



PU/Lignocellulosic Composites Produced from Recycled Raw Materials

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Abstract

Lignocellulosic composites are biodegradable, have low cost, neutrality to CO₂ emission, easily processed, easily available and pose no health risks, therefore these materials have been the subject of an increase of interest. In addition, there is a continuous demand of materials obtained from renewable resources and waste recycling. In that sense, in this study polyurethane (PU) residues were mixed with residues of cork and pine (up to 70 wt/wt) to produce 100% recycled composites. Cork is well known to be a light and a thermal insulator material, so the addition of cork granulates decreased both density (circa 51%) and thermal conductivity (circa 61%) of the composites. In turn, pine fibers are hydrophilic and have cylindrical shapes, thus their presence increased the water absorption and improved the mechanical properties of the composites. From the results, these composites proved to be suitable to be used as structure and thermal insulation materials with the advantage of being produced from 100% recycled raw-materials.

Keywords Composites · Cork · Pine fibers · Recycled polyurethane · Polymer composites

Introduction

Lignocellulosic polymer composites which are composed by a polymer matrix and lignocellulosic reinforcing fillers are replacing many components in automobiles, aircrafts or spacecrafts which are normally produced using metals and alloys [1]. This type of bio-based composites have been produced from many lignocellulosic resources, such as abaca, kenaf, flax, hemp, sisal, coir, bagasse, jute, cork or pine, among many others [2]. Lignocellulosic fillers offer many advantages over synthetic fillers, such biodegradability, low cost, neutrality to CO₂ emission and low health risks. In addition, lignocellulosic composites present excellent thermal stability, chemical resistance, good strength, low density, good toughness, ability to be molded and can be customized to suit a range of temperature and environmental conditions [3]. This type of composites can be re-melted and

re-processed, the damaged structures can be repaired by the application of heat and pressure, reduces the weight without compromising structural strength and can be used to produce complex design geometries [4]. Hence, they are used as structural and insulating panels, floors, chairs, benches tables, window panel, doors as well as tiles, among many others [5].

One commonly lignocellulosic material used to produce composites is cork, which is the outer bark of *Quercus suber L.*, a plant tissue which can be found in the southern Mediterranean countries of Europe, being Portugal the main cork producer in the World [6]. Cork is composed of suberin (30–60%), lignin (19–22%), polysaccharides (12–20%) and extractives (9–20%), has a very low density, low thermal conductivity, good sound insulation properties, an elastic behavior and it is hydrophobic [7]. The industry consumes annually *ca* 280 000 tons of Cork worldwide [8], being mainly used to produce cork stoppers [6], however 20–30% of the Cork is rejected, especially because the low granulometry fractions have no industrial interest. Nonetheless, the interest in the production of cork composites has been increasing [6]. Instead of burning it for energy production, the valorization of this industrial residue is an economically and environmentally potential option. In that sense, cork granulates can be bound together to produce floor coverings,

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shoes soles or sandwich composites, to be used for thermal and acoustic insulation, among many others [6].

Another important lignocellulosic material that can be used to produce bio-based composites is pine wood. The Maritime Pine (*Pinus Pinaster Ait.*) is a dominant species in western Mediterranean forests, especially in the Iberian Peninsula, but also in western Italy, southwest of France or in Tunisia [9]. The Maritime Pine wood is normally composed by cellulose (46%), lignin (29%), hemicellulose (24%) and extractives [10] and has been traditionally explored for resin and wood production [11]. Despite of its high density, this kind of wood has little acceptance for structural applications due to the presence of several defects in its structure, such as knots, resin canals or inadequate forms and dimensions [12]. Nonetheless, Pinus wood can be used to produce furniture, pallets, posts, panels, pulp, paper or glued-laminated wood beams or composites [12–14].

In turn, many polymers can be used as matrix to produce lignocellulosic composites, such as polyurethane (PU), polystyrene (PS), polyisocyanurate (PIR), polyethylene (PE), polypropylene (PP), ethylene–vinyl acetate (EVA), nitrile rubber (NBR), poly(vinyl chloride) (PVC), or others [1, 15]. PU represent a diverse group of materials, including hard plastics, elastomers, foams or adhesives, being PU adhesives used for laminating thermal sandwich panels, bonding gypsum boards, bonding veneers or for gluing plywood [16]. However, the PU industry is heavily petroleum-dependent, so to improve the eco-efficiency of PU materials, the PU wastes must be recycled [17, 18]. Even though the mechanical recycling of PU to produce lignocellulosic composites has been patented [19] several years ago, this process has not been frequently used at industrial scale. Moreover, the fact that the pollution derived from the plastics used in general has become one of the most important environmental issue, since the disposal of these products overwhelms the world's ability to deal with them. As a result of that it affects the biodiversity, accumulates at sea and is consumed by animals and organisms [20]. In that sense, many petroleum-based products are starting to be produced from renewable feedstocks or residues [21–24]. Therefore, in this study, PU/Lignocellulosic composites were produced from 100% recycled raw-materials. PU wastes were used as polymer matrix, cork granulates and pine fibers, without any chemical treatment, were used as fillers and the ensuing composites presented potential applications as construction materials.

