



# Insights into PU/EVA Blends Produced Using Industrial Residues Towards Eco-efficient Materials

Nuno Gama<sup>1</sup> · B. Godinho<sup>1</sup> · Ana Barros-Timmons<sup>1</sup> · Artur Ferreira<sup>2</sup>

Accepted: 3 September 2021 / Published online: 14 September 2021

© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

## Abstract

Aiming at minimizing the issues associated with the disposal of polymers, in this study, elastomeric materials derived from 100% recycled feedstocks were produced. Residues of polyurethane (PU) foams (from 0 to 100%) were blended with residues of ethylene–vinyl acetate (EVA) derived from the shoe-soles industry (from 0 to 100%) to produce films by hot compression. The experimental values obtained by the characterization of the blends were compared with the predicted values derived from the rule of mixtures. Despite of the two-phase morphology observed, the high correlation between the experimental and predicted values suggest that phase segregation did not have a significant effect on the properties of the blends. Voids were also observed on the PU derived materials, due to the source of PU (foams), which reduced their density and increased the water absorption. Yet, this did not jeopardize the mechanical performance of the ensuing materials. In addition, higher amounts of PU resulted in stiffer materials, while higher amounts of EVA induced higher thermal stability. From the results, it was demonstrated that the PU/EVA blends, produced from 100% recycled feedstock, presented suitable properties to be used in shoe-soles applications.

**Keywords** Circular economy · Polymer blending · Recycled EVA · Recycled polyurethane · Renewable raw-materials

## Introduction

Polymer blending consists in mixing two or more polymers and is used since polymers were first synthesized as it is an easy and cost-effective method to develop new materials [1, 2]. One reason for that, is the fact that the properties of the final material can be adjusted by selecting the type and quantity of the neat polymers, increasing in that way the range of their applications [2–4]. However, the compatibility between polymers can limit the use of polymer blending. The boundaries between polymers in a blend is characterized by interfacial tension and large interfacial tensions may lead to phase separation, decreasing the performance of the material [2, 5]. Nonetheless, the interfacial tension

can be reduced by the addition of interfacial agents known as compatibilizers. These molecules have hydrophobic and hydrophilic regions that can reduce the interfacial tension, improving the compatibility between polymers [6].

Many types of polymers can be used to produce blends, such as polyurethane (PU), polystyrene (PS), polyisocyanurate (PIR), polyethylene (PE), polypropylene (PP), ethylene–vinyl acetate (EVA), nitrile rubber (NBR), polyvinylchloride (PVC), or others [7–11]. PU is one of the most versatile polymers which can be used in a wide range of properties, such as elastomers, adhesives, paints or foams (PUF) [8, 12–14]. PU exhibit a considerable number of superior physical properties like high tensile modulus, resilience, abrasion resistance, wear and tear resistance, good compression set, good chemical and solvent resistance along with low-temperature elasticity [12]. In turn, EVA is a copolymer synthesized from ethylene and vinyl acetate (VA) monomers whose weight percent of VA usually may vary from 10 to 45%. The numerous desirable features of EVA are high polarity (due to the polar nature of the acetoxy side group), excellent aging resistance, weather resistance, good mechanical properties, resistance to color change and relatively low cost [15].

✉ Nuno Gama  
nuno.gama@ua.pt

<sup>1</sup> CICECO - Aveiro Institute of Materials and Department of Chemistry, University of Aveiro – Campus Universitário Santiago, 3810-193 Aveiro, Portugal

<sup>2</sup> CICECO - Aveiro Institute of Materials and Escola Superior de Tecnologia e Gestão de Águeda - Rua Comandante Pinho e Freitas, no 28, 3750-127 Águeda, Portugal

PU can be blended with EVA and due to the superior properties of the ensuing blends, its use in for example shoes applications, is widely reported in literature. Zhang et al. [16] used EVA/PU blends for shoe-sole applications with enhanced friction and wear characteristics. The hardness and resilience, friction coefficients and abrasion resistance were improved by adding PU to the EVA. In turn, Trein and Silva [17] produced lightweight mortars based on PU/EVA aggregates as a replacement for conventional construction sand counterparts. The PU/EVA based mortars presented bulk density between 2.10 and 2.48 kg m<sup>-3</sup> and water absorption in the range from 8 to 17%, which is in accordance with the range specified for ceramic blocks. From the results, the PU/EVA based mortars proved to have potential to be used in the manufacture of sealing blocks, side walls or finish mortars.

As a consequence of its high demand, it was forecast that the global market of PU will grow to 27.61 million tons in the year 2026, which after used, most of it is still disposed in landfills or incinerated [18]. Similarly, nearly 200,000 tons of EVA waste are generated worldwide every year needing a large land surface for placement and storage [19]. In that sense, the consumption of these polymers represent environmental issues. Furthermore, most of these polymers are derived from fossil resources, hence the use of scraps to produce new materials, represents an environmental solution to overcome the issue of the pollution associated to the plastics. In fact, potential solutions have been developed and example is the patent by Borredon et al. [20] which describes the treatment of polymeric materials containing EVA waste. According to the authors, it is possible to break certain chemical bonds of the polymer without damaging the functional groups and therefore, reuse the end product in the production of shoe-soles. In a similar manner, acidolysis can be used to recover the polyol of PU wastes, in order to produce new materials [21–23]. Yet, all these methods require high energy demands or chemical reactants. In turn, the use polymer residues (without chemical treatment), can improve the eco-efficiency of the new materials. Indeed, this approach is widely reported in literature since polymers were first synthesized, as mentioned above. As regards the specific combination of EVA and PU, the work of Sipaut et al. [24] is an example. These authors produced foams using residues of EVA and PUF and concluded that PU and EVA can be used as filler, enhancing the sustainability of the ensuing foams.

Following our interest in the enhancement of the eco-efficiency of polymers, in this study, PU/EVA blends were produced from 100% renewable raw materials, without using any compatibilizers. The results suggest potential applications in athletic and casual shoe-shoes industry.

## Experimental

### Materials

PU flakes derived from PUF, kindly provided by Flexipol Espumas Sintéticas, were milled resulting in a powder (see Figure S1) 5.1% humidity. EVA derived from the sole shoes industry were kindly provided by local manufactures, has a worm like form (see Figure S1), containing circa 20% of inorganic matter (titanium oxides determined by X-ray diffraction (XRD) analysis) and 3.6% humidity. Further information about the chemical composition of these materials, namely Fourier-transform infrared spectroscopy (FTIR), <sup>13</sup>C solid-state Cross Polarization-Magic Angle Spinning Nuclear Magnetic Resonance (<sup>13</sup>C CPMAS NMR) spectra, thermal conductivity and XRD) results can be found in supporting information.

