Effect of organoclay and corn straw on the properties of poly (butylene adipate-co-terephthalate) (PBAT) hybrid composites

Efeito da argila organofílica e palha de milho nas propriedades de compósitos híbridos de poli (butilen adipato-co-tereftalato) (PBAT)

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Abstract
The packaging industry requires permeable materials capable of offering freshness of the packaging content. The use of fillers can enhance these permeable properties to the polymeric material. This work investigates the effect of incorporating different fillers (organophilic clay and corn straw) on the rheological, mechanical, permeability, water absorption and

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biodegradability characteristics of poly (butylene adipate-co-terephthalate) (PBAT) processed in an internal laboratory mixer. Extruded films and specimens injection molded were produced. The results of torque rheometry suggest polymer matrix degradation during processing slightly increase, also evidenced by MFR results. Composite films showed a drop in tensile strength, higher stiffness and lower elongation. Incorporation of the fillers in the PBAT matrix enhanced the permeability to oxygen gas of the produced films. The presence of fillers significantly increased the capacity of water absorption. The incorporation of C20A and, mainly, CS tends to accelerate the biodegradation of PBAT. Adding small amounts of organoclay C20A and CS to PBAT leads to a material that combines maintenance or improvement of biodegradation combined with higher permeability to oxygen, which indicates the potential use of these systems in packaging industry for maintenance of freshness of content.

**Keywords**: PBAT. Organophilic Clay. Corn Straw. Biodegradability. Permeability.

**Resumo**
A indústria de embalagens requer materiais permeáveis capazes de oferecer frescor ao conteúdo. O uso de cargas pode melhorar a permeação do material polimérico. Este trabalho investiga o efeito da incorporação de diferentes cargas (argila organofílica e palha de milho) nas propriedades reológicas, mecânicas, permeabilidade, absorção de água e biodegradabilidade do poli (butilenio adipato-co-tereftalato) (PBAT) processado em um misturador interno de laboratório. Filmes extrusados e corpos de prova moldados por injeção foram produzidos. Os resultados de reometria de torque sugerem um discreto aumento da degradação da matriz polimérica durante o processamento, evidenciada pelos resultados de índice de fluidez. Os filmes compósitos apresentaram uma queda da resistência à tração, enrijecimento, e menor alongamento. A incorporação das cargas ao PBAT aumentou a permeação ao gás oxigênio. A presença das cargas aumentou significativamente a capacidade de absorção de água. A incorporação da argila C20A, principalmente, e da palha de milho tende a acelerar a biodegradação do PBAT. A adição de pequenas quantidades de C20A e palha de milho ao PBAT leva a um material que combina a manutenção ou melhoria da biodegradação, combinado com uma maior permeabilidade ao oxigênio, que indica o uso potencial deste compósito híbrido na produção de embalagens que requerem a passage de ar para o seu interior, na busca de manter o frescor do conteúdo acondicionado.

Introduction

The search for environmentally correct polymeric materials becomes a choice that meets the needs of the current generation, but that guarantees the integrity of the ecosystem in the future, and biodegradables polymers are able to degrade in relatively short times compared to conventional polymers generally used in packaging (Silva et al., 2022). One of these polymers is poly (butylene adipate co-terephthalate) (PBAT), synthetic, biodegradable, flexible, thermally stable and with high elongation at break, being widely used in packaging films (Nóbrega et al., 2013; Bardi et al., 2014; Mondal et al., 2015; Almeida et al., 2016).

Composites using nanoparticulate organophilic clays that interact at the nanometric scale with the polymeric matrix are materials that normally generate products with high mechanical, thermal and barrier properties, at low loading levels. Therefore, the development and use of nanocomposites having biodegradable polymers as a matrix, stable during processing, is one of the ways to expand the applications of these materials and contribute to their use in a more environmentally correct way (Fukushima et al., 2012; Almeida et al., 2016; Falcão et al., 2017; Bettio et al., 2012).

