Influence of the morphology and viscoelasticity on the thermomechanical properties of poly(lactic acid)/thermoplastic polyurethane blends compatibilized with ethylene-ester copolymer

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ABSTRACT: Viscoelastic, interfacial properties, and morphological data were employed to predict the thermal and mechanical properties of compatibilized poly(lactic acid) (PLA)/thermoplastic polyurethane (TPU) blends. The combination of interfacial thickness measured by contact angle and entanglement density determined by dynamical mechanical analysis analyze data was employed to evaluate the mechanical behavior of PLA/TPU blends with and without ethylene-butyl acrylate-glycidyl methacrylate (EBG) compatibilization agent. The PLA/TPU blend (70/30 wt %) was prepared in a Haake internal mixer at 190 °C and compatibilized with different contents of EBG. The evaluation of the interfacial properties revealed an increase in the interfacial layer thickness of the PLA/TPU blend with EBG. The scanning electronic microscopy images showed a drastic reduction in the size of the dispersed phase by increasing the compatibilizer agent EBG content in the blend. The compatibilization of the PLA/TPU blends improved both the Izod impact strength and yield stress by 38 and 33%, respectively, in comparison with neat PLA/TPU blend. The addition of EBG into PLA/TPU blends significantly increased the entanglement density and the PLA toughening but resulted in a decrease of PLA deformation at break. The PLA and TPU glass transitions were affected by the EBG, suggesting that the PLA and TPU domains were partially miscible. © 2020 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2020, 137, 48926.

KEYWORDS: biodegradable; elastomers; morphology; surfaces and interfaces; structure-property relationships

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INTRODUCTION

Poly(acid lactic) (PLA) is currently one of the most important and employed biodegradable polymers obtained from renewable resources. PLA is notable for its high elastic modulus and stiffness, as well as biocompatibility and biodegradability. However, drawbacks such as brittleness and low thermal stability, require PLA be modified to fulfill project requirements, especially for physical properties. These changes can be done through bulk modification (copolymerization), crosslinking, and blending, as reported by Saini et al.

Polymer blending, in contrast to other routes, is the most usual option for improving PLA mechanical properties, especially as it enables a better balance of the tensile strength and toughness. In general, PLA is blended with thermoplastic elastomers (TPEs) such as thermoplastic polyurethane (TPU), ethylene-based elastomers (for instance, ethylene-vinyl acetate (EVA), ethylene-acrylic acid copolymer (EAA), and ethylene-methyl acrylate-glycidyl methacrylate (EMAGMA) and polyesters (i.e., poly(butylene adipate-terephthalate) (PBAT) and poly(butylene succinate) (PBS)). The incorporation of flexible polymers, especially TPEs, decreases the PLA elastic modulus and increases both impact absorption and deformation at break. Jia et al., in a study about PLA/TPU blends reinforced with mica, revealed that 50 wt % of TPU reduced the PLA tensile modulus from 240 to nearly 120 MPa and increased the PLA deformation at break from around 30% to approximately 810%. TPE also tends to increase the polymer matrix chain entanglement density due to higher viscosity and stronger intermolecular forces. Oommen et al. investigated natural rubber (NR)/poly(methyl methacrylate) (PMMA) (50/50 wt %) blends compatibilized with NR-g-PMMA and reported an entanglement density increase from 761 to 729 mol m⁻³ by adding 5% of NR-g-PMMA. The higher entanglement density was due to the compatibilization agent reducing the interfacial tension and promoting a better adhesion between the phases. The mechanical performance of a polymer blend during its application is influenced by the thermodynamic and intermolecular
forces aspects. The difference in terms of chemical affinity between the blend components results in the immiscibility of polymer blends and a “sea-island” type morphology, in which one phase is composed by droplets dispersed into the second phase or matrix weakly/moderately adhered. Thus, it is expected that this type of polymer blend exhibits a weak interfacial adhesion and a thin interfacial thickness, which result in a poor stress-transferring process between the phases. To improve interfacial adhesion in heterogeneous blends, compatibilization agents are usually incorporated during the mixing process, which increases the blend components miscibility and reduces the surface tension between the phases. Consequently, the polymer blend interfacial thickness is increased and the stress-transferring mechanism is improved, resulting in a material with superior impact absorption. Lin et al. investigating PLA/TPU blends reported an impact strength increase from 4.2 to 49.5 kJ m−2 for the PLA/TPU (90/10 wt %) blend compatibilized with 5% of EMA. Zhao et al. studied the influence of the compatibilizer 4,4-methylene diphenyl disocyanate (MDI) on the mechanical properties of PLA/TPU (80/20) blends and reported that 0.8% of MDI increased the deformation at break from 139.8 to 392.4%. Fourati et al. investigated the compatibilization of poly(butylene adipate-co-terephthalate) (PBAT)/thermoplastic starch (TPS) (60/40) blend using different contents of maleic anhydride (MA), citric acid (CA), and maleated PBAT (PBAT-g-MA). The use of maleic anhydride or citric acid, regardless of the content employed, reduced PBAT/TPS tensile strength and strain at break, indicating these additives were not suitable for improving the PBAT/TPS interface. On the other hand, the use of 2 wt % PBAT-g-MA barely modified the PBAT/TPS blend tensile strength but remarkably increased both its elastic modulus and strain at break.

In our previous paper, we investigated the thermomechanical, rheological and mechanical properties of PLA/TPU and PLA/ethylene elastomer (EE) blends with 10 and 30% TPE contents, as well as the efficiency of the compatibilizer agent ethylene-butyl acrylate-glycidyl methacrylate (EBG) in the modification of PLA/TPU 70/30 wt and PLA/EE 70/30 wt blends. We concluded EBG was only effective in the modification of the interface of the PLA/TPU blend, and that the interfacial properties of the PLA/TPE blends could be related with their rheological and morphological data. As a continuation of our previous investigation, this investigation aims at evaluating the relationship between viscoelastic and interfacial properties and morphology and their influence on the mechanical and thermal properties of PLA/TPU blend (70/30 wt %) compatibilized with different contents of EBG compatibilizer agent. In general, some researchers tend to use interfacial thickness to entanglement density to correlate and explain the mechanical properties of polymer blends or composites. However, the combination of both interfacial thickness and entanglement density information was the least explored in detail in the literature, and the combination of both data could be a very powerful and useful set of information to predict the mechanical performance of a polymer blend system. In this article, the interfacial thicknesses of PLA/TPU with and without EBG were determined by contact angle measurements and used in conjunction with the entanglement density measured by DMA analyze as an attempt to explain the modification of PLA/TPU blends energy absorption (based on the improvements of Izod impact strength and yield stress after the blend compatibilization).