### Production of Blends

PU scraps were milled using a 0.5 mm mesh in a Retsch cross beater mill SK1 (Haan, Germany). Next, the PU powder (0–100% wt/wt) was mixed with EVA (0–100% wt/wt) in a high-speed mixer and the mixtures were dried overnight in an oven at 105 °C to remove the moisture. Blends were produced using 100% wt/wt PU + 0% wt/wt EVA; 75% wt/wt PU + 25% wt/wt EVA; 50% wt/wt PU + 50% wt/wt EVA; 25% wt/wt PU + 75% wt/wt EVA and 0% wt/wt PU + 100% wt/wt EVA. Finally, the blend derived films were produced in a hot press (CARVER model 3851-0) at 180 °C, using 3 tons of pressure, during 10 min. The process of production of blends is described in Fig. 1.

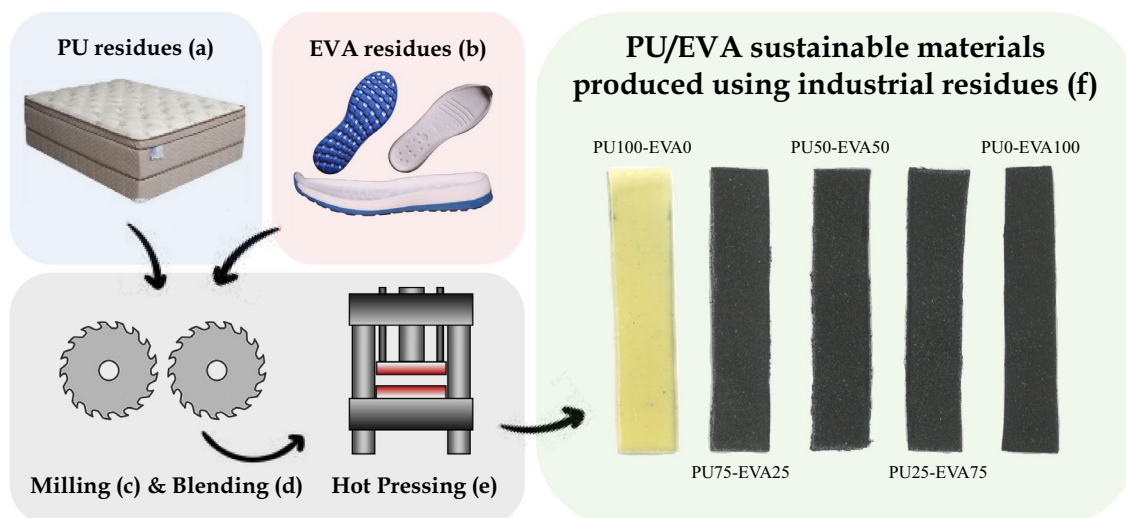
### Characterization

SEM images of the surface of the films in the compression direction were obtained in a SU-70 (Hitachi) scanning electron microscope after vacuum-coating with gold to avoid electrostatic charging during examination, and at accelerating voltage of 15.0 kV.

Specimens (50 × 10 × 1 mm<sup>3</sup>) were cut and weighed to determine the density. Densities were obtained, dividing the weight of the specimens by the calculated volume. The values presented correspond to the average density determined for 10 specimens of each specimen.

Mechanical analyses were performed in a SHIMADZU AGS-X using a load cell of 10 kN and a deformation rate of 5.0 mm min<sup>-1</sup>. Five specimens were tested for each sample.

Dynamic mechanical analyses (DMA) were carried out using a Tritec 2000 equipment (Triton Technologies). Samples with dimensions of 10 × 9 × 6 mm<sup>3</sup> were compressed



**Fig. 1** Scheme of production steps of the polymer blends: first PU (a) and EVA (b) are milled (c) and blended (d). Next hot press (e) is used to produce the PU/EVA films (f)

from  $-50\text{ }^{\circ}\text{C}$  up to  $50\text{ }^{\circ}\text{C}$  at a constant heating rate of  $2\text{ }^{\circ}\text{C min}^{-1}$  and at a frequency of  $1\text{ Hz}$ .

For the determination of hardness Shore A, the specimen was placed on a hard flat surface. The indenter of the instrument (CV Instruments hardness tester) was then pressed into the specimen making sure that it was perpendicular to the surface. The hardness was read within one second of firm contact with the specimen.

For the determination of water absorption, samples were immersed in 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 thickness of the films was measured using a digital caliper, and the increase of thickness was determined using Eq. 1:

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

where  $t_f$  is the thickness of sample after the immersion and  $t_i$  is the thickness of sample before the immersion. The increase of weight was determined using Eq. 2:

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

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 films were left overnight in an oven at  $105\text{ }^{\circ}\text{C}$  and weighed. The weight variation of samples was determined using Eq. 3:

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

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

Thermogravimetric analysis (TGA) of the blends were performed using a SETSYS Evolution 1750

thermogravimetric analyzer (Setaram) from room temperature up to  $800\text{ }^{\circ}\text{C}$ , at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  and under oxygen flux ( $200\text{ mL min}^{-1}$ ).

### Rule of Mixtures

The properties of blended polymers can be predicted from the contribution of each polymer using mathematic models, such as the rule of mixtures [25] given by the Eq. 4:

$$Y = X_A P_A + X_B P_B \quad (4)$$

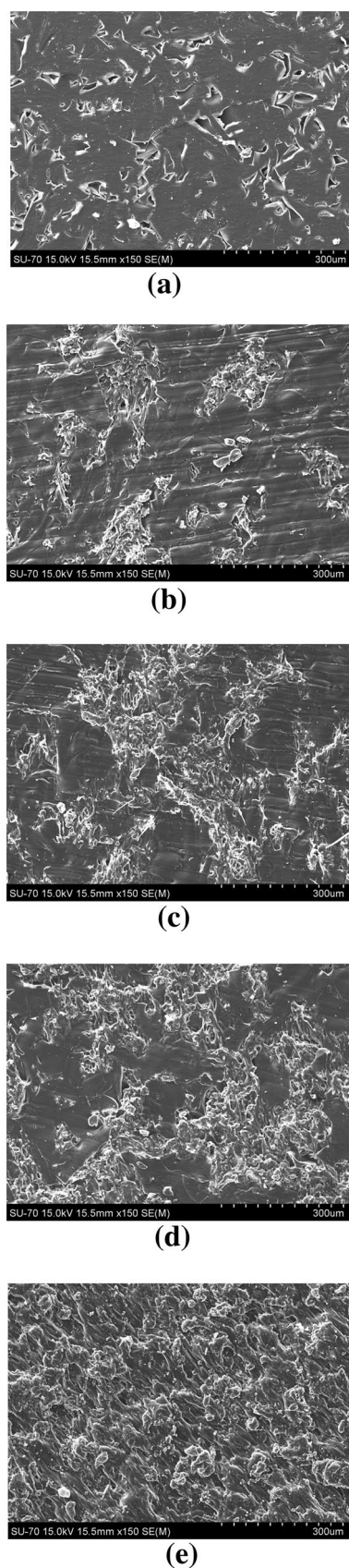
where  $Y$  is the predicted property of the blend,  $X_A$ ,  $X_B$ ,  $P_A$  and  $P_B$  are the mass fraction and properties values of polymer A and B, respectively. The rule of mixtures was applied to the density, thermal conductivity, mechanical properties and water absorption of polymer blends.