Experimental

Materials

In this study PU residues were blended with residues of cork and pine to produce 100% recycled composites. PU scraps

(residues from the production of methylene diphenyl diisocyanate based flexible foams) with a density of 0.17 g.cm^{-3} and the particle size distribution (D50 of 1.76 mm) shown in Fig. 1 were kindly provided by Flexipol Espumas Sintéticas, S. A. Cork granulates (residues of the production of cork stoppers) derived from the outer bark of *Quercus suber L.* were kindly supplied by Corticeira Amorim while pine fibers from the Maritime Pine tree (*Pinus Pinaster Ait.*) were kindly supplied by Sonae.

Production of Composites

PU scraps were milled down to 0.5 mm mesh in a Retsch cross beater mill SK1 (Haan, Germany). Next, the PU powder was dried mixed at room temperature with cork granulates (50–70% wt/wt) or with pine fibers (50–70% wt/wt) in a high-speed mixer and the mixtures were left over night in an oven at $105 \text{ }^\circ\text{C}$ to remove moisture. Afterwards, the composites were produced in a hot press (CARVER model 3851-0) at $180 \text{ }^\circ\text{C}$, using 3 tons of pressure, during 10 min. The conditions used to produce the composites are the result of a series of preliminary tests using different parameters (temperature from 130 to $200 \text{ }^\circ\text{C}$; pressure from 1 to 5 tons; time from 2 to 30 min). In Table 1, the composites formulations and their properties are listed.

Characterization of Composites

The FTIR spectra, contact angle measurements (CA), SEM images, density, static and dynamic (DMA) mechanical properties, Shore hardness and thermogravimetric analysis (TGA) were carried out as described elsewhere [18].

A Mitutoyo model SJ-210 roughometer was used to analyze the roughness of materials surface. The roughness (Ra) was determined according to ISO 1997 standard, being the results presented, the average of six replicates.

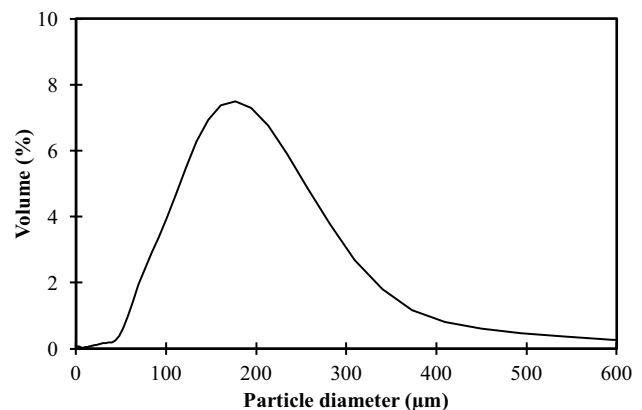


Fig. 1 Particle size distribution [25]

Table 1 Formulations of composites

Sample	% PU	% Cork granulates	% Pine fibers
PU	100		
PU-50Cork	50	50	
PU-60Cork	40	60	
PU-70Cork	30	70	
PU-50Pine	50		50
PU-60Pine	40		60
PU-70Pine	30		70

The theoretical density of the composites was determined using the rule of mixtures, according to Eq. 1 [26]:

$$d_{theo} = X_A P_A + X_B P_B \quad (1)$$

where d_{theo} is the theoretical density of the composite, X_A , X_B , P_A and P_B are the mass fraction and density of polymer and filler, respectively. Afterwards, the porosity of composites was determined using Eq. 2:

$$\%_{porosity} = \frac{d_{theo} - d_{deter}}{d_{deter}} \times 100 \quad (2)$$

where d_{deter} is the measured density of the materials previously measured.

For the determination of water absorption, samples were immersed in a de-ionized water bath at room temperature. After 24 h, the samples were taken out from the bath and dried using a paper tissue to remove the excess of water. The increase of thickness was determined using Eq. 3:

$$\Delta t = (t_f - t_i) / t_i \times 100 \quad (3)$$

where t_f is the thickness of sample (measured using micrometer) after the immersion and t_i is the thickness of sample before the immersion. The increase of weight was determined using Eq. 4:

$$\Delta w = (w_f - w_i) / w_i \times 100 \quad (4)$$

where w_f is the weight of sample after the immersion and w_i is the weight of sample before the immersion. After water absorption measurements, the composites were left overnight in a ventilated oven at 105 °C and weighed. The weight variation of samples was determined using Eq. 5:

$$\Delta w_{dry} = (w_a - w_i) / w_i \times 100 \quad (5)$$

where w_a is the weight of sample after drying and w_i is the weight of sample before the immersion.