**EXPERIMENTAL**

**Materials**

PLA [density: 1.24 g cm−3; melt flow index (MFI): 35 g 10 min−1 (190 °C/2.16 kg); glass transition temperature (Tg): 55–60 °C; melting temperature (Tm): 155–170 °C] was donated by DuPont. Thermoplastic polyurethane (TPU) [density: 1.20 g cm−3; MFI: 2 g 10 min−1 (190 °C/2.16 kg); Tg: −37 °C; Tm: 162 °C] was donated by Prisma Montelur. Ethylene-butyl acrylate-glycidyl methacrylate (EBG) [density: 0.94 g cm−3; MFI: 12 g 10 min−1 (190 °C/2.16 kg); Tg: −45 °C; Tm: 73 °C] was donated by DuPont.

**PLA/TPU Blends Preparation**

The polymer blend (PLA/TPU) and the compatibilizer (EBG) were carried out by one-step in the melted state at 190 °C under 50 rpm for 8 min in an internal mixer chamber (Haake Rheodrive 7 Rheomix OS). PLA and TPU were dried at 50 °C and EBG at 30 °C in an oven for 24 h before being processing to avoid moisture. The blends were prepared with a fixed TPU content of 30% and with 2.5, 5.0, and 7.5 wt% of EBG, as already reported in the literature. The PLA/TPU blends nomenclature and composition are displayed in Table I, where 3T means 30% of TPU and the E represents the compatibilizer EBG. The specimens for physical–mechanical tests and contact angle measurements were obtained by injecting PLA and PLA/TPU samples in a mini-injector Thermo Scientific Haake model Minijet II. [Correction added on 3 February 2020 after first online publication: Text removed at end of sentence for correctness.] The parameters were injection pressure of 60 MPa (10 s) and post pressure of 55 MPa (10 s), and the barrel and mold temperatures were, respectively, 200 °C and 70 °C.

**Characterization**

**Interfacial Properties.** The determination of PLA, TPU, and EBG surface energies was carried out by contact angle measurements of in a contact angle analyzer (Phoenix Mini P10001) at 25 °C following the sessile drop method and Wu’s harmonic mean equation. The interfacial tension between the “i” and “j” domains (γij, jγ) was calculated considering the polymer surface energy (γs) and its polar (γp) and nonpolar components (γl) for each polymer. The solvents were distilled water (H2O) and diiodomethane (CH2I2) [eq. (1)].

<table>
<thead>
<tr>
<th>Table I. Nomenclature and Compositions (Weight and Volume) of PLA/TPU Blends</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td><strong>(wt %)</strong></td>
</tr>
<tr>
<td>PLA</td>
</tr>
<tr>
<td>PLA3T</td>
</tr>
<tr>
<td>PLA3T-2E</td>
</tr>
<tr>
<td>PLA3T-5E</td>
</tr>
<tr>
<td>PLA3T-7E</td>
</tr>
</tbody>
</table>
\[
\gamma_{ij} = \gamma_i + \gamma_j - 2\sigma \left( \left( \frac{\gamma_i^D + \gamma_j^D}{2} \right)^2 + \left( \frac{\gamma_i^P + \gamma_j^P}{2} \right)^2 \right)^{\frac{1}{2}} 
\]

The surface and interfacial tensions at 90 °C were estimated using the Guggenheim relationship \[eq. (2)\].

\[
\gamma_{S,T} = \gamma_{S,T_{exp}} \left( 1 - \frac{T_R}{T} \right)^{\frac{1}{2}} 
\]

where “\(\gamma_{S,T}\)” is the surface (or interfacial) tension at 90 °C, “\(\gamma_{S,T_{exp}}\)” is the surface (or interfacial) tension at 25 °C (298 K), “\(T_R\)” and “\(T\)” are the experiment (90°C/363 K), and the reference (defined as R.T. = 25 °C/298 K) temperatures, respectively.

The work of cohesion (\(W_c\)) and adhesion (\(W_{ad}\)) (in m²) was calculated, respectively, by eqs. (3) and (4)\[27\].

\[
W_{C,j} = 2\sigma \gamma_i 
\]

\[
W_{AD,i,j} = \gamma_i + \gamma_j - \gamma_{ij} 
\]

The Girfalco–Good interaction parameter (\(\phi\)) was also calculated [eq. (5)], based on the Uthaipan et al.\[27\] investigation on surface properties of ethylene-propylene-diene-monomer (EPDM)/ethylene-octene copolymer (EOC)/polypropylene (PP) blends.

\[
\phi = \frac{W_{AD,i,j}}{\sqrt{W_{C,i}W_{C,j}}} 
\]

The interfacial thicknesses (\(L_{ij}\)) (in nm) of PLA/TPU, PLA/EBG, and TPU/EBG interfaces were estimated based on the investigation of Wu\[22\] about interfacial and rheological properties of polymer blends [eq. (6)].

\[
\gamma_{ij} = 7.6 \times 10^{-0.86} L_{ij} 
\]

**Differential Scanning Calorimetry.** The polymer’s thermal transitions were evaluated in a differential scanning calorimeter (DSC Q20; TA Instruments), and the data acquisition and analysis were carried out through a Universal V4.5A software. Samples (±5 mg) of the PLA and PLA/TPU blends were heated to 190 °C at a heating rate of 10 °C min⁻¹ and held at this temperature for 5 min, and then cooled at the same rate to 30 °C and held at this temperature for 5 min, to remove their thermal history. Following, the samples were reheating from 30 °C to 190 °C for the measurements of the thermal transitions (glass transition, phase transitions, crystallization, and melting temperatures) and cold crystallization and melting enthalpies.

