Evaluation of the Poly (Lactic Acid) and Calcium Carbonate Effects on the Mechanical and Morphological Properties in PBAT Blends and Composites

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Abstract
In this study, the effect of the organic (poly(lactic acid)) and the inorganic (calcium carbonate (CaCO₃)) fillers were evaluated in mechanical, thermal, morphological and surface properties of the poly(butylene adipate-co-terephthalate) (PBAT) matrix. Mechanical results showed that the fillers have an influence on the PBAT matrix. The use of CaCO₃ showed higher elongation at break than PLA. However, the blends showed higher elastic modulus, resulting in greater stiffness to the PBAT matrix. Both fillers thermally destabilized the matrix. The morphological properties showed a uniform dispersion of the fillers in the composites and blends, however it is weaker with PLA. Because the PBAT matrix surface is, intrinsically, hydrophobic, the composites presented a smaller degree of hydrophobicity, while the PLA makes the blends hydrophilic.

Keywords: poly(butylene-adipato-co-terefalato), poly(lactic acid), PBAT/PLA blends, CaCO₃, composites.

1. Introduction

Concern over the amount of solid waste generated in the last decades has significantly increased research in biodegradable materials field to reduce impacts worldwide in the most different areas such as packaging, films and medical applications including orthopedic devices, tissue engineering, and wound management [1-9]. Poly (butylene adipate-co-terephthalate) (PBAT) is an aliphatic-aromatic biodegradable copolyester commercialized under the tradename Ecoflex® by BASF that exhibits high toughness and biodegradability [2]. PBAT is used as a biodegradable packaging material due to thermoplastic and fully biodegradable properties, low water vapor permeability, and good processing properties suitable for preparation of packaging films, compost bags, and agricultural mulching films [10]. PBAT has been widely used also in the production of blown films and its associated membrane products [9]. Concerning the preparation processes, PBAT films can be prepared using casting methods, extrusion-casting, extrusion blowing and thermocompression. Despite extrusion is the preferred method for industrial production of films, thermocompression is also a simple method for production of films without use of a solvent [10]. Nevertheless, PBAT has a limited use because it is expensive compared with others commercial polymers. To overcome such problems, blending PBAT with other biodegradable polymers or add inorganic fillers can minimize these limitations. PLA (poly (lactic acid)) appears to be one of the most attractive polymers to promote economic advantages besides exhibits some interesting features to make it appropriate for PBAT blends. In general, studies show that the PBAT is usually add in PLA matrix in the range of 5 to 25 wt. % in order to obtain toughened PLA and film processability, besides to improve performance properties such as impact strength, flexibility, gas barrier properties, and thermal stability [2,9,11-16].

In recent studies involving PBAT /PLA blends show that the PLA is the minor phase dispersed within the continuous PBAT phase are rare but allow identifying several advantages [17-19]. First, the introduction of PLA could reduce the consumption of non-renewable resources. Moreover, PLA component and its hydrolytic degradation products efficiently catalyze the hydrolytic degradation of PBAT, which allows accelerating the biodegradability of material [19, 20]. In their study, Li et al. [21] analyzed the dynamic rheological behavior and morphology of PLA/PBAT blends with various composition ratios. They concluded that when the PBAT content was lower than 20 wt. % or when exceeded 70 wt%, the morphology of the blend featured small droplets suspended in the continuous phase with the size of the dispersed particles was small, and their distribution was relatively uniform. When the PBAT content was increased from 20 to 50 wt. %, the blend system became heterogeneous, and a co-continuous phase structure was formed when the PBAT content was at 50 wt.%. Otherwise for reducing the price of PBAT and making it economically viable it is filled with natural materials e.g. natural fiber, calcium carbonate (CaCO₃), or another...
inorganic or organic fillers, that has lower cost than PBAT. Thus, the objective of this work was to investigate the effects of PLA, compared with CaCO₃, on mechanical and morphological properties of PBAT matrix.

