a scale for each of these characteristics was set, being this scale presented in Chapter 4.

3.2.2.2 Twin-screw extrusion

The up-scale of several compositions was tested, having narrowed down the possibilities to the formulations using PP and PLA as matrix phase. WF without any previous treatment, referred to as unmodified wood flour (U-WF), and previously transesterified with 5 wt.% soybean oil/ethanol solution (Oil-WF), were used as natural based reinforcing phases. To some compositions using PLA, the respective plasticizer, Citroflex A-4 (C.A4), was also added. Before compounding, PLA granules and all the natural residues were dried in oven at 45 °C and 70 °C, to reduce moisture content, during approximately 5 h and 24 h, respectively. All compounding processes were carried out using a co-rotating twin-screw extruder (Rondol), with a screw diameter of 21 mm and a L/D of 25. The resulting composites, leaving the extruder in filament form, were further cooled in a water bath, and finally fed to a grinder (Rondol), to obtain the intended green composites in pellet form. **Table 4** summarizes all the tested formulations and the processing conditions used.

Table 4 | Percent composition of the mixtures processed by twin-screw extrusion and respective processing conditions. The presented temperature profile describes the temperatures set in the several heating zones of the extruder, from the main feeding zone to the die.

Code	**Composition**			**Extrusion Conditions**	
	Polymer (wt.%)	*Residue* (wt.%)	*Plasticizer* (wt.%)	*Temperature profile* (°C)	*Screw speed* (rpm)
PP/U-WF (10)	90	10	-	165/165/170/175/230/235	300
PP/U-WF (15)	85	15			
PP/U-WF (20)	80	20			
PP/U-WF (25)	75	25			
PP/Oil-WF (10)	90	10	-	165/165/170/175/230/235	300
PP/Oil-WF (15)	85	15			
PP/Oil-WF (20)	80	20			
PLA/C.A4 (10)	90	-	10	165/170/170/170/170/170	150
PLA/U-WF (10)	90	10	-	165/170/170/170/170/170	250
PLA/U-WF (15)	85	15	-	165/170/170/170/170/170	150
PLA/U-WF (10)/C.A4 (10)	80	10	10		
PLA/U-WF (15)/C.A4 (10)	75	15	10	165/170/170/170/170/160*	200
PLA/Oil-WF (10)	90	10	-	165/170/170/170/170/160*	270
PLA/Oil-WF (15)	85	15	-		
PLA/Oil-WF (10)/C.A4 (10)	80	10	10		

* Temperatures of the die were reduced to avoid WF degradation, since in these compositions, as screw speed was increased, the temperatures of mixtures in the extruder path are above the established.

For the compounding processes, the extruder was equipped with two automatic volumetric feeders (Rondol), used to add the polymers and the WF separately, whose feeding rate was synchronized, so that the leaving extrudates held the intended polymer/residue ratio. The calibration curves of the two polymers, U-WF and Oil-WF used for the calculations are presented in **Appendix B.** For the formulations using PP as matrix, the two feeders were placed at different areas in the extruder, as schematized in

Figure 22, where the polymer granules were added at the beginning of the path, by the main feeder, whereas the WF was added later, at the second feeding zone, to reduce the residence time in the extruder. On the other hand, for the formulations using PLA as matrix, given the low MFI of the used grade, all the components were added with the respective volumetric feeder at the main feeding zone. For the compositions including plasticizer, this was also added at the main feeding zone, by a synchronized peristaltic pump (**Appendix B**). Moreover, **Figure 22** also presents a schematization of the screw profile, holding two different types of elements, which ensure that the different components of the formulations are well mixed, while also being boosted towards the die of the equipment.

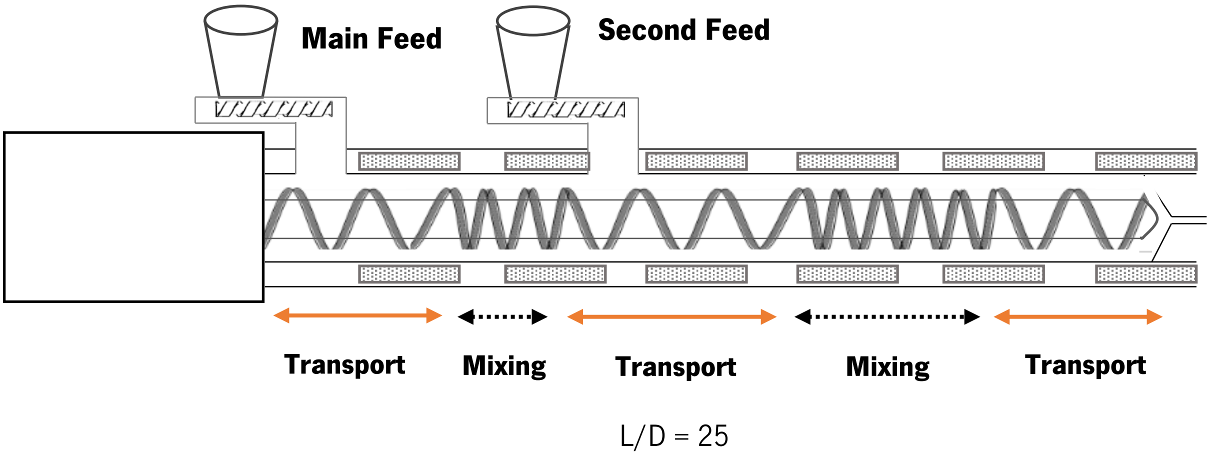


Figure 22 | Illustration of the equipment used to obtain the different composites.

3.2.2.3 Compression moulding

Adequate surfaces were required to evaluate the wettability through water contact angles measurement, thus these were prepared by compression moulding of granules of the different compositions obtained by twin-screw extrusion. A Galaxy XL0508 hydraulic press from Acosgraf (Portugal) was used to produce plates with rectangular geometry of approximately 6.5x11 cm and 1 mm of thickness. The pellets, previously dried for 24 h at 40 °C, were placed between two aluminium plates, used as mould, with the same dimensions, and heated at 210 °C, 4.5 bar, for 2.30 min. After pressure removal, the system was cooled at ambient temperature for about 5-10 min, and the aluminium plates were finally removed (**Figure 23**).

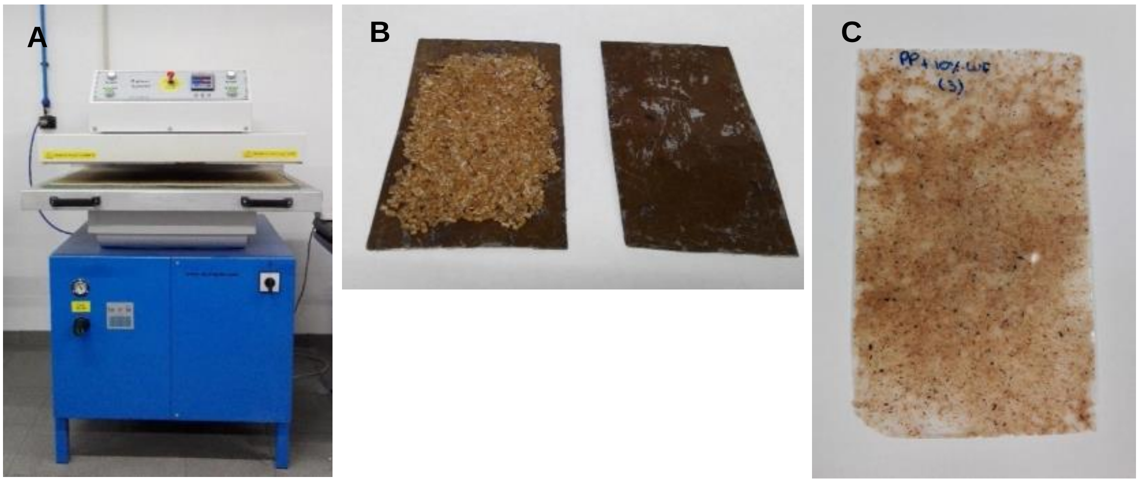


Figure 23 | Galaxy XL0508 hydraulic press **(A)** and forming system used, with aluminium plates where the granules are placed between them **(B)**. This result in compression moulded plates, with 6.5x11 cm, as exemplified in **(C)**.

3.2.3 Characterization methods

3.2.3.1 Chemical properties

Fourier transform infrared spectroscopy (FTIR)

To study the effect of the natural residues' functionalization with soybean oil solutions, the samples were analysed with a Spectrum 100 (Perkin Elmer) spectrometer with an attenuated total reflectance (ATR) accessory. For each sample, 8 scans were recorded at wavenumbers between 650 cm^{-1} and 4000 cm^{-1}, with a resolution of 4 cm^{-1}.

3.2.3.2 Thermal properties

Thermogravimetric analysis (TGA)

To study the thermal stability and degradation profile of different samples TGA analysis were carried out using a Pyris 1 thermogravimetric analyser (Perkin Elmer). Each measurement was carried out under a nitrogen atmosphere from 25 °C to 700 °C, at a 10 °C min^{-1} or 20 °C min^{-1} heating rate. The unmodified and treated natural residues, the matrix polymers, and all formulations obtained by twin-screw extrusion, were analysed by this method.

Differential scanning calorimetry (DSC)

The DSC experiments were performed in a differential scanning calorimeter Pyris Diamond (Perkin Elmer) for the evaluation of thermal transitions of the developed compositions. Samples of 6-12 mg were used. Two heating scans were performed, with one cooling step between them, under nitrogen atmosphere (20 mL min^{-1}), from 0 °C to 200 °C, at a 10 °C min^{-1} heating rate. The first heating rate was used to eliminate the history of the samples acquired during compounding, and the second was used to determinate the glass transitions temperatures (Tg) of the PLA composites, the melting temperatures (Tm), and the respective melting enthalpy values (ΔHm) of the PP composites. The temperature of crystallisation (Tc) and the crystallisation enthalpies (ΔHc) were obtained from the cooling scan. From the ΔHm values, it was possible to determine the degrees of crystallinity (Xc) of each composition with PP basis, based on a 100 % crystalline polymer, using the following equation:

$$Xc\ (\%) = \frac{\Delta Hm}{\Delta Hm^{\circ} \times (1 - w)} \times 100 \qquad (2.1)$$

where ΔHm is the observed melting enthalpy per gram of sample, ΔHm° is the melting enthalpy of fully (100 %) crystalline polypropylene (209 J g^{-1}), and w is the weight fraction of wood in the composites [57].

3.2.3.2 Physical properties

Water compatibility

To qualitatively evaluate the hydrophobization efficiency of the residues treated with soybean oil solutions, an approximate amount of 10 mg of each residue, unmodified and treated with the different oil solutions prepared, were added to 5 mL flasks. The flasks contained equal amounts of two immiscible solvents, water (1 g cm^{-3}) and petroleum ether (0.65 g cm^{-3}), with different densities and polarities. After adding the residues, the solutions were vigorously mixed and left to rest for residues deposition in the compatible liquid.

Moisture content (MC)

The percentage of moisture content of each composition was determined, using a MAC 110/2/NH balance (RADWAG, Poland), where approximately 10 g of each sample were heated from ambient temperature to 115 °C, until constant weight was reached. Before the analysis, all samples were heated for 24 h at 40 ˚C. Then, the humidity gain measurements of the samples were performed, at 2 h intervals, during 6 h of air exposure. The temperature and relative humidity in the room were near 25 °C and 50-55 %, respectively. A final measurement was performed after 24 h of air exposure and at least 3 measurements were recorded for each sample.

Water absorption (WA)

To determine the capacity of the developed composites to absorb water, approximately 15 and 20 g of granules of the different materials, with PP and PLA basis respectively, were immersed in distilled water, at 25 °C for 24 h. Two specimens of each composition were analysed. Before being immersed in water, all materials were dried in an oven at 40 °C for 24 h, and each specimen was then weighted. After the 24 h immersion period, the samples were removed from water, gently blotted with tissue paper to remove the excess of water at the surface, and were immediately weighed. The WA levels were calculated as follows:

$$WA\ (\%) = \frac{Ww - Wd}{Wd} \times 100 \tag{2.2}$$

where Ww is the wet weight, in grams, of each specimen after being immersed in water, and Wd corresponds to the dry weight, in grams, of the same specimen before the immersion and after being dried in the oven.

Water contact angle (WCA)

The wettability evaluation of the materials was determined by measuring the contact angles between the surfaces of the compression molded plates and water droplets. The measurements were performed on six selected compositions, on uniformly dispersed surface areas, (the two bare polymers; PP compounded with 15 wt.% of U-WF and Oil-WF; and PLA compounded with 10 wt.% of U-WF and Oil-

WF). The analysis were conducted by sessile drop method, using a One Attensio contact angle meter (Biolin Scientific, Finland). The WCA were measured using water droplets of 3 μL placed in at least six positions of the samples.

3.2.3.3 Rheological properties

Melt flow index (MFI)

To evaluate the fluidity of each composition, as well as the fluidity of the two neat polymers used as matrix phase, a CEAST MF20 (Instron, USA) was used. The measurements were conducted according to ASTM D1238, at 230 °C and 190 °C, for PP and PLA compositions respectively, both under a 2.16 kg load. In each measurement, a pre-heating time of two minutes was carried, before applying the pressure. The determination of the MFI values was obtained by weighting the melts that left the die with a defined volume. Each measurement was repeated at least three times.

3.2.3.4 Morphological properties

Scanning electron microscopy (SEM)

To analyse the interfaces of the compositions obtained by twin-screw extrusion, a small quantity of granules from each composition was embedded in an epoxy resin (EpoFix Kit, from Struers). The resin allowed the hardening and immobilization of the granules, so plastic deformation could be minimized during fracturing. It was ensured that granules were in fact fractured and not only separated from the resin.

The fractured surfaces from each composition were then characterized using a desktop scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) analysis (Phenom ProX with EDS detector (Phenom-World BV, Netherlands)). All results were acquired using the ProSuite software.

The samples were added to aluminium pin stubs with electrically conductive carbon adhesive tape (PELCO Tabs™), with the excess removed using compressed air. Samples were imaged without coating. The aluminium pin stub was then placed inside a Phenom Charge Reduction Sample Holder, and different points or areas for each sample were analysed.

4. RESULTS AND DISCUSSION

4.1 Laboratorial scale extrusion

Several mixtures were first tested using small-scale extrusion aiming to scrutinise the wide range of combining possibilities and thus, understand how the resultant mixtures behaved depending on those conditions. As the characterization of all mixtures was obtained in a qualitative manner, i.e. by simple observations of their processing characteristics and mechanical behaviour, a classification range for all tested features was established to accomplish a more consistent evaluation, being presented in **Table 5**. The results attributed to these properties, for all the tested mixtures, including those where no natural residues were added, are summarized in **Appendix C** for a more in-depth examination.

Table 5 | Defined scale for evaluation of the four properties under study in laboratorial scale mixtures. All mixtures were scored with a value between 0 and 5, for each of the properties listed.

Property	**0**	**5**
Processing	Very viscous mixtures; Difficult to process, presenting high resistance to flow through the die.	Very fluid mixtures; Mixtures present low resistance to flow, easily passing through the die.
Resistance to break	No resistance; Filaments break by any force applied.	Very tough mixtures; Filaments withstand intense applied forces without breaking.
Flexibility	Very stiff mixtures; Filaments don't bend when flexural force is applied.	Very flexible mixtures; Filaments easily bend, without breaking, when flexural force is applied.
Surface roughness	Smooth surface.	Very rough surface.

4.1.1 Processing

One of the first effects observed when processing natural residues together with bare polymers, independently of their type, is that the actual processing of mixtures is hindered. The addition of these reinforcements may work as barrier to the normal flow of the material through the die, generating more resistance and increasing the pressure on the extruder output. Thus, the exit of materials from the equipment is hindered. This effect is noticeably dependent on residue content. Namely, more viscous mixtures were obtained for higher contents of residues, and so, for mixtures possessing 20 wt.% of the reinforcing phase, lower flow rates were achieved, and lower levels of ease of processing were registered. Due to different MFI's, the three bare polymers flow with different rates when in the molten state. For that reason, the levels of ease of processing attributed to mixtures using each one of them is, as expected, also different. Mixtures containing the polymer PP, are expected to flow more easily than mixtures with PE or PLA, with the same amount of residue, given the lower MFI of these two polymers. This information is gathered in **Appendix C.2**. Indeed, as way of example, a higher level of ease of processing was attributed to the mixture containing 20 wt.% of WF and PP as matrix phase, relatively to those having the same composition but with PE or PLA (a level of 2 was registered for the PP mixture, and 1 for the other two polymers). This easier flow of PP mixtures at small scale already indicates that this polymer will be a good choice as matrix, for reproduction of mixtures by twin screw extrusion, since it is expected to offer fewer complications during processing.

Despite the particle size and shape differences of the natural residues used, very similar levels of ease of processing were attributed to mixtures using the same polymer and the same amount of the different residues. This thus suggests that the residue amount exhibits a greater observable impact than the type of residue *per se*. However, for a more accurate evaluation, further studies on the MFI of the different mixtures would be valuable to correlate these residues' shape and size parameters to their impact on the ease of flow of the resultant mixtures. Despite the similar results, it is known that these parameters, among others, play important role on the viscosity of composites, as already stated by Klyosov [58].

During processing of the different mixtures at laboratorial scale, one key outcome was also observed for all mixtures, i.e. independently of polymer or residue nature. This outcome greatly influenced not only the processing phase but also most of mixtures' properties (mechanical performances and visual aspects). After manual mixing of polymer granules with the residues, at the intended proportions, the formulations were added to the extruder feeder. These could then reach the extruder screw, by gravity, and be melt-mixed while being forced to leave the equipment through the die. However, being the polymer granules considerable denser than the residues, these reached the screw of the extruder first, leaving most of the residue on the feeder, which would then reach the screw mainly in the later phase of the process. This inconsistent feeding of components completely changed the intended proportions of the mixtures, resulting in filaments mainly composed by polymers or residue particles, depending if they were collected in earlier, or later stages of the process, respectively. This inconsistent composition of filaments, in the same mixtures, is represented in **Figure 24**. As expected, this effect is also intensified for mixtures with higher residue content. In these mixtures, the filaments collected at final stages are mainly composed by compacted residues. These are therefore more difficult to process, since the elements that play major role on carrying the residues throughout the extruder are the polymers in their molten state, which are almost absent in this later stage.

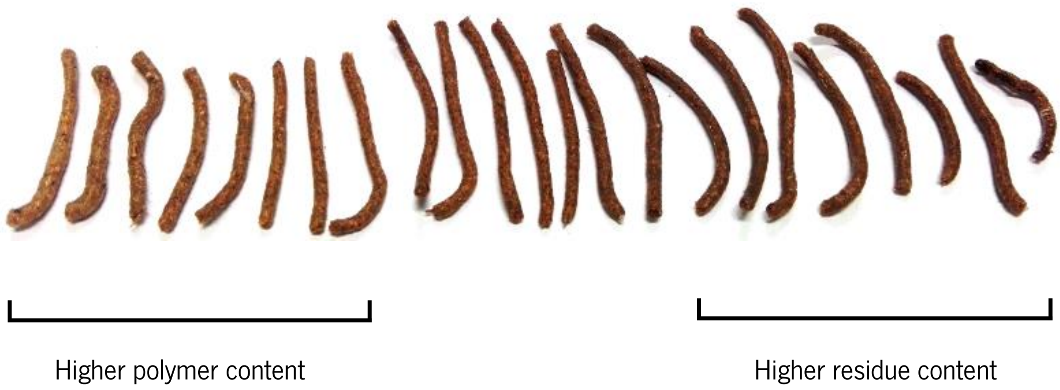


Figure 24 | Composition of mixtures obtained by laboratorial scale extrusion. The represented filaments correspond to the mixture of polyethylene with 20 wt.% in content of wood flour.

4.1.2 Physical properties and mechanical performance

Besides influencing the processing stages, the residues content can also affect other mixtures properties. The visual aspect of the resulting materials, namely the colour and surface roughness of filaments, are among these properties. As can be seen in **Figure 25**, for higher loads of the reinforcing phases, colour and surface roughness are clearly intensified.

Figure 25 | Colour and roughness intensification with increasing residue contents. Polypropylene with 10 wt.% **(A)** and 20 wt.% **(B)** of wood flour.

However, for mixtures with different polymer basis, these properties are felt differently. While surface roughness of mixtures with PP are more affected by residue content, the same is not true for mixtures with PE or PLA, for which slightly more smooth surfaces are achieved. This can be observed in **Figure 26**, where the surface of filaments resultant from mixtures of the three different polymers with 20 wt.% of WF particles are shown. The smoother surfaces obtained in mixtures with PLA and especially with PE may be driven by the lower MFI of these polymers, which, by flowing at slower paces, enabled better dispersions of the residues in the laboratorial scale tests. However, to our knowledge, no correlation between these parameters have been reported.

Figure 26 | Roughness of mixtures with 20 wt.% of wood flour and the three polymer basis: polypropylene **(A)**, polyethylene **(B)** and polylactic acid **(C)**.

Regarding the type of residue, differences on surface roughness are once again more evident for mixtures using PP as matrix phase. CP seems to provide more rough surfaces than WF particles, while CF have no significant influence on the roughness of mixtures' filaments, remaining quite smooth. This differential visual aspect of PP mixtures according to residue nature can be observed in **Figure 27**. For

PE or PLA mixtures, roughness levels between mixtures with CP and WF are very similar, although lower levels of this aspect are also achieved for mixtures with CF.

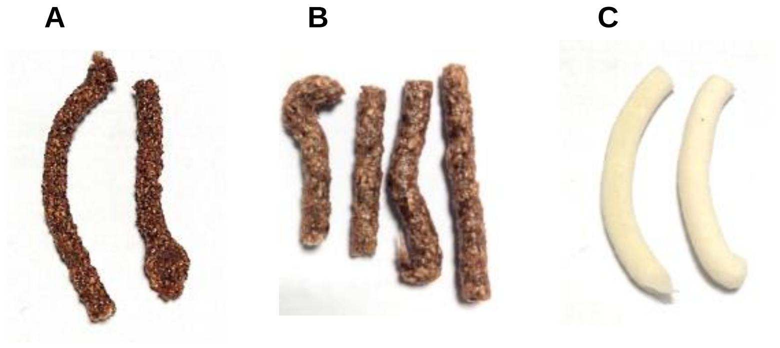


Figure 27 | Roughness of mixtures with polypropylene and 20 wt.% of the three residues: cork powder **(A)**, wood flour **(B)** and cellulose fibres **(C)**.

