Development of Bio- and Eco-Composites for the Footwear Industry

Palloma Carvalho dos Santos

Final dissertation report submitted to

Escola Superior de Tecnologia e Gestão
Instituto Politécnico de Bragança

to obtain the Master Degree in

Chemical Engineering

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DEVELOPMENT OF BIO- AND ECO-COMPOSITES FOR THE FOOTWEAR INDUSTRY

por

Palloma Carvalho dos Santos

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Profa. Dra. Maria Filomena Barreiro
IPB

Profa. Dra. Isabel Patrícia Fernandes
IPB

Juliana Martins Teixeira de Abreu Pietrobelli
UTFPR - Orientadora

Profa. Dra. Juliana de Paula Martins
Responsável pelo TCC do Curso de Engenharia Química

- A FOLHA DE APROVAÇÃO ASSINADA ENCONTRA-SE ARQUIVADA NA SECRETARIA DO CURSO -

“It is said that even before a river falls into the ocean, it trembles with fear.
It looks back at the whole journey, the peaks of the mountains,
the long winding path through the forests,
through the people, and it sees in front of it such a vast ocean that
entering into it is nothing but disappearing forever.
But there is no other way. The river cannot go back.
No one can go back. Going back is impossible in existence.
The river has to take the risk and go into the ocean.
And only when it enters the ocean will the fear disappear
because only then will the river know that it is not disappearing
into the ocean; rather, it is becoming the ocean”.
Osho

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Abstract

The evolution of consumers' environmental awareness, allied to the demand for bio-products, is considered a challenge for the footwear sector. In this context, the development of novel composites, based on natural materials and by adopting green productive processes, is an area of great interest. Based on this motivation, the present work aims to develop cork composites where the toxic TDI-based binder traditionally used for cork agglomeration, is substituted by an aqueous water-based polyurethane adhesive reinforced with Melissa officinalis L. extract. The work was divided into three stages. The first one was dedicated to the synthesis of water-based polyurethane adhesives (PUD) following a modified pre-polymer method. Three adhesives were produced, namely a formulation with no added extract, and two formulations incorporating Melissa officinalis L. hydrophilic extract, at contents of 3 and 5% (w/w, prepolymer-basis). In the second stage of this study, based cork composites were produced using adhesives at contents of 20, 30 and 40% (w/w, cork-basis, adhesive weight based on its solids content). The final stage comprised the production of cork composites (30% of adhesives content of the three formulations were used) added with biomass residues (sugarcane bagasse (CA), malt bagasse (MA), coconut fibers (CO) and chia seeds (CH)) at contents of 5 and 10% (w/w, cork-basis).

The obtained results pointed out for the viability of using PUDs to substitute the traditionally used TDI-based binders, which also added several advantages. Namely, a remarkable increment of the water absorption capacity was identified, particularly when the adhesives were incorporated with the extract. It was observed that all the produced composites fulfill the imposed value of 70 mg/cm^2*. For the water desorption capacity, and with the exception of the composite produced with the adhesive added with 5% of extract at a content of 20%, all of the adhesives were below to the limit of 80%. This means that the adhesive hydrophilic nature lead to an increase of the composite drying time. Regarding the dimensional stability, almost all the produced composites presented shrinkage lower or close to 2%. The results evidenced also the increasing of film’s flexibility due to the extract incorporation. In a general way, the adding of biomasses results in the decrease of both water adsorption and desorption properties, even very close to the corresponding base-composites. Concerning shrinkage values, and flexibility, better results were generally achieved. Namely, in terms of flexibility, the biomasses conducting to the best results were CA, CO or CH at contents of 5% combined with the PU3C adhesive at a content of 30%.*

Resumo

A evolução da consciência ambiental dos consumidores, aliada à procura por bio-produtos, constituiu um desafio para o setor do calçado. Neste contexto, o desenvolvimento de novos compósitos, baseados em materiais naturais e adotando processos produtivos verdes, é uma área de grande interesse. Com base nesta motivação, o presente trabalho visa desenvolver compósitos de cortiça onde o ligante tóxico à base de TDI, tradicionalmente usado na aglomeração da cortiça, é substituído por um adesivo aquoso de poliuretano reforçado com um extrato de Melissa officinalis L. O trabalho foi dividido em três etapas. A primeira foi dedicada à síntese dos adesivos aquosos de poliuretano (PUD) seguindo o método do pré-polímero modificado. Três adesivos foram produzidos, nomeadamente uma formulação sem adição de extrato, e duas formulações incorporando o extrato hidrofílico de Melissa officinalis L., com teores de 3 e 5% (m/m, base pré-polímero). Na segunda etapa, os compósitos de cortiça foram produzidos utilizando adesivos num teor de 20, 30 e 40% (m/m, base cortiça, massa do adesivo baseado no teor de sólidos). A fase final visou a produção de compósitos de cortiça (teor de adesivo 30%) adicionados com resíduos de biomassa (bagaço de cana (CA), bagaço de malte (MA), fibras de coco (CO) e sementes de chia (CH), com teores de 5 e 10% (m/m, base cortiça).

Os resultados obtidos apontam para a viabilidade da utilização de PUDs para substituir os ligantes baseados em TDI, o que também agregou várias vantagens. Foi identificado um incremento substancial da capacidade de absorção de água, particularmente quando os adesivos continham o extrato. Observou-se que todos os compósitos produzidos cumprem o valor imposto de 70 mg/cm^2. Para a capacidade de dessorção de água, e com exceção do compósito produzido com o adesivo adicionado com 5% de extrato a um teor de 20%, todos os adesivos ficaram abaixo do limite de 80%. Isto significa que a natureza hidrofílica do adesivo aumenta o tempo de secagem do compósito. Quanto à estabilidade dimensional, quase todos os compósitos produzidos apresentaram uma retração inferior ou próxima de 2%. Os resultados evidenciaram também um aumento da flexibilidade do filme devido à incorporação do extrato. A adição de biomassa resultou na diminuição da capacidade de adsorção e dessorção de água, contudo muito próximas das obtidas para os correspondentes compósitos base. Em relação aos valores de retração e flexibilidade, de uma forma geral foram alcançados melhores resultados. Em termos de flexibilidade, as biomassas que conduzem aos melhores resultados foram as CA, CO ou CH num teor de 5% combinado com o adesivo PU3C a um teor de 30%.

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List of Abbreviations

CA Sugarcane bagasse

CH Chia seeds

CO Coconut fiber

CTCP Centro Tecnológico do Calçado de Portugal

DBA N-dibutylamine

DMPA Dimethylolpropionic acid

DMF Dimethylformamide

DSC Differential Scanning Calorimetry

FTIR Fourier Transform Infrared Spectroscopy

HS Hard segment

IPDI Isophorone diisocyanate

MA malt bagasse

MEK Methyl ethyl ketone

NMP N-methyl pyrrolidone

NCO Isocyanate group

PUB Base adhesive

PU3C Adhesive modified with 3% of *Melissa officinalis* L. extract

PU5C Adhesive modified with 5% of *Melissa officinalis* L. extract

PUD Polyurethane-urea aqueous dispersions

PU Polyurethane

SS Soft segment

TDI Toluene diisocyanate

TG Thermogravimetric analysis

T_g Glass transition temperature

T_m Melting temperature

THF Tetrahydrofuran

VOC Volatile organic compound

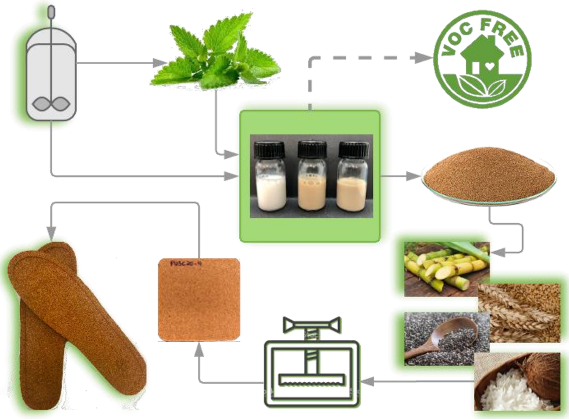
$\Delta \boldsymbol{H_m}$ Melting enthalpy variation

E Young modulus

$\boldsymbol{\sigma_b}$ Stress at break

$\boldsymbol{\varepsilon_b}$ Strain at break

w/w Mass ratio



1 Introduction

1.1 Motivation and Objectives

The Portuguese footwear industry is an important economic sector once it represents one of the most active national business areas, with an annual exporting value of 1.9 billion euros, as referenced in 2016, setting up a new record (APPICAPS, 2017). This evolution evidences the valorization of the footwear industry, as a result of the investment made in the production of footwear with high technological performance, high technical-scientific requirements, superior added-value and high quality standards. Furthermore, the evolution of consumers' environmental awareness pose also attractive challenges for the sector, as the demand for bio products is a reality and represents an opportunity for the development of innovative products. Certifications as the European Ecolable are reflections of the response to this demand. This label provides consumers with products characterized by comfort, quality and durability and based on materials free of toxic substances, which represent unquestionable advantages for the users and the environment.

Considering the industry demand for new eco- and bio-products, the development of novel composites, based on natural materials and by adopting green productive processes, represents an area of great interest. In this sense, the present work will be focused on the production of cork composites with enhanced physico-mechanical properties, having in view the development of footwear components, as insoles and soles, with innovative properties. Moreover, as far as it was possible to verify in the available literature, no studies were published considering this novel approach for cork composites production.

Traditionally, agglomerated cork-based products are made by an agglomeration process which uses a reactive polyurethane-based adhesive. The generated products are known by presenting low flexibility and limited water absorption/desorption characteristics, resulting in low comfort properties. These characteristics are related with both, the cork and the adhesive properties. Therefore, the present work has as main objective the production of eco- and bio-composites based on cork granulates, where the traditionally used adhesive will be replaced by a green water-based polyurethane adhesive. This adhesive will be synthesized by a process developed by the research group where this work is being carried out, and it will be completely exempt of volatile organic compounds (VOC). Beyond this, and based on recent studies of the group, the adhesive performance will be enhanced by the incorporation of natural extracts, in order to improve the mechanical properties. Moreover, in order to increment the content of biobased materials and also to enhance the water absorption/desorption capacity of the composites, the incorporation of biomass residues will be also tested. Thus, this work will be organized in three main stages:

- The first part of the work will be focused on the replacement of the reactive adhesive by a water-based polyurethane adhesive. For this purpose, a water-based adhesive, VOC-free, will be produced trough the modified prepolymer process. Three different adhesive formulations will be tested: base formulation (without the adding of extracts), and modified adhesives with 3 and 5% of an aqueous extract of *Melissa officinalis L.* The adhesives will be characterized in what concerns the most relevant properties for the agglomeration process.
- The second part of this study will be devoted to the cork composites production having in view the obtainment of composites with improved properties. This will be done by using cork granulates with two different granulometries, following the current procedures used at industrial level. First, a screening of the best cork/adhesive ratio will be evaluated by testing different adhesive contents (20, 30 and 40%; w/w, cork-basis, adhesive weight based on its solids content); all the 3 previously produced adhesives will be tested. The resultant properties (dimensional stability, water absorption/desorption and mechanical behavior) will be evaluated in order to select the best adhesive content.
- In the final stage, and taking advantage of the previous results, new cork composites will be produced by using the produced adhesives for the most relevant adhesive/cork composition (30%). These composites will be added with biomass residues (sugarcane bagasse, malt bagasse, coconut fibers and chia seeds) and their impact studied according to the properties presented in the last point.

1.2 Thesis organization

The present work is divided in 7 main chapters organized as follows:

- Chapter 2 “Adhesives” presents a review about the adhesives historical facts, different adhesives classifications and literature review about the water-based polyurethane adhesives main synthesis processes and characterization methodologies;
- Chapter 3 “Cork composites” is devoted to the overview of the cork production and use, together with the cork composites production through agglomeration processes and their properties evaluation. The composites reinforcement through residual biomass incorporation is also focused;
- Chapter 4 “Materials and Methods” describes the materials used during this work, the synthesis process of the adhesives, the procedures adopted for the composites production, as well as the characterization methodologies;
- Chapter 5 “Results and Discussion” presents the obtained results of the adhesives, base cork composites and biomass modified cork composites characterization results, accompanied by a critical discussion;
- Chapter 6 “Conclusions and future work” contains the final considerations and the synthesis of the most relevant obtained results. Additionally, some future perspectives are stressed out.

Finally, Chapter 7 presents the bibliographic references supporting the present work.

2 Adhesives

2.1 Historical facts about adhesives

It is not possible to state exactly the date when the use of adhesive materials began, since there are archaeological evidences for thousands of years, which point to the application of adhesives in the bonding of several objects. The first compounds used for this purpose were natural glue substances and only later the first simple adhesives were prepared, being these derived from culinary products (Adams, 2009). In 1700, the production of adhesives was carried out at industrial scale, being Holland the pioneer country at this level, followed by England. The first patent focusing the term "glue" dates back to 1754 and it has British origin, where the adhesive is defined as "a type of fish glue". Animal glues began to be used later. Adhesives derived from animal and vegetable sources were used during the following century for bonding wood or paper-based products. Great part of the adhesives used until 1920 were from natural sources, obtained through leather, bone or animal hull, fish glue, glue made from oil, shellac, casein glues, vegetable glues, among others. These materials were progressively replaced by synthetic polymer-based adhesives over the next two decades (Adams, 2009).

The most significant event in the history of structural adhesives is the development of epoxy resins in the late 1930s. A swiss researcher called Pierre Castan synthesized the first resins in 1936. In 1939, resins based on epichlorohydrin and bisphenol A were produced by Greenlee in the United States. At that time, polyvinyl acetate, polyvinyl chloride and acrylic adhesives were also developed. In 1937, Otto Bayer developed the synthesis process of polyurethanes. This process has been patented giving rise to a wide variety of new materials suitable for an extensive range of applications, including coatings, paints, foams and elastomers, among others. In 1940, the adhesive properties of polyurethanes were identified and its use started in applications such as glass bonding, composites agglomeration, rubber, wood and leather (Adams, 2009).

Nowadays, among the several types of adhesives, high temperature adhesives and sealants are indispensable for a wide range of industries, from automobile and aeronautics to footwear, packaging, etc. Factors such as production costs, energy consumption and, above all, the preservation of the environment have led to the development of new adhesives and/or modification of the synthesis processes. Summarizing, the use of a given adhesive in a specific application requires the evaluation of the cost/benefit ratio and the type of adhesive bonding required between substrates, which may be superficial or structural (Falco, 2007).

2.2 Relevant definitions

Adhesives are classified in different typologies, according to the following properties (Falco, 2007):

- Viscosity: the adhesive bond strength depends on the viscosity as follows: low viscosity adhesives might flow out from substrate surface, reducing its amount present in the bonding point, while high viscosity adhesives have a low substrate penetration; both cases result in weak bond strength development;
- Solid content corresponds to the content of polymer (adhesive material) dispersed in a solvent and is related with the drying time and bonding strength of the adhesive;
- Drying time is the time taken between the adhesive application on the substrate surface and the total evaporation of the solvent;
- Open time: it is the period elapsed between the adhesive application and the effective bond development between the substrates.

Additionally, adhesives can be classified also according to their physical form (form in which they are commercialized and applied), as follows (Falco, 2007):

- Film adhesive: it contains all curing agents essential for the bond development, being usually activated by heat;
- Paste adhesive: it can be single or bi-component, presented in paste or viscous liquid form;
- Liquid adhesive: it is cured by contact with ambient moisture. This adhesive can be mono or bi-component products, whereas bi-component systems require the simultaneous application of a primer (the curing agent) for the bonding formation;
- Adhesive in solution (water or solvent): it is cured by solvent evaporation, coalescence and crystallization of the polymer particles, resulting in the adhesive film formation and substrate bonding. Like paste and liquid

adhesives, they may be commercialized as mono- or bi-component systems, depending on the application to which they are intended.

From the perspective of the footwear components production, the most used adhesives are polyurethane-based products in different physical forms, i.e. hotmelt, reactive and solution (organic solvent or water) adhesives. Hotmelt adhesives are applied at high temperatures (about 200 °C) in the liquid state. The adhesive bonding is developed by solidification upon temperature decrease. The bonding process occurs in a short time interval. However, the major drawback on its utilization for footwear components production is related with the high temperatures required for their application. Part of the used materials are organic, which do not withstand such elevated temperatures (Hwang and Lee, 2011; Khairushany et al., 2017; Paiva et al., 2016).

Regarding the reactive adhesives, they are usually bi-component systems, whereas the bonding is developed through the reaction between both components and the substrates, after the mixing step. These types of adhesives are usually applied in processes where the formation of strong adhesive bonds, with high resistance to environmental conditions, is required. Despite this, these adhesives are characterized by a very short pot-life after the component’s mixture is prepared, which represents the major drawback for their utilization (Petrie, 2007).

Regarding to adhesives in solution form, traditionally, these products have solid contents between 15 and 50%. The bonding process occurs by solvent evaporation and due to polymer crystallization. These adhesives are characterized by a good wettability of most substrates and by exhibiting an initial adhesion (tack) prior to the total evaporation of the solvent. However, it is important to mention the environmental restrictions imposed in the recent years on solvent-based adhesives, in particular on the volatile organic compounds content (VOCs) release. Moreover, the European legislation has limited the maximum VOCs amount in the production of footwear as 18 g/pair of shoes. These limitations raised the interest for water-based adhesives or polyurethane-urea aqueous dispersions (PUD) (Fernandes, 2017; Martınéz, 2011). Considering water-based polyurethane adhesives, these products are formulated on an aqueous base, being therefore exempt or including only residual amounts of organic solvents, which minimizes the flammability and toxicity problems of the traditional solvent based products. Thus, the compliance with the legal requirements regarding the VOC release is guaranteed. Furthermore, the excellent properties of water-based polyurethane adhesives, namely in what concern high elasticity, good thermal and chemical resistance, good adhesion to a great part of the substrate materials, have driven their use in several industrial areas over traditional solvent-based products (Fernandes, 2017).

2.3 Aqueous polyurethane-urea dispersions (PUD)

Waterborne adhesives are aqueous dispersions composed by two phases, one formed by the polymer particles (the dispersed phase), and another formed by water (the dispersant medium). These adhesives are linear thermoplastic polyurethane-ureas, containing ionic groups (internal emulsifier), in order to allow the dispersion of the polyurethane in the aqueous medium (Pérez-Limiñana et al., 2006). The use of small contents, or no cosolvents, in PUD formulations is a great environmental advantage, guaranteeing properties such as atoxicity, non-flammability and non-atmospheric polluting. In addition to these environmental advantages, their price can be more affordable, because of organic solvent prices increase. Moreover, their use decrease workers' health and flammability risks (Kim, 1996; Maciel et al., 2017).

Polyurethane properties can be adapted by changing the used composition, isocyanate/hydroxyl ratio, and the structure of raw materials. For this reason, this polymeric materials have many utilities, such as adhesives, coatings, foams, liquid crystals, medical applications, and others (Gurunathan and Arukula, 2018).

Synthesis procedures

Polyurethanes (PU) are polymers containing the urethane (or carbamate) group, which is produced by the reaction of the isocyanate group (NCO) with the hydroxyl group (OH). They can involve the reaction between a compound containing two or more isocyanate groups with another bi- or polyfunctional alcohol, currently named polyol. Different polyurethanes with a wide range of properties can be synthesized, since many isocyanates and polyols can be applied in their synthesis (Falco, 2007). The isocyanates react with compounds having active hydrogens, and their relative reactivity is ranked as follows:

$$RNH_2 > ROH > H_2O > C_6H_5OH > RSH > RCOOH$$

The NCO group also reacts with amines forming ureas, with water forming an intermediate with subsequent decomposition into an amine and CO_2, and also with organic acids generating amines and CO_2. Furthermore, isocyanate can react with urethane groups forming allophanates and with urea groups generating biurets. These reactions should be avoided when the obtainment of linear polyurethanes is desired, because the formation of these groups correspond to chemical crosslinking points in the polyurethane molecular structure (Fernandes, 2017).

One of the most interesting polyurethane-based materials are the polyurethane-urea aqueous dispersions (PUD). Since the early 1970s, the PUD have gained an important market quote, becoming one of the most used materials for coatings and adhesives (Harjunalanen and Lahtinen, 2003; Hourston et al., 1997). Presently, the emphasis on the VOC reduction increased the use of these products and give rise to the intensification of research in this field. While waterborne polyurethanes feature zero or low VOC, since water is the dispersant medium, solvent-based PUs contains over 600g/L of VOC (Liang et al., 2018b).

PUDs are defined as binary colloidal systems in which the PU particles are dispersed in a continuous aqueous phase. The PUD viscosity is generally independent on the polymer molecular weight, being mostly related with the particle size distribution. PUD can be made with high solids content, high molecular weight in which the film forming mechanism is dependent on the water evaporation and polymer crystallization. Once the polyurethanes are not water soluble, their molecular chain must be modified by the incorporation of hydrophilic moieties, in order to allow their dispersion in water. Thus, the PU molecular chain will be composed by hydrophobic parts containing hydrophilic points (Kim, 1996; Najafi et al., 2011).

The raw materials used for PUD synthesis are long-chain polyether, polyester or polycarbonate polyols, diisocyanates (manly aliphatic ones in order to reduce the reactivity towards the water during the dispersion stage), low molecular weight glycols and/or diamines, bis–hydroxycarboxylic acids (internal emulsifier) and a neutralizing base. Long-chain polyol units structure represent the soft segments (SS), while hard segments (HS) are built from the reaction of diisocyanates with glycols or diamines and bis-hydroxycarboxylic acid (Cakić et al., 2012; Manvi and Jagtap, 2010).

Depending on the type of emulsifying agent, PUD can be divided into ionic and nonionic types. While nonionic species are composed by hydrophilic segments (polyethylene oxide), ionic type consists of anionic or cationic centers (pendant acid or tertiary nitrogen) along the polymer chain. Among the ionic types, the dimethylolpropionic acid (DMPA) is an anionic emulsifier, being one of the most used due to its easy commercial availability (Barikani et al., 2007; Manvi and Jagtap, 2010). The DMPA carboxylic acid groups are neutralized by adding a base (usually tryethylamine), resulting in the formation of a salt group. However, one of the important features of using DMPA as internal emulsifier is related with its low solubility into the reactive mixture. Until a few years ago, N-methyl pyrrolidone (NMP) was most used solvent since it has high capacity to dissolve DMPA together with good compatibility with the reactive mixture. Beyond this solvent, others like dimethylformamide can be used for DMPA dissolution. The particle size of the dispersion can be reduced by increasing the DMPA content, once it will increase the amount of ionic centers in the PUD backbone, allowing the formation of smaller particles. However the increase of DMPA amount will also increase polymer hydrophilicity, which, in turn, will reduce the resistance of the adhesive bond in the presence of water (Cakić et al., 2012; Dieterich, 1981).