2. Experimental

The poly (butylene adipate-co-terephthalate) (PBAT) was produced and supplied by BASF with a weight average molecular weight of 66,500 g.mol⁻¹. The poly (lactic acid) (PLA) produced by Ingeo, 3800 rpm). The CaCO₃ PA was supplied by Proquimios with molecular weight of 100,19 g.mol⁻¹. PBAT and PLA were dried at 50°C in a vacuum oven for 12 h before preparation of the formulations. The neat polymer and their composites were prepared according to the compositions of Table 1 using a quick K-Mixer homogenizer (MH - 50hIR) with controls for temperature, time and rotation speeds (low and high: 2000 rpm and 3000 rpm).

The samples were compression molded into sheets at 190°C and 6 MPa for 5 min using a hot compression molding machine. The hot compression molded samples were subsequently cooled down to room temperature under ambient atmosphere. Then, the test specimens were prepared from sheets using counter-cut.

The elastic modulus (E), ultimate tensile strength (σₘₐₓ) and elongation at break (εₘₐₓ) were determined using a universal testing machine (Instron S/A Ind. e Com. Ltda.) at 50 mm/min with 500 kgf (ASTM D638). Thermal degradation behavior was performed in a Mettler Toledo TGA module TGA/SDTA851e with N₂ from 20°C to 800°C at 10°C/min.

Contact angle (CA) test was performed using a Dynamic contact angle tensiometer (DCAT) with three phases (air/water/sample) to determine the static contact angle (θₛₐₜ) and dynamic contact angle (θ₅₀) using the Young-Laplace equation with droplets of 4.00 μl during 300 s. The data, obtained in triplicate, were evaluated by the Bluehill and Origin-8 programs [22].

Field emission-scanning electronic microscopy (FE-SEM) images of the composites and blends samples were recorded on a JEOL-JSM-6701F microscope with an accelerating voltage of 1-30 kV, using EDS Thermo-Scientific mod. Noran System Six software, in carbon sputtered samples kV.

3. Results and Discussion

3.1 Tensile properties

Table 2 and Figure 1 (a) shows the mean values and their respective standard deviations of the elastic modulus (E), ultimate tensile strength (σₘₐₓ) and elongation at break (εₘₐₓ) for all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E (MPa)</th>
<th>σₘₐₓ (MPa)</th>
<th>εₘₐₓ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBAT</td>
<td>51.0±1.6</td>
<td>25.1±1.2</td>
<td>1269.3±147.6</td>
</tr>
<tr>
<td>PBAT/CaCO₃ 80/20</td>
<td>68.2±3.1</td>
<td>18.2±0.6</td>
<td>914.4±11.9</td>
</tr>
<tr>
<td>PBAT/CaCO₃ 70/30</td>
<td>77.0±2.4</td>
<td>12.1±0.3</td>
<td>427.4±47.4</td>
</tr>
<tr>
<td>PBAT/PLA 80/20</td>
<td>71.8±2.7</td>
<td>13.9±0.8</td>
<td>609.3±99.0</td>
</tr>
<tr>
<td>PBAT/PLA 70/30</td>
<td>93.5±2.3</td>
<td>9.0±0.2</td>
<td>183.1±40.9</td>
</tr>
<tr>
<td>PLA</td>
<td>2068.0±27.7</td>
<td>58.1±1.6</td>
<td>6.4±0.6</td>
</tr>
</tbody>
</table>

As CaCO₃ content was increased of 20 and 30 wt.%, Young’s modulus of the composites increased in 33.7 and 51%, respectively, comparing with PBAT matrix. This is due the addition of rigid filler to the polymeric matrix, that consequently decreased the tensile strength and elongation at break. The increase in the stiffness of the samples justifies the reduction of the elongation at break. On the other hand, probably the reduction of the tensile strength was attributed to the poor adhesion of CaCO₃, especially at higher CaCO₃ content as shown in Fig. 3 (c) and (e) [23].
The addition of PLA, which is a brittle polymer, results in an increase of the E in 40.8 and 83 % for the addition of 20 and 30 wt. %, respectively. It was an expected behavior since PLA is a polymer with high tensile strength (58.1 MPa) [18]. With increasing PLA content, there is a tendency to enhance the size of the rigid phase, which restricts matrix mobility and makes the mixture heterogeneous and incompatible as can be seen in Fig. 3(d) and (f). As a result, the interaction between PLA and PBAT is poor [21].

