Evaluation of the Reinforcing Effect of Ground Wood Pulp in the Preparation of Polypropylene-Based Composites Coupled with Maleic Anhydride Grafted Polypropylene

J. A. Méndez, F. Vilaseca, M. A. Pèlach, J. P. López, L. Barberà, X. Turon, J. Gironès, P. Mutjé

Laboratory of Paper Engineering and Polymer Materials (LEPAMAP) Group, Department of Chemical Engineering, University of Girona, Campus Montilivi, Building PI, 17071, Girona, Spain

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ABSTRACT: Polypropylene-based composites reinforced with ground wood pulp (pulp stone) were prepared in the reinforcing range of 20–50 wt %. The mechanical properties of the system were evaluated through the observation of a stiffening effect of the prepared materials, which reached Young's moduli up to 2.3 times higher than that of plain polypropylene, for formulations with 50 wt % ground wood pulp as a reinforcement. In contrast to this result, the ultimate tensile strength decreased because of the different polarities of the components of the composite. To overcome this problem, maleic anhydride grafted polypropylene was added as a coupling

agent (6 wt %, with respect to the ground wood pulp content, as the optimal composition), giving rise to an important improvement in the ultimate tensile strength close to 125%, in comparison with the uncoupled composite, for the composite filled with 50 wt % ground wood pulp. The addition of maleic anhydride grafted polypropylene also diminished the capacity for absorbing water, improving the durability of the composite under wet conditions. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3588–3596, 2007

Key words: biofibers; composites; poly(propylene) (PP)

INTRODUCTION

Everyday, our society is requiring new materials to satisfy the usual and innovative applications of our common life. Polyolefins are a group of polymer matrices derived from petroleum that are considered commodities in applications such as packaging,¹ agriculture films,² food contact,³ and car accessories.⁴ These materials show good chemical resistance, good dimensional stability, and good processability. On the other hand, polyolefins develop limited mechanical properties because of their very simple chemical structure based on long aliphatic macromolecules without any functional group to allow intermolecular interactions. The limitation has been overcome by the preparation of composites based on polymer matrices modified with reinforcing agents.^{5,6} Thus, the use of highresistance reinforcements such as fiberglass, carbon fibers, and polymer-derived fibers is one of the most effective alternatives for improving the mechanical

Correspondence to: J. A. Méndez (jalberto.mendez@ udg.es).

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behavior of polymer matrices. Fiberglass, which is the reinforcement of polyolefins par excellence, increases the ultimate tensile strength and Young's modulus of polypropylene (PP), giving rise to competitive materials for load-bearing applications.⁷

However, fiberglass reinforcement is associated with some disadvantages derived from its null biodegradability. Once the material has finished its working life, its elimination from the environment is quite difficult, and it is stored for a long time. Another disadvantage is its aggressive character against processing equipment.

Because of these limitations, new alternative reinforcing agents must be found, and in this sense, cellulose natural fibers have attracted more attention as reinforcements of polymer matrices. Nonwooden fibers such as hemp,⁸ flax,⁹ jute,¹⁰ and abaca have been used as reinforcements of polymer matrices, giving rise to an effective stiffening effect on the mechanical properties of the derived composites. Wooden fibers are also useful for reinforcing purposes. There are different types of wood fibers depending on the production process. Thus, ground wood pulp (GWP) is obtained by the mechanical treatment of wood, without any extra thermal or chemical treatment, providing a fibrous material useful in fields such as the paper industry for obtaining newspaper paper. Other wood pulps, obtained by thermomechanical treatments (thermomechanical wood pulp), have been reported by other authors as reinforced components of polymer matrices.^{11,12} GWP is obtained by a less expensive methodology and represents an economically favorable alternative ($0.3 \notin /kg$).

However, the ultimate tensile strength of composites reinforced with natural fibers has not been improved because of the low compatibility between the materials, which is related to the high difference in their chemical structures. Polyolefins have nonpolar character that is the opposite of that of natural fibers, which because of the presence of hydroxyl groups of cellulose awards them high hydrophilicity. To solve this eventual disadvantage, coupling agents have been included in the formulations of composites to contribute to the establishment of chemical interactions between the matrix and reinforcement. Several authors^{13–15} have reported the good benefits of the use of maleic anhydride grafted polypropylene (MAH– PP) to bond covalently the surface of fibers and PP.

In this work, PP-based composites reinforced with GWP fibers (pulp stone) were developed by means of an internal mixer and later processed by injection molding. The mechanical properties, water sensitivity, polarity, and interface morphology were studied to provide a wide vision for the use of this reinforcement in the preparation of PP-based composites.