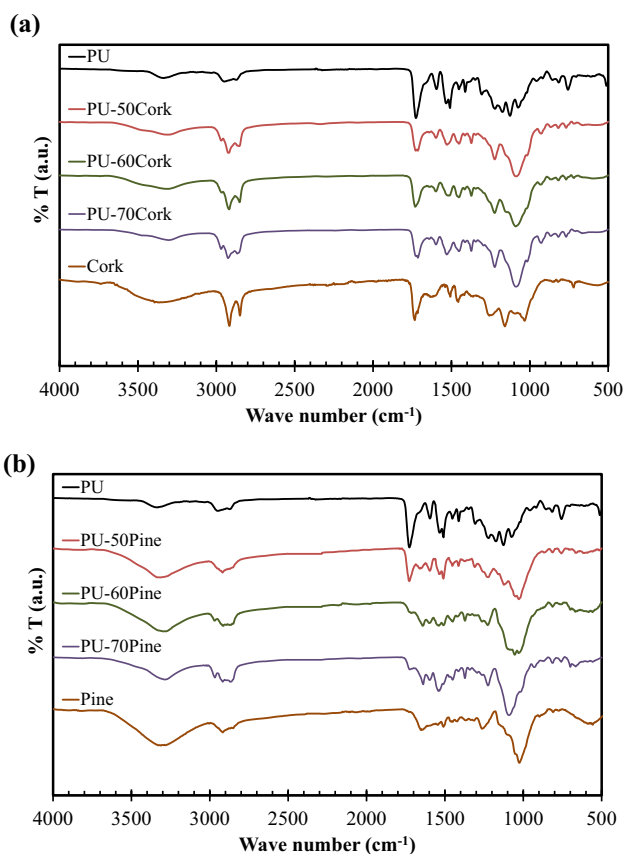


Fig. 2 Normalized FTIR spectra of PU-Cork composites (a) and PU-Pine composites (b)

Results and Discussion

Chemistry of the Surface

Spectrophotometry analysis were used to inspect the chemical composition of the composites being the resulting normalized FTIR spectra presented in Fig. 2.

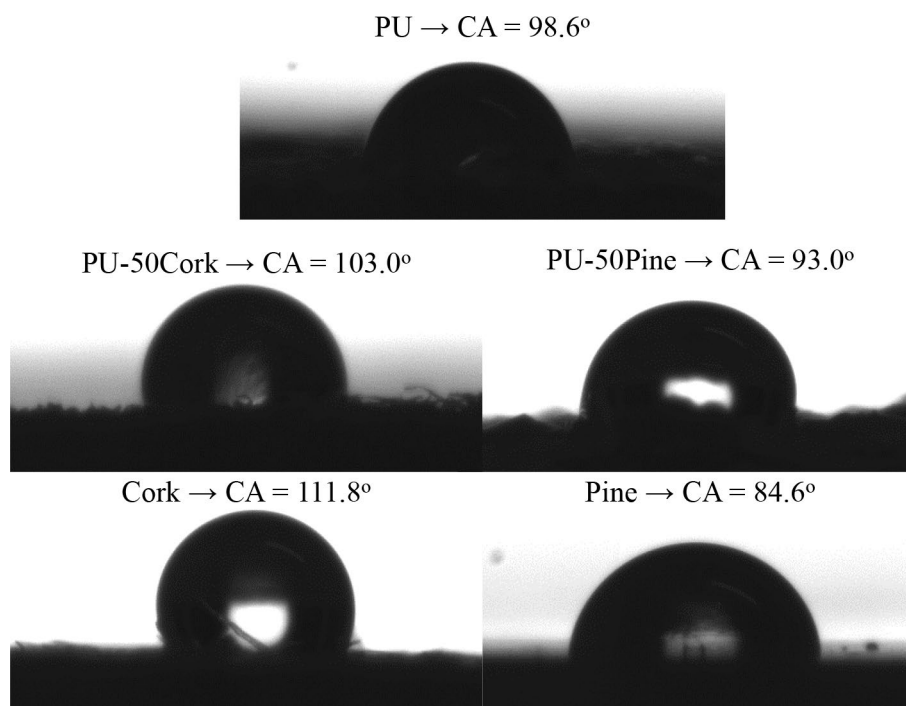
As it can be seen, the FTIR spectra of the PU sample presented the band in the 3200–3450 cm⁻¹ region which is attributed to the symmetric and asymmetric stretching vibrations of the N–H of the urethane and of urea groups [27, 28]. The peak at 1730 cm⁻¹ is due to the stretching vibrations of the C=O associated with ester groups of the polyester bases polyol used in its preparation whilst the nearly overlapped bands between 1540 and 1517 cm⁻¹ are attributed to the stretching and bending vibrations of the C–N and N–H of the urethane moieties, respectively [27, 28]. Regarding the FTIR spectra of the lignocellulosic materials, it can be observed that the cork and pine composites maintained most of the peaks associated with the matrix and the fillers, such as the O–H groups which overlap with the N–H of the urethane and of urea groups at 3100–3600 cm⁻¹, the C–H stretching vibrations at 2950–2850 cm⁻¹, the C=O ester

groups at 1730 cm^{-1} , the $\text{CH}=\text{CH}$ groups at $1607\text{--}1513\text{ cm}^{-1}$, the aromatics $\text{C}=\text{C}$ at $1010\text{--}1300\text{ cm}^{-1}$, the $\text{C}-\text{N}$ and $\text{N}-\text{H}$ of the urethane bands at 1540 and 1517 cm^{-1} [29, 30]. Moreover, all composites samples presented the $\text{C}=\text{C}$ of lignin aromatics at $1010\text{--}1300\text{ cm}^{-1}$ bands (carbohydrate and lignin $\text{C}-\text{O}$ bonds) [31]. However, in contrast to pine, the cork containing samples present the $\text{C}=\text{O}$ ester groups at 1730 cm^{-1} which overlap with those of the PU and the $\text{CH}=\text{CH}$ groups at 1607 and 1513 cm^{-1} of suberin [32]. Indeed, for the cork-based composites the intensity of the $\text{C}=\text{O}$ band at 1730 cm^{-1} hardly changes as a function of filler whilst in the pine based composites, the intensity of that band drops as a function of filler content. This lignin and suberin moieties are associated with the hydrophobic character of cork. Interestingly the $\text{O}-\text{H}$ band of cork derived composites seems to decrease in intensity, with the addition of higher amounts of matrix, contrarily to the pine counterparts. This reinforces the observations about wettability, as it will be discussed next.

