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Flexible thermoplastic composite of Polyvinyl Butyral (PVB) and waste of rigid Polyurethane foam

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Abstract

This study reports the preparation and characterization of composites with recycled poly(vinyl butyral) (PVB) and residue of rigid polyurethane foam (PUr), with PUr contents of 20, 35 and 50 wt %, using an extruder equipped with a Maillefer single screw and injection molding. The components of the composites were thermally characterized using differential scanning calorimetry (DSC) and thermogravimetry. The composites were evaluated by melt flow index (MFI), tensile and hardness mechanical tests and scanning electron microscopy (SEM). Tg determined by DSC of PVB sample (53 °C) indicated the presence of plasticizer (Tg of pure PVB is 70 °C). MFI of the composites indicated a viscosity increase with the PUr content and, as the shear rate was held constant during injection molding, higher viscosities promoted higher shear stresses in the composites, thereby causing breaking or tearing of the PUr particles. The SEM micrographs showed low adhesion between PVB and PUr and the presence of voids, both inherent in the rigid foam and in the interphase PVB-PUr. The SEM micrographs also showed that PVB/PUr (50/50) composite exhibited the smallest particle size and a more homogeneous and compact structure with fewer voids in the interface. The stiffness of the composites increases with addition of the PUr particles, as evidenced in the mechanical tests.

Keywords: *rigid Polyurethane foam (PUr), Polyvinyl Butyral (PVB), composites, recycling.*

1. Introduction

Polyurethanes are extremely versatile polymers that can be used as a flexible thermoplastic or as a rigid foam with low density and low coefficient of thermal conductivity. This versatility promotes the application of polyurethanes in several industries, including automotive, construction, medical, footwear, adhesives and elastomers[1,2]. The production and the post-consumer disposal of PUr products generate significant volumes of solid residues due to the low density of the polymer[2]. The reuse of these products is complicated by the presence of reticulations in the polyurethane structure, so PUr creates a great disposal problem and is highly polluting to the environment. PUr residues are not adequately reprocessed to obtain new product, as they are thermoset polymers with low density[3-5].

Polyvinyl butyral (PVB) is an amorphous random copolymer of vinyl butyral, vinyl alcohol, and vinyl acetate, mainly used in laminated safety glass in automotive, aerospace and architectural glass sections[6,7]. The chemical structure of PVB is very important because it deeply influences the properties of the polymer. The vinyl butyral unit is hydrophobic and promotes good processibility, toughness, elasticity and compatibility with many polymers and plasticizers. The hydrophilic vinyl alcohol and vinyl acetate units are responsible for high adhesion to inorganic materials such as glass[8]. Commercial PVB contains approximately, 17-22% vinyl alcohol, 1-3% vinyl acetate and 75-82% vinyl butyral units. The PVB used in windshields is highly plasticized, and different plasticizers, such as alkyl phthalate, dibutyl sebacate, and di-2-ethylhexanoate of triethylene glycol can be present to different extents[9].

The recycling of PVB is hampered by the elimination of plasticizer and/or degradation during the recycling process. Degradation generates new functional groups of the polymer, which, in addition to variations in composition caused by the loss of plasticizer, can cause deterioration of the polymer properties[6,9].

The main objective of this study was to develop flexible thermoplastic composites with a plasticized and recycled PVB filled with residues of rigid polyurethane foam through extrusion and injection molding. The PVB is a residue from the automotive industry, and the PUr is from the footwear sector. The development of the composite could offer possible applications in the footwear industry as a sustainable alternative for the reuse of PUr residues.

2. Experimental

2.1 Materials

PVB in flake form was obtained from automotive glass sandwich residue with a density of 1.20 g/cm^3 and 16% plasticizer (obtained by Sohxlet extraction). The PUr was a residue from the footwear industry. PUr was milled in a plastic granulator with knives from Wittmann Battenfeld, model MAS1. After milling, the PUr particles were selected through sieves between 0.25 and 1.68 mm.