The resistance to break of mixtures' filaments is one of the most important features to evaluate, given that it represents part of the mechanical performance of the compositions. This feature is also one of the most influenced by the content on the reinforcing phases. The resistance of mixtures is lower for higher contents of residues, since the volume of polymer granules that keeps residues together is lower. For that reason, the filament mixtures are more easily separated and more prone to fail when pressure is applied. Zhang, Zhang & Choi [59] demonstrated this, having reported lower strain at break percentages in PE composites with increasing wood content, i.e materials with higher WF content hold less distorting forces (fail more easily). Analysing the values of resistance at break attributed to control mixtures on **Appendix C.1**, it can be observed that the levels were similar for the three tested polymers, however the polymer PP showed to be slightly less resistant. For this reason, it is predictable that the addition of natural residues to this polymer will result in more fragile materials, which could be verified, for instance in mixtures containing 20 wt. % of CP. Here, for filaments containing PP as matrix phase it was attributed a resistance level of 3, while for those having PE or PLA, higher values were registered, namely 4/5 and 4, respectively. On the other hand, regarding the type of residue, CP seemed to be the least valued residue when analysing this property, This is probably due to CP granular format that do not allow good depositions on the melted polymers, as a result of less available surface area, but also to its lower cellulose content [21], [28]. In fact, to mixtures containing cellulose fibres as reinforcing phases, it was attributed the highest levels of resistance at break, thus emphasizing that this component is, as expected, essential for better mechanical performances.

When adding natural residues to polymers, considering the reported works on this matter, it was expected to achieve stiffer materials [21], [59]. Nevertheless, in the filaments resultant from the mixtures herein used, to our perception, an increase in their flexibility was observed, since it was possible to bend them more easily than the bare polymers. This effect was more easily noticed for mixtures using PE as matrix, since the bare polymer was very difficult to bend. As an example, when adding 20 wt.% of WF to this polymer, the registered flexibility level increased from 0/1, achieved by the control mixture with no residue added, to 2/3 (**Figure 28**). The increase in flexibility with the addition of natural residues was also noticed for PP mixtures. However, it is important to notice that the bare polymer already exhibits some flexibility *per se* and therefore the changes were not so evident. On the other hand, mixtures containing PLA as matrix phase were those experiencing the lowest levels of flexibility, which seems reasonable considering that PLA is the stiffer polymer among the three used. Moreover, it could be noticed that the higher levels of flexibility were achieved for mixtures with 10 wt.% in residue content, for all polymer basis used, given the fact that, for higher residue contents, the filaments would break more easily when force was applied. This increase in flexibility of filaments, especially for PP and PE mixtures, seems a very interesting feature when evaluating application opportunities for the materials, enlarging their possible fields of application. However, regarding the influence of the type of residue on mixtures' flexibility, no correlation could yet be identified for compositions containing only polymer and residue particles.

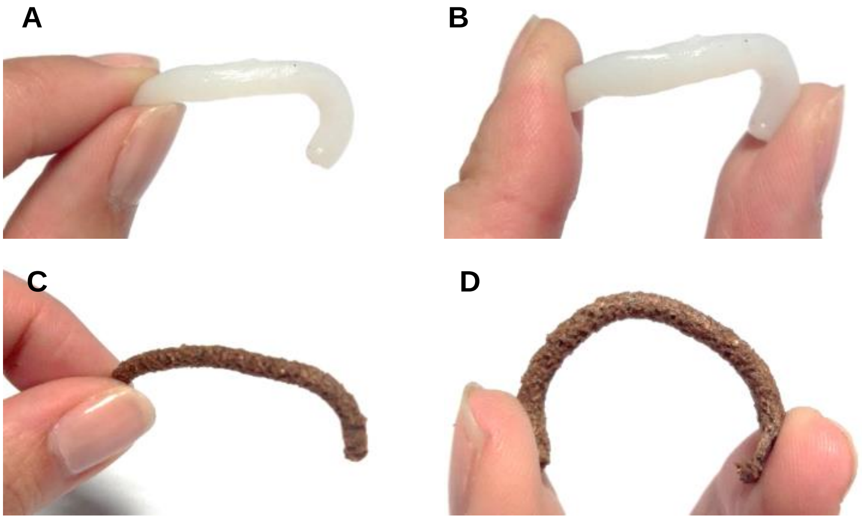


Figure 28 | Initial position and flexibility of polyethylene **(A)**, **(B)** and polyethylene compounded with 20 wt.% of wood flour.

4.1.3 Addition of plasticizers

To enhance the composition inconsistency of the extruded mixtures obtained during processing, additional components were added, being referred to as plasticizers. Given their viscous nature, these aid the adhesion of residues to the polymer granules. Different plasticizers were used, according to each polymer type, namely Durasyn 180 for PP and PE, and C.A4 for PLA mixtures. These plasticizers were manually pre-mixed with the granules, before adding the residues. Once the residues were more in contact with polymer granules, the separation of the different components in the feeder was not so evident, leading to mixtures' filaments with more consistent composition and better dispersions of the residues, as demonstrated in **Figure 29.** When compared to those achieved from mixtures without plasticizers, previously shown in **Figure 24**, the effective role of these components is evidenced.

Figure 29 | Composition of mixtures obtained with plasticizers supplementation, by laboratorial scale extrusion. The represented filaments correspond to the mixture of polyethylene with 20 wt.% in content of wood flour and 10 wt.% of Durasyn 180.

This effect was clearly observed for mixtures using PP or PE as matrix phase. In the case of PLA, the compatible plasticizer was more liquid, and thus, the adhesion of residues to polymer granules was less efficient, leading to weaker dispersions. Therefore, the filaments of these mixtures leaving the extruder in the final stages, still possessed higher amounts of residues than the former. Even so, the addition of C.A4 to PLA mixtures diminished the heterogeneity of the composition during processing.

It was observed that, for mixtures possessing 10 and 20 wt.% of residues, independently of the type of polymer or residue, the most suitable amounts of plasticizer were 5 and 10 wt.%, respectively. With these amounts of plasticizer, better dispersions of residues were obtained, while maintaining other properties at acceptable levels, such as the ease of processing. As the accumulation of residues in the feeder during processing was, as expected, higher for mixtures composed of 20 wt.% of residues, higher amounts of plasticizers were tested. However, as the volume of residue was much higher than that of polymer granules, this strategy proved to be insufficient. In these mixtures, the surfaces of polymer granules were already completely covered by residue particles, thus, the addition of extra amounts of plasticizer only led to aggregation of the residue particles.

By promoting better dispersions, the addition of plasticizers to the mixtures had an expected positive effect on their ease of processing, facilitating their flow through the equipment. Yet, despite the weaker dispersions obtained by PLA's compatible plasticizer, the positive effect of its addition was especially evident, having been observed an incredible leap on mixtures' processing levels. Given its low MFI, the processing of PLA by itself was already difficult, which was then aggravated by the addition of residues. Thereby, the easier flow (easier processing) observed on PLA mixtures with the plasticizer, represent the powerful role of this additive as lubricant, justifying its addition, even though it did not serve efficiently the initial intended purpose (improvement of residues dispersion). In **Appendix C.1**, this cooperative influence of C.A4 can be easily noticed, since the registered processing levels of PLA's control mixtures shifted from 1/2, in its absence, to 4, by adding 5 or 10 wt.% of this plasticizer. Maiza et al. [60], also observed an improvement on processing of PLA formulations with a compatible plasticizer, by the achievement of higher MFI values (easier flow). This effect is observable given the higher mobility of polymer chains obtained with the addition of the plasticizer.

As for the remaining properties under study, the addition of plasticizers to the mixtures was also helpful. Higher levels of flexibility, and lower levels of surface roughness were registered, in comparison to mixtures having the same composition, but without plasticizer. This can be confirmed by **Figure 30**. The improvements observed are most probably driven from the plasticizers themselves, which have a special impact on flexibility. In fact, plasticizers are known to improve polymers flexibility and ductility, amongst other properties, by lowering their Tg [17]. However, the better dispersions of residues achieved with the use of these additives are also responsible for the improvement of mixtures' properties, as previously discussed.

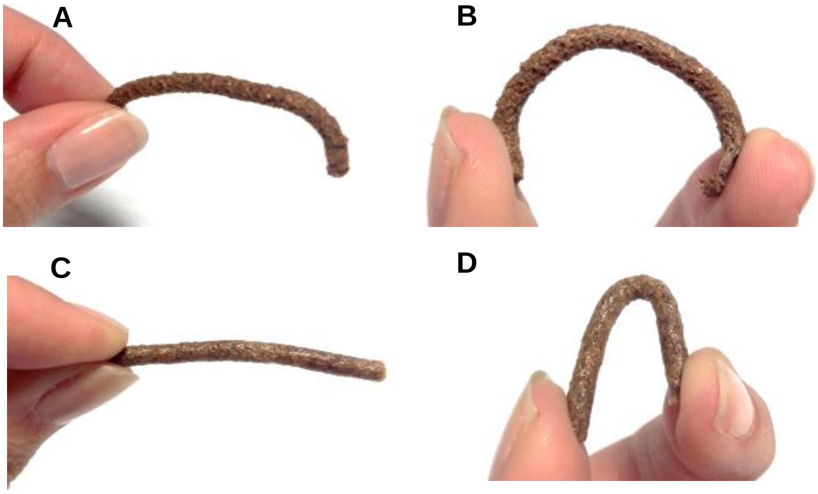


Figure 30 | Surface roughness, initial position, and flexibility of polyethylene compounded with 20 wt.% of wood flour **(A)**, **(B)** and with the supplementation of 20 wt.% of plasticizer **(C)**, **(D)**.

The plasticizers used exhibited different effects on the polymers to which they were added. For instance, by adding only 5 wt.% of plasticizer to PP, the flexibility levels of the control extruded filaments rise from 2 to 4/5, or from 0/1 to 2, for PE control filaments with the same amount of plasticizer. However, the same is not observed for the addition of plasticizer to PLA, since 20 and 30 wt.% amounts of this additive are needed to visualize an increment on the flexibility levels. Nevertheless, for mixtures with this polymer and plasticizer, the increases on flexibility levels observed are abrupt, because with 5 and 10 wt.% of the additive the flexibility of filaments is minimal. In **Figure 31**, filaments of PLA with different quantities of plasticizer (0, 5, 10 and 30 wt. %) are presented, and the abovementioned abrupt influence on flexibility of filaments is demonstrated.

Furthermore, the addition of plasticizers also highlighted the differences on mixtures' flexibility, according to the type of residue used, which without this supplementation was not possible. Following this, CP seems to have a greater impact on the flexibility of filaments, namely higher levels of this property for mixtures using this natural residue were registered. This effect is most probably observed due to the high content in suberin, being this the component responsible for the characteristic flexibility of cork itself [44]. In fact, Fernandes et. al [61], using suberin as coupling agent for cork composites with HDPE polymer basis, also reported improvements on the flexibility levels of materials with the supplementation of this component.

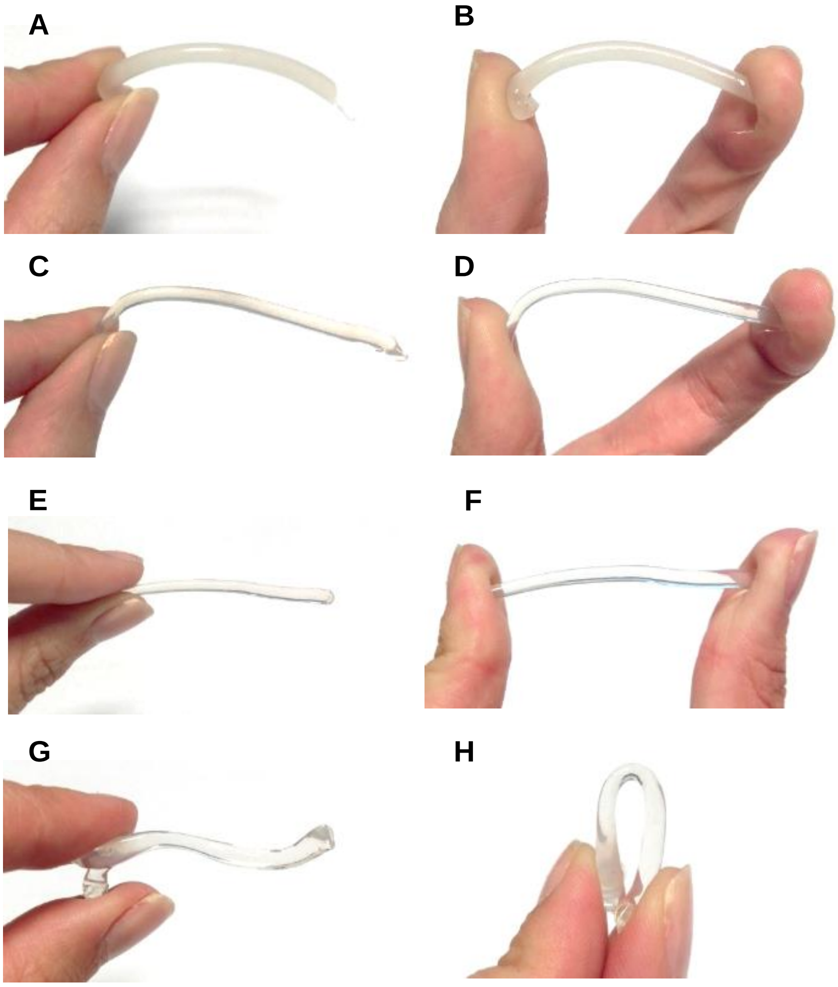


Figure 31 | Initial position and flexibility of polylactic acid **(A, B)** and with the supplementation of 5 wt.% **(C, D)**, 10 wt.% **(E, F)** and 30 wt.% **(G, H)** of the plasticizer Citroflex A4.

Despite the registered higher levels of flexibility for mixtures supplemented with plasticizers, in some cases, especially for mixtures with higher contents of residue and using PE as matrix phase, the filaments, although didn't break when bended, were deformed. This deformation is shown in **Figure 32**.

Figure 32 | Deformation observed on the mixture polyethylene with 20 wt.% of wood flour and 20 wt.% of plasticizer, when maximum flexural force was applied.

4.1.4 Residues’ surface modification

Despite the several functionalization attempts, based on previously reported works [46], [48], [51], no significant improvements on mixtures performances were observed for mixtures containing the same type and quantity of polymer, residue, and plasticizer. The small differences obtained for all the tested mixtures are probably owed to the low dispersions obtained in the laboratorial scale extruder, as it is composed by a single screw, with very small length, that does not enable good mixing of mixtures’ components.

However, considering processing, one particular set of mixtures stood out, showing higher flows due to the addition of the long-used adhesion promotor MAPP. This component was only added to mixtures with PP as matrix phase. MAPP influenced the ease of processing of mixtures, due to the high MFI experienced by the coupling agent itself. In fact, considering that the polymer has already a high MFI, and that the plasticizer also increases the flow rate, for mixtures with lower residue content, the addition of MAPP hindered their processing for turning them too fluid. Despite the numerous reports designating this coupling agent as efficient at improving mechanical performances [26], [46], this could not be confirmed at the laboratorial scale tests herein performed. Contrary to what was expected, similar levels of resistance at break were attributed to these mixtures, comparatively to those using unmodified natural residues. However, in some cases, small reductions on flexibility levels were registered, which could be related with the expected improvement on adhesion between the residues and the polymer.

Given that the results could be influenced by perception (subjective comparisons), small variations on the attributed levels may not prove that different treatments influenced differently the interaction between the mixtures’ phases. Nevertheless, small reductions on flexibility and general reduction on surface roughness of filaments were also observed for the remaining functionalization experiments. It was observed that residues’ surface modification with silane at higher concentration (4 wt.%) led to slightly lower flexibility levels than the treatment with lower concentration (1 wt.%), and also than the alkaline treatment with NaOH. In some cases, higher resistance at break levels were also found, thus implying that the concentrated treatment was more effective on promoting the intended adhesion.

Likewise, the same was observed for the treatment with soybean oil, for which higher adhesions probably occurred, especially with mixtures using WF as natural residue, since those showed lower levels of flexibility and surface roughness. In mixtures treated by this method, it was not possible to define a oil concentration or type of solvent that was more effective. For that reason, and furthermore, for being a less explored, low-priced, and ecological functionalization, a more detailed study on the surface modification of residues by this treatment was performed.

4.2 Surface modification with soybean oil

Different transesterification reactions between soybean oil solutions and residues were tested, targeting the modification of their surfaces and the induction of hydrophobicity. The characterization of the new materials was performed by FTIR-ATR spectroscopy and TGA analyses, to better understand the efficiency of each attempted test. In the next sections are discussed the impact of: the used solvent on the oil solutions, duration of the reaction, and the use of a base catalyst. However, for a better and clearer analysis, the results of chemical and thermal characterizations of the residues and vegetable oil used are firstly addressed.

4.2.1 Residues' characterization

4.2.1.1 Chemical characterization

The two solid substrates used for this study, WF and α-cell are related, since cellulose itself is the major component of wood species, and therefore it comes as no surprise that the absorptive patterns of the two are similar, as can be confirmed in **Figure 33**. Three strong bands can be observed in both spectra, namely at 3500-3200 cm^{-1} corresponding to OH groups [62],[63], near 2855 cm^{-1}, related with C-H stretching of methyl and methylene groups [62],[63], and around 1024 cm^{-1}, associated to C-OH vibrations experienced in cellulose chains [62].

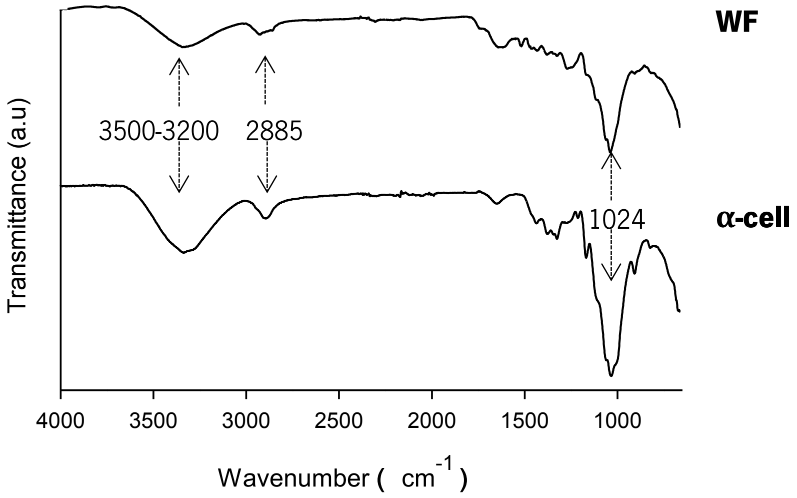


Figure 33 | Absorption spectra of wood flour and α-cellulose obtained by FTIR-ATR.

The analysis of the soybean oil spectrum is also essential for the transesterification studies (**Figure 34**). In this spectrum, two strong peaks appear between 3000 cm^{-1} and 2850 cm^{-1}, indicative of the high amounts of C-H bonds present in the alkyl chains of triglycerides. An also strong peak appears around 1745 cm^{-1}, being related to the C=O interactions present in the ester linkages established between fatty acids and glycerol molecules [51],[62]. As for the remaining strong peaks, these are also attributed to the interactions established within the long alkyl chains.

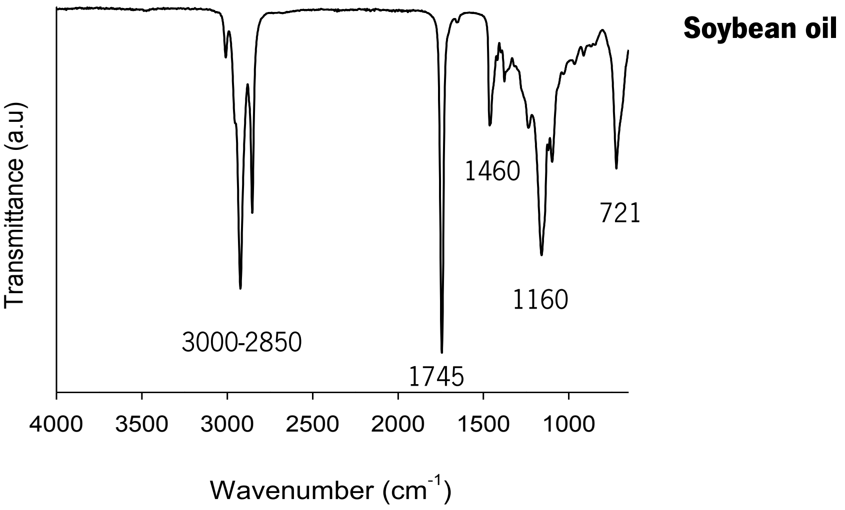


Figure 34 | Absorption spectrum of soybean oil obtained by FTIR-ATR.

4.2.1.2 Thermal characterization

The thermogravimetric analysis of all samples mainly allows determinations on their thermal stability, which is important to recognize the temperature window at which the residues can be handled. However, in some cases, it also permits the determination of different components in a sample and their percent composition, by observing different degradation steps with temperature and their percent mass losses.

In **Figure 35 (A),** the thermograms of the two residues used are provided. In both thermograms, two major degradation steps are observed The first, occurring between ambient temperature and approximately 100 °C, emerges due to the elimination of moisture content [64], where mass losses around 8 wt.% were registered for WF and α-cell. Although the thermogram of the WF sample only shows one degradation step besides that driven by moisture elimination, the earlier degradation temperature obtained when compared to that of α-cell, reveals the presence of other components in this residue. In fact, the lower initial degradation temperature is mainly due to its hemicellulose content, which degrades approximately in the range of 200-260 °C, being therefore the component responsible for the lower thermal stability of WF when compared to α-cell [64]. Analysing the derivative of the mass loss curves, known as derivative thermogravimetric curves (DTG), presented in **Figure 35 (B)**, it can be observed that the WF sample presents a shoulder to the left of the main peak, which corresponds to the degradation of hemicellulose.