Chain extenders have the role of reacting with the residual isocyanates in order to increase the molecular weight of the final polyurethane. Chain extenders are short chain compounds, usually diols (1,4-butanediol, 1,6-hexanediol) or diamines (1,2-ethylene diamine, hydrazine), allowing obtaining predominantly linear polymers. In cases where some degree of crosslinking is desired, tri- or polyfunctional chain extenders, for example diethylene triamine, are used. If the chain extender is a diol, urethane groups are formed, while if it is a diamine, urea groups are formed, in the latter case giving rise to a polyurethane-urea product. The use of diamines in the synthesis of PUD is more usual due to its high reactivity with the NCO groups, which allows the chain extension reaction to be carried out in aqueous medium (Cakić et al., 2010; Pérez-Limiñana et al., 2006). Beyond this, natural polymers like water-soluble chitosan can be used as chain extenders, rendering antibacterial properties to the PUD (Arshad et al., 2018; Atef El-Sayed et al., 2010; Muzaffar et al., 2016; Xu et al., 2008).

The raw materials used in PUD synthesis are mostly derived from petroleum feedstock, being thus considered as non-sustainable. For this reason, efforts are being made regarding the use of alternatives from renewable resources. In this context, several studies were published focusing the synthesis of bio-based polyurethanes using cellulose, natural oils, and lignin. Vegetable oils are one of the most studied raw materials for polyol synthesis purposes due to their low cost and availability (Liang et al., 2018a).

In what concerns PUD synthesis, there are four main processes: the acetone process, the prepolymer process, the ketamine/ketazine and the melt dispersion processes. All these four processes have a first stage in common: the synthesis of a low molecular weight prepolymer by reacting a polyol with a diiocyanate in excess (Harjunalanen and Lahtinen, 2003; Barni and Levi, 2003). Generally speaking, these processes are based on three main stages:

- Synthesis of a NCO-terminated prepolymer in bulk;
- Prepolymer dispersion in water;
- Chain extension.

The most used processes for PUD synthesis at industrial level are the acetone and prepolymer processes. In the acetone process, a PU prepolymer isocyante-terminated is prepared in an organic solvent, being acetone the most used. The chain extension is done by using a sulphonated diamine, which, beyond acting as chain extender also works as an internal emulsifier. Next, the polymer solution is mixed with water to form the water dispersion. The organic solvent is removed by distillation and finally the PUD with high molecular weight, and free of solvent, is obtained (Dang et al., 2007; Pérez-Limiñana et al., 2006; Remya et al., 2016). As acetone has low-boiling point, it can be removed easily, yielding a final product with low content of VOCs (Sardon et al., 2011).

The prepolymer process starts by preparing a NCO-terminated prepolymer, containing the hydrofilic groups on its backbone. In this stage, the polyol, the internal emulsifier (dissolved in N-methyl pyrrolidone (NMP)), catalyst and the dissocyanate are fed to the reaction vessel. Usually, the reaction occurs at 70-90ºC in the presence of a solvent (NMP) used to compatibilize the internal emulsifier with the reactive mixture. After, the ionic groups are neutralized at 30-60ºC by using a tertiary amine, in order to activate the ionic sites (conversion of carboxyl groups to their salt form). Next, the polymer is dispersed in water under vigorous stirring at 25-35ºC until the phase inversion occurs and a stable polymer dispersion is formed. The next stage correspond to the chain extension stage aiming to increase the molecular weight of the polymer, by the addition of a diamine in order to react with the residual NCO groups of the prepolymer and to finish the molecular chain built (Fernandes, 2017; Remya et al., 2016). In Table 1 and Table 2, a survey of raw materials and studied formulations is presented, when using the described prepolymer process, and also a modified prepolymer process. This former was developed in order to allow the chain extension stage in homogeneous medium, i.e. before the prepolymer dispersion in water.

Concerning the solvents used in PUD synthesis, acetone, methyl ethyl ketone (MEK), tetrahydrofuran (THF), NMP and dimethylformamide (DMF) are the most applied. Acetone and MEK have low boiling point, which allows an easier removal from the final dispersion. However, these solvents have low capacity to dissolve the internal emulsifier DMPA. On the other hand, NMP has a higher ability to dissolve DMPA, but cannot be removed from the final dispersion due its high boiling point (around 220 °C). Nevertheless, legal impositions limiting the presence of organic solvents in PUD, namely the European Commission Regulation 1272/2008 (European Commission, 2008a), restricted the NMP content in PUD. NMP was classified as carcinogenic, mutagenic and toxic for reproduction. In addition, the EU market has imposed, since July 2015, that products with levels higher than 5% (w/w) of NMP must be labeled as toxic and that those with lower levels must be classified as irritants (Fernandes, 2017). Moreover, NMP is costly, has tendency to oxidize, the residues remaining on the dried film causes yellowing, and can provoke disintegration or swelling of protective gears in industrial equipment (Chimankar et al., 2010). These impositions lead to the modification of one of the most used processes in the PUD industry, resulting in the production of PUD with small traces of VOC or even in products free of organic solvents.

In order to fulfill the restrictions imposed by the legislation related to the NMP use, a modification of the prepolymer process was developed by the research group where this work was developed (Fernandes, 2017). In this process, the prepolymer synthesis stage was modified in order to allow the introduction of pre-neutralized DMPA in acetone (i.e. DMPA was previously dissolved in a small quantity of acetone in the presence of the neutralizing agent, triethylamine), as this mixture was not compatible with the synthesis temperature (80 °C). Thus, this stage was divided in two sequential steps: (1) Reaction of the polyol with the isocyanate at 80 °C; (2) Reaction of the pre-neutralized DMPA with the residual isocyanate from step (1) at 55 °C. The next stages of the process were the prepolymer dispersion in water and the chain extension. A last stage of acetone removal was introduced. A schematic representation of this process is shown in Figure 1. In brief, comparatively to the traditional prepolymer process, DMPA is added to the reactive mixture in pre-neutralized form, making the neutralization step dispensable. Since acetone is removed in the last stage, this process gives rise to a PUD VOC-free.

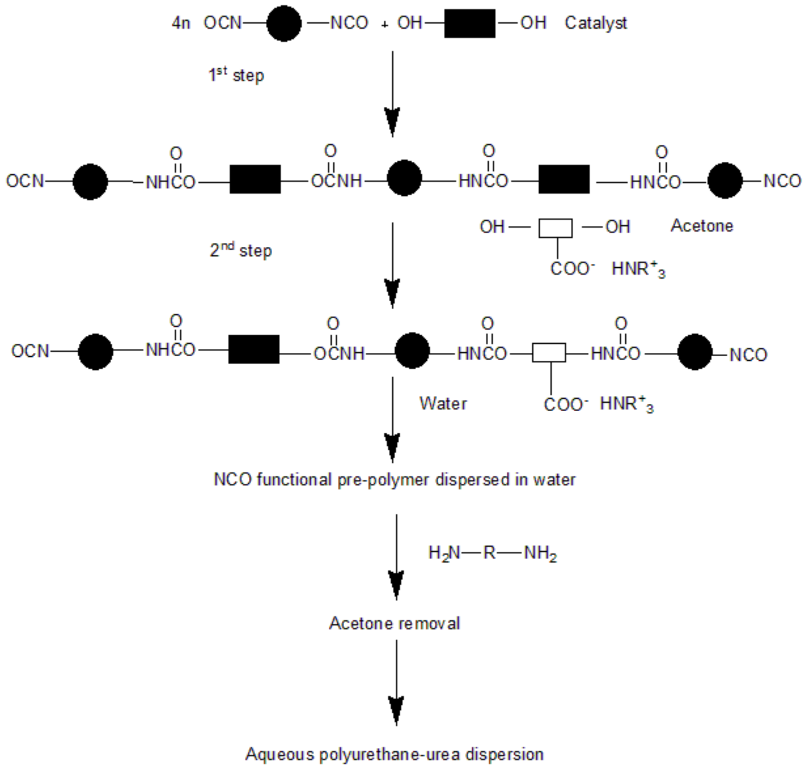


Figure 1 Scheme of the NMP-free process (Fernandes, 2017).

Table 1 Typical reactants and formulations used in PUD synthesis by the prepolymer process.

Process	Raw Materials/Formulation								References
	Isocyanate	Polyol	Catalyst	Solvent	Internal emulsifier	$\frac{NCO}{OH}$ ratio	Neutralization agent	Chain extender	
Prepolymer	HMDI	PPG; BDO	DBTDL	Acetone	DMPA	3.5; 3; 2.9; 2.8; 2.7; 2.6	TEA	EDA	(Tao et al., 2018)
	IPDI	PBAG; TMP	DBTDL	DMF	DMPA; AAS salt	1.7	TEA	HZ; AAS salt	(Cao et al., 2017)
	IPDI	PCL2000; BDA	Not used	NMP	DMPA	1.4; 1.5; 1.6; 1.7	TEA	EDA; DETA; TETA	(Lei et al., 2016)
	IPDI	PPG	DBTDL; ZrCat; manganese catalyst	NMP; DMF	DMPA	3	TEA	EG; PG	(Cakić et al., 2010)
	IPDI	Poly(hexamethylene adipate)	Not used	NMP	DMPA	1.1; 1.2; 1.4; 1.6	TEA	HDA	(Yoon Jang et al., 2002)

Table 2 Typical reactants and formulations used in PUD synthesis by the modified prepolymer process (cont.).

Process	Raw Materials/Formulation								References
	Isocyanate	Polyol	Catalyst	Solvent	Internal emulsifier	$\frac{NCO}{OH}$ ratio	Neutralization agent	Chain extender	
Modified prepolymer	IPDI	PCL3000	Not used	Acetone	LDMPA; AAS salt	1.7	TEA	EDA; AAS salt	(Wu and Chen, 2018)
	IPDI	PCD; 1,4-butanediol polyadipate	DBTDL	Acetone	DMPA	1.5	TEA	HZ[4]	(Fuensanta et al., 2018)
	IPDI	1,4-butanediol polyadipate	Not used	Acetone	DMPA; DEG	1.2	TEA	HZ; 1,4-butanediol; 1,6-butanediol	(Orgilés-Calpena et al., 2012)
	IPDI	DEG	Not used	Acetone	DMPA	1.3; 1.5; 1.7	TEA	HZ	(García-Pacios et al., 2010)

HMDI: Methylene bis(4-cyclohexylisocyanate); PPG: Polypropylene oxide glycol; BDO: 1,4-butanediol; DBTDL: Dibutyltin dilaurate; TEA: Triethylamine; EDA: Ethylene diamine; PBAG: Poly-1,4-butylene adipate glycol; TMP: Trimethylol propane; AAS salt: N- (2-aminoethyl) -2-aminoethane sulfonic acid; PCL2000: Polycaprolactone diol (Mw=2000); BDA: 1,4-butane diamine; DETA: Diethylene triamine; TETA: Triethylene tetramine; ZrCat: Zirconium catalyst; EG: Ethylene glycol; PG: Propylene glycol; HDA: 1,6-hexane diamine; PCL3000: Polycaprolactone diol (Mw=3000); LDMPA: Liquefied dimethylol propionic acid; PCD: 1,6-hexanediol; HZ: Hydrazine monohydrate; DEG: Diethylene glycol.

PUD characterization methodologies

PUD properties are usually addressed according to two physical forms: dispersion itself and produced films and under final application conditions.

The dispersion is usually characterized by evaluating:

- The particle size distribution and the mean particle size: this is directly related to the internal emulsifier content and degree of neutralization of the ionic groups. The particle size affects the dispersion storage stability, the film forming ability, and the performance in the final application;
- pH: which depends on the content of free residual amines present in the dispersion, thus its value reflects the chain extension efficiency;
- Viscosity: this property is related with the solids content of the dispersion and is strongly dependent of the particle size.

The film properties can be characterized in terms of thermal behavior by Differential Scanning Calorimetry (DSC); chemical composition, through the identification of the characteristic functional groups by Fourier Transform Infrared Spectroscopy (FTIR), and thermal stability by thermogravimetric analysis (TG).

Regarding the final application characterization, specific mechanical tests are usually performed according to the application requirements. Properties like density, hardness, abrasion resistance, tear strength, traction and elongation at the break point, flexural strength and fatigue strength, among others are evaluated (Fernandes, 2008; Santamaria-Echart et al., 2016). Table 3 presents a survey of the PUD characterization results based on selected published works.

Table 3 Examples of PUD characterization: dispersions and films.

Process	Dispersion properties				Film properties		References
	Solids content (%)	pH	Particle size (nm)	Viscosity (cps)	T_g (°C)	T_m (°C)	
Modified prepolymer	40	8-9	102-245	4-132	-30	46	(Kwak et al., 2004)
	38.2-38.6	7.8-8.2	73-128	18.1-172	-10 - 7; 38*	165-200; 139-147	(García-Pacios et al., 2011)
	30	n.d.	33-48	0.9	-22- -15.9; 50- 100	n.e.	(Wang et al., 2010)
Prepolymer	35	n.d.	84-165	22-54	n.e.	45-73	(Harjunalanen and Lahtinen, 2003)
	40	n.d.	42-86	75-3302	n.e.	25; n.e.**	(Rahman and Kim, 2006)
	50	n.d.	40-1422	150	-51 – -35	48.89-58.02	(Li and Sun, 2007)

T_g: glass transition temperature; T_m: melting temperature; n.e.: no evidences; n.d: not determined; *two glass transition temperatures due to the soft segments and the carbonate moieties; **temperature of soft and hard segments, respectively.

PUDs modification by natural extracts incorporation

Due to the hydrophilic character of polyurethane dispersions, the incorporation of water-soluble natural additives, allows the introduction of innovative and interesting properties into it. An example is *Salvia officinalis L.* (known as sage) extract, which presents antibacterial and anti-inflammatory properties and can confer these functionalities to the polymer matrix where being incorporated. This plant extract can be obtained in the liquid or powder form (e.g. after lyophylization). Another example is *Melissa officinalis L.*, or commonly called lemon balm, which is also an interesting option due to its antibacterial, anti-inflammatory and antioxidant properties. In addition, and based on previous experience of the research group, it is expected that adhesive mechanical properties increase (Santamaria-Echart et al., 2018a). Thus, when these adhesives are used for cork agglomeration, properties such as antibacterial and antifungal activities are expected to be imparted to the final materials, acting as preservatives of the composite and also providing added protection to the consumer, once microorganism growth on the foot can be minimized.

Considering the wide range of chemical compounds contained on the plants’ extracts, several works reported that alkaloids, flavonoids, tannins and phenolic compounds are the main component present. These compounds are known by its antibacterial and antioxidant activities (Moradkhani et al., 2010; Oprean et al., 2016; Xu et al., 2008). The use of this type of compounds in polymer formulations is being tested in recent years, having in view different objectives. In this context, Liu and co-workers (2013) tested the use of lignin amines as natural antioxidants in order to retard PU degradation, replacing the traditional synthetic antioxidant additives. Moreover, according to the work of Peng et al., (2013), the addition of phenolic compounds to polyurethanes improves the adhesion properties in an extent similar to the obtained when using other chemical adhesion promoters. Additionally, this strategy resulted on the adhesive curing time reduction. Similarly, Cerruti et al., (2009) evaluated the effect of the carotenoids obtained from tomato skins and seeds, on the polypropylene processing stability improvement, once lycopene can act as neutralizer of the tested alkyl radicals. In the same manner, Al-Malaika et al., (1994), tested α-tocopherol and Ambrogi et al., (2011) tried the application of flavonoids as natural reactive oxygen stabilizers for polypropylene, resulting on a long-term stabilization. Beyond this, other works are focused on the use of extracts as antioxidant additives for polyolefines (Agustin-Salazar et al., 2017; Dopico-García et al., 2011). López-Rubio and Lagaron (2010) stated that β-carotene could be used as plasticizer for biopolymers, particularly for poly (ε-caprolactone), acting as UV stabilizer, avoiding the biopolymers photodegradation.

Regarding the incorporation of natural extracts in PUD, the available literature is scarce. Great part of the published studies focused on the benefits of the natural extract’s incorporation on other polymeric matrices. However, analogies can be made by comparing the advantages resulting from this strategy.

3 Cork composites

3.1 Cork production and use

Cork is the cork oak bark (*Quercus suber L.*), which is normally harvested every 9-12 years depending on the country. The cork oak is grown in areas where the climatic conditions are characterized by low rainfall, low humidity and high sunlight exposition (Abenojar et al., 2014). Table 4 presents a survey of the countries with higher cork production and the respective annual production, according to the information of the Portuguese Cork Association (APCOR):

Table 4 Cork production by Country (APCOR, 2016).

Country	Annual production (tons)	Percentage (%)
Portugal	100000	49.60
Spain	61504	30.50
Morocco	11686	5.80
Algeria	9915	4.90
Tunisia	6962	3.50
Italy	6161	3.10
France	5200	2.60
TOTAL	201428	100.00

Cork forests are not only an ideal habitat for a lot of animals and vegetable species, but they also prevent desertification, allow water penetration into the soil, as well as their preservation. Due to its importance for the environment, the area of production, the improvement of the quantity and quality of this material, as well the development of new cork-based products, are of utmost importance for cork producers (Gil, 2015). Additionally, cork products have the advantages of being long-life products based on natural raw materials, contributing for a green carbon footprint. The cork harvesting promotes the cork production, since a normal cork oak produces about four fold more cork bark than a normal tree that has never been stripped before (Gil, 2015). The cork also has a high calorific value and when incinerated, the CO_2 produced is the same that was fixed during the cork growth on the tree, being known as “neutral carbon”.

The use of cork to make different products lead to an increased demand of this material, promoting the harvesting and the consequent growth, rising the CO_2 sequestration from the environment (Gil, 2014).

Cork is characterized as being a natural material with excellent acoustic insulation properties, due to its cellular structure. The cellular structure of cork is alveolar, similar to a honeycomb, while the cellular structure of cork cell walls consists of three different compound layers: a primary internal wall rich in lignin; a thick secondary wall made up from alternating suberin and wax lamella, and a thin tertiary wall composed of polysaccharides (Silva et al., 2005). Some studies suggest that the secondary wall is lignified and for this reason may not consist exclusively of suberin and waxes. Figure 2 shows the chemical composition of the cell wall. The cell structure of cork gives properties such as liquid and air impermeability, good compressibility, resilience, chemical inertia, low density, low permeability and low energy transfer coefficients. It is also characterized by good elastic behavior, and great physical, chemical and biological stability. Cork offers fracture resistance when used as composite filler. It can also be used as insulating material in building construction and in the production of stoppers for beverage packaging. This set of properties makes cork also attractive for use in car interiors and in footwear. Also, transport industry has been using the cork due to its lightweight structure with a high strength to weight ratio (Abenojar et al., 2014; Castro et al., 2010) .

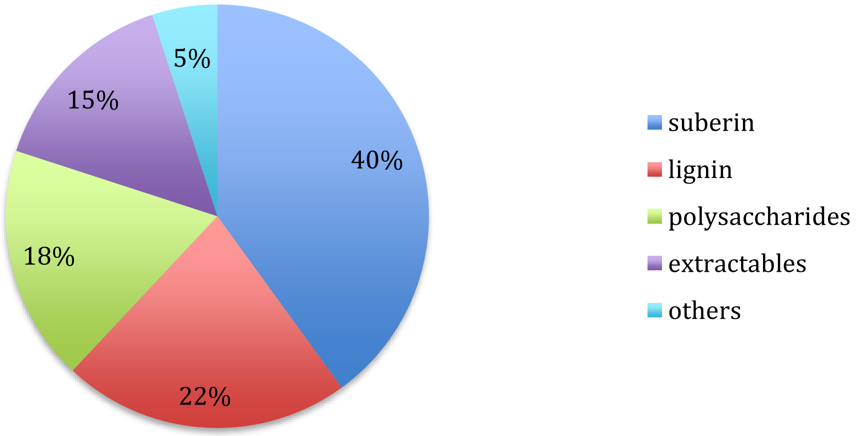


Figure 2 Cell wall components of the cork (Silva et al., 2005).

The hydrophobicity of cork is related to the presence of suberin (hydrophobic) on its chemical composition. However, this fact causes a decrease in the adhesion of cork to other materials. The reduction of hydrophobicity can be achieved by the application of surface treatments such as through the application of atmospheric pressure plasma (APPT), low-pressure plasma chamber (LPPC) and silanization. These treatments aim to modify the properties of the cork surface where the generation of reactive groups occurs. These modifications increase the compatibility between the cork and the binding agent, without changing the cork intrinsic properties (Abenojar et al., 2014).

Considering the different types of cork produced, three different qualities can be distinguished during the cork oak life cycle. The first one, virgin cork, is extracted when the tree is around 25 years old. The second one is the summer virgin, followed by the winter virgin, from the pruned brunches, consisting of fiber fragments and ligneous tissue. Only the summer virgin is used for cork stoppers while all the others can be used in agglomeration processes (Gil and Moiteiro, 2003).

The cork impermeability to liquid and gases, its flexibility and compressibility, make it an ideal material for bottles sealing, especially for reserve wines (Duarte and Bordado, 2015). However, new applications have been sought, since cork stopper production only uses around 25% of the raw material. Therefore, cork composites and new cork-based materials are a prosperous field under development. The cork industry had a significant advance at the end of 19th century, when an American manufacturer of lifejackets produced composite cork unintentionally, conferring to this product, and its waste, an economic value (Gil, 2009; Gil and Moiteiro, 2003).

Comparatively with synthetic foams, cork has a limited variation in properties, restricting its engineering applications. Nonetheless, the specific strength of cork can compete with any rigid synthetic foam. Its low thermal conductivity and its moderate compressive strength make it an attractive material for thermal insulation supporting high compressive loads (Silva et al., 2005).

3.2 Cork agglomeration processes

Cork is used as raw material for different products, depending on their physical and chemical properties. The characteristics of pure cork are maintained, while the incorporation of other materials add additional properties. The production of composites starts by grinding the cork in order to obtain a granulometry in accordance with the desired size and density. Then, the bonding processes comprises: (1) agglomeration with a binder (adhesive or thermosetting resin); (2) agglomeration by extrusion under high temperature and steam (without binders) of expanded agglomerates; and (3) agglomeration by copolymerization with rubber (the less used process) (Duarte and Bordado, 2015; Pereira, 2007). The two main bonding process conditions and cork agglomerate properties are summarized in Table 5. The best bonding process to use will depend not only on the desired physical and mechanical properties for the composite, but also on the raw materials, size and density of the chosen cork granulate. Furthermore, some processing lines demand that raw materials and process control have high quality, especially when avoiding contamination of the final product (Duarte and Bordado, 2015; Mestre et al., 2011; Pereira, 2007).

The thermosetting adhesives used include urea-formaldehyde, melamine or phenolic adhesives, while the thermoplastic ones are traditionally based on polyurethanes (mainly reactive adhesives). Phenolic resins are commonly used for indoor products, such as parquet tiles and wall panels, but the emission of residual phenol and furfural, known as volatile organic compounds (VOC), should be reduced (Horn et al., 1998; Pereira, 2007). Other example of cork agglomerates application is the production of technical cork stoppers, where the toluene diisocyanate (TDI)-based adhesives with free isocyanate contents of 3.5 to 5% are used. Typically, these TDI-based adhesives are also used to produce cork-based composites for footwear soles and insoles. The agglomeration is done by weighing the required amount of cork, adhesive and a small amount of water, being followed by the mixture homogenization by mechanical stirring. Afterwards, the mixture is transferred to a mold, which is then pressed under heating in order to promote the adhesive curing and cork agglomeration. These products are characterized by having good physical-mechanical characteristics, but due to the aromatic nature of TDI, they have also a considerable lack of flexibility. Moreover, the high toxicity of TDI represents a major drawback (Júlio, 2016).