The contact angle (CA) which a drop of water forms when deposited on a surface is a conventional method to evaluate the hydrophobicity of materials. In the case of lignocellulosic composites their hydrophobicity character can be associated to their components, i.e. to the organic moieties present on the surface of the composites. Since the hydrophobicity of composites components can dictate the affinity between them, in Fig. 3, the CA values of the main components and of corresponding 50% wt/wt composites are presented.

From Fig. 3, it can be observed that the CA values for PU, cork and pine fibers is 98.6° , 111.8° and 84.6° , respectively and as expected, the ensuing composites present CA values between those measured for the corresponding raw materials: 103.0° and 93.0° for PU-50Cork PU-50Pine, respectively. It is known that cork is a very hydrophobic material, being in fact, impermeable to liquids and gases. This behavior is attributed to the closed cell walls and to suberin, which is a hydrophobic component [33]. In turn, most natural fibers, such as pine fibers are hydrophilic due to the presence of cellulose, hemicelluloses and lignin, rich in OH groups thus associated with lower CA [34]. Comparing the results shown in Fig. 3 with those found in literature, the same trend is detected. Martins and Gil [35] studied the structure–properties of cork polymer composites, reporting that the incorporation of cork resulted in the increase of the CA value to above 100° . According to the authors, water did not wet the surface reflecting a pronounced hydrophobic and impermeable behavior of the ensuing composites. In turn, Lazrak et al. [36] produced composites from maritime Pine wood and recycled high-density polyethylene, reporting that the CA value decreased when the wood content was higher than the matrix. The decrease of CA values was attributed to the hydrophilicity of the wood flour. In addition, the results obtained can be associated to the roughness of the surfaces, as it will be discussed later.

Fig. 3 Contact angle with water of PU, lignocellulosic materials and 50% wt/wt derived composites



Water Absorption

The water absorption of the lignocellulosic composites is dependent on numerous aspects such as the filler content, permeability of fibers, area of the exposed surfaces, diffusivity, porosity and voids, hydrophilicity of the fibers, among others [37, 38]. It is also known that some lignocellulosic materials are normally hydrophilic due to the hydroxyl groups on the surface of cellulose, hemicellulose or lignin, in contrast with the polymer matrix that is hydrophobic [39]. Espert et al. [40] reported that due to the hydrophilic character of the lignocellulosic material, the ensuing composites presented higher amount of water absorption. Moreover, numerous studies can be found in literature, relating the water absorption of lignocellulosic composites with their degradation. Fakhrol et al. [41] studied the degradation of natural fiber reinforced composites and reported that the addition of both sawdust and wheat flour considerably improved the biodegradability. Similar results were reported by Ndazi et al. [42] who studied the hydrolytic degradation of poly(lactic acid)/rice hulls composites in water. Since the lignocellulosic materials are hydrophilic, they allow water to diffuse into the polymer matrix even in the inner regions, increasing the water absorption. In other words, the increase of hydrophilicity of the composites can result in the increase of the degradation rate of the material [43].

From the results presented in Table 2, it can be seen that the presence of the fillers, increased the water absorption of the composites in different extends. In the case of composites prepared with pine fibers, besides of the hydrophilic character of these fillers, the water absorption is largely dependent on the porosity of the composites, i.e. to the presence of free space between the fillers and the matrix, as it was observed in pine composites SEM images (see Fig. 3). Moreover, the higher water absorption of pine-based composites can be a result of the high surface area of the filler. Nourbakhsh et al. [37] studied the effect of bagasse and beech fibers on the water absorption of PP composites and reported that bagasse fibers presented higher water absorption as a result of the larger surface area.

In turn, from Table 2, it can be observed that the cork-based composites presented lower water absorption (Δt (%)). As mentioned, cork is a hydrophobic material, being in fact, impermeable to liquids and gases, hence the water absorption of cork-based composites can be explained by two physical mechanisms competing with each other: (i) the presence of suberin in cork granulates which is hydrophobic, (Pinus fibers are mostly composed by cellulose which is hydrophilic) prevents the water absorption; (ii) yet the limited wettability of the fillers by the matrix allows water to diffuse through the interface. In summary, from the results presented in Table 2, it can be seen that the composites presented a significant loss of mass, after the water absorption