The following observed mass losses in the WF sample are driven from the decomposition of cellulose, completed between 300 °C and 500 °C, being therefore the range of temperatures in which the α-cell sample also experiences its major mass losses [64], [65]. The higher and abrupt mass loss experienced by this latter sample at this temperature range are due to the composition of this sample being entirely cellulose. Above 400 °C, the mass percentages observed in the α-cell thermogram are mainly driven from the residual char formed during the analysis [65]. However, we are aware that the same is not true for the WF sample, which possesses other components, like lignin, degrading at higher temperature ranges. Lignin initiates its degradation at 180 °C, till near 450 °C, therefore being a more thermally stable component and enlarging the thermal degradation range of this sample [65].

The identification of the different stages of degradation experienced by the soybean oil used would also be very useful, however the equipment used did not allow this evaluation.

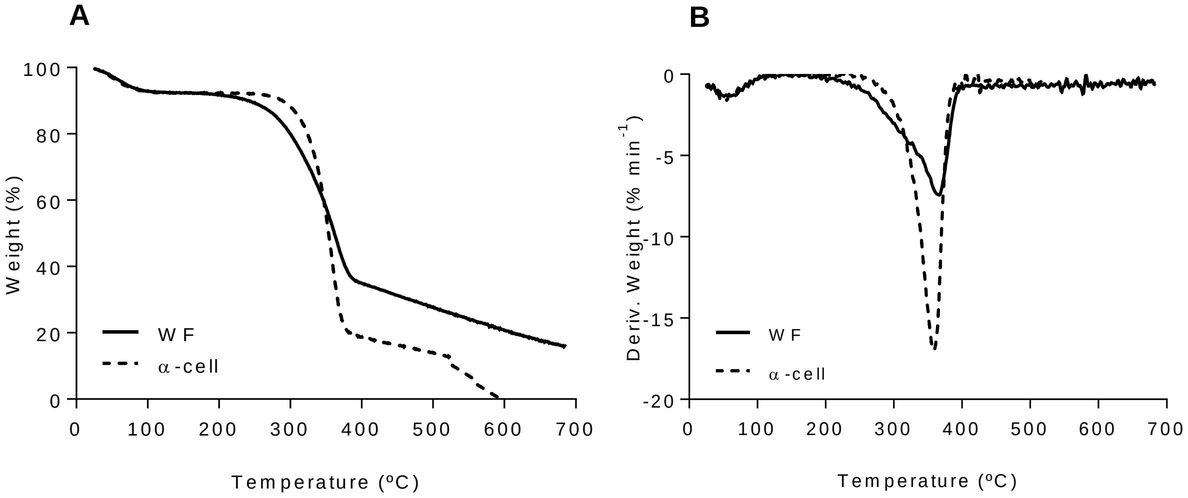


Figure 35 | TGA thermograms **(A)** and respective DTG curves **(B)** of wood flour and α-cellulose samples, obtained under nitrogen atmosphere at 10 °C min^{-1}.

4.2.2 Effect of solvent of oil solutions on residues' hydrophobicity

4.2.2.1 Chemical characterization

The treatment of residues with oil solutions was initially attempted using two different solvents. In **Figure 36**, the spectra of WF samples treated with soybean oil solutions using ethanol (**A**) or acetone (**B**) as solvent are represented. New absorption peaks can be observed as compared to the spectrum in **Figure 33**. These peaks, being more perceptible those appearing at 3000-2850 cm^{-1} and at 1745 cm$^{-1,}$ and thus corresponding to the characteristic of the soybean oil spectrum, are indicative that efficient transesterification reactions may have occurred, as we intended.

The concentration of soybean oil on the treatment solutions appears to have an effect on the absorption intensities of these peaks. Higher intensities were obtained with higher oil concentrations. However, comparing only the spectra of WF samples treated with solutions at 5 wt.% in oil, but with the two different solvents, it can be inferred that the type of solvent used also plays a role in the absorption intensities of oil peaks. The more intense absorptions obtained on samples treated with oil/ethanol solutions, might indicate that the bonds within fatty acid chains and ester linkages were more easily detected in these samples. These observations thus lead to suppositions on the higher abundance of transesterification reactions in samples treated with this type of solvent. As more transesterification reactions have probably occurred, ethanol appears to be more efficient than acetone at increasing residues' hydrophobicity through soybean oil solutions.

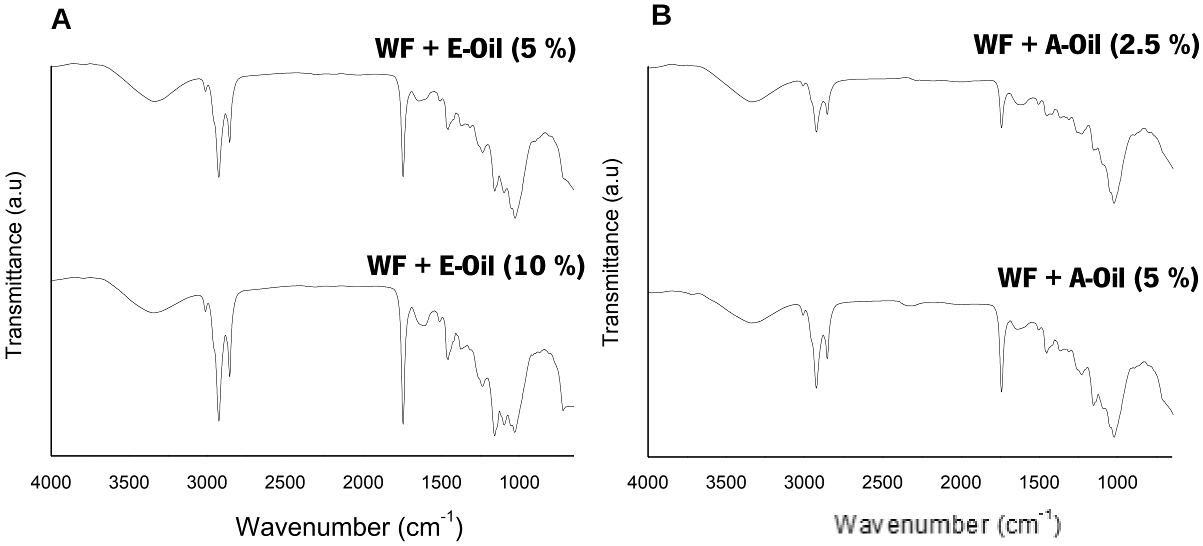


Figure 36 | FTIR-ATR absorption spectra of wood flour treated with soybean oil solutions at different concentrations, using ethanol (**A**) or acetone (**B**) as solvent.

Analysing the FTIR spectra obtained by α-cell samples (**Figure 37**), it was found that this solid substrate was affected in less extent by the soybean oil treatment. In these samples, the oil peaks, if detected, appeared with lower intensities than those observed in WF samples (**Figure 36**). This effect might, once more, indicate that fewer transesterification reactions have occurred, resulting in fewer fatty acids attached to cellulose chains, and therefore, a lower degree of surface modification and hydrophobicity. The difference in absorption intensities of oil peaks, between samples with WF and α-cell as solid substrate, is probably due to the presence in WF of other components, besides cellulose, that possess hydroxyl groups, capable of being substituted by fatty acids, like hemicelluloses and lignin.

Despite the low intensities, the analysis of FTIR spectra of oil treated α-cell samples allowed confirming that ethanol (**A**) was the most efficient solvent used in this treatment, since with acetone (**B**) it was not possible to detect the peaks characteristic of soybean oil. Interestingly, contrary to what our study suggests, Dankovich and Hsieh [50], aiming to improve the hydrophobicity of cotton by following the same treatment, achieved lower water absorptions when treating cotton with oil solutions using acetone as solvent, at only 1 wt.%. In that study, the water absorptions were compared to those obtained on cotton treated with oil/ethanol solutions with oil contents slightly lower than 5 wt.%, therefore suggesting that acetone was more efficient at promoting transesterification. However, the differences in water absorptions obtained with the two solvents were not significant, being therefore not sufficient to correlate with our results.

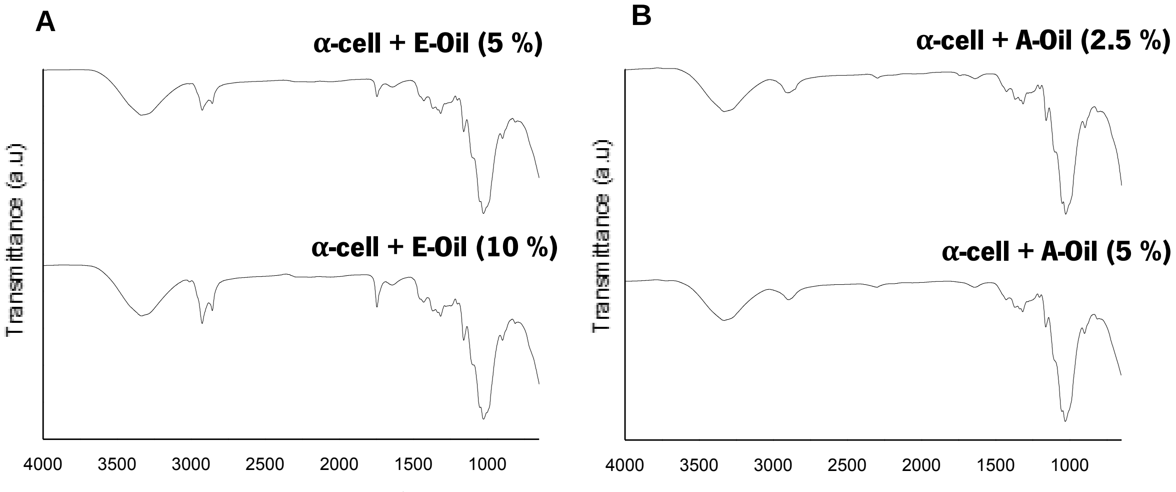


Figure 37 | FTIR-ATR absorption spectra of α-cellulose samples treated with soybean oil solutions at different concentrations, using ethanol (**A**) or acetone (**B**) as solvent.

Despite the promising results, uncertainties on the nature of the oil peaks obtained by most of the samples arise, particularly with the peak appearing at 1745 cm^{-1} resultant from the presence of ester bonds in the samples, for being somewhat inconclusive. This peak may suggest that ester linkages between fatty acids and the hydroxyl groups of cellulose chains were formed, and therefore that transesterification reactions occurred as intended. Even though, it may also only represent the ester linkages already present in triglycerides molecules. Therefore, to better understand if the peaks present in the samples, in fact appear due to the occurrence of transesterification reactions, a second wash of WF samples with the respective solvent was preformed, and the residues were once more analysed by FTIR-ATR. The second analysis revealed that the intensities of oil peaks decreased for all samples. However, the WF samples treated with oil/ethanol solutions retained the higher intensities (*data not shown*). This reduction on oil peaks intensity may have two causes. Firstly, it may indicate that the surfaces of residues were not modified, being oil particles simply adhered to the surfaces, and detached and washed out with the second rinse, hence not influencing the absorption spectra. Secondly, it may indicate that the second wash reversed the transesterification reactions previously occurred, replacing the fatty acids on cellulose chains and resetting de O-H bonds, thus also washing out the fatty acids.

Most certainly, it must be more favourable that fatty acids become linked to cellulose chains rather than just adhered to the surfaces, considering that it is more likely that hydrophobicity, if granted to the residues, is maintained. Therefore, a further study on the chemical composition of the differently treated residues by more detailed techniques, like solid-state nuclear magnetic resonance (SS-NMR), would be very useful.

4.2.2.2 Thermal characterization

Analysing the thermograms (**Figure 38**) corresponding to WF **(A)** and α-cell **(C)** samples, untreated and treated with 5 wt.% oil solutions, with the two different solvents under study, it can be perceived that the oil treatments increased the thermal stability of residues. This can be inferred since all treated samples start to degrade at higher temperatures than their untreated counterparts. The onset temperatures of residues treated with 5 wt.% oil solutions shifted approximately from 296 to 318 °C, and from 323 to 340 °C, relatively to untreated WF and α-cell samples, respectively. Hence, the temperature range at which residues experience their major mass losses is enlarged with the oil treatment, probably driven from the fact that oil components degrade at higher temperatures (400-410 °C). In fact, this can be confirmed from the DTG curves of the oil treated samples (**Figure 38 (B)** and **(D)**), since peaks corresponding to major rates of mass loss are slightly shifted to higher temperatures. Hence, analysing the DTG curves of WF samples **(B)** it can be observed that a shoulder to the right of the peak referent to cellulose degradation appears, probably corresponding therefore to the degradation of the vegetable oil. This shoulder is especially evident on the WF sample treated with oil solution using ethanol as solvent.

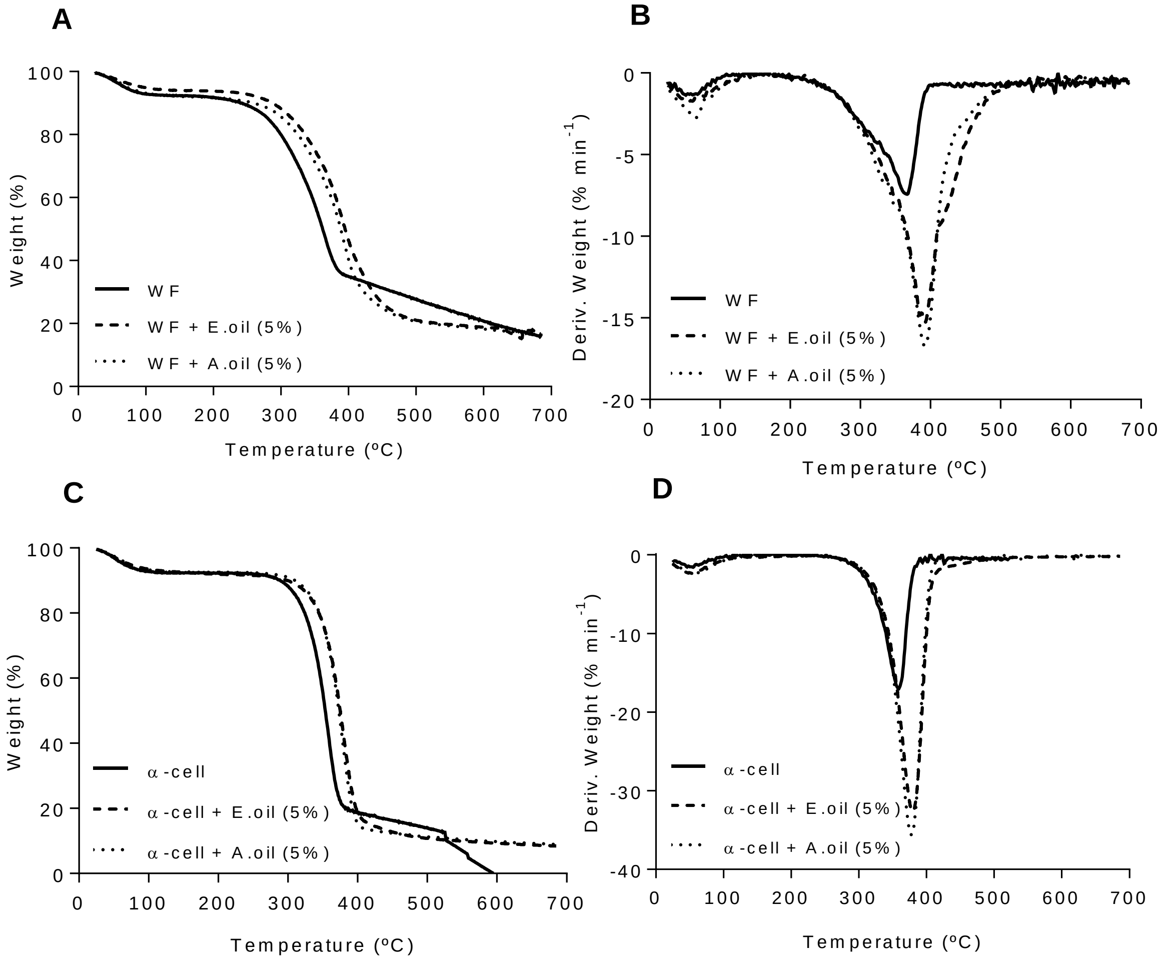


Figure 38 | TGA thermograms and DTG curves of wood flour **(A)**, **(B)** and α-cellulose **(C)**, **(D)** samples, untreated or treated with 5 wt.% soybean oil solutions using ethanol or acetone as solvent. All samples were analysed under nitrogen atmosphere at 20 °C min^{-1}.

Similar to what was suggested by the chemical characterization, ethanol was found to be a more valuable solvent to be used in the oil treatment, since more thermally stable residues are obtained when this type of solvent is applied. This is more clearly observed for WF thermograms, where degradation of the oil/ethanol treated sample occurs at higher temperatures compared to that treated with oil/acetone solution. Furthermore, when analysing specifically the first level of degradation, corresponding to moisture elimination (near 25-100 °C), it can be observed that lower mass losses were obtained for the WF sample using ethanol, thus suggesting that the hygroscopicity of this sample was lower. This thus emphasizes that this solvent is more efficient at promoting transesterification and conferring the intended hydrophobicity to the residues. Lower hygroscopicities of cellulose samples treated with soybean oil, relatively to pristine cellulose were also reported by Jang and Kim [51].

Following the results of chemical and thermal characterizations, obtained for residues treated with oil solutions using the two different solvents, that evidenced ethanol as the best option, the further surface modification studies used only this solvent.

4.2.3 Reaction time for oil solutions

4.2.3.1 Chemical characterization

Aiming to improve the yields of residues' surface modification we studied the effect of the reaction time of the oil treatment solutions, before being applied to the residues. In **Figure 39**, the effects of this variable on both WF **(A)** and α-cell **(B)** as solid substrates, are compared. It is clear that the two residues were influenced differently. Moreover, it was expected that by allowing the oil solutions to react for 1 h, more fatty acids could be released from triglycerides molecules, thus leading to a higher amount available in solution. This would therefore, possibly result in higher degrees of residues' surface modifications. From **Figure 39 (A)**, it can be seen that WF behaved as expected, since more intense oil peaks were achieved in the sample with 1 h reaction, thus suggesting that more transesterification reactions occurred. However, the same was not observed for α-cell samples. Even though the differences in intensities of oil peaks may be attributed to different washing intensities of residues, as above suggested, no conclusion could be outlined on the influence of the reaction time on the yield of residues' hydrophobicity.

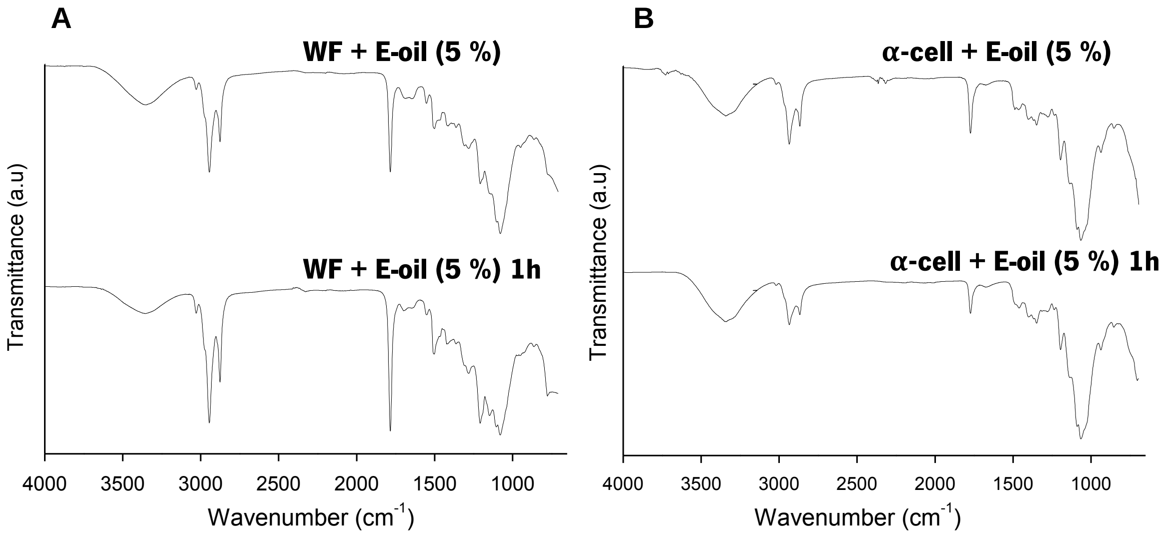


Figure 39 | FTIR-ATR absorption spectra of wood flour **(A)** and α-cellulose **(B)** samples treated with soybean oil solutions at 5 wt.% which were immediately added to residues or kept reacting for 1 h before the addition.

4.2.3.2 Thermal characterization

The TGA analysis of the different samples corroborated the results obtained in the chemical characterization. From **Figure 40 (A)**, corresponding to thermograms obtained from the WF samples, we can observe that the more thermally stable residue corresponds to that treated with oil solution that was kept in reaction for 1 h. From the thermogram of this sample, it was found that it initiates the degradation process at higher temperatures, and also that the range of degradation temperatures is larger, comparatively to the other two. Consequently, the results indicate that higher amounts of fatty acids from the soybean oil are attached to WF components, and therefore that a higher number of transesterification reactions occurred, as also suggested by the FTIR-ATR spectra. As previously shown, lower mass losses corresponding to moisture elimination were once again obtained for WF samples treated with oil solutions, thus suggesting that efficient improvements in hydrophobicity were introduced.

From **Figure 40 (B)**, it can be observed that no significant differences between the three α-cell samples were obtained. Nevertheless, the slightly lower mass losses obtained in the first step of degradation, in the sample treated with oil solution immediately added to the residues, corroborate the results obtained from the chemical analysis, in which this sample exhibited more intense oil peaks. Therefore, given the contradictory results between samples with different solid substrates, no significant correlation between time of reaction and efficiency of surface modification could again be established.

