FULLY BIODEGRADABLE POLYLACTIC COMPOSITES REINFORCED WITH BLEACHED SOFTWOOD FIBERS

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The increasing environmental awareness of the society has led to the development of materials with a lower environmental impact. Polylactic acid (PLA) is a biodegradable polymer with higher mechanical properties than PP. The scientific literature shows some interest in PLA reinforced biocomposites, but the published mechanical properties of such materials are comparatively low. In fact, the generation of a good interface, when the reinforcement contents are higher than 30%, is nowadays unsolved. The main objective of this study is to obtain PLA biocomposites with a good interface and with satisfactory improvements in their mechanical properties against reinforcement contents. Bleached pine fibers, used as reinforcement, were prepared and shred with 1/3 and 2/3 of diglyme, in order to avoid the formation of hydrogen bonds among the cellulose fibers. Then, composite materials were obtained through kinetic mixing. The composites were injection molded to make standard specimens and were submitted to tensile tests. The results showed that the addition of diglyme favored the formation of hydrogen bonds between the reinforcement and the PLA. Only the fibers treated with 2/3 diglyme followed a linear positive progression of its tensile strength when increasing reinforcement contents were added. Although suitable results were obtained, it seems that these composites allow further improvement.

Keywords: biocomposites, softwood fibers, polylactic acid

INTRODUCTION

The use of fibers to increase the mechanical properties of composite materials has been a prominent direction of research. Mineral or synthetic based fibers, such as aramid, carbon or glass fibers, are the most common reinforcements. The most commonly used reinforcement, due to its good mechanical properties and its relatively low price, is glass fiber. However, glass fiber is a very abrasive reinforcement, which could reduce the operating life of the screws and barrels of the manufacturing equipment. Furthermore, because of its fragility, glass fiber length shortens during the processing of the composite materials, reducing its mechanical properties, and its recyclability.[1]

Polymeric matrices could be classified in thermoplastic and thermoset polymers. Thermoset composites, like polyester reinforced with glass fiber, are widely used to manufacture boats, bicycles, helmets etc. In the case of thermoplastics, the most used polymers are polypropylene, polyamide 6 and polyamide 6.6, and are usually reinforced with glass fiber.[2-5] These matrices are not biodegradable and do not degrade easily, causing a big environmental impact. Moreover, the increasing environmental awareness has led to manufacturing more environmentally friendly materials.[6-9] A large amount of research has been done on replacing glass fibers by natural fibers, especially in the case of polyolefins, such as polypropylene and high density polyethylene.[10-15] This replacement reduces the mechanical properties of the composites, when compared with glass fibers. Nevertheless, the resulting materials show good specific properties due to the lower density of the natural fibers. Moreover, these fibers are more flexible and less abrasive than glass fibers, protecting the machinery and allowing higher recyclability rates. Furthermore, eliminating the final product by incineration has a higher energetic yield than in the case of the glass fiber,

which is inert and does not burn, leaving a higher amount of residue as well.

With respect to matrices, the same environmental awareness has led research to develop more environmentally friendly polymers, which degrade under particular conditions, reducing the amount of residues accumulated in natural environments. Some of these polymers are starch, polyhydroxyalkanoates, aliphatic polyesters, polycaprolactone or polylactic acid. Polylactic acid is a polyester, which could be obtained by open ring polymerization of the lactide or by polycondensation of the lactic acid monomers. It has a glass transition temperature around 60 ºC and a melting temperature of 180 ºC. Its good mechanical properties, higher than those of PPs, make them appropriate for the packing or the textile industries.[16,17]

All the above mentioned properties make polylactic acid an attractive candidate to substitute some polyolefins and to be used as a matrix in natural-fiber based composites. However, the compatibility between the PLA and the natural fibers is a problem not yet solved. The literature shows that reinforcing PLA with natural fibers could cause drops in the mechanical strength of the composite materials. Nonetheless, the presence of fibers always enhances the Young modulus.[18] The literature indicates a non-linear behavior of the tensile strength of the composite when the amount of fiber is increased,[19] especially when the fiber content is raised over 30 wt%.[17,20]

The objective of the paper is to investigate methods to improve the individualization of fibers, their dispersion into a matrix and the enhancement of the interphase between PLA and natural fibers.