**Dynamical Mechanical Analysis.** The viscoelastic behaviors of the polymers and blends were evaluated in a dynamic mechanical analyzer (DMA model 2980; TA Instruments), employing double cantilever deformation mode and frequency of 1 Hz. The temperature was swept from −80 to 100 °C at a heating rate of 5 °C min⁻¹. The specimen dimensions were 63.5 × 12.6 × 3.2 mm. It was investigated the storage modulus (\(E\)) and damping factor (\(\tan \delta\)) as functions of temperature. The \(T_g\) value was taken as the corresponding temperature for the \(\tan \delta\) peak in the \(\tan \delta\) versus temperature curves.

Based on the proposition of Komalan et al.\[24\] [eq. (7)], the entanglement density (\(N\)) (in mol m⁻³) was measured at 90 °C in the onset temperature of the PLA elastomeric behavior plateau.

\[
N' = \frac{E_{\text{elastomeric region}}}{6\pi R^*T} 
\]

“\(E_{\text{elastomeric region}}\)” (in MPa) is the storage modulus value in the elastomeric region of \(E’\) versus \(T\) curve, and “\(R\)” is the universal gas constant (8.314 kJ mol⁻¹ K⁻¹).

**Scanning Electron Microscopy.** The morphology and TPU particle dispersion in the PLA/TPU blends were evaluated in a scanning electron microscope (JSM 6060, JEOL) at 10 kV, using a magnification of 1000x. The cryogenically fractured surfaces of the Izod impact test specimens of the PLA/TPU blends were coated with gold before SEM evaluation. The estimation of the TPU particle size \((d_u)\) (in μm) was carried out through the Image software. The TPU particle size homogeneity in the PLA3T-E blends was evaluated through the particle-size distribution parameter \((\sigma)\) [eq. (8)].

\[
\sigma = \exp \left( \frac{\sum_{i=1}^{N} n_i \ln(d_i) - \ln d_u N}{N} \right) 
\]

where “\(N\)” is total amount of TPU particles evaluated, “\(n_i\)” is the quantity of TPU particles with a particle size equal to “\(d_i\)”, and “\(d_u\)” is the TPU particle size.

The interparticle distance (\(ID\)) was used to investigate the brittle–ductile transition (BDT) of the PLA/TPU blends and to identify in which EBG content the PLA/TPU blend has more toughness, based on Wu’s equation\[28\] [eq. (9)].

\[
ID = d_u \left[ \frac{\pi}{6} \left( \frac{1}{V_{TPU}} \right) \right]^{\frac{1}{3}} \exp(\ln^2 \sigma) 
\]

where “\(\sigma\)” is the particle-size distribution parameter, “\(ID\)” is the interparticle distance (in μm), and “\(V_{TPU}\)” is the TPU volumetric fraction in the PLA/TPU blends.

**Izod impact strength test.** The Izod impact strength measurements of the PLA and the PLA/TPU blends were carried out with an instrumented impact tester (CEAST Resil Impactor II) at 25 °C, and all samples were previously notched, according to ASTM D256. The hammer energy used was 2.75 J. The measurement of the impact strength of PLA and PLA/TPU blends was taken as the average of 10 specimens of each tested sample.

**Tensile Test.** The tensile measurements of the PLA and the PLA/TPU blends were carried out in a universal testing machine (Instron 3382) at 25 °C by following ASTM D638.
specimen’s dimensions were 7.62 × 2.85 × 2.85 mm (regarded to gage length, width of narrow section, and thickness, respectively), and the length of narrow section was 9.53 mm. The velocity test employed was 10 mm min⁻¹ until the specimens broke. Seven specimens were tested to achieve an average value for the property evaluated.

The interfacial interactions between the PLA-EBG and EBG-TPU domains were also investigated through the Nicolai–Narkis model [eq. (10)] as was similarly investigated by Singla et al. In this model, the polymer blend tensile strength (σ_{TS, blend}) is mainly influenced by the second-phase volumetric fraction and by the polymer matrix tensile strength (σ_{TS, m}), as well as by the weightage factor (K).

\[ \sigma_{TS, blend} = \sigma_{TS, m} \times \left( 1 - K \times \sqrt{V_{TPU}} \right) \]  

Analysis of Variance. Analysis of variance (ANOVA) statistical tool was employed to test whether the EBG content was significant for the PLA/TPU blends’ mechanical properties. The statistical data were analyzed using Excel software. The Duncan method was chosen to analyze the data through the p-value test. The significance was taken as p < 0.05. The confidence interval was considered as 0.95.

RESULTS AND DISCUSSION

PLA/TPU Blends’ Interfacial Properties

Table II shows the values of the surface energy and work of cohesion for the PLA, TPU, and EBG at 25 °C and 90 °C. Comparing the values, PLA has higher surface energy and work of cohesion in both temperatures (about 30%) because it has higher polarity. At 25 °C, the PLA chains have stronger intermolecular interaction, while TPU and EBG, despite the differences in their chemical structures and density (1.20 and 0.94 g cm⁻³, respectively), exhibited the same values of surface energy and work of cohesion. At 25 °C, PLA is under its T_g (55–60 °C), in which the chain movement is frozen. On the other hand, the TPU (T_g = 37 °C) and EBG (T_g = 47 °C) are above their glass transition, and, therefore, both exhibit chain mobility in their amorphous fraction, which could have resulted in lower intermolecular forces’ density. In contrast, at 90 °C, all the polymers exhibited very low values of surface energy and work of cohesion, but still the same difference in magnitude despite the increase in the temperature. At 90 °C, PLA has also overtaken its glass transition temperature (T_g), increasing the free volume of amorphous fraction and molecular movement with consequent reduction of the intermolecular forces’ density. Although at this temperature, PLA and TPU still have a crystalline fraction, EBG is above its T_m (73 °C) and in the molten state, resulting in a higher free volume of the amorphous fraction (and, therefore, increasing molecular movement) and a decrease of its intermolecular forces’ density.