2.2 Preparation of PVB/PUr composites

Prior to the extrusion process, the PVB flakes and PUr were dried in an oven at 60 ºC for 6 h to remove moisture and prevent the degradation of the polymers under heating during further processing. This drying step is important due to the hygroscopic nature of the materials. Then, the two materials were mechanically mixed in the solid state in three mass proportions of PVB/PUr (80/20, 65/35, and 50/50) and processed in an extruder equipped with a Maillefer screw with a 45 mm diameter, L/D = 25, from Miotto, Brazil, using a flat die measuring 150.0 mm in width and 2.0 mm in thickness. A pineapple type mixer block was added to the screw in the metering zone. The Maillefer screw and the pineapple mixer increase the shear rate of the mixture, improving the incorporation of various additives and fillers into the thermoplastic matrix[10]. The temperature profile was 155 °C /170 °C / 175 °C in the extrusion barrel and 180 °C in the extrusion die, and the screw speed was 20 rpm. After extrusion, the composite plates were milled in a plastic granulator. Finally, the composites were injection molded in a Battenfeld 25/75 Unilog B2 injector, producing specimens for tensile test (ASTM D638). The temperature profile was 160 °C/170 °C/180 °C, and the mold temperature was 60 °C. To maintain the same injection velocity or shear rate during injection, it was necessary to set higher values of injection pressure (65 bar-115 bar) as the composite viscosity increased due to the addition of PUr.

2.3 Characterization and testing

PVB and PUr were thermally characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass transition (Tg) of the PVB was identified by a DSC Mettler-Toledo, model 822E. Heating rates of 10 °C/minute were used in a nitrogen atmosphere. The TGA analysis was performed in a TA Instruments model Q500. The temperature ranged from 30 °C to 600 °C with heating rates of 10 °C/minute in a nitrogen atmosphere.

Tensile tests were performed on an INSTRON instrument, model 5569R1789, with an optical extensometer. The tests were performed according to ASTM D638 at room temperature at a velocity of 500 mm min^{-1}. The Shore A hardnesses of the composites were measured using a Bareinss hardness tester, model Digitest, following ASTM D2240.

The melt flow index (MFI) was measured in a Gottfert 011043/2009 instrument using a weight of 21.6 kg at 175 °C according to ISO 1133 to prove the viscosity increase.

The morphology of the cryogenically fractured composites was examined using a scanning electron microscope (FEI LX400) at an accelerating voltage of 20 kV.

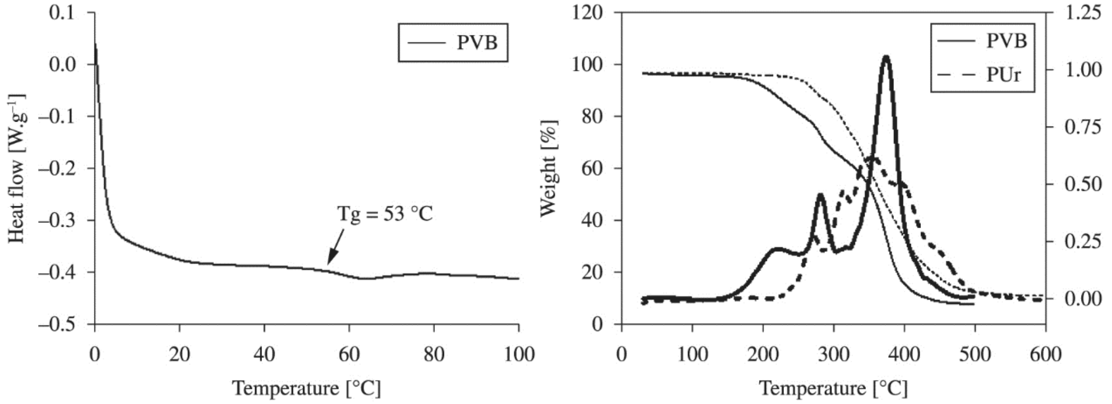
All the tests of neat PUr were performed using machined foam from the footwear industry that was not extruded or injection molded.