## Results and Discussion

### Surface Characterization of Films

Almost every property of polymer blends depends on the properties of the individual polymers and the compatibility between them [2, 26]. If the polymers are incompatible, it can result in phase separation, compromising their properties [2, 26]. Therefore, SEM analysis is an important and versatile tool to inspect the material. In Fig. 2, the SEM images of polymers and polymer blends are presented.

As it can be observed in Fig. 2, the neat polymers present very distinct morphologies. The PU sample presents a smooth surface with voids, while the EVA sample presents



**Fig. 2** SEM images of PU100-EVA0 (a), PU75-EVA25 (b), PU50-EVA50 (c), PU25-EVA75 (d) and PU0-EVA100 (e)

a rough surface without voids. The SEM images also reveal that the polymer blends present voids and a distinguishable two-phase morphology is detected. The presence of voids is attributed to the cellular structure of the foam used as source of PU. Usually, the presence of void affects the mechanical performance of materials, since voids are initiation sites for shear bands and crazes [27]. In turn, the two-phase morphology is associated with the fact that two immiscible polymers can originate phase segregation [28]. As mentioned earlier, EVA presents high polarity (hydrophilic character) due to the polar nature of the acetoxy side group [15]. In turn, PU is produced using long aliphatic chains of polyol and aromatic groups, therefore it presents lower polarity (hydrophobic character) [29]. Hence, the differences of hydrophobicity of polymers can result in poor miscibility and thus phase segregation, as observed in SEM images. Furthermore, from the mechanical tests intergranular fracture was observed (see Figure S4) which can be associated with weak boundaries due to immiscibility. Yet, the presence of voids and two-phase morphology apparently did not affect significantly the properties of the blends, as it will be discussed later. The two phase morphology on TPU/EVA blends was also observed by Dutta and Naskar [30]. Similarly to the observations of Fig. 2, the homogeneous distribution of polymers matrices resulted in suitable interfacial adhesion and effective stress transfer, leading to good mechanical properties.

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. Since the hydrophobicity of polymers can dictate the affinity between them, in Fig. 3, the CA values of PU100-EVA0, PU50-EVA50 and PU0-EVA100 are presented.

From Fig. 3, it can be observed that the CA values of PU, PU50-EVA50 and PU0-EVA100 with water are 92.4°, 85.2° and 79.5°, respectively. In other words, the results suggest that EVA present lower hydrophobicity which can be associated to the polar nature of the acetoxy side groups present in its surface. In turn, PU presents higher hydrophobicity, which can be due to the long alkyl chains derived from the polyol component. Similar results were reported in literature [31, 32]. Hence, the differences on the hydrophobic character of PU and EVA, may contribute to the phase segregation observed in Fig. 2. Nonetheless, other factors such as hydrogen bonding, interfacial area or which polymer acts as a matrix or as a filler (depends on the proportions of each in the sample), must not be neglected.

## Density

In Table 1, the density of the materials is listed, in which it can be observed that the PU sample presents a density

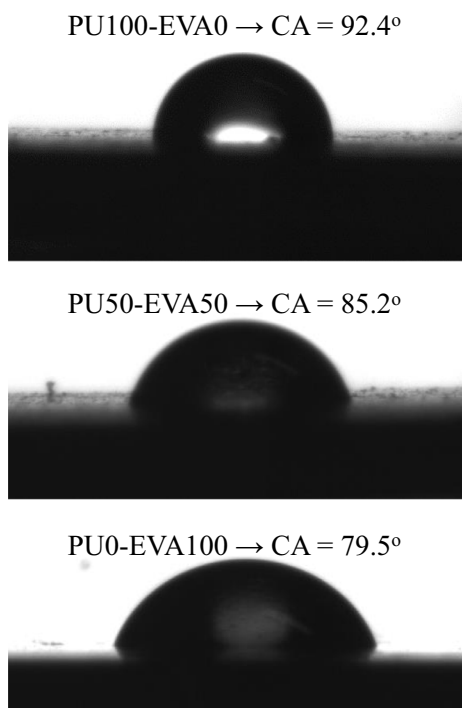


Fig. 3 CA values of PU100-EVA0, PU50-EVA50 and PU0-EVA100

of  $1133.2 \text{ kg m}^{-3}$ , while the neat EVA presents a density of  $879.0 \text{ kg m}^{-3}$ . In turn the blends presented intermediate values. As mentioned, Trein and Silva [17] used PU/EVA aggregates as a replacement of conventional construction materials. The so-called lightweight mortars presented a bulk density range between 2000 and  $2500 \text{ kg m}^{-3}$ , which is considerably higher than the results presented in Table 1. In other words, the lower density of these blends can be suitable for the production of lightweight mortars. Next, the rule of mixtures was applied to the density of the blends and the correlation between of experimental and predicted values are presented in Fig. 4.

From the results presented in Fig. 4, it can be seen that the experimental and theoretical values are similar. Moreover,

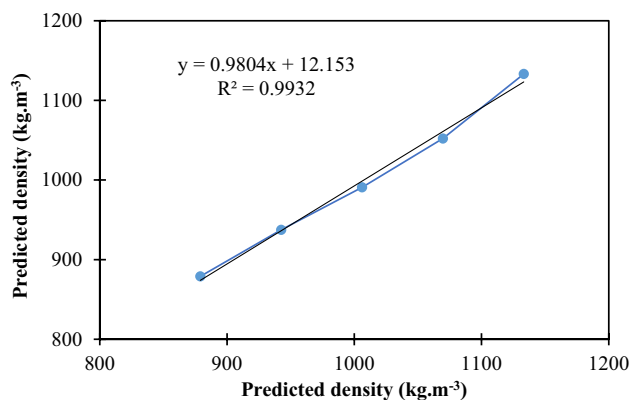


Fig. 4 Relationship between of the experimental and theoretical values of density

the graphs present slopes of  $\approx 1$ , and the predicted value presents excellent correlation with the experimental values (high  $R^2$ ), therefore the rule of mixture can be applied to predict the properties of the polymer blends.