Table 2 Properties of composites

Sample	PU	PU-50Cork	PU-60Cork	PU-70Cork	PU-50Pine	PU-60Pine	PU-70Pine
Calculated porosity (%)	0.0	18.7	12.2	0.7	5.9	4.7	2.9
Density (kg m^{-3})	1146.5 ± 46.6	610.2 ± 21.5	570.5 ± 40.6	551.5 ± 24.7	877.5 ± 49.5	845.9 ± 53.8	817.7 ± 39.7
Roughness (μm)	0.425 ± 0.048	6.578 ± 0.346	8.354 ± 0.411	9.948 ± 0.633	3.633 ± 0.184	5.470 ± 0.467	8.439 ± 0.468
Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	0.1861 ± 0.0009	0.0869 ± 0.0005	0.0807 ± 0.0003	0.0726 ± 0.0004	0.1406 ± 0.0004	0.1327 ± 0.0003	0.1188 ± 0.0005
Young's modulus (MPa)	143.5 ± 4.1	47.0 ± 3.6	39.4 ± 2.5	32.2 ± 1.0	285.1 ± 4.9	349.3 ± 6.6	416.4 ± 6.4
Maximum stress (MPa)	20.7 ± 6.2	2.6 ± 0.3	2.4 ± 0.1	2.2 ± 0.1	11.7 ± 1.9	11.3 ± 1.2	9.9 ± 1.2
Elongation at maximum stress (%)	44.1 ± 0.8	16.1 ± 0.9	12.8 ± 0.9	12.6 ± 0.8	4.9 ± 0.4	4.6 ± 0.6	3.9 ± 0.3
Shore A (pts)	30.5 ± 0.0	35.0 ± 1.0	38.5 ± 0.5	39.5 ± 0.5	31.5 ± 0.5	33.0 ± 0.0	37.5 ± 0.5
Water absorption Δt (%)	3.6 ± 0.0	15.7 ± 0.2	16.0 ± 1.1	19.3 ± 1.5	22.3 ± 1.7	28.8 ± 2.7	32.3 ± 2.3
Water absorption Δw (%)	2.8 ± 0.2	40.9 ± 1.1	48.5 ± 1.3	58.4 ± 0.0	40.6 ± 2.6	47.9 ± 1.6	55.2 ± 1.1
Weight variation after water absorption tests (%)	-1.1 ± 0.2	-1.0 ± 0.0	-0.9 ± 0.1	-1.0 ± 0.0	-4.9 ± 0.0	-5.8 ± 0.3	-6.8 ± 0.4

tests, indicating their potential for faster degradation in the environment at the end of use.

Morphology

Almost every property of lignocellulosic/polymer composites depends on the elastic properties of the fillers and polymer matrix, the size and shape of the fillers, the aspect ratio of the fillers, the interfacial adhesion between the fillers and the matrix or the amount of filler used [1]. Therefore, SEM analysis is an important and versatile tool to inspect the composites structure and the filler/matrix interface. The SEM images of composites are presented in Fig. 4.

From the SEM images presented in Fig. 4, it can be seen that the neat PU sample has a smooth surface, while the PU/Cork and PU/Pine composites present very distinct morphologies. Cork granulates are large spherical grains whilst pine fibers present cylindrical shape and more homogeneous dimensions. Whilst the cork granulates are randomly distributed in the matrix the pine composites are orientated in two dimensions. These differences have significant effect of the properties of the composites, such as their mechanical properties as will be discussed ahead [44]. From the pine composites images, it can also be observed some agglomeration of the particles and empty spaces in the region of contact between the filler and matrix (voids). As mentioned, the differences in hydrophobicity can compromise the filler/matrix affinity, resulting in voids [45, 46]. In fact, as it can be observed from SEM images and Table 2, the addition of fillers results in the presence of voids. Moreover, natural fibers tend to agglomerate due to the formation of hydrogen bonding, leading to poor dispersion within the matrix and consequently poor matrix-fiber interaction [47]. In addition, the differences of the hydrophilic nature of fillers and matrix, previously discussed, can also contribute to their poor dispersion. These observations can be attributed to the higher surface area (high surface area can result in the aggregation/agglomeration [48]) which limits the wetting of the fillers by the matrix, resulting in the presence of air bubbles and fibrillation.

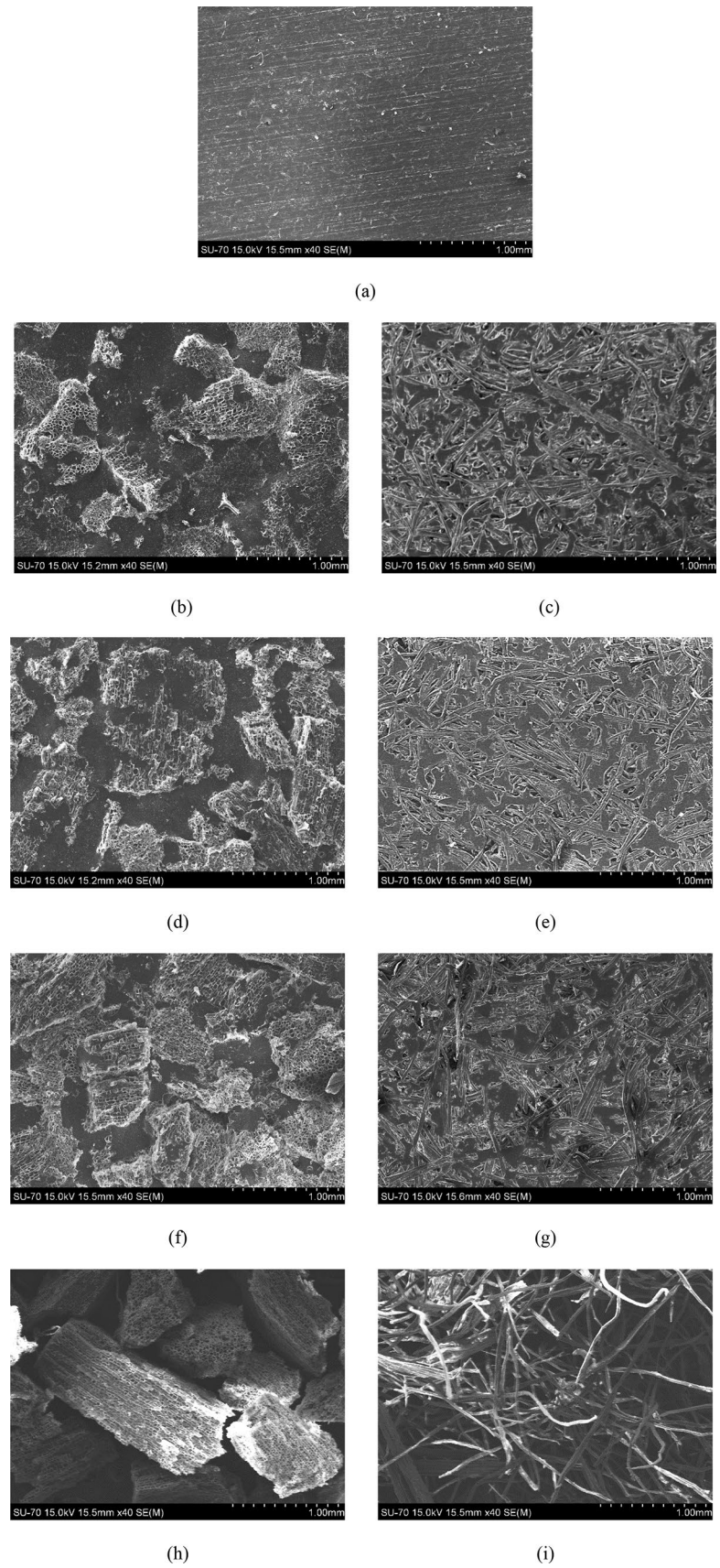
Analyzing the results presented in Table 2, it can be seen that the neat PU material presents a smooth surface (Ra of 0.425 μm) and the addition of fillers increases the roughness. Furthermore, using higher amounts of filler has a pronounced effect on roughness surface, as already observed in the SEM images. Similar results were reported by Lazrak et al. [36] who studied the structural properties of pine wood and recycled high-density polyethylene composites or by Sajith et al. [49] who compared the mechanical properties of lignocellulosic flour epoxy composites. In turn, the cork-based composites present rougher surfaces when compared to the pine-based counterparts. The dissimilarity in surface roughness of composite materials is mainly attributable to