3. Results and Discussion

3.1 Thermal characterization

The DSC analysis indicated that the glass transition temperature (Tg) of the PVB is 53 °C; the thermogram is presented in Figure 1a. The presence of a plasticizer in a polymer increases the mobility of the polymer chains[6,9,11], thus influencing the Tg of the polymer. According to the literature, the Tg of unplasticized PVB is higher than 70 °C[9,12], and thus the Tg = 53 °C measured for the recycled flake of PVB used in this study, provides strong evidence that the recycled PVB contains a plasticizer. The PVB used in windshields usually includes different plasticizer additives, such as alkyl phthalate, dibutyl sebacate, and di-2-ethylhexanoate of triethylene glycol[9].

The TGA analysis of the PVB and PUr is shown in Figure 1b. The PVB was stable up to a temperature of approximately 200 °C, above which a mass loss occurred related to decomposition of the PVB and plasticizer. It is possible to see, in Figure 1b, a pronounced weight loss in PVB above 350 °C. Dhaliwal and Hay[9] studied the thermal decomposition of PVB using a thermogravimetric unit attached to a thermolab mass spectrometer. They concluded that the weight loss below 250 °C is due to the loss of plasticizer. Above 260 °C, the major products of decomposition were initially butyraldehyde and butenal, produced by the elimination of butyral groups. Above 380 °C, there was also acetic acid as a minor component, from the elimination of acetate [9].



(a) (b)

Figure 1. Thermal characterization of the base materials: (a) differential scanning calorimetry (DSC) of PVB and (b) thermogravimetric analysis (TGA) of PVB and PUr.

The decomposition of PUr starts at higher temperatures, approximately 260 °C. Through this analysis, it is possible to determine that PVB and PUr are stable under the maximum processing temperature used to obtain the composites.

3.2 Morphological characterization

As the rigid polyurethane foam (PUr) is reticulated and does not melt during processing, it was considered as filler in the matrix of polyvinyl butyral (PVB). Higher concentrations of filler promoted increased viscosity of the composite, as shown by the MFI results in Table 1, and therefore it was necessary to increase the injection pressure during processing. Notice the high weight adopted in the MFI analysis, which indicate the high viscosity of the composites.

The flow behavior of a melt polymer can be represented by the power law according to Equation 1. In this equation, the shear stress (τ) and the shear rate ($\dot{\gamma}$) are directly proportional to the pressure gradient and speed of the fluid (feed rate), respectively. The power law index (n) indicates the pseudoplasticity level of the polymer, while the consistency parameter (m) corresponds to the shear stress when the shear rate is extrapolated to 1 s^{-1}, indicative of the polymer viscosity[13]. During the injection molding of the PVB/PUr composites, the injection velocity was the same for all samples, and thus the shear rate ($\dot{\gamma}$) was also held constant for all samples. Therefore, the increased viscosity (m) of the material resulted in the increase of the shear stress (τ) on the composite, considering a pseudoplastic material (Equation 1). High shear stress during processing can modify the PUr particle morphology and consequently affect the mechanical properties.

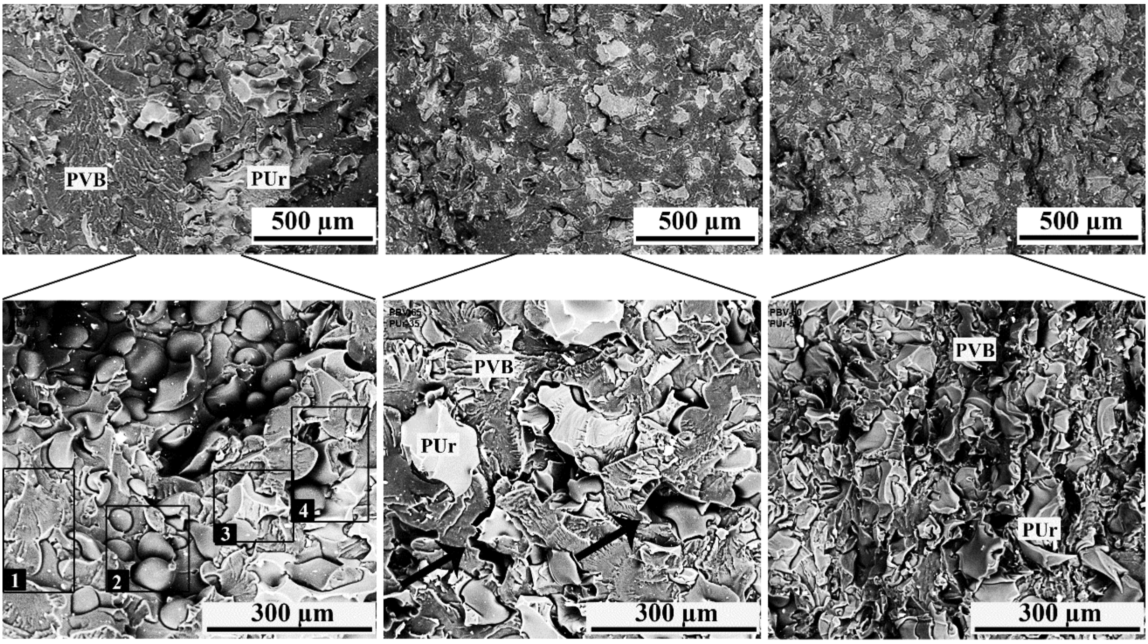
Table 1. Melt flow index and injection pressure set during injection molding of neat PVB and PVB/PUr composites.