Considering that CaCO$_3$ is salt, with ionic character, it could promote more interaction with the polar groups of the PBAT. This interaction may justify that the “inorganic filler” was better dispersed in the PBAT than the PLA (“organic filler”), which can be observed in the photomicrographs in Fig.3 (c) and (e). These Figures show that the “inorganic filler” has a smaller size than the “organic filler” (PLA) (Fig 3 (d) and (f)). The influence of the size of the fillers could alter the mobility restriction. The smaller particle sizes result in lower interference in the entanglement of PBAT chains. This may explain that the elongation at break values of the PBAT/CaCO$_3$ composites were higher than the PBAT/PLA blends. Besides, the ultimate tensile strength was higher for the composites with “inorganic filler” than for the “organic filler”.

Concerning the elastic modulus, the PBAT/PLA composites show higher values, probably because the PLA is a polymer with a high elastic modulus (2068.0 MPa), resulting in greater stiffness to the polymer matrix.

3.2 TGA Analysis

The thermal stability of the samples was studied by TGA. Figure 2 (a) and (b) show the TG and DTG curves, respectively, for the PBAT, PLA, and their composites and blends. The thermal degradation curves of PBAT and PLA samples present a decomposition process in one step. Regarding the blends PBAT/PLA 80/20 and 70/30, a two-step decomposition process occurred due to the different thermal resistance of PBAT and PLA, where the first decomposition step, between 306-352°C, corresponded to the decomposition of PBAT. This indicates that the compatibility between PLA and PBAT was poor, which is consistent with the results of morphological observation (See Fig. 3 (d) and (f)). From the raw data the decomposition temperature for 10% mass loss ($T_{10\%}$) and onset degradation temperature (corresponding to the crossover of tangents drawn on both sides of the decomposition trace) ($T_{onset}$) decrease when CaCO$_3$ and PLA were added. It is evident that CaCO$_3$ and PLA thermally destabilize PBAT, so it might be concluded that the PBAT/CaCO$_3$ and PBAT/PLA interfaces are the possible weak points of the composites. Besides, the non-uniform dispersion of the “inorganic filler” in the composites and the PLA rigid phase (organic filler) in the blends changes the diffusion pathway of degradation products of PBAT and affects the thermal stability [24].
3.3 Field Emission Scanning Electron Microscopy (FE-SEM)

FE-SEM micrographs of the cryofractured surfaces of PBAT, PLA, PBAT/CaCO$_3$ composites and PBAT/PLA blends are shown in Fig. 3 (a)-(f). The PBAT matrix presented plastic deformation on the surface Fig. 3 (a). After adding CaCO$_3$ or PLA into PBAT, many droplets/spheres were found in the PBAT matrix, which is very common in two-phase systems with largely different melt viscosities [23, 25]. These results indicated that the composites were a kind of immiscible two-phase system [26]. That was also observed, more pronounced, in blends. Moreover, the sizes of phase-separated CaCO$_3$ or PLA increased significantly with increasing minor phase content [27,28], which can explain the mechanical properties.

3.4 Contact angle (CA)

The CA value is usually used as an indicator of surface hydrophilicity or hydrophobicity of polymers. Table 3 shows the results for CA for neat PBAT, neat PLA, PBAT/CaCO$_3$ composites and PBAT/PLA blends.

