

# PU composites based on different types of textile fibers

Nuno Gama<sup>1,2</sup> , B Godinho<sup>1,2</sup> , Ana Barros-Timmons<sup>1,2</sup> and Artur Ferreira<sup>1,3</sup>

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## Abstract

In this study polyurethane (PU) residues were mixed with residues of textile fibers (cotton, wool and synthetic fibers up to 70 wt/wt) to produce 100% recycled composites. In addition, the effect of the type of fiber on the performance of the ensuing composites was evaluated. The presence of fibers showed similar effect on the density, reducing the density in the 5.5–9.0% range. In a similar manner, the addition of fillers decreased their thermal conductivity. The 70 wt/wt wool composite presented 38.1% lower thermal conductivity when compared to the neat matrix, a reduction that was similar for the other type of fibers. Moreover, the presence of fillers yields stiffer materials, especially in the case of the Wool based composites, which with 70 wt/wt of filler content increased the tensile modulus of the ensuing material 3.4 times. This was attributed to the aspect ratio and stiffness of this type of fiber. Finally, the high-water absorption and lower thermal stability observed, especially in the case of the natural fibers, was associated with the hydrophilic nature of fibers and porosity of composites. Overall, the results suggest that these textile-based composites are suitable for construction and automotive applications, with the advantage of being produced from 100% recycled raw-materials, without compromised performance.

## Keywords

Textile fibers composites, textile fibers, recycling, circular economy, renewable raw-materials

## Introduction

Textile fibers composites are a class of advanced materials composed by a matrix reinforced with textile fibers. These materials can be flexible or rigid depending of the matrix and the type and quantity of the fiber used. In that sense, these materials can be used in a broad range of applications, such as in the transportation, construction or even medical fields.<sup>1</sup>

The textile fibers can be classified as synthetic (such as polyester (PeS), nylon or acrylic, among others) or natural, being the natural fibers obtained from animal (such as wool, silk or camel, among others) or plant (such as cotton, flax, hemp or sisal, among others) resources.<sup>2</sup> Considering that millions of kilograms of fibers residues are generated annually from the clothing industry, the fiber wastes represent an environmental problem.<sup>3</sup> Yet, due to government regulations, its disposal in landfills is not a valid option, so the development of textile fiber composites may have environmental and economic benefits.

Cotton cultivation and its use to produce fabrics dates since thousands years ago and its production reached 18.45 million tons per year.<sup>4</sup> Therefore, the use of cotton fibers to produce reinforced polymers has

potential to reduce the accumulation of textile residues. As a matter of fact, the use of cotton fibers as reinforcement filler has already been studied. Alomayri and Low<sup>5</sup> produced cotton fiber composites and reported that a fiber content of 0.5 wt% was enough to achieve the best mechanical properties of composites. Lin et al.<sup>4</sup> utilized cotton as polypropylene (PP) reinforcing material by hot pressing and the results suggested that the ensuing composites can be potential used to produce furnish.

Wool fibers are soft, durable, retain their shape and are flame and wrinkle resistant.<sup>6</sup> For these reasons, many authors have used wool fibers to produce composites. Yukselglu and Çaliskan<sup>7</sup> produced wool reinforced composites and reported that wool wastes can

<sup>1</sup>CICECO – Aveiro Institute of Materials, Portugal

<sup>2</sup>Department of Chemistry, University of Aveiro, Portugal

<sup>3</sup>Escola Superior de Tecnologia e Gestão de Águeda of University of Aveiro, Portugal

## Corresponding author:

Nuno Gama, Department of Chemistry, University of Aveiro – Campus Universitário Santiago, 3810-193 Aveiro, Portugal.

Email: nuno.gama@ua.pt

be used as a reinforcement material with applications in the construction industry.

PeS fibers consist in a long chain of a synthetic polymer, normally poly(ethylene terephthalate) (PET). Suitable mechanical and thermal properties and chemical resistance are some of the characteristics of these fibers, making them interesting for the production of fiber composites.<sup>8</sup> Guleryuz and Eryurek<sup>9</sup> utilized PeS fibers (such as, yarns, woven, and knitted fabrics) to reinforce an urea formaldehyde matrix which increased the bending strength and water absorption of the neat material. Besides PeS fibers, other synthetic fibers such glass, nylon or PP fibers, among others, have also been used as filler in composites.<sup>10</sup>

Natural fibers are hydrophilic and to enhance their compatibility with a hydrophobic polymer matrix several mechanical, chemical, and biological approaches have been reported.<sup>11,12</sup> Lu et al.<sup>13</sup> treated bamboo fibers with alkyl solution to produce epoxy composites and reported that the mechanical performance of composites was enhanced after modification. Balla et al.<sup>14</sup> produced modified soybean fiber composites and reported strong dependence of the composites performance after fiber treatment. Filgueira et al.<sup>15</sup> modified pulp fibers via enzymatic reaction. It was reported that the fibers modification was responsible for reducing the water absorption of composites and for the improvement of the fiber-matrix adhesion.

**Table 1.** Dimensions of the fibers.

Property	Cotton fiber	Wool fiber	Synthetic fiber
Length (mm)	1.484	1.180	0.959
Diameter ( $\mu\text{m}$ )	23.3	28.5	32.9
Aspect ratio	63.7	41.4	29.1
Density ( $\text{kg} \cdot \text{m}^{-3}$ )	1118.9	1014.1	1025.7

In turn, almost every polymer can be used as matrix to produce composites.<sup>16,17</sup> Polyurethanes (PU) represent a diverse group of materials, including hard plastics, elastomers, foams or adhesives.<sup>18–22</sup> PU adhesives are used for laminating thermal sandwich panels, bonding gypsum boards, bonding veneers or for gluing plywood.<sup>23,24</sup> However, the PU industry is heavily petroleum-dependent, so to improve the eco-efficiency of PU materials, the PU wastes must be recycled.<sup>19,25–29</sup>

Aiming at the development of eco-efficient materials, in this study, PU/textile fibers composites were produced, without any treatment, from 100% recycled raw materials. PU wastes were used as polymer matrix, while wool, cotton and polyesters fibers were used as fillers reinforcing materials. The results suggest that these composites can be used in many applications, such as structural components for construction or automotive sectors. Since they were produced using 100% recycled raw materials and no chemical treatments were required, these materials can contribute to the preservation of environment.

## Experimental

### Materials

PU scraps were kindly provided by Flexipol Espumas Sintéticas, S. A. Cotton, wool and synthetic textile fibers were purchased in local store. In Table 1, the properties of fibers are listed.

### Production of composites

PU powder was mixed with textile fibers (50–70% wt/wt) in a high-speed mixer and left-over night at 105°C to removal moisture. Afterwards, the composites were produced in a hot press (CARVER model 3851-0) at 180°C, using 3 tons of pressure, during 10 min. In Table 2, the composites formulations are listed.