Sample	MFI (175°C/21,6 kg) [g/min]	Injection Pressure [bar]
Neat PVB	69.8	65
PVB/PUr (80/20)	20.8	80
PVB/PUr (65/35)	6.6	95
PVB/PUr (50/50)	2.2	115

$$\tau = m \cdot \dot{\gamma}^{n} \qquad (1)$$

Figure 2 shows micrographs of the PVB/PUr composites. To distinguish PVB and PUr, note that the PVB is darker than the PUr. Comparing the morphology of composites with different proportions of PUr in Figures 2a-c, one can note that as the PUr content increases, the particles become smaller. The PUr particles have pores or cavities, which under high shear stress can act as defects and points for crack initiation. The high shear stress imposed on the composite during processing could have broken or torn the PUr particles, explaining the decrease in size with addition of PUr. The decrease in PUr size during processing was also observed by Gonella et al.[14], who studied the reclaiming process of PUr using a Drais mixer. When the foam is broken or torn, the cavities or pores are destroyed, reducing the foam porosity. Furthermore, the superficial area of the foam particles increases as the size decreases, which can be important for a system with no compatibilizer and poor interfacial adhesion between the components.

Figure 2a shows the morphology of the PVB/PUr (80/20) composite. The molten PVB with high mobility and low viscosity was able to partially fill the pores of PUr, as shown by the zoom image in Figure 2a. The rounded shapes observed in Figure 2a are PVB that filled the pore during



(a) (b) (c)

Figure 2. Micrographs of the cryogenically fractured surface of the composites (a) PVB/PUr (80/20); (b) PVB/PUr (65/35) and (c) PVB/PUr (50/50).

process, assuming the shape of the pore. The diameter of these rounded shapes ranged from 60 μm to 90 μm. This diameter is consistent with the pore diameter distribution observed in PUr, as seen in Figure 3.

When the material was cryogenically fractured, crack propagation occurred through the filled pore (Figure 2a-1), through the PUr particle (Figure 2a-3) or through the PVB/PUr interface (Figure 2a-2), creating fractured surfaces with empty pores and PVB molded with pore form. At higher viscosity and consequently higher shear stress, the PUr particles are torn or broken by the flow, becoming smaller and less porous. As the particles become less porous, the penetration of polymer into the pores becomes more difficult, as observed in Figures 2b and 2c. Thus, PVB/PUr (50/50) composite presented the smallest particles and no pore penetration.

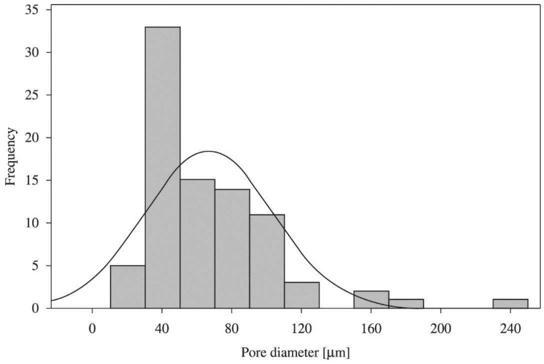


Figure 3. Distribution of pore diameter observed in the PUr.

