Synthesis of Polymeric Composites Reinforced with Unidirectional and Bidirectional Bamboo Fibers

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Abstract Due to environmental problems and exhaustion related to materials provided from non-renewable sources, the development of recycling technologies using residue as raw material has grown increasingly. Polypropylene (PP), a thermoplastic polymer, despite being easily recycled, presents a decrease in their mechanical properties after reprocessing cycles. In order to solve this problem, reinforcements may be added, producing a composite with better properties. The choosing of the dispersed phase aimed to consider, especially, its mechanical properties. Moreover, it was also considered the orientations of the incorporated fibers at the composite mechanical strength. In this scenario, a composite material of polymer matrix from recycled PP reinforced unidirectionally and bidirectionally with bamboo fibers were prepared. The fibers were treated with modifiers in order to increase the adhesion between polymer/fiber. The results showed that the use of reinforcement improves the mechanical properties of the polymer. Also, the superficial treatments were effective, indicating that there was an increase of the compatibility between the materials. It can be also inferred that the orientation of the fibers has directly influence at the final properties of the composite.

Keywords Recycled Polypropylene, Bamboo Fibers, Reinforcement Orientation, Polymeric Composites, Surface Modifiers

1. Introduction

Polymers are formed by macromolecules constituted by the repetition of short chemical units called monomers [1]. Conventionally, polymers are prepared from petroleum fractions, non-renewable and not biodegradable source, contributing a lot for the residues generation. Therefore, researchers and industry have been seeking alternatives to minimize the impacts caused by improper and exaggerated disposal of these materials. Thus, the reuse and recycling are presented as management strategies of these residues, also involving the deployment of industrial ecology, which means that nothing is residue, but a raw material for a new product [2, 3]. In addition, other aspects motivate these processes, such as economy of energy (the manufacturing of recycled plastic saves about 70% of energy), of financial (reduction of expenses with cleaning and public health) and environmental (reduction with the recovery of impacted areas, such as rivers and lakes) [4].

According to surveys conducted in major Brazilian cities, the recycling of plastics remains slow due to the lack of selective waste collection associated with an efficient waste sorting. The main polymers found in these urban residues are high and low density polyethylene (HDPE and LDPE), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC) and polypropylene (PP) [4, 5].

The PP is a polymer synthesized from propylene monomer. It is a colorless material with excellent mechanical properties related to its crystallinity. The atactic PP, with all methyl groups allocated irregularly along the chain, is the most used in the market [6, 7]. This polymer is a semi-rigid, translucent, with a good mechanical, electrical, thermal and chemical strength, etc. [6, 8]. Furthermore, because it is a thermoplastic, the PP has a great usability and can be formed easily, that is, a widely recyclable material. However, the recycling of polymers causes depletion of its mechanical properties because it increases the amount of defects. These did not significantly interfere with mechanical behavior until the maximum force was reached. From this point, where the propagation of cracks has a great influence on the deformation until the rupture, the defects were determinants in the deformation [8, 9]. This problem can be solved with the mixture of the virgin and recycled PP, which has yielded good results [9], or with the addition of reinforcements in polymer matrix. This method aims to increase the mechanical strength of materials, resulting in composite materials with wide applicability.

There are numerous materials used as reinforcement of composites, among them the fibrous one deserve attention. The fibers are effective means for reinforce due to its low thickness, tending thus to provide fewer defects that may
induce failures and its resistance tends to be equal to the theoretical material strength [10]. In addition of enhancing the composites mechanical properties, the use of natural fibers stands out due to environmental, technological, social and economic issues [11]. They may be of animal, vegetable or mineral origin. The vegetable fibers are natural composites, consisting of cellulose fibers incorporated into a matrix of lignin. Therefore, they are also known as lignocellulosic fibers. They have low cost; are soft and non-abrasive; are flexible; have low densities; are recyclable, non-toxic and biodegradable; have low energy consumption in their production; and do not emit carbon dioxide (CO₂), instead, their photosynthesis process consumes CO₂ from the air [10, 12, 13].