**Table 2.** Formulations of composites.

Sample	% PU (wt/wt)	% Cotton fibers (wt/wt)	% Wool fibers (wt/wt)	% Synthetic fibers (wt/wt)
PU	100%			
PU-50Cotton	50%	50%		
PU-60Cotton	40%	60%		
PU-70Cotton	30%	70%		
PU-50Wool	50%		50%	
PU-60Wool	40%		60%	
PU-70Wool	30%		70%	
PU-50Syn	50%			50%
PU-60Syn	40%			60%
PU-70Syn	30%			70%

## Characterization

The FTIR spectra, contact angle (CA), SEM analyses, densities, thermal conductivity measurements, mechanical analyses, and thermogravimetric analysis (TGA) were carried out as described elsewhere.<sup>30</sup> Also, XRD patterns and Shore A values were obtained as previously reported.<sup>31–34</sup>

The fiber dimensions (lengths and widths) were measured using a FiberMaster device. The fibers dimensions are determined by image analysis of fibers in a dilute suspension.

For the determination of water absorption, samples were immersed in de-ionized water bath at room temperature. After 24 h, the samples were dried using a paper tissue to remove the excess of water. The increase of thickness was determined using equation (1)

$$\Delta t = (t_f - t_i) / t_i \times 100 \quad (1)$$

where  $t_f$  is the thickness of specimen after the immersion and  $t_i$  is the thickness of specimen before the immersion. The increase of weight was determined using equation (2)

$$\Delta w = (w_f - w_i) / w_i \times 100 \quad (2)$$

where  $w_f$  is the weight of specimen after the immersion and  $w_i$  is the weight of specimen before the immersion. After water absorption measurements, the materials were left over night in an oven at 105°C and weighed. The weight variation of samples was determined using equation (3)

$$\Delta w_{dry} = (w_a - w_i) / w_i \times 100 \quad (3)$$

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

The theoretical density of the composites was determined using the rule of mixtures, according to equation (4)

$$d_{theo} = X_A P_A + X_B P_B \quad (4)$$

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 equation (5)

$$\%porosity = \frac{d_{theo} - d_{deter}}{d_{deter}} \times 100 \quad (5)$$

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

## Results and discussion

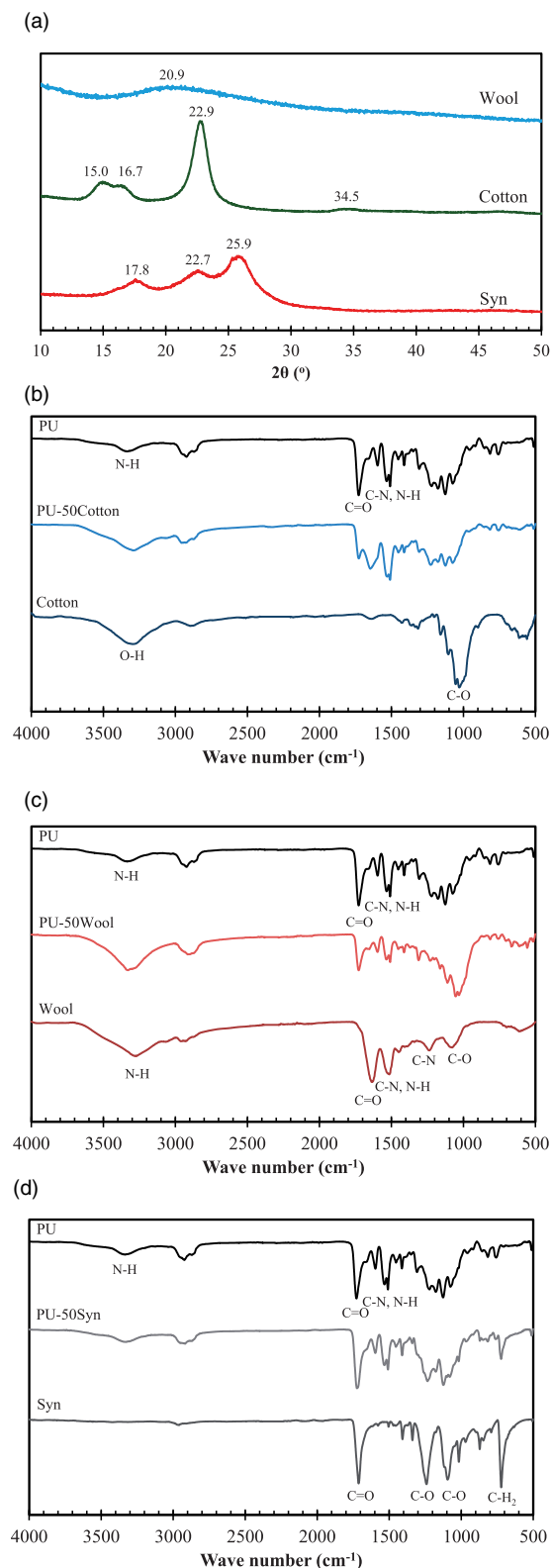
### Chemical and structural analysis

FTIR spectrophotometry and X-ray diffraction were used to inspect the crystallinity and chemical composition of the fibers and composites surfaces. In Figure 1, the resulting XRD patterns and normalized FTIR spectra are presented.

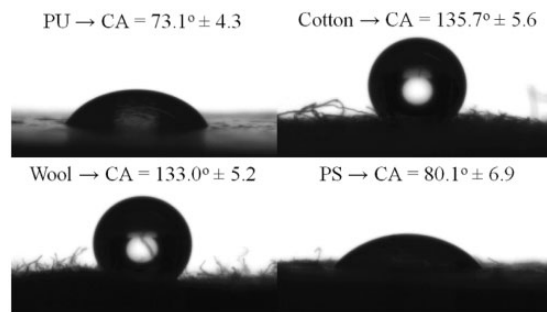
The crystallinity of the fibers has a great influence on the performance of the ensuing materials, as it will be discussed later.<sup>35</sup> From Figure 1(a), it is possible to observe that the fibers present very distinct XRD patterns. In the wool XRD diffractogram a broad scattering peak centered around 20.9° can be observed, indicating that wool fibers are hardly crystalline. Regarding the cotton fibers XRD diffractogram peaks at 15.0° (101), at 16.7° (110), at 22.9° (200) and at 34.5° (004) of cellulose<sup>36</sup> can be observed, while in the PET fibers XRD peaks at 17.8° (101), at 22.7° (10 $\bar{1}$ ) and at 25.9° (002)<sup>37</sup> are observed, meaning that the last two types of fibers present a more crystalline structure.<sup>38</sup>

Regarding the FTIR spectra, as it can be seen the PU sample presented the typical bands or urethanes and urea moieties: the 3200–3450 cm<sup>−1</sup> band due to the vibrations of the N–H; the 1710 cm<sup>−1</sup> peak due to the C=O vibrations; the 1540 and 1517 cm<sup>−1</sup> bands due to the C–N and N–H vibrations. In the FTIR spectra of cotton composites (Figure 1(b)) it can be observed the band at 3100–3600 cm<sup>−1</sup> due to O–H groups of Cotton. In addition, the peak at 1640 cm<sup>−1</sup> is due to water absorbed, as well as the broad peak at 1030 cm<sup>−1</sup> which is attributed to the vibration of C–O groups of cellulose moieties. In the FTIR spectra of wool composites (Figure 1(c)), it can be observed the main COOH, NH<sub>2</sub> and OH functional groups of wool. The band at 3100–3400 cm<sup>−1</sup> is attributed to the vibration of N–H groups, the peak at 1651 cm<sup>−1</sup> is attributed to the vibration of C=O groups and the peak at 1519 cm<sup>−1</sup> is due to the vibration of C–N and N–H groups. Finally, the peaks at 1230 cm<sup>−1</sup> and 1080 cm<sup>−1</sup> are attributed to the vibration of C–N and C–O groups, respectively. From the FTIR spectra of the synthetic fibers (Figure 1(d)), it can be observed the strong peak at 1710 cm<sup>−1</sup> which is attributed to the C=O vibration and the peaks at 1090 cm<sup>−1</sup> and 1240 cm<sup>−1</sup> which are due to the vibrations C–O, typically of PeS. Finally, the peak at 720 cm<sup>−1</sup> is attributed to the CH rocking vibration.