The use of vegetable fiber residues in biodegradable polymer matrix composites tends to reduce the pollution caused by these products when discarded in the environment. In addition, they produce lighter parts that are safer to handle, as these fibers do not form sharp edges when broken, are low cost, are non-toxic, have lower density and cause less wear and tear on conventional polymer processing equipment than synthetic fibers. Another relevant aspect is that they are products from a renewable source, considering that their production depends on the energy of sunlight (Sanyang et al., 2016; Rubio-López et al., 2017). Corn straw is one of the main agricultural products of Brazil. It is a vegetal fiber composed mainly of cellulose, lignin and hemicellulose, with relatively high modulus and tensile strength, used as reinforcement in composites and demonstrating its potential for industrial use (Guimarães et al., 2010).

Hybrid composites formed by combined use of corn straw and organophilic clay, forming hybrid PBAT composites are an option to optimize the performance of composites, associated to biodegradation. The use of these materials makes the reduction of costs achieved through the use of natural fibers, as reinforcement, in polymeric composites, more easily obtained. Hybrid thermoplastic polymeric composites are important to research, exploring its potential and possible industrial application.
The aim of this work is to innovate in the development of biodegradable PBAT composites using organophilic clay and corn straw vegetable fiber as fillers and, in this way, to evaluate the effect of different types and contents of fillers on the structure, permeability, rheological, mechanical properties, water absorption and biodegradability of these composites, and thus collaborate with the development of new materials from PBAT, expanding the opportunities for applying these materials, and contributing to reducing the negative impacts of these materials when discarded in the environment.

**Methodology**

The polymeric matrix employed was poly (butylene adipate co-terephthalate) (PBAT), trade name ECOFLEX® FC1200 supplied by BASF (Germany), density of 1.25-1.27 g/cm³ at room temperature, with a melt flow rate of 2.7-4.9 dg/min (ISO 1133, 190 ºC/2.16 kg), melting point between 110 and 120ºC, according to the manufacturer (Yamamoto et al., 2002; Perez et al., 2008). The chemical structure of PBAT is shown below in Figure 1.

![Chemical structure of PBAT](image)

**Figure 1 – Chemical structure of PBAT.**
Source: From the authors (2023).

The organoclay used was Cloisite®20A (C20A) purchased from Southern Clay Products (USA). It is a natural layered silicate (montmorillonite) with cation exchange capacity 0.95 meq/g, modified with quaternary ammonium salt with two long-chain (C₁₆ to C₁₈) aliphatic residues. It has a basal interplanar distance of 2.42 nm and a density of 1.72 g/cm³, average particle diameter of 8.2 µm, with particles ranging in size from 1.7 to 15.7 µm (Falcão et al., 2017).

Corn straw (CS) collected from Campina Grande/PB (Brazil) was used as lignocellulosic vegetable filler, without pre-processing. The true density of the filler is 1.157 ± 0.06, measured with hexane in a pycnometer at ambient temperature (Reul et al., 2018).

Samples with 1, 3 and 5% organoclay and hybrid systems with 2, 6 and 10% organoclay and corn straw content (by weight 1:1) were prepared in a Haake Rheomix 3000 laboratory internal mixer, fitted with high-intensity (roller type) rotors. The processing chamber wall was kept at a constant temperature of 160ºC and the fill factor was estimated at
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70%. The mixer was operated at 60 rpm for 10 min. Samples of the neat PBAT matrix were also processed to provide a baseline for comparison. The compounds were ground and fed to a 16 mm bench scale single screw extruder Lab-16 Chill-Roll from AX Plásticos (Brazil) with a flat die, operating at 180°C and 45 rpm, to prepare films for further characterization. Film thickness between 80 and 189 µm was measured for the different compounds. The materials processed in the internal mixer were injection molded in a Yizumi (Alfamach) A5 equipment operated at 150/170/170/170/170°C in its heating zones, with cooling time of 50 seconds and mold temperature of 20°C. Type I tensile test specimens according to ASTM D638 standard were obtained.