Bamboo is a plant that, compared to materials used in construction, such as steel, concrete and wood, has good mechanical strength (particularly tensile strength) combined with high hardness and lightness, and presents easy reforestation and a great planting area per amount of material [14, 15]. The disadvantage of the bamboo fibers (BF) uses is concentrated in their low compatibility with polymer matrices, resulting in a vulnerable and a short life composite [12]. However, studies have been developed with the aim of finding efficient surface modifiers that reach the superficial chemical structure of the fibers, inserting chemical groups or removing some constituents, such as waxes, pectin and lignin [16].

Face of this context and of the data presented, composites of recycled PP reinforced with unidirectionally and bidirectionally oriented BF were developed. Its mechanical properties were evaluated in order to identify the best combination of surface modifier and fiber orientation.

2. Materials and Methods

2.1. Materials

Virgin polypropylene (PP) and recycled polypropylene (PPr), mechanically recycled from virgin material, was prepared and provided by Plastsan Plásticos do Nordeste LTDA. The polymers were provided in the form of granules without the presence of additives.

Bamboo fibers (BF) were obtained from some clumps present at Federal University of Ceará (UFC). Their culms were measured, sized and sawed for internodes extraction. Their culms are woody, hollow and present the fibers arranged in the form of bundles. From each sized region, consecutive internodes were removed and their walls were laminated longitudinally by hands. The defibration was performed in the internodes closer to the husk, where there are more visible fibers. The removed fibers have 200 mm of length and 0.5 mm, approximately, of diameter.

The surface modifiers used for removal of waxes, lignin, pectin and other undesirable constituents present in BF were Sodium Hydroxide (NaOH), Sodium Hypochlorite (NaClO), Sulfuric Acid (H₂SO₄), Acetic Acid (CH₃COOH), Acetic Anhydride ((CH₃CO)₂O) and deionized water. They were all provided by Laboratory of Products and Processes Technology (LPT) of Federal University of Ceará/Brazil (UFC).

2.2. Processing of PP and PPr Specimens

In order to characterize the raw material base, a PP and PPr specimens were prepared. Considering the density of PP (0.905 g/cm³), it was weighed a sufficient amount to prepare a specimen with 260 mm x 80 mm x 4 mm. The material in form of pellets was dispersed in a metallic mold (it was designed for processing these materials) and heated to 180 °C. With the complete polymer melting, the apparatus was closed and the heat flow stayed continuous a few minutes and then began to decrease. The next step was introducing a constant pressure (2.5 to 3.5 bar) until the complete apparatus cooling. The processing of PP and PPr specimens occurred at Laboratory of Mechanic of Fracture and Fatigue (LAMEFF) of UFC.

2.3. Chemical Treatment of BF

The treatment of fibers consisted in two parts: mercerization and acetylation. Mercerization has the purpose of removing part of lignin, waxes and sugars. This chemical treatment exposes the internal fibrillar structure of the fiber, increasing their surface area and thus increasing the roughness of the surface, which promotes the mechanical anchoring of the fiber by the matrix. Acetylation has the purpose of introducing non-polar groups in bamboo fiber, providing greater adherence with the polymer matrices that are non-polar.

Initially, the fibers were pretreated by immersing in deionized water and heating to 80 °C for 30 min.

The next step, mercerization, consisted in immersing the wet fibers in aqueous solution of NaOH 5% (w/v) under 60-65 °C for 1 h. After this, the fibers were washed several times until close to neutral pH, being subjected to the acetylation process.

This constituted in a chemical treatment with a solution consisting of 1.5 g (CH₂CO)₂, 1.0 g of CH₃COOH 0.2% (w/v) and 7 drops of H₂SO₄ for each 250 mL of solution. The fibers were totally immersed in the solution at 100 °C for 1 h. After the reaction, the fibers were continuously washed until pH closer to neutral, and then they were dried at 100°C for 30 min.

The mercerized and acetylated BF was named, respectively, as BFM and BFA. The treatments were performed at Laboratory of Mechanic of Fracture and Fatigue (LAMEFF) of UFC.