The interfacial properties values at different temperatures (25 °C and 90 °C) of the polymer pairs PLA/TPU are listed in Table III. At 25 °C, PLA/TPU and PLA/EBG showed the lowest interfacial tensions and the highest works of adhesion in comparison with TPU/EBG. These results suggested EBG interacted more intensely with PLA in comparison with TPU. These tendencies were equally observed at 90 °C for the same polymer pairs, despite the probable reduction in the intermolecular force’s density.

The Girifalco–Good interaction parameter (ϕ) was also employed to evaluate the intermolecular interaction between the polymeric domains. According to Uthaipan et al., polymer blends usually exhibit ϕ values between 0.50 and 1.15, and higher ϕ values imply a greater interfacial adhesion. The PLA-TPU, PLA-EBG, and TPU-EBG ϕ values at 25 °C indicated that EBG strongly interacted with both polymers, despite the TPU-EBG pair showing a slightly lower ϕ value. Moreover, the Girifalco–Good parameter at 90 °C could also provide an insight into the PLA/TPU blends entanglement density. Polymer chain entanglement is heavily influenced by temperature, chain ramification, viscosity, and intermolecular interaction. As already discussed in our previous article, the compatibilization of PLA/TPU blends by EBG has increased the PLA/TPU intermolecular interaction. Based on this, it would be expected that the PLA-TPU blends entanglement density would be increased as more EBG is added, possibly resulting in PLA/TPU blends with higher impact absorption and improved yielding stress.

The interfacial thickness (L_ij) at 25 °C of PLA/TPU, PLA/EBG, and TPU/EBG interfaces is exhibited in Table III. The presence of EBG compatibilizer agent increased the PLA/TPU interfacial thickness, as seen in PLA/EBG and EBG/TPU L_ij values. These results suggested that EBG was an efficient compatibilization agent for improving the PLA-TPU interfacial interaction, as was also observed by Wang et al. during their research about the compatibilization of polyurethane/polyolefins blends on the morphology and mechanical properties. According to these authors, compatibilization agents, besides reducing interfacial tension, also increase the polymer blend interfacial thickness. Furthermore, it is expected that increasing the EBG content improves the impact strength and yield stress of the PLA/TPU blend, due to the intermolecular forces density increasing between the PLA and the TPU promoted by the EBG.

Influence of EBG Content on PLA/TPU Thermal Transitions

Figure 1(a) shows the DSC second heating run curves of PLA and of noncompatibilized and compatibilized PLA/TPU blends, while the DSC cooling and second heating run curves of EBG are shown in Figure 1(b). The temperature range for both figures was 30–190 °C. The thermal parameters of PLA and PLA/TPU blends are displayed in Table IV. PLA T_g was observed in the range of 55–65 °C and was not influenced by the TPU presence or the EBG content, in
accordance with Shi et al.\textsuperscript{30} investigation about PLA/TPU blends, in which the incorporation of up to 25\% TPU into the PLA matrix did not shift the PLA $T_g$. The compatibilization of PLA/TPU blends, as well as the increase of EBG content, did not affect the PLA $T_g$, disagreeing with the Lu et al.\textsuperscript{31} study about compatibilized PLA/PBAT blends with dicumyl peroxide (DCP). According to these authors, increasing the DCP fraction by up to 0.7\% reduced the PLA $T_g$, which was attributed to the compatibilization of the PLA/PBAT blends. Therefore, considering PLA $T_g$ was unshifted, regardless of the TPU addition or EBG content, PLA3T-Eblends are expected to exhibit a heterophase morphology in which TPU particles are dispersed over the PLA matrix.

Despite the strong intermolecular interaction between PLA and TPU, which was attributed to the compatibilization of the PLA/PBAT blends, as previously discussed, 20 the TPU addition did not affect the PLA cold crystallization process. This result diverged from Qu et al.’s\textsuperscript{32} research on PLA/TPU blends, in which the addition of 20\% TPU into PLA/TPU blends resulted in the PLA $T_{cc}$ being shifted from 117 °C to 128 °C. According to these authors, the higher $T_{cc}$ was probably caused by restricting the PLA macromolecules due to PLA-TPU hydrogen bond. On the other hand, the PLA $T_{cc}$ had increased slightly in the PLA/TPU blend with higher EBG fraction (sample PLA3T-7E). A stronger intermolecular interaction between PLA-EBG-TPU macromolecules might have changed the PLA crystallization process, as verified by the $\Delta H_{cc}$ values of the PLA/TPU blend without and with EBG (PLA3T-7E).

PLA and PLA/TPU blends exhibited a small exothermic peak at 155--157 °C followed by an endothermic melting curve. This phenomenon was indicative that PLA has formed both $\alpha'$ and $\alpha$ crystallites and has also possibly undergone an $\alpha'$ to $\alpha$ phase transformation.\textsuperscript{20} The presence of TPU and EBG did not shift the PLA $T_m$ in the PLA/TPU blends, which was attributed to PLA and PLA/TPU blends being practically cold crystallized at the same temperature. In addition to that, the increase in EBG content in the PLA/TPU blends decreased PLA $\Delta H_{pt}$, confirming the hypothesis that a combination of stronger intermolecular interaction and improved chain entanglement density could have affected the PLA $\alpha'$--$\alpha$ crystallites transformation process. PLA and PLA/TPU blends melting processes were observed between 158 and 175 °C. As previously discussed,\textsuperscript{20} the contribution of TPU crystallites melting enthalpy was not considered in the melting enthalpy of the PLA/TPU blends. The incorporation of TPU or the EBG presence did not affect the PLA $T_m$. Jing et al.\textsuperscript{33} identified the same trend while studying PLA/TPU blends thermal properties in which increasing the TPU fraction up to 40\% TPU in PLA/TPU blends did not affect PLA $T_m$. Nonetheless, the presence of TPU reduced the PLA/TPU blend $\Delta H_m$ which could have resulted in a decrease in the size of the PLA crystallites formed in PLA/TPU blends, in comparison with the ones in neat PLA. The EBG only barely modified the PLA/TPU blends $\Delta H_m$ at 2.5\%EBG, which indicated that this content could have modified the PLA crystallization process and/or crystallite size, while larger EBG contents reduced PLA/TPU blends $\Delta H_m$.