The melt flow rate (MFR) of the extruded samples was determined according to ASTM D 1238 at 180 °C with weight 2.16 kg. The films were analyzed by optical microscopy to measure the degree of dispersion with a LED Digilab optical microscope operating in transmission mode and 50× magnification. Permeability to oxygen and carbon dioxide gases were measured at 25°C in a GPD-C Brugger instrument according to ASTM D 1434 e ISO 15105/1 standards. Tensile tests were done according to ASTM D 882-02 and D 638, using an Instron EMIC 2320 machine with a 5 kN load cell operating at 50 mm/min constant rate of extension at ambient temperature. Samples were weighed on an analytical balance and placed in an oven at 80°C for 24 hours to determine the moisture content, and to observe the influence of particulate and fibrous loads on water absorption in films and specimens. Water absorption analyzes were performed gravimetrically, in duplicate, with samples cut from injection molded tensile, with all side surfaces sealed by hot cutting. The samples were immersed in distilled water, and weighted weekly to determine sample mass increase as a function of time. Biodegradation was performed by burial in soil prepared with manually mixed fertile soil and sand (1:3). Biodegradation testing was conducted in an incubator operating at 23-29°C with air and soil relative humidity kept at 80% and 50%, respectively.

Results and Discussion

3.1 Torque Rheometry

Temperature inside the processing chamber (T) and total torque (Z) were measured as a function of time (t) during compounding in the internal mixer. Results are presented in Figures 2 and 3.
Figures 2 and 3 indicate that, after 4 minutes of processing, the matrix is substantially molten. Torque changes due to increasing degree of dispersion (if any) are negligible during the final stage of melt processing, identified here as the last two minutes inside chamber (8 to 10 min processing time). Since at constant rotor speed torque is directly proportional melt viscosity at this stage, decrease of torque with time may be attributed to increases in melt temperature and decreases in molar mass of the polymer due to degradation during processing (Canedo, 2017). A drop in the temperature is observed up to 2 min of processing, associated with the introduction of inputs into the processing chamber.
According to Canedo (2017), the relative rate of change of the adjusted torque is considered as a measure of the degradation rate. Temperature effects on the viscosity (that is, on torque) may be eliminated by adjusting the torque to a constant reference temperature ($T^*$):

$$Z^* = Z \exp\{\beta(T - T^*)\}$$  

Where

$Z^*$ is the adjusted torque and $\beta$ is the exponential temperature coefficient of the viscosity, taken here as 0.020°C$^{-1}$ (Costa et al., 2015). Table 1 presents the calculated parameters in the final interval of processing (8-10 min) at 160°C. These include, respectively, the average temperature and adjusted torque in that range ($\bar{T}$ and $\bar{Z}$*) and two versions of the degradation rate: the relative rate of reduction of the adjusted torque ($R_Z$) and the relative rate of reduction of weight average molar mass ($R_M$), evaluated according to the procedure described to Canedo (2017).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{T}$ (°C)</th>
<th>$\bar{Z}^*$ (Nm)</th>
<th>-$R_Z$ (min$^{-1}$)</th>
<th>-$R_M$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBAT</td>
<td>177.11 ± 0.13</td>
<td>43.84 ± 0.23</td>
<td>0.008</td>
<td>0.002</td>
</tr>
<tr>
<td>PBAT/1%C20A</td>
<td>178.98 ± 0.22</td>
<td>42.85 ± 0.27</td>
<td>0.011</td>
<td>0.003</td>
</tr>
<tr>
<td>PBAT/3%C20A</td>
<td>176.88 ± 0.06</td>
<td>33.33 ± 0.36</td>
<td>0.019</td>
<td>0.005</td>
</tr>
<tr>
<td>PBAT/5%C20A</td>
<td>176.72 ± 0.06</td>
<td>30.89 ± 0.55</td>
<td>0.031</td>
<td>0.009</td>
</tr>
<tr>
<td>PBAT/1%C20A/1%CS</td>
<td>175.86 ± 0.38</td>
<td>33.33 ± 0.32</td>
<td>0.014</td>
<td>0.004</td>
</tr>
<tr>
<td>PBAT/3%C20A/3%CS</td>
<td>174.59 ± 0.34</td>
<td>30.41 ± 0.04</td>
<td>0.023</td>
<td>0.006</td>
</tr>
<tr>
<td>PBAT/5%C20A/5%CS</td>
<td>172.80 ± 0.18</td>
<td>27.41 ± 0.52</td>
<td>0.030</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Table 1 – Torque rheometry parameters during the final stage (8-10 min)

Source: From the authors (2023).

