Estudio de la influencia de tratamientos superficiales en papel kraft para la compatibilización con polímeros termoplásticos

La industria de los transportes ha estado presentando un conjunto de soluciones que integran las fibras naturales y su compatibilidad con materiales estructurales, como los polímeros. Sin embargo, es fundamental garantizar el cumplimiento de los requisitos mecánicos. Una de las razones principales que impulsa el uso de este tipo de fibras, en lugar de las fibras sintéticas, está relacionada con algunas tendencias recientes, como la reducción de peso, que está ligada con su menor densidad. Además, la reducción de peso también contribuye, indirectamente, a la sostenibilidad y la disminución de las emisiones de gases de efecto invernadero, ya que hace posible reducir el consumo de combustible de los transportes. Sin embargo, debido a las diferentes polaridades verificadas entre los polímeros termoplásticos apolares, como el polipropileno (PP), y las fibras naturales, como el papel kraft, se realizó un estudio del efecto de los tratamientos físicos y químicos de la superficie para verificar su influencia en las propiedades de la interfaz fibra-matriz.

El proceso físico, tratamiento de corona, se aplicó en el papel kraft con diferentes dosis de descarga, mientras que el tratamiento químico se realizó utilizando soluciones alcalinas con diferentes concentraciones de NaOH. Los resultados obtenidos de las pruebas realizadas muestran que los tratamientos con soluciones alcalinas mejoraron, hasta un 57%, las propiedades mecánicas de la resistencia a la tracción y el módulo de Young del material compuesto, comparativamente con las amostras que tuvieron tratamientos corona. Estos resultados inducen un aumento de la compatibilidad de la interfaz entre la matriz y el papel kraft.

Study of the influence of surface treatments in kraft paper for the compatibilization with thermoplastic polymers

The transports industry has been presenting a set of solutions that integrates natural fibers and their compatibility with structural materials, like polymers. However, it is fundamental to ensure the fulfillment of mechanical requirements. One of the main reasons that is driving the use of this type of fibers, instead of synthetic fibers, is related to some actual trends, such as weight reduction, which is linked with its lower density. Moreover, weight reduction also contributes, indirectly, to the sustainability and decrease of greenhouse gases emissions, since it makes possible to reduce the fuel consumption of transports. However, due to the different polarities verified between apolar thermoplastic polymers, such as polypropylene (PP), and natural fiber reinforcements, such as kraft paper, a study of the effect of physical and chemical surface treatments was carried out in order to verify their influence on the fiber-matrix interface properties.

The physical process, corona treatment, was applied in the kraft paper with different discharge dosages, while the chemical treatment was performed through the use of several alkali solutions with different concentrations of NaOH. The obtained results from the performed tests shows that the alkali solution treatments improved, up to 57%, the mechanical properties of tensile strength and Young Modulus of the composite material, comparatively with the effect of corona treatment on its surface. These results induce an increase of interface compatibility between the matrix and kraft paper.
1 Introduction

Natural fibers are increasingly used as reinforcement, rather than synthetic fibers, in polymer matrix composites. The growing interest in the use of this type of fibers as reinforcement in composites is mainly due to the fact that they are raw materials from renewable natural resources, having relatively high specific strength and modulus, low weight (low density) and low cost, being also biodegradable, comparing with synthetic fibers [1]. However, a great problem of natural fibers comes from the large amount of cellulose that they contain in their chemical structure, which makes the natural fibers are polar hydrophilic materials (trend to moisture absorption), while the polymers are apolar and hydrophobic (trend to not absorb moisture). These different characteristics between natural fibers and polymeric matrices make the compatibility between these two types of materials harder, resulting in composites that have low mechanical properties. The low mechanical properties of polymeric composites reinforced with natural fibers are a consequence of the weak adhesion that occurs at the fiber/matrix interface [2].

1.1 Fiber/matrix interface strength

The interfacial connection between fiber and polymer plays a vital role in the mechanical properties of composites. The stress that a compound is subject is transferred from the matrix to the fibers through their interface, so it’s essential that there is a good interfacial connection to obtain an optimized reinforcement.