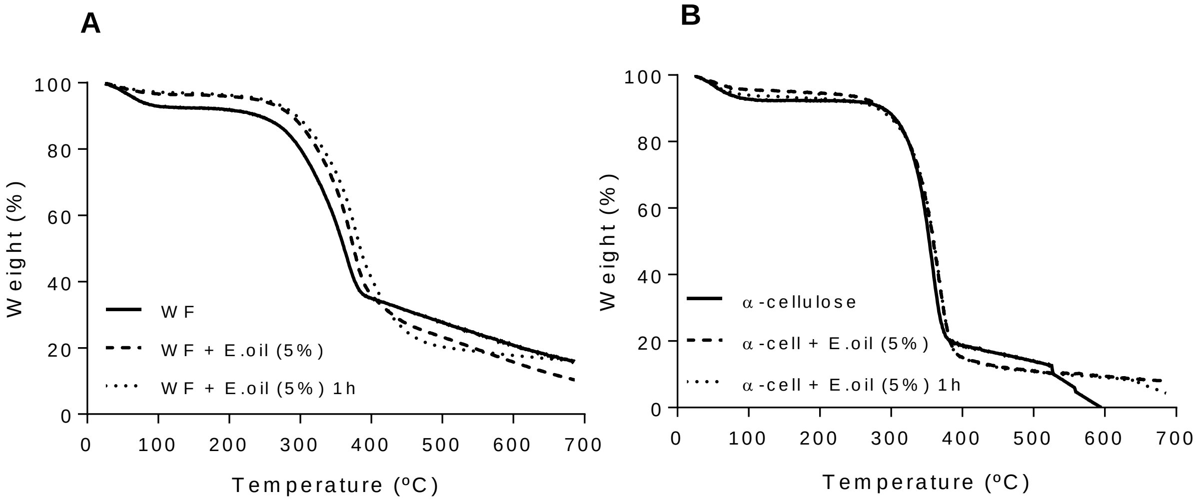


Figure 40 | TGA thermograms of wood flour **(A)** and α-cellulose **(B)** samples, untreated or treated with 5 wt.% soybean oil/ethanol solutions which were immediately added to residues or kept reacting for 1 h before the addition. All samples were analysed under nitrogen atmosphere at 10 °C min^{-1}.

4.2.4 Addition of base catalyst

To achieve higher yields of transesterification reactions, we evaluated the use of a base catalyst in the oil solutions. For that purpose, before the addition of soybean oil, ethanol solutions were previously mixed with NaOH at 1 wt.%. NaOH molecules act by attracting the hydrogen atoms of ethanol molecules, giving rise to more reactive species (ethanol anions). These have higher capacity to efficiently attack the carbon atoms in triglycerides molecules, promoting transesterification after oil is added to the solutions. This attack will therefore result in a greater release of fatty acids to the solution, in the form of ethyl esters [66]. Aiming at a better accessibility to the cellulose chains of residues, so more transesterification reactions could occur, an alkaline pre-treatment of both residues was also attempted. Nevertheless, this was beforehand expected to impact majorly the WF samples. Attempting to improve the yields even further, the reaction time of oil solutions was studied again, and FTIR-ATR and TGA analysis were performed on all samples.

4.2.4.1 Chemical characterization

Contrary to what was anticipated, as can be seen in **Figure 41**, the introduction of the base catalyst into the oil solutions was not efficient on the surface modification of any of the tested residues. In the spectra corresponding to these samples, none of the characteristic oil peaks (particularly those at 3000, 2850, and 1745 cm^{-1}) could be observed. In fact, when the oil solutions were added to residues, and after partial ethanol evaporation, it could be observed that the solutions formed greasy white aggregates, which were present in all the samples tested, independently of the time of reaction of the oil solutions. Consequently, these aggregates deposited as a layer on the surface of residues, not allowing modifications on the cellulose chains. These aggregates were then rinsed out when residues were washed with ethanol, justifying the absence of the oil peaks.

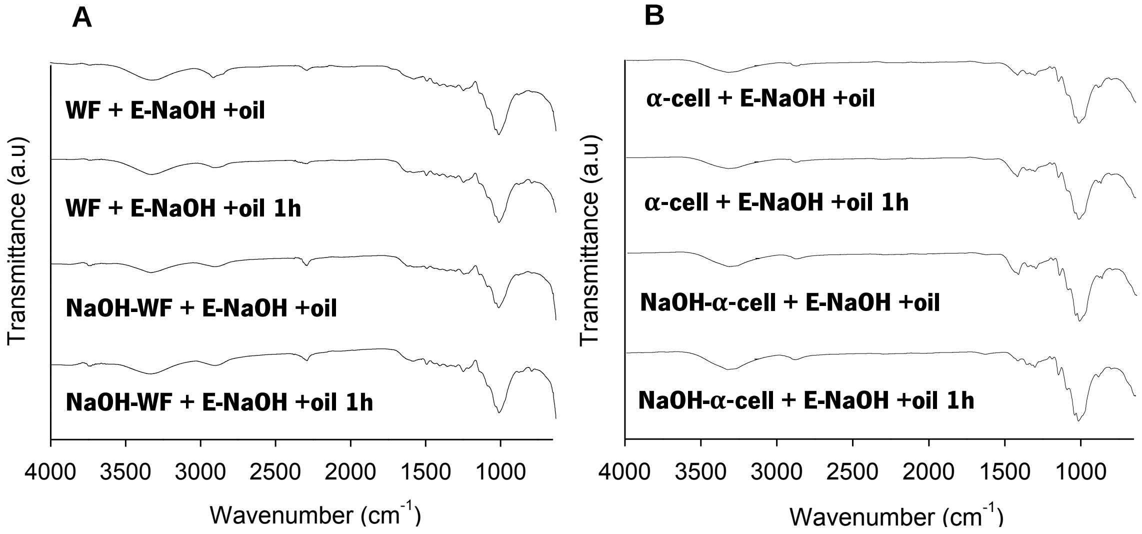


Figure 41 | FTIR-ATR absorption spectra of unmodified or previously alkalinized wood flour **(A)** and α-cellulose **(B)** samples treated with soybean oil solutions at 5 wt.% using NaOH at 1 wt.% as catalyst.

To better understand the formation of the greasy aggregates, before washing the residues, samples of the layers formed on top of them were retrieved and also analysed by FTIR-ATR (**Figure 42**). It was found that the two peaks near 3000 and 2850 cm^{-1}, corresponding to the C-H bonds established in the alkyl chains were conserved, while the peak resultant from the C=O bonds in ester linkages faced a significant reduction on its intensity. On the other hand, two different peaks appeared, near 1560 cm^{-1} and 1425 cm^{-1}, probably due to the presence of C=O bonds of carboxylic acid salts [62]. A possible reason that led to the formation of these salts is that, instead of releasing higher amounts of ethyl esters to the solution, the addition of NaOH induced the hydrolysis of triglycerides from the soybean oil, also known as saponification reaction, resulting in fatty acids salts release. The occurrence of this reaction indicates that the amount of base catalyst used was much higher than that of soybean oil (triglycerides), the latter functioning as limiting reagent [67]. Therefore, to efficiently achieve the intended purpose, studies on the residues hydrophobization using solutions with lower amounts of base catalyst should be conducted.

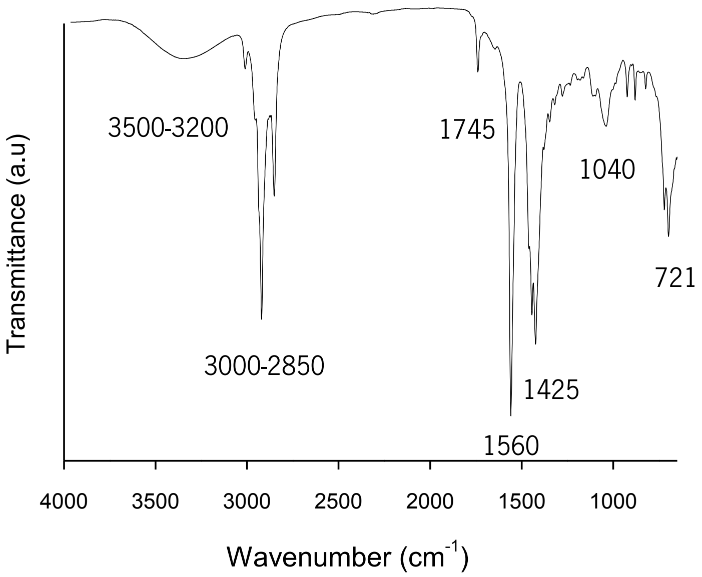


Figure 42 | FTIR-ATR absorption spectra of lipid layer deposited on the surface of wood flour samples treated with oil solutions containing NaOH as base catalyst.

Analysing the remaining peaks appearing in the spectra of all samples (**Figure 41**), it could be inferred that NaOH did not affect the normal structure of residues, since no significant differences were observed when compared to the spectra of the untreated residues. The characteristic peaks of cellulose are still observed at 3500-3200 cm^{-1}, at 2885 cm^{-1}, and at 1024 cm^{-1}, despite the lower intensities. However, when narrowed the wavelength of the spectra to wavenumbers between 1900 cm^{-1} and 650 cm^{-1}, small but significant differences can be observed in WF samples. In **Figure 43**, the spectra of the U-WF and NaOH-WF samples, both treated with oil solution with the base catalyst, are presented. From the absorbance spectrum of the untreated WF, a small peak near 1729 cm^{-1} can be observed, assigned mainly to the stretching of C=O linkages of carbonyl groups in hemicelluloses. As it was expected, this peak is absented in the spectrum of the pre-treated WF sample with alkaline solution, thus suggesting that the hemicelluloses were removed for being soluble in alkali, as also experienced by Chang, Sain, and Kortschot [63], and Zierdt et. al [68]. In the WF sample treated only with oil solution with the catalyst, a decrease in intensity of the peak at 1729 cm^{-1} is also noticeable, suggesting that the use of NaOH as catalyst also contributed to the removal of hemicelluloses. On the other hand, the conservation of the band near 1266-1224 cm^{-1}, this corresponding to C-O-C stretching of the ether linkages in lignin [68], suggest that these components were not affected neither by the alkali pre-treatment, nor by using the base catalyst. This stands as a positive point considering that lignin also serves as barrier component for water penetration.

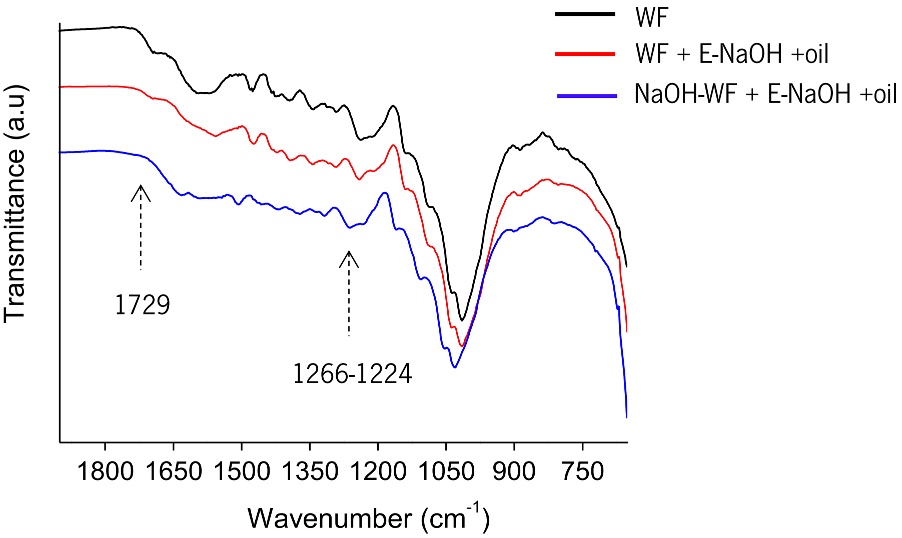


Figure 43 | Narrowed FTIR-ATR absorption spectra of wood flour samples unmodified or pre-alkalinized and treated with oil solutions with base catalyst.

4.2.4.2 Thermal characterization

From **Figure 44** and **Figure 45**, showing the thermograms of residues treated with oil solutions containing the base catalyst in its composition, for WF and α-cell samples, respectively, the first observable effect is that the thermal stability of all samples was reduced as compared to the unmodified residues. The lower thermal stabilities achieved by these samples, which suggest that no transesterification reactions occurred on the surfaces of residues, emphasize the results obtained in the chemical characterization, where no oil peaks could be observed on any sample. This effect of lowered thermal stability, pointed out by the lower onset temperatures of degradation, is even more evident for residues pre-treated with alkali solutions (**Figure 44 (B)** and **Figure 45 (B)**).

From the chemical analysis, it was suggested that both the alkali pre-treatment and the use of base catalyst induced hemicelluloses removal from the WF samples. Therefore, it was expected that, in these samples, higher thermal stabilities would be observed, since hemicelluloses are among the first components to degrade in WF (starting near 200 °C). This expected initial degradation at higher temperatures of NaOH-WF samples, was observed by Zierdt et. al [68], even so, the same could not be verified in our study. One possible explanation for these results is that this treatment also led to the removal of other components, like waxes, that have a protective effect against thermal degradation.

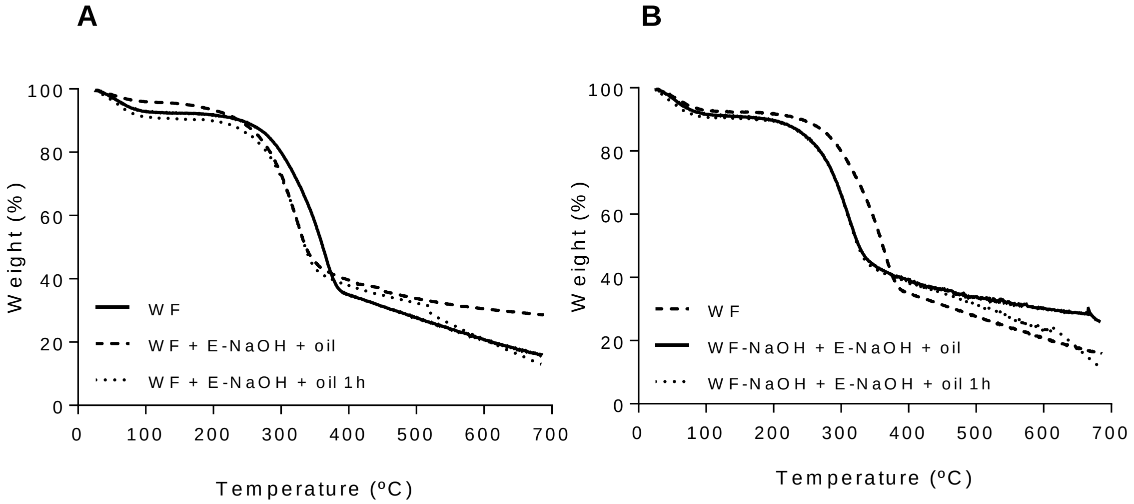


Figure 44 | TGA thermograms of unmodified **(A)** and previously alkali-treated **(B)** wood flour samples, treated with 5 wt.% soybean oil/ethanol solutions containing 1 wt.% of NaOH as base catalyst, which were immediately added to residues or kept reacting for 1 h before the addition. All samples were analysed under nitrogen atmosphere at 10 °C min^{-1}.

On the other hand, no significant differences were expected on the thermal stabilities of α-cell samples, since this solid substrate is merely composed of cellulose. Nevertheless, similar decreases of thermal stability were found in the different samples using this solid substrate. For this reason, one possible explanation for the obtained results is that changes in cellulose chains occurred by using the base catalyst, thus promoting earlier degradations of this component.

Once more, no correlation with the reaction duration of the oil solutions and their effect on residues' modifications could be outlined, since very similar results were obtained for samples in which this variable was not introduced.

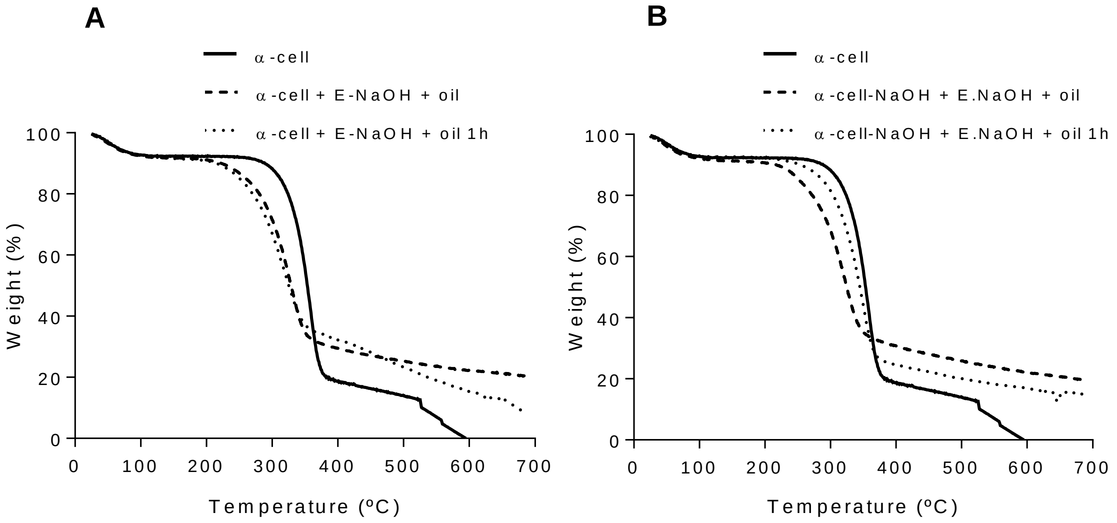


Figure 45 | TGA thermograms of unmodified **(A)** and previously alkali-treated **(B)** α-cellulose samples, treated with 5 wt.% soybean oil/ethanol solutions containing 1 wt.% of NaOH as base catalyst, which were immediately added to residues or kept reacting for 1 h before the addition. All samples were analysed under nitrogen atmosphere at 10 °C min^{-1}.

Analysing the DTG of both residues (**Figure 46**) the lower thermal stabilities obtained in both residues with the oil treatment containing the base catalyst is confirmed. The peaks corresponding to the maximum rate of mass losses are shifted to lower temperatures, in all samples. Furthermore, despite the results from the thermograms of the WF samples being different from what was expected, when analysing their DTG curves (**Figure 46 (A)**), it was observed that the shoulder at left from the main peak, present in the untreated sample and attributed to the degradation of hemicelluloses, disappears in the samples treated with the base catalyst and pre-treated with alkali. This effect suggests that these components were in fact removed and hence support the results achieved by chemical analysis.

Both the results from the chemical and thermal analysis proved that the addition of NaOH as catalyst for the transesterification reactions, was not only uncooperative on delivering fatty acids to residues' surfaces, but also damaging, given the lower thermal stabilities achieved. For that reason, this component was not further used in soybean oil solutions for residues surface modification.

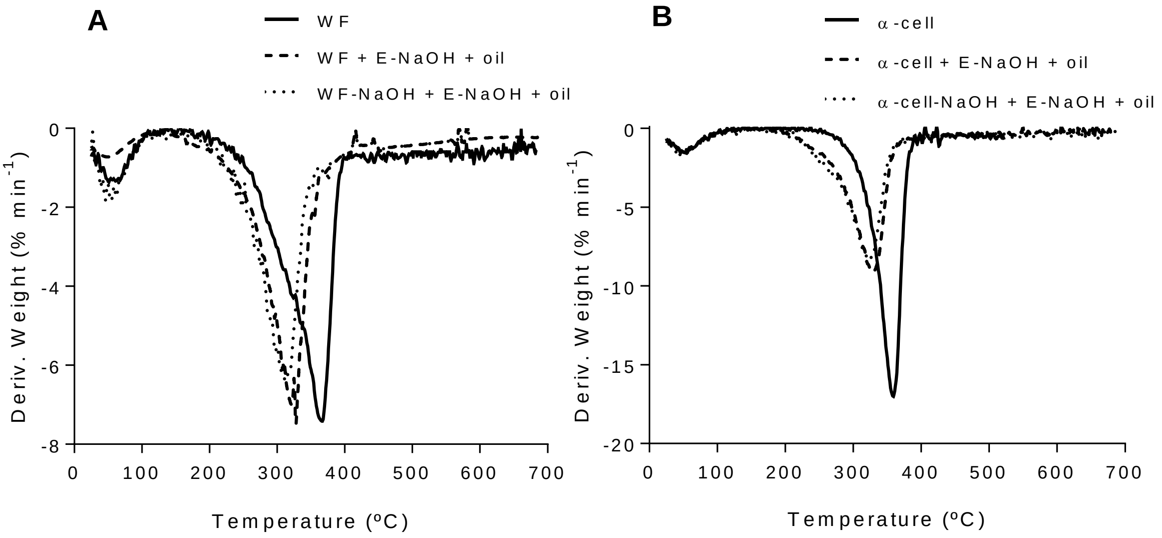


Figure 46 | DTG curves of wood flour **(A)** and α-cellulose samples **(B)**, untreated or pre-treated with alkali and then treated with 5 wt.% soybean oil/ethanol solutions containing 1 wt.% of NaOH as base catalyst. All samples were analysed under nitrogen atmosphere at 10 °C min^{-1}.

4.2.5 Compatibility test

To evaluate, among the different treatments with soybean oil solutions, which were in fact efficient at conferring the intended hydrophobicity to the residues, a simple test based on compatibility was performed. In this test, small amounts of WF and α-cell samples, untreated and treated with the several oil solutions, were added to heterogeneous solutions, composed of equal amounts of two immiscible solvents. The two different solvents presented different densities and polarities: water and petroleum ether. This test is based on the fact that residues, according to their polarity, will settle on the solvent with similar polarity.

From **Figure 47**, gathering the results obtained for the differently treated WF samples, it is observable that only the residues treated with soybean oil/ethanol solutions at 5 wt.% granted hydrophobicity. Both solutions, that which was immediately added to residues and that which was kept reacting for 1 h, were efficient. In these samples the residues remained in the upper solvent, corresponding to the non-polar petroleum ether, which is less dense than water. Therefore, this suggests that transesterification reactions occurred as intended, i.e. surfaces of WF were probably modified, with the attachment of long alkyl chains, as it was previously suggested by the chemical and thermal analysis.

On the other hand, all samples treated with solutions using NaOH as base catalyst migrated to the lower polar phase, therefore indicating that no transesterifications occurred, and that hydrophobicity was not granted to residues, as already predicted by the FTIR-ATR analysis. In fact, the untreated WF sample already settles in the non-polar phase, demonstrating that this residue possesses certain components that confer a given degree of hydrophobicity to itself, like waxes. Therefore, it was found that the addition of base catalyst hinders the natural polarity of residues, probably by removing these naturally present waxy components, as also predicted by the thermal characterization.