In Figure 1(b) are exhibited the DSC thermograms of the cooling and the second heating of EBG in the temperature range of 30–190 °C. A single and sharp crystallization peak near 51 °C of the PLA/TPU blends thermal properties in which increasing the TPU fraction up to 40\% TPU in PLA/TPU blends did not affect PLA $T_m$. Nonetheless, the presence of TPU reduced the PLA/TPU blend $\Delta H_m$ which could have resulted in a decrease in the size of the PLA crystallites formed in PLA/TPU blends, in comparison with the ones in neat PLA. The EBG only barely modified the PLA/TPU blends $\Delta H_m$ at 2.5\%EBG, which indicated that this content could have modified the PLA crystallization process and/or crystallite size, while larger EBG contents reduced PLA/TPU blends $\Delta H_m$.

In Figure 1(b) are exhibited the DSC thermograms of the cooling and the second heating of EBG in the temperature range of 30–190 °C. A single and sharp crystallization peak near 51 °C.

### Table III. Interfacial Properties at 25 °C and at 90 °C of the PLA/TPU Blends

<table>
<thead>
<tr>
<th>Polymer pair</th>
<th>Interfacial tension ($\gamma_{ij}$) (mJ m$^{-2}$) (25 °C)*</th>
<th>Work of adhesion ($W_{ad}$) (mJ m$^{-2}$) (25 °C)</th>
<th>Girifalco–Good interaction parameter ($\phi$) (25 °C)</th>
<th>Interfacial thickness ($L_{ij}$) (nm) (25 °C)</th>
<th>Interfacial tension ($\gamma_{ij}$) (mJ m$^{-2}$) (90 °C)</th>
<th>Work of adhesion ($W_{ad}$) (mJ m$^{-2}$) (90 °C)</th>
<th>Girifalco–Good interaction parameter ($\phi$) (90 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/TPU</td>
<td>1.7</td>
<td>67.9</td>
<td>0.99</td>
<td>5.7</td>
<td>1.3</td>
<td>53.4</td>
<td>0.78</td>
</tr>
<tr>
<td>PLA/EBG</td>
<td>1.5</td>
<td>68.1</td>
<td>0.99</td>
<td>6.6</td>
<td>1.2</td>
<td>53.5</td>
<td>0.78</td>
</tr>
<tr>
<td>TPU/EBG</td>
<td>2.0</td>
<td>55.6</td>
<td>0.97</td>
<td>4.7</td>
<td>1.6</td>
<td>43.7</td>
<td>0.76</td>
</tr>
</tbody>
</table>

* Reference 20.

### Table IV. PLA and PLA/TPU Blends Thermal Transitions (Second Run)

<table>
<thead>
<tr>
<th>Sample</th>
<th>PLA glass transition ($T_g$) (°C)</th>
<th>Cold crystallization ($T_{cc}$ (°C)</th>
<th>$\Delta H_{cc}$ (J g$^{-1}$)</th>
<th>Phase transformation ($T_{pt}$ (°C)</th>
<th>$\Delta H_{pt}$ (J g$^{-1}$)</th>
<th>Melting ($T_m$ (°C)</th>
<th>$\Delta H_m$ (J g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>61</td>
<td>103</td>
<td>25.6</td>
<td>157</td>
<td>2.3</td>
<td>169</td>
<td>36.0</td>
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<tr>
<td>PLA3T</td>
<td>61</td>
<td>104</td>
<td>20.0</td>
<td>157</td>
<td>1.4</td>
<td>169</td>
<td>25.8</td>
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<tr>
<td>PLA3T-2E</td>
<td>61</td>
<td>103</td>
<td>26.7</td>
<td>157</td>
<td>1.4</td>
<td>169</td>
<td>32.4</td>
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<tr>
<td>PLA3T-5E</td>
<td>60</td>
<td>101</td>
<td>18.6</td>
<td>156</td>
<td>1.1</td>
<td>168</td>
<td>25.5</td>
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<tr>
<td>PLA3T-7E</td>
<td>60</td>
<td>106</td>
<td>25.0</td>
<td>158</td>
<td>0.4</td>
<td>169</td>
<td>22.8</td>
</tr>
</tbody>
</table>

* Reference 20.
and a small melting peak around 74 °C was verified for EBG, in agreement with data reported by Benhamida et al.34 These results indicated EBG should have probably formed small crystallites in size during its crystallization, once EBG ΔH_m was very low in comparison with PLA.

Viscoelastic Behavior of PLA and PLA/TPU Blends
The viscoelastic behavior of PLA and PLA/TPU blends was evaluated by the variation of storage modulus (E') [Figure 2(a)] and tan δ [Figure 2(b)] as functions of temperature. The storage modulus curves of PLA/TPU blends exhibited two sharp inflections, which were attributed to the glass transition of each component (TPU, near −20 °C, while PLA approximately 70 °C), as already by Liu et al.35 Furthermore, regardless of EBG content, any modification in the TPU and PLA T_g's positions was verified. The PLA/TPU blend exhibited lower storage modulus values in comparison with PLA over all the temperature range evaluated (as exemplified by PLA and PLA/TPU blends E' values at 25 °C in Table V). A similar result was also reported by Yazdaninia et al.'s36 study about PLA/TPU, in which increasing the TPU fraction in the PLA/TPU blends resulted in lower PLA/TPU blends storage modulus values in comparison with neat PLA. However, as analogously reported by Jašo et al.,37 PLA/TPU blends still exhibited high storage modulus values up to 60 °C. The influence of TPU on the PLA storage modulus could be attributed to TPU great chain flexibility than PLA, once in that temperature range TPU had already underwent its glass transition. The EBG influence on PLA/TPU blends storage modulus was affected by the percentage of EBG. For example, non-compatibilized PLA/TPU and PLA/TPU-2E blends have shown similar E' curve profiles, indicating the incorporation of EBG barely influenced the PLA/TPU blends’ storage modulus. On the other hand, a larger EBG content resulted in a greater decrease of the PLA/TPU blends’ storage modulus, especially for the PLA3T-7E sample.