Considering all the above mentioned, it is easy to note a lack of green alternatives for cork agglomeration. Thus, the application of PUD adhesives represents a good pathway for the obtainment of composites with increased flexibility. The simplicity of the typical agglomeration process allows the direct replacement of the TDI-based adhesive by the PUD, without requiring major modifications.

Table 5 The main two bonding process used in cork agglomeration.

Bonding process	Process conditions				Materials used	Properties	References
	Temperature (˚C)	Pressure (MPa)	Adhesive content (%)	Cork content (%)			
Thermoplastic materials (resins or adhesives)	150-170	1.42	50	50	Polyethylene (PE), Polypropylene homopolymer (PP), Recycled polyolefins	High tensile modulus and tensile strengths	(Fernandes et al., 2010)
	80	1.5-6	24-30	70-76	Epoxy resin	High core shear limit, high load values, excellent recovery capacity	(Castro et al., 2010)
	100	2	95-99	1-5	Epoxy adhesive Araldite® 2020	Improved toughness, impact resistance, high impact absorption	(Barbosa et al., 2012)
	150	1.42	44-50	44-50	Polyethylene (HDPE), coconut fibre, coupling agent	Increased tensile maximum strength, maximum strain values and tensile modulus	(Fernandes et al., 2013a)
Extrusion	90	-	-	100	Suberin acts as binder	Higher heating value and density than other pellets produced from conventional types of wood (pine and eucalyptus)	(Nunes et al., 2013)

3.3 Cork composites characterization methods

Generally speaking, the cork composites characterization is usually done according to the intended specific final application. Regarding the mechanical behavior of natural cork, this is generally influenced by its density, porosity or moisture, resulting in distinct mechanical behavior under different loading direction (radial, axial and tangential) (Anjos et al., 2008; Gameiro et al., 2007). Most of cellular materials, such as expanded polystyrene (EPS), expanded polypropylene (EPP) or even metal foams, absorb energy by suffering a permanent deformation, and under compression conditions they support large deformations and present low stress levels (Fernandes et al., 2014; Jardin et al., 2015).

Usually the mechanical behavior of agglomerated cork is evaluated by characterizing its static mechanical responses, such as compression, tensile, shear, three-point bending and creep tests under compression conditions. Several parameters are obtained through the material behavior evaluation when it is subjected to the action of external strength (Mata, 2008; Sanchez-Saez et al., 2011). Furthermore, this cellular material presents a mechanical behavior under quasi-static compression. This means that a linear elastic behavior is identified, due to the bending resistance of the cell walls. This leads to a progressive bending which makes the stress almost independent of the strain. However, when the cells collapse, the stress increases due to the material densification (Sanchez-Saez et al., 2015).

Beyond the static behavior, the dynamic evaluation is also very helpful for the assessment of the cork composites properties, under specific conditions. In this context, Sanchez-Saez et al. (2011) analyzed the ballistic behavior of agglomerate-cork-cored structures, by studying the effects of the cork core according to the projectile residual velocity and energy absorption during penetration. In another study, Sanchez-Saez et al. (2015) evaluated dynamic crushing behavior of agglomerated cork, by analyzing the influence of the specimen thickness on the energy-absorption capacity, contact force, displacement, and strain. In the same manner, Jardin et al. (2015) studied multi-impact behavior of agglomerated cork, by performing several consecutive impact tests in a drop-weight tower.

Considering the application of the cork composites to produce footwear components like shoes’ uppers, outsoles, insoles, eyelets, decorative pieces and other materials, tests such the elongation strength are used (CTCP, Laboratory Tests). Beyond this, there are several other physical properties highly relevant for their validation such as abrasion resistance, hardness, thickness, tear strength, impact resistance, water resistance, among others (Falco, 2007; CTCP Laboratory Tests). Accurate footwear testing is important to ensure that footwear product meets the standards. One of these tests is the water absorption/desorption behavior. The water absorption is essential because it removes the moisture from the foot surface, giving comfort the end-user while wearing the shoes. The water desorption is related with the water drying rate after shoe usage (CTCP Laboratory Tests). Another important group of properties are the flexibility and the adhesion to other materials. The flexibility is evaluated by subjecting the composite sample to a simulation of the foot movement during a standard number of cycles. The test is stopped when the pre-established number of cycles is reached or when the material suffers degradation (usually detected by the appearance of superficial cracks) (CTCP Laboratory Tests). T-peel and creep tests are usually used to check the adhesion performance in shoe bonding. T-peel determines the bonding characteristics between the insole and the sole (Martınéz, 2011). Another important property is the impact absorption capacity. In this test, an impact apparatus that falls into the test piece is used, being its penetration on the material measured along with the maximum deceleration of the test piece (Fernandes et al., 2014).

3.4 Cork composites modification by incorporation of residual biomass

Considering the industry demand for new eco- and bio-products, the development of novel composites, based on natural materials and by adopting green productive processes, represents an area of great interest. Moreover, in order to increment the biobased content and also to enhance the water absorption/desorption capacity to reinforce the composites, the addition of biomass residues can be an important strategy. Among the several kinds of biomass, natural fibers are receiving an increasing attention. Natural fibers collected from plants or animals, like oil palm, sisal, flax, and jute, have being studied (Mohammed et al., 2015). Cellulose fiber plant producers are divided in bast fibers (jute, flax, ramie, hemp, and kenaf), seedfibers (cotton, coir, and kapok, leaf fibers- sisal, pineapple, and abaca), grass and reed fibers (rice, corn, and wheat), and core fibers (hemp, kenaf, and jute), and other types like wood and roots (Faruk et al., 2012).

The use of natural fibers to reinforced composites has increased in recent years because of their low density, attractive thermal properties, low cost, biodegradability, and non-toxicity. Because of their features, plant fiber-based materials have increased over conventional reinforcing materials, such as glass fibers and particle minerals, being found already in different applications (e.g. furniture and nonstructural building applications) (Fernandes et al., 2013a, 2013b). Despite these features, natural fiber composites are incompatible with hydrophobic polymer matrices forming aggregates during processing, thus generating problems with final material properties. Polymer matrix cannot transfer the stress to the filler through the interface when it is subjected to a mechanical load, especially because they are of nonpolar character, while natural fibers have polar nature (Fernandes et al., 2013b). In order to change natural fibers surface, strategies as pre-treatments have been developed. Alkaline treatment, or mercerization, is one theses procedures, which removes a certain quantity of lignin, wax and oils wrapping the external surface of the fiber cell wall, removing natural and artificial impurities, leading the fiber bundle to smaller fibers, thus improving tensile properties (Faruk et al., 2012). A single matrix can combine distinct kinds of fibers, creating hybrid composite materials, which bring together the benefits of the fibers and complement what is lacking in the other. The resourcefulness of the hybrid composite will depend on its fiber content, length and internal orientation within the resultant polymeric matrix (Thomas and Pothan, 2009).

Regarding biomass residues such as sugarcane bagasse, malt bagasse, coconut fibers and chia seeds, their usage can increase water absorption of cork composites and act as a physical reinforce, increasing the mechanical resistance. Sugarcane bagasse, or the fibrous residue of sugarcane, is one of the largest agriculture residues. It is obtained after crushing and extracting the juice. The bagasse is composed of cellulose, hemicellulose, lignin, ash, and wax, which can be used as reinforcement fibers in composite materials with improved chemical and physical properties (Loh et al., 2013). Sugarcane is a fast growth plant that has a short development cycle, which is very attractive for composite reinforcement purposes. In the sugar production, the sugarcane is crushed in mills with heavy rollers. The broken cane stalks, or bagasse fibers, are the by-products from sugar industries (Bilba and Arsene, 2008). New applications are required to valorize these by-products, since approximately 85% of the bagasse is burned as fuel while the remaining is putted on landfills. The development of new applications for these residues can increase the whole economic value of sugarcane bagasse (Hajiha and Sain, 2014).

Malt bagasse is the main by-product of the brewing industry, being one of the components of the solid part that comes from wort filtration before boiling, corresponding to 85% of the waste resulting from the production process. It is a lignocellulosic material, rich in fibers and proteins, being composed, in general, by 28% lignin, 28% hemicellulose and 17% cellulose. The malt bagasse is composed by leftover peels and pulp of malt, grains and some additives (rice, corn, and wheat) (Mello and Mali, 2014). The reuse of the malt bagasse, considered as a problematic agro-industrial residue due to its high carbohydrate, protein, fat and fiber contents, results on a effluent with a chemical demand of oxygen (about one hundred times greater than the domestic sewage) (de Oliveira et al., 2016).

Other natural products that can be used to obtain fibers is coconut shell. Coconut fiber comes from the fibrous husk (mesocarp) of the coconut (*Cocas Nucifera*) from the coconut palm. It has high lignin and cellulose content, being a resilient material, strong and very durable (Fernandes et al., 2013a). Coconut shells are easily found in tropical countries due to the consumption of coconut water and meat. Its easily availability is an advantage when considering the request for filler based composites, avoiding waste production (Sathish et al., 2017). Coconut fiber can take 4-6 times more strain than other natural fibers, and is largely used in boards, roofing elements, concrete and other building materials (Hwang et al., 2016). Usually, the weight of a coconut is around 1 kg, being the husk weight from 300-400g. About 30% of the husk is composed by textile quality fiber, remaining small fibers (Pits) and fragments (Pith). Different factors may influence the quality of coconut fiber, such as rainfall, humidity, soil, and other agro-ecological circumstances, diversification of seedlings and fiber extraction. The green coconut husk, before drying, allows the obtainment of fibers of good quality, since they have higher flexibility, are softer, and less resistant (Sengupta and Basu, 2016).

Chia (*Salvia hispanica L.*) is an annual herbaceous plant native from southern Mexico and northern Guatemala. Chia, or chia sage, has been used in the food industry, in flavorings, in body emollient, in painting oil and also in folk medicine. The chia seeds contain proteins, lipids, ash, carbohydrates and high fiber content. The seed is composed of approximately 20% of proteins and 37% of fibers, and these values vary with the production conditions, among other factors (Capitani et al., 2013, 2012). Although it is widely used in the food area due to its nutritional properties, chia seeds can also be used as a residual biomass for other applications (Inglett et al., 2014; Inglett et al., 2013).

4 Materials and Methods

4.1 Materials

Melissa officinalis L. plant was purchased from Happy Flora Plantas Medicinais (Alcanede, Portugal) and was used for the extract production.

For the PUD adhesives synthesis, the following raw materials were used: polypropylene glycol with molecular weight 2000 (PPG2000) was the macrodiol, being supplied by DOW Chemical Company (Midland, Michigan, USA). Isophorone diisocyanate (IPDI) was supplied by Alfa Aesar (Karlsruhe, Germany) while the internal emulsifier dimethylol propionic acid (DMPA) and the neutralizing agent triethylamine (TEA) were both purchased from Fluka (Milwaukee, USA). Dry acetone was used as co-solvent and 1,2-ethylene diamine (EDA) was the chain extender, being both supplied by Panreac (Barcelona, Spain).

Toluene from analytical grade and the catalyst tin (II) 2-ethylhexanoate (SO) were purchased from Sigma-Aldrich (St. Louis, USA). 2-propanol was obtained from Honeywell (Germany), n-dibutylamine (DBA) and bromophenolblue were purchased from Riedel-deHaën (Seelze, Germany).

The biomass residues (sugarcane bagasse, malt bagasse, coconut fibers and chia seeds) were recovered from Brazilian industries.

4.2 Methods

4.2.1 Extract production and adhesives synthesis

Melissa officinalis L. extracts obtainment

The extract of *Melissa officinalis* L. was obtained by the infusion method from dry plant. Briefly, 20 g of gridded plant was added to 800 mL of boiling distilled water during 5 minutes. The obtained solution was then filtered and freeze-dried (Scanvac, Lynge, Denmark), in order to recover the extract in powder form.

PUD synthesis process

PUDs were produced using the modified prepolymer method, developed by Fernandes and co-workers (2017). For this procedure, the prepolymer synthesis was done at a scale of 100 g using a reactor previously designed for this purpose by the LSRE-LCM group (Figure 3). This reactor is equipped with temperature, stirring and reactant's addition control, and pH monitoring. Three different adhesive formulations were synthesized: base formulation, and formulations modified with 3 and 5% of the aqueous extract of *Melissa officinalis* L. The extract was added to the PUD formulation during the inversion stage, in order to be partially inserted on the polymer particles inner, together with some remaining dissolved on the outer aqueous medium. The first stage of the synthesis process corresponded to the prepolymer synthesis, where polyether-based polyol (PPG2000), IPDI and catalyst (SO) were added to the reactor, followed by their homogenization under stirring (200 rpm) at 80 °C under a nitrogen atmosphere. During the reaction, the NCO conversion was monitored by the dibutilamine back-titration method (Appendix B). After reaching the theoretical NCO conversion, the reactive mixture was cooled to 50 °C in order to allow the addition of the pre-neutralized DMPA in acetone solution. This former neutralized DMPA was prepared by partially dissolving the DMPA (5%, w/w, pre-polymer basis) in 20 ml of dry acetone, under stirring. After, the required amount of TEA for neutralizing 95% of the DMPA's COOH groups, the solution was kept under stirring until the complete dissolution of DMPA was achieved. After feeding this solution to the synthesis reactor, the reaction was maintained until the theoretical conversion to the NCO (typically 0.60) was reached. The following stage corresponded to the dispersion of the prepolymer in water through a phase inversion process, at 25 °C, where the water was added at controlled flow rate under stirring at 500 rpm, being the total used volume 100 ml. For the modified formulations, the required amount of extract (3, or 5%, with the exact amount calculated based on the prepolymer weight of each assay), was dissolved in water before starting the addition. If viscosity constrains were noticed during the phase inversion process, more acetone was added to dilute the medium. After the dispersion was formed, the stirring rate was decreased to 200 rpm and the temperature increased to 35 °C. Then, the chain extension was made adding an EDA aqueous solution (total volume of 25 ml) at a flow rate of 0.505 ml/min, being the amount of EDA calculated based on the NCO conversion achieved after the dispersion stage. This reaction was maintained during 2 hours, in order to promote the reaction of the NCO groups with the amine (NH_2) groups of EDA. The last stage of the process corresponded to the acetone evaporation under reduced pressure, by using a rotary evaporator (Buchi Rotavapor R114 (Flawil, Switzerland)) at 50 °C and 300 mbar. The obtained PUD was stored at ambient conditions for further characterization.

Figure 3 Reactor designed by the LSRE-LCM group for the synthesis of aqueous polyurethane dispersions.

4.2.2 Dispersion characterization

Solids content determination

The PUD solids content was determined by adopting the procedure described in the standard EN 827:1996. Briefly, 1g of dispersion was added to a previously weighted petri dish and the weight registered (m_i). Then, the sample was placed in an oven at 100 °C for 30 minutes. At the end of this period, the sample was placed in a desiccator until it was cooled to ambient temperature. Afterwards, the sample was weighted until the difference between two consecutive weighing's did not exceed 2 mg. The residual mass of the last weighing (m_f) is related with the initial mass according to Equation (1):

$$solid\ content(\%) = \frac{m_f}{m_i}\ x\ 100 \qquad \text{Eq. (1)}$$

pH determination

The PUD pH was measured according to the procedure described in standard EN 1245:1998. Summarily, the pH electrode (WTW, Weilheim, Germany) was placed into the dispersion kept under stirring. The pH was registered when a constant value was achieved during 2 minutes.

Particle size distribution determination

The PUD particle size distributions (in number and volume) were measured by using a Malvern Mastersizer 3000 laser diffraction apparatus, equipped with a Hydro MV dispersion unit (Malvern, UK), using water as solvent. The obtained data was registered with Mastersizer software version 3.10. The results are presented as average values from five measurements, for each sample.

Viscosity determination

The PUD viscosities were measured by using a Visco Star Fungilab Brookfield viscometer (Barcelona, Spain), equipped with an Electro Temp heating/cooling bath to assure a constant temperature during the measurement. The measurements were made according to the guidelines of the 12092:2001 standard and the spindle used was TL5 (8 mL sample volume). The general procedure consists in the heating of the viscometer cylinder to the working temperature (23.0 ±0.5 °C); after, the PUD sample was added to the cylinder, and the temperature was left to stabilize. Then, the measurement was started at the lowest rotational speeds. The correct speed is the one that allows obtaining values of % EOS (viscometer parameter) close to 95%. When a measurement was finished, the viscometer was stopped and left to reach the steady state before a new measurement was done. The measurement was repeated until a difference no greater than 3% between two consecutive assays were obtained. The PUD viscosity value corresponds to a mean value between two consecutive measurements.

4.2.3 PUD films characterization

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were carried out in order to analyze the thermal behavior of the PUD films. The measurements were performed using a DSC 204 F1 Phoenix equipment from Netzsch (Selb, Germany), equipped with an electric intracooler as refrigerator unit. The samples were weighted (7-8 mg) in aluminum pans and were heated from -75 to 250 ºC at a heating rate of 20 ºC.min^{-1} under a constant nitrogen flow.

Fourier Transform Infrared Spectroscopy

Fourier Transform infrared spectroscopy (FTIR) was performed in order to get information about the chemical structure of the films. Spectra were obtained on ABB Inc. FTIR, model MB3000 (Quebec, Canada), operating in ATR mode (ATR cell equipped with a diamond crystal). The spectra acquisition was made by co-adding 32 scans, with a resolution of 16 cm^{-1}, between 4000-550 cm^{-1}. The spectra were obtained by using the software Horizon MB v.3.4. No baseline correction was done.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) was made using a TG model 209F3 Tarsus equipment (Selb, Germany). Approximately 10 mg of the sample were weighted to alumina crucibles. The analyses were made by heating the sample from 32 until 750 ºC at a constant heating rate of 10 ºC.min^{-1}, under nitrogen flow (20 mL.min^{-1}). Thermograms were treated with Netzsch Proteus thermal analysis software, version 5.2.1.

Mechanical behavior

The stress-strain curves of the PUD films were evaluated by using a Shimadzu Autograph AGS-X series Europa testing machine, equipped with a 500N load cell and grips to hold sample (Figure 4). PUD film samples had dimensions 115 mm x 25 mm x 3 mm (l x w x h). Tests were made at room temperature. Young modulus (E), stress at break (σ_b) and strain at break (ε_b) were determined from stress–strain curves obtained at a crosshead speed of 50 mm.min^{-1}.

Figure 4 Shimadzu Autograph AGS-X series Europa testing machine used for the adhesive films and cork composites characterization.

4.2.4 Composites production and characterization

The composites were produced using a hydraulic press equipped with heated plates (Figure 5). The total amount of cork used was set at 10 g. Two cork granulometries (0.2-0.5 mm and 0.5-1 mm) were used, being mixed for each trial at a 50:50 ratio. The tested adhesives content (w/w, cork-basis; adhesive weight based on its solids content) were 20, 30 and 40% (the composites nomenclature was set based on the type of used adhesive and content, e.g. the sample PU3C20 is the composite made with PU3C adhesive using a content of 20%). For composites production, first both corks were weighed (5 g of each granulometry) and hand mixed. When biomass was added (5 or 10%), the required amount was also mixed with the cork (composites nomenclature was distinguished based on the biomass type and content, e.g. the sample PUB30CA5 is the composite made with 30% of the PUB adhesive and 5% of sugarcane bagasse). After, the required amount of adhesive was weighted and added to the previously prepared mixture, being then homogenized during 10 minutes using a mechanical stirrer. Then, the obtained mixture was transferred to the mold and pressed at 15 bar (135 °C), during 2 minutes. After cooling, the mold was opened, and the composite removed. The samples were stored at ambient temperature during one week, before testing.

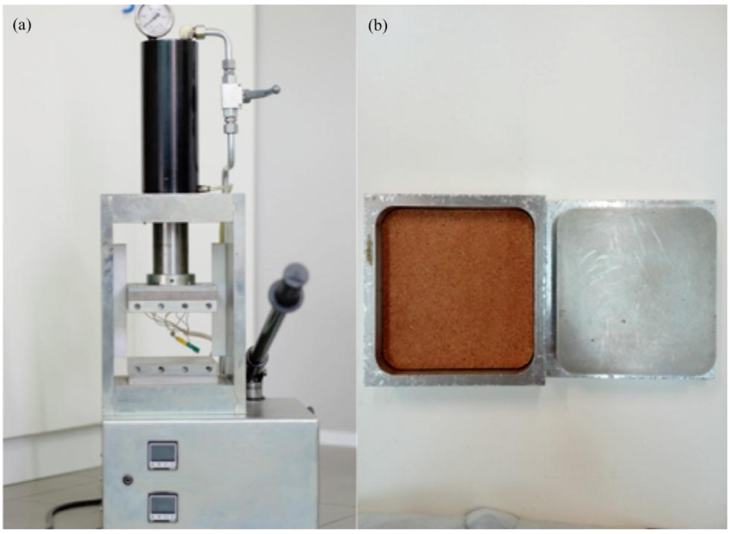


Figure 5 Experimental system used for the composites production: (a) hydraulic press; (b) mold.

Water absorption/desorption capacity

The water absorption evaluation was made according to the ISO 22649:2016 standard guidelines. Herein the composite samples were cut with dimensions 50 mm x 50 mm (l x w) as shown in Figure 6(a). Afterwards the samples were initially weighted (m_i) and then immersed in distilled water during six hours, as shown in Figure 6(b). Next, the samples were weighted (m_f) in order to calculate water absorption. The next stage corresponded to the samples drying during sixteen hours at room temperature. After this period, the samples were weigthed (m_r). The water absorption (W_a) and desorption (W_d) were calculated using the equations (2) and (3), respectively. According to ISO/TR 20882 specifications, the sample is classified as having adequate water absorption and desorption properties if the absorption is higher than 70.0 mg/cm^2 and the desorption is at minimum 80.0%.

$$W_a = \frac{m_f - m_i}{sample\ area} \qquad \text{Eq. (2)}$$

$$W_d(\%) = \frac{(m_f - m_r)}{(m_f - m_i)} * 100 \qquad \text{Eq. (3)}$$

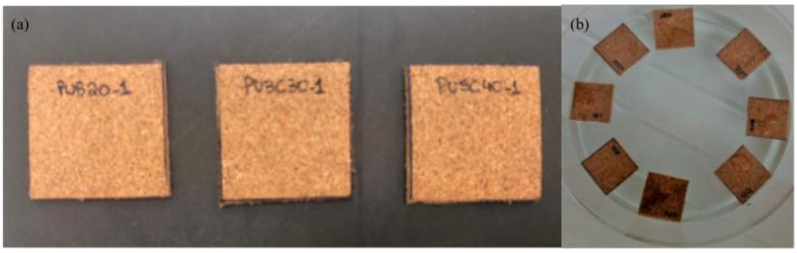


Figure 6 (a) Specimens prepared to test water absorption/desorption; (b) specimens immersed in water.