As mentioned, the crystallinity and chemical composition of the fibers may influence the properties of the ensuing composite.<sup>1</sup> Normally, (i) highly crystalline



**Figure 1.** XRD patterns (a) of the textile fibers used and normalized FTIR spectra of PU-Cotton composites (b), PU-Wool composites (c) and PU-Syn composites (d).



**Figure 2.** Contact angle with water of PU and fibers.

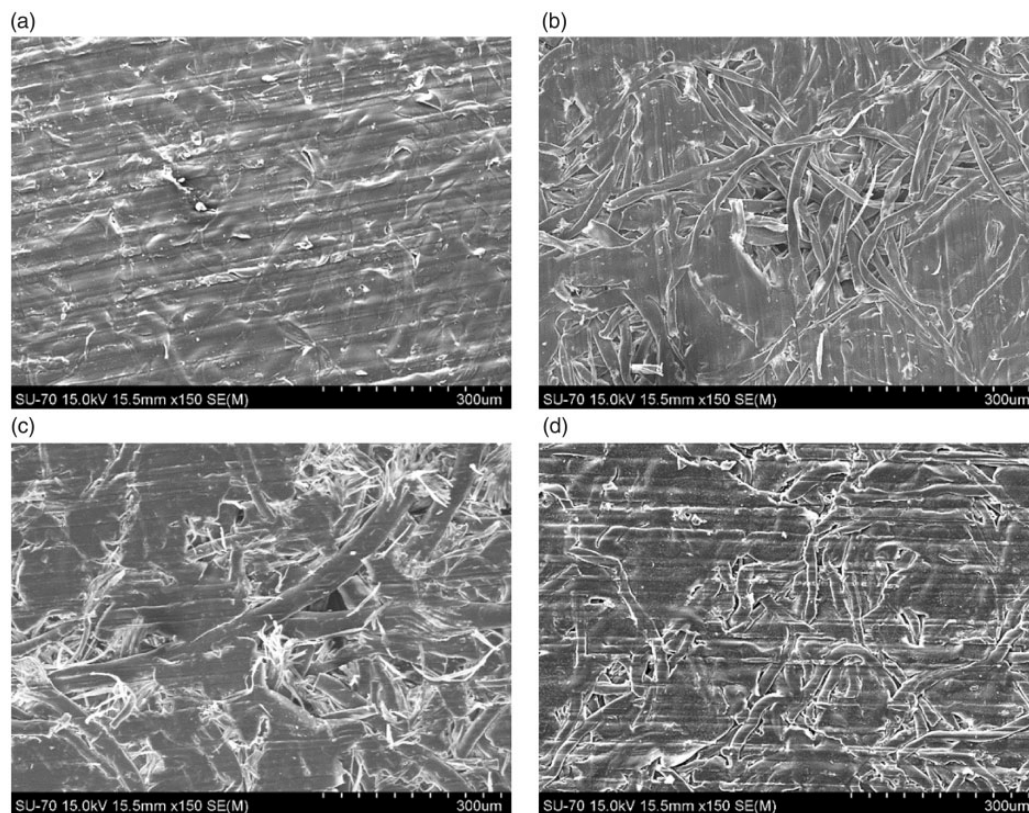
fibers present higher tensile strength, which can increase the stiffness of the composites; (ii) the functional groups, can react with the NCO groups of the PU matrix which can result in a better bonding; (iii) the functional groups make these fibers hydrophilic, limiting the interfacial adhesion with the hydrophobic matrix and/or increasing water absorption, as it will be discussed later.

### Contact angle

Typically, most of natural fibers are hydrophilic due to the presence of cellulose, hemicelluloses and lignin on its surface, while polymer matrices are normally hydrophobic, since they are composed by long aliphatic and or aromatic chains.<sup>39</sup> The lack of adhesion between filler and matrix may jeopardize the properties of the ensuing composites. Hence, the incorporation of hydrophilic fillers in the hydrophobic matrix can result in a heterogeneous system with inferior properties.<sup>40</sup> Therefore, the evaluation of the hydrophobic/hydrophilic character of these materials is of paramount importance and is relevant in all fields of application of composites. 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 Figure 2, the CA values of PU and fibers are presented.

From Figure 2, interesting results can be observed. PU presents a CA of  $73.1^\circ$ , the natural fibers present a CA around  $135^\circ$  and the synthetic fiber presents a CA of  $80.1^\circ$ . As mentioned, most natural fibers are hydrophilic, yet the CA which water formed with cotton and wool suggest that they are hydrophobic. Nonetheless, the results are in accordance with literature. Birzu et al.<sup>41</sup> reported that the pristine wool presented a CA of  $155^\circ$  with water, while Kwon et al.<sup>42</sup> reported that raw cotton fabric presented a CA of  $154^\circ$ . This may be due to the roughness of the surfaces. The differences of hydrophobicity observed between the natural





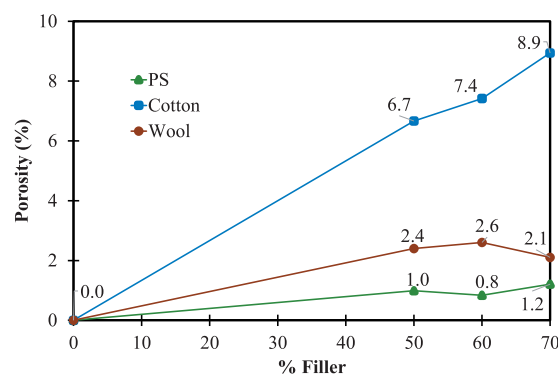
**Figure 3.** SEM images of PU (a), PU-60Cotton (b), PU-60Wool (c) and PU-60Syn.

fibers and the matrix may influence the interfacial adhesion between fibers and PU, contrarily to PeS fibers which present similar CA to that of the matrix.

### Morphology and porosity

In Figure 3, the SEM images of PU and textile fibers composites are presented.

From SEM images presented in Figure 3, it can be observed that the composites presented an identical morphology, being the fibers randomly distributed in the matrix. As expected, it can also be observed that with the increase of the amount of fibers, the matrix that bonds the fibers is reduced. In addition, due to the presence of fibers, voids in the interfacial region are detected. Contributing to the void formation is the different hydrophobic character of the fibers and the matrix, as it will be discussed later, which can be reflected in the mechanical properties of materials.<sup>43,44</sup> To overcome this problem, normally the fibers are chemically modified to improve the interfacial adhesion.<sup>30</sup> Lacerda et al.<sup>34</sup> modified cork with poly (methyl methacrylate) moieties to produced 3D printed



**Figure 4.** Porosity of composites.

materials. It was reported that the grafting of cork thus enhanced the distribution of cork on the composites.