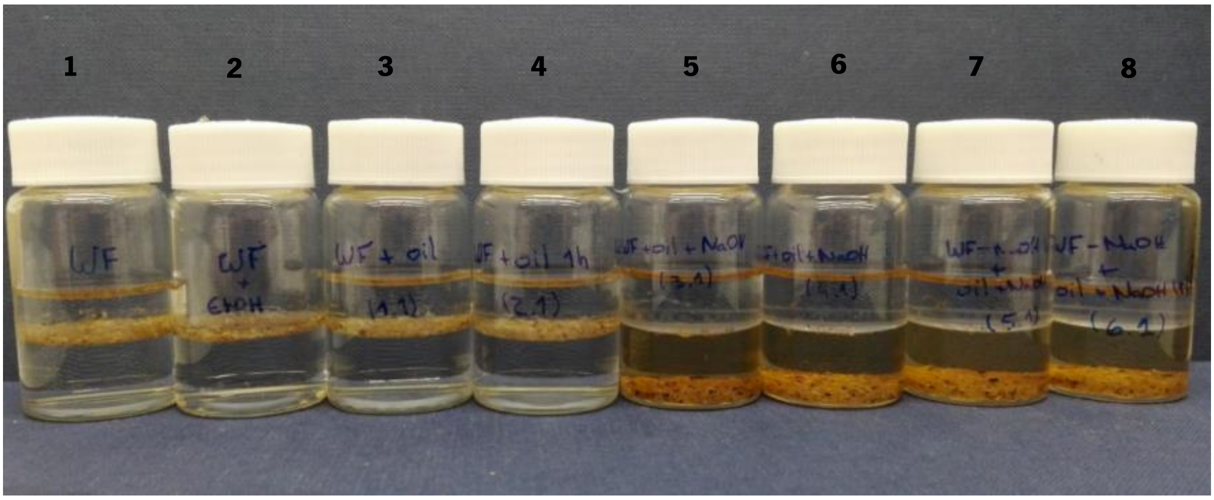


Figure 47 | Compatibility of wood flour samples, treated with different soybean oil solutions, for non-polar solvents. All samples were added to heterogeneous solutions with two immiscible solvents: water and petroleum ether. The number on each sample were attributed as follows:

1: WF; **2:** WF + E; **3:** WF + E-oil; **4:** WF + E-oil 1h; **5:** WF + E-NaOH + oil;
6: WF + E-NaOH + oil 1h; **7:** NaOH-WF + E-NaOH + oil; **8:** NaOH-WF + E-NaOH + oil 1h

The efficiency of the treatment of residues with soybean/ethanol solutions is more evident when observing the compatibility test results of α-cell samples (**Figure 48**). In these, the untreated residue, for being merely composed by the polar component cellulose, settles on the lower, polar phase of the flasks, contrary to what observed by the untreated WF sample. Therefore, it was observed that the treatment with oil solutions was in fact efficient at conferring hydrophobicity, since these samples remained in the upper non-polar phase of the flasks. The remaining samples treated with oil solutions using NaOH as catalyst, once more remained in the lower phase, thus indicating that no hydrophobization was obtained, as already predicted.

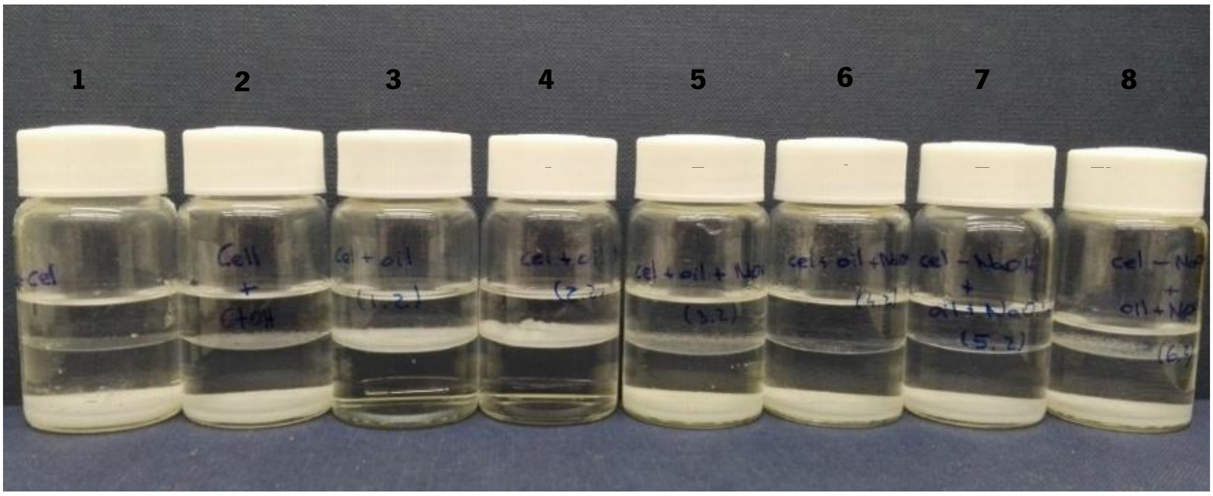


Figure 48 | Compatibility of α-cellulose samples, treated with different soybean oil solutions, for non-polar solvents. All samples were added to heterogeneous solutions with two immiscible solvents: water and petroleum ether. The number on each sample were attributed as follows:

1: α-cell; **2:** α-cell + E; **3:** α-cell + E-oil; **4:** α-cell + E-oil 1h; **5:** α-cell + E-NaOH + oil;
6: α-cell + E-NaOH + oil 1h; **7:** NaOH- α-cell + E-NaOH + oil; **8:** NaOH- α-cell + E-NaOH + oil 1h.

Given the apparent efficiency of the resorted soybean oil/ethanol solutions at conferring hydrophobicity to the residues, this strategy was employed to functionalize WF for compounding with the polymer matrices PP or PLA. This treated WF thus functioned as the reinforcing phase of the resultant green composites. By conferring hydrophobicity, thus making the WF less polar, it is expected that higher interactions between the two different components are achieved, which will probably result in materials with better mechanical performances. Besides the improved mechanical performances, this treatment is also expected to reduce the water absorption levels of the materials, thus facilitating their processing, and enlarging their potential applications.

4.3 Processing of composites by twin-screw extrusion

To evaluate the influence of the oil treated residues and the amount of reinforcing phase on the achievement of valuable sustainable materials, the two above referred polymers were used as matrix phase, which were compounded with different amounts of functionalized or untreated WF.

A very fluid grade of PP was used to enable the feeding of the residue at the second opening in the extruder, without occurring refluxing of the polymer. In compositions using this polymeric basis, the plasticizer used in the laboratorial scale phase was not used since it promoted aggregation of the polymer granules in the feeder, making it difficult to continue the path along the extruder. For compositions with PLA basis, both the polymer and the residue were fed in the first opening of the extruder. This strategy was applied for these compositions since, when feeding of the residues at the second opening was attempted, reflux of the melted polymer occurred, driven by its low MFI (high viscosity). However, in these compositions, the plasticizer used in the preceding phase could also be used in the compounding processes at larger scale, thus facilitating it.

For the evaluation of the developed materials, thermal, rheological, and morphological analysis were conducted and the results compared with the neat polymers.

4.3.1 Thermal analysis

4.3.1.1 TGA

From the thermograms of the developed compositions, using WF with any pre-treatment, presented in **Figure 49 (A)** for those with PP basis and in **(B)** for PLA, it was found that the thermal stability of the materials is reduced with the increasing content on residues. This effect was already expected since WF starts to degrade at lower temperatures than both the polymeric matrices. A decrease on thermal stability of wood composites with increasing wood content has already been reported [69]. In **Table 6**, all the onset temperatures related to different degradation steps are presented, as well as the respective mass loss percentages, experienced by both the untreated and oil-treated WFs, the two used polymers, and by each composition tested. Therefore, this lower thermal stability of WF relatively to the polymers can be confirmed, since the untreated residue starts to degrade approximately between 200-260 °C, as previously referred, exhibiting an onset temperature of 296 °C, whereas PP and PLA degrade, in a single step, near 445 °C and 366 °C, respectively.

Furthermore, in **Figure 49 (B)**, it was also found that the addition of plasticizer C.A4 to the PLA compositions, despite improving the processing, considerably reduces their thermal stability since they start to degrade at lower temperatures. This lower thermal stability is experienced in higher extent in formulations were WF was added. C.A4 is chemically composed of acetyl tributyl citrate, whose compound was also used as plasticizer by Maiza et al. [60]. These authors also experienced lower thermal stabilities relatively to neat PLA for compositions containing the plasticizer, due to the earlier evaporation of the additive.

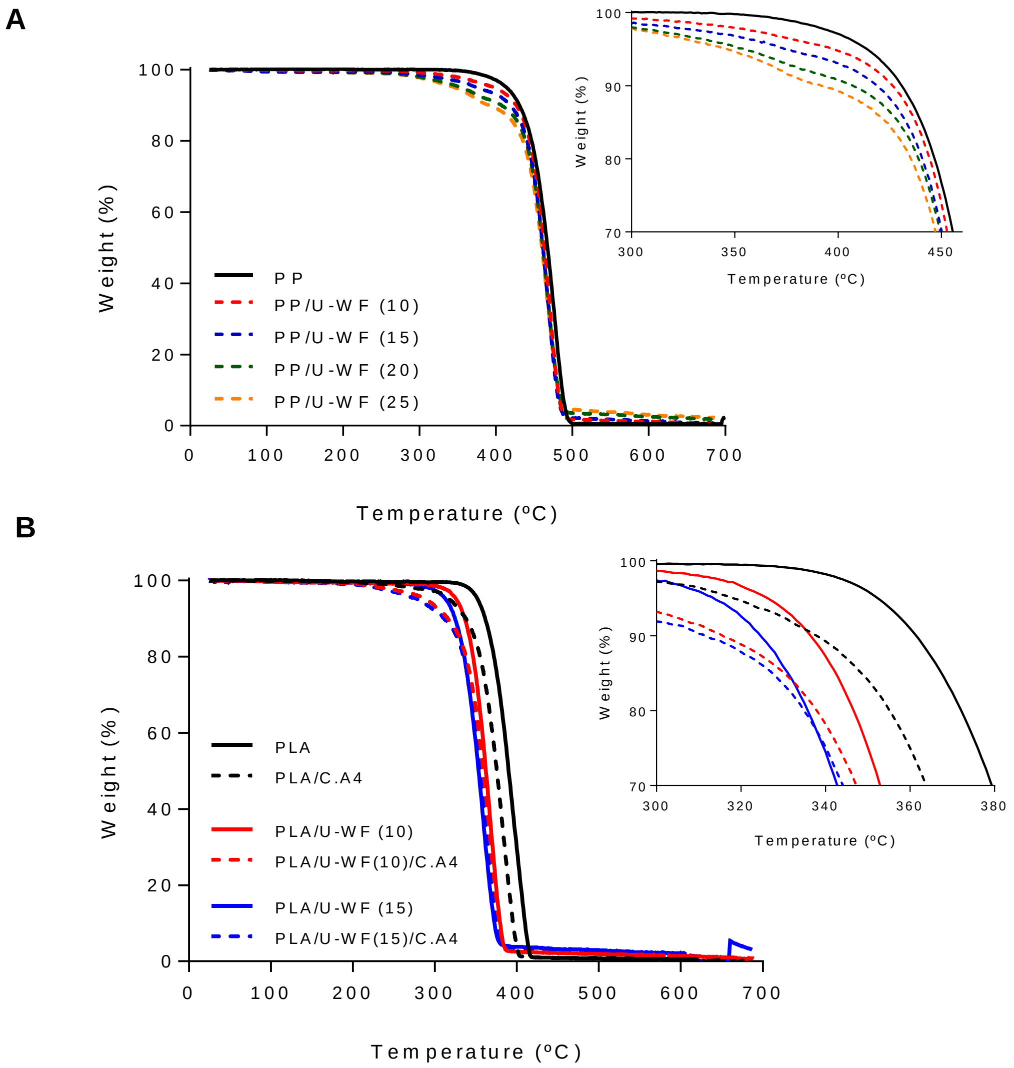


Figure 49 | TGA thermograms of compositions with untreated wood flour, processed by twin-screw extrusion, possessing polypropylene **(A)** or polylactic acid **(B)** as matrix phase. The inserts represent the thermograms with smaller temperature ranges for a clearer analysis of the initial degradation of the different compositions. For polylactic acid compositions, the thermograms of those supplemented with the plasticizer are also presented. All samples were recorded at 10 °C min^{-1} under nitrogen atmosphere.

When analysing the DTG curves of the PP compositions, a very small peak appeared to the left of the main peak of degradation, for all compositions. This is related to cellulose degradation, considering that it appears between the temperature range of degradation of this component (300-400 °C). As way of example, the DTG curve of the composition using 20 wt.% of U-WF as reinforcement is shown in **Figure 50 (A)**, where this small peak is highlighted. For this reason, in **Table 6**, for compositions with PP basis, two degradation steps are presented, the first being related to the degradation of WF and the second to the degradation of the polymer itself. Herein, the mass loss percentages experienced by compositions among the first temperature range are expected to translate the weight percentages of WF that were added to each composition during processing by twin screw-extrusion. However, as can be seen, the percentages revealed by the mass losses during TGA analysis are below those intended. Nevertheless, the oil-treated compositions showed higher WF percentages than their untreated counterparts. Even though, it must be kept in mind that TGA analyses are performed on very small amounts of each composition, which might not be representative of the whole process.

As PLA degrades in a temperature range similar to that of cellulose, the two peaks corresponding to the reinforcement and the matrix could not be distinguished. The two peaks overlapped (**Figure 50 (B)**), and therefore it was not possible to confirm the weight percentages of the reinforcements present in these compositions.

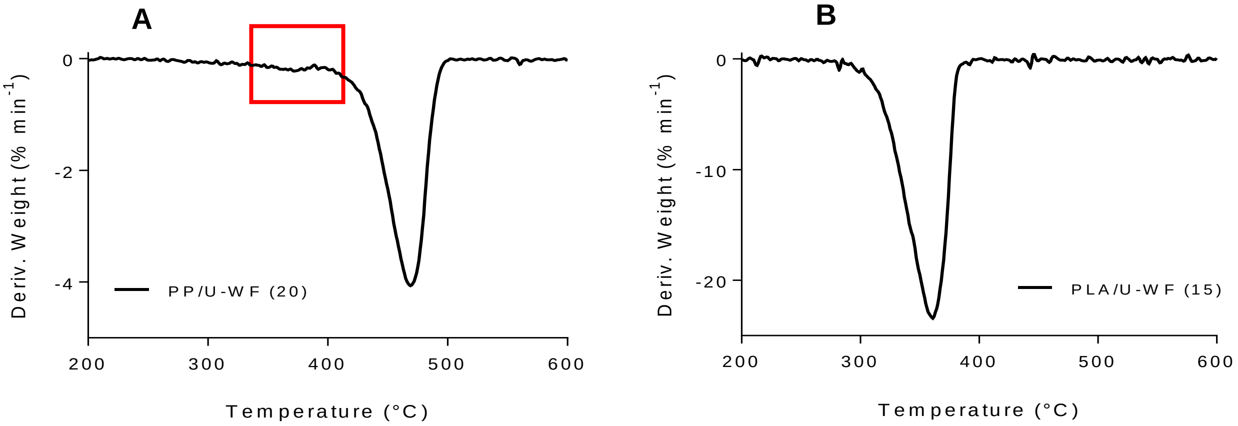


Figure 50 | DTG curves of two compositions with untreated wood flour possessing polypropylene **(A)** or polylactic acid **(B)** as matrix phase, recorded at 10 °C min^{-1} under nitrogen atmosphere. In Figure **(A)** a small peak is highlighted, which is discussed in the text.

Table 6 | Temperature onsets and respective weight loss percentages of each step of degradation experienced by the untreated and oil-treated residues, neat polymers, and each attempted composition. The values of residual weight percentages are also presented.

Sample	Onset$_1$ Temp. (°C)	Weight Loss$_1$ (%)	Onset$_2$ Temp. (°C)	Weight Loss$_2$ (%)	Onset$_3$ Temp. (°C)	Weight Loss$_3$ (%)	Residue (%)
WF	28	8.3	296	69.2			16
Oil-WF	27	3.9	318	56.8	388	13.7	9.3
PP	445	99.3			-		0.4
PP/U-WF (10)	318	8.4	445	90.1			0.5
PP/Oil-WF (10)	332	9.1	442	89.8			0.2
PP/U-WF (15)	319	10.7	445	87.6			0.7
PP/Oil-WF (15)	318	11.9	445	86.4			0.6
PP/U-WF (20)	315	12.5	444	84.8			1.8
PP/Oil-WF (20)	343	19.8	422	78.1			0.7
PP/U-WF (25)	317	15.6	443	80.1			2.2
PLA	366	99.2	-		-		0.6
PLA/C.A4	352	99.3					0.1
PLA/U-WF (10)	344	98.4					0.7
PLA/U-WF (10)/C.A4	335	98.2					0.1
PLA/Oil-WF (10)	335	98.1					0.1
PLA/Oil-WF (10)/C.A4	339	98.6					0.7
PLA/U-WF (15)	333	96.8					2.1
PLA/U-WF (15)/C.A4	334	97.5					0.6
PLA/Oil-WF (15)	340	98.5					0.5

Considering the results of the thermal analysis present in section 4.2.2.2, in which higher thermal stabilities were found for WF samples treated with 5 wt.% soybean oil solutions, it was also expected to observe slight increases in the thermal stability of compositions with oil-WF, when compared to their counterparts with the same amounts of U-WF. Even so, for compositions with PP as matrix phase, no significant differences were observed on the initial temperature of degradation, except for the composition with 20 wt.% of Oil-WF (**Figure 51**). In this sample, the thermogram clearly shows that the composition experiences degradation at lower temperatures. However, as shown in **Table 6** by the percentage of mass loss in the first step of degradation, this oil-treated composition appears to have higher residue content than the composition of PP with 20 wt.% of U-WF, namely 19.8 and 12.5 wt.% respectively, this representing a possible reason for its earlier degradation.

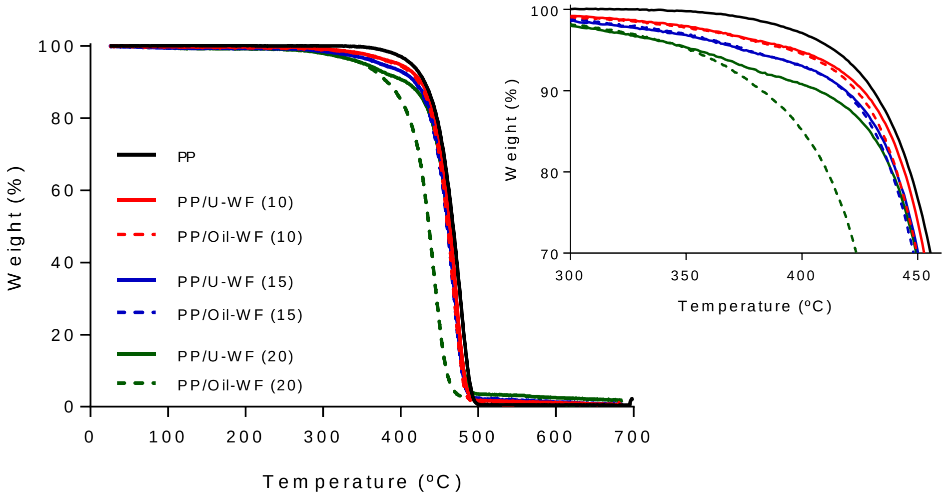


Figure 51 | TGA thermograms of compositions with untreated or oil-treated wood flour, processed by twin-screw extrusion, possessing polypropylene as matrix phase. The insert represents the thermograms with smaller temperature ranges for a clearer analysis of the initial degradation of the different compositions. All samples were recorded at 10 °C min^{-1} under nitrogen atmosphere.

Interestingly, in PLA compositions, lower thermal stabilities were also observed on the two formulations with oil-treated WF (**Figure 52**). However, as the two peaks from the different components could not be distinguished in the DTG curves, no correlation between the degradation profile and the residue content of the compositions could be confirmed.

Based on these results, despite the evident influence of residue content on the thermal stability of the materials, no concrete correlation could be outlined relatively to the influence of the oil treatment. However, it appears to negatively affect the compositions using PLA as polymer matrix, while exhibiting little or no influence on the stability of those with PP basis. This effect is maybe driven from the latter polymer possessing lower polarity, possibly establishing more and stronger interactions with the hydrophobized residues, therefore stabilizing the structures and resisting higher temperatures more effectively than PLA [48].

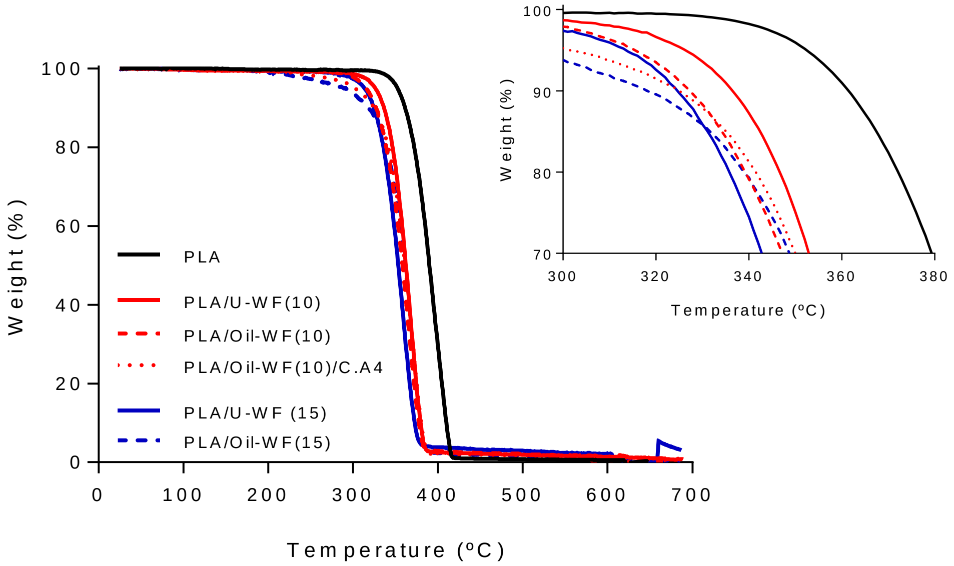


Figure 52 | TGA thermograms of compositions with untreated or oil-treated wood flour, processed by twin-screw extrusion, possessing polylactic acid as matrix phase. The insert represents the thermograms with smaller temperature ranges for a clearer analysis of the initial degradation of the different compositions. All samples were recorded at 10 °C min^{-1} under nitrogen atmosphere.