The data indicate an increase in the degradation rate as the clay content increases from 0% (neat matrix) to 5% of C20A and that the increase in the degradation rate becomes more pronounced as corn straw was added to these compositions. These changes in rates are attributed to the increase in matrix degradation due to the presence of fillers (C20A and CS). The same can be observed in the rate of change in weight average molar mass.

Figure 4 shows that the average torque set in the final processing stage is directly proportional to the viscosity.
In general, the viscosity of composite materials increases markedly with the concentration of solid particles (Shenoy, 2013; Santos et al., 2019). However, the results show that the viscosity of the neat PBAT is higher than that of the PBAT/C20A nanocomposites, that is, the introduction of the filler, contrary to expectations, caused a reduction in the viscosity of the system. This behavior is attributed to the degradation of the matrix caused by the incorporation of the filler and that this effect surpassed the predicted increase in viscosity. The viscosity of the compounds with clay and corn straw also decreased as the percentage of fiber increased, also an unexpected behavior.

According to Almeida et al. (2016), a possible explanation for this fact is based on the instability of the matrix, as the PBAT degrades during processing and the degradation is affected by the type and concentration of the filling material. All observed trends are consistent with the preceding analysis of the rate of degradation. The presence of the filler contributed to increase the degradation of the matrix, reducing its viscosity and this effect was enough to overcome the increase that would be expected due to the presence of solid particles suspended in the molten polymer.

In the present case, a slight increase of the rate of degradation is observed (Table 1) as the clay content or corn straw increases from 0% (neat matrix) to 5%. However, the rates are low and degradation under processing may be disregarded in first approximation. Similar results have been observed in the literature (Reul et al., 2018; Falcão et al., 2017; Almeida et al., 2016).
3.2 Melt Flow Rate (MFR)

Figure 5 shows the MFR results obtained for neat PBAT and PBAT/C20A and PBAT/C20A/CS composites.

![Melt Flow Rate (MFR) for neat PBAT and PBAT/C20A and PBAT/C20A/CS composites.](source: From the authors (2023).

It is evident that the melt flow rate of the systems decreased with the addition of clay. The viscosity of the systems increased with the incorporated filler content. This result was expected, since the incorporation of rigid loads increases the viscosity of the systems. Surprisingly, the incorporation of 1% of corn straw to the systems containing clay, raised its flow index when the expected would be a reduction in this value. A possible explanation for this behavior is that the introduction of corn straw favored matrix degradation, resulting in a higher system flow index. The lowest MFR value occurred in composites with the highest filler content, that is, the one containing 5% clay and 5% corn straw. The results obtained for the melt flow rate of the matrix were considerably different from those reported by the manufacturer (2.7 – 4.9 g/10 min). The melt index value found for neat PBAT was approximately 22 g/10 min, which represents a value six times greater than that provided by the manufacturer. This pronounced increase in the value found is attributed to the degradation suffered by the polymer during processing and also during storage, which reduced the viscosity of the PBAT, and directly affected the properties of the material, since it contributed to the degradation of the polymeric matrix. These results corroborate those found in the study of torque rheometry.
3.3 Optical Microscopy (MO)

Figures 6 to 11 show optical micrographs of films prepared from PBAT/C20A and PBAT/C20A/CS compounds processed in the extruder and injection machine, taken at 50× magnification.

![Figure 6](image1)

**Figure 6** – Optical microphotographs of PBAT/1%C20A (50×) processed in the extruder (left) and injection machine (right).
Source: From the authors (2023).

![Figure 7](image2)

**Figure 7** – Optical microphotographs of PBAT/3%C20A (50×) processed in the extruder (left) and injection machine (right).
Source: From the authors (2023).

![Figure 8](image3)

**Figure 8** – Optical microphotographs of PBAT/5%C20A (50×) processed in the extruder (left) and injection machine (right).
Source: From the authors (2023).
The images reveal relatively well-distributed charge particles. Significantly larger and elongated particles were found in the corn straw composites.