Dimensional stability

The dimensional stability was evaluated by measuring the samples length and width before and after conditioning at 37 °C for 24 hours, according to the guidelines of ISO 22651:2002 standard guidelines. Figure 7(a) shows the four dimensions (AB, CD, AC and BD) evaluated, in which AB and CD have 60 mm and AC and BD 20 mm, at the initial time. Figure 7(b) shows the biomass composite samples before starting dimensional stability tests. The dimensional stability (DS) was calculated according to equation (4), (5) and (6). The dimensional variation S is the mean value calculated between Sa and Sb. Where a_0 is the AB and CD mean distances at the beginning of the test; a_{24} the AB and CD mean distances after conditioning; b_0 the AC and BD mean distances at the beginning of the test; and b_{24} the AC and BD mean distances after conditioning. According to the ISO/TR 20882 specification for assembly insoles, a material is considered as dimensionally stable when it exhibits shrinkage equal or lower than 2.0%.

$$Sa = \frac{(a_0 - a_{24})}{a_0} \qquad \text{Eq. (4)}$$

$$Sb = \frac{(b_0 - b_{24})}{b_0} \qquad \text{Eq. (5)}$$

$$DS(\%) = \frac{(S_a + S_b)}{2} * 100 \qquad \text{Eq. (6)}$$

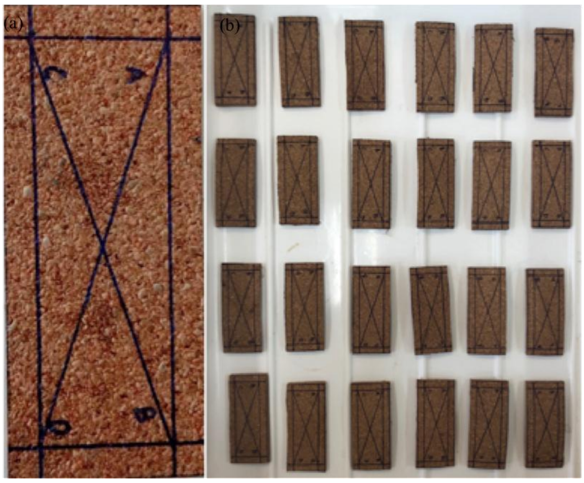


Figure 7 (a) Four dimensions of a specimen evaluated in dimensional stability analysis; (b) specimens prepared for characterization.

Mechanical behavior

The mechanical behavior of composites followed the methodology described in the section 4.2.2. PUD films characterization. In this case, cork composite samples had dimensions of 100 mm x 20 mm x 4 mm (l x w x h). Young modulus (E), stress at break (σ_b) and strain at break (ε_b) were determined from stress–strain curves obtained at a crosshead speed of 2 mm.min^{-1}.

5 Results and Discussion

Three different PUD formulations were used in order to obtain three adhesives: base formulation (PUB) and formulations modified with 3 and 5% of Melissa extract. In order to obtain around 1 liter of each adhesive, the synthesis process was repeated 5 times for each formulation, being then mixed in a container and the final dispersion characterized. For each assay, the amount of reactants and the NCO conversion obtained by the DBA method, are described in Table A1 and Table B1 of Appendix A and Appendix B, respectively. PUD adhesives were characterized in the dispersion itself and in the film physical forms. For the dispersion, pH, viscosity, solid content and mean particle size were evaluated. Regarding the films, FTIR was used to access the chemical structure, while DSC and TGA were used to evaluate the thermal behavior. Mechanical properties were also evaluated using tensile tests.

5.1 PUD characterization

Regarding the dispersions visual appearance, the base PUB presented a typical white color, while PU3C and PU5C presented a browner-like aspect, which is related with the extract color itself, as it can be seen in Figure 8. The results of the dispersions PUB, PU3C and PU5C characterization, namely pH, viscosity and solids content are summarized in Table 6.

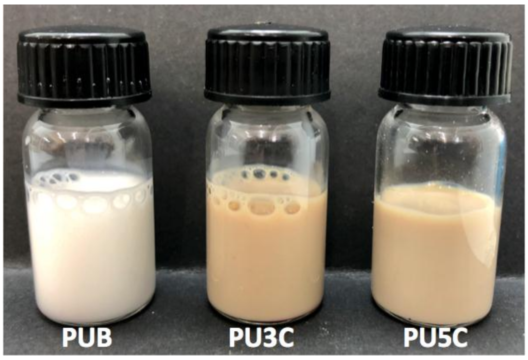


Figure 8 PU base and formulation (PUB) and formulations modified with 3 (PU3C) and 5% (PU5C) of the aqueous extract of Melissa officinalis L.

Analyzing the pH of 7.75 registered for the PUB dispersion, it can be stated that this is in good agreement with the pH range found in the literature and it confirms the success of the chain extension step, once the presence of free EDA will result in the pH increment. Regarding the extract-based dispersions, PU3C and PU5C, the value of 7.55 was obtained for both samples, indicating higher chain extension efficiency.

However, the extract presence can have also influenced the pH value, once this was progressively incorporated during the phase inversion step, when the PUD nanoparticles are formed, being partially retained at the PUD particles inner, while the extract contained outside, in the aqueous medium, can contribute for lowering the pH value of the dispersions (Fernandes, 2017; Santamaria Echart, 2017).

Table 6 Results PUB, PU3C and PU5C dispersion characterization: pH, viscosity and solids content.

Sample	pH	Viscosity (mPa.s)*	Solids content (%, m/m)
PUB	7.75	18.55 ± 0.45	38.80
PU3C	7.55	61.50 ± 0.20	39.70
PU5C	7.55	18786.50 ± 3.00	36.60

*Values expressed as mean ± standard deviation.

Viscosity

Analyzing the viscosity values registered in Table 6, it can be noticed that the increase of the extract content resulted in the viscosity growth from 18.55 mPa.s (PUB), to 61.50 mPa.s (PU3C), and 18786.5 mPa.s (PU5C), being this associated with the variation in the particle's surface shear stress and interactions occurred in the system. This means that the solubilized extract present ionized compounds that might interact with the negatively charged polyurethane-urea nanoparticles, resulting on the ionic interactions increase and consequently, on the viscosity rise (Nanda and Wicks, 2006; Rahman and Kim, 2006).

Solids Content

With respect to the solids content, values around 40% were obtained for the PUB and PU3C, being close to the typically registered for commercial products. However, for the dispersion PU5C, only 36.60% was obtained. This was due to the higher viscosity of this dispersion, which required a higher water amount to achieve its stabilization (60 ml were further added during the phase inversion (Appendix A, Table A1).

Particle size

Regarding particle size measurements, Figure 9 shows the size distributions in volume and in number. The mean values of the particle size distribution and the percentiles D_{10}, D_{50} and D_{90} are presented in Table 7.

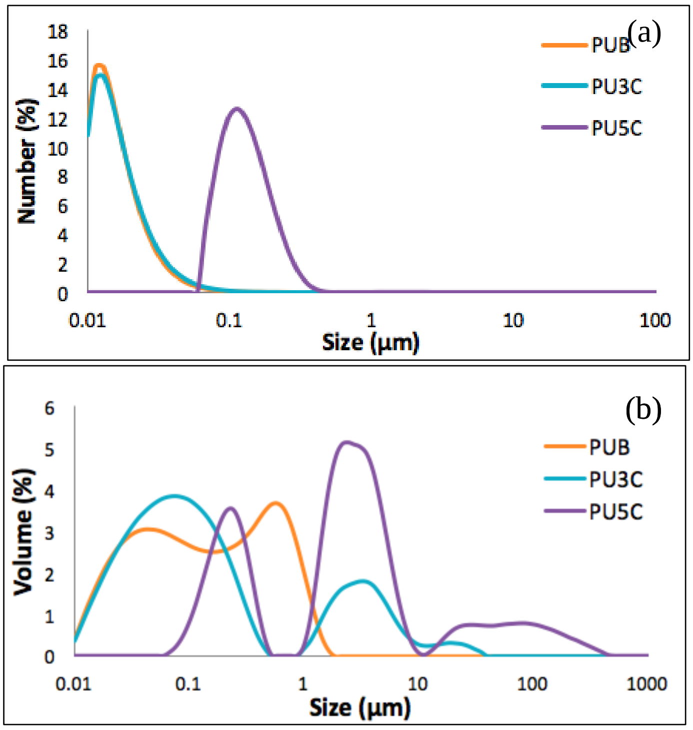


Figure 9 Particle size distributions of PUB, PU3C and PU5C: (a) volume distribution and (b) number distribution.

Analyzing the particle size distribution in volume (Figure 9(a)), a bimodal pattern is identified for sample PUB, while for the PU3C and PU5C these distributions are multimodal. Regarding the number distributions (Figure 9(b)), a unimodal pattern is noticed for all of samples. The D_{10} and D_{90} percentiles values of the PUB volume distribution registered were 0.0238 and 0.794 µm, and the mean particle size calculated based on this distribution was 0.145 µm. Similarly, for the volume distribution of the samples PU3C and PU5C, the percentile values varied from 0.0247 to 4.02 µm (mean size of 0.107 µm) and 0.1920 to 45.7 µm (mean size of 2.51 µm), respectively. Analyzing these results, it can be noticed that when comparing the PUB sample with the extract containing dispersions, PU3C and PU5C, the particle size distribution, both in number and in volume, broaden and shift to greater particle sizes as a consequence of *Melissa* extract incorporation, which is related to the surfactant effect attributed to the used extracts, according to the findings of Santamaria-Echart et al. (2018b). This means that some part of the water solubilized extract compounds can be electronegatively active, interacting with the anionic charged PUD nanoparticles, leading also to a more viscous system, as previously discussed.

Table 7 Values of D_{10}, D_{50}, and D_{90} for the distributions in volume and in number of the PUB, PU3C and PU5C samples.

Sample	Volume Distribution			Number Distribution		
	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)
PUB	0.024± 2.260x10^{-5}	0.145± 3.590x10^{-4}	0.794± 2.590x10^{-3}	0.011± 2.820x10^{-7}	0.016± 1.320x10^{-6}	0.030± 7.520x10^{-6}
PU3C	0.025± 1.280x10^{-5}	0.107± 2.290x10^{-4}	4.020± 2.420x10^{-2}	0.011± 8.470x10^{-8}	0.016± 3.860x10^{-7}	0.031± 1.950x10^{-6}
PU5C	0.192± 1.540x10^{-3}	2.510± 6.280x10^{-2}	45.700± 2.320	0.085± 1.010x10^{-4}	0.132± 2.360x10^{-4}	0.233± 6.300x10^{-4}

Values expressed as mean ± standard deviation.

5.2 *PUD films characterization*

Analyzing the appearance of the films, which is shown in Figure 10, some remarkable differences can be noticed being related with the extract incorporation. For PUB, a transparent film was obtained, being a typical aspect of PUD films. With the extract incorporation, the films became browner with both modified formulations (PU3C and PU5C), meaning that the extract increase on the formulations results in the color intensification of the films. Despite this, the translucent aspect prevails for both PU3C and PU5C films.

Figure 10 Films obtained after drying the dispersions PUB, PU3C and PU5C.

FTIR

The FTIR spectra of PUB, PU3C and PU5C films are presented in Figure 11, together with the one of the *Melissa officinallis* L. extract. For the extract spectrum, a broad peak between 3700 and 3000 cm^{-1} is identified, being associated with the hydroxyl groups from the phenolic compounds, while the vibration around 1590 cm^{-1} is assigned to the C=C of the aromatic rings. Moreover, a shoulder identified around 1700 cm^{-1} is attributed to the C=O of the extract phenolic acids. Melissa extract is known by having a chemical composition mainly comprised by phenolic compounds such as phenolic acids and flavonoids (Dias et al., 2012). The extract FTIR analysis confirms the presence of these types of compounds.

Considering dispersions PUB, PU3C and PU5C film´s spectra, the following features can be assigned: the vibration detected between 3500-3100 cm^{-1} correspond to N-H of urethane and urea groups, while the peak around 1720 cm^{-1} is assigned to the C=O vibrations of the urethane, urea and DMPA ionized acid groups (Santamaria Echart, 2017; Tsou et al., 2017). Moreover, the prominent peak identified between 1300-1000 cm^{-1} is attributed to the C-O vibration from PPG ether group. Additionally, the non-appearance a vibration at 2270 cm^{-1} indicates the absence of the NCO groups, proving its complete conversion during the synthesis process.

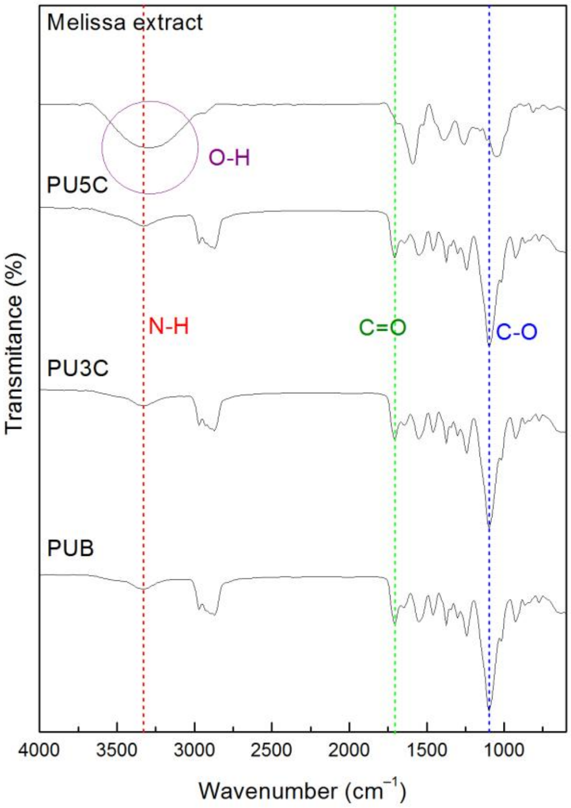


Figure 11 FTIR spectra of Melissa officinallis L. extract, PU5C, PU3C and PUB films.

Differential scanning calorimetry

The thermal behavior of PUD films was evaluated by differential scanning calorimetry (DSC) being the obtained thermograms shown in Figure 12. The glass transition temperature (T_g), melting temperature (T_m) and melting enthalpy variation (ΔH_m) are summarized in Table 8.

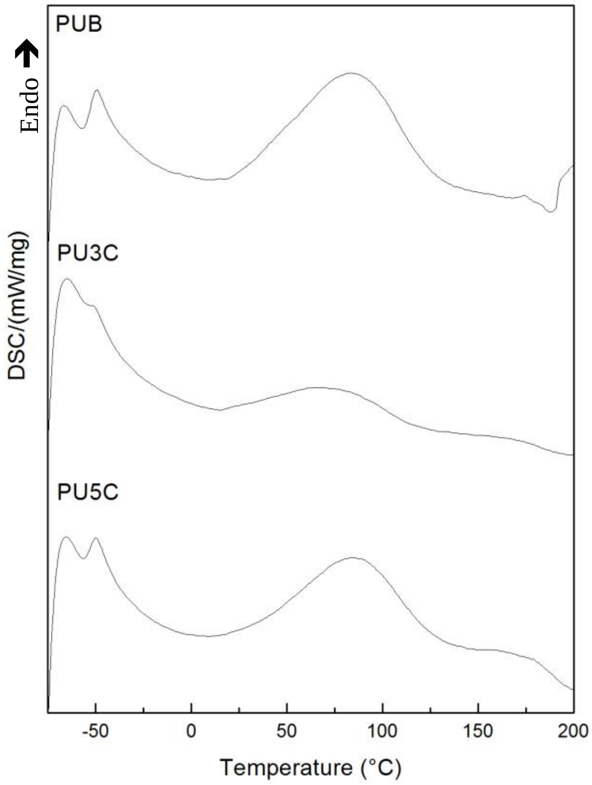


Figure 12 DSC thermograms of PUB, PU3C and PU5C.

Table 8 Thermal properties of the PUB, PU3C and PU5C films.

Sample	T_g (°C)	T_m (°C)	ΔH_m (Jg^{-1})
PUB	-52.7	83.4	33.4
PU3C	-52.7	68.4	22.4
PU5C	-52.6	83.8	27.9

For the PUB film the values of T_g and T_m were -52.7 °C and 83.4 °C, respectively, while the enthalpy of 33.4 Jg^{-1} was registered. For the extract-containing dispersions, PU3C and PU5C, the T_g values were equal to the obtained for the PUB, meaning that no differences of the thermal behavior at low temperatures was achieved due to the extract incorporation. However, regarding the T_m values of the three samples, a diminution for 68.4 °C was registered for the PU3C sample, while for the PU5C was 83.8 °C, being similar to the one obtained for the PUB sample. In the case of the ΔH_m values, the one registered for the PUB was 33.4 Jg^{-1}, while for the PU3C the ΔH_m value decreased to 22.4 Jg^{-1}, increasing again to 27.9 Jg^{-1} for the PU5C sample. This behavior might be related with the extract presence on both the PUD nanoparticles inner and out phase. Thus, when 3% of extract was added, both the T_m and the ΔH_m values lowered, probably due to the extract distribution that interfered with hard segments rearrangement occurring at molecular level, leading to a decrease of both the T_m and ΔH_m, comparatively with the PUB. However, when the extract amount was increased to 5%, an increment of both T_m and ΔH_m was noticed, which might be attributed to the favoring of the hard segments rearrangement, leading to more organized structures that will result in both T_m and ΔH_m increase. These observations are in good agreement with the findings of Santamaria-Echart and co-workers (2018).

Thermogravimetric analysis

The TGA analysis was applied to evaluate the thermal stability of the extract and the dispersions. The obtained results are registered in Table 9, while the TG and DTG curves are shown in Figure 13. Considering the Melissa extract, this type of sample is composed by a multicomponent mixture of organic and inorganic compounds, which have different thermal stabilities. Analyzing the extract TG degradation pattern, it can be seen that the degradation zone between 30 and 121 °C (weight loss of 10.4%) is related with the water loss. The second and the third stages, between 121 to 228 and 228 to 316 °C, is due to the degradation of phenolic acids and flavonoids (Cordeiro et al., 2013), corresponding to a weight loss of 30.1%. The last identified degradation stage corresponds to the decomposition of the carbonaceous char resulting from previous degradation stages. The final residue obtained was 36.8%, at 750 °C, being related with the remaining carbonaceous char together with the inorganic compounds presence.

Looking at the thermal degradation profile of the films samples PUB, PU3C and PU5C, three main decomposition stages can be identified. For the PUB sample, the first degradation stage starts at 200 °C, being related with the urethane group decomposition. Next, the second degradation stage starting at 267 °C, correspond to the urea decomposition, while the third one starting at 338 °C is related with the soft segment decomposition. This is a typical degradation pattern of water-based polyurethane-ureas, since two different hard segments were formed during the synthesis, due to the reaction of the polyol and the diamine with the NCO, resulting on the formation of urethane and urea groups. Comparing the thermal stability of both groups, it is well established that ureas have higher stability than the urethanes, therefore the urethane degradation occurs at lower temperatures (Fang et al., 2014; Pérez-Limiñana et al., 2006).

Analyzing the degradation pattern of the PU3C sample, a displacement of the first and second degradation stages for higher temperatures is noted (maximum temperature of the PUB increases from 255 and 325 °C, to 261 and 345 °C for the PU3C), as it can be seen in Figure 13. This is also detected for the PU5C sample and can be related with the extract incorporation, which contains compounds able to increase the thermal stability of the polymer (López-de-Dicastillo et al., 2010; López-de-Dicastillo et al., 2011). The presence of the extract on the PU3C and PU5C films is also visible through the residue obtained at 750 °C, once values of 0.3 and 3.8% were registered, while for the PUB a total degradation was achieved at this temperature (Table 9) (no residue was obtained).

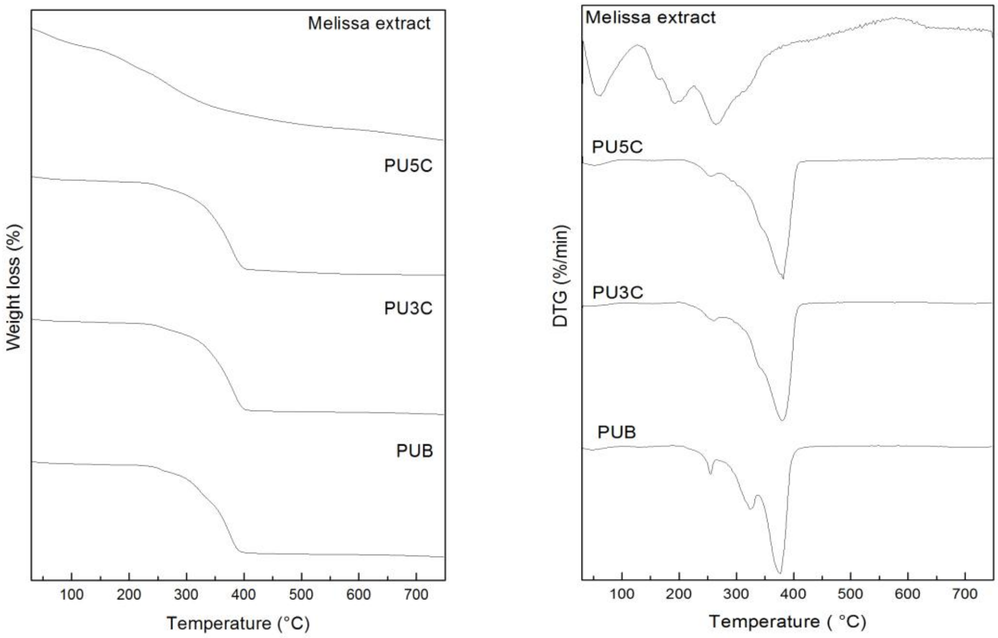


Figure 13 TG and DTG curves of the Melissa extract, PU5C, PU3C and PUB films.

Table 9 Weight loss, initial (T_i), maximum (T_{max}) and final (T_f) degradation temperatures, and residue of the extract, PUB, PU3C and PU5C.

Sample	Residue (%)	T_i (°C)	T_{max} (°C)	T_f (°C)	Weight loss (%)
Melissa extract	36.8	30	60	121	10.4
		121	198	228	13.9
		228	265	316	16.2
		316	386	575	16.3
PUB	0.0	200	255	267	7.6
		267	325	338	28.1
		338	377	440	57.6
PU3C	0.3	207	261	278	8.6
		278	345	347	21.8
		347	380	430	62.5
PU5C	3.8	202	255	270	7.3
		270	342	345	24.9
		345	377	430	60.0

Mechanical behavior

Regarding the films mechanical behavior evaluation, it is important to mention that all the samples reached the maximum extension (equipment limit), not being possible to achieve film rupture. Considering mechanical behavior, the stress-strain evaluation of the PUB films are shown in Figure 14 The ultimate stress (σ_u), ultimate strain (ε_u) and Young modulus (E) were determined from stress-strain curves (Figure 15), for the PUB, PU3C and PU5C, as well these results of σ_u, ε_u and E are described in Table 10. It is worth to mention that no film rupture was achieved when the used load cell was 500N (the maximum available). Hence, the σ_u and ε_u values recorded corresponded to the ultimate values achieved and not to the breaking point. Regarding to the ε_u, all the films achieved an ultimate elongation superior to 600%, while the σ_u varied from 16.07 MPa for the PUB, to 14.88 and 11.31 MPa for the PU3C and PU5C, respectively. With respect to the Young modulus, the values decreased with the extract amount incorporated into the PUD increasing, varying from 6.62 MPa for the PUB to 6.16 MPa for the PU3C and reaching 5.36MPa for the PU5C. These results evidence the increasing of the films flexibility due to the extract incorporation.