EXPERIMENTAL
Materials
A polylactic acid (PLA) based polymer, PLA Ingeos Byopolymer 3251D, supplied by Nature Works, was used as a biodegradable thermoplastic matrix. Bleached kraft fibers derived from softwood (*Pinus radiata*), prepared by Celulosa Arauco y Constitución (Chile) and supplied by Torraspapel S.A. (Spain), were used as lignocellulosic reinforcement.

Diethyleneglicol dimethyl ether (diglyme), with a 134.17 g/mol molecular weight, and a 162 ºC boiling point, was provided by Clariant.

Composite preparation
Bleached pine fibres (PBF) were prepared and shred with 1/3 and 2/3 of diglyme in order to avoid the

formation of hydrogen bonds among the cellulose fibers after shredding.

Composite materials comprising 15 to 35 wt% PLA-PBF were obtained. The materials were prepared in a Gelimat multikinetic mixer, at 2500 rpm, until a 195 ºC discharge temperature was obtained. The discharge temperature allowed for a total evaporation of the diglyme.

Test specimens were prepared on a Meteor-40 injection-moulding machine (Mateu&Soler, Barcelona, Spain), using a steel mould complying with ASTM: D3641 specifications.

Mechanical characterization
The specimens were stored in a Dycometal conditioning chamber at 23 ºC and 50% relative humidity during 48 h, prior to mechanical testing, in agreement with ASTM D638. The composites were tested on an InstronTM 1122, fitted with a 5kN load cell, operating at a rate of 2 mm/min. Tensile properties were analyzed according to the ASTM D638 standard. Results were obtained from the average of at least 5 samples.

Fiber extraction from composites
Reinforcing fibers were extracted from composites by using a Soxhlet apparatus and decalin as solvent. Small pieces of composites were cut and placed inside a cellulose filter and set into the Soxhlet equipment. Once the fibers were extracted, they were rinsed with acetone and then with distilled water in order to remove the solvent residue. Finally, the fibers were dried in an oven at 105 ºC for 24 hours.

Determination of fiber length and diameter
After extraction, fiber length and diameter distribution were determined by means of a Morfi analyzer. A diluted aqueous suspension (1 wt% consistency) of fibers was analyzed for 2 to 5 minutes, and the lengths and diameters of the fibers were evaluated considering an amount of individual fibers in the range of 2500 to 3000 units. A minimum of 2 samples were analyzed.

RESULTS AND DISCUSSION
Previous to the composite preparation, the fibers were submitted to an XPS analysis. The analysis rendered an O/C (oxygen/carbon) relation of about 0.82, showing that the fibers had almost 100% cellulose content. The result also indicated that the fiber treatments eliminated almost all the lignin and extractives. Consequently, a higher accessibility to the chemical components and a higher ease to generate hydrogen bonds or Van der Waals interaction were expected.

Table 1
Tensile properties of the tested materials

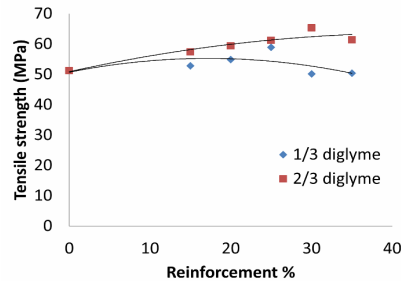|	1/3 diglyme			2/3 diglyme		
PBF (%)	σ_t^C (MPa)	E_t^C (GPa)	ε_t^C (%)	σ_t^C (MPa)	E_t^C (GPa)	ε_t^C (%)
0	51.2	3.40	3.2	51.2	3.40	3.2
15	52.84	4.18	2.7	57.4	4.64	2.65
20	54.91	5.01	2.50	59.35	5.20	2.50
25	58.96	5.60	2.39	61.2	5.79	2.3
30	50.17	5.97	2.05	65.3	6.19	2.2
35	50.39	6.36	2.05	61.4	6.53	2.1