4.3.1.2 DSC

Considering the influence of the degree of crystallinity (Xc) on the mechanical performance of polymers, this parameter was evaluated on the developed materials, by DSC. The determination of the temperatures of crystallization (Tc) and melting (Tm), and the respective enthalpies of crystallisation (ΔHc) and melting (ΔHm) were also assessed. The results obtained for composites with PP basis are summarized in **Table 7**.

No significant differences were obtained on the Tc values of the different composites relatively to the neat polymer. However, slight decreases on the Tm values were registered with the increase of wood content. Following this pattern, lower values of melting enthalpy were registered for composites with increasing content in wood, which was reflected in higher degrees of crystallinity relatively to the neat polymer. The increase in Xc values was only manifested on compositions with 20 and 25 wt.% of WF, both unmodified or treated with soybean oil. This thus supports the capacity of wood to act as nucleating agent and therefore, to promote valuable materials with interesting mechanical properties. Materials with higher degree of crystallinity, i.e whose polymer chains are organised in a more ordered manner, are generally harder materials, with higher tensile strength [70]. This nucleation effect of wood, or the capacity of wood particles to act as sites that induce the crystallization of the matrix, was already observed by many authors, as is the case of Butylina, Martikka, and Kärki [57]. Those authors reported higher levels of degree of crystallinity for wood composites, using both bare and recycled PP as matrix.

Table 7 | Crystallinity (Tc) and melting (Tm) temperatures and respective enthalpies (ΔHc, ΔHm) obtained in the DSC scans from the cooling and second heating runs of polypropylene compositions. The degrees of crystallinity (Xc), calculated from **equation 2.1**, are also presented.

Sample	**Tc (°C)**	**ΔHc (J g^{-1})**	**Tm (°C)**	**ΔHm (J g^{-1})**	**Xc (%)**
PP	120.38 (± 1.78)	-91.99 (± 0.97)	167.45 (± 3.99)	88.78 (± 2.44)	42.48 (± 1.17)
PP/U-WF (10)	118.60 (± 0.69)	-86.87 (± 3.72)	166.68 (± 1.14)	78.83 (± 2.49)	41.91 (± 1.32)
PP/Oil-WF (10)	117.88 (± 0.92)	-85.06 (± 0.29)	164.19 (± 2.45)	75.39 (± 3.15)	40.08 (± 1.68)
PP/U-WF (15)	118.97 (± 0.86)	-83.39 (± 1.80)	166.49 (± 2.01)	72.54 (± 2.97)	40.83 (± 1.67)
PP/Oil-WF (15)	118.75 (± 0.08)	-81.21 (± 1.20)	164.59 (± 0.88)	72.50 (± 1.70)	40.81 (± 0.96)
PP/U-WF (20)	118.71 (± 0.19)	-80.31 (± 0.84)	164.12 (± 0.83)	73.01 (± 1.82)	43.67 (± 1.10)
PP/Oil-WF (20)	118.57 (± 1.04)	-81.58 (± 1.91)	163.85 (± 1.59)	76.21 (± 1.59)	45.58 (± 0.95)
PP/U-WF (25)	118.77 (± 0.65)	-78.61 (± 2.61)	165.70 (± 1.86)	74.53 (± 1.07)	44.57 (± 0.64)

The influence of WF content and its surface modification on the thermal transitions of PLA composites was not so evident. Given the grade of PLA used for the preparation of the different compositions being amorphous, i.e not possessing ordered polymer chains (0 % of crystallinity), no peaks related to crystallisation or melting transitions could be observed. Even so, differences on the heat of flow of samples could be observed near 60 °C. At this temperature, the polymer undergoes its glass transition (Tg), passing from a brittle state to a rubberier material. The identifiable Tg's from the several PLA compositions are presented in **Table 8**. No identification of Tg was possible on the remaining samples since the differences in their heat flow was rather small. Therefore, for a more concise and descriptive analysis, other techniques should be used, like dynamic mechanical analysis (DMA), to evaluate the influence of the different components on the thermal transitions of materials with PLA as matrix phase. Nevertheless, the results obtained mainly indicate that the plasticizer used significantly reduces the Tg of the polymer, from near 60 °C to 44 °C. Apparently, this component exhibits more impact than the wood content or the surface treatment of the residues, as similar values of Tg were determined for the two other compositions. A reduction on the Tg of PLA when acetyl tributyl citrate was added as plasticizer was previously observed. This effect was attributed to the low molecular size of the plasticizer, which allows it to occupy intermolecular spaces between polymer chains, reducing the formation of hydrogen bonding between chains. Therefore, the free volume and molecular mobility is increased, allowing the polymer to reach its rubberier state more easily [60].

Table 8 | Glass transition temperatures (Tg) obtained in the DSC scans from the second heating run of polylactic acid compositions.

Sample	Tg (°C)
PLA	59.65
PLA/C.A4	44.25
PLA/Oil-WF (10)/C.A4	44.91
PLA/U-WF (15)/C.A4	43.15

In fact, a small endotherm can be seen on the PLA compositions analysed, instead of the common step in heat flow that is characteristic of the glass transition of amorphous and semi-crystalline materials on DSC curves. This effect is probably related with the storage of the polymer. Indeed, during storage, and due to exposure to different temperatures, rearrangements on the structure of the polymer might have occurred to reach an equilibrium state. Therefore, when analyzing the polymer by DSC and when its Tg is reached, it is necessary to provide a greater amount of heat to the polymer so that the transition can be completed, resulting in the observed endotherm. This phenomenon, also known as physical ageing, can have particular influence on the properties of the polymer. In fact, due to this phenomenon, reduced impact resistance and ductility of the materials are often reported [71].

4.3.2 Rheological analysis

4.3.2.1MFI

The study of the MFI of the materials herein developed, allows recognizing the influence of the different components on their overall ease of flow. The results obtained from those materials with PP basis are presented in **Figure 53**, being the columns grouped by WF content, and compared to the MFI value of the neat polymer. It is mainly observed that the MFI tends to decrease with the increase on residue content, which is more pronounced for the compositions with untreated WF. This reduction on the ease of flow was already expected, considering that the used reinforcements increase the shear forces occurring during the extrusion process. Hence, this effect supports the lower values of ease of processing previously registered, on the extrusion at laboratorial scale phase, to mixtures containing higher content of residues.

From the compositions using the oil-treated WF it is also possible to observe the effect of the residue content on the reduction of the materials MFI. Although, higher values were obtained for these compositions when compared to those with the same amount but with untreated WF. These results thus indicate that the treatment has an effect on the fluidity of the materials, probably driven from the oil attached to the surface of the WF particles, acting as lubricant.

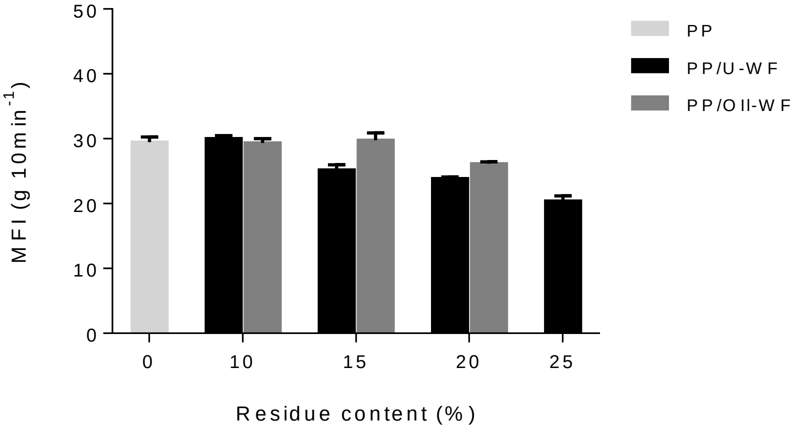


Figure 53 | Melt flow index values obtained for the compositions with polypropylene as matrix phase and untreated or soybean oil treated wood flour as reinforcing phase. The results are compared to the melt flow index values obtained for the neat polymer. All tests were performed at 230 °C with a 2.16 kg load.

For PLA compositions, the results were not so coherent (**Figure 54**). Nevertheless, for those using untreated WF, it can be observed that the MFI also decreased with the increasing content of wood. However, the registered values were higher than those obtained for the neat polymer.

In fact, the analysis of the neat polymer itself was difficult. The tests were performed at a temperature lower than that stated as optimum by the technical data sheet (210 °C), since at that temperature the polymer was too fluid and no valid tests could be accomplished. Even so, it was found that the MFI values obtained for the neat polymer, at 190 °C, were much higher than those pointed by the technical data sheet (10 g 10 min^{-1}). This might, once more, be attributed to the storage of the polymer, since, considering its ability to absorb moisture, it might have degraded during storage time, thus reducing the length of polymer chains, which justifies the higher observed fluidity. However, this incoherency might also be driven from degradation of PLA during processing of composites.

Besides the incoherent results, the influence of the used plasticizer on the ease of flow of the materials is clear, representing its role as lubricant, as already observed on the laboratorial scale tests.

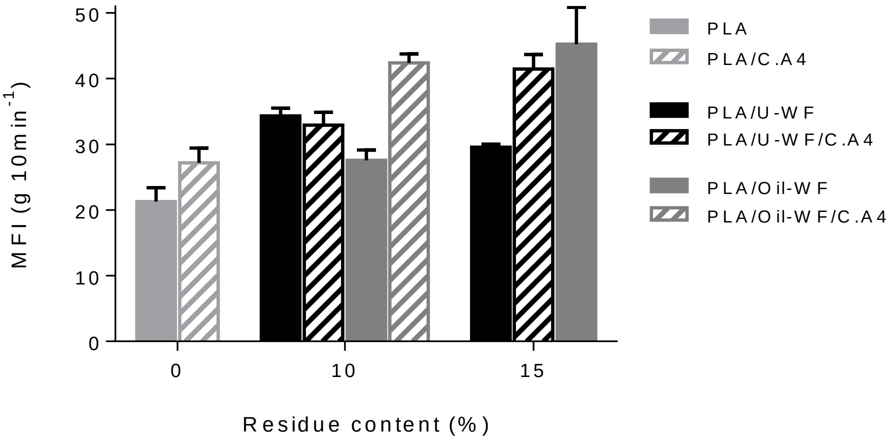


Figure 54 | Melt flow index values obtained for the compositions with polylactic acid as matrix phase and untreated or soybean oil treated wood flour as reinforcing phase. The results obtained for the compositions using the plasticizer (C.A4) are also presented, being all compared to the melt flow index values of the neat polymer. All tests were performed at 190 °C with a 2.16 kg load.

4.3.3 Physical properties

4.3.3.1 Moisture and water absorption

One of the main critical characteristics of wood materials that may reduce their applicability, for example for outdoor applications, is their tendency to absorb water and moisture. These capacities lead to swelling of the materials and often hinders their mechanical performance [72]. Therefore, to evaluate how the developed materials deal with these parameters and if the attempted pre-treatment of residues was beneficial for this matter, the absorption of moisture and water was accessed by two different methods.

The results obtained for the materials with PP basis are presented in **Figure 55**. The hydrophilicity of wood is, as expected, mostly experienced in materials with higher WF content. In these, higher levels of moisture (**Figure 55 (A)**) and water (**Figure 55 (C)**) absorptions were registered. On the other hand, as PP does not have tendency to absorb moisture, the registered values of percent of humidity for this material kept null during time. The level of water absorption obtained for this material is therefore related with the method used, in which, after being immersed in water, the materials are simply blotted with tissue paper and weighted. Given this, it is possible that some residual water is still adhered to the surface of the materials, thus influencing the weighting and consequently the results.

In **Figure 55 (B)**, it is noticeable that there is not a concrete correlation between the compositions with untreated and oil-treated residues. For those with 10 wt.% of reinforcing phase, contrary to what was intended, the oil-treated composition appears to be more sensitive to moisture absorption. This is supported by the water absorption results, in which higher levels of this parameter were also registered when compared to the composition with same amount but with untreated residue. Consequently, for this percentage of WF, the soybean oil pre-treatment appears to have been disadvantageous. For the compositions with 15 wt.% of WF, considering the errors associated to each measurement, the levels of moisture and water absorption appear to have been very similar, suggesting that the oil treatment had little or no influence on the hydrophilicity of the composites. Lastly, considering the compositions with 20 wt.% of WF, it appears that the oil-treated material, despite possessing higher wood content than its untreated counterpart, absorbed lower levels of moisture and water during the tests. These results thus indicate that the oil treatment was effective for the PP composite with 20 wt.% of reinforcing phase. However, it must be considered that the errors associated to the measurements in these compositions are also higher, which reveals the heterogeneity of the materials obtained during processing.

Jang and Kim [51], studying the water absorption of PP composites with 20 wt.% of cellulose fibres, also observed a reduction on WA levels for soybean oil treated materials, when compared to those obtained in materials with untreated reinforcing phase. In their study, a greater reduction of these levels was obtained (approximately 18 %, whereas, in our study, the WA levels of the oil-treated composition was only 6 % lower). Even though, it must be kept in mind that, in our study, the test was performed on granules obtained from the extrusion processes, whereas theses authors used specimens with defined and regular dimensions, being therefore less subjected to error.

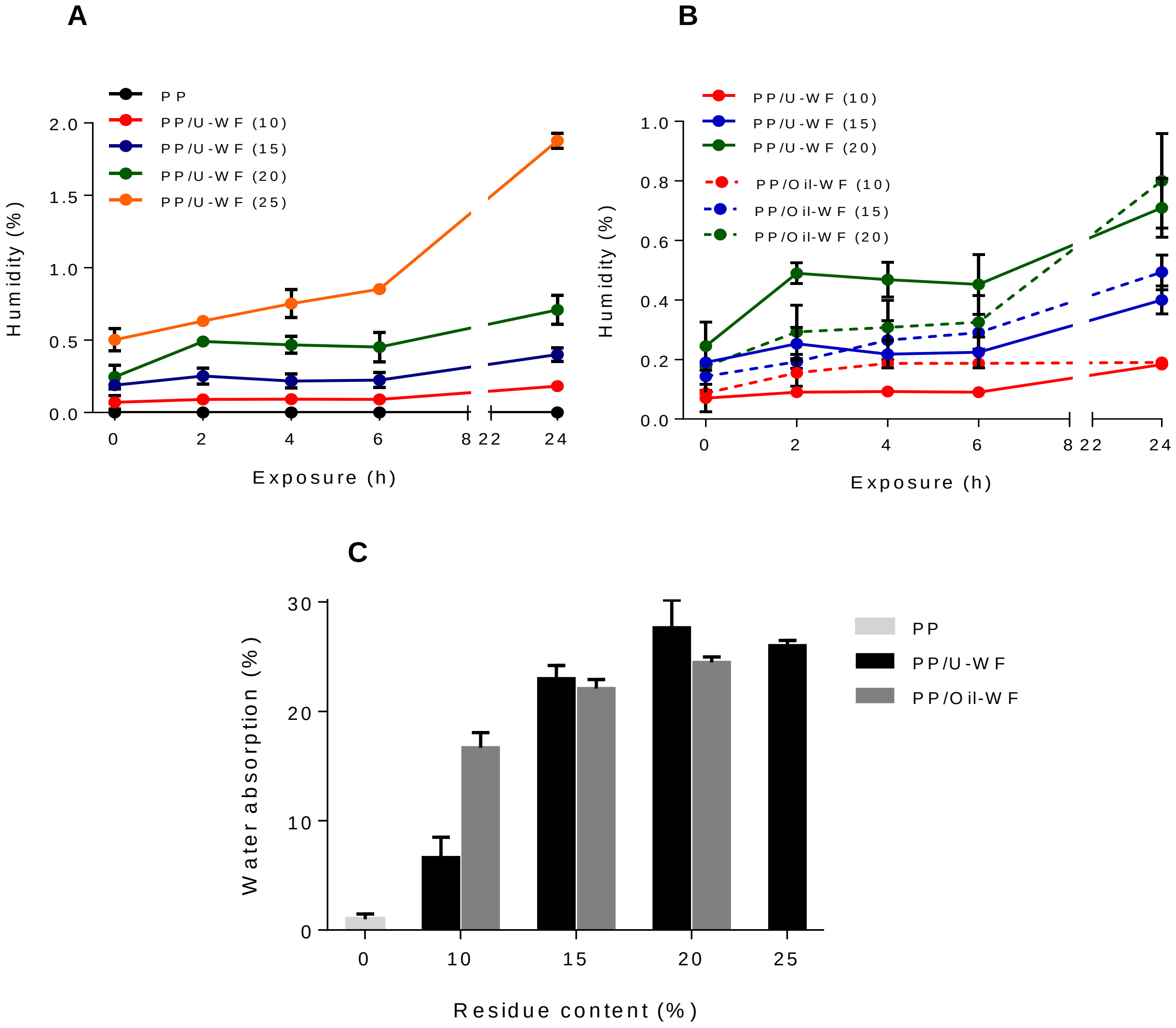


Figure 55 | Levels of humidity (**A** and **B**) and water absorption (**C**), gained for 24 h, by polypropylene composites using untreated or soybean oil treated wood flour as reinforcing phase, after drying in oven at 40 °C for 24 h.

The analysis of the compositions with PLA basis was considerably more difficult given the higher errors associated to the measurements performed on these materials (**Figure 56**). The sensibility for moisture absorption of this polymer can be seen in **Figure 56 (A)**, in which the MC levels of PLA rise from zero to approximately 1 % in 24 h. Even though, the MC levels obtained for composites with this polymer matrix were very similar to those obtained with their PP counterparts. As an example, both composites with 10 wt.% of U-WF and PP or PLA as matrix phase showed increases in humidity levels from 0.2 % to near 0.4 %.

Interestingly, despite the similar humidity gains, the water absorption levels registered for PLA composites were significantly lower than those obtained in PP composites. This possibly indicates that higher interactions were established between WF and PLA, or that lower quantities of voids, formed by moisture evaporation during processing, are present. Furthermore, since the TGA thermograms did not allow the confirmation of the WF content on PLA compositions, the possibility of these compositions possessing lower wood contents than the PP samples must not be excluded. However, these different and unexpected results may also be driven from the different format of PP and PLA composites granules, in which the tests were performed. The granules from PLA compositions were significant smaller, having therefore less area exposed to water, which might have influenced the test. Following this, for a more accurate analysis and comparison between materials with different polymer basis, the test should be repeated, using more uniform samples.

The effect of the addition of plasticizer is not clear. While it seemed to have not influenced the moisture absorption when added to PLA alone, the results from the water absorption reveal the opposite, i.e. higher levels were obtained for the plasticized sample (**Figure 56 (B)**). However, for the remaining compositions it seems to have reduced their hydrophilicity. This effect is clearer for the composition with 15 wt.% of U-WF. With this sample, both lower levels of humidity gain during time, and water absorption after 24 h, were obtained relatively to the un-plasticized composition with the same amount of residue.

Regarding the influence of the WF treatment, similar levels of humidity gain and water absorption were registered for compositions with 10 wt.% of WF. On the contrary, for the material with 15 wt.% of oil-treated residue, lower levels were obtained in both tests when compared to those achieved by the composition with the same amount of untreated residue. The results thus infer that the oil treatment was more effective for compositions with higher WF content, as it was already hypothesized by the results achieved in the PP compositions. This higher efficiency of the treatment in materials with higher wood content is possibly driven from the consequent higher oil content present.

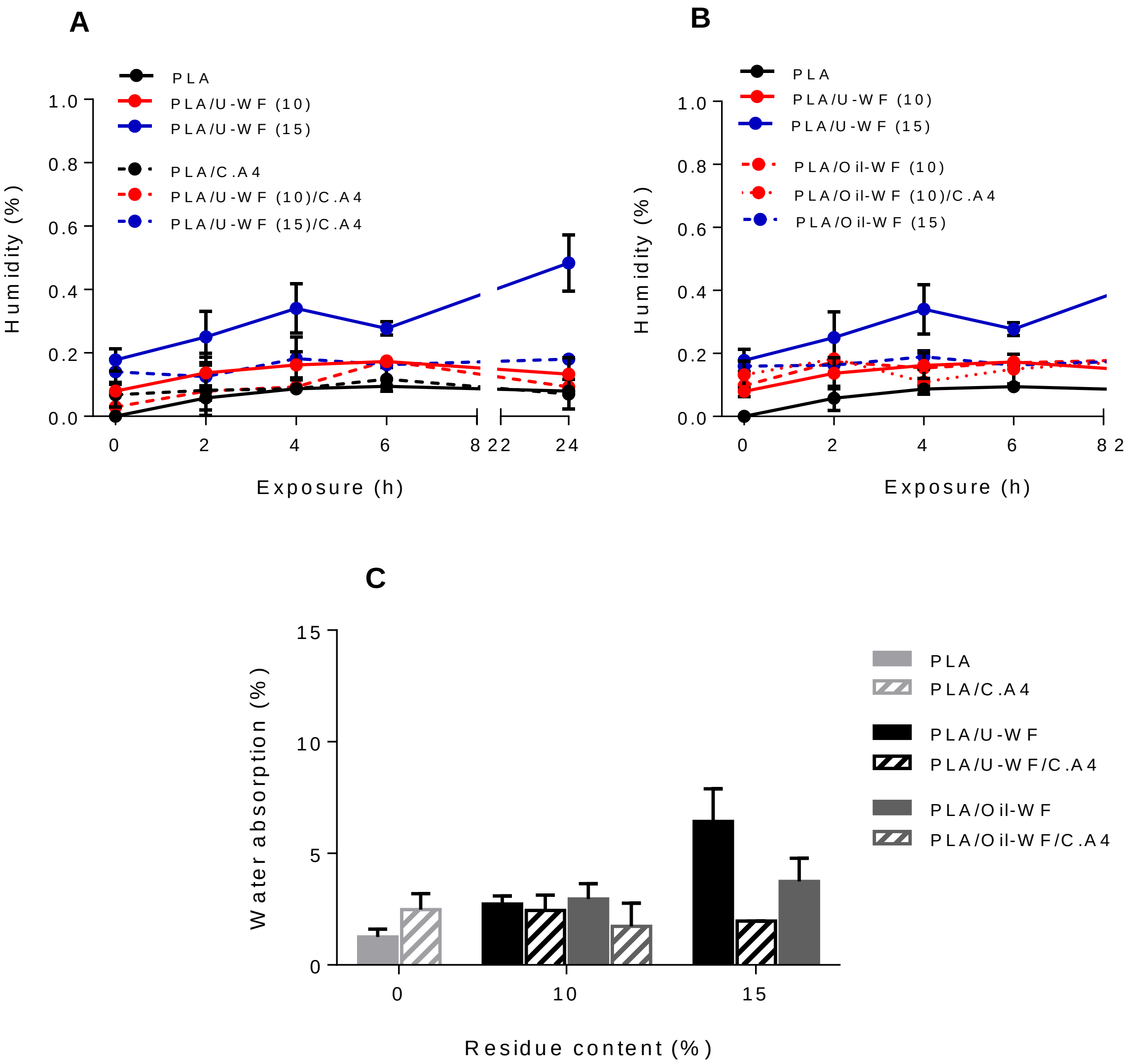


Figure 56 | Levels of humidity (**A** and **B**) and water absorption (**C**), gained for 24 h, by polylactic acid composites using untreated or soybean oil treated wood flour as reinforcing phase, after drying in oven at 40 °C for 24 h.