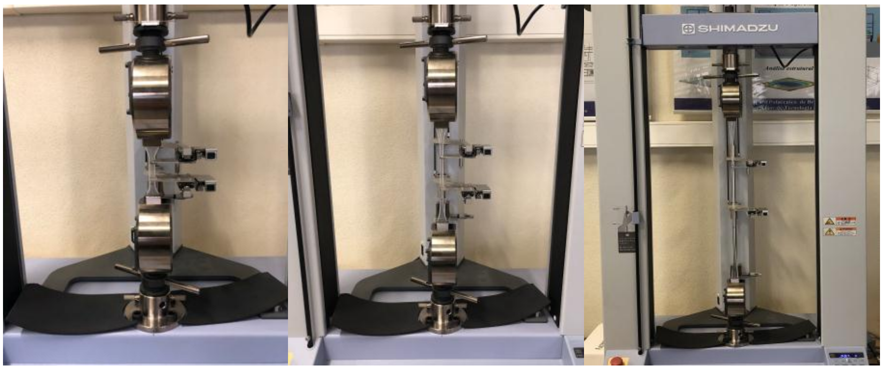


Figure 14 Stress-strain evaluation of the PUB film.

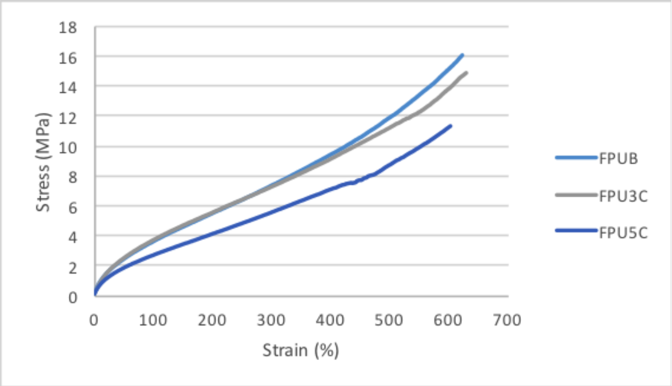


Figure 15 Stress-strain curves of PUB, PU3C and PU5C films.

Table 10 Values of σ_u, ε_u and E of the PUB, PU3C and PU5C films.

Sample	σ_u (MPa)	ε_u (%)	E (MPa)
PUB	16.07	623.13	6.62
PU3C	14.88	629.96	6.16
PU5C	11.31	603.76	5.36

5.3 Base cork composites characterization

The base cork composites were produced by using the three adhesives PUB, PU3C and PU5C, at contents of 20, 30 and 40% (w/w, cork-basis, adhesive weight based on its solids content), in order to select the best adhesive content for the following steps. After the production, the cork composites were characterized in terms of water absorption/desorption, dimensional stability and mechanical behavior through the tensile tests. It is important to mention that the production of homogeneous composites using 40% of the adhesives was difficult due to the higher amount of water evaporation, with experimental setup used. This could be solved by changing the type of mold by another with larger leakage points.

Water absorption/desorption behavior

The complete data of the samples used for water absorption and desorption evaluation (dimensions, namely length, width, area, weights before, after six hours in water and after sixteen hours drying at room temperature) are described in Appendix C, Figure C1. The composite samples were named based on the different adhesives and contents tested and the type of test made, e.g. the sample PUB30-1 is the composite made with PUB adhesive, using a content of 30% and the number 1 represents water absorption/desorption test. Number 2 was used to the dimensional stability tests (to be discussed next). The absorption results are represented in Figure 16, while Figure 17 shows the desorption results.

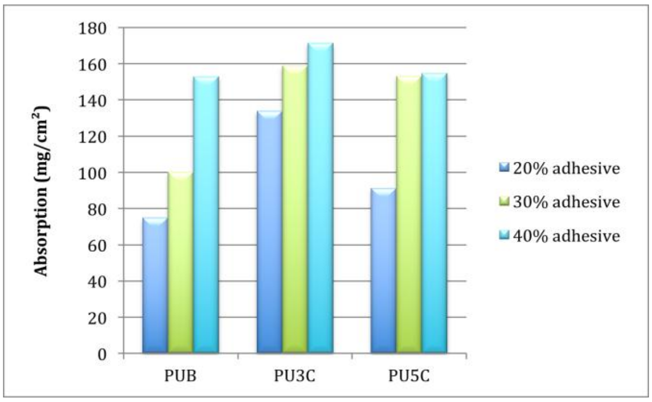


Figure 16 Absorption results of cork composites produced with PUB, PU3C and PU5C, using adhesives contents of 20, 30 and 40%.

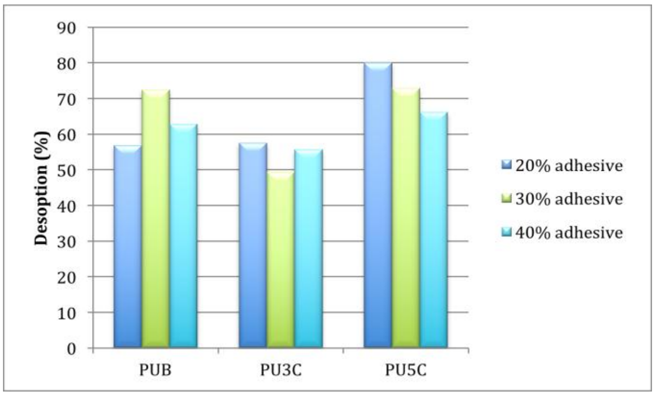


Figure 17 Desorption results of cork composites produced with PUB, PU3C and PU5C adhesives, using contents of 20, 30 and 40%.

With respect to the water absorption results, the standard ISO/TR 20882 specification imposes an absorption value higher than 70 mg/cm^2, and a water desorption of 80% minimum. The composites produced with the traditionally used TDI-based adhesive have a very low water absorption capacity, typically around 8-10 mg/cm^2, while the desorption usually achieves the value imposed (80%). This is related to the hydrophobic character of the cork itself and the used binder, which results in low absorption of the sweat, promoting a sensation of discomfort when footwear incorporating these types of materials. However, by changing the adhesive by a more hydrophilic material, the water absorption is expected to increase. In this context, the composites produced with the PUD adhesive are expected to have higher water absorption. Moreover, the extract incorporation can lead to an increase of this capacity also. Based on these considerations, and analyzing the results shown in Figure 16, the following observations can be made:

- The composite produced with 20% of PUB had the lowest water absorption (75.1 mg/cm^2); while when using 30 and 40%, values of 100.2 and 152.9 mg/cm^2 were registered. These results put in evidence the importance of the adhesive nature on the water absorption of the cork composites;
- The composites produced with PU3C gave the highest water absorption among the three tested adhesives, being the maximum value 171.4 mg/cm^2 obtained for the composite produced with an adhesive content of 40%;
- When the PU5C adhesive was used, the water absorption varied from 91.3 to 154.8 mg/cm^2, when the adhesive content was changed from 20 to 40%.

Looking to the overall results, a remarkable increment of the water absorption capacity is identified due to the extract incorporation on the adhesives. However, a diminution of water absorption is noticed when the PU5C is used, being still higher than the ones registered for the PUB composites. Despite this, all the composites produced fulfill the imposed value of 70 mg/cm^2 defined by the specification ISO/TR 20882.

Regarding to the water desorption values, from the analysis of Figure 17, it can be mentioned:

- The values of desorption obtained with the composites produced with the PUB were 56.9, 72.5 and 62.8%, respectively for the contents of 20, 30 and

40%, respectively; being below to the limit of 80% imposed by the standard. This means that the adhesive hydrophilic nature lead to an increase of the composite drying time;

- The composites produced with the PU3C adhesive had the following desorption values, 57.6, 49.3 and 55.7%, respectively for the adhesive contents of 20, 30, and 40%, being the lowest ones obtained;
- The composites produced with the PU5C adhesive had a water desorption of 80.0, 72.9 and 66.3%, respectively for 20, 30 and 40% of adhesive. The maximum value achieved corresponded to 80%, fulfilling the value imposed by the standard.

Analyzing the obtained values, it can be seen that the lowest water absorption is achieved when the PUB adhesive is used, for the three tested contents. The composites produced with the PU5C adhesive gave the best water desorption results.

Dimensional stability

The sample dimensions registered during the dimensional stability test are detailed in Appendix C, Figure C2, C3 and C4. The results of the composites shrinkage are listed in Table 11. The composites are considered as dimensional stable when the shrinkage is less than 2%. Looking at the shrinkage values, it can be seen that the composites produced with the PUB have different behavior, once the sample containing 20% of adhesive presented a shrinkage of 2.30% while for the other tested contents, the values were lower than 2%. In the case of the PU3C composites, only the one produced with 20% of adhesive had shrinkage lower than 2%, while for the PU5C composites, only the sample produced with 30% of adhesive had a shrinkage higher than 2%. In general way, the composites present a good dimensional stability, since the shrinkage is lower than 2% for the great part of the samples.

Table 11 Dimensional stability results of cork composites produced with PUB, PU3C and PU5C using adhesives contents of 20, 30 and 40%.

Sample	Sa (%)	Sb (%)	S (%)
PUB20-2	2.09	2.50	2.30
PUB30-2	0.84	2.50	1.67
PUB40-2	0.42	2.38	1.40
PU3C20-2	0.42	0.00	0.21
PU3C30-2	2.12	2.53	2.33
PU3C40-2	1.68	2.44	2.06
PU5C20-2	0.43	1.28	0.85
PU5C30-2	1.69	2.50	2.10
PU5C40-2	1.24	1.30	1.27

Mechanical behavior

Considering mechanical behavior, stress at break (σ_b), strain at break (ε_b) and Young modulus (E), were determined from stress-strain curves (Figure 18), where (a), (b) and (c) represent the curves for cork composites produced with PUB, PU3C and PU5C adhesives at contents of 20, 30 and 40%, respectively. The results of σ_b, ε_b and E are represented in Figure 19 for each adhesive.

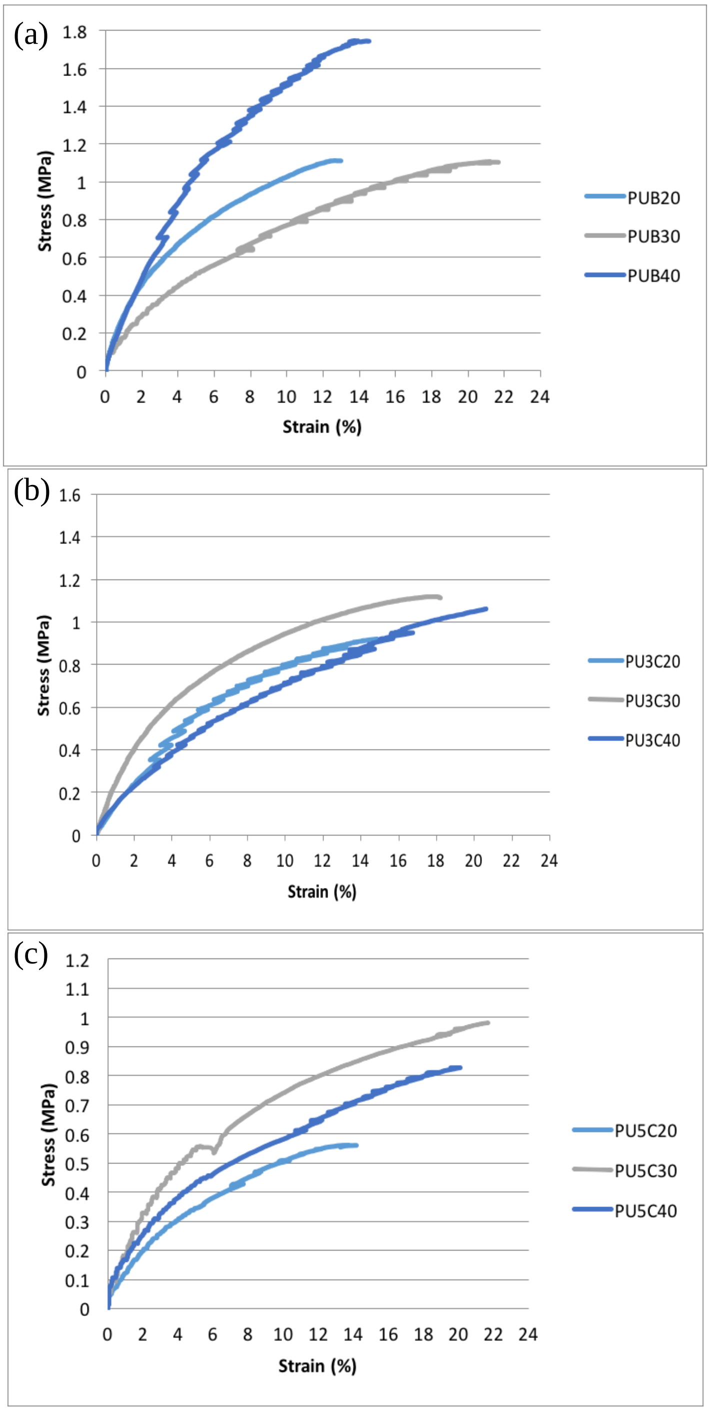


Figure 18 Stress-strain curves from base cork: (a) PUB composites; (b) PU3C composites and (c) PU5C composites.

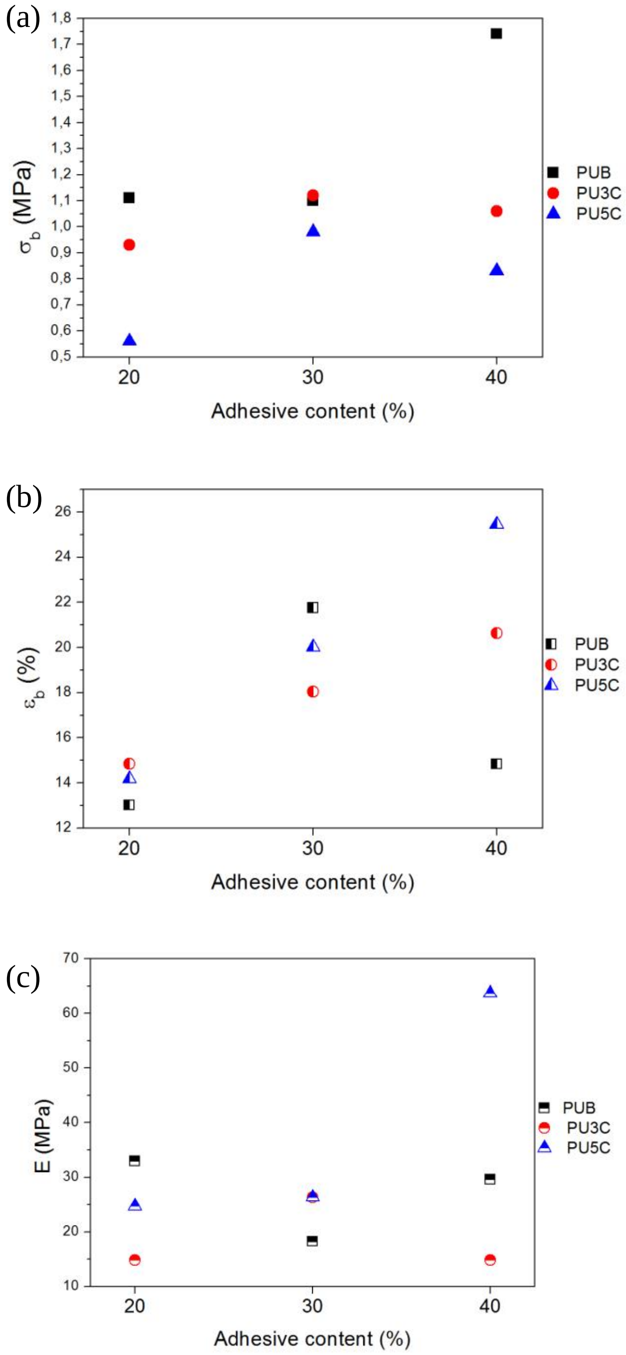


Figure 19 Mechanical behavior of the base cork composites comparisons relatively to the adhesive type and content: (a) Stress at break; (b) Strain at break, and (c) Young Modulus.

Looking to the graphical representation of Figure 19, the stress at break of the PUB composites presented a growing trend from 1.10 to 1.74 MPa, when the adhesive content increased from 20 to 40%. In contrast, for the ε_b, a maximum value of 21.75% was achieved for an adhesive content of 30%. With respect to the Young Modulus values, the higher is 32.96 MPa, corresponding to the adhesive content of 20%, while the minimum value is 18.21 MPa for the 30% of adhesive. In the case of the PU3C composites, the stress at break has a maximum value of 1.12 MPa for the adhesive content of 30%, while the ε_b increases from 14.84 to 20.63% as the adhesive content rise from 20 to 40%. The Young Modulus has a maximum value of 26.28 MPa for 30% of adhesive. Finally, for the PU5C composites, the stress at break has a maximum value of 0.98 MPa when the adhesive content is 30%, while the ε_b increases from 14.18 to 25.45% as the adhesive content rise from 20 to 40%. The Young Modulus have the same trend, once the minimum value is 24.70 MPa, increasing with the adhesive content increase, reaching 63.70 MPa when 40% of adhesive is used.

Based on the overall Young Modulus results it can be concluded that when the adhesive contents were 20 and 40%, PU3C the composite presented higher flexibility. In a general way, the minor discrepancy between the Young Modulus values was achieved when the adhesive content was 30%. Furthermore, this adhesive content led to high water absorption values. So according to all the above mentioned, the adhesive content selected for the following studies was 30%.

5.4 Biomass modified cork composites characterization

Cork composites containing biomasses residues were produced using the PUB, PU3C and PU5C adhesives, at a content of 30%. The biomasses were incorporated at contents of 5 and 10% (w/w, cork-basis). Sugarcane bagasse (CA), coconut fiber (CO), malt bagasse (MA) and chia seeds (CH) were tested. The samples nomenclature was set based on the different adhesives and contents tested, the content of biomass and the number of the produced sample (2 samples of each composite). For example, the sample PUB30CO5-2 is the composite made with 30% of PUB adhesive and 5% of coconut fiber, used in dimensional stability tests. Then, the produced composites were characterized in terms of water absorption/desorption, dimensional stability and mechanical behavior.

This study has as main objective to test the effect of the biomass on the cork-based composites final properties. This is a strategy already studied for polymers reinforcement but not tested with cork composites, as far as it is our knowledge. Herein, the effect of biomass type and content, together with the adhesive formulation on the composites water absorption/desorption, dimensional stability and mechanical behavior will be analyzed and discussed.

Water absorption/desorption behavior

The complete data obtained within the water absorption and desorption evaluation (dimensions (length, width, area), weight (before, after six hours in water and after sixteen hours drying at room temperature)) are described in Appendix D. The results obtained for the water absorption are shown in Figure 20 while water desorption data is shown in Figure 21.

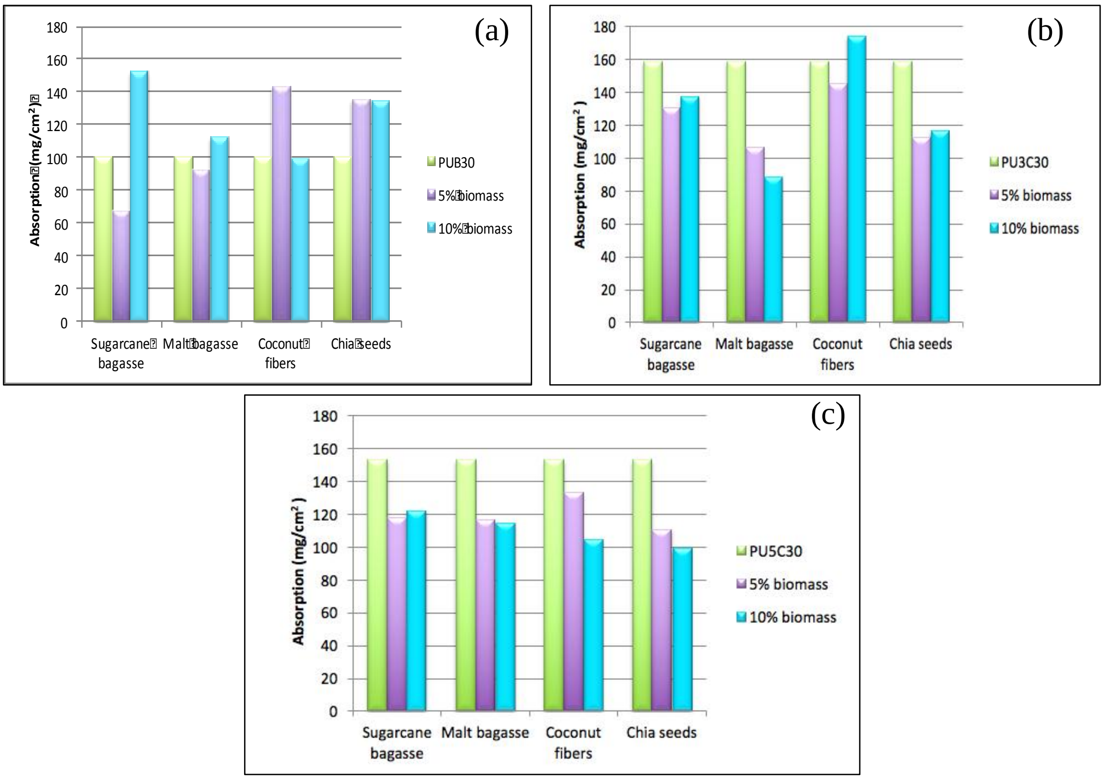


Figure 20 Water absorption results of the biomass-containing composites produced using: (a) PUB, (b) PU3C and (c) PU5C adhesives.