Figure 1: Tensile strength of the composites versus reinforcement content
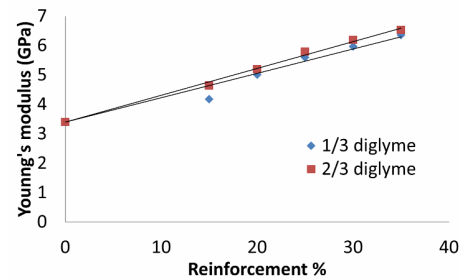

Figure 2: Young's modulus of the composites versus reinforcement content

Following this, the tensile properties of the composite materials were tested. Table 1 shows the results. Both, 1/3 and 2/3 diglyme treated PBF based composites were tested and compared.

It was observed that the composite materials reinforced with 2/3 diglyme treated fibers rendered better properties than those with 1/3 diglyme treated fibers. The reason could lie in the fact that the addition of diglyme favored the formation of hydrogen bonds between the reinforcement and the PLA. This was achieved by avoiding the generation of hydrogen bonds between the cellulose chains, and then increasing the number of potential fiber-matrix interactions. During the composite preparation diglyme vaporizes when the fibers are already dispersed in the matrix.

Figure 1 shows the evolution of the tensile strength of the composites against fiber contents.

The 1/3 diglyme fiber-based composites showed slight tensile strength increases up to 25% reinforcement content. At this point, the tensile strength of the composite was higher (15%) than that of pure PLA. Higher percentages of reinforcement rendered sudden decreases of the tensile strength of the materials. The 2/3 diglyme fiber-based composites showed increases of the tensile strength up to 30% reinforcement contents. The property decreased for higher reinforcement contents. The 25 and 35% values were very

similar. The peak value, obtained with the 30% reinforcement content, was 27% higher than that for the pure PLA matrix. The cause of the lower value can be the saturation of the available surface bonds. Compared with SGW/PP composites,[15,21] the PP-based composites showed higher increases of tensile strength against fiber contents, but the initial tensile strength of the PP (27.6 MPa) was lower than that of PLA. The 50% SGW/PP composite reached a tensile strength of 68.1 MPa. Figure 1 shows that if a good interface between PLA and reinforcement is obtained, then 35% fiber content could lead to similar tensile strength values. The values obtained with 30% reinforcement are similar to that reached with 30% sized glass fiber/PP composite (58.5 MPa) and inferior to that obtained with 30% e-glass fiber/PP composite (79.85 MPa).[15]

Both kinds of composites showed increases in Young's modulus, reaching values of 87% and 93% with respect to the matrix modulus for the 35% reinforced composites. It was found that the values of Young's modulus increased linearly with the reinforcement percentages (Figure 2).

Moreover, the slope of the 2/3 diglyme treated composites was found to be slightly superior to that of the 1/3 diglyme treated ones. While the linear behavior suggests a good dispersion of the reinforcement inside the matrix, the lower slope of the 1/3 diglyme composites could be due to the

creation of fiber bundles, and to a bad dispersion of these bundles. On the other hand, the mechanical properties of the 2/3 diglyme composites denoted better individualization of the fibers and then a good dispersion of these individualized fibers inside the matrix.

It is known that Young's modulus of a composite material is little influenced by the quality of the fiber matrix interface.[22] On the contrary, the tensile strength of a composite material is greatly influenced by the quality of the above mentioned interface. The 1/3 diglyme treated composites showed the highest tensile strength for the 25% fiber content. The obtained tensile strength was slightly similar to the matrix value, only 8 MPa higher. The values showed a linear behavior, which decreased for the 15 to 25% fiber contents. This may be due to a lack of free bonds or the creation of bonds between the cellulose fibers. On the other hand, the 2/3 diglyme treated fibers showed a more linear behavior for the 15 to 30% fiber contents. The obtained tensile strength for the 30% reinforced composite was 27% higher than that of the matrix. The 35% reinforced composite showed a decrease in its tensile strength, probably due to a saturation of all the free available bonds. However, the problem needs more research.