4.3.3.2 Water contact angle

Measuring the wettability of the materials might also stand as a useful tool to understand the influence of the addition of wood to polymers, and also to evaluate the contribution of surface modification of wood to this parameter. The wettability of materials is measured by contact angle, that is, the angle that is established between a certain volume of a given solvent, in this case water, and the surface of the materials. This thus represents the ability of the materials to absorb water at their surfaces. Higher WCA are generally related to more hydrophobic materials. The wettability of wood and their composites is influenced by different factors, among them surface roughness, surface tension, and moisture content [73].

In **Figure 57**, it is represented the visual aspect of the wettability of both the neat polymers used as matrix. It is observable that PP (**Figure 57 (A)**) forms slightly more spherical droplets on their surface than PLA, resulting in higher WCA values, as demonstrated in **Figure 58** (89 ° and 79 °, respectively). This outcome is due to the lower surface tensions experienced in the PP surface, resulting in a more hydrophobic material. In PLA, as the surface tensions are higher, overcoming the cohesion forces between the water molecules, the result is that more water is spread in the surface of the material (**Figure 57 (B)**), reducing its WCA, being consequently more hydrophilic.

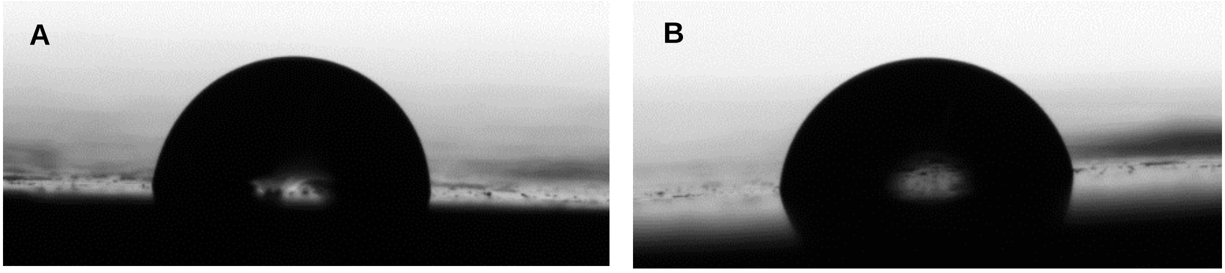


Figure 57 | Wettability of polypropylene (**A**) and polylactic acid (**B**) surfaces, measured by water contact angle.

When adding wood to the polymers, being this a hydrophilic material due to its lignocellulosic content, it was expected to observe a reduction on the WCA of composites. However, no differences were detected on the wettability. Indeed very similar values were obtained relatively to the respective neat polymers (**Figure 58**). In fact, in PP composites, slightly increased WCAs were observed, even having the tested samples higher wood content than that present on the tested PLA samples (20 and 10 wt.% respectively). Even though, it must be considered that the errors associated with the measurements are also higher, due to irregularities of the surfaces. Ideally, if the treatment of the residues resulted as expected, the higher hydrophobicity experienced by WF would probably result in higher interactions with the polymer matrix. Then, higher WCAs would be probably experienced by these composites, considering that they would be more stable and uniform [73]. However, no differences between composites with untreated and oil-treated WF were also detected.

The similar results obtained for all tested samples with the same polymer basis, are possibly due to the method used for their preparation. The compression molding of the different compositions led to higher accumulation of the polymer fractions on the surfaces of the plates, becoming the wood particles entrapped between polymer layers. Therefore, the surfaces were very similar among different compositions, which was especially evident for those with PLA basis, therefore resulting in also similar WCAs. To obtain a more comprehensive evaluation, the study of the WCA on the different compositions within a defined time period would be valuable, and differences on the rate of water absorption could be observed, consequently allowing a better identification of the wettability of the materials.

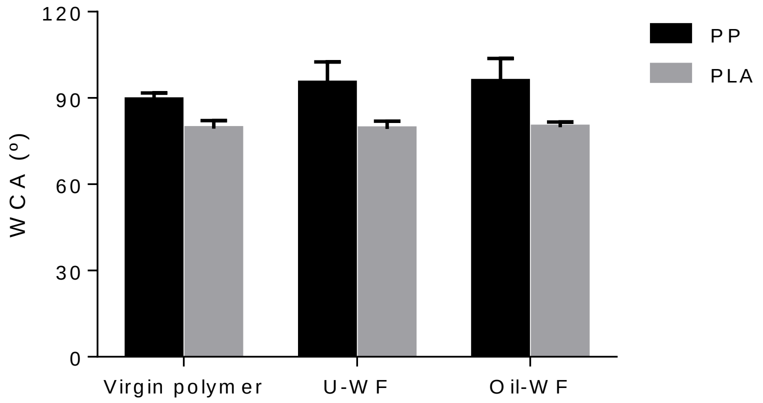


Figure 58 | Water contact angles obtained for both the used polymers and respective composites using untreated or oil-treated wood flour. For polypropylene composites, the tested samples possessed 20 wt.% of wood flour, whereas those with polylactic acid basis possessed 10 wt.% in content of the reinforcing phase.

4.3.4 Morphological analysis

4.3.4.1 SEM

The study of fractured surfaces of composites allows the evaluation of the reinforcement/matrix interface and how these two components interact and adhere to each other. The degree of interaction between the two components has an effect on the mechanical performance of the materials, dictating their possible fields of application. Therefore, SEM analyses were carried out to evaluate the addition of WF to polymer matrix, as well as to understand the influence of the performed functionalization with soybean oil on the interaction of the components.

In **Figure 59**, the depositions of untreated **(A)**, and oil-treated **(B)** WF particles on PP basis are shown. It can be observed that, in the untreated sample, the WF particles are more separated, existing depressions between the fibres. These gaps suggest the occurrence of fibre pull-outs when fractioning, an effect characteristic of weak interactions. On the other hand, in **Figure 59 (B)**, the WF particles appear to be more adhered between them, not showing evidence of fibre pull-outs. This is possibly driven from the presence of the vegetable oil that act as bonding agent.

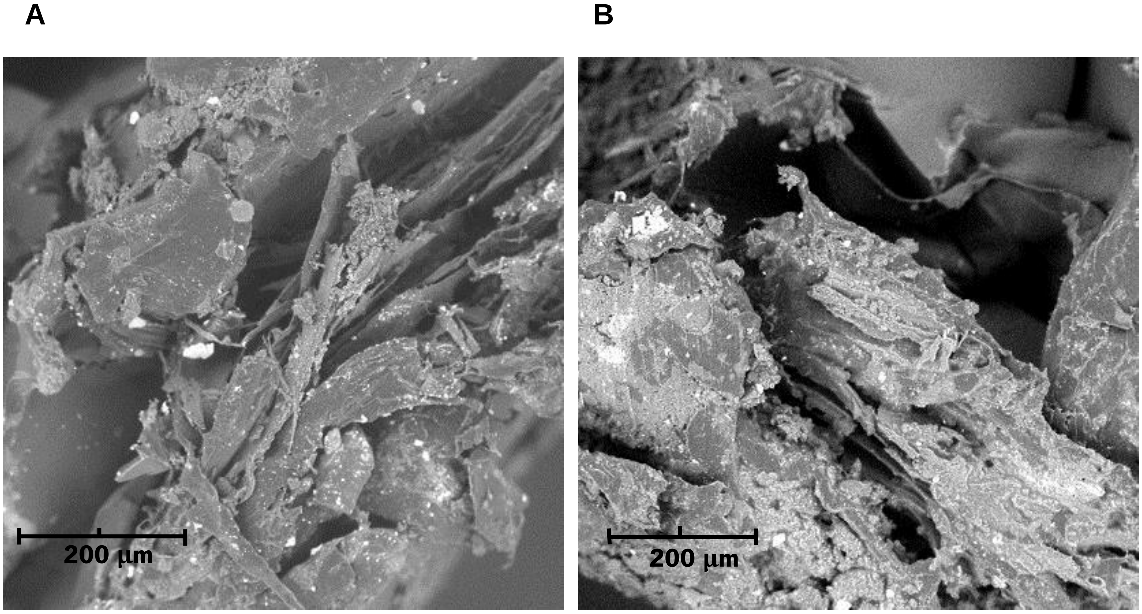


Figure 59 | Deposition of untreated **(A)** and oil-treated **(B)** wood flour particles on polypropylene matrices. The images were acquired on PP composites with 15 wt.% in content of wood flour.

In **Figure 60**, the interactions of WF with the PP matrix can be assessed in more detail, being visible that, in the untreated sample **(A)**, besides the suggested fibre pull-outs, a gap between the WF particles and the polymer was established. This gap existing between the two phases emphasizes the presence of weak adhesions between the components, most probably owed to their different polarities, which hinder affinity. This low affinity between components suggests therefore that the material holds weak mechanical properties. On the other hand, in the oil-treated sample **(B)**, the WF particles seem to be significantly more adhered to the polymer, indicating that the treatment was effective on improving the interaction of the two components. This therefore suggests that higher mechanical performances would be probably achieved with this material, when compared to its untreated counterpart. The improved adhesion of the components was already expected since the oil treatment improves the hydrophobicity of WF particles, reducing their polarity, as demonstrated in section 4.2.5, consequently improving the affinity to interact with the polymer matrix.

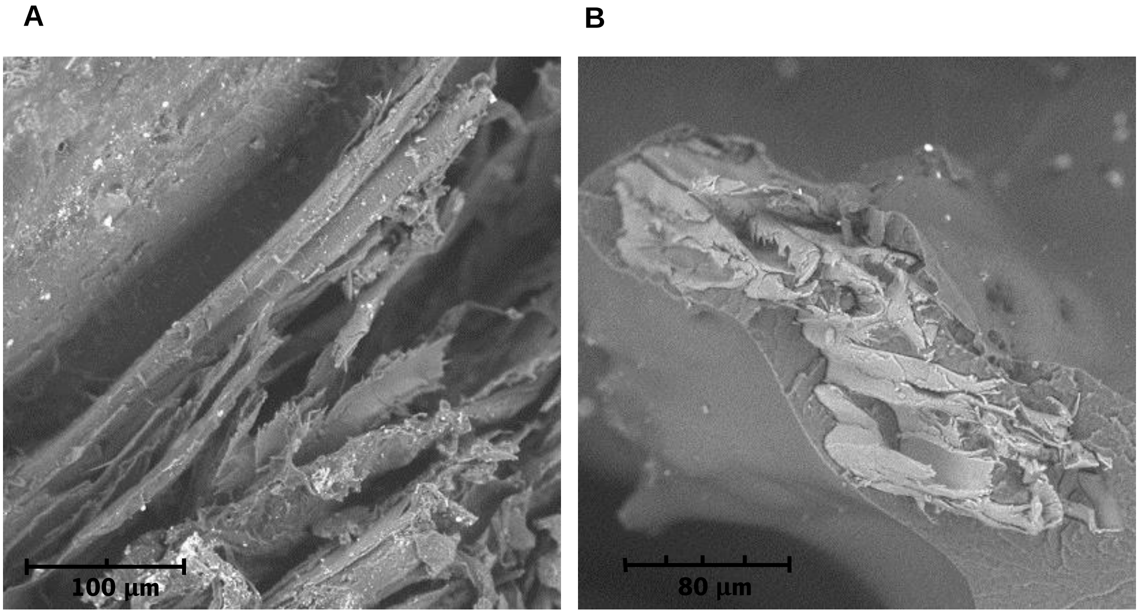


Figure 60 | Interaction of untreated **(A)** and oil-treated **(B)** wood flour particles on polypropylene matrices. The images were acquired on PP composites with 15 wt.% in content of wood flour.

In PLA compositions, the evaluation of the interfaces was more difficult since the WF particles were scarce. Even though, from **Figure 61**, it is suggested that the treated sample **(B)** once more possessed improved interface adhesion, given the more accessible identification of WF particles that remained in the fractured surface surrounded by polymer. In the untreated sample **(A)**, wood appears to have been pulled out once more during fraction. In both samples it can be spotted the existence of voids, which can be caused by the evaporation of water molecules during processing, due to insufficient drying of the materials. These voids were also present in PP samples.

In PLA compositions, plastic deformation has also occurred, as indicated by the prolongations of the smoother surfaces that correspond to the polymer. The plastic deformation might be an indicator of good adhesions between the components, since, the overall material may offer more resistance during fracture, deforming before breaking. Based on this supposition, as the plastic deformation occurred in higher extent in the treated sample, this effect supports the beneficial action of soybean oil solutions for the functionalization of WF and development of valuable green composites.

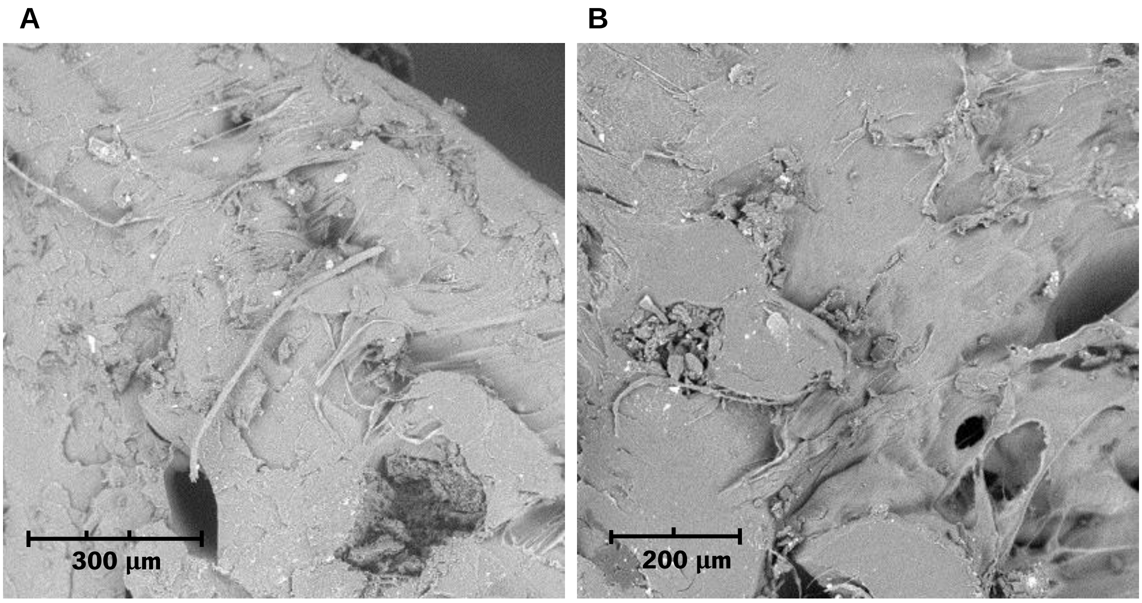


Figure 61 | Interaction of untreated **(A)** and oil-treated **(B)** wood flour particles on polylactic acid matrices. The images were acquired on PLA composites with 10 wt.% in content of wood flour.

From PLA compositions containing the plasticizer, the major differences is related to higher plastic deformations for samples containing plasticizer, when compared to their un-plasticized counterparts (**Figure 62**). This effect, besides being a possible indicator of higher adhesions between components, might also be caused by higher flexibilities experienced by these samples. Herein, for the untreated sample, it was possible to identify more areas with WF particles, suggesting that this component improves the dispersion of WF in the polymer, as already pointed out in section 4.1.3. In this sample **(A)**, the gap between WF and the polymer can be also observed. However, the comparison of the adhesion with that obtained in the plasticized and treated sample **(B)** cannot be done efficiently, since few areas with WF could be identified in the latter.

Herein, considering that SEM analysis were only performed on one or two granules of each composition, which are not representative of the overall composition, further analysis on other granules should be performed so a more accurate correlation of the influence of residue addition, pre-treatment, and plasticizer addition, on the adhesion of the components can be outlined.

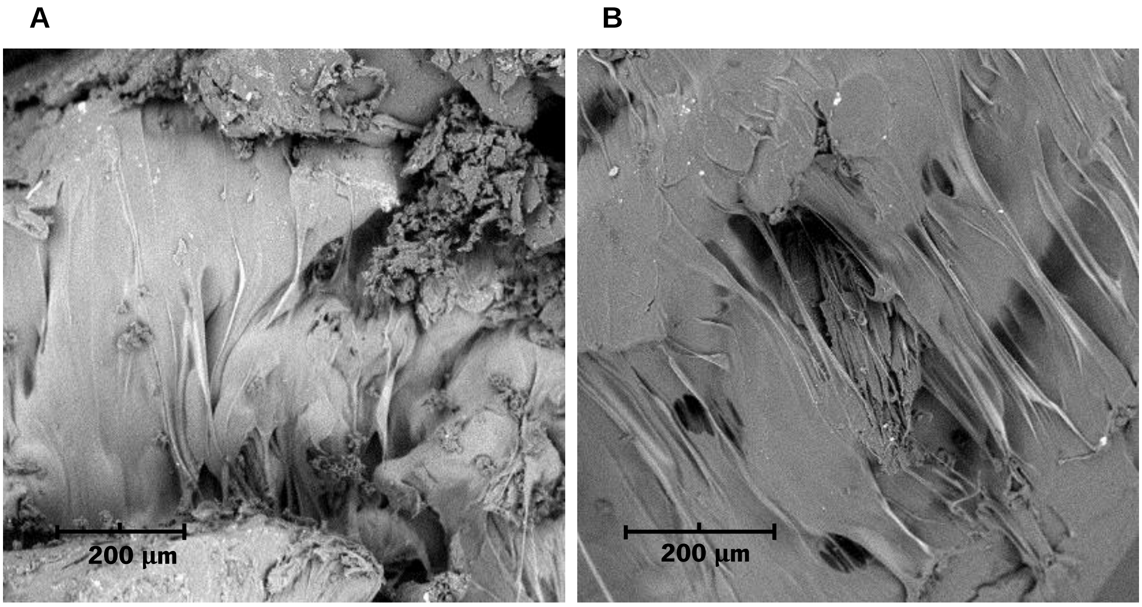


Figure 62 | Interaction of untreated **(A)** and oil-treated **(B)** wood flour particles and plasticizer on polylactic acid matrices. The images were acquired on PLA composites with 10 wt.% in content of wood flour and 10 wt.% of the plasticizer C.A4.

5. CONCLUDING REMARKS AND FUTURE PROSPECTS

The developed work consisted in three core stages, directed at the preparation of green polymer composites, with interesting properties, capable of competing with the currently leading plastic materials. From a first laboratorial scale phase, it was possible to narrow the possibilities of compositions and select the more interesting components and conditions to be reproduced at larger scale. For its ease of process, PP proved to be a good choice of polymer to be used as matrix phase in the subsequent stage, along with PLA, for its biodegradable nature and resistance to break. The higher cellulose content and the shape of WF particles proved to be advantageous, leading to stronger and better dispersed mixtures, with lower surface roughness. Despite the very similar results among mixtures assembled with differently treated residues, the surface modification with soybean oil solution stood out displaying interesting properties.

The study carried on the surface modification of WF and α-cell with the vegetable oil hold very promising results that supported its use as treatment of WF in twin-screw extrusion. The FTIR-ATR spectra of the treated residues displayed new absorption peaks at 3000-2850 cm^{-1} (C-H bonds of triglycerides' alkyl chains) and 1745 cm^{-1} (ester linkages), indicating that effective transesterification reactions had probably occurred. This surface modification translated into more thermally stable residues, starting to degrade at higher temperatures than the untreated ones. 5 wt.% soybean oil/ethanol solutions proved to be the more efficient treatment, having conferred hydrophobicity to the residues.

The characterization of the composites developed by twin-screw extrusion showed that their properties are mainly influenced by residue content. Compositions with higher WF content has reduced the ease of flow of the materials in melt state, hindering their process, and lead to higher water and moisture absorptions. However, both the characteristics are in some cases improved with the oil treatment. PP with 15 or 20 wt.% in content of oil-treated WF seem to be the most promising compositions, for having a small reduction on the MFI relatively to the neat polymer, similar or reduced moisture and water absorption than their untreated counterparts, and specially for having improved adhesion of their constituents, as indicated by SEM. The properties of PLA compositions were more inconsistent, but the addition of plasticizer clearly proved to have a positive effect on processing, reducing, however, both the initial thermal decomposition temperature and the Tg, which can be an impediment for their application.

The used batch of PLA possibly faced some degradation during storage, and for that reason, new compositions should be developed and characterized using a different batch for more accurate evaluations.

For future work, the optimisation of the processing conditions to minimise the existence of voids in the compositions is of major importance, considering that these voids significantly affect most properties of the materials. Optimisation of WF feeding is also needed, since the strategy followed in the present work was inconsistent.

Products assembled from green composites generally experience changes in their form when exposed to different conditions, for example to water, which limits their application outdoors. Therefore, the study of the dimensional stability of the developed materials would also be appreciated to evaluate their applicability.