In microphotographs 6 to 8, the surfaces of the extruded films show a rougher surface when compared to the injected specimens, and this roughness tends to increase in the films as the clay content increases.
Rough surfaces and non-uniform morphologies and the presence of defects in their structure are observed in samples of hybrid composites (Figures 9 to 11), which may be associated with humidity absorption and formation of agglomerates by parts of corn straw fibers.

C20A clay and corn straw are different fillers and the morphological difference is preserved in the composites. These morphological differences, together with chemical differences, perhaps related to the incipient load degradation, may be responsible for the greater effect of corn straw on the increase of PBAT degradation, when compared to organophilic clay.

3.4 Permeability

Permeability to oxygen measured at 25°C for the neat PBAT and PBAT composite films with 1, 3 and 5% C20A and CS is plotted in Figure 12.

The data indicate that the permeability of the PBAT films to oxygen gas increased with the incorporation and content of clay and corn straw, being greater for the PBAT film containing only 5% clay and 3% clay and corn straw in its composition. It was not possible to calculate the permeability for the PBAT/5%C20A/5%CS due to the non-uniformity of the film obtained, as well as the presence of pores, which facilitate the passage of gas.

Generally, the presence and concentration of inert fillers reduces the permeability of films. Falcão et al. (2017) evaluated properties of PBAT/clay composites and found that the
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The barrier properties are sensitive to the interface compatibility of the inorganic and organic phases. An incompatibility in this interface can lead to the creation of micro empty spaces that allow greater permeation between the constituents, due to the increase in the volumetric fraction of the charge. Furthermore, the barrier properties are dependent on the particle size and dispersion of the clays (Avérous & Pollet, 2012). When it comes to semicrystalline polymers, some factors can influence the permeation process, for example, size and shape of crystallites, crystalline structure and degree of crystallinity. It is attributed that crystallites consist of the impermeable phase for gaseous molecules, so that diffusion occurs only in the amorphous phase of the matrix (Morales et al., 2010).

Thus, the results indicate a probable bad interaction of the charges, both clay and corn straw, in the PBAT matrix, presenting a possible incompatibility at the interface and, consequently, an increase in gas diffusion through the films. Such results agree with the analysis of the mechanical properties of these films, where it was possible to perceive that the increase in the filler content in the polymeric matrix resulted in a loss of these properties.

Oxygen is the main component causing oxidation and initiates several undesirable changes in food such as color, taste, odor and nutrient deterioration. Films providing an adequate oxygen barrier can help improve food quality and increase shelf life (Falcão et al., 2017). The results indicate that the composites under study may not have efficient barrier properties for application in food packaging and protective coatings, for example, but may be indicated for permeable packaging that favors the freshness of some vegetables and meats.

3.5 Tensile Properties

Tensile properties for PBAT, PBAT/C20A and PBAT/C20A/CS compounds of films are shown Figure 13.
Figure 13 - Tensile strength (a) and modulus (b) and elongation at break (c) of neat PBAT and C20A and C20A/CS composites of films.
Source: From the authors (2023).

The results indicate that the mechanical properties of the PBAT films were affected by the incorporation of clay and corn straw. Figure 13a shows that there was no significant reduction in the tensile strength for the systems with the addition of 3% and 5% of clay, when compared to the neat PBAT film. The addition of 1% of C20A increased the maximum stress value, indicating that the clay acted as a reinforcer, since the nanoclay used in the preparation of the nanocomposites is organophilic and it is expected that a better interaction between polymer and clay will be established, in addition to small amounts of clay favor its dispersion and exfoliation in the matrix, better transferring tensions. For hybrid systems with addition of clay and corn straw, it was observed that the incorporation of corn straw fibers to the nanocomposites significantly reduced the tensile strength of the systems, which can be associated with poor dispersion and poor adhesion of the fiber to the matrix, reducing the fiber/polymer matrix interaction.