the differences in the size, geometry and content of filler particles, as reported by Filho et al. [50]. In fact, Cademartori et al. [51] studied the roughness of wood polymer composites filled with waste of mate-tea (spherical shape) and eucalypt fibers (elongated shape) and reported that the particle size and geometry are major factors that play a significant role in surface roughness of wood-based composites, being rougher surfaces observed in the mate-tea based composites.

Porosity and Density

As the porosity of composites can affect their performance, the rule of mixture was used to calculate the theoretical density which was then correlated with the measured values using Eq. 2. As shown in Table 2, the porosity of the cork composites is much higher, with a maximum value of 18.7% for the composite prepared using 50% of filler, whilst the addition of pine fibers to PU results in a maximum value of porosity of 5.9% for the same filler content. Considering that the differences of CA between PU and Cork (13.3°) and PU and Pine (14.0°) is similar, the differences of hydrophobicity cannot explain the values of porosity achieved. The fact that the maximum porosity was achieved using 50% of filler for both types of composites suggests that further addition of fillers results in the decrease of the porosity, which is not commonly observed, nor intuitive. Moreover, these results are not in accordance with the SEM images, where higher amount of voids were observed in the materials produced using higher contents of filler. This is more evident in the case of the cork composites, where high porosity values were determined. The fact that cork is a very porous material itself may justify this discrepancy. In other words, the results suggests that the rule of mixtures, commonly used to predict the porosity of composites, probably cannot be used in this case. Hence, the results obtained cannot be used to explain the performance of the materials produced. Yet, the density of the lignocellulosic composites presented in Table 2 are coherent with the textural characteristics of the fillers. Whilst the density of the PU is 1146.5 kg m^{-3} , the addition of cork granulates and pine fibers decreased the density of composites (551.5 kg m^{-3} and 817.7 kg m^{-3} respectively, for 70% wt/wt content). In fact, it is very common to observe that the increase of lignocellulosic fillers content, decreases the density of the ensuing composites [52]. From the results presented in Table 2, it also can be seen that the cork/composites presented lower density, compared with the pine/composites which is in agreement with the fact that cork is a lighter material, due to their honeycomb structure, i.e. the voids in its cellular structure [53], whilst pine fibers are more compact. Moreover, the decrease of the density of the composites may also be due to the void formation which was observed in the SEM images of the pine composites [1]. Cork composites with a density of 400–500 kg m^{-3} and

Fig. 4 SEM images of PU (a), PU-50Cork (b), PU-50Pine (c), PU-60Cork (d), PU-60Pine (e), PU-70Cork (f), PU-70Pine (g), Cork granulates (h) and Pine fibers (i)



fiberboards with density greater than 800 kg m^{-3} (classified as hardboard) are normally used as floor coverings, as panels and cover materials for buildings and construction applications [6, 54]. The density of the materials produced are appropriated for structural applications.