2.4. Composite Processing

Six specimens were prepared:
The first four were performed by dispersing the recycled polymer at the metallic mold and heated to 180ºC. With the complete fusion of the polymer, the fibers were placed at 0º (unidirectionally and longitudinally) and others at 90º (unidirectionally and transversally) under the molten PPr layer, and they were pressed manually until adhered to the matrix. The apparatus was closed and the heat flow stayed continuous a few minutes and then began to decrease, introducing a constant pressure, 2.5 to 3.5 bar, in order to make the matrix penetrates between the fibers. This compression was maintained until the complete cooling of the apparatus.

The last two were prepared by dispersing one part of the recycled polymer at the metallic mold and heated to 180 ºC. With the complete fusion of the polymer, part of the fibers was placed at 0º (longitudinally) under the molten PPr layer, and they were pressed again until adhered to the matrix. Another part of the fibers was now arranged at 90 º (transversally) under the second molten PPr layer. They were pressed again until adhered to the matrix. The apparatus was closed and the heat flow stayed continuous a few minutes and then began to decrease, introducing a constant pressure, 2.5 to 3.5 bar, in order to make the matrix penetrates between the fibers. This compression was maintained until the complete cooling of the apparatus.

Figure 1 shows one illustration of the composite performed.

Approximately 20% (v/v) of fibers were incorporated into the composites.

The processing of composites occurred at Laboratory of Mechanic of Fracture and Fatigue (LAMEFF) of UFC.

2.5. Characterization

2.5.1. Microstructure Morphology

The fibers morphology characterization was performed using a scanning electron microscope (SEM), model S-3400N Hitachi with a vacuum of 15.0 kV at Laboratory of Mechanic and Technology (LMT) of University of Paris-Saclay/France (UPS). Samples were metallized before the analyses.

The fibers morphology characterization was performed using a scanning electron microscope (SEM), model S-3400N Hitachi with a vacuum of 15.0 kV at Laboratory of Mechanic of Fatigue (LAMEFF) of UFC.

2.5.2. Mechanical Behavior

Tensile tests were carried out to control displacements and deformations to characterize the real mechanical behavior of produced materials.

The standards used to characterize the mechanical behavior of the polymeric materials were ASTM D638 and D3039 [17, 18]. The first standard was used for the matrix specimens and the second one was used for the composites specimens. The test speed was 2 mm/min.

The tests were conducted in an EMIC testing machine (100 series). The testing temperature was 298 K (25 ºC) and the relative air humidity was between 70 and 80%.

The composites mechanical characterization was performed at National Service of Industrial Learning/Brazil (SENAI/CE).
3. Results and Discussions

Figure 2 illustrates SEM micrographies from mercerized (BFM) and acetylated bamboo fibers (BFA). For BFM, cementing substances (lignin and hemicellulose) were partial removed, influencing the modification around the surface layer. Which favors the exposure of microfibrils (indentations) and globular traits (protrusions) promotes a long-lasting effect on their mechanical properties and facilitates the impregnation with polymeric matrix, improving, this way, the composite useful life. For BFA, the fiber presented an aspect more porous, which is consistent with the performed reaction which promotes the stabilization of the cell walls, improving dimensional stability and environmental degradation.

The maximum tensile strength ($\sigma_m$, for matrix, and $\sigma_c$, for composite) was determined as the maximum stress before the rupture. Young’s modulus was determined in the elastic linear phase of the stress-strain curve. Table 1 summarizes the main results of the PP and PPr specimens’ tensile tests.

According to these results, both tensile strength and Young’s modulus of PPr decreased when compared with the PP. This corroborates the hypothesis that recycled polymers, due to the recycling cycle and recycling selection itself, present a decrease in their mechanical properties.

Table 2 summarizes the mechanical results of the polymeric composites performed. As it is presented, the addition of BF to PPr matrix actually promotes a strengthening of its mechanical properties when in a longitudinal configuration (or in same direction of the applied force). This can be explained by the transfer capacity of the efforts in the matrix to the reinforcement, such that we can observe increases in the maximum stress in PPr composites performed with fibers oriented in 0° and in 0° and 90°.