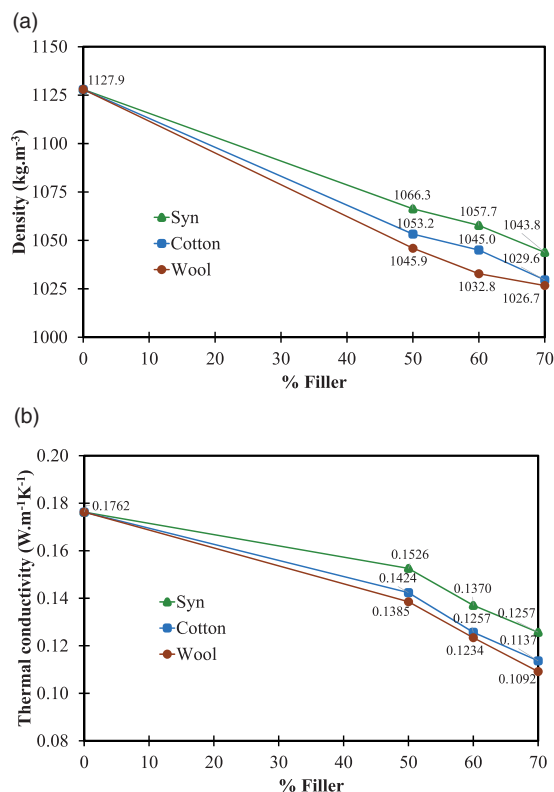
In Figure 4, the porosity of the composites are presented.

As mentioned, the differences in hydrophobicity can decrease the filler/matrix affinity, resulting in voids.<sup>45,46</sup> In fact, from the results presented in Figure 4, it can be observed that the addition of textile fibers results in the presence of voids. Namely, the wool based composites present a porosity of ~2.5%, while

the addition of cotton to PU results in a porosity of 8.9%. Since wool and cotton fibers present similar CA, the hydrophobic solely cannot justify the differences observed on the porosity of the ensuing composites. Yet, other aspects may contribute to the higher porosity of cotton based composites, as observed by Habibi *et al.*,<sup>47</sup> who reported that longer fiber increase the porous size. In turn, PeS fibers present similar hydrophobicity when compared to PU, therefore higher compatibility between these fibers and matrix is expected.<sup>45,46</sup> Analyzing the results presented in Figure 4, it can be observed that the PeS based composites present a porosity of  $\sim 1\%$ , suggesting higher compatibility. As reported, fiber composites contain typically a relative large amount of voids, which considerably influences their properties.<sup>48,49</sup> On the one hand, the porosity of the textile fibers composites can be associated to the hydrophobicity fibers and on the other hand with their dimensions. While high porosity can decrease the density and jeopardize the mechanical performance,<sup>50</sup> it can contribute to enhance the sound absorption of the ensuing materials.<sup>51</sup>

### Density and thermal conductivity

In Figure 5(a) and Figure 5(b), respectively, the density and the thermal conductivity of the composites are presented.



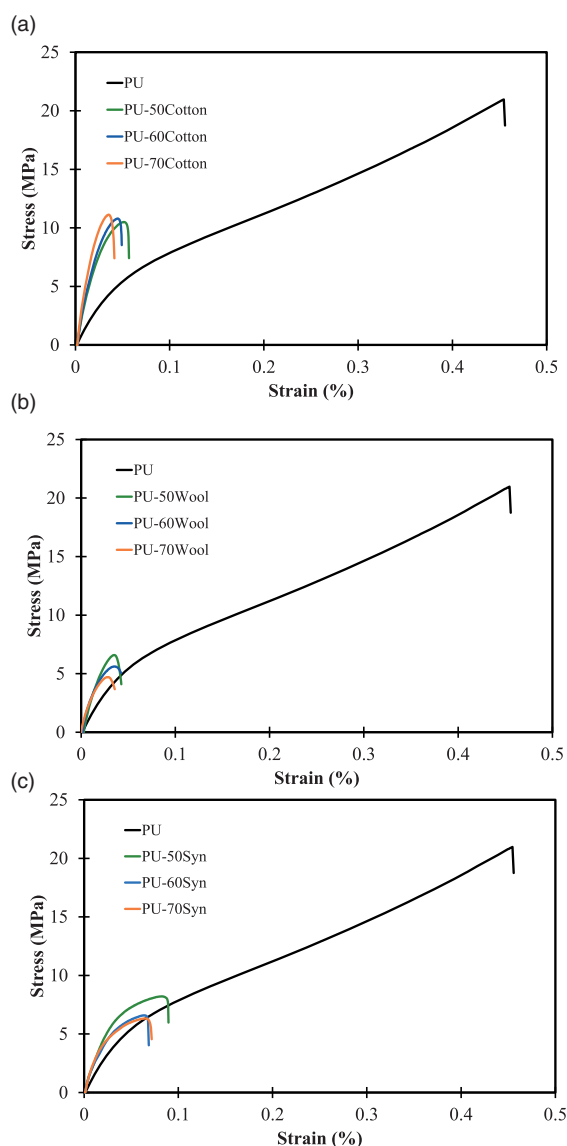
**Figure 5.** Effect of fiber type and quantity on the density (a) and thermal conductivity (b) of the composites.

From the results presented in Figure 5(a), it can be observed that the density of the PU is  $1127.9 \text{ kg.m}^{-3}$  and that the addition of fibers, decreased the density of the ensuing composites ( $1029.6 \text{ kg.m}^{-3}$ ,  $1026.7 \text{ kg.m}^{-3}$  and  $1043.8 \text{ kg.m}^{-3}$  for 70% wt/wt content of cotton, wool and synthetic fibers, respectively). Even though cotton fibers ( $1118.9 \text{ kg.m}^{-3}$ ) are denser than synthetic fibers (PeS –  $1025.7 \text{ kg.m}^{-3}$ ), followed by wool fibers ( $1014.1 \text{ kg.m}^{-3}$ ),<sup>52</sup> others aspects can justify the density of the composites. As observed earlier, both cotton and wool fibers composites presented voids in their morphologies, hence the resulting composites presented lower density. In a similar manner, despite of the fact that synthetic fibers are the second denser fiber studied, the lower porosity of these materials contributed to the higher density of the ensuing composite. Similar results were observed by Yang and Li<sup>51</sup> who reported that the lower density of fiber-based composites was associated with porosity.