Thermal Conductivity

The thermal conductivity is probably the key property of thermal insulating materials and depends on many factors, such as the properties of fillers and matrix, the filler size and direction, the filler content, the quality of adhesion between fillers and matrix, etc. [55]. The thermal conductivity results of the lignocellulosic composites are presented in Table 2 and as it can be seen, the presence of the lignocellulosic fillers reduces the thermal conductivity of the composites, reaching the minimum values for the highest contents of fillers. Moreover, as expected, it was observed that cork composites presented lower thermal conductivity than pine composites. Indeed, it is well known that Cork is an excellent thermal insulation material [6] due to their honeycomb structure, i.e. due to the air which fills the cells in the cork structure, which provides good thermal insulation. In turn, pine fibers are a more compact in their structure thus, do not have air trapped, and for that reason have higher thermal conductivity. Therefore, the relationship between the thermal conductivity of these composites and their density cannot be neglected. Shah *et al.* [56], studied the thermal conductivity of bamboo composites and reported a relationship between the thermal conductivity of composites which increases linearly with density. In fact, this statement is in agreement with the results presented in Table 2, considering that denser composites (lower amounts of fillers) presented higher thermal conductivity. Although cork agglomerates normally present thermal conductivity values of $0.040\text{—}0.050 \text{ W.m}^{-1} \text{ k}^{-1}$ [57, 58], and the values obtained in the present study are higher, the effect of granulometry must be taken into account. In fact, cork particles commonly used to produce cork agglomerates are 2–10 mm [59, 60] but Carvalho *et al.* [60] using granulometry fractions of 0.5–1 mm to produce cork composites reported that the resulting materials presented a thermal conductivity from 0.070 up to $0.150 \text{ W.m}^{-1} \text{ k}^{-1}$, which is in agreement with the results presented in Table 2. In turn, the pine/PU composites presented higher thermal conductivity comparing with the cork/PU composites, but lower values than those reported in literature. However, it should be kept in mind that the thermal conductivity is an anisotropic property hence, various parameters can affect the performance of composite such as fiber orientation, length of the fibers, and level of aggregation. For example, Limam *et al.* [61] produced composites from pine wood for building insulation, which presented thermal conductivity values of $0.200\text{—}0.280 \text{ W.m}^{-1} \text{ k}^{-1}$

in the perpendicular direction to the fibers whilst in our composites the fibers being randomly orientated presented conductivity values of $0.1406 \text{ W.m}^{-1} \text{ k}^{-1}$ or less, depending on the fiber content. Overall, the thermal conductivity of these lignocellulosic composites is suitable for thermal insulation applications with the advantage of being produced from 100% recycled raw materials.

Mechanical Properties

As mentioned, the addition of lignocellulosic material to polymer matrices results in a significant change of their mechanical properties, which depends on many factors, such as the elastic properties of the fillers and polymer matrix, the size, shape and orientation of the fillers, the aspect ratio of the fillers or the amount of filler used [37, 44, 62]. In addition, the mechanical properties of lignocellulosic composites are dependent on interfacial adhesion between the filler and the matrix. If the adhesion is not perfect, it is expected the presence of voids in the interfacial region, making these regions weaker, favoring the failure of the composite under stress [63]. Besides the presence of voids, the reduction of tensile strength with the increase of filler content may be due to agglomeration of the particles, which reduces the wettability of the particles by the matrix and therefore weakens the filler–matrix interface, as already discussed [44]. From the results presented in Table 2, it can be observed that the cork and pine composites presented different mechanical behavior.

The addition of pine fibers increased the Young modulus, increased the maximum stress and reduced the elongation at maximum stress of the composites, which is a result of the limited movement of the fibers in the matrix, as reported by Salasinska *et al.* [62]. Interestingly, the results suggest that the effect of formation of voids and agglomeration on pine are counterbalanced by the shape (cylindrical) of the filler and the fact that the filler has higher stiffness than the polymer matrix. In other words, the use of Pine fibers increased the strength of the composites, suggesting a considerable reinforcing effect from these fibers. Similar results, from wood/polymer composites have been published [64, 65]. In turn, the addition of cork granulates had the opposite effect to that registered for the pine fibers. The results, suggested that due to the fact that Cork granulates have spherical shape with elastic character, the addition of this filler reduced the stiffness of the ensuing composites [38]. Even though voids were not observed in the cork composites SEM images, the results obtained for the water absorption tests suggest that the matrix did not fully wet the fillers which can limit load transfer. Moreover, it is well known from literature that due to their geometric characteristics, spherical particles are less effective as reinforcing materials compared to fibers [66]. The mechanical properties of the composites can also be

related to the higher cellulose content in pine fibers, since a higher number of OH groups on the fibers' surface is available to interact with the PU matrix resulting in a better bonding. In fact, in a recent study [67], it was demonstrated that heat enables the rearrangement of the network topology of the PU foam, favoring in that way, the formation of bonds between the PU network and fillers. Even though distinct applications may need to be considered, the mechanical performance of these composites is suitable to be used as structural materials.

DMA experiments were carried out in order to obtain further information on the viscoelastic properties of the composites.

In Fig. 5, the DMA results of PU and PU filled with 70 wt/wt of cork granulates and pine fibers are presented. At lower temperatures the materials behave as hard solids showing high storage modulus (E') values: 1×10^{10} , 5.5×10^9 and 2×10^{10} Pa for PU, PU-70Cork and PU-70Pine, respectively. The DMA results corroborate the static mechanical results, since the pine fibers increase the stiffness of the PU, in contrast with the cork granulates. The increase of the storage modulus of the Pine composites can be related to the filler reinforcing effect, while the decrease of the modulus of the cork composite can be related to the elastic behavior of cork, as well as to the shape of the particles, as previously mentioned. From Fig. 5, it can also be observed a well-defined peak of the tan (δ) curve of the cork composite, which can be related to the well-known damping properties of this material as well as the better interaction between the filler and matrix. In turn, the pine composite presents a broad peak, which can be due to the high stiffness of fillers as well as the presence of the voids, as previously mentioned. Finally, from Fig. 5, it can also be seen that the presence of lignocellulosic materials increased the glass transition temperature (T_g) (measured at the top of the tan (δ)), which is associated with the decrease of mobility of the PU chains.