However, in composites reinforced with natural fibers there is, generally, a limited interaction between the hydrophilic fibers and the matrices, which are typically hydrophobic, leading to a weak connection at the interface, which limits the mechanical performance, as well as decreases the resistance to moisture absorption, affecting their long-term properties. For a good connection at the interface, the fiber and the matrix must be in intimate contact, and the wettability can be considered as an essential precursor for this contact. Low wetting of fibers results in interfacial defects that can act as stress concentrators. It has already been shown in studies carried out previously that the wettability of fiber affects the tenacity, tensile and flexural resistances of composites. Then, surface treatments can improve the wettability of the fiber and thus improve interfacial strength [3].

1.2 Surface treatments

Several techniques have been tested to modify the surface of natural fibers, mainly to reduce their water absorption and improve their adhesion with polymeric matrices. To improve the adhesion between the matrix and the fiber, the surface of the fiber is modified through surface treatments, which is commonly done by physical or chemical methods that lead to the reduction of moisture gain, as well as changes in fiber surface.

1.2.1 Physical treatments

Physical treatments modify the structural and surface properties of the fiber and, therefore, affect the mechanical bond with the matrix. The physical methods involve surface fibrillation of the fiber through an electric discharge (plasma or corona). The plasma treatment offers a unique approach for the modification of the chemical and physical structures of both fibers and polymeric surfaces, without changing the characteristics of the resulting materials. Plasma treatment is mainly applied to the cleaning, sterilization and surface conditioning of films in the applications of food packaging. In fact, the hydrophilicity of the surface and the adhesion capacity of the films increase dramatically after plasma treatment, because polar groups are formed on the surface of the film [4].

The corona treatment is one of the most interesting techniques for the activation of surface oxidation. This treatment changes the energy of the surface in cellulosic fibers, which affects the resulting composites. The corona treatment modifies the composition of the surface and, therefore, the properties of the surface of the composites.

1.2.2 Chemical treatments

Chemical treatments are applied to natural fibers to improve fiber-matrix adhesion. The changes promoted in the natural fibers promotes the increase of the their wettability, originating a better impregnation of the polymer in the fibers. As a result, the moisture absorption by the composites in which natural fibers are used is indirectly reduced [5]. Most chemical modifications of natural fibers involve silanization, alkalization (mercerization), acetylation, cyanomethylation, benzoylation, isocyanate treatment, dewaxing, esterification, etherification and graft copolymerization. The chemical composition of these compounds allows them to react with the surface of the fiber, forming chemical bonds between the fiber and the matrix [6].

Alkali treatment or mercerization is one of the oldest, but more effective treatment in terms of costs, and, because of that, this is the most used chemical method to treat natural fibers. The efficiency of this treatment depends on the type and concentration of the alkaline solution, the treatment time and the used temperature. If the alkali concentration is greater than the optimum condition, excess delignification of the fiber may occur, resulting in the weakening or deterioration of the fiber. The alkalin treatment removes constituents of the fiber, including hemicellulose, lignin, pectin, grease and wax, which exposes the cellulose and increases the roughness and surface area of the fiber to provide interfacial connection. The development of a rough surface results in a better mechanical interconnection that promotes the improvement of fiber-matrix interfacial adhesion in the resulting composites [4].

2 Experimental

2.1 Materials

The sheets of kraft paper, with the grammage of 213 g.m⁻², were treated with two different types of surface treatments. Chemical treatments were carried out using alkali solutions with different concentrations of sodium hydroxide, while the physical treatment was carried out using a corona discharge, with different dosages of discharge.

The sheets of paper that were treated, as well as the control sample (without surface treatments), were impregnated with a thermoplastic polypropylene (PP) matrix in the form of a film.
2.2 Surface treatments

The kraft paper sheets were subjected to a physical treatment (corona) and a chemical treatment (mercerization).

2.2.1 Physical treatment

The two sheets that were used in this test were subjected to different test conditions, so the sample of the first corona treatment (C1) was treated with a power of 300 W at a speed of 5 m/min for 4 turns and with a discharge dose of 480 W min m\(^{-2}\). The sample of the second corona treatment (C2) was treated with a power of 300 W, at a speed of 5 m/min, for 17 turns and with a discharge dosage of 2040 W min m\(^{-2}\) [7].