The PLA tan δ curve (Figure 2(b)) exhibited a single peak near 70 °C related to the PLA glass transition and the PLA/TPU blends exhibited two tan δ peaks, which were related to the TPU (~ −20 °C) and PLA (~70 °C) glass transitions. These results confirmed that PLA3T blend has shown the phase separation phenomenon (previously observed in the DSC analyses), so agreeing with Liu et al.'s35 investigation about PLA/TPU blends. Moreover, the PLA and TPU T_g values were comparable to the ones reported by Feng and Ye,38 who attributed PLA and TPU tan δ peaks to an α-relaxation process caused by the chain movement from the amorphous regions of the PLA and TPU macromolecules.

The comparison of the TPU and PLA T_g values in the PLA/TPU blends (Table V) showed EBG slightly shifted the TPU and PLA T_g to lower temperatures, which could be an indication that the PLA/TPU domains achieved partial miscibility after being

Table V. PLA/TPU Blends’ Main Viscoelastic Properties Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>E' (MPa) (25 °C)</th>
<th>E' (MPa) (90 °C)</th>
<th>N' (mol m⁻³)</th>
<th>T_g TPU (°C)</th>
<th>tan δ (TPU)</th>
<th>T_g PLA (°C)</th>
<th>tan δ (PLA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>2972</td>
<td>6.6</td>
<td>364</td>
<td>-</td>
<td>-</td>
<td>71.5</td>
<td>1.45</td>
</tr>
<tr>
<td>PLA3T</td>
<td>1715</td>
<td>9.2</td>
<td>508</td>
<td>-20.6</td>
<td>0.06</td>
<td>71</td>
<td>0.88</td>
</tr>
<tr>
<td>PLA3T-2E</td>
<td>1657</td>
<td>18.2</td>
<td>1005</td>
<td>-25.0</td>
<td>0.08</td>
<td>67.9</td>
<td>0.91</td>
</tr>
<tr>
<td>PLA3T-5E</td>
<td>1425</td>
<td>19.9</td>
<td>1099</td>
<td>-23.5</td>
<td>0.08</td>
<td>67.8</td>
<td>0.79</td>
</tr>
<tr>
<td>PLA3T-7E</td>
<td>1332</td>
<td>16.2</td>
<td>894</td>
<td>-23.3</td>
<td>0.08</td>
<td>68.3</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Figure 1. DSC thermograms of PLA/TPU blends (second run) (a), and cooling and second heating curve of EBG (b).
modified the PLA–TPU intermolecular interaction and strengthened the PLA–TPU interface.

The incorporation of TPU into PLA increased the PLA/TPU blend chain entanglement density in comparison with neat PLA (by nearly 39.5%). Moreover, the chain entanglement density of PLA/TPU blends rose as more EBG was added into the PLA/TPU blends, which was attributed to an increased PLA–TPU intermolecular interaction. A similar trend was reported by Komalan et al., who employed ethylene-propylene rubber grafted with maleic anhydride (EPM-g-MA) as a compatibilization agent for ethylene propylene diene (EPDM)/polyamide 6,66 (PA 6,66) (70/30) blends. According to these authors, the entanglement density of EPDM/PA 6,66 blend was increased from 123 to 273 mol m⁻³ after adding 5.0% EPM-g-MA. Therefore, based on $N$ values, it is expected that PLAST-5E shows the highest impact absorption and the most well-balanced elastic modulus-impact strength relation in contrast to the other evaluated samples.

**PLA/TPU Blends Fracture Surface Morphology**

Figure 3 shows the SEM micrographs of the fracture surface of non-compatibilized and compatibilized PLA/TPU blends. The PLA/TPU blends were considered as heterogeneous and EBG was considered as an efficient compatibilization agent for PLA/TPU blends, verified by the good adherence of TPU particles into the PLA matrix, as previously reported. The PLA/TPU blends exhibited a morphology called “sea-island,” in which the TPU droplets are dispersed in the PLA matrix, regardless of the TPU presence or the content of EBG. Yazdaninia et al., in their study of PLA–TPU blends reinforced with trifluoropropyl-substituted polyhedral oligomeric silsesquioxane (POSS), also identified this morphology when 30%TPU was incorporated into the PLA matrix. The PLA/TPU blends micrographs showed that the TPU particles were well adhered into the PLA matrix, as verified by the reduction of the TPU particle pull-out degree as the EBG content increased. The comparison of the surface fractures of noncompatibilized and compatibilized PLA/TPU blends showed that all the blends exhibited the “sea-island” morphology regardless of EBG content, indicating the compatibilization of the PLA/TPU blends did not induce the formation of a co-continuous morphology. A similar result was reported by Kang et al., while studying the effect of ethylene-butyl acrylate-glycidyl methacrylate (EBAGMA) compatibilization agent on the morphology of PLA-polyplopropylene (PP) blends, in which increasing the EBAGMA content from 0 to 10% in the PLA/PP (70/30) blend reduced the PP particle size.

The particle size ($d_p$) and particle distribution parameter ($\sigma$) of the PLA/TPU blends are displayed in Table VI. As expected from a good compatibilization agent, the increase in EBG content in PLA/TPU blends implicated in the reduction of TPU particle size, especially for the PLAST-7E blend. A possible explanation for the reduction of TPU particle size could be attributed to the EBG reducing the interfacial tension of PLA/TPU, resulting in the formation of smaller TPU particles, as already reported. However, this modification was also affected by EBG content. PLAST and PLAST-2E micrographs exhibited very similar TPU particle size and particle distribution, suggesting that the EBG presence barely influenced the reduction of the TPU particle size. On the other hand, PLAST-5E and PLAST-7E micrographs...
showed a significant decrease in TPU particle size, indicating that both blends are expected to show the highest impact absorption.