Commonly, synthetic fibers (polyesters -  $0.1400 \text{ W.m}^{-1}\text{K}^{-1}$ ) presents higher thermal conductivity than cotton ( $0.0710 \text{ W.m}^{-1}\text{K}^{-1}$ ) and wool fibers ( $0.0540 \text{ W.m}^{-1}\text{K}^{-1}$ ).<sup>52</sup> In addition, the fibers present lower thermal conductivity than the neat PU ( $0.1762 \text{ W.m}^{-1}\text{K}^{-1}$ ). Therefore, it was expected that the composites would present lower thermal conductivity. In fact, the decrease of thermal conductivity of composites filled with natural fibers is very common, as observed in Figure 5(b). As it can be observed, the addition of fibers, reduced the thermal conductivity of the ensuing composites ( $0.1092 \text{ W.m}^{-1}\text{K}^{-1}$ ,  $0.1237 \text{ W.m}^{-1}\text{K}^{-1}$  and  $0.1257 \text{ W.m}^{-1}\text{K}^{-1}$  for 70% wt/wt content of cotton, wool and synthetic fibers, respectively). Similar results were achieved by Chandana *et al.* (Altaf Hussian<sup>53</sup>) who studied the thermal conductivity of a bamboo fiber reinforced epoxy resin or Kumar Gudapati *et al.*<sup>54</sup> who studied the thermal conductivity of palm fiber reinforced composites. The lower thermal conductivity of these materials can also be attributed to the presence of voids and to the lower density. As previously mentioned, the cotton based composites presented higher porosity. Yet, the results suggest that porosity has no significant effect on the thermal conductivity of composites, since the cotton based composites present intermediate thermal conductivity. However, as Rebolledo *et al.*<sup>55</sup> reported, the fiber size has a significant effect on thermal conductivity of fiber-board materials. It was reported that the thermal conductivity of coarse fibers was higher than the medium and fine fibers. This observation is in agreement with the results presented in Table 1 and Figure 5(b), since higher thermal conductive composites were obtained using fibers with higher diameter. Nonetheless, various parameters can influence the thermal conductivity of fibers. Overall, it was observed that the properties

**Table 3.** Mechanical properties of composites.

Sample	Tensile modulus (MPa)	Maximum stress (MPa)	Elongation at maximum stress (%)
PU	134,6 ± 6,5	18,2 ± 0,9	44,0% ± 1,1%
PU-50Cotton	349,1 ± 2,9	10,1 ± 0,4	4,9% ± 0,2%
PU-60Cotton	389,4 ± 3,2	10,1 ± 0,5	4,5% ± 0,4%
PU-70Cotton	457,2 ± 4,8	10,2 ± 0,5	4,3% ± 0,1%
PU-50Wool	258,4 ± 7,0	6,4 ± 0,3	3,6% ± 0,3%
PU-60Wool	271,9 ± 5,9	5,6 ± 0,7	3,3% ± 0,3%
PU-70Wool	325,1 ± 4,4	4,9 ± 0,6	3,2% ± 0,6%
PU-50Syn	243,5 ± 3,5	8,5 ± 0,7	8,8% ± 0,8%
PU-60Syn	255,0 ± 3,4	6,9 ± 0,5	6,6% ± 0,9%
PU-70Syn	285,1 ± 4,4	6,2 ± 0,8	5,1% ± 0,7%

**Figure 6.** Mechanical properties of composites cotton composites (a), wool composites (b) and synthetic composites (c).

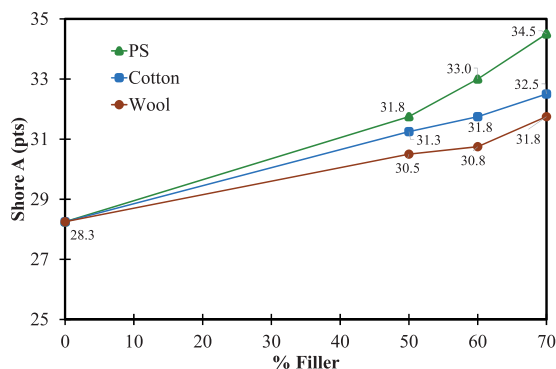
and characteristics of the fibers and density of composites contributes to the thermal conductivity of these materials.

### Mechanical properties

The mechanical properties of the textile fibers composites were measured and the results are presented in Table 3 and Figure 6.

The mechanical performance of fiber composites depends on the quantity and type of the fibers, orientation and dispersion of fibers, type of polymer matrix, the interaction between both, among many others.<sup>44</sup> As mentioned, the lack of compatibility between natural fibers and synthetic polymers can compromise the interfacial adhesion and subsequently the mechanical performance of composites. Yet, this was not observed, since cotton based composites presented higher stiffness. Nonetheless, the presence of the functional groups on the surface of fibers must not be neglected, as these groups are available to bonding with the PU matrix resulting in a better adhesion. Furthermore, the low filler/matrix compatibility can induce the presence of voids, favoring the failure of materials.<sup>44,56</sup> In fact, Stamopoulos et al.<sup>57</sup> evaluated the effect of the porosity on the mechanical properties of carbon fiber-reinforced plastic, reporting that the presence of pores reduces the properties of the ensuing materials. Again, this is not in agreement with the results obtained, since the higher porosity composites proved to be stiffer. In turn, the mechanical properties of the fibers have a major influence the mechanical performance of composites. For instance cotton fibers normally present tensile modulus of 5500–12600 MPa, while wool fibers present tensile modulus of 2300–3400 MPa.<sup>46</sup> Indeed, stiffer fibers yielded stiffer composites, which is in accordance with the results presented. Furthermore, the mechanical performance

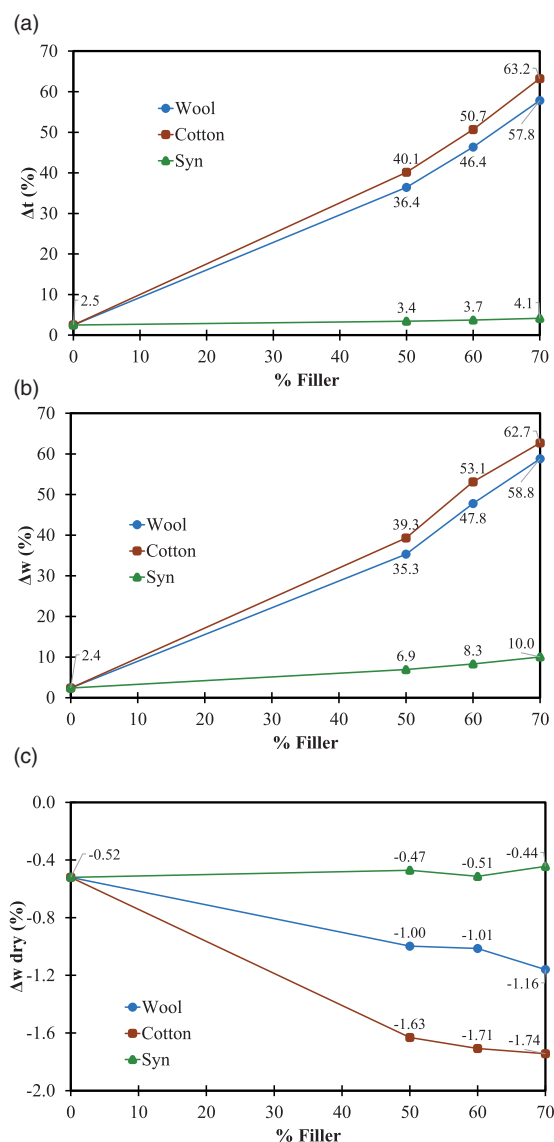
of composites is dependent on the fiber dimensions.<sup>58</sup> Capela et al.<sup>58</sup> studied the effect of the fiber length on the mechanical properties of composites, reporting that the stiffness of the ensuing materials increases in order of 25% when the fiber length increases from 2mm to 4 mm. Again, this observation is in accordance with the results presented in Table 3 and Figure 6. The cotton fibers present higher length, followed by wool fibers and synthetic fibers, and the stiffness of the resulting composites followed the same trend. From Table 3 and Figure 6, it can also be observed that the stiffer composites are obtained using fibers with smaller diameter. Büyükkaya<sup>59</sup> studied the fiber diameter effect on the performance of goose feather composites and reported that the increase of the fiber diameter reduced the stiffness of composites. In other words, the mechanical performance of the composited increased with the aspect ratio of the corresponding textile fibers. Finally, crystalline fibers presents higher tensile strength, since the fiber molecular arrangement results in stronger bonding forces between the molecules.<sup>60</sup> This is in accordance with the results presented in Figure 1(a) and Figure 6(a), since cotton presented higher crystallinity and the ensuing composites are stiffer. Identical observations were made by Zhang et al.<sup>61</sup> who produced bamboo fiber reinforced epoxy composites and reported that increasing the crystallinity of cellulose fibers, affords materials with higher tensile and modulus values. Overall, the results suggest that higher stiffness, higher aspect ratio and higher crystallinity of natural fibers counterbalance the possible lack of adhesion between fibers and matrix. In addition, other aspects, such as roughness and mechanical interlocking can play an important role on the mechanical properties of composites. In that sense, chemical treatments may not be required to obtain composites with high mechanical performance.