After the tests were completed, the samples were removed and carefully stored in a dark opaque plastic bag, so that they were not in contact with any object and with UV rays, which would cause the loss of the effect that the corona treatment caused.

2.2.2 Chemical treatment

In the chemical treatment (mercerization) three sheets of kraft paper were treated, for which three aqueous solutions of sodium hydroxide (NaOH) were used with different concentrations, 1%, 3% and 5% w/w, one for each sheet [8].

The aqueous solution (with distilled water) was prepared with the respective concentration of NaOH (1%, 3% and 5% w/w) and this solution was placed in a metal tray where the sheet of kraft paper was emerged. The kraft paper sheet remained in the NaOH solution for 5 min, in order to improve the impregnation capacity. After 5 minutes, the kraft paper sheet was removed from the NaOH solution and rinsed abundantly with water, until the sheet was maintained with a pH slightly lower than 7, which was verified using strips of pH indicator paper.

2.3 Production of composites

After the surface treatments on the sheets of kraft paper, the compounds were produced with PP, in the form of a film. For this, a kraft sheet with dimensions of 300 x 300 mm was used, between two PP films, with the same dimensions of paper. The compounds were produced through the hot compression molding technique, using a hydraulic press, with the following processing conditions: 180℃ for 10 min at a pressure of 30 bar, followed by cooling to 60℃ at a pressure of 30 bar.

A total of six compounds were produced, Table 1, namely a reference sample (Ref) that did not have any treatment, two samples that had the corona treatment (C1 and C2) and three samples that had the alkaline treatment with aqueous solutions of NaOH, with 1% w/w (Alc 1%), 3% w/w (Alc 3%) and 5% w/w (Alc 5%).

<table>
<thead>
<tr>
<th>Composite</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>-</td>
</tr>
<tr>
<td>Alc 1%</td>
<td>Alkaline treatment with 1% w/w NaOH solution</td>
</tr>
<tr>
<td>Alc 3%</td>
<td>Alkaline treatment with 3% w/w NaOH solution</td>
</tr>
</tbody>
</table>

Table 1. Samples produced.

2.4 Tensile test

The six composites produced were subjected to tensile tests, in a universal dynamometer, according to EN ISO 527-4, at a speed of 5 mm min\(^{-1}\), with a distance between grips of 150 mm. The five specimens used for each sample have the following dimensions: L = 250 mm and W = 25 mm, where L is the length of the test pieces and W is their width. The thickness of the composites is approximately 2 mm, for each different sample type.

2.5 Scanning Electron Microscopy

In order to morphologically characterize the developed composites, Scanning Electron Microscopy (SEM) tests were carried out. In this test the differences observed in the impregnation of the polymer matrix in the different compounds were analyzed, depending on the type of treatment (alkaline or corona), applied in the kraft paper. These tests were performed with a high vacuum resolution of 1.8 nm to 1 kV (SE), an acceleration voltage of 200 V up to 30 kV, an electron beam current of 0.3 pA at 22 nA and a pressure in the sample chamber less than 10\(^{-6}\) mBar.