In addition to the particle size, the micrographs show the poor quality of the interface between PVB and PUr. The arrows in the zoom in Figure 2b highlight the voids in the interface. The use of compatibilizer could improve the adhesion between PVB and PUr, decreasing the presence of voids in the interface[15]. By analyzing the images, it was possible to conclude that PVB/PUr (50/50) composite, due to the higher injection pressure, higher shear stress and smallest particle size, has a more homogeneous and compact structure with fewer voids in the interface.

3.3 Mechanical characterization

The results of the tensile and hardness mechanical tests are presented in Figure 4. According to Figure 4a, the elastic moduli of neat PVB and PUr are very close, so the addition of this recycled foam should not significantly modify this mechanical property, as occurred in the composites containing

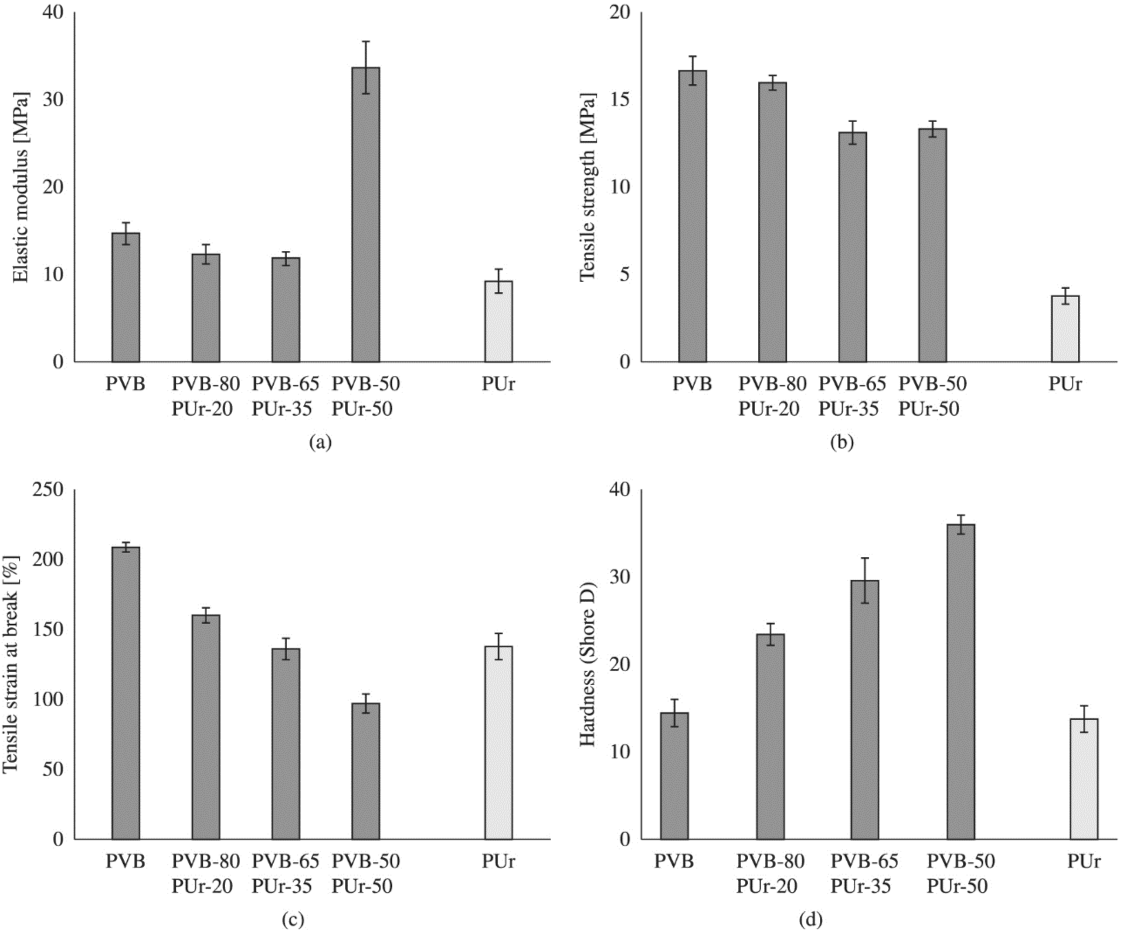


Figure 4. Mechanical characterization of the composites, PVB and PUr: (a) Elastic modulus; (b) Tensile Strength and (c) Tensile Strain at break obtained in the tensile test and (d) Hardness – Shore D Test.