Given the apparent higher interactions established between components on PP compositions with oil-treated WF, the evaluation of their mechanical performance, namely the tensile, flexural and impact strengths, would be very valuable to effectively understand and correlate the influence of the treatments in the materials' performance, and their possible application. Hence, the further evaluation and optimisation of the performance with residues treated with oil solutions at different concentrations would also be interesting.

The portrayed theme holds great relevance when considering the current efforts on sustainable materials, offering a cost-effective alternative, and may serve as good basis for further advances

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APPENDICES

Appendix A: Composition of mixtures tested by laboratorial-scale extrusion

In Appendix A are discriminated the percent compositions of all mixtures tested by laboratorial scale extrusion.

A.1- Control mixtures

In **Table A.1** are described the compositions of control mixtures, obtained by processing of neat polymers, or supplemented with the respective plasticizers (Durasyn 180 for the polyolefins, and Citroflex A4 for PLA mixtures). All were compounded at 190 °C.

Table A.1 | Percent composition of control mixtures, of polymers without residue, tested on a laboratorial scale extruder.

Composition					
PP (wt.%)	*Plasticizer* (wt.%)	*PE* (wt.%)	*Plasticizer* (wt.%)	*PLA* (wt.%)	*Plasticizer* (wt.%)
100	-	100	-	100	-
95	5	95	5	95	5
90	10	90	10	90	10
85	15	85	15	70	30

A.2- Mixtures with untreated residues

In **Table A.2** are described the compositions of mixtures obtained with residues without any pre-treatment. Mixtures with and without plasticizer were attempted. All were compounded between 170-190 °C.

Table A.2 | Percent composition of mixtures tested on a laboratorial scale extruder, using wood flour, cork powder, or cellulose fibres, without any previous functionalization, as reinforcement.

Residue		**Composition**									
Treatment		*PP* (wt.%)	*Residue* (wt.%)	*Plasticizer* (wt.%)	*MAPP* (wt.%)	*PE* (wt.%)	*Residue* (wt.%)	*Plasticizer* (wt.%)	*PLA* (wt.%)	*Residue* (wt.%)	*Plasticizer* (wt.%)
Without treatment	WF	95	5	0	0	95	5	0		-	
		90		5	0	90		5			
		85		5	5						
		90	10	0	0	80	10	10	90	10	0
		85		5	0				85		5
		75		10	5				80		10
		80	20	0	0	80	20	0	80	20	0
		75		5	0	60		20	75		5
		55		20	5				70		10
	CP	95	5	0	0	90	5	5		-	
		90		5	0						
		85		5	5						
		90	10	0	0	80	10	10	90	10	0
		85		5	0				85		5
		75		10	5						
		80	20	0	0	60	20	20	80	20	0
		75		5	-				70		10
		55		20	5						
	CF	85	10	5	0		-		85	10	5
		70	20	10					70	20	10
									60		20
									50		30

A.3- Mixtures with silane and alkaline treated residues

In **Table A.3** are described the compositions of mixtures obtained with residues pre-functionalized with alkaline or silane treatments. For the silane treatment, two concentrations of APTES solutions were tested (1 and 4 wt.%). In all mixtures the respective plasticizer, according to the polymer in use, was added. All mixtures were compounded at 170 °C.

Table A.3 | Percent composition of the different mixtures tested on a laboratorial scale extruder, using wood flour or cork powders, previously functionalized with alkaline or silane treatments, as reinforcement.

Residue		**Composition**									
Treatment		*PP* (wt.%)	*Residue* (wt.%)	*Plasticizer* (wt.%)	*MAPP* (wt.%)	*PE* (wt.%)	*Residue* (wt.%)	*Plasticizer* (wt.%)	*PLA* (wt.%)	*Residue* (wt.%)	*Plasticizer* (wt %)
NaOH (5 %)	WF	85	10	5	-	85	10	5		-	
		70	20	10		70	20	10			
	CP	85	10	5	-	85	10	5		-	
		70	20	10		70	20	10			
Silane (1 %)	WF	85	10	5	-	85	10	5		-	
		70	20	10		70	20	10	70	20	10
									60		20
									50		30
			-				-		40	30	30
	CP	85	10	5	-	70	20	10		-	
		65	20	15			-				
Silane (4 %)	WF	85	10	5	-	85	10	5		-	
		70	20	10	-	70	20	10			
		60			10						
	CP	85	10	5	-	85	10	5		-	
		70	20	10	-	70	20	10			
		60			10						

A.4- Mixtures with soybean oil treated residues

In **Table A.4** the compositions of mixtures obtained with residues pre-treated with soybean oil solutions are described. Mixtures with residues treated by two different solvents were attempted: ethanol and acetone. For ethanol solutions, two different oil concentrations were tested (2.5 and 5 wt.%), whereas acetone solutions possessed an oil concentration of 1 wt.%. In all mixtures the respective plasticizer, according to the polymer in use, was added. In PP mixtures, the addition of the coupling agent MAPP was also tested. All mixtures were compounded at 170 °C.

Table A.4 | Percent composition of the different mixtures tested on a laboratorial scale extruder, using wood flour, cork powder, or cellulose fibres, previously functionalized by transesterification methods, as reinforcement.

Residue		**Composition**						
Treatment		*PP* (wt.%)	*Residue* (wt.%)	*Plasticizer* (wt.%)	*MAPP* (wt.%)	*PLA* (wt.%)	*Residue* (wt.%)	*Plasticizer* (wt.%)
E-Oil (2.5 %)	WF	85	10	5	-		-	
		70	20	10	-			
		60			10			
	CP	85	10	5	-		-	
		70	20	10	-			
		60			10			
	CF	85	10	5	-		-	
		70	20	10				
E-oil (5 %)	WF	70	20	10	-	70	20	10
	CF	70	20	10		50	20	30
A-oil (1%)	WF	70	20	10	-	60	20	20
	CF	70	20	10	-	70	20	10

Appendix B: Calibration curves for twin-screw extrusion

In Appendix B the calibration curves used to synchronise the equipment during compounding of green composites, for the achievement of the intended compositions, are presented. The volumetric feeder 1 was used for the polymers (PP and PLA), volumetric feeder 2 for the residues (U-WF and Oil-WF), and the peristaltic pump was used, for PLA compositions, to supplement the plasticizer C.A4.

B.1- Polymers

In **Figure B.1.1** and Figure **B.1.2** the calibration curves obtained for PP and PLA, respectively, are presented. The curves represent the debit of polymer, in grams per minute, according to the positions set on the volumetric feeder 1 (VFP).

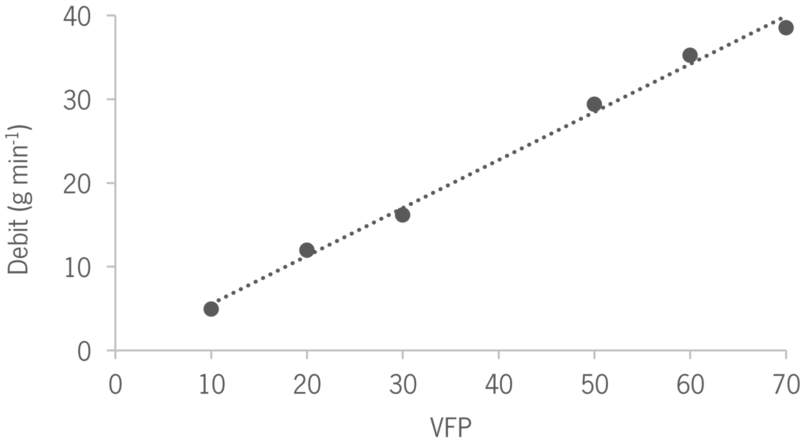

Figure B.1.1| Calibration curve of the debits obtained for polypropylene according to the position set on volumetric feeder. The relation between the two is defined by the equation: Debit=0.5732 (± 2.7923) VFP - 0.1902 (± 0.0614), with an associated R^2 of 0.98941.

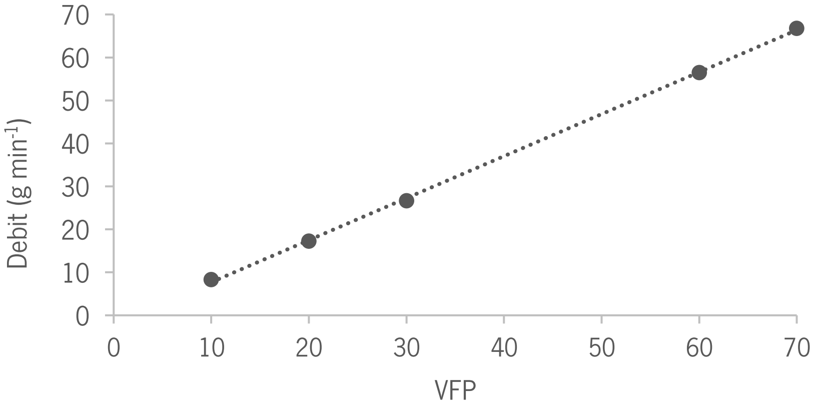

Figure B.1.2 | Calibration curve of the debits obtained for polylactic acid according to the position set on volumetric feeder. The relation between the two is defined by the equation: Debit=0.9775 (± 1.6583) VFP – 2.0683 (± 0.0350), with an associated R^2 of 0.9996.

B.2- Residues

In n **Figure B.2.1** and Figure **B.2.2** the calibration curves obtained for U-WF and Oil-WF, respectively, are presented. The curves represent the debit of polymer, in grams per minute, according to the positions set on the volumetric feeder 2 (VFP).

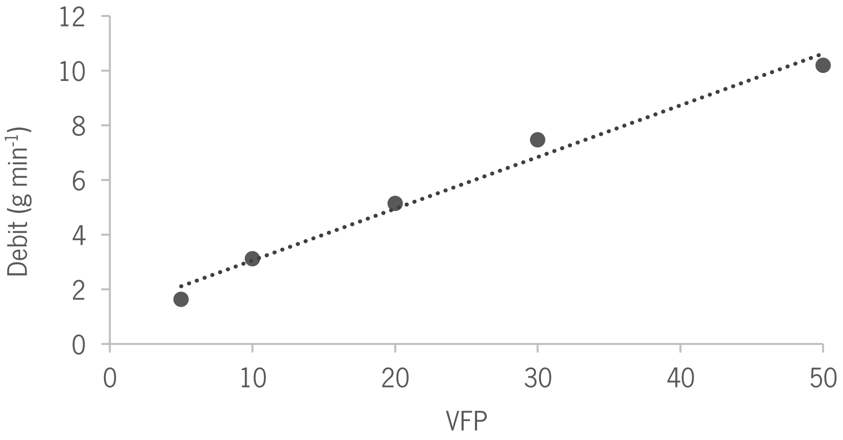

Figure B.2.1 | Calibration curve of the debits obtained for untreated wood flour according to the position set on volumetric feeder. The relation between the two is defined by the equation: Debit=0.1892 (± 1.3347) VFP + 1.1632 (± 0.0476), with an associated R^2 of 0.9816.

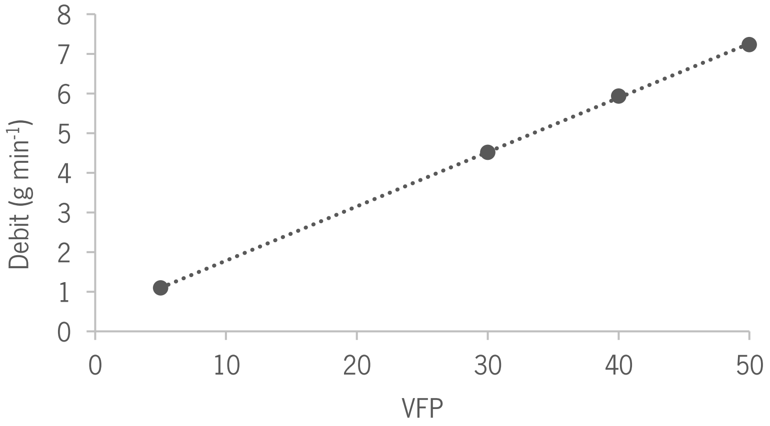

Figure B.2.2 | Calibration curve of the debits obtained for soybean oil-treated wood flour according to the position set on volumetric feeder. The relation between the two is defined by the equation Debit=0.1369 (±0.1736) VFP + 0.4132 (± 0.0049), with an associated R² of 0.9999.

B.3- Plasticizer

In **Figure B.3** the calibration curve obtained for the plasticizer C.A4 is presented. The curve represents the debit of plasticizer, in grams per minute, according to the positions set on the peristaltic pump (PPP).

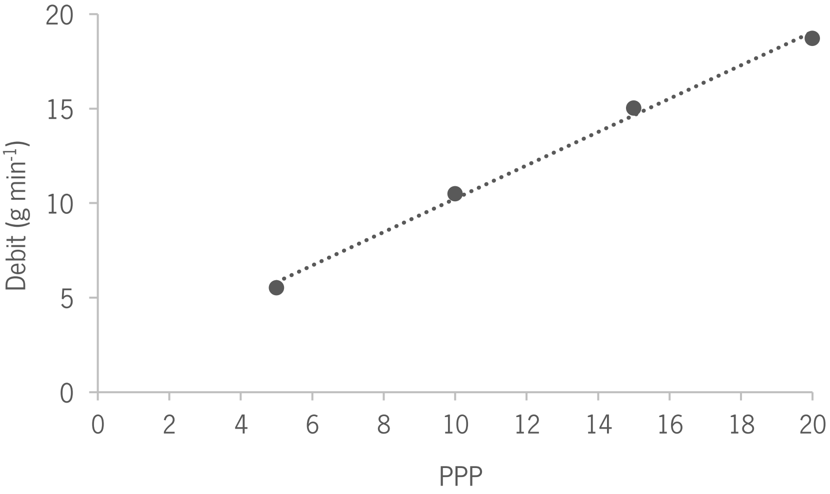

Figure B.3 | Calibration curve of the debits obtained for the plasticizer Citroflex A4 according to the position set on the peristaltic pump. The relation between the two is defined by the equation: Debit=0.8825 (± 2.4413) PPP + 1.41 (± 0.1783), with an associated R² of 0.9956.

Appendix C: Properties of mixtures tested by laboratorial-scale extrusion

In Appendix C the levels attributed to the properties in study of all mixtures tested by laboratorial scale extrusion are discriminated. Properties like ease of processing, resistance to break, flexibility and surface roughness were evaluated, having been attributed different levels according to the scale presented in Chapter 4.

In some cases the filaments presented particularities, having been labelled as follows:

a) The filaments, when leaving the extruder, presented a gluey behaviour, thus making the processing difficult.

b) The extruded mixture wasn't consistent throughout the procedure. Initial filaments, possessing more quantity of polymer, were more resistant, whereas the final filaments, constituted essential by residue, were more fragile.

c) The extruded mixture wasn't consistent throughout the procedure. Initial filaments, possessing more quantity of polymer, were more rigid, whereas the final filaments were more flexible and more easily bended.

C.1- Control mixtures

Table C.1 | Properties observed on mixtures obtained from the virgin polymers and, if present, the respective plasticizer, by laboratorial scale extrusion.

Composition		**Properties**											
	Plasticizer (wt.%)	*Processing*			*Resistance*			*Flexibility*			*Roughness*		
		PP	PE	PLA	PP	PE	PLA	PP	PE	PLA	PP	PE	PLA
No residue	0	3/4	2	1/2	4	5	5	2	0/1	0	0	0	0
	5	3/4	2	4	5	5	5	4/5	2	0/1	0	0	0
	10	3/4	2	4	5	5	5	4/5	2	0/1	0	0	0
	15	4	2	-	5	5	-	5	2/3	-	0	0	-
	30	-	-	4/5[a)]	-	-	4/5	-	-	5	-	-	0

Table C.2 | Properties observed on mixtures obtained by laboratorial scale extrusion, where the used residues did not pass through any previous treatment.

	Composition		**Properties**											
	Residue (wt.%)	*Plasticizer (wt.%)*	*Processing*			*Resistance to break*			*Flexibility*			*Roughness*		
			PP	PE	PLA	PP	PE	PLA	PP	PE	PLA	PP	PE	PLA
Without treatment	WF (5 %)	0	3/4	2	-	4	5	-	3/4	2	-	3	3	-
		5	4	2	-	4	5	-	4	3	-	2	2/3	-
	WF (10 %)	0	3	-	1/2	3	-	3	3/4	-	1/2	4	-	3/4
		5	3/4	-	4	4	-	5	4	-	1	3	-	2/3
		10	-	2	4/5	-	5	5	-	4	1	-	3	2/3
	WF (20 %)	0	2	1	1	2/3	2/3	2	2/3	2/3	1/2	5	4/5	4/5
		5	3	-	2/3	3	-	5	3	-	1	4/5	-	3
		10	-	-	3/4	-	-	4/5	-	-	0/1	-	-	3
		20	-	1/2	-	-	3	-	-	3	-	-	3/4	-
	CP (5 %)	0	3	-	-	4	-	-	4	-	-	4	-	-
		5	3/4	2	-	4	5	-	4	2/3	-	4	1	-
	CP (10 %)	0	3	-	1/2	4	-	3	4	-	2/3	4	-	4/5
		5	3/4	-	3	3/4	-	4/5	4	-	1	5	-	2
		10	-	2	-	-	5	-	-	4	-	-	2/3	-
	CP (20 %)	0	2	-	1	**b)**	-	1/2	3	-	2	5	-	5
		5	2/3	-	-	3	-	-	4	-	-	5	-	-
		10	-	-	3	-	-	4	-	-	1/2	-	-	2/3
		20	-	1/2	-	-	4/5	-	-	4	-	-	2	-
	CF (10 %)	5	3/4	-	3	5	-	5	3	-	0/1	1	-	1
	CF (20 %)	10	2	-	2	4	-	4/5	3/4	-	1	1/2	-	1
		20	-	-	2/3	-	-	4	-	-	**c)**	-	-	1
		30	-	-	3	-	-	5	-	-	5	-	-	1

Table C.3 | Properties observed on mixtures obtained by laboratorial scale extrusion, where the used residues were previously functionalized by alkaline or silane treatments.

Composition			**Properties**											
	Residue (wt.%)	*Plasticizer (wt.%)*	*Processing*			*Resistance to break*			*Flexibility*			*Roughness*		
			PP	PE	PLA	PP	PE	PLA	PP	PE	PLA	PP	PE	PLA
NaOH (5 %)	WF (10 %)	5	4	2	-	3/4	4	-	3	3/4	-	3	2	-
	WF (20 %)	10	3	1/2	-	3	3/4	-	3/4	3	-	4	3	-
	CP (10 %)	5	4/5	2	-	4/5	5	-	3	3/4	-	3	2	-
	CP (20 %)	10	3/4	1/2	-	3	4	-	3	3/4	-	3	2	-
Silane (1 %)	WF (10 %)	5	3/4	2	-	4	4/5	-	3	4	-	3/4	2	-
	WF (20 %)	10	3	1/2	3/4	3	3/4	4/5	3	4	0/1	4/5	3	4
		20	-	-	3	-	-	3	-	-	**c)**)	-	-	4
		30	-	-	4/5	-	-	4	-	-	4/5	-	-	4
	WF (30 %)	30	-	-	2	-	-	**b)**	-	-	**c)**	-	-	4
	CP (10 %)	5	3/4	2	-	3/4	5	-	3	4	-	4	2	-
	CP (20 %)	10	-	1/2	-	-	3/4	-	-	4	-	-	3/4	-
		15	3	-	-	2/3	-	-	4	-	-	4/5	-	-
Silane (4 %)	WF (10 %)	5	4	2	-	4/5	5	-	3	4	-	2	2	-
	WF (20 %)	10	3	1/2	-	3	4	-	3	4	-	3	2	-
	CP (10 %)	5	4	2	-	4	5	-	3	4	-	3	2	-
	CP (20 %)	10	3	1/2	-	2	4	-	3	4	-	4/5	2	-

Table C.4 | Properties observed on mixtures obtained by laboratorial scale extrusion, where the used residues were previously functionalized by transesterification with soybean oil solutions, differing on the oil content and the used solvent.

Composition			**Properties**							
	Residue (wt.%)	*Plasticizer (wt.%)*	*Processing*		*Resistance to break*		*Flexibility*		*Roughness*	
			PP	PLA	PP	PLA	PP	PLA	PP	PLA
E-oil (2.5 %)	WF (10 %)	5	4	-	4/5	-	3	-	2/3	-
	WF (20 %)	10	3	-	4	-	2	-	3/4	-
	CP (10 %)	5	4	-	4	-	3	-	3	-
	CP (20 %)	10	3	-	2/3	-	2/3	-	4	-
	CF (10 %)	5	3/4	-	4/5	-	3	-	1	-
	CF (20 %)	10	2/3	-	4	-	3	-	1/2	-
E-oil (5 %)	WF (20 %)	10	4	3/4	3/4	1	2	1	3/4	3
	CF (20 %)	10	3	3	4	4/5	3	5	1/2	1
A-oil (1 %)	WF (20 %)	10	3	2/3	4	3/4	3	3	3/4	3/4
	CF (20 %)	10	2/3	2	4/5	4/5	3/4	1	3/4	1

C.5- Mixtures with MAPP

Table C.5 | Properties observed on mixtures obtained by laboratorial scale extrusion, using unmodified residues, or treated with silane (4 wt.%) or soybean oil/ethanol (2.5 wt.%) solutions. All compositions were supplied with MAPP.

	Composition			**Properties**			
	Residue (wt.%)	*MAPP (wt.%)*	*Plasticizer (wt.%)*	*Processing*	*Resistance to break*	*Flexibility*	*Roughness*
				PP			
Without treatment	WF (5 %)	5	0	4/5	4/5	4	3
			5	5	4/5	4	1
	WF (10 %)	5	0	4	3/4	3	4
			10	4	3/4	4	3
	WF (20 %)	5	0	3/4	3	3	4/5
			20	4	2	1/2	4
	CP (5 %)	5	5	4/5	4	4	2
	CP (10 %)	5	10	4	3/4	4	3
	CP (20 %)	5	20	3/4	1/2	2	5
Silane (4 %)	WF (20 %)	10	10	4/5	3	3	4
	CP (20 %)	10	10	4	3	3	4/5
E-oil (2.5 %)	WF (20 %)	10	10	3/4	3/4	2/3	3/4
	CP (20 %)	10	10	3/4	2/3	2	4/5