**PLA and PLA/TPU Blends' Mechanical Behavior**

The PLA and PLA/TPU blends tensile stress versus strain curves, as well as the correlation elongation at break–chain entanglement density are illustrated in Figure 4(a,b), respectively. According to Figure 4(a), PLA exhibited a high elastic modulus (2.2 GPa) and low deformation at break (5.1%) (as listed in Table VII), as well as the presence of the yielding point, which diverged from the reported by Bedő et al.'s investigation about PLA/TPU blends.

TPU incorporation drastically improved the PLA deformation at break (from 5.1 to 53.7%). This modification caused by TPU could be attributed to the combination of an increased chain entanglement density (in contrast to neat PLA) and to the strong PLA—TPU intermolecular interaction (as seen in the PLA—TPU interfacial tension and Girifalco—Good interaction parameter in Table III). However, the presence of TPU also reduced PLA elastic modulus from 2.2 GPa to 1.8 GPa (nearly 20%), resulting in a large decrease of both PLA tensile strength (nearly 48%) and tensile load at break (nearly 75%). The reduction of these properties could be explained by the difference between the PLA and TPU mechanical behavior under tensile load. This hypothesis was based on Jing et al.'s research about the mechanical behavior and morphology of PLA/TPU blends, in which it was observed that the lower TPU tensile strength (compared to neat PLA) was responsible for reducing the PLA/TPU blend's tensile strength.

The influence of EBG on the tensile behavior of PLA/TPU blends was affected by the EBG content used. For example, the PLA/TPU blends elastic modulus values (Table VII) suggested that the presence of EBG itself was more prominent for this property than the EBG content. On the other hand, EBG was responsible for a larger improvement in both impact absorption and resistance of PLA/TPU blends, as seen by the higher yielding strength, tensile strength, and tensile load at break values of compatibilized PLA/TPU blends in comparison with the PLA3T blend, especially for PLA/TPU blends with EBG content above 2.5%. These modifications could be attributed to a stronger PLA/TPU interface promoted by EBG due to an increase in EBG content in PLA/TPU blend. This hypothesis was...
also supported by the study of Simões et al. about the interface adhesion in fluence on the polymer blend mechanical behavior using the Nicolais–Narkis (related to K parameter) model. According to these authors, the interphase adhesion occurs when K is smaller than 1.21. Based on their investigation, EBG has successfully improved both the PLA/TPU interface adhesion and the stress-transferring process by reducing the K values of the PLA/TPU blends, especially for PLA3T-5E and PLA3T-7E blends (Table VII). Regard to the yielding point of PLA/TPU blends, the PLA/TPU blend yielding point was shifted to higher stress and strain values after the compatibilization by EBG above 2.5% EBG [see the magnification in Figure 4(a)]. The EBG content, however, did not influence both yielding stress and yielding strain values for PLA3T-5E and PLA3T-7E blends, as corroborated by ANOVA analysis result in Table VII. This result was also similar to the reported by Fourati et al. study about compatibilized PBAT/TPS blends, in which the content of maleic anhydride or citric acid barely affected the mechanical behavior of PBAT/TPS blends.

Figure 4(b) illustrates the correlation between elongation at break and entanglement density of the PLA and PLA/TPU blends. It can be seen that both the PLA elongation at break and chain entanglement were drastically increased after the addition of TPU, which could be attributed to a higher viscosity of the PLA/TPU blend, in contrast to neat PLA, combined with a stronger intermolecular interaction between PLA and TPU macromolecules. The use of EBG compatibilization agent reduced PLA/TPU blends elongation at break as the percentage of EBG increased, despite EBG having improved the PLA/TPU interfacial adhesion. A similar trend was identified by Lin et al.’s investigation about PLA/TPU blends compatibilized with ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA). According to these authors, increasing E-MA-GMA content from 0 to 20% in PLA/TPU blends also reduced the elongation at break ~500% (PLA/TPU 90/10 blend) to ~ 450% (PLA/TPU/E-BA-GMA 70/10/20 blend). The reduction in deformation at break promoted by EBG could be attributed to the increase of PLA/TPU blends entanglement density after the addition of EBG, resulting in a lower chain length bond deformation due to the stronger intermolecular interaction between PLA-EBG-TPU chains.

The correlation of PLA/TPU blends impact strength and interparticle distance is shown in Figure 5. The presence of TPU improved the PLA impact absorption by approximately 160% (from 1.9 to 5.3 kJ m⁻²), which could be attributed to the combination of well-dispersed TPU particles over the PLA matrix (as seen by the PLA/TPU blend SEM micrograph in Figure 3) and to the low PLA–TPU interfacial tension (Table III), as already reported in our previous article. An analogous result was reported by Zhao et al.’s investigation about PLA/TPU blend’s mechanical properties, in which the PLA impact strength was increased from 3.1 to 54.2 kJ m⁻² after addition of 20 wt %.