20 wt% and 35 wt% PUr. However, the composite with 50 wt% PUr exhibited an increase in stiffness greater than 200%. PUr is thermoset foam with crosslinked bonds, which are an obstacle to fusion melting/softening during processing, and thus it can be imagined as a rigid filler in the composite compared to the plasticized PVB matrix. In the PVB/PUr (50/50) composite, due to the breaking or tearing of the PUr particles caused by the higher injection pressure and compression of the composite, there was a reduction of porosity and a bigger fraction of rigid filler considering a certain volume, which improved the composite stiffness. Furthermore, the PVB/PUr (50/50) composite presented a higher superficial area and better homogeneity and dispersion of PUr particles.

Figure 4b shows the tensile strength of the composites. One can see a small decrease in the mechanical property with increasing PUr content. The tensile strength of the foam is lower than for the neat PVB. Furthermore, the tensile strength depends on the interface between matrix and filler. A good interface promotes good transference of stress from the matrix to the filler resulting, in a good mechanical performance[16-18]. As seen in the micrographs in Figure 2, there was no proper interface between PVB and PUr, which would compromise the tensile strength of the composites even if the foam had a higher mechanical property. The same decrease can be seen in the tensile strain at break in Figure 4c. As PUr is less flexible than PVB, the deformation occurs mostly in the PVB matrix. The addition of rigid particles to a flexible matrix tends to compromise the deformation of the composite[18].

Figure 3d shows the hardness results. The hardness tests of PUr were performed in the foam, and therefore the results were affected by the pores. If PUr hardness had been correctly measured in a sample with no pores, the values obtained should be higher. In the composites, there was an increase in hardness with the addition of PUr particles. This result is consistent with the increase of the elastic modulus observed in PVB/PUr (50/50) composite. As the hardness is evaluated at the material surface, the internal defects of the composite could not deeply affect this property, as occurred in the elastic modulus. Furthermore, the porosity of the PUr decreased during processing, which can improve the hardness of the foam.

It is important to highlight that the addition of the recycled PUr did not deeply compromise the mechanical properties of PVB. In addition to the increase in properties such as the as hardness and elastic modulus, there was a small decrease in the tensile strength, and the smallest tensile strain at break presented by the composites is still compatible with a flexible material. Therefore, the mechanical properties of the composites should not be an obstacle to the recycling of this highly polluting foam.

4. Conclusions

The DSC analysis of the PVB indicated the presence of plasticizer once the Tg measured (53 °C) was below the Tg of the unplasticized PVB (70 °C). Through TGA analysis of PVB and PUr, it was possible to deduce that the matrix and filler were thermally stable under the maximum processing temperature used to obtain the composites.

The viscosity of the composites increased with the PUr content, as shown by the MFI. As the shear rate was held constant during injection molding, higher viscosities promoted higher shear stress in the composites, causing breaking or tearing of the PUr particles. The morphological characterization by SEM showed that the PVB/PUr (50/50) composite presented more homogeneous and compact structures with smaller particles, less porosity, fewer voids in the interface and less pore penetration. The morphological characterization through SEM showed poor adhesion between PVB and PUr.

Most of the mechanical results were consistent for composites of a flexible matrix and a rigid filler. There was an increase in the hardness properties and decrease in the tensile strain at break, which is still compatible with a flexible material. The small decline in the tensile strength of the composites was due to the poor interface between PVB and PUr. The elastic modulus results may be explained by the different morphology of the composites. The higher shear stresses imposed on the PVB/PUr (50/50) composite promoted decreases in particle size and porosity, better dispersion of PUr, an increase in superficial area and a higher volume fraction of rigid particles, which resulted in a higher elastic modulus.

Generally, the mechanical properties were satisfactory, suggesting that composites of recycled materials can be applied in the industries, which have disposal problems with PUr.

5. References

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