3 Results and Discussion

3.1 Tensile test

The results of the tensile tests are shown in Table 2. As can be verified from these data, the samples in which corona treatments were carried out (C1 and C2) in the kraft paper, have much lower values in the tensile strength and in the Young's module, compared to the reference sample, which had no treatment. These values can reflect a degradation of kraft paper, due to the action of corona discharge, which resulted in the loss of mechanical properties of the developed composites. In the composites in which the kraft paper sheets suffered alkali treatments, the samples treated with aqueous solutions of 1% (Alc 1%) and 3% (Alc 3%) of sodium hydroxide presents better tensile strength and elongation above break than the reference sample. On the other hand, the Young's modulus of the Alc 1% and Alc 3% samples is slightly lower than that presented for the reference sample. The Alc 5% sample presents worse mechanical properties, with the exception of the elongation, possibly due to the concentration of sodium hydroxide used in the alkali solution, causing the degradation and consequent weakness of the kraft paper, which resulted in the loss of mechanical properties. In the present work, the results obtained in the analysis of the samples show that the alkali treatments caused the improvement of the mechanical properties of their composites in values between 20 and 57%, in comparison with the composites produced with kraft paper that had corona treatment.
Figure 1. SEM images of the reference sample (A and D), the Alc 3% sample (B and E) and of the C1 sample (C and F) with 200x and 5000x enlargements, respectively.
Table 2. Tensile test results.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (MPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>29.18 ± 1.53</td>
<td>0.77% ± 0.06%</td>
<td>5.21 ± 0.25</td>
</tr>
<tr>
<td>Alc 1%</td>
<td>35.69 ± 3.68</td>
<td>1.22% ± 0.07%</td>
<td>4.70 ± 0.57</td>
</tr>
<tr>
<td>Alc 3%</td>
<td>36.53 ± 1.98</td>
<td>1.29% ± 0.07%</td>
<td>4.49 ± 0.20</td>
</tr>
<tr>
<td>Alc 5%</td>
<td>22.92 ± 1.49</td>
<td>2.68% ± 0.61%</td>
<td>2.43 ± 0.35</td>
</tr>
<tr>
<td>C1</td>
<td>17.01 ± 1.83</td>
<td>0.95% ± 0.19%</td>
<td>2.59 ± 0.47</td>
</tr>
<tr>
<td>C2</td>
<td>15.86 ± 0.95</td>
<td>0.76% ± 0.02%</td>
<td>2.63 ± 0.20</td>
</tr>
</tbody>
</table>

3.2 Scanning Electron Microscopy

The results from the SEM tests, presented at Figure 1, shows that the reference sample surface was not impregnated with PP, since its possible to see the dried fibers without polymer (Figure 1A). Comparing the surface of the reference sample with the surfaces of Alc 3% (Figure 1B) and C1 (Figure 1C) samples, it can be seen that the last ones have surfaces better impregnated with PP, since the fibers from the kraft paper are less visible, which indicates that the surface treatments have a positive effect on these samples. In Figure 1, it is possible to observe that the cross section of the Alc 3% (E) sample has a better impregnation than the cross section of the C1 sample (F), because the latter has more voids (zones without polymer) than the sample who had the alkali treatment. Even though the C1 sample has a better impregnated surface than any of the other samples, it seems like the polymer did not penetrate in the interior of the sample (due to many voids in the cross section of this composite). Therefore, with a cross section with so many voids the composite becomes weaker, hence it has lower mechanical properties. The cross section of the Alc 3% sample has less voids than all the other composites developed, since the alkali treatment allowed the polymer to penetrate and impregnate the paper, promoting better connection between the fibers present on the paper and the polymer, making this composite as the best in terms of mechanical properties, as its possible to observe from the results of the tensile test.

4 Conclusions

The alkali solutions with concentration of 1% and 3% NaOH removed components from the surface of kraft paper, such as lignin, a hydrophobic element, increasing the wettability of the paper, which allowed to the polymer more effectively impregnate the fibers. The improve of the paper impregnation allows to reduce the voids where the water could penetrate. Thus, indirectly, the moisture absorption of the paper was reduced, which allowed a more mechanically resistant composite to be formed. The removal of the lignin also led to an increase in the roughness (and wettability) of the surface of the kraft paper, which allowed the PP to impregnate on the sheet of paper, as could be observed in the analysis of the SEM. This aspect results in the improvement of the tensile strength and the elongation, compared to the reference sample that had no surface treatment. The treatment with alkali solution of 5% concentration of NaOH applied to the kraft paper resulted in the loss of mechanical properties compared to the reference sample, which is probably due to the excessive concentration of NaOH that led to the removal of part of the cellulose, beyond other constituents of kraft paper, which is the structural element and largest constituent of natural fibers. The corona treatments carried out on the kraft sheets improved the impregnation of the PP only on the surface of the paper. However, they did not allow the matrix to penetrate and impregnate the fibrils that are inside the kraft paper. On the other hand, the dosage of corona discharge that was used in the different treatments may have damaged the kraft paper, resulting in lower mechanical properties, up to 57%, of the compounds made with this paper, compared to the samples with alkali treatment (Alc 1% and Alc 3%).

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