EXPERIMENTAL

Materials

PP (Isplen PP070 G2M), provided by Repsol-YPF (Tarragona, Spain), was used as a polymer matrix. This polymer had a medium–high melt flow index focused for injection-molding purposes. GWP (type PX2), derived from pine (*Pinus radiata*), was supplied by Zubialde S.A. (Aizranazabal-Guipúzcoa, Spain) and was applied for reinforcing PP. The specific characteristics of this pulp are shown in Table I.

MAH–PP (Epolene G 3015) from Eastman España (Las Rozas, Spain), S.L., with an acid number of 15 mg of KOH/g and a molecular weight of 24.8×10^3 Da, was used as a coupling agent. Phenylisocyanate (PI), provided by Acros Organics (Barcelona, Spain), and dibutyltin dilaurate, from Aldrich (Madrid, Spain), were used for GWP modification as received.

TABLE I Specific Properties of the GWP Used in This Work as a Reinforcing Agent for PP-Based Composites

Property	Value
Schopper Riegler degree (°SR)	60–65
Breaking length	2100/2400
Explosion index	1.0/1.2
Tear index	45
Somerville index	0.6%
Fiber classification (Bauer-McNett)	16-29-18-10-26%

Methods

Fiber individualization

GWP was disintegrated in a pulper device (Púlcel, Tolosa, Spain) to induce fiber individualization. A suspension of GWP in diethylene glycol dimethyl ether (diglyme) and water (2/1 v/v; 5 wt % consistency) was placed in the pulper for 1100 revolutions. Once GWP was disintegrated, the resulting fibers were dried at 80°C until a constant weight was obtained.

Fiber surface modification

GWP fibers were dispersed in diglyme to obtain a consistency of 20 g/L. At room temperature, PI was added to the dispersion along with dibutyltin dilaurate as a catalyst. The reaction was stirred for 48 h. The modified fibers were filtered, washed, and dried in an oven until a constant weight was obtained. The modified fibers were characterized with Fourier transform infrared (FTIR) spectroscopy.

Composite preparation

PP, GWP, and MAH–PP were dried before use in an oven (at 80°C without a vacuum for 48 h). The composite was prepared by the addition of the polymer matrix and the reinforcement inside a Brabender plastograph internal mixer (Duisburg, Germany). The mixing procedure was carried out at 180°C at 80 rpm for 8 min. The obtained composite was pelletized with an Agrimsa pelletizer (Sant Adrià de Besos, Spain). The pellets were dehumidified with an oven at 80°C for 24 h. To identify the different composites prepared in this work, the following labels have been used: GWPXX denotes composites based on PP and GWP [XX is the GWP content (wt %)]; GWPXX–MPY denotes the same composites coupled with MAH–PP [Y is the MAH–PP content (wt %) with respect to the GWP content].

Injection molding

Pellets were injection-molded into a Meteor-40 injection molder (Mateu & Solé, Barcelona, Spain) to obtain tensile, flexural, and impact specimens. The injectionmolding temperatures were in the range of 168–186°C. The first and second pressures were 120 and 37.5 kgf/ cm².

Mechanical characterization

Composite specimens were conditioned at 23°C and 50% humidity for 24 h before testing (ISO D618). Tensile and flexural tests were carried out by with an Instron 1122 universal testing machine (Zamudio, Spain) according to ASTM D 638 and ASTM D 790 standard specifications, respectively. The impact test was per-