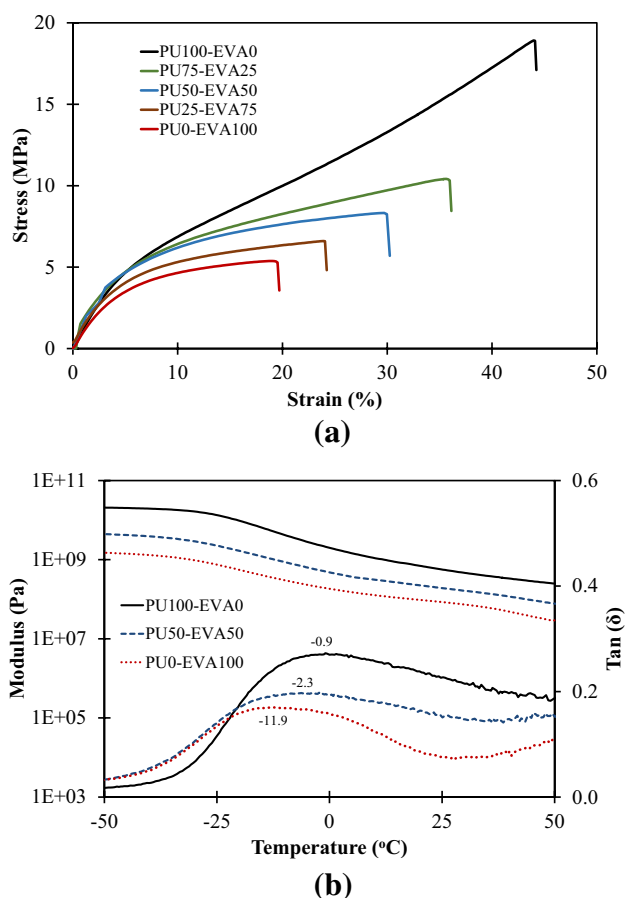
### Mechanical Properties

The mechanical properties of polymer blends can dictate their application and depend on many factors, such as the quantity and properties of the neat polymers, among many others [26]. The static and dynamic mechanical properties of the polymers blends were measured, being the results are presented in Table 1 and Fig. 5, respectively.

From the results presented in Table 1 and Fig. 5a it can be seen that the neat PU presents a Young modulus of  $111.6 \pm 5.2 \text{ MPa}$ , whereas the neat EVA presents a Young modulus of  $87.6 \pm 4.9 \text{ MPa}$ . It can be also observed that the neat PU presents a tensile strength of  $18.9 \pm 1.7 \text{ MPa}$  and an elongation at break of  $44.2 \pm 1.1\%$ , while the neat EVA presents a tensile strength of  $5.0 \pm 1.8 \text{ MPa}$  and an elongation at break of  $40.8 \pm 1.9\%$ . Maity et al. [33] produced PU/EVA blends, reporting that their mechanical

Table 1 Formulations and properties of blends

Sample	PU100-EVA0	PU75-EVA25	PU50-EVA50	PU25-EVA75	PU0-EVA100
Density ( $\text{kg m}^{-3}$ )	$1133.2 \pm 25.6$	$1052.1 \pm 32.1$	$990.8 \pm 36$	$937.5 \pm 20.6$	$879 \pm 24.3$
Young modulus (MPa)	$111.6 \pm 5.2$	$107 \pm 5.8$	$101.3 \pm 3.6$	$96.2 \pm 6.4$	$7.6 \pm 4.9$
Tensile strength (MPa)	$18.9 \pm 1.7$	$13 \pm 0.4$	$9.1 \pm 0.4$	$7 \pm 0.5$	$5 \pm 1.8$
Elongation at break (%)	$44.2 \pm 1.1$	$36.1 \pm 1.8$	$30.2 \pm 3.8$	$24.2 \pm 4.1$	$19.7 \pm 7.6$
Toughness ( $\text{J m}^{-3}$ )	$740,500 \pm 9643$	$429,318 \pm 7385$	$309,700 \pm 4345$	$151,252 \pm 6234$	$45,020 \pm 7055$
Shore A (pts)	$30.5 \pm 1.8$	$33.3 \pm 1.9$	$36 \pm 1.4$	$37.5 \pm 1.1$	$40.8 \pm 1.9$
Water absorption— $\Delta t$ (%)	$4.5 \pm 1.2$	$3.8 \pm 0.3$	$3.2 \pm 0.1$	$2.3 \pm 0.1$	$1.8 \pm 0.4$
Water absorption— $\Delta w$ (%)	$2.6 \pm 0.1$	$2.4 \pm 0.2$	$2 \pm 0.1$	$1.5 \pm 0.3$	$1 \pm 0.1$
Mass loss— $\Delta w$ dry (%)	$0.5 \pm 0$	$0.4 \pm 0.1$	$0.4 \pm 0$	$0.4 \pm 0$	$0.3 \pm 0.1$



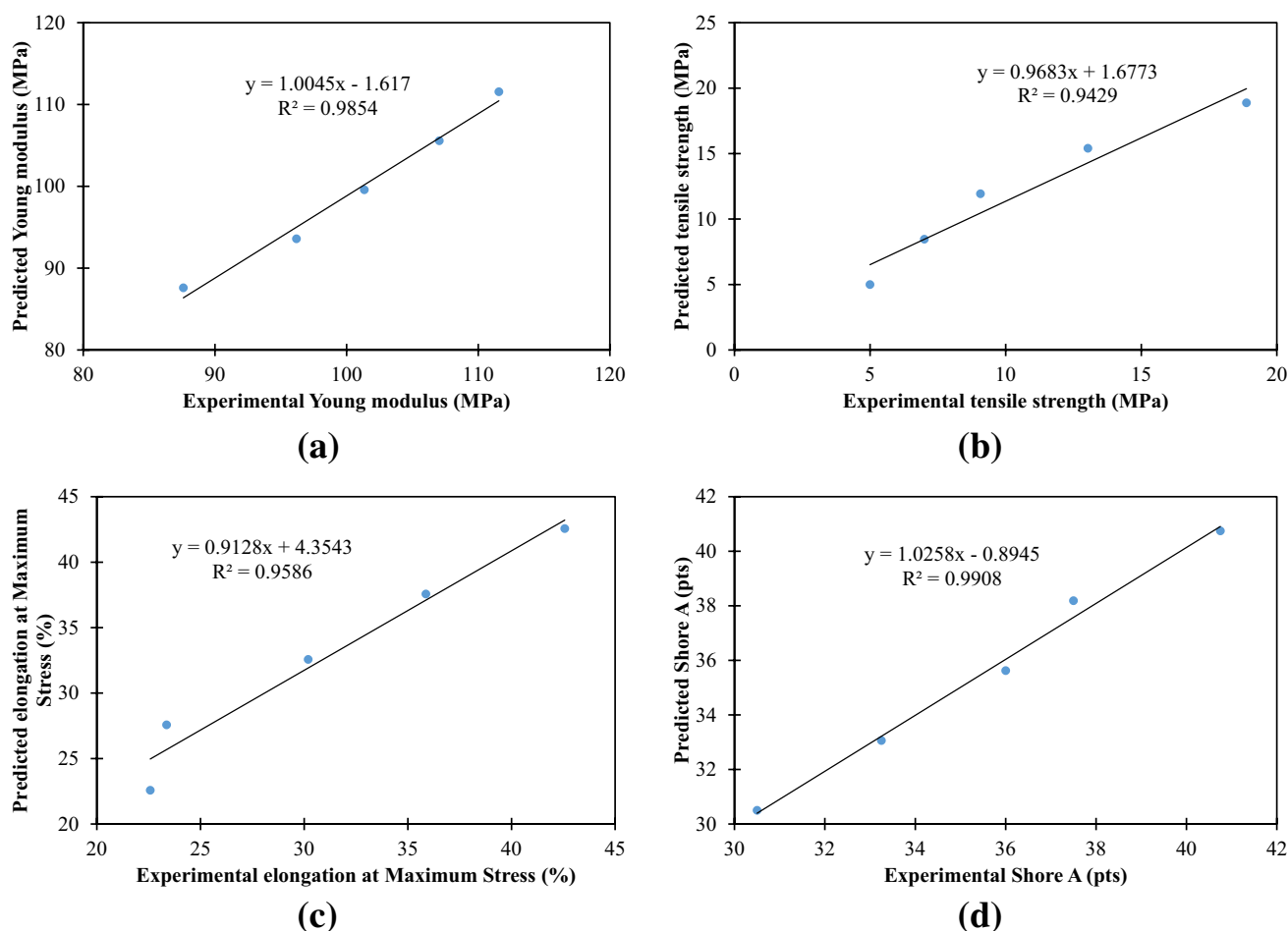
**Fig. 5** Static (a) and dynamic (b) mechanical properties of polymers and polymers blends