The tensile modulus of the composite films (Figure 13b) increased with the addition of clay at levels of 1 and 3%, which was expected, since the filler has a higher tensile modulus.
than the PBAT matrix and reduces the free movement of the chains of the polymer. However, the incorporation of 5% of C20A reduced the modulus, which may be associated with the formation of agglomerates and/or greater degradation of the matrix. In turn, the tensile modulus of composite films decreased with fiber content and was lower than that of all other compositions. It is believed that the reason for this behavior is the tendency for the fibers to agglomerate, which end up acting as stress concentrators in these regions, in addition to reducing the interaction of the polymer and clay interface at the agglomeration points.

The elongation of the films (Figure 13c) decreases in all systems compared to the PBAT matrix, as the fillers and fibers stiffened the polymeric matrix. The composition containing 1% clay did not show significant change regarding to the neat polymer. Ferreira et al. (1997) describe that elongation is a property extremely dependent on the interfacial adhesion between the present phases.

Tensile properties for PBAT, PBAT/C20A and PBAT/C20A/CS compounds of injection molded specimens are shown Figure 14.

![Graphs showing tensile strength, modulus, and elongation at break of neat PBAT and C20A and C20A/CS composites of injection molded specimens.](image)

*Figure 14 - Tensile strength (a) and modulus (b) and elongation at break (c) of neat PBAT and C20A and C20A/CS composites of injection molded specimens. Source: From the authors (2023).*
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The tensile strength results show that the clay incorporation of 3 and 5% increase in this property when compared to the neat matrix, indicating that all the loads used were reinforcing. The C20A is an organophilic clay and, therefore, it is expected that a good interaction will be established between the polymer and the clay, which can lead to the formation of exfoliated nanocomposites. For the systems with addition of clay and corn straw, it was observed that the introduction of fibers to the PBAT/C20A systems led to a slight loss in the maximum resistance of the material. The loss observed is considered insignificant. It is believed that this behavior is related to poor fiber/matrix adhesion and probable poor dispersion of corn straw in the polymeric matrix.

The tensile modulus of the specimens no vary significantly with filler content. PBAT/5%C20A/5%CS composition showed a significant increase, which was expected, since the filler and fiber have a higher elastic modulus than the PBAT matrix and its introduction reduces the free movement of the chains of the polymer. These results suggest that the introduction of filler and fiber stiffened the elastic phase of the composites.

The elongation at break of the specimens did not suffer significant alteration of this property in the nanocomposite with 1% of C20A and in the hybrid composite with 5% of C20A and 5% of corn straw in the PBAT matrix. In the other compositions, contrary to expectations, there was an increase in elongation, it is believed that this behavior is associated with the breakage of load agglomerates and sliding of clay lamellae.

Differences in the mechanical properties of composites of the same composition processed in the different forms studied are observed. Injection processing generated homogeneous samples with considerable mechanical resistance of the composites and nanocomposites, a result confirmed by the mechanical tensile test performed. This may be associated with the geometry of the specimen and the pressure/flow exerted during this process. The extrusion processing of the films generated more heterogeneous samples that, in general, showed loss of mechanical properties of the investigated systems. It is believed that the extruder used (benchtop) and the processing conditions adopted were not sufficient to disperse the loads well in the polymeric matrix. In addition, the nominal values of modulus and stress in films are subject to greater experimental uncertainties due to inconsistencies in the determination of the actual dimensions of the samples and variations in thickness with the introduction of the load. The most correct would be to compare the properties of films of the same thickness. However, with the introduction of fillers, this is only achieved by changing the extrusion conditions which, in turn, can significantly change the orientation and crystallinity of the films.
3.6 Humidity Content

Humidity content was measured with the objective of observing the influence of particulate and fibrous loads on water absorption in films and specimens, mainly because humidity causes hydrolytic degradation of the polymeric resin, resulting in loss of physical properties and making it difficult to processing (Das et al., 2000). Table 2 presents the moisture values of neat PBAT, composites and hybrids produced.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Humidity (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Films</td>
<td>Specimen</td>
<td></td>
</tr>
<tr>
<td>PBAT</td>
<td>0.56 ± 0.03</td>
<td>0.36 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>PBAT/1%C20A</td>
<td>0.87 ± 0.31</td>
<td>0.42 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>PBAT/3%C20A</td>
<td>1.06 ± 0.03</td>
<td>0.45 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>PBAT/5%C20A</td>
<td>1.75 ± 0.33</td>
<td>0.48 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>PBAT/1%C20A/1%CS</td>
<td>1.83 ± 0.25</td>
<td>0.50 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>PBAT/3%C20A/3%CS</td>
<td>2.22 ± 0.02</td>
<td>0.66 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>PBAT/5%C20A/5%CS</td>
<td>3.26 ± 0.02</td>
<td>0.82 ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 – Humidity content for PBAT and composites.
Source: From the authors (2023).