The strain to break remained almost the same, slightly increasing with regard to the neat matrix. Other matrices, like PP, show high decreases on the strain to break with the increases of the reinforcements.

A micromechanics analysis was carried out to investigate the quality of the interphase. The objective was to know the interfacial shear strength (τ) between the fiber and the matrix. The Tresca ($\sigma_t^m/2$) and Von Misses ($\sigma_t^m/3^{1/2}$) criteria provide a 25.61 to 29.57 MPa τ value.
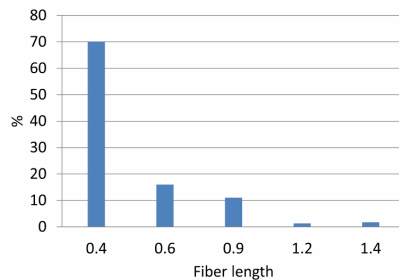
The proposed model to compute the intrinsic Young's modulus of the fibers (E_t^f) was the Hirsch model:

$$E_t^C = \beta \cdot \left(E_t^f V^f + E_t^m \left(1 - V^f\right)\right) + \left(1 - \beta\right)\frac{E_t^f \cdot E_t^m}{E_t^m \cdot V^f + E_t^f \left(1 - V^f\right)}$$

where E_t^C, E_t^f, E_t^m are the elastic moduli of the composite, the reinforcement, and the matrix, respectively, and V^f is the volume fraction of the reinforcement. In the model, β is the parameter that determines the stress transfer between the fiber and the matrix. It has been reported that the value of β is mainly influenced by the orientation of the fibers, and by the stress concentration effects at the end of the fibers.[23] A value of β=0.4 has been reported to adequately reproduce results obtained experimentally for natural fiber composites.[24,25]

The value was then used to solve the modified Kelly and Tyson equations with the solution provided by Bowyer and Bader(eq.2):[26]

$$\sigma_t^C = \chi_1 \left(\sum_i \left[\frac{\tau \cdot l_i^f \cdot V_i^f}{d^f} \right] + \sum_j \left[\sigma_t^f \cdot V_j^f \left(1 - \frac{\sigma_t^f \cdot d^f}{4 \cdot \tau \cdot l_j^f} \right) \right] \right) + (1 - V^f) \cdot \sigma_t^{m*}$$

In Eq. 2, σ_t^C and σ_t^f represent the ultimate tensile strength of the composite and the reinforcing fibers. The term σ_t^{m*} is the contribution of the matrix to the composite breaking strain. The d^f and l_j^f terms represent the fiber diameter and length, respectively. V^f is the volume fraction of reinforcement in the composite. In order to solve the equation, the Bowyer–Bader method was used (Bowyer and Bader, 1972), evaluating χ_1 and τ.

The fibers were extracted from some 20% fiber content specimens to obtain the fiber length distribution inside the composite matrix (Figure 3). It is known that during composite processing, the fibers are subjected to attrition phenomena, which decrease their length.

Figure 3: Fiber length distribution inside the composite material; length percentage versus fiber length
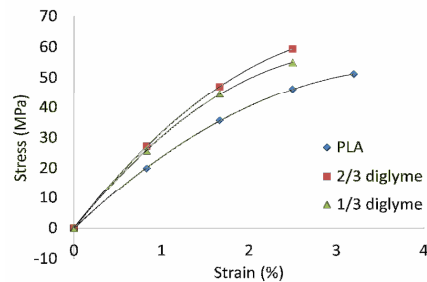

Figure 4: Mean stress-strain curves for the 20% composite materials and the PLA matrix