### Table VII. PLA/TPU Blends’ Main Tensile Properties Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic modulus (GPa)</th>
<th>Yielding strain (%)</th>
<th>Yielding strength (MPa)</th>
<th>Tension strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tension load at break (MPa)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>2.2 ± 0.2</td>
<td>4.4 ± 0.6</td>
<td>67.0 ± 3.4</td>
<td>69.0 ± 3.0</td>
<td>5.1 ± 0.4</td>
<td>60.0 ± 5.7</td>
<td>-</td>
</tr>
<tr>
<td>PLA3T</td>
<td>1.8 ± 0.0a</td>
<td>2.8 ± 0.1a</td>
<td>35.6 ± 0.5a</td>
<td>35.6 ± 0.5a</td>
<td>53.7 ± 0.8a</td>
<td>14.8 ± 1.1a</td>
<td>1.1</td>
</tr>
<tr>
<td>PLA3T-2E</td>
<td>1.6 ± 0.0b</td>
<td>4.1 ± 0.3b</td>
<td>39.8 ± 3.4b</td>
<td>39.8 ± 3.4b</td>
<td>44.3 ± 1.2b</td>
<td>23.0 ± 1.3b</td>
<td>0.9</td>
</tr>
<tr>
<td>PLA3T-5E</td>
<td>1.4 ± 0.1c</td>
<td>4.7 ± 0.4c</td>
<td>49.4 ± 3.0c</td>
<td>49.4 ± 3.0c</td>
<td>27.6 ± 1.0c</td>
<td>24.7 ± 1.9b</td>
<td>0.6</td>
</tr>
<tr>
<td>PLA3T-7E</td>
<td>1.4 ± 0.0c</td>
<td>4.8 ± 0.2c</td>
<td>48.7 ± 1.6b</td>
<td>48.7 ± 1.6b</td>
<td>20.2 ± 1.6d</td>
<td>22.9 ± 1.2b</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Means with different superscript letters in the same column exhibited significant difference (p-value < 5%).
Impact strength and interparticle distance versus EBG content in PLA3T-E blends.

The PLA/TPU blends impact absorption was improved as the EBG content increased, especially for the PLA3T-7E blend. A similar trend was also reported by Ma et al. in their evaluation of poly(ethylene terephthalate) (PET)/ethylene-methyl acrylate-glycidyl methacrylate random terpolymer (E-MA-GMA) blends compatibilized by PET grafted with methyl acrylate (PET-g-PMA). The authors fixed the E-MA-GMA content at 20 wt % while varying both PET-g-PMA contents. The increase of PET-g-PMA fraction up to 10% improved the PET/E-MA-GMA blend impact strength from 14.7 to near 19 kJ m⁻². The improvement in PLA/TPU blend’s impact strength, promoted by EBG, could be explained by the combination of a decreased TPU interparticle distance as the EBG content increased (Table VI), resulting in smaller, well-dispersed, TPU particles [Figures 3(b)-(d)], and an increased PLA–TPU interfacial thickness promoted by the EBG presence (as seen in interfacial thickness values in Table III), which would imply a more efficient stress-transferring process. Moreover, p-test analysis revealed that only PLA3T and PLA3T-2E blends did not exhibit a significant difference in comparison with all PLA/TPU-EBG blends.

According to the Wu toughness criterion, a polymer blend undergoes the brittle–ductile transition (BDT) when its interparticle distance (ID) is equal to the critical interparticle distance (IDc). Furthermore, in the condition of the polymer blend ID being smaller than IDc, it is said that this polymer blend is considered tough. In the case of the PLA matrix, IDPLA is 1.0 μm, based on Anderson et al. Figure 5 showed that the BDT for the PLA/TPU blends occurred when no EBG compatibilizer agent was added into PLA/TPU blends, once IDPLA3T blend = IDc. However, the increase in the EBG fraction only resulted in the toughening of PLA/TPU blends for EBG contents greater than 2.5% EBG. The PLA3T-7E blend exhibited the lowest interparticle distance and the highest impact absorption, confirming the previous tendency observed in PLA/TPU blends SEM micrographs [Figures 3(a–d)], in which the decrease of TPU particle size and the improvement of TPU dispersion over PLA matrix would contribute to better impact absorption.

CONCLUSIONS

The interfacial and viscoelastic properties of PLA/TPU blends with and without EBG were investigated, and both properties were used to analyze and to predict the thermal and mechanical behaviors of PLA/TPU blends. The evaluation of interfacial properties of PLA/TPU blends components indicated that EBG has successfully modified and improved PLA/TPU interface, which was corroborated by the increase of PLA/TPU interfacial thickness. The DSC analyses showed EBG did not influence PLA Tg location, regardless of EBG content used. PLA/TPU blends cold crystallization temperature range were barely affected by the EBG used, which indicated EBG did not act as a plasticizer for PLA chains. The PLA/TPU blends ΔHm values were changed as EBG content increased, suggesting EBG might have acted as a nucleating agent during the PLA crystallization process only in low content (2.5%EBG).

The PLA/TPU blends viscoelastic properties measured by storage modulus versus temperature and tan δ versus temperature curves indicated PLA/TPU domains could have achieved a low-degree of miscibility in the presence of EBG. The PLA entanglement density increased after adding TPU, and this property largely increased after the compatibilization of PLA/TPU, which was attributed to the stronger intermolecular interaction between PLA-EBG-TPU chains.

The PLA/TPU blends SEM micrographs revealed the TPU particles were well dispersed and well adhered into the PLA matrix. In addition to that, as EBG fraction increased in PLA3T-E blends, the TPU particle size was decreased and a finer TPU particle morphology was observed. The similarity of TPU particle size values in the PLA3T and PLA3T-2E SEM micrographs indicated that a low EBG content could have been not effective to improve the toughness of PLA/TPU blends.

According to the Wu toughening criteria, the PLA/TPU blends’ BDT was observed in the PLA3T blend. The compatibilized PLA/TPU blends were only considered toughened above 2.5% EBG, indicating that lower EBG contents were not effective for improving PLA/TPU toughness. The PLA/TPU blends impact strength were increased as more EBG was added, especially for the PLA3T-7E blend. There was no significant difference between PLA3T and PLA3T-2E blends, which could have been also attributed to the combination of low EBG content employed and by the similarity of TPU particle size values in both PLA3T and PLA3T-2E blends.

The PLA/TPU blends elastic moduli were barely modified by the presence of EBG. EBG presence has improved PLA/TPU blend yield stress and confirmed the improvement of PLA/TPU energy absorption seen in Izod impact strength values. However, the deformation at break of PLA/TPU blends was reduced as EBG content increased, which was explained by the increase in PLA/TPU blend’s entanglement density.

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REFERENCES