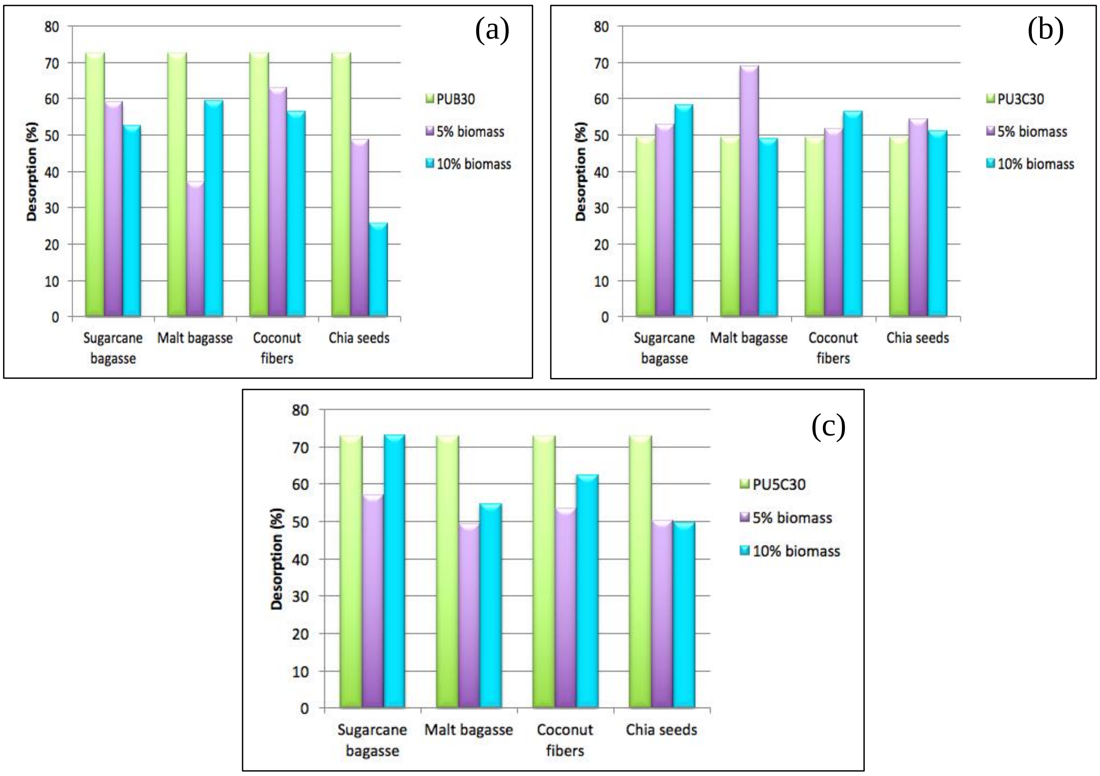


Figure 21 Water desorption results of the biomass-containing composites produced using: (a) PUB, (b) PU3C, and (c) PU5C adhesives.

Looking at the water absorption results, several observations can be made:

- For the PUB composites, it can be noticed that the sample produced with 10% of CA (sugarcane bagasse) led to the highest water absorption (152.0 mg/cm^2) while the one containing 5% had lowest one (67.8 mg/cm^2). When 5% CO (coconut fiber) was used, the water absorption was 143.4 mg/cm^2, followed by CH (chia seeds) (135.4 mg/cm^2). Among the tested biomasses, the 5% of CA gave the lowest water absorption results, which together with the 5% of MA (malt bagasse) led to water absorption values lower than the obtained for the base composites (100.2 mg/cm^2);
- For the composites produced with PU3C adhesive, the CO used at a content of 10% led to highest water absorption (174.6 mg/cm^2), being superior to the one registered for the base composite (158.8 mg/cm^2). Among the other biomasses, the lowest water absorption was 88.6 mg/cm^2, achieved when10% of MA was used;
- For the composites produced with PU5C, the highest absorption was 132.9 mg/cm^2, for 5% of CO, while the lowest one was 99.81 mg/cm^2,

corresponding to the composite with 10% of CH. It is worth to mention that all the composites produced with biomasses had lower water absorption than the base composites (153.2 mg/cm^2);

Regarding the water desorption results shown in Figure 21, it is possible to verify that:

- All the composites produced with PUB, and containing the different biomasses, had a water desorption behavior inferior to the one of the corresponding base composite (72.5%);
- Among the composites produced with PU3C, the highest water desorption was 69.0%, obtained for the composite containing 5% of MA, while all the other biomasses led to water desorption values near to the one of base composite (49.3%);
- For the PU5C composites, only the CA used in a content of 10% led to a water desorption of 73.3%, being this close to the one of base composite (73.0%).

Dimensional stability

The sample dimensions registered during the dimensional stability test are detailed in Appendix D. The results are described on Table 12 for the composites produced with CA (sugarcane bagasse) and CO (coconut fiber), while the one obtained with CH (chia seeds) and MA (malt bagasse) are described in Table 13. Analyzing the shrinkage values, it can be noticed that these are lower than 2%, fulfilling the standard specification. From a general perspective, the incorporation of the selected biomasses led to composites with higher dimensional stability than the obtained for the base composites. This pointed out for the dimensional stability increase due to the biomass incorporation at contents of 5 and 10%.

Table 12 Dimensional stability results of cork and biomass composites produced with 30% of adhesive content and 5 and 10% of sugarcane bagasse and coconut fiber.

Sample	S (%)	Sample	S (%)
PUBCA5-2	0.42	**PUBCO5-2**	0.42
PUBCA10-2	2.09	**PUBCO10-2**	1.26
PU3CCA5-2	0.63	**PU3CCO5-2**	1.07
PU3CCA10-2	0.42	**PU3CCO10-2**	1.06
PU5CCA5-2	0.42	**PU5CCO5-2**	1.46
PU5CCA10-2	1.64	**PU5CCO10-2**	0.42

Table 13 Dimensional stability results of cork and biomass composites produced using 30% of adhesives and 5 and 10% of malt bagasse and chia seeds.

Sample	S (%)	Sample	S (%)
PUBM5-2	0.21	**PUBCH5-2**	1.02
PUBM10-2	0.21	**PUBCH10-2**	1.06
PU3CM5-2	1.05	**PU3CCH5-2**	0.63
PU3CM10-2	0.42	**PU3CCH10-2**	0.42
PU5CM5-2	0.42	**PU5CCH5-2**	0.42
PU5CM10-2	1.44	**PU5CCH10-2**	1.27

Mechanical behavior

The values of stress at break (σ_b), strain at break (ε_b) and Young Modulus (E) determined from stress-strain curves of the cork and biomass composites are shown in Figure 22, where they are organized by adhesive type and biomass content. The graphics comparing the biomass composites produced with different contents (5 and 10%) are presented separately for each adhesive and can be consulted in Appendix E.

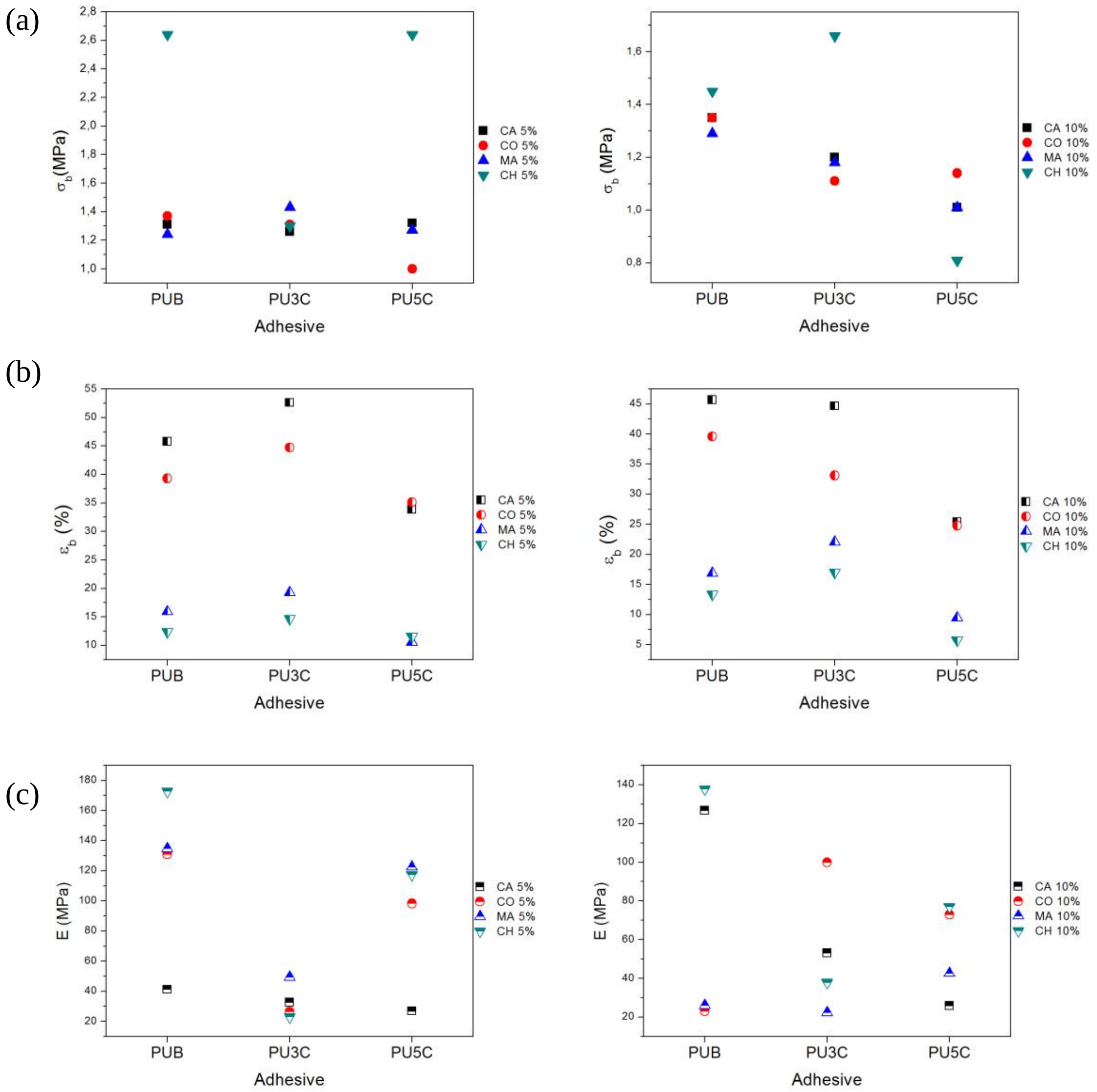


Figure 22 Mechanical behavior of the biomasses cork composites comparisons relatively to the adhesive type and different biomasses contents: (a) Stress at break; (b) Strain at break, and; (c) Young Modulus.

Observing the behavior of the 5% biomass composites, it is possible to note:

- The σ_b values of the CA containing composites had slight variations among the three adhesives, being the value around 1.30 MPa. For the CO, the minimum value was 1.0 MPa, obtained for the sample produced with the PU5C adhesive. In contrast, for the MA composite, a maximum value of 1.43 MPa was obtained for the PU3C adhesive, while for the CH containing composite a minimum value of 1.30 MPa was obtained also with the PU3C. In the case of the ε_b values, a maximum was obtained for all the composites when the PU3C adhesive was used, being the obtained highest value 52.6%, achieved with the CA-based composite. The lowest values were registered for the MA and CH composites, when the PU5C adhesive was used. Regarding the Young Modulus, in the case of the CA composite, a decrease from 41.2 to 26.8 MPa was verified when the adhesives changed from PUB to PU5C. For the CO, CH and MA composites maximum values were achieved when the PUB adhesive was used, decreasing after for minimum values when the PU3C was used and increasing again, in a lower extent, when PU5C was used. Based on the Young Modulus values, it can be concluded that the most flexible composites were the ones produced with PU3C, together with 5% of CH, CO and CA. In contrast, the stiff composite was produced using the PUB adhesive with 5% of CH.

Looking to the results obtained with the composites containing 10% of biomass, the following analysis can be done:

- The σ_b of the CA and MA containing composite had a decreasing pattern, varying from 1.35 MPa for CA and 1.3 MPa for MA, when PUB was used, to 1.0 MPa for both CA and MA, when PU5C was used. For the CO composite a minimum (1.1 MPa) was observed when the adhesive applied was PU3C, while the CH had a maximum value (1.7 MPa) in the same conditions, decreasing after for 0.8 MPa when PU5C was applied. In the case of the ε_b values, for the composites produced with CA and CO, a decreasing pattern was noted from 45.7 and 39.6 % when PUB was adopted, to 25.4 and 24.8%, when PU5C was used. The MA and CH composites had a similar behavior, presenting a maximum value of 22.1 and 17.0% when the PU3C adhesive was applied. Regarding the Young Modulus, the highest values were 126.7 and 137.8 MPa encountered for the composites produced with CA and CH, when the PUB adhesive was used. In opposition, the CO containing composite had a maximum value of 99.9 MPa when the PU3C was used, while the MA composite had a maximum value of 42.6 MPa, obtained when the PU5C was chosen. Based on the Young Modulus values, it can be concluded that the most flexible composites were produced when the PUB and the PU3C were used, together with 10% of MA and CO. In opposition, the stiff composites were produced with the PUB adhesive when 10% of CA and CH were used.

From the overall results analysis, it can be considered that the best formulation to achieve composites with higher flexibility corresponds to the use of the PU3C at a content of 30%. Moreover, and also from the perspective of the composites flexibility increment, the best biomass content is 5% when using CA, CO or CH.

Comparing the base composites properties with the ones modified with biomasses, the following differences can be highlighted:

- The base composites made with 30% of PUB adhesive presented shrinkage of 1.8% while the biomass composites using the same adhesive content led to values between 0.2 and 2.1%. In the same manner, the base composites produced using 30% of the PU3C adhesive had shrinkage of 2.3%, whereas biomass composites using the same adhesive content presented lower values, namely varying between 0.4 and 1.1%. Finally, for the base composites produced with 30% of the PU5C adhesive a shrinkage of 2.1% was noticed, whereas the biomass composites using the same adhesive content presented lower values, being between 0.4 and 1.6%. In general, the composites produced through the biomass incorporation presented a shrinkage lower than 2% being considered dimensionally stable according to the TR/ISO20882 standard specification. The only identified exception was PUBCA10 composite, where a shrinkage of 2.09% was obtained. Based on these results it can be concluded that the selected biomasses led to composites with higher dimensional stability;
- Regarding water absorption, the base composite produced with 20% of PUB had the lowest water absorption (75.1 mg/cm^2), among all the base composites. The CO used at a content of 10% combined with the PU3C adhesive led to highest water absorption values (174.6 mg/cm^2), being superior to the one registered for the base composite with same adhesive content (158.8 mg/cm^2). However, for the composites produced with PU5C and the biomasses, a lower water absorption was observed comparatively with the base composites with same adhesive content (153.2 mg/cm^2);
- With respect to the water desorption, in a general way, the base composites presented higher values if compared to the biomass-containing ones. For instance, all the biomass-containing composites produced with PUB had a

water desorption inferior to the one of the base composite for the same adhesive content. The same pattern was detected for the ones produced with the PU5C, where only the CA used at a content of 10% led to a water desorption close to the value obtained for the base composite with same adhesive content. For the composites produced with PU3C, almost all the biomasses led to water desorption values near to the ones obtained for the base composites. These results pointed out for a decrease of the water desorption due to the biomass incorporation. The mechanical behavior of the composites pointed out for an increase of the flexibility due the use of the extract modified adhesives. Despite this, when comparing the Young Modulus of all the 3 produced adhesives, the variation was lower when the used content was 30%. Regarding biomass-containing composites, the one with the highest flexibility corresponds to the one produced with PU3C (30%) together with 5% of CH.

6 Conclusions and future work

The main objective of the present work was to study the production of bio and eco-composites with enhanced physico-mechanical properties, having in view their integration in footwear components (e.g. insoles and soles). The approach to the problem considered, firstly, the production of cork composites replacing the traditional TDI-base adhesive by a water-based polyurethane-urea adhesive (3 PUD formulations were previously synthesized and tested), and thereafter the reinforcement of the cork composites through the incorporation of residual biomasses.

Concerning the water-based polyurethane adhesive synthesis, three formulations were tested (a base formulation (PUB), and formulations modified by the incorporation of 3% (PU3C) and 5% (PU5C) (w/w, prepolymer-basis) of a *Melissa officinalis* L. hydrophilic extract. The extract incorporation aimed to enhance the adhesive's properties. The adhesives were characterized as dispersions itself and as films. The dispersion characterization evidenced the effect of the extract addition on the viscosity, pH and particle size, once its incorporation gave dispersions with higher mean particle size (0.107 μm and 2.510 μm for dispersions modified with 3 and 5% of Melissa extract, respectively, (volume distributions)), and more viscous dispersions as the extract content increased from 3 to 5%.

With respect to films characterization, the polyurethane-urea chemical structure was confirmed through Fourier Transform Infrared Spectroscopy. Differential Scanning Calorimetry analysis evidenced the effect of the extract on the thermal behavior of the PUDs, once when 3 and 5% of extract were added the values of melting temperature (T_m) and the melting enthalpy variation (ΔH_m) changed, fact associated to the extract distribution that interferes with the hard segment rearrangement occurring at molecular level, comparatively with the one observed for PUB film. The thermogravimetric analysis showed an increase of the films thermal stability related with the incorporation of the extract.

The evaluation of the films mechanical behavior through the stress-strain curves allowed the obtainment of the ultimate stress, ultimate strain and the Young modulus values. The results evidenced the increasing of the films flexibility due to the extract incorporation, once the Young modulus values decreased with the used extract amount, varying from 6.62 MPa for the PUB to 6.16 MPa for PU3C, and reaching 5.36 MPa for the PU5C.

The second part of the study was focused on the cork composites production and characterization. In a first stage, base cork composites were produced by using adhesive contents of 20, 30 and 40% (w/w, cork-basis, adhesive weight based on its solids content). Then, the composites were characterized in terms of water absorption and desorption properties, dimensional stability and mechanical behavior. The water absorption/desorption and dimensional stability results were compared against the specifications posed by the ISO/TR 20882 standard that specifies values of water absorption ≥ 70mg/cm^2, desorption ≥ 80% and shrinkage ≤ 2%. The values of water absorption varied from 75.1 mg/cm^2 to 171.4 mg/cm^2 when the adhesive content varied from 20% to 40%, being the highest values with the PU3C and PU5C adhesives. The desorption varied from 56.9% to 80% for the PUB, from 57.6% to 55.7% for the PU3C, and from 80.0% to 66.25% for the PU5C. Regarding the dimensional stability, almost all the produced composites presented shrinkage lower or close to 2%, fulfilling the standard specification. From a general perspective, it can be stated that the hydrophilic character of the adhesives led to the increase of the water absorption properties, which is an interesting feature for footwear applications.

Regarding the mechanical behavior evaluation, the overall Young modulus results showed that when the adhesive content was 20 and 40%, the more flexible composites were produced with PU3C and PU5C. Moreover, the Young Modulus values presented minor variations when the adhesive content was 30%. Based on these results, together with the ones of water absorption/desorption, the adhesive content of 30% was selected for the following studies related with the incorporation of residual biomass.

The last stage of the study aimed at evaluates the effect of adding residual biomasses to the base cork composites previously produced (only the ones produced with 30% adhesive were considered). The following residual biomasses were used: sugarcane bagasse (CA), malt bagasse (MA), coconut fibers (CO) and chia seeds CH). The tested contents were 5 and 10% (w/w, cork-basis). Then, the obtained composites were characterized in terms of water absorption/desorption characteristics, dimensional stability and mechanical behavior. The water absorption revealed that for the PUB-based composites, the highest water absorption was 152.0 mg/cm^2, being obtained with 10% of CA. Among the tested biomasses, 5% of MA incorporation gave the lowest water absorption results, being lower than the ones obtained for PUB base composite (100.2 mg/cm^2). For the composites produced with PU3C adhesive, the use of CO at 10% content led to the highest water absorption (174.6 mg/cm^2) while the lowest achieved value was 88.6 mg/cm^2 (10% MA). In the case of the PU5C composites, the highest absorption was 132.9 mg/cm^2 (5% CO), while the lowest was 99.81 mg/cm^2 (10% CH). It is worth to mention that all the composites incorporating biomasses had lower water absorption than the corresponding base composites. Regarding the water desorption results, it was observed that all the composites produced with PUB, and incorporating the different biomasses, had water desorption properties inferior to the ones of the base composite (72.5%). In the case of the composites produced with PU3C, the highest water desorption was 69.0 (5% MA), while the use of the others biomasses led to water desorption values near to the ones of the base composite (49.3%). For the PU5C composites, only CA used at a content of 10% led to a water desorption of 73.3%, being this close to the one of the base composite (73.0%).

Analyzing the shrinkage values, cork composites reinforced with biomass presented values lower than 2%, fulfilling the standard specification. From a general perspective, the incorporation of the selected residual biomasses led to composites with higher dimensional stability comparatively with the base composites. This pointed out for the dimensional stability increasing due to biomass incorporation.

Regarding to the mechanical behavior evaluation, the Young modulus of the composites incorporating 5% of biomass pointed out for the production of more flexible samples, in particular when the PU3C adhesive was combined with CH, CO and CA biomasses. In contrast, a stiff composite was produced using the PUB adhesive combined with CH. In the same manner, when 10% of biomass was used, the most flexible composites were produced when the PUB and the PU3C were used with MA and CO. In opposition, the stiff composites were produced with the PUB adhesive when CA and CH were used.

From the overall results analysis, it can be considered that the best formulation used towards the achievement of higher flexibility corresponds to the use of the PU3C adhesive at a content of 30%. Moreover, and also from the perspective of the composites flexibility, the biomasses conducting to the best results were CA, CO or CH at contents of 5%.

As future work, it would be very interesting to study the morphology of PUD films and composites, namely the distribution of the extract in the PUD films and the residual biomass within the composite structure. It would be also important to complement the mechanical properties study of both films and composites, by performing thermomechanical studies in order to evaluate the viscoelastic behavior. Moreover, and regarding the antimicrobial activity of the *Melissa officinalis* L. extract, it can be also suggested the evaluation of the fungal strains *Trichoderma* and *Fusarium* inhibition due to the extract presence. This would be important from the perspective of cork-based composites preservation, once these fungal strains are known to grow in a mid-term period in cork, affecting the aesthetic appearance of the final products and generating the 2,4,6-trichloroanisole, which usually contaminates the wine and gives it a moldy off-odor.

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8 Appendices

8.1 Appendix A

PUD characterization data

Table A 1 Experimental records of the reagent quantities used throughout the PUD synthesis.

Sample		m_{PPG} (g)	m_{ISO} (g)	V_{SO} (μl)	m_{DMPA} (g)	v_{TEA} (ml)	v_{water1} (ml)	m_{me} (g)	v_{EDA} (ml)	v_{water2} (ml)	$v_{total\ acetone}$ (ml)
PUD base	**PUB-1**	68.48	26.91	37.50	5.08	5.10	100.00	-	1.22	23.78	80.00
	PUB-2	67.76	26.37	37.50	5.07	5.00	100.00	-	0.96	24.04	80.00
	PUB-3	67.54	26.50	37.50	5.09	5.02	100.00	-	0.90	24.10	90.00
	PUB-4	67.83	27.90	37.50	5.04	4.97	100.00	-	1.50	22.50	80.00
PUD 3% Melissa extract	**PU3C-1**	67.72	28.16	37.50	5.00	4.94	120.00	2.86	0.96	24.04	20.00
	PU3C-2	67.86	28.17	37.50	5.04	4.98	120.00	2.88	1.37	23.63	100.00
	PU3C-3	68.32	27.62	37.50	5.04	4.98	120.00	2.88	1.00	24.00	100.00
	PU3C-4	68.40	28.14	37.50	5.06	4.99	120.00	2.89	0.94	24.06	100.00
	PU3C-5	68.51	27.89	37.50	5.05	4.98	120.00	2.88	1.09	23.91	100.00
PUD 5% Melissa extract	**PU5C-1**	68.43	27.07	37.50	5.05	4.99	180.00	4.75	0.65	24.35	40.00
	PU5C-2	68.53	27.52	37.50	5.04	4.98	180.00	4.75	1.03	23.97	80.00
	PU5C-3	68.47	27.84	37.50	5.02	4.96	180.00	4.81	1.05	23.95	120.00
	PU5C-4	68.55	27.80	37.5	5.03	4.97	180.00	4.76	0.92	24.08	80.00

*v_{water1}: dispersion of the prepolymer in water stage; m_{me}: Melissa extract mass; v_{water2}: chain extension stage.