Table 3. CA and water adhesion tension ($\tau^0$) results for neat PBAT, neat PLA, PBAT/CaCO$_3$ 80/20, PBAT/CaCO$_3$ 70/30, PBAT/PLA 80/20 and PBAT/PLA 70/30.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CA (°)</th>
<th>$\tau^0$ (dyn/cm)</th>
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<tbody>
<tr>
<td>PBAT</td>
<td>73.4±2.4</td>
<td>20.8</td>
</tr>
<tr>
<td>PBAT/CaCO$_3$ 80/20</td>
<td>65.8±2.7</td>
<td>29.8</td>
</tr>
<tr>
<td>PBAT/CaCO$_3$ 70/30</td>
<td>68.6±1.8</td>
<td>26.6</td>
</tr>
<tr>
<td>PBAT/PLA 80/20</td>
<td>60.5±1.4</td>
<td>35.8</td>
</tr>
<tr>
<td>PBAT/PLA 70/30</td>
<td>64.9±1.7</td>
<td>30.8</td>
</tr>
<tr>
<td>PLA</td>
<td>71.2±1.2</td>
<td>23.4</td>
</tr>
</tbody>
</table>

According to Li et al., the contact angle for PBAT films was in the range of 68.9-72.9°, depending on the preparation method [10]. A surface is considered as hydrophobic when the CA is greater than 65° [30]. Based on these criteria, both neat PBAT and neat PLA could be considered as hydrophobic. With the addition of CaCO$_3$ there was a decrease in the CA, and when the carbonate content is increased, the CA increases. It should be noted that, for all these samples, the degree of hydrophobicity was not high. However, the addition of PLA to the PBAT matrix decreases the CA and, consequently making the blends hydrophilic, but higher the PLA content, higher the contact angle.

One way of solving this problem is the incorporation of compatibilizer agents, which improve interfacial adhesion by decreasing the surface tension between the phases. Many additives have been used to improve thermal stability as well as to work as compatibilizers in polymer blends or composites. They promote the formation of copolymers during compounding in the molten state that work as physical compatibilizers by reducing the size of the dispersed phase in the matrix [12-14, 18, 25, 27, 29].

The interphase is well defined in the blend and composites, which is indicative of low adhesion between the PBAT matrix and PLA or CaCO$_3$ [23]. The stiffness of the PBAT matrix can be improved with the addition of CaCO$_3$ or PLA as reinforcing agents. However, their compatibility is poorer for PLA than carbonate [29] (see Fig. 3 (e) and (f)). Besides, this result confirms the lower properties obtained in the composites and blends studied. In this way, it can be stated that it is essential to have good interface adhesion and compatibility between the phases to obtain satisfactory properties.

One way of solving this problem is the incorporation of compatibilizer agents, which improve interfacial adhesion by decreasing the surface tension between the phases. Many additives have been used to improve thermal stability as well as to work as compatibilizers in polymer blends or composites. They promote the formation of copolymers during compounding in the molten state that work as physical compatibilizers by reducing the size of the dispersed phase in the matrix [12-14, 18, 25, 27, 29].
matrix, the $\tau^p$ increased and made the blends surface hydrophilic, because $\tau^p$ is 35.8 and 30.8 dyn/cm, for PBAT/PLA 80/20 and PBAT/PLA 70/30, respectively.

4. Conclusions

The tensile properties results showed that as CaCO$_3$ content was increased of 20 and 30 wt.%, Young’s modulus of the composites increased in 33.7 and 51%, respectively. The addition of PLA, which is a rigid polymer, results in an increase of 40.8 and 83% for the addition of 20 and 30 wt.%, respectively, comparing with PBAT matrix. However, the tensile strength and elongation at break decreased more to the blends PBAT/PLA than to the composites PBAT/CaCO$_3$. Its occurs because CaCO$_3$ (inorganic filler) was best dispersed than PLA (organic filler). This would promote lower mobility restriction, considering that better dispersed particle result in smaller interference in the entanglement and consequently, its affects the thermal stability. Besides, the micrographs show the low adhesion and immiscibility between the PBAT matrix and CaCO$_3$. This behavior is more pronounced in PLA. Besides, the non-uniform dispersion of the fillers in the composites and blends changes the diffusion pathway of degradation products of PBAT and consequently, its affects the thermal stability. Besides, the micrographs show the low adhesion and immiscibility between the PBAT matrix and the dispersed phase, whether PLA. This is also observed for carbonate, however, in lesser intensity. This result confirms the lower properties obtained in the blends and composites studied. Both materials are good alternatives to increase the stiffness of the material and to reduce the cost, being that the CaCO$_3$ stands out for its low cost.

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References


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