As said before, considering the unidirectional and longitudinal composites (PPr_BFM_0 and PPr_BFA_0), the tensile strength results showed that the fibers properly reinforced the recycled polymeric matrix (increase of 255% and 291%, respectively), providing even better results than the ones obtained for the virgin polymer without reinforcement (increase of 22% and 34%, respectively). However, taking in account the unidirectional and transversal composites (PPr_BFM_90 and PPr_BFA_90), the mechanical properties presented a decrease.

These results can be understood by the “mixture law”, an empirical relation that represents the composite system constituted by two phases [19, 20]. The system consisted of the composites reinforced unidirectionally and longitudinally follows the Parallel model (Voigt model), that imposes uniform strain conditions, Eq. (1):

$$ E_c = E_f \cdot V_f + E_m \cdot V_m $$

Where $E$ and $V$ are the Young’s modulus and the volume fraction, respectively, and $c$, $f$ and $m$ are the indices corresponding to composite, fiber and matrix. Thus, we can find a greater value for this modulus and, this way, also greater value for tensile strength.

However, for the composite system consisting of two phases with continuous reinforcements oriented in the transverse direction follows the Serial model (Reuss model), that imposes uniform stress conditions, Eq. (2):

$$ 1/E_c = (V_f / E_f) + (V_m / E_m) $$

This way, for the same $E_f$ and $V_f$ in both cases, the mechanical property resultant ($E_c$) is expected to be greater than $E_m$ in Eq. 1, but it is expected to be smaller in Eq. 2.

For the composites reinforced bidirectionally with part oriented in the direction of the request and part in perpendicular direction, the mechanical properties remain between the two extreme mixture models, the Voigt model (upper limit) and the Reuss model (limit below), resulting in mechanical values between the both results.

About the treatment, the both performed great results
promoting better adherence between fiber and matrix, even resulting in similar data. This way, aiming fewer steps, the better treatment, in the case of using PPr as matrix and BF as reinforcement, was mercerization.

Table 1. Uniaxial tensile test results of virgin (PP) and recycled (PPr) polypropylene specimens.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\sigma_m) (MPa)</th>
<th>(E_m) (GPa)</th>
</tr>
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<tbody>
<tr>
<td>PP</td>
<td>26.8 ± 4.5</td>
<td>1.39 ± 0.14</td>
</tr>
<tr>
<td>PPr</td>
<td>9.2 ± 2.0</td>
<td>1.47 ± 0.19</td>
</tr>
</tbody>
</table>

Table 2. Uniaxial tensile test results of the polymeric composites specimens.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\sigma_c) (MPa)</th>
<th>(E_c) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPr_BFM_0</td>
<td>32.7 ± 7.0</td>
<td>3.4 ± 0.3</td>
</tr>
<tr>
<td>PPr_BFM_90</td>
<td>5.5 ± 0.8</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>PPr_BFM_090</td>
<td>20.0 ± 11.2</td>
<td>1.3 ± 0.2</td>
</tr>
<tr>
<td>PPr_BFA_0</td>
<td>36.0 ± 10.0</td>
<td>6.9 ± 1.0</td>
</tr>
<tr>
<td>PPr_BFA_90</td>
<td>8.3 ± 1.3</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>PPr_BFA_090</td>
<td>34.6 ± 4.0</td>
<td>0.6 ± 0.1</td>
</tr>
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4. Conclusions

After all the processes of composites preparation and performance of the tests, clear results could be observed.

According to tensile tests, as it was expected, the matrix showed an increase of the maximum stress at rupture with the addition of bamboo fibers when compared to unreinforced polymer. Furthermore, there is also an improvement of the composites mechanical properties when the fibers are mercerized and acetylated, because, as explained above, these treatments promotes a chemical modification in the fiber surface, making them more compatible with the polymeric matrix, which promotes a better adhesion.

With this, in the case of the reinforcements unidirectionally and longitudinally oriented, the phases function as a unit, obtaining a compound with superior performance and properties to those of their individual components. In the case with the reinforcements bidirectionally oriented, the compound presents a medium performance, because its behavior stays between systems which corresponds a unit and a system that corresponds a less than that, as explained above.

This way, the treated BF orientated unidirectionally and longitudinally presented itself as an alternative to reinforce and to improve the mechanical resistance of recycled polymeric matrix in general.

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