In all cases, moisture content increased with clay and clay/fiber content, which is associated with the hygroscopic character of both clay and lignocellulosic fiber. The incorporation of fillers increases the water absorption capacity of the material when compared to the isolated matrix. The hydroxyls present in hemicellulose are considered to be primarily responsible for water absorption, although non-crystalline cellulose and lignin also play an important role in this process. Moisture swells the cell wall of the lignocellulosic fiber until it is saturated with water. Then, the water starts to occupy the free spaces between the bundles of fibers and change their dimensions. Moisture is higher in films than in injected parts, which is related to the exposed surface and the area/volume ratio. The films have a small thickness and therefore have higher humidity than the injected compound whose relative surface becomes smaller than that of the film (Das et al., 2000; Moura et al., 2014).

3.7 Water Absorption

Table 3 shows the results obtained for water absorption as a function of time of neat PBAT, composites and hybrids produced.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hours)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>PBAT</td>
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<td>0.0280</td>
<td>0.0420</td>
<td>0.0490</td>
<td>0.0840</td>
</tr>
</tbody>
</table>

Revista Gestão e Secretariado (GeSec), São Paulo, SP, v. 14, n. 7, 2023, p. 11309-11332.
Effect of organoclay and corn straw on the properties of poly (butylene adipate-co-terephthalate) (PBAT) hybrid composites

Table 3 – Water absorption (%) for PBAT and composites.
Source: From the authors (2023).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Water Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBAT/1%C20A</td>
<td>0.0000</td>
</tr>
<tr>
<td>PBAT/3%C20A</td>
<td>0.0000</td>
</tr>
<tr>
<td>PBAT/5%C20A</td>
<td>0.0000</td>
</tr>
<tr>
<td>PBAT/1%C20A/1%CS</td>
<td>0.0000</td>
</tr>
<tr>
<td>PBAT/3%C20A/3%CS</td>
<td>0.0000</td>
</tr>
<tr>
<td>PBAT/5%C20A/5%CS</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Water absorption is rapid in the initial stages (in the first 5 hours), tending to decrease for longer exposure times until saturation is reached. Figure 15 shows the variation in percentage of water absorption after 4 weeks of the study.

Samples of specimens of the PBAT/5%C20A/5%CS hybrid composite and the PBAT/5%C20A composite showed a higher rate of water absorption, which can be explained by the hydrophilic character of the fillers used. The results indicate that the higher the percentage of added load, the greater the tendency for water absorption in the samples. The hybrid composites showed greater water absorption capacity due to the synergy of the two hydrophilic materials in the composition, clay and corn straw (Ming et al., 2021; Sousa et al., 2021). Same behavior was found for humidity content.

3.8 Biodegradation

Figure 16 shows the results of mass variation for the biodegraded samples studied.
Effect of organoclay and corn straw on the properties of poly (butylene adipate-co-terephthalate) (PBAT) hybrid composites

Figure 16 – Mass variation as a function of biodegradation time of neat PBAT and compounds. Source: From the authors (2023).

Neat PBAT samples have their weight slightly increased (up to about 1%) during the first 20 days, probably due to the absorption of water from the moist soil. The mass begins to decrease slowly, and after 140 days the samples have a weight 3.44% and 1.76% lower than the initial dry injection molded samples and films, respectively. Moraes Filho (2020) obtained a mass variation of 33% in neat PBAT samples, after 168 days of burial in soil. Other authors obtained a mass loss of PBAT of 49 to 62% after submitting the films to UV aging, around 5 weeks, as well as a mineralization of 18% of the PBAT films after 182 days in soil (Falcão et al., 2017; Souza et al., 2019). However, in a study carried out by Falcão et al. (2019), on the influence of the filler content in PBAT/organophilic clay nanocomposite films, it was found that the mass loss of the films was 1.23% for neat PBAT, after 14 weeks of incubation. Although discreet, considering the study time, it is noted that the neat polymer undergoes biodegradation. Higher mass loss value of neat PBAT found by other authors may be associated with matrix degradation during storage.