performance decreased with the addition of EVA. Analogous trend was observed by Li et al. [34] who studied the microstructure of PU/EVA elastomers reporting that the addition of EVA, decreased the stiffness of blends. Likewise, Dutta and Naskar [30] who developed blends based on EVA and TPU for cable and footwear industry, reported that the modulus becomes gradually higher with the increase of TPU content. Kim et al. [35] produced mortars based on EVA, and reported Young modulus values close to 10 MPa, which is considerably lower than the results presented in Table 1. From the results presented in Table 1, it can also be observed that toughness, which is the ability of a material to absorb energy and corresponds to the area underneath the stress–strain curve, is clearly higher for the PU richer blends. Overall, the mechanical properties results suggest that these materials present suitable elastic and damping performance suitable for footwear applications. Nonetheless, DMA experiments were carried out in order to obtain further information on the viscoelastic properties of blends. From Fig. 5b it can be observed that at lower temperatures the materials behave as hard solids showing high storage modulus ( $E'$ ) values:

$2.0 \times 10^{10}$ ,  $4.1 \times 10^9$  and  $1.4 \times 10^9$  Pa for PU100-EVA0, PU50-EVA50 and PU0-EVA100, respectively. Hence, the DMA results corroborate the static mechanical results, since the addition of EVA reduces the stiffness of the PU. These results are in agreement with Dutta et al. [30] who reported that the addition of TPU resulted in an increment of the storage modulus of TPU/EVA blends. As the temperature goes through the glass transition temperature ( $T_g$ ) (measured at the top of the  $\tan(\delta)$ ), the increase of molecular motion causes the storage modulus to drop. Thus, the neat PU presents a  $T_g$  of  $-0.9$  °C attributed mainly to the glass to rubber transition of polyester based soft segments while the neat EVA presents a  $T_g$  of  $-11.9$  °C corresponding to the amorphous region glass–rubber relaxation [30]. The higher  $T_g$  value of PU can be associated with crosslinking and aromatic moieties which limits the motion of polymer chains. In turn, EVA is a linear flexible polymer, so higher molecular motion is expected. Dutta et al. [30] reported that the higher content of EVA results in higher  $T_g$  value. However, notice should be made that the PU used in the Dutta study was a linear polymer (TPU), while the PU used in this study is derived from a crosslinked polymer and its aromatic moieties (PUF), so the molecular motion is limited, justifying the higher  $T_g$  of PU100-EVA0. Furthermore, from Fig. 5b it can also be observed that the 50/50 blend presents a  $T_g$  of  $-2.3$  °C being characterized by only one  $\tan(\delta)$  indicating suitable compatibility of the PU and EVA, i.e. technological miscibility [10, 11].

In addition, from Table 1 it can also be seen that EVA presents a harder surface. The Shore A hardness of PU is  $30.5 \pm 1.8$  pts, while the Shore A hardness of EVA is  $40.8 \pm 1.9$  pts. In contrast, Zhang et al. [16] studied the mechanical, friction, and abrasion properties of EVA/PU blend for shoe-sole applications and reported that the EVA richer blends has lower hardness while the PU richer blends has the higher hardness. Yet, the PU used in this study is derived from a cellular structure (PUF) and voids were still observed in the films produced. Furthermore, the EVA sample used in this study has circa 20% of inorganic filler (as it will be discussed later), which can justify the harder surface of the ensuing films. Finally, the damping effect (higher toughness) as a result of void may contribute to the lower hardness.

The results presented on Table 1 suggest that the PU sample is stiffer and the addition of EVA reduces the Young modulus, tensile strength, the elongation at break of the blends and increased the Shore A hardness. Moreover, since the blends presented intermediate values which fit well with those predicted by the law of mixture (see Fig. 6), it can be concluded that the compatibility of the two polymers is appropriated.



**Fig. 6** Relationship between of the experimental and theoretical values of young modulus (a), tensile strength (b), elongation at break (c) and shore A hardness (d)

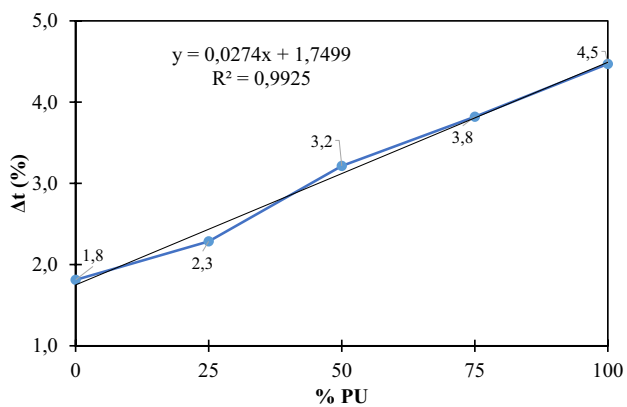
As for the density, from the results presented in Fig. 6, it can be observed that the predicted values of mechanical properties present excellent correlation with the experimental values (high  $R^2$ ) and slopes  $\approx 1$ . Moreover, from the results presented in Fig. 6, it can be concluded that the voids and segregation of domains, observed in SEM images (Fig. 2), did not affected significantly the mechanical properties of the blends, since their properties are intermediate of the neat polymers.