Table 2
Input data used to solve the modified Kelly and Tyson equation

	1/3 diglyme	2/3 diglyme
Reinforcement weight content (%)	20%	20%
Reinforcement volume fraction	0.171	0.171
Average fiber length (µm)	514	514
Weighted average fiber length (µm)	604	604
Average fiber diameter (µm)	26.6	26.6
Composite strength (Mpa)	54.9	59.35
Fiber modulus (Gpa)	21.2	24.1
Elongation at break (%)	2.5	2.5
Strain level 1 analyzed (%)	0.83	0.83
Composite stress at strain level 1 (MPa)	25.8	27.2
Strain level 2 analyzed (%)	1.67	1.67
Composite stress at strain level 2 (MPa)	44.6	47.0
Matrix stress at strain level 1 (MPa)	19.9	19.9
Matrix stress at strain level 2 (MPa)	35.7	35.7
Matrix stress at break (Mpa)	46.12	46.12

Table 3
Micromechanical properties of the composites

	1/3 diglyme	2/3 diglyme
Reinforcement weight content (%)	20%	20%
Orientation factor -χ_1	0.367	0.369
Interface shear strength (Mpa) - τ	12.0	14.05
Fiber's tensile strength at maximum stress (Mpa)	456	668
Critical length (µm)	505	632

Figure 4 shows the curve of the tensile strength for the 20% reinforced composites and the PLA matrix. The figure also shows the analyzed strain 1 and 2 levels, allowing to apply the solution proposed by Bowyer and Bader.[26] The remaining data necessary to solve the equation are shown in Table 2.

All the tensile data were obtained from the strength-strain analysis of the matrix and the composites. Table 3 shows the obtained micromechanical properties.

It was found that the orientation factors were similar in both cases. This was expected, as the characteristic is related to the equipment used to manufacture the test specimens, and in both cases the equipment was the same. Considering that the orientation factor is accepted to be: $\chi_1=\cos^4(\alpha)$, then the equivalent orientation angle is around 39º. The obtained solution is also proper to 3/8, a typical value of the orientation factor for a 2D semi-oriented composite.

The value of the interfacial shear strength showed clearly that the 1/3 diglyme treated fibres had a feeble interface, being very far from the value provided by the Von Mises criteria. On the other hand, the 2/3 diglyme treated fibres showed

a slightly higher value of this property. The value showed that it is possible to increase the quality of the interface. It also showed that more research is needed to create a high quality interface.

The 2/3 diglyme treated fibres showed a 25% higher intrinsic strength than the 1/3 diglyme treated ones. This fact denoted that the relative efficiency of the 2/3 treated fibres was higher than that of the 1/3 treated fibres. It also indicates that the more aggressive 2/3 diglyme treatment of the fibre surface rendered better interaction between the fibre and the matrix, allowing a better exploitation of the fibre reinforcing capabilities. Nonetheless, similar chemical fibres are known to render intrinsic tensile strengths close to 850 MPa, also leaving the door open for manufacturing composite materials with higher tensile strengths.

The critical length ($L_c=(\sigma_t^C \cdot d^f)/(2 \cdot \tau)$) is a measure of the length to totally load a fiber. The results showed that the value of the 2/3 diglyme treated fibres was higher than that of the 1/3 treated ones. The value is related to the bonds created on the surface of the fibres. As the 1/3 treated fibres presented a worse interface, less intrinsic tensile strength and presumably fewer

bonds per area unit, fewer lengths to totally load the fibre are needed.

CONCLUSION

The fibers were treated with 1/3 and 2/3 diglyme. The 1/3 treatment was insufficient to provide a good interface between the fibers and the matrix. The 2/3 treatment provided reinforcement fibers that increased the tensile properties of the composite materials. This could be due to a deficient fiber individualization in the 1/3 diglyme materials, causing the creation of fiber bundles inside the matrix.

The tensile strength of the composite materials increased until a 30% fiber content, and then decreased, presumably due to the saturation of the available surface bonds.

The micromechanical properties showed a better exploitation of the fibers' reinforcing potential when a more aggressive treatment was applied to the surfaces.

Research on the optimization of the interface between the studied fibers and the PLA matrix is still necessary.

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