8.2 Appendix B

Determination of the NCO content through Dibutylamine (DBA) method

The residual NCO groups were quantified according to the guidelines of the EN 1242:1993 standard. The adopted procedure can be described as follows:

1. 25 ml of toluene were added to 4 erlenmeyers with lids;
2. 6.3 ml of the dibutylamine/toluene solution (108 ml DBA + 400 ml toluene) were added to the erlenmeyers;
3. For each reaction time (15, 30, 45 min and after the dispersion production), approximately 2g of prepolymer were collected and weighted into each Erlenmeyer.
4. Next, the Erlenmeyer was kept under heating at 60 °C during 5 minutes. Then, the sample solution was left to cool until ambient temperature under stirring.
5. Next, 50 ml of 2-propanol and 0.25 ml of bromophenol blue were added to the samples solution before the titration with HCl 1N until a persistent yellow color appear.

A Blank sample was also prepared following the same procedure, without the sample addition. The NCO content was calculated and expressed as a percentage using Equation (7), where V_B is the volume of titrant consumed in the blank titration (ml), V_A is the volume of titrant consumed in the sample titration (ml), N_{HCl} is the concentration of the titrant solution expressed in normality (N), and m_A is the mass of the sample (g). The obtained NCO conversion is calculated by Equation (8):

$$NCO(\%) = \frac{(V_{B-}V_A)\ x\ N_{HCl}\ x\ 4.2}{m_A} \qquad \text{Eq. (7)}$$

$$\rho_{NCO} = \frac{(NCO)_i - (NCO)_f}{(NCO)_i} \qquad \text{Eq. (8)}$$

Table B 1 Experimental records of the NCO groups used throughout the PUD synthesis.

Sample		Reaction NCO:OH $_{PPG}$		Reaction NCO:OH$_{DMPA}$		After phase inversion
		Theoretical Conversion	Experimental Conversion	Theoretical Conversion	Experimental Conversion	Experimental Conversion
PUD base	**PUB1**	0.28	-*	0.60	0.65	0.74
	PUB2	0.29	0.30	0.60	0.69	0.79
	PUB3	0.28	-*	0.60	0.62	0.79
	PUB4	0.27	0.30	0.57	0.68	0.68
PUD 3% Melissa extract	**PU3C1**	0.27	0.22	0.56	0.65	0.80
	PU3C2	0.27	0.29	0.56	0.70	0.72
	PU3C3	0.27	0.30	0.58	0.73	0.78
	PU3C4	0.27	0.28	0.57	0.70	0.80
	PU3C5	0.27	0.30	0.57	0.70	0.77
PUD 5% Melissa extract	**PU5C1**	0.28	0.28	0.59	0.71	0.87
	PU5C2	0.28	0.28	0.58	0.68	0.78
	PU5C3	0.27	0.28	0.57	0.72	0.81

*values not available.

8.3 Appendix C

Base composites characterization data

Table C 1 Absorption/desorption results of cork composites made with base formulation and three different adhesives contents: 20, 30 and 40%.

Standard	Sample	Length (cm)	Width (cm)	Area (cm^2)	Initial weight (mg)	Final weight* (mg)	Reconditioned sample** (mg)	Absorption (mg/cm^2)	Desorption (%)
ISO22649: 2016	**PUB20-1**	5.06	5.07	25.64	3439.00	5365.00	4270.00	75.12	56.85
	PUB30-1	5.01	5.03	25.20	3819.00	6343.00	4514.00	100.17	72.46
	PUB40-1	4.90	5.01	24.54	3664.00	7417.00	5060.00	152.91	62.80
	PU3C20-1	4.93	4.98	24.58	3421.00	6714.00	4818.00	133.96	57.58
	PU3C30-1	5.00	5.14	25.70	3639.00	7719.00	5707.00	158.75	49.31
	PU3C40-1	4.93	5.01	24.69	3926.00	8158.00	5803.00	171.38	55.65
	PU5C20-1	4.99	5.10	25.46	3128.00	5452.00	3592.00	91.27	80.03
	PU5C30-1	4.93	4.99	24.61	3591.00	7361.00	4612.00	153.19	72.92
	PU5C40-1	4.95	5.00	24.76	3832.00	7666.00	5126.00	154.82	66.25

* After 6h in water; ** after 16h drying at room temperature.

Table C 2 Dimensional stability results of cork composites made with base formulation and three different adhesives contents: 20, 30 and 40%.

Standard	Sample	Length/ width	Length / width (mm)	Length / width (after 24h at 37 °C) (mm)	Dimensional stability (%)	Sa (%)	Sb (%)	S (%)
ISO 22651: 2002	**PUB20-2**	**AB**	59.50	58.50	1.68	2.09	2.50	2.30
		CD	60.00	58.50	2.50			
		AC	20.00	19.50	2.50			
		BD	20.00	19.50	2.50			
	PUB30-2	**AB**	59.00	58.50	0.85	0.84	2.50	1.67
		CD	59.50	59.00	0.84			
		AC	20.00	19.50	2.50			
		BD	20.00	19.50	2.50			
	PUB40-2	**AB**	59.00	59.00	0.00	0.42	2.38	1.40
		CD	59.00	58.50	0.85			
		AC	21.00	20.50	2.38			
		BD	21.00	20.50	2.38			

Table C 3 Dimensional stability results of cork composites made with formulation modified with 3% of the aqueous extract of Melissa officinalis and three different adhesives contents: 20, 30 and 40%.

Standard	Sample	Length/ width	Length / width (mm)	Length / width (after 24h at 37 °C) (mm)	Dimensional stability (%)	Sa (%)	Sb (%)	S (%)
ISO 22651: 2002	**PU3C20-2**	**AB**	59.50	59.00	0.84	0.42	0.00	0.21
		CD	59.00	59.00	0.00			
		AC	21.00	21.00	0.00			
		BD	20.00	20.00	0.00			
	PU3C30-2	**AB**	59.50	58.00	2.52	2.12	2.53	2.33
		CD	58.50	57.50	1.71			
		AC	20.00	19.50	2.50			
		BD	19.50	19.00	2.56			
	PU3C40-2	**AB**	59.50	58.50	1.68	1.68	2.44	2.06
		CD	59.50	58.50	1.68			
		AC	21.00	20.50	2.38			
		BD	20.00	19.50	2.50			

Table C 4 Dimensional stability results of cork composites made with formulation modified with 5% of the aqueous extract of Melissa officinalis and three different adhesives contents: 20, 30 and 40%.

Standard	Sample	Length/ width	Length / width (mm)	Length / width (after 24h at 37 °C) (mm)	Dimensional stability (%)	Sa (%)	Sb (%)	S (%)
ISO 22651: 2002	**PU5C20-2**	**AB**	58.50	58.50	0.00	0.43	1.28	0.85
		CD	58.50	58.00	0.85			
		AC	20.00	19.50	2.50			
		BD	19.00	19.00	0.00			
	PU5C30-2	**AB**	59.00	58.00	1.69	1.69	2.50	2.10
		CD	59.00	58.00	1.69			
		AC	20.00	19.50	2.50			
		BD	20.00	19.50	2.50			
	PU5C40-2	**AB**	60.00	59.50	0.83	1.24	1.30	1.27
		CD	60.50	59.50	1.65			
		AC	19.50	19.00	2.56			
		BD	19.00	19.00	0.00			

8.4 Appendix D

Composites modified with biomasses characterization data.

Table D 1 Absorption/desorption results of cork composites made with base formulation and three different 30% of adhesives contents using sugarcane bagasse and malt bagasse with 5 and 10% of biomass content.

Standard	Sample	Biomass	Length (cm)	Width (cm)	Area (cm^2)	Initial weight (mg)	Final weight* (mg)	Reconditioned sample** (mg)	Absorption (mg/cm^2)	Desorption (%)
ISO22649: 2016	**PUB30CA5-1**	**Sugarcane bagasse**	5.02	5.03	25.20	3779.00	5487.00	4478.00	67.78	59.07
	PUB30CA10-1		4.91	4.92	24.17	3747.00	7421.00	5487.00	151.99	52.64
	PU3C30CA5-1		5.01	4.99	25.00	3733.00	7001.00	5266.00	130.69	53.09
	PU3C30CA10-1		4.95	5.00	24.74	3652.00	7060.00	5078.00	137.78	58.16
	PU5C30CA5-1		4.99	4.99	24.92	3858.00	6791.00	5116.00	117.72	57.11
	PU5C30CA10-1		4.98	4.89	24.35	3916.00	6896.00	4711.00	122.37	73.32
	PUB30M5-1	**Malt bagasse**	5.11	5.11	26.11	3630.00	6053.00	5151.00	92.79	37.23
	PUB30M10-1		5.10	5.05	25.74	3746.00	6619.00	4910.00	111.59	59.48
	PU3C30M5-1		4.99	5.08	25.35	3869.00	6571.00	4708.00	106.59	68.95
	PU3C30M10-1		5.04	5.13	25.89	3652.00	5944.00	4822.00	88.54	48.95
	PU5C30M5-1		5.07	5.08	25.76	3819.00	6823.00	5338.00	116.61	49.43
	PU5C30M10-1		5.10	5.02	25.61	4081.00	7018.00	5404.00	114.69	54.95

* After 6h in water; ** after 16h drying at room temperature.

Table D 2 Absorption/desorption results of cork composites made with base formulation and three different 30% of adhesives contents using coconut fiber and chia seeds with 5 and 10% of biomass content.

Standard	Sample	Biomass	Length (cm)	Width (cm)	Area (cm^2)	Initial weight (mg)	Final weight* (mg)	Reconditioned sample** (mg)	Absorption (mg/cm^2)	Desorption (%)
ISO22649: 2016	**PUB30CO5-1**	**Coconut fiber**	4.96	5.07	25.15	3627.00	7232.00	4962.00	143.35	62.97
	PUB30CO10-1		4.96	4.99	24.76	3826.00	6273.00	4893.00	98.83	56.40
	PU3C30CO5-1		5.05	4.99	25.20	3690.00	7349.00	5454.00	145.20	51.79
	PU3C30CO10-1		5.00	4.99	24.95	3902.00	8258.00	5800.00	174.59	56.43
	PU5C30CO5-1		5.03	4.99	25.10	3282.00	6618.00	4826.00	132.91	53.72
	PU5C30CO10-1		5.04	4.99	25.14	3656.00	6299.00	4645.00	105.13	62.58
	PUB30CH5-1	**Chia seeds**	5.02	5.03	25.28	3713.00	7136.00	5460.00	135.40	48.96
	PUB30CH10-1		5.03	5.03	25.32	3650.00	7040.00	6168.00	133.91	25.72
	PU3C30CH5-1		4.98	5.01	24.95	3880.00	6695.00	5159.00	112.80	54.56
	PU3C30CH10-1		4.94	5.02	24.78	3811.00	6708.00	5230.00	116.89	51.02
	PU5C30CH5-1		4.82	4.80	23.14	3660.00	6218.00	4933.00	110.56	50.23
	PU5C30CH10-1		4.95	4.88	24.19	3762.00	6176.00	4973.00	99.81	49.83

* after 6h in water; ** after 16h drying at room temperature.

Table D 3 Dimensional stability results of cork composites made with base formulation and three different 30% of adhesives contents using sugarcane bagasse with 5 and 10% of biomass content.

Standard	Sample	Length/ width (mm)	Length / width (mm)	Length / width (after 24h at 37ºC) (mm)	Dimensional stability (%)	Sa	Sb	S
ISO 22651: 2002	**PUB30CA5-2**	**AB**	59.00	58.50	0.85	0.84	0.00	0.42
		CD	59.50	59.00	0.84			
		AC	19.50	19.50	0.00			
		BD	19.50	19.50	0.00			
	PUB30CA10-2	**AB**	59.00	58.50	0.85	1.68	2.50	2.09
		CD	60.00	58.50	2.50			
		AC	20.00	19.50	2.50			
		BD	20.00	19.50	2.50			
	PU3C30CA5-2	**AB**	59.50	59.50	0.00	0.00	1.25	0.63
		CD	59.50	59.50	0.00			
		AC	20.00	19.50	2.50			
		BD	20.00	20.00	0.00			
	PU3C30CA10-2	**AB**	59.50	59.00	0.84	0.84	0.00	0.42
		CD	59.50	59.00	0.84			
		AC	19.50	19.50	0.00			
		BD	19.50	19.50	0.00			
	PU5C30CA5-2	**AB**	59.50	59.00	0.84	0.84	0.00	0.42
		CD	59.50	59.00	0.84			
		AC	19.50	19.50	0.00			
		BD	19.00	19.00	0.00			
	PU5C30CA10-2	**AB**	59.50	59.00	0.84	0.84	2.44	1.64
		CD	59.50	59.00	0.84			
		AC	20.50	20.00	2.44			
		BD	20.50	20.00	2.44			

Table D 4 Dimensional Stability results of cork composites made with base formulation and three different 30% of adhesives contents using malt bagasse with 5 and 10% of biomass content.

Standard	Sample	Length/ width (mm)	Length / width (mm)	Length / width (after 24h at 37ºC) (mm)	Dimensional stability (%)	Sa	Sb	S
ISO 22651: 2002	**PUB30M5-2**	**AB**	60.00	59.50	0.83	0.42	0.00	0.21
		CD	59.50	59.50	0.00			
		AC	20.00	20.00	0.00			
		BD	20.00	20.00	0.00			
	PUB30M10-2	**AB**	59.00	59.00	0.00	0.42	0.00	0.21
		CD	59.00	58.50	0.85			
		AC	19.00	19.00	0.00			
		BD	19.00	19.00	0.00			
	PU3C30M5-2	**AB**	59.50	59.00	0.84	0.84	1.27	1.05
		CD	59.50	59.00	0.84			
		AC	20.00	19.50	2.50			
		BD	19.50	19.50	0.00			
	PU3CM10-2	**AB**	59.50	59.00	0.84	0.84	0.00	0.42
		CD	59.50	59.00	0.84			
		AC	19.50	19.50	0.00			
		BD	19.50	19.50	0.00			
	PU5C30M5-2	**AB**	59.50	59.00	0.84	0.84	0.00	0.42
		CD	59.00	58.50	0.85			
		AC	20.00	20.00	0.00			
		BD	19.50	19.50	0.00			
	PU5C30M10-2	**AB**	59.50	59.50	0.00	0.42	2.47	1.44
		CD	59.50	59.00	0.84			
		AC	20.00	19.50	2.50			
		BD	20.50	20.00	2.44			

Table D 5 Dimensional stability results of cork composites made with base formulation and three different 30% of adhesives contents using coconut fiber with 5 and 10% of biomass content.

Standard	Sample	Length/ width (mm)	Length / width (mm)	Length / width (after 24h at 37ºC) (mm)	Dimensional stability (%)	Sa	Sb	S
ISO 22651: 2002	**PUB30C05-2**	**AB**	59.50	59.00	0.84	0.84	0.00	0.42
		CD	59.50	59.00	0.84			
		AC	20.00	20.00	0.00			
		BD	19.50	19.50	0.00			
	PUB30CO10-2	**AB**	59.50	59.00	0.84	1.26	1.27	1.26
		CD	59.50	58.50	1.68			
		AC	19.50	19.50	0.00			
		BD	20.00	19.50	2.50			
	PU3C30CO5-2	**AB**	59.50	59.00	0.84	0.84	1.30	1.07
		CD	59.50	59.00	0.84			
		AC	19.00	19.00	0.00			
		BD	19.50	19.00	2.56			
	PU3C30CO10-2	**AB**	590	58.50	0.85	0.85	1.27	1.06
		CD	58.50	58.00	0.85			
		AC	20.00	20.00	0.00			
		BD	19.50	19.00	2.56			
	PU5C30CO5-2	**AB**	59.00	58.50	0.85	0.43	2.50	1.46
		CD	58.50	58.50	0.00			
		AC	20.00	19.50	2.50			
		BD	20.00	19.50	2.50			
	PU5C30CO10-2	**AB**	59.50	59.00	0.84	0.84	0.00	0.42
		CD	59.50	59.00	0.84			
		AC	19.50	19.50	0.00			
		BD	19.50	19.50	0.00			

Table D 6 Dimensional stability results of cork composites made with base formulation and three different 30% of adhesives contents using chia seeds with 5 and 10% of biomass content.

Standard	Sample	Length/ width (mm)	Length / width (mm)	Length / width (after 24h at 37ºC) (mm)	Dimensional stability (%)	Sa	Sb	S
ISO 22651: 2002	**PUB30CH5-2**	**AB**	60.50	60.00	0.83	0.83	1.22	1.02
		CD	60.50	60.00	0.83			
		AC	20.50	20.50	0.00			
		BD	20.50	20.00	2.44			
	PUB30CH10-2	**AB**	59.50	59.00	0.84	0.84	1.28	1.06
		CD	59.50	59.00	0.84			
		AC	19.00	19.00	0.00			
		BD	20.00	19.50	2.50			
	PU3C30CH5-2	**AB**	60.00	59.00	1.67	1.26	0.00	0.63
		CD	59.50	59.00	0.84			
		AC	19.50	19.50	0.00			
		BD	20.00	20.00	0.00			
	PU3C30CH10-2	**AB**	59.00	58.50	0.85	0.85	0.00	0.42
		CD	59.00	58.50	0.85			
		AC	19.50	19.50	0.00			
		BD	19.50	19.50	0.00			
	PU5C30CH5-2	**AB**	59.50	59.00	0.84	0.84	0.00	0.42
		CD	59.00	58.50	0.85			
		AC	20.00	20.00	0.00			
		BD	19.50	19.50	0.00			
	PU5C30CH10-2	**AB**	60.00	59.00	1.67	1.25	1.28	1.27
		CD	60.00	59.50	0.83			
		AC	19.50	19.00	2.56			
		BD	19.50	19.50	0.00			

8.5 Appendix E

Cork composites stress-strain curves

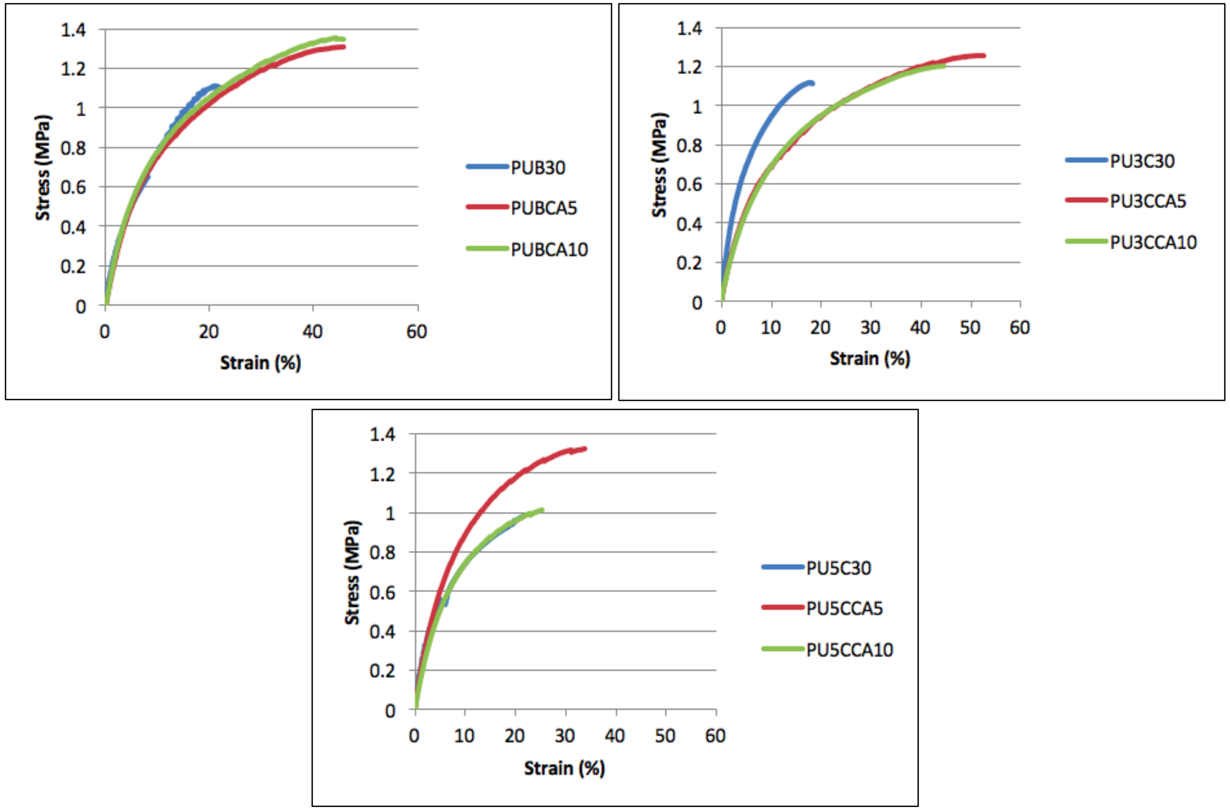

Figure E 1 Cork composites stress-strain curves obtained from tensile tests: (a) composite made with PUB and containing 5 and 10% of CA; (b) composite made with PU3C and containing 5 and 10% CA; (c) composite made with PU5C and containing 5 and 10% CA.