Typically, the materials used to produce shoe-soles have [36]: (i) a density of 900–1230  $\text{kg m}^{-3}$ ; (ii) tensile strength of 7–28 MPa, (iii) a elongation at break of 25–800% and (iv) a shore hardness A of 60–80 pts. Comparing the results presented in Table 1 to those reported in literature, it can be concluded that the materials produced can fulfill the shoe-soles requirements.

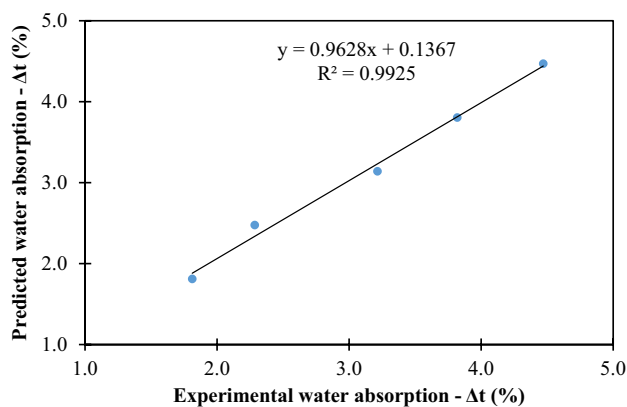
## Water Absorption

It is well known that the water absorption of polymers is very dependent of its hydrophobic character [37]. In addition, the wettability is influenced by morphology and capillarity of surfaces [38]. In Fig. 7, the water absorption results of the polymer blends are presented.

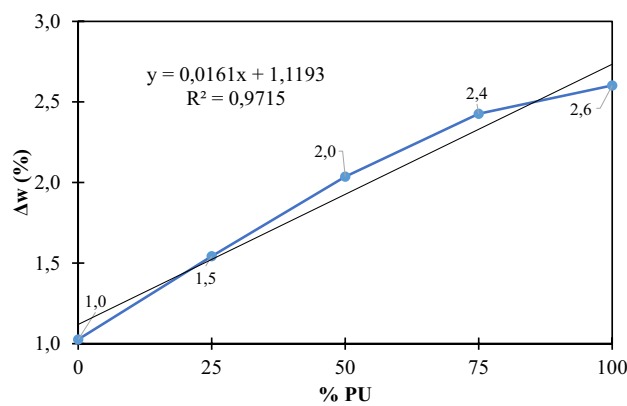
As mentioned, PU present a CA of 92.4°, while EVA present a CA of 79.5°. This would suggest that EVA has higher affinity to water i.e. higher water absorption, yet, this statement is not in agreement with the results presented in Fig. 7. Bidsorkhi et al. [39] studied the properties of EVA composites, reporting water absorption of 1.37% after 24 h, which is in similar to the results presented in Fig. 7. In turn, in recent studies [31, 40], PU derived from cellular feedstocks (PUF) was used to produce composites, being reported that water absorption of 3.6% after 24 h, which is again in agreement with the results presented in Fig. 7. Regardless of the hydrophilic character of the materials, the water absorption of PU can be essentially attributed to its porosity, i.e. to



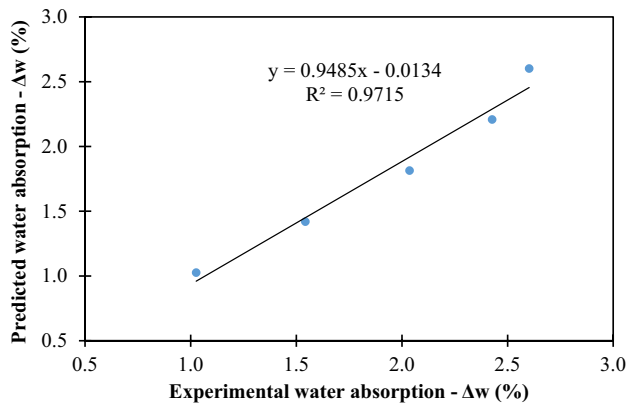
(a)



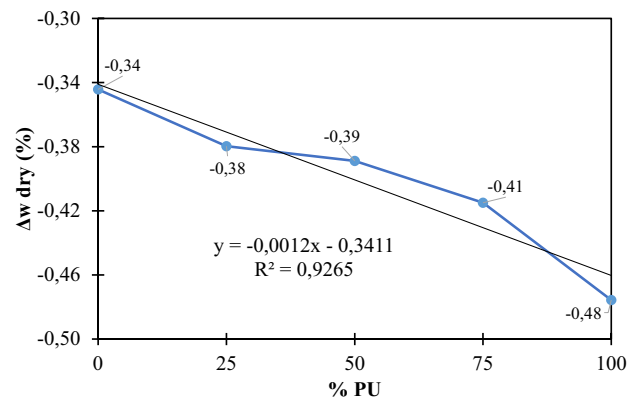
(a)



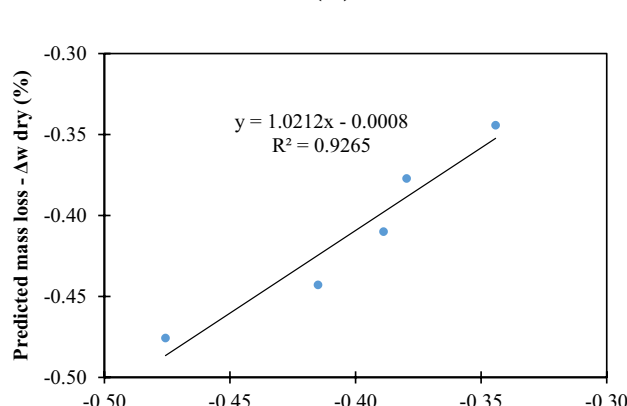
(b)



(b)



(c)



(c)

Fig. 7 Water absorption of blends:  $\Delta t$  (a),  $\Delta w$  (b) and  $\Delta w_{dry}$  (c)