The composites PBAT/C20A and PBAT/C20A/CS also exhibit weight gain (0.2 to 7%) during the initial stage. After 20 and 60 days the samples containing PBAT/C20A/CS and PBAT/C20A, respectively, begin to lose mass. After 140 days, the PBAT/C20A composites weigh 0.7% less than the initial dry samples, while the PBAT/C20A/CS composites lose 6 to 8% of their initial mass. Losses in corn straw composites are greater than in composites containing only organophilic clay, which acted by slowing up the biodegradation of the neat matrix, since they became about 79.6% less biodegradable when compared to neat PBAT, which presented 3.44% of biodegradation, in the same incubation period, for the specimens, and 1.76% for films. Such results corroborate the data obtained by Falcão et al. (2017), where a loss of 1.57% in weight, for PBAT/5%clay film samples, after 14 weeks of burial in simulated soil, was observed.
For composites incorporated with clay and corn straw, a mass loss of around 6.84% and 3.47% was observed for specimens and films, respectively, after 6 weeks of burial in soil. These results show an increase in the biodegradation of these systems, when compared to the neat PBAT, being about 100.3% more biodegradable than the neat polymer. Fernandes et al. (2013), studied the biodegradation of Polyester/starch/corn straw composites and obtained a maximum loss of 56.92% in weight, for polyester/10% corn straw composites, after 15 weeks of burial in simulated soil. Paiva et al. (2015) evaluated the biodegradability of polyester/corn straw composites and, after 4 weeks of incubation, obtained losses of 43.6% for composites with 10% straw. It was thus found that all samples are susceptible to microbial attack and that the addition of corn straw accelerates the mass loss of polymer when in the soil, under the evaluated conditions.

Visual observation of the samples (Figure 17) shows color changes, roughness surface, fissures and deterioration, which indicate degradation, more evident in hybrid composites. In view of the slight degradation of the neat matrix, the mass loss observed in the composites can be attributed to the biodegradation of the filler. Similar results have been published in the scientific literature (Falcão et al., 2019).

**Figure 17** – Visual appearance of the surface of neat PBAT samples and PBAT/C20A and PBAT/C20A/CS composites at different times of biodegradation.
Source: From the authors (2023).

**Conclusions**

The data obtained indicate that PBAT and PBAT/C20A and PBAT/C20A/CS composites are quite stable and minimally degrade during processing. The incorporation of more than 1% of C20A in the films weakened the PBAT. The effects could be improved, with
better processing of the fiber and/or use coupling agents, making it smaller in an attempt to synthesize more homogeneous films. Optimized results of the properties of the injected specimens of nanocomposites and hybrid composites were obtained with the incorporation of organophilic clay and corn straw in the PBAT matrix. The fillers are presented as excellent natural resources for the synthesis of the unprecedented hybrid material PBAT/C20A/CS and may possibly be used in commercial products. The addition of fillers increased O$_2$ gas permeation, which may make their use in food packaging and protective coatings unfeasible, but they may be indicated for permeable packaging that favors the freshness of some vegetables and meats. The formulation of the unprecedented hybrid compound showed relevance by increasing its biodegradation capacity in simulated soil, and may be a future alternative for replacing non-biodegradable synthetic polymers. The addition of small amounts of C20A and CS to PBAT is a useful material alternative that combines the improvement of O$_2$ gas permeation allied to the excellent biodegradation properties, having potential application in the packaging industry.

Acknowledgments

The authors thank to Federal University of Pernambuco (UFPE) for support and are grateful for the fellowships provided by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) in favor of Costa Júnior (PhD) and Almeida (PDJ#160909/2019-8).

References


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Submetido em: 19.06.2023
Aceito em: 18.07.2023