Mechanical Properties of PP-Based Composites Reinforced with GWP							
Tensile test			Flexural test			Impact test	
Ultimate tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)	Ultimate flexural strength (MPa)	Elongation at break (%)	Flexural modulus (GPa)	Impact strength (kJ/m ²)	
28.1 (0.5)	>20	1.4 (0.1)	40.0 (0.1)	9.0 (0.8)	1.4 (0.5)	_	
28.7 (0.5)	3.8 (0.2)	1.9 (0.1)	48.9 (0.0)	7.1 (0.5)	2.1 (0.5)	18 (2.9)	
27.2 (0.8)	2.8 (0.2)	2.2 (0.1)	48.9 (1.4)	5.2 (0.8)	2.7 (1.4)	11.5 (0.6)	
25.9 (0.8)	2.1 (0.2)	2.5 (0.2)	47.4 (1.6)	3.7 (0.3)	3.4 (1.6)	8.8 (1.4)	
24.4 (0.7)	1.5 (0.1)	3.2 (0.0)	46.2 (1.6)	2.7 (0.2)	4.0 (1.6)	7.4 (0.1)	
	V Ultimate tensile strength (MPa) 28.1 (0.5) 28.7 (0.5) 27.2 (0.8) 25.9 (0.8) 24.4 (0.7)	Ultimate tensile strength (MPa) Elongation at break (%) 28.1 (0.5) >20 28.7 (0.5) 3.8 (0.2) 27.2 (0.8) 2.8 (0.2) 25.9 (0.8) 2.1 (0.2) 24.4 (0.7) 1.5 (0.1)	Mechanical Properties of PP-Bat Tensile test Ultimate tensile Elongation at break (%) Young's modulus (GPa) 28.1 (0.5) >20 1.4 (0.1) 28.7 (0.5) 3.8 (0.2) 1.9 (0.1) 27.2 (0.8) 2.8 (0.2) 2.2 (0.1) 25.9 (0.8) 2.1 (0.2) 2.5 (0.2) 24.4 (0.7) 1.5 (0.1) 3.2 (0.0)	Mechanical Properties of PP-Based Composites R Tensile test Tensile test Ultimate tensile Elongation at break (%) Young's modulus (GPa) Ultimate flexural strength (MPa) 28.1 (0.5) >20 1.4 (0.1) 40.0 (0.1) 28.7 (0.5) 3.8 (0.2) 1.9 (0.1) 48.9 (0.0) 27.2 (0.8) 2.8 (0.2) 2.2 (0.1) 48.9 (1.4) 25.9 (0.8) 2.1 (0.2) 2.5 (0.2) 47.4 (1.6) 24.4 (0.7) 1.5 (0.1) 3.2 (0.0) 46.2 (1.6)	Mechanical Properties of PP-Based Composites Reinforced with Tensile test Flexural test Ultimate tensile strength (MPa) Elongation at break (%) Young's modulus (GPa) Ultimate flexural strength (MPa) Elongation at break (%) 28.1 (0.5) >20 1.4 (0.1) 40.0 (0.1) 9.0 (0.8) 28.7 (0.5) 3.8 (0.2) 1.9 (0.1) 48.9 (0.0) 7.1 (0.5) 27.2 (0.8) 2.8 (0.2) 2.2 (0.1) 48.9 (1.4) 5.2 (0.8) 25.9 (0.8) 2.1 (0.2) 2.5 (0.2) 47.4 (1.6) 3.7 (0.3) 24.4 (0.7) 1.5 (0.1) 3.2 (0.0) 46.2 (1.6) 2.7 (0.2)	Mechanical Properties of PP-Based Composites Reinforced with GWP Tensile test Flexural test Ultimate tensile strength (MPa) Elongation at break (%) Young's modulus (GPa) Ultimate flexural strength (MPa) Elongation at break (%) Flexural modulus (GPa) 28.1 (0.5) >20 1.4 (0.1) 40.0 (0.1) 9.0 (0.8) 1.4 (0.5) 28.7 (0.5) 3.8 (0.2) 1.9 (0.1) 48.9 (0.0) 7.1 (0.5) 2.1 (0.5) 27.2 (0.8) 2.8 (0.2) 2.2 (0.1) 48.9 (1.4) 5.2 (0.8) 2.7 (1.4) 25.9 (0.8) 2.1 (0.2) 2.5 (0.2) 47.4 (1.6) 3.7 (0.3) 3.4 (1.6) 24.4 (0.7) 1.5 (0.1) 3.2 (0.0) 46.2 (1.6) 2.7 (0.2) 4.0 (1.6)	

TABLE II Mechanical Properties of PP-Based Composites Reinforced with GWP

The standard deviations are shown in parentheses.

formed with a Charpy pendulum according to ISO 178, providing the impact strength.

Evaluation of the fiber length/diameter ratio

The GWP fiber length was determined before (fresh fibers) and after processing (isolated fibers from the composite). The isolation of the fibers from the matrix was carried out by the Soxhlet extraction of the processed composite in toluene at 130°C for 24 h. Later, the fibers were dried to a constant weight, and the lengths of the fresh and isolated fibers were evaluated with a Kajanni FS-100 analyzer (Helsinki, Finland). A diluted aqueous suspension of fibers was eluted, and the average fiber length was calculated from an analysis of about 3000 fibers for each analysis. The diameters of the fresh and isolated fibers were characterized with a Leica DMR-XA optical microscope (Wetzlar, Germany).

The critical length (l_c) was calculated according to the Kelly–Tyson theory [eq. (1)] and defined as the minimum fiber length with which the maximum allowable fiber tensile stress can be achieved:¹⁶

$$l_c = \frac{\sigma_t^{\dagger} D}{2\tau_i} \tag{1}$$

where σ_t^I , *D*, and τ_i are the intrinsic tensile strength, diameter, and interfacial tension of the fiber, respectively.

Determination of