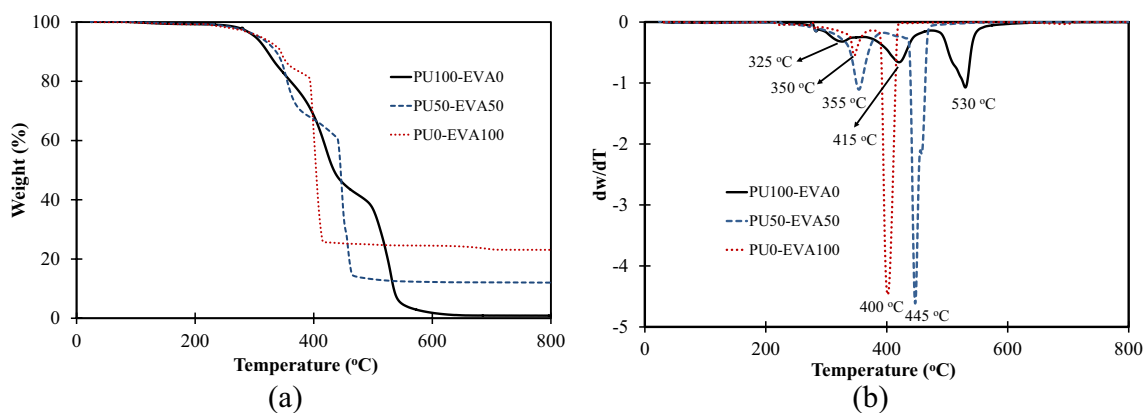
the presence of voids, as it was observed in SEM images. Furthermore, the wettability is influenced by capillarity of surfaces. In fact, one of the mechanisms for water penetration into polymer blends is governed by capillary action, in which water molecules flow into the interface between polymer phases. This mechanism is particularly important when the interfacial adhesion between the polymer phases is weak [41]. Yet, from the results presented in Table 1, it

Fig. 8 Relationship between of the experimental and theoretical values of  $\Delta t$  (a),  $\Delta w$  (b) and  $\Delta w_{dry}$  (c)

can be observed low water absorption, suggesting strong interfacial adhesion between the polymer phases.

The rule of mixtures was applied as well to the water absorption of the blends and the relationships between of the experimental and predicted values are presented in Fig. 8.





**Fig. 9** Thermal degradation (a) and  $dw/dT$  (b)

From the results presented in Fig. 8, it can be observed again slopes  $\approx 1$  and high correlation between the experimental and predicted values, meaning that the rule of mixture can be applied to predict the water absorption of these materials as well.

### Thermogravimetric Analysis

The blend composition can affect the thermal stability of a polymer blend and can differ from the degradation profile of the neat polymers since interactions among different species in the blends and degradation products, can occur. These reactions can accelerate or retard the degradation rate of the blend [42]. In that sense, the thermal stability of the neat polymers and the 50/50 blend was analyzed by TGA.

As it can be seen from Fig. 9, 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 decompositions steps: (i) a 11% mass lost at 325 °C, related to the thermal decomposition of the hard segments of PU (e.g. urethane groups); (ii) a 28% mass lost at 415 °C related to the thermal decomposition of the soft segments of PU and (iii) a 46% mass lost at 530 °C related to the degradation of aliphatic polyol chains [43–46]. Up to 800 °C, the PU sample lost 98% of its mass. In turn, the thermal degradation of EVA presents two stages of degradation: (i) a 12% mass lost at 350 °C due to the evolution of acetic acid and (ii) a 62% mass lost at 400 °C due to the transvinylene formation associated to the main chain scission [47]. At 800 °C a 26% of residue was obtained, which is attributed to inorganic matter present in the EVA residue. Similarly, Zattera et al. [48] characterized residues of expanded EVA generated by shoes' industries and from TGA results, circa 20% of inorganic matter was detected. XRD analysis identified the char obtained as titanium oxides. Regarding the TGA curve of the 50/50 blend, it was also observed two degradation steps: (i) a 20% mass lost at 355 °C which can be associated to the

deacetylation and (ii) a 68% mass lost at 400 °C associated to the dissociation of TPU into diisocyanate and polyols [30]. At 800 °C a 12% of residue was obtained. In brief, EVA is thermally more stable than the TPU and the thermal stability of the 50/50 blend lies in between them (355 °C). The higher thermal stability of EVA was also observed by Dutta Naskar et al. [30]. From the TGA of TPU/EVA blends it was observed that the 50% weight loss temperature for TPU was achieved at 392 °C whereas the 50% weight loss temperature for EVA was achieved at 457 °C. From the TGA results, it was demonstrated that all materials are thermally stable at the processing temperatures (160 °C), which is a typical processing temperature for shoe-soles.

### Conclusions

In this work, PU/EVA blends were produced using recycled raw materials. From SEM images it is observed that the PU/EVA blends are immiscible, since a two-phase morphology was clearly observed. In addition, voids on the morphology of the PU derived materials were observed. Incompatibility between polymers could limit the application of the materials produced, yet, the mechanical properties, water absorption and thermal degradation of the blends were further characterized and presented intermediate values of the neat polymers. In other words, it was observed that the phase segregation did not affected significantly the properties of the blends. Furthermore, PU based blends are stiffer, while EVA based counterparts presents higher thermal stability. In addition, higher quantities of PU reduced density, while higher quantities of EVA reduced the water absorption of polymer blends. Finally, the rule of mixtures was used to compare experimental with predicted values and high correlation was observed, which is evidence of the good compatibility of polymers, even though no compatibilizer was used. From the results, it was demonstrated that these materials

can present a broad range of applications, with the advantage of being produced from industrial residues.

In summary, from the results obtained, it can be concluded that the materials produced can fulfill the shoe-soles requirements.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s10924-021-02289-x>.

**Acknowledgements** This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES and by ERDF Funds through Operational Competitiveness and Internationalization Programme – COMPETE 2020 in the frame of the project FlexiRecover – POCI-01-0247-FEDER-003369.