**Figure 7.** Shore A hardness of cotton, wool and synthetic based composites.

The mechanical response of the composites was also evaluated by the determination of its Shore A hardness, which measures the resistance of the material to a permanent indentation.<sup>62</sup>

From the results presented in Figure 7, it can be seen that the Shore A hardness follows the same trend of the mechanical performance. In other words, stiffer materials are associated with harder surfaces and with higher fibers content. This is in line with what was observed by Megha et al.<sup>63</sup> from his study on the hardness of banana and jute PeS composites, as well as the studies of Pantamanatsopa et al.<sup>64</sup> who studied the effect of jute fiber on mechanical properties of rubber composites, reporting that the increase of



**Figure 8.** Water absorption of composites and PU:  $\Delta t$  (a),  $\Delta w$  (b) and  $\Delta w_{dry}$  (c).



filler content tended to increase the hardness of composites.

### Water absorption and thermal degradation

The degradation of polymers can be fastened by water absorption, since it results in hydrolysis of the polymer chains. The water absorption of these materials is dependent on numerous aspects such as the filler content, diffusivity, porosity, permeability and hydrophilicity of the fibers, area of exposition, among others.<sup>65,66</sup> In Figure 8, the water absorption results are presented.

From the results presented in Figure 8 it can be seen that the neat matrix has low water absorption. The 2.4% wt/wt water absorption of PU is derived from the moisture still present in the raw material, even after moisture removal. In turn, wool and cotton based composites present high water absorption. These results are in accordance with Espert et al.<sup>67</sup> who compared the water absorption of PP composites and reported that the water absorption was associated to natural fibers. In turn, synthetic fibers are hydrophobic so the water absorption is lower. Pandian et al.<sup>68</sup> studied the water absorption of basalt fiber composites and reported low water absorption due to the fact that no functional groups are present on surface of filler. Besides the hydrophilic character of the fibers, the water absorption is largely dependent on the porosity of the composites. As it can be observed, higher porosity materials presented higher water absorption. Numerous studies can be found in literature, relating the water absorption of composites with their degradation. The degradation rate of the material can be associated with the water diffusion into the polymer matrix.<sup>69</sup> Fakhrul et al.<sup>70</sup> produced reinforced composites and reported enhanced degradability associated with the presence of wheat flour and sawdust. Identical results were reported by Ndazi and Karlsson.<sup>71</sup> From the results presented in Figure 8(c), it can be seen that the composites presented a

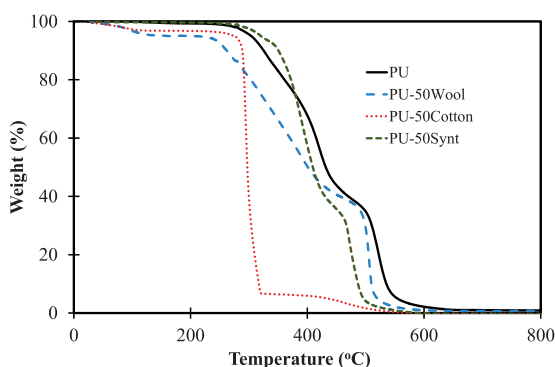
significant mass loss after the water absorption tests, especially the natural fibers composites.

Besides water absorption, the degradation of composites can be studied by submitting them to high temperature. In Figure 9, the TGA of the PU and PU reinforced with 50% wt/wt of fibers are presented.

As observed in Figure 9, the thermal degradation of PU consists in two main steps: (i) between 200–290°C, associated to the degradation of the hard segments of PU (e.g. urea and urethane moieties) and (ii) at 450°C associated to the degradation of the soft segments of PU.<sup>72–74</sup> Regarding the composites, it is observed that the presence of cotton and wool fibers, reduced the thermal stability of the ensuing composites, while the presence of synthetic fibers has the opposite effect. As observed by Ferreira et al.<sup>75</sup> who produced eucalyptus/PeS composites, the presence of the natural filler decreased the thermal stability of materials. In addition, Kim et al.<sup>76</sup> studied the thermal degradation of neat PP and wool/PP composites, observed that neat PP started to decompose at 280°C while the 30 wt% wool composite started to decompose at 240°C. In turn, the synthetic fibers composite seems to present enhanced thermal stability. Suhara et al.<sup>77</sup> studied the thermal behavior of PeS and PU composites reporting similar results. It was observed that the onset of degradation shifted from 230°C to 238°C due to the addition of 30 phr of PS fiber. From the water absorption and TGA results, it was proven that the presence of natural fillers can enhance the degradation of the materials, resulting in environmentally friendly materials.

### Conclusions

In this study, composites were produced from PU residues and different type of textile fibers. Despite of the differences on the composition and morphology of the fibers, the ensuing composites presented similar morphologies. In addition, it was observed that their addition yield lower density and lower thermal conductive materials, independently of the type of fiber. Yet, the type of fiber has relevant effect on the mechanical performance and degradability of the ensuing composites. The higher stiffness, higher aspect ratio and higher crystallinity of natural fibers afford stiffer materials. Likewise, the porosity of the natural fibers-based composites results in higher water absorption and lower the thermal stability, as opposed to the synthetic fibers counterparts. From the results, it can be concluded that these composites can find many applications with the advantage of being produced from 100% recycled raw materials. In that sense, chemical treatments may not be required to obtain composites with good mechanical performance, enhancing that way the sustainability of these materials.



**Figure 9.** Thermal degradation of PU, PU-50Cotton, PU-50Wool and PU-50Syn.

## Declaration of Conflicting Interests


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## ORCID iDs

Nuno Gama  <https://orcid.org/0000-0002-1865-098X>

B Godinho  <https://orcid.org/0000-0002-7949-7739>

Artur Ferreira  <https://orcid.org/0000-0003-1785-4048>

## References

- Binetruy C and Boussu F. *Recent advances in textile composites*. Lancaster: DEStech Publications, 2010.
- Houck MM. *Identification of textile fibers*. Cambridge: Woodhead Publishing Ltd, 2009.
- Mulinari DR, Voorwald HJC, Cioffi MOH, et al. Composite materials obtained from textile fiber residue. *J Compos Mater* 2011; 45: 543–547.
- Lin T, Wang Z and Guo WJ. Cotton fiber-reinforced polypropylene composites. *Appl Mech Mater* 2011; 138–139: 581–587.
- Alomayri T and Low IM. Synthesis and characterization of mechanical properties in cotton fiber-reinforced geopolymer composites. *J Asian Ceram Soc* 2013; 1: 30–34.
- Bharath K, Pasha M and Nizamuddin B. Characterization of natural fiber (sheep wool)-reinforced polymer-matrix composites at different operating conditions. *J Ind Text* 2016; 45: 730–751.
- Yukselglu SM and Çaliskan M. Mechanical and thermal properties of wool waste fabric reinforced composites. *J Text Eng* 2015; 22. DOI: 10.7216/130075992015229703.
- Vigneswaran C, Ananthasubramanian M, Kandhavadivu P, et al. Bioprocessing of synthetic fibres. In: *Bioprocessing of textiles*. Delhi: Woodhead Publishing India, 2014, pp. 189–250.
- Guleryuz CG and Eryurek B. Usage of polyester textile wastes in composites. *J Sci Ind Res* 2003; 62: 462–467.
- Habib A, Begum R and Alam MM. Mechanical properties of synthetic fibers reinforced mortars. *Int J Sci Eng Res* 2013; 4: 923–927.
- Kaur N, Saxena S, Gaur H, et al. A review on bamboo fiber composites and its applications. In: *2017 international conference on Infocom technologies and unmanned systems: trends and future directions, ICTUS 2017*, 2018, pp. 843–849. IEEE Xplore. ISBN: 978-1-5386-0514-1.
- Liu D, Song J, Anderson DP, et al. Bamboo fiber and its reinforced composites: structure and properties. *Cellulose* 2012; 19: 1449–1480.
- Lu T, Jiang M, Jiang Z, et al. Effect of surface modification of bamboo cellulose fibers on mechanical properties of cellulose/epoxy composites. *Compos Part B Eng* 2013; 51: 28–34.
- Balla VK, Tadimeti JGD, Kate KH, et al. 3D printing of modified soybean hull fiber/polymer composites. *Mater Chem Phys* 2020; 254: 123452.
- Filgueira D, Holmen S, Melbø JK, et al. Enzymatic-assisted modification of thermomechanical pulp fibers to improve the interfacial adhesion with poly(lactic acid) for 3D printing. *ACS Sustain Chem Eng* 2017; 5: 9338–9346.
- Mohanty AK, Misra M and Drzal LT. *Natural fibers, biopolymers, and biocomposites*. Milton Park: Taylor & Francis, 2005.
- Thakur VK. *Lignocellulosic polymer composites: processing, characterization, and properties*. Hoboken: Wiley & Sons, 2014.
- Gama N, Costa LC, Amaral V, et al. Insights into the physical properties of biobased polyurethane/expanded graphite composite foams. *Compos Sci Technol* 2017; 138: 24–31.
- Gama N, Ferreira A and Barros-Timmons A. Polyurethane foams: past, present, and future. *Materials* 2018; 11: 1–35.
- Gama N, Amaral C, Silva T, et al. Thermal energy storage and mechanical performance of crude glycerol polyurethane composite foams containing phase change materials and expandable graphite. *Materials* 2018; 11: 1896.
- Gama NV, Silva R, Costa M, et al. Statistical evaluation of the effect of formulation on the properties of crude glycerol polyurethane foams. *Polym Test* 2016; 56: 200–206.
- Gama NV, Soares B, Freire CS, et al. Effect of unrefined crude glycerol composition on the properties of polyurethane foams. *J Cell Plast* 2017; 54: 633–649.
- Gama N, Ferreira A and Barros-Timmons A. Cure and performance of castor oil polyurethane adhesive. *Int J Adhes Adhes* 2019; 95: 102413.
- Stokke DD, Wu Q and Han G. *Introduction to wood and natural fiber composites*. New Delhi: John Wiley & Sons, Ltd, 2014.
- Gama Nuno, Ferreira A and Barros-Timmons A. 3D printed thermoplastic polyurethane filled with polyurethane foams residues. *J Polym Environ* 2020; 28: 1560–1570.
- Gama N, Godinho B, Marques G, et al. Recycling of polyurethane scraps via acidolysis. *Chem Eng J* 2020; 395: 125102.
- Gama N, Godinho B, Marques G, et al. Recycling of polyurethane by acidolysis: the effect of reaction conditions on the properties of the recovered polyol. *Polymer*. Epub ahead of print 2021. DOI: 10.1016/j.polymer.2021.123561.
- Godinho B, Gama N, Barros-Timmons A, et al. Recycling of polyurethane wastes using different

- carboxylic acids via acidolysis to produce wood adhesives. *J Polym Sci* 2021; 59(8): 1–9.
29. Soares B, Gama NV, Freire CSR, et al. Spent coffee grounds as a renewable source for ecopolyols production. *J Chem Technol Biotechnol* 2014; 64: 250–275.
  30. Gama N, Barros-Timmons A, Ferreira A, et al. Surface treatment of eucalyptus wood for improved HDPE composites properties. *J Appl Polym Sci* 2019; 137: 48619.
  31. Gama N, Ferreira A and Barros-Timmons A. 3D printed cork/polyurethane composite foams. *Mater Des* 2019; 179: 107905.
  32. Gama N, Santos R, Godinho B, et al. Triacetin as a secondary PVC plasticizer. *J Polym Environ* 2019; 27: 1294–1301.
  33. Gama NV, Santos R, Godinho B, et al. Methyl acetyl ricinoleate as polyvinyl chloride plasticizer. *J Polym Environ* 2019; 27: 703–709.
  34. Lacerda PSS, Gama N, Freire CSR, et al. Grafting poly (methyl methacrylate) (PMMA) from cork via atom transfer radical polymerization (ATRP) towards higher quality of three-dimensional (3D) printed PMMA/cork-g-PMMA materials. *Polymers* 2020; 12: 1867.
  35. Summerscales J. *Microstructural characterisation of fibre-reinforced composites*. Cambridge: CRC Press, 1998.
  36. Park S, Baker JO, Himmel ME, et al. Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnol Biofuels* 2010; 3: 10.
  37. Noritake A, Hori M, Shigematsu M, et al. Recycling of polyethylene terephthalate using high-pressure steam treatment. *Polym J* 2008; 40: 498–502.
  38. Firoz Babu K, Siva Subramanian SP and Anbu Kulandainathan M. Functionalisation of fabrics with conducting polymer for tuning capacitance and fabrication of supercapacitor. *Carbohydr Polym* 2013; 94: 487–495.
  39. Pereira PHF, De Freitas Rosa M, Cioffi MOH, et al. Vegetal fibers in polymeric composites: a review. *Polimeros* 2015; 25(1): 9–22.
  40. Ali A, Shaker K, Nawab Y, et al. Hydrophobic treatment of natural fibers and their composites – a review. *J Ind Text* 2018; 47: 2153–2183.
  41. Birzu M, Frunza L, Zgura I, et al. Wettability by water contact angle upon the surface of wool fabrics covered with oxide nanoparticles. *Digest J Nanomater Biostruct* 2017; 12: 921–931.
  42. Kwon J, Jung H, Jung H, et al. Micro/nanostructured coating for cotton textiles that repel oil, water, and chemical warfare agents. *Polymers* 2020; 12: 1826.
  43. El Messiry M. *Natural fiber textile composite engineering*. Oakville: CRC Press, 2017.
  44. Pickering KL, Efendy MGA and Le TM. A review of recent developments in natural fibre composites and their mechanical performance. *Compos Part A Appl Sci Manuf* 2016; 83: 98–112.
  45. Salit MS, Jawaid M, Yusoff N Bin, et al. *Manufacturing of natural fibre reinforced polymer composites*. Selangor: Springer International Publishing, 2015.
  46. Sanjay MRR, Madhu P, Jawaid M, et al. Characterization and properties of natural fiber polymer composites: a comprehensive review. *J Clean Prod* 2018; 172: 566–581.
  47. Habibi M, Ruiz É, Lebrun G, et al. Effect of surface density and fiber length on the porosity and permeability of nonwoven flax reinforcement. *Text Res J* 2018; 88: 1776–1787.
  48. Madsen B, Thygesen A and Lilholt H. Plant fibre composites – porosity and volumetric interaction. *Compos Sci Technol* 2007; 67: 1584–1600.
  49. Mehdikhani M, Gorbatiikh L, Verpoest I, et al. Voids in fiber-reinforced polymer composites: a review on their formation, characteristics, and effects on mechanical performance. *J Compos Mater* 2019; 53: 1579–1669.
  50. Madsen B, Thygesen A and Lilholt H. Plant fibre composites – porosity and stiffness. *Compos Sci Technol* 2009; 69: 1057–1069.
  51. Yang WD and Li Y. Sound absorption performance of natural fibers and their composites. *Sci China Technol Sci* 2012; 55: 2278–2283.
  52. Morton WE and Hearle JWS. *Physical properties of textile fibres*. New York: CRC Press, 2008.
  53. Altaf Hussain D. Thermal conductivity characterization of bamboo fiber reinforced in epoxy resin. *IOSR J Mech Civil Eng* 2013; 9: 7–14.
  54. Kumar Gudapati SP, Supraja K and Ratna Prasad A. Thermal conductivity characterization of areca palm fiber reinforced polymer composites. *Int J Pure Appl Math* 2018; 119: 1871–1880.
  55. Rebolledo P, Cloutier A and Yemele M-C. Effect of density and fiber size on porosity and thermal conductivity of fiberboard mats. *Fibers* 2018; 6: 81.
  56. Mirmehdi S, Henrique G, Tonoli D, et al. Lignocellulose-polyethylene composite: influence of delignification, filler content and filler type. *Cellulose Chem Technol* 2017; 51: 341–346.
  57. Stamopoulos A, Tserpes K, Prucha P, et al. Evaluation of porosity effects on the mechanical properties of carbon fiber-reinforced plastic unidirectional laminates by X-ray computed tomography and mechanical testing. *J Compos Mater* 2016; 50: 2087–2098.
  58. Capela C, Oliveira SEE, Pestana J, et al. Effect of fiber length on the mechanical properties of high dosage carbon reinforced. *Proc Struct Integrity* 2017; 5: 539–546.
  59. Büyükkaya K. Effects of the fiber diameter on mechanic properties in polymethyl-methacrylate composites reinforced with goose feather fiber. *Mater Sci Appl* 2017; 8: 811–827.
  60. Wang C, Bai S, Yue X, et al. Relationship between chemical composition, crystallinity, orientation and tensile strength of kenaf fiber. *Fibers Polym* 2016; 17: 1757–1764.
  61. Zhang K, Wang F, Liang W, et al. Thermal and mechanical properties of bamboo fiber reinforced epoxy composites. *Polymers* 2018; 10: 608.
  62. Srinivasa CV and Bharath KN. Impact and hardness properties of areca fiber-epoxy reinforced composites. *J Mater Environ Sci* 2011; 2: 351–356.
  63. Megha BE, Gowda BSK and Prasad GLE. A study on hardness attributes of banana and jute polyester composites. *Int J Eng Res Mech Civil Eng* 2017; 2: 172–176.

64. Pantamanatsopa P, Ariyawiriyanan W, Meekeaw T, et al. Effect of modified jute fiber on mechanical properties of green rubber composite. *Energy Proc* 2014; 56: 641–647.
65. Nourbakhsh A and Kouhpayehzadeh M. Mechanical properties and water absorption of fiber-reinforced polypropylene composites prepared by bagasse and beech fiber. *J Appl Polym Sci* 2009; 114: 653–657.
66. Tserki V, Matzinos P and Panayiotou C. Novel biodegradable composites based on treated lignocellulosic waste flour as filler. Part II. Development of biodegradable composites using treated and compatibilized waste flour. *Compos Part A Appl Sci Manuf* 2006; 37: 1231–1238.
67. Espert A, Vilaplana F and Karlsson S. Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties. *Compos Part A Appl Sci Manuf* 2004; 35: 1267–1276.
68. Pandian A, Vairavan M, Jebbas Thangaiah WJ, et al. Effect of moisture absorption behavior on mechanical properties of basalt fibre reinforced polymer matrix composites. *J Compos* 2014; 2014: 1–8.
69. Correlo VM, Pinho ED, Pashkuleva I, et al. Water absorption and degradation characteristics of chitosan-based polyesters and hydroxyapatite composites. *Macromol Biosci* 2007; 7: 354–363.
70. Fakhrol T and Islam MA. Degradation behavior of natural fiber reinforced polymer matrix composites. *Proc Eng* 2013; 56: 795–800.
71. Ndazi BS and Karlsson S. Characterization of hydrolytic degradation of polylactic acid/rice hulls composites in water at different temperatures. *Exp Polym Lett* 2011; 5: 119–131.
72. Miller JW, Tang Z, Maroto-valer MM, et al. Thermal degradation behavior of rigid polyurethane foams prepared with different fire retardant concentrations and blowing agents. *Polymer* 2002; 43: 6471–6479.
73. Shufen L, Zhi J, Kaijun Y, et al. Studies on the thermal behavior of polyurethanes. *Polym Plast Technol Eng* 2006; 45: 95–108.
74. Xu Y, Petrovic Z, Das S, et al. Morphology and properties of thermoplastic polyurethanes with dangling chains in ricinoleate-based soft segments. *Polymer* 2008; 49: 4248–4258.
75. Ferreira MVF, Neves ACC, de Oliveira CG, et al. Thermogravimetric characterization of polyester matrix composites reinforced with eucalyptus fibers. *J Mater Res Technol* 2017; 6: 396–400.
76. Kim NK, Lin RJT and Bhattacharyya D. Extruded short wool fibre composites: mechanical and fire retardant properties. *Compos Part B* 2014; 67: 472–480.
77. Suhara F, Kutty SKN and Nando GB. Thermal degradation of short polyester fiber-polyurethane elastomer composite. *Polym Degrad Stab* 1998; 61: 9–13.