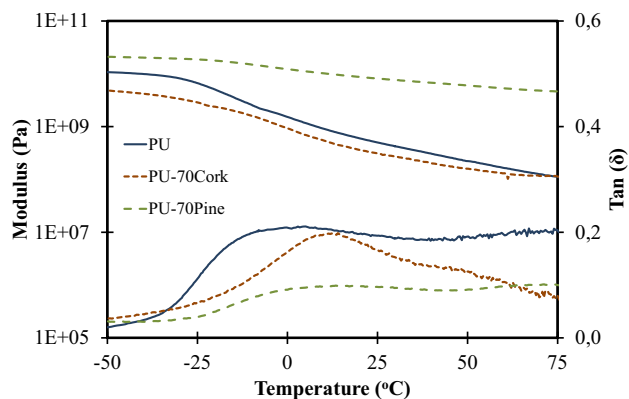


Fig. 5 DMA of PU filled with 70 wt/wt of cork granulates and pine fibers

The mechanical properties of the composites were also evaluated by Shore A hardness which measures the resistance of the material to a permanent indentation. From the results presented in Table 2, it can be seen that the effect of the pine fillers on the hardness, follows the same trend observed for the mechanical properties. The increase of the Shore A hardness with the increase of lignocellulosic filler content was also observed by Megha et al. [68] from its study of the on the hardness attributes of banana and jute PS composites.

Thermogravimetric Analysis

TGA analysis were carried out under oxygen atmosphere, being the TGA curves of the composites presented in Fig. 6.

As it can be seen from Fig. 6, the decomposition of PU shows a very small weight loss at around 100 °C due to the release of residual water, followed by the three main decomposition steps. The first degradation step (centered at 320 °C) is related to the degradation of the hard segments (e.g. urethane groups). The second degradation step (centered at 410 °C) is related to the ester/ether bond (polyol) decomposition through chain scission and the last degradation step (centered at 520 °C) is attributed to C–C bond cleavages of the polyol [69, 70]. As regards the lignocellulosic composites, although it has been previously demonstrated [30] that *Eucalyptus* fibers can be considered as a radical scavenger in radical aging reactions of high-density polyethylene (HDPE), due to the notable amounts of polyphenolics moieties (mainly lignin and tannins), providing an increased thermal stability to derived composites, in the present study this was not verified. In turn, Monteiro et al. [71] who reviewed the thermogravimetric stability of other lignocellulosic/polymer composites reported that the thermal degradation of cellulose and hemicellulose plays a crucial aspect, reducing the thermal stability of natural fiber reinforced polymer composites. From Fig. 6, it can be seen that the addition of pine fibers or cork granulates, reduced the

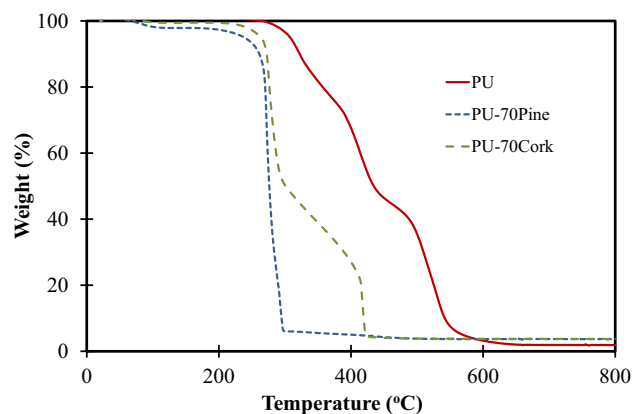


Fig. 6 TGA of PU and 70 wt/wt lignocellulosic composites

thermal stability of the ensuing composites, being this observation more evident in the case of pine composites. Despite the fact that both fillers contain a significant amount of lignin (cork—19–22%; pine—29%), pine fibers are mainly composed of cellulose (46%) and hemicellulose (24%) [7, 11], justifying the lower thermal stability of the ensuing composites. In summary, even though the addition of lignocellulosic materials decreased the thermal resistance of the composites, all materials are thermally stable up to 275 °C, which is suitable for automotive, household or construction applications.

Conclusions

In this study, composites were produced using PU and cork and pine residues. Due to the differences in the composition and morphology of the fillers, the ensuing composites presented different morphologies and distinct properties. The presence of both types of lignocellulosic materials reduced the density and thermal conductivity of the ensuing composites, due to the honeycomb structure of cork and the presence of voids and eventually the random orientation of the pine fibers, respectively. In turn, the higher hydrophilic character of pine fibers makes the ensuing composites more prone to hydrolytic decomposition. Due to the cylindrical shape and higher strength of fibers, the resulting pine composites are stiffer whilst the elastic behavior of cork afforded composites with better damping properties. Overall, the results suggest that these composites are suitable to be used as structural and thermal insulation materials with the advantage of being produced from 100% recycled raw materials.

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Authors' contributions All authors contributed equally to this work.

Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflict of interest.

Consent for Publication All authors consent for publication.

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