## References

- Ryan AJ (2002) Designer polymer blends. *Nat Mater* 1:8–10
- Sharma KR (2017) Polymer thermodynamics: blends, copolymers and reversible polymerization. CRC Press, Boca Raton
- Utracki LA (2003) Thermodynamics of polymer blends. Springer, Dordrecht
- Mikitaev AK, Ligidov MK, Zaikov GE (2006) Polymers, polymer blends, polymer composites, and filled polymers: synthesis, properties, and applications. Nova Science Publishers, New York
- Gama N, Barros-Timmons A, Ferreira A, Evtuguin D (2019) Surface treatment of eucalyptus wood for improved HDPE composites properties. *J Appl Polym Sci* 137:48619
- Altstädt V (2017) Polymer blends and compatibilization. MDPI AG, Basel
- Visakh PM, Markovic G, Pasquini D (2017) Recent developments in polymer, macro micro and nano blends. Elsevier, Amsterdam
- Gama NV, Soares B, Freire CS et al (2017) Effect of unrefined crude glycerol composition on the properties of polyurethane foams. *J Cell Plast* 54:633–649
- Amaral C, Gama NV, Mohseni F et al (2020) Development of structural layers PVC incorporating phase change materials for thermal energy storage. *Appl Therm Eng* 179:115707
- Gama N, Santos R, Godinho B et al (2019) Triacetin as a secondary PVC plasticizer. *J Polym Environ* 27:1294–2101
- Gama NV, Santos R, Godinho B et al (2019) Methyl acetyl ricinoleate as polyvinyl chloride plasticizer. *J Polym Environ* 27:703–709
- Gama N, Ferreira A, Barros-Timmons A (2018) Polyurethane foams: past, present, and future. *Materials (Basel)* 11:1–35
- Gama N, Amaral C, Silva T et al (2018) Thermal energy storage and mechanical performance of crude glycerol polyurethane composite foams containing phase change materials and expandable graphite. *Materials (Basel)* 11:1896
- Gama N, Ferreira A, Barros-Timmons A (2019) Cure and performance of castor oil polyurethane adhesive. *Int J Adhes Adhes* 95:102413
- Erbil HY (2000) Vinyl acetate emulsion polymerization and copolymerization with acrylic monomers. CRC Press, Boca Raton
- Zhang ZX, Zhang T, Wang D et al (2018) Physicomechanical, friction, and abrasion properties of EVA/PU blend foams foamed by supercritical nitrogen. *Polym Eng Sci* 58:673–682
- Trein FA, Vargas AS, Rodrigues MAS, Gomes JPC (2015) Evaluation of the influence of PU/EVA waste-based lightweight aggregates on the physical properties of alkali-activated mortars. *Key Eng Mater* 634:278–287
- Garside M (2021) Polyurethane global market volume 2015–2026. In: *Glob. polyurethane Mark*, vol 2015–2021
- United Nations Industrial Development Organization (2020) Wastes generated in the leather footwear industry. United Nations Industrial Development Organization, Vienna
- Borredon E, Delmas M, Gaset A et al (1994) Process for the treatment of polymers based on cross-linked E.V.A. and applications. 1–8
- Gama N, Godinho B, Marques G et al (2020) Recycling of polyurethane scraps via acidolysis. *Chem Eng J* 395:125102
- Gama N, Godinho B, Marques G et al (2021) Recycling of polyurethane by acidolysis: the effect of reaction conditions on the properties of the recovered polyol. *Polymer (Guildf)* 219:123561. <https://doi.org/10.1016/j.polymer.2021.123561>
- Godinho B, Gama N, Barros-Timmons A, Ferreira A (2021) Recycling of polyurethane wastes using different carboxylic acids via acidolysis to produce wood adhesives. *J Polym Sci* 59:697
- Sipaut CS, Halim HA, Jafarzadeh M (2017) Processing and properties of an ethylene-vinyl acetate blend foam incorporating ethylene-vinyl acetate and polyurethane waste foams. *J Appl Polym Sci*. <https://doi.org/10.1002/app.44708>
- Meaurio E, Sanchez-Rexach E, Zuza E et al (2017) Predicting miscibility in polymer blends using the Bagley plot: blends with poly(ethylene oxide). *Polymer (Guildf)* 113:295–309
- Utracki LA, Wilkie CA (2011) Polymer blends handbook. Wiley, Medford, MA
- Cheng L, Guo TF (2007) Void interaction and coalescence in polymeric materials. *Int J Solids Struct* 44:1787–1808
- Serrano B, Pierola IF, Bravo J, Baselga J (2003) Effect of the morphology of two phase polymer blends on glass transition temperature. *J Mater Process Technol* 141:123–126
- Król P, Król B (2012) Surface free energy of polyurethane coatings with improved hydrophobicity. *Colloid Polym Sci* 290:879–893
- Dutta J, Naskar K (2014) Investigation of morphology, mechanical, dynamic mechanical and thermal behaviour of blends based on ethylene vinyl acetate (EVA) and thermoplastic polyurethane (TPU). *RSC Adv* 4:60831–60841
- Gama N, Godinho B, Barros-Timmons A, Ferreira A (2021) PU/Lignocellulosic composites produced from recycled raw materials. *J Polym Environ*. <https://doi.org/10.1007/s10924-021-02191-6>
- Kim JS, Kim YK, Lee KH (2004) Effects of atmospheric plasma treatment on the interfacial characteristics of ethylene-vinyl acetate/polyurethane composites. *J Colloid Interface Sci* 271:187–191
- Maity M, Das CK, Pandey KN, Mathur GN (2000) Polyblends of polyurethane and EVA elastomers (peroxide cure). *Int J Polym Mater* 45:123–133
- Bin LY, Huang JT (2013) The microstructure of polyurethane (PU)/ethylene-vinyl acetate (EVA) polymer lastomer of analysis. *Adv Mater Res* 652–654:475–480
- Kim HJ, Park JY, Suh HW et al (2019) Mechanical degradation and thermal decomposition of ethylene-vinyl acetate (EVA) polymer-modified cement mortar (PCM) exposed to high-temperature. *Sustainability* 11:500
- Kyriacos D, Materials for shoe soles. In: *Polymer technology, engineering, science and marketing*. <http://www.gem-chem.net/artpubsoles.html>. Accessed 2 Aug 2021
- Vasile C (2000) Handbook of polyolefins. CRC Press, Boca Raton
- Noda I, Rubingh DN (1992) Polymer solutions, blends, and interfaces, 1st edn. Elsevier, Amsterdam
- Bidsorkhi HC, Soheilmooghaddam M, Pour RH et al (2014) Mechanical, thermal and flammability properties of ethylene-vinyl acetate (EVA)/sepiolite nanocomposites. *Polym Test* 37:117–122

40. Gama N, Godinho B, Barros-Timmons A (2021) PU composites based on different types of textile fibers. *J Compos Mater*. <https://doi.org/10.1177/00219983211031656>
41. Kushwaha PK, Kumar R (2009) Studies on water absorption of bamboo-polyester composites: effect of silane treatment of mercerized bamboo. *Polym Plast Technol Eng* 49:45–52
42. La Mantia FP, Morreale M, Botta L et al (2017) Degradation of polymer blends: a brief review. *Polym Degrad Stab* 145:79–92
43. Shufen L, Zhi J, Kaijun Y et al (2006) Studies on the thermal behavior of polyurethanes. *Polym Plast Technol Eng* 45:95–108
44. Xu Y, Petrovic Z, Das S, Wilkes GL (2008) Morphology and properties of thermoplastic polyurethanes with dangling chains in ricinoleate-based soft segments. *Polymer (Guildf)* 49:4248–4258
45. Miller JW, Tang Z, Maroto-valer MM et al (2002) Thermal degradation behavior of rigid polyurethane foams prepared with different fire retardant concentrations and blowing agents. *Polymer (Guildf)* 43:6471–6479
46. Jiao L, Xiao H, Wang Q, Sun J (2013) Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS. *Polym Degrad Stab* 98:2687–2696
47. Costache MC, Jiang DD, Wilkie CA (2005) Thermal degradation of ethylene–vinyl acetate copolymer nanocomposites. *Polymer (Guildf)* 46:6947–6958
48. Zattera AJ, Bianchi O, Zeni M, Ferreira CA (2005) Caracterização de resíduos de copolímeros de etileno-acetato de vinila—EVA. *Polímeros* 15:73–78

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.