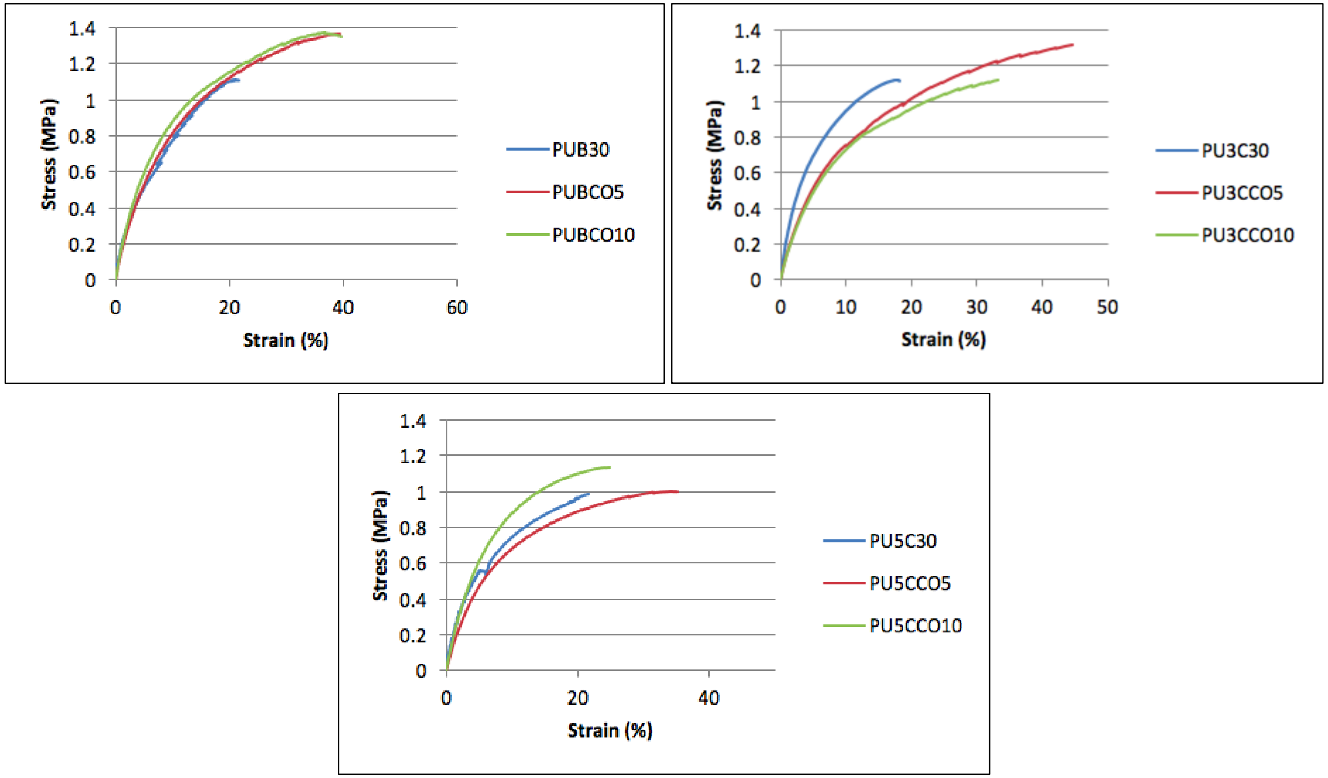

Figure E 2 Cork composites stress-strain curves obtained from tensile tests: (a) composite made with PUB and containing 5 and 10% of CO; (b) composite made with PU3C and containing 5 and 10% CO; (c) composite made with PU5C and containing 5 and 10% CO.

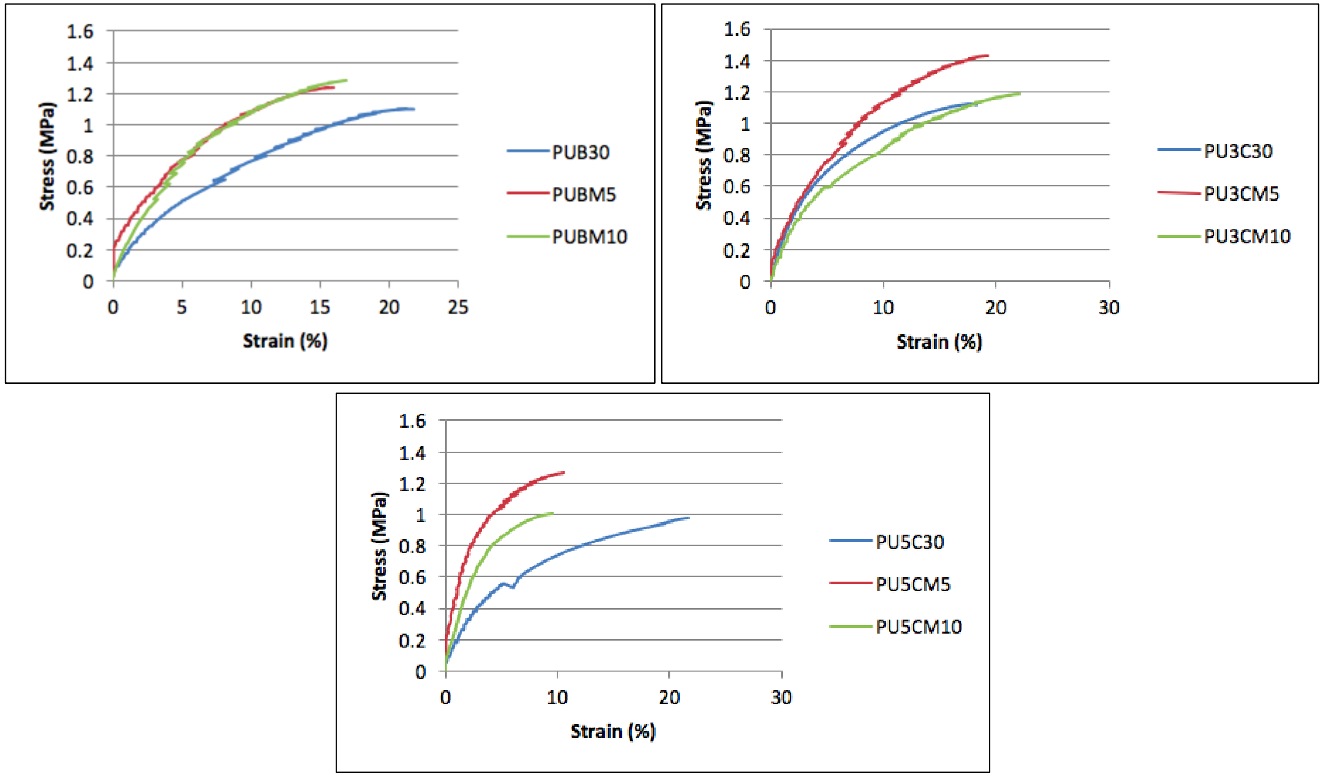

Figure E 3 Cork composites stress-strain curves obtained from tensile tests: (a) composite made with PUB and containing 5 and 10% of M; (b) composite made with PU3C and containing 5 and 10% M; (c) composite made with PU5C and containing 5 and 10% of M.

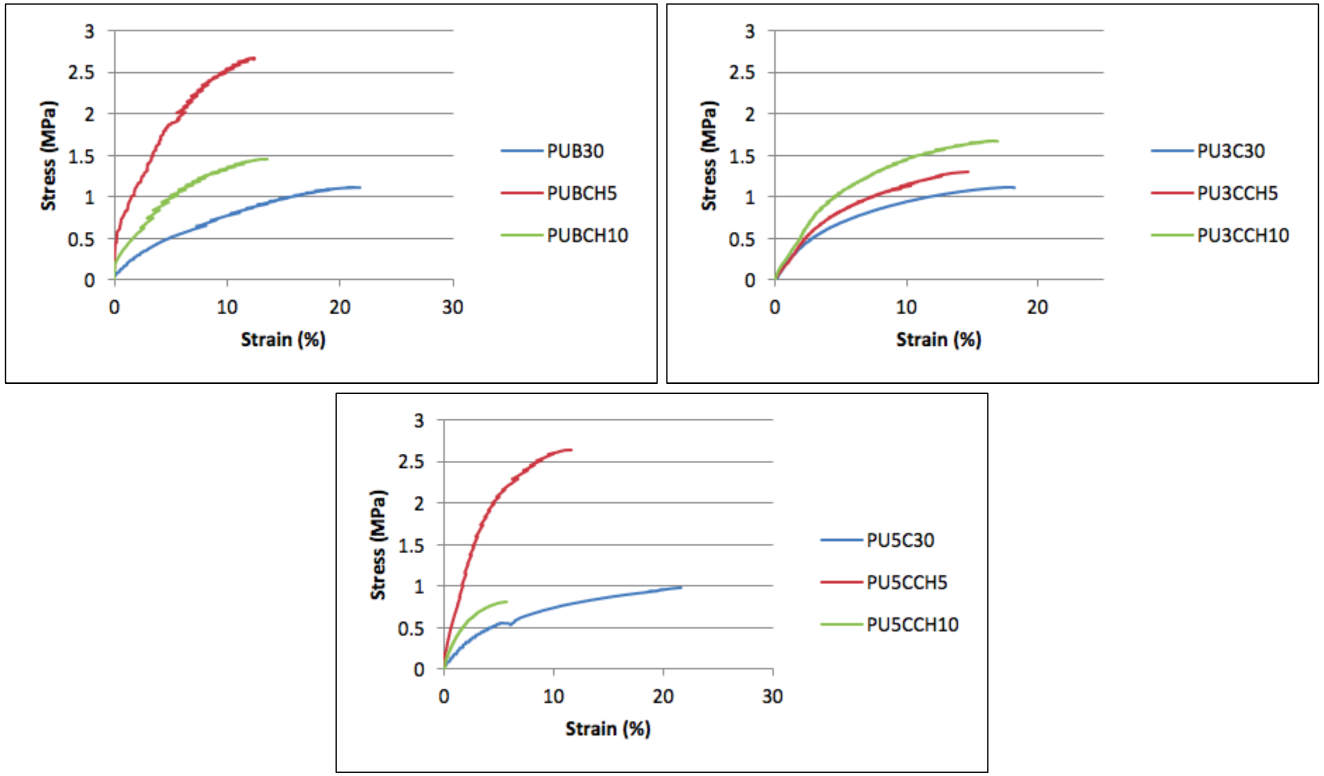

Figure E 4 Cork composites stress-strain curves obtained from tensile tests: (a) composite made with PUB and containing 5 and 10% of CH; (b) composite made with PU3C and containing 5 and 10% CH; (c) composite made with PU5C and containing 5 and 10% of CH.

8.6 Appendix F

Participation in Symposium and Conference

1ª Escola de Verão & Simpósio de Dupla Diplomação DD2018
1st Summer School & Symposium Double Degree DD2018

DEVELOPMENT OF BIO- AND ECO-COMPOSITES FOR THE FOOTWEAR INDUSTRY

✉ P.C. Santos[1,2], I.P. Fernandes[3], M.F. Barreiro[3,4], J.M.T.A. Pietrobelli[5]

[1]Chemical Engineering Master Degree, School of Technology and Management, Polytechnic Institute of Bragança, Portugal
[2]Chemical Engineering Graduation Degree, Campus de Ponta Grossa, Federal University of Technology-Paraná, Brazil
pallomaeq@gmail.com (P.C. Santos)
[3]Mountain Research Centre (CIMO) and Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Polytechnic Institute of Bragança, Campus de Santa Apolonia - 5300-253 Bragança Portugal
ipmf@ipb.pt (I.P. Fernandes)
[4] Chemical and Biological Technology,Department, School of Technology and Management, Polytechnic Institute of Bragança, Campus de Santa Apolonia - 5300-253 Bragança Portugal
barreiro@ipb.pt (M.F. Barreiro)
[5]Chemical Engineering Department, Federal University of Technology-Paraná (UTFPR), Campus of Ponta Grossa, 84016-210 Ponta Grossa, PR - Brazil
jpietrobelli@utfpr.edu.br (J.M.T.A. Pietrobelli)

ABSTRACT

The Portuguese Footwear industry is one of the most active national business areas. Considering this industry demand for eco- and bio-products, the development of novel composites, based on natural materials and by adopting green productive processes, represents an area of great interest. In this context, the work developed in the DD course is focused on the production of cork composites with enhanced physico-mechanical properties, having in view the development of cork-based footwear components, e.g. insoles and soles. The first stage of the work correspond to the synthesis of the waterbased polyurethane adhesives according to a modified prepolymer process developed at the IPB research group. These adhesives are based on polypropylene glycol (PPG) polyol, isophorone diisocyanate (IPDI), dimethylolpropionic acid (DMPA) as internal emulsifier, trimethylamine (TEA) as neutralizing agent and ethylenediamine (EDA) as chain extender. Moreover, beyond the base adhesive, two modified formulations were produced through the incorporation of *Melissa officinalis L.* hydrophilic extract, in contents of 3 and 5% (w/w), in order to enhance properties such as adhesion strength and to impart functionalites such as antibacterial and antifungal activities [1]. Afterwards, the adhesives were characterized in terms of solid content, pH and viscosity. The second stage of this study comprises the development of composite materials using different adhesive:cork ratios (20:80, 30:70 and 40:80, w/w). The properties of the produced composites such as flex resitance, dimensional stability and water absorption/desorption are being evaluated in order to select the best adhesive and composite formulations. Then, based on these results, cork composites reinforced with biomass residues, namely sugarcane bagasse, malt bagasse, coconut fibers and chia seeds will be produced and characterized. Afterwards, the best formulation will be validated in the production of footwear insoles containing a superficial leather coating, traditionally applied in footwear construction. This work is being done in collaboration with the Portuguese Footwear Technological Center (CTCP).

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Development of bio- and eco-composites for the footwear industry

P.C. Santos[1,2,3], I. P. Fernandes[1,2], J. E. Ribeiro[2], J.M.T.A. Pietrobelli[3], M. F. Barreiro[12,*]
[1]LSRE-LCM, Polytechnic Institute of Bragança, Campus Santa Apolonia Ap 1134, 5301-857 Bragança, Portugal; [2]CIMO, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; [3]Chemical Engineering Department, Federal University of Technology-Paraná (UTFPR), Campus of Ponta Grossa, 84016-210 Ponta Grossa, PR – Brazil
[*]barreiro@ipb.pt

Nowadays consumer´s demands for more ecological footwear, impacts on components like shoe insoles materials. In this context, cork composites are often used for this application. However, the traditional agglomeration process uses a reactive polyurethane-based binder (containing TDI), generating composites with low flexibility and poor water absorption/desorption characteristics, resulting in products with low comfort properties. Furthermore, the presence of TDI, is another important drawback due to its high toxicity. Therefore, the present work is devoted to the development of cork composites, where the TDI-based binder was replaced by an aqueous PUD reinforced with *Melissa officinalis* L. extract. Cork-composites were produced using different adhesive/cork ratios, and characterized in terms of dimensional stability, water absorption/desorption properties, and mechanical behavior. After the selection of the best adhesive content, composites reinforced with sugarcane bagasse, malt bagasse, coconut fibers, and chia seeds were also produced and characterized.

Introduction

The footwear industry is an important economic area in Portugal, with recent investments centered in the production of high performance footwear, which demand high technical-scientific expertise. Moreover, this sector is nowadays seeking to respond to consumer's demands for more ecological footwear, namely by developing novel components based on natural materials and supported by green productive processes. In this context, footwear components such as shoe insoles are being increasingly produced from cork, due to its impermeability, good compressibility, resilience and low density. Traditionally, the cork agglomeration process uses a reactive polyurethane-based adhesive, generating composites with low flexibility and poor water absorption/desorption characteristics, resulting in products with low comfort properties. Additionally, this type of binder is based on toluene diisocyanate (TDI), a highly toxic compound. Efforts are being made to replace this adhesive by more environmentally friendly products. In this context, the use of water-based polyurethane-urea dispersions free of NMP (N-methyl-2-pyrrolidone), and exempt of volatile organic compounds (VOC), can be envisaged. Therefore, the present work had as main objective the production of cork composites, where the traditionally used adhesive was replaced by a water-based polyurethane. This former adhesive was synthesized by a process developed at our research group, which generates a final product, both NMP and VOC-free. Moreover, in order to improve composites performance, the adhesive formulation was modified with *Melissa officinalis* L. extracts [1]. Also, water absorption/desorption properties, as well as mechanical properties, were tested as a function of the added biomass residue.

This work is organized according to the following stages: (1) synthesis and characterization of the water-based polyurethane-urea dispersions. Three formulations were produced: base PUD (PUD), and modified PUDs using 3 (PU3C) and 5% (PU5C) (w/w, prepolymer-basis) of *Melissa officinalis* extract. (2) Testing of the adhesive content for composite production. Contents of 20, 30 and 40% (w/w, cork basis; adhesive weight based on its solids content). Following the characterization results, the best adhesive content was selected for further studies; (3) testing of the biomass content: for that composites incorporating 5 and 10% (w/w, cork-basis) of biomass residues (sugarcane bagasse, malt bagasse, coconut fibers and chia seeds), were produced and characterized in terms of stress at break (σ_b) and strain at break (ε_b), dimensional stability and water absorption/desorption behavior. The main objective was to select the composites with the best properties, and validate their use in the production of footwear insoles.

Materials and Methods

The *Melissa officinalis* L. dry plant used to produce the extract was purchase in a local market. For the production of the PUD adhesives the following raw-materials were used: Polypropylene glycol with molecular weight 2000 (PPG 2000) as the macrodiol, isophorone diisocyanate (IPDI) as the diisocyanate, 2,2-Bis(hydroxymethyl) propionic acid (DMPA) as the the internal emulsifier, triethylamine (TEA) as the the neutralizing agent, dry acetone as a co-solvent, 1,2-Ethylene diamine as the chain extender and tin (II) 2-ethylhexanoate (SO) was the catalyst. PPG2000 and DMPA were dried under vacuum at 50 °C overnight previously to the synthesis process. The tested biomasses were sugarcane bagasse, malt bagasse, coconut fibers and chia seeds.

Melissa officinalis L. extracts obtainment

The extract of *Melissa officinalis* L. was obtained by the infusion method from dry plant material. Briefly, 20 g of gridded plant was added to 800 mL of boiling distilled water during 5 minutes. The obtained solution was then filtered and freeze-dried, in order to recover the extract in powder form.

PUD synthesis process

PUDs were produced using the modified prepolymer method, developed by Fernandes and co-workers [2]. Three different formulations were produced: base formulation (PUB), and modified formulations with 3 and 5% of *Melissa officinalis* extract (PU3C and PU5C, respectively). The used NCO/OH ratio was 1.7, and DMPA content was 5% (w/w, prepolymer basis). The PUD adhesives (100 g of prepolymer) were synthesized by using a 500mL four neck jacketed reactor equipped with heating, thermocouple and mechanical stirring. The synthesis was carried out under nitrogen atmosphere and the reaction progress was monitored by the dibutylamine back titration method, according to ASTM D 2572-97. Briefly, the required amounts of PPG2000, SO and IPDI were added to the reactor, heated at 80 °C under stirring until the theoretical NCO value was reached. Thereafter, the mixture was cooled to 50 °C to add the pre-neutralized DMPA in acetone solution. The reaction was left to proceed until the NCO conversion reached the theoretical value. Then the NCO-terminated prepolymer was cooled to 25 °C, and distilled water containing the required amount of *Melissa officinalis* added dropwise under vigorous stirring (prepolymer dispersion phase). The resultant dispersion was heated to 35 °C, and EDA aqueous solution (concentration dependent on the NCO conversion after the dispersion stage) added at a flow rate of 0.3mL/min. Finally, acetone was removed in a rotary evaporator (40 °C, 350 mbar).

Cork composites production

The composites were produced using a hydraulic press equipped with heated plates and a scale based on 10 g of cork. Two cork granulometries (0.2-0.5mm and 0.5-1mm) were used at a 50:50 ratio. The tested adhesive content (w/w, cork basis; adhesive weight based on its solids content) was 20, 30 and 40% (this content was reflected in the composites nomenclature, e.g. the sample PU3C20 is the composite with PU3C adhesive at a content of 20%). For composites production, first both corks were weighed (5g of each granulometry) and hand mixed. When biomass was added, the applied amount was also mixed with the cork. After, the required amount of adhesive was weighted and added to the previously prepared mixture, and mixed during 10 minutes using a mechanical stirrer. Then, the obtained mixture was transferred to the mold and pressed at 15 bar (135 °C), during 2 minutes. After cooling, the mold was opened and the composite removed. The samples were stored at ambient temperature during one week, before testing. After the selection of the best adhesive content, cork composites added with residual biomass (contents of 5 and 10%) were produced.

PUD and composites characterization

PUD adhesives were characterized in terms of the produced dispersions and films. For the dispersion, solid content, pH, viscosity, and mean particle size were determined. Films were evaluated concerning chemical structure (FTIR) and thermal behavior (DSC and TGA). Composites were evaluated in what concerns water absorption/desorption behavior and dimensional stability according to the standards ISO 22649:2016 and ISO 22651:2002, respectively. The stress-strain curves and the stress at break (σ_b) and the strain at break (ε_b) of the composites were obtained by using a Shimadzu Autograph AGS-X series Europa testing machine.

Results

Table 1 summarizes the properties of the obtained dispersions. The pH values for all the dispersions were around 7, reflecting the absence of free chain extender, showing the good efficiency of the chain extension process. The viscosity values were influenced by the solids content, once a viscosity increment was noticed as the extract content increases. The effect of the extract is also perceptible on the particle size increment, once the PU5C presented higher mean particle size among the three produced PUD formulations (Table 1).

The dimensional stability is evaluated by measuring the length and width of the sample specimen before and after conditioning at 37 °C for 24 hours. The established specification for shoe soles requires a variation inferior to 2% (ISO 22651:2002). The obtained results show a change from 0.21% (PU3C20) to 2.33% (PU3C30) for cork composites without biomass, and between 0.21%, for the PUB30 with 5% of malt bagasse, and 2.09% for the PUB30 containing 10% of sugarcane bagasse, for the biomass containing composites. Biomass addition improves the dimensional stability. For the water absorption/desorption tests, the ISO22649:2016 standard specifies a water absorption higher than 70 mg/cm^2 and a minimum water desorption of 80%. The water absorption results for the cork composites without biomass varied from 75.12 mg/cm^2 (PUB20) to 171.38 mg/cm^2 (PU3C40), while water desorption was between 49.31 (PU3C30) and 80.03% (PU5C20). When biomass is added, absorption values varied from 67.78 mg/cm^2 (PUB30 with 5% of sugarcane bagasse) to 174.59 mg/cm^2 (PU3C30 with 10% of coconut fiber), while water desorption varied between 25.72% (PUB30 with 10% of chia seed) to 73.32% (PU5C30 with 10% of sugarcane bagasse). Considering these results, the biomass giving the best effect on water absorption is the coconut fiber at a content of 10%, while for desorption, 10% of chia seeds gave the best results.

Table 1. Results of PUB, PU3C and PU5C characterization.

Sample	pH	μ (mPa.s)	Solids (%, w/w)	Average particle size (μm)	
				Number	Volume
PUB	7.75	18.55	38.8	0.0157	0.145
PU3C	7.55	61.5	39.7	0.0161	0.107
PU5C	7.55	1878.7	36.59	0.132	2.510

Stress at break (σ_b) and strain at break (ε_b) were determined from stress-strain curves of the composites produced with the different adhesive contents. The results are described in Table 2. The highest σ_b values were registered for the composite samples containing 30 and 40% of the adhesives PUB and PU3C, while for the PU5C lower values were obtained. The highest value for σ_b was 0.99 MPa (PU5C30 composite). Based on these results, the selected adhesive content was 30%, once it gave rise to the highest σ_b with both PU3C30 and PU5C30 adhesives.

Table 2. Cork composites mechanical properties.

Sample (*)	σ_b (MPa)	ε_b (%)
PUB20	1.10	12.45
PUB30	1.12	15.40
PUB40	1.76	14.56
PU3C20	0.93	14.84
PU3C30	1.13	18.03
PU3C40	1.10	22.11
PU5C20	0.57	13.52
PU5C30	0.99	21.55
PU5C40	0.85	25.45

Conclusions

In a general way, it was observed that water-based polyurethane adhesives presented suitable properties for the production of cork-based composites. At the moment, the work is devoted to the validation of the best composite formulations on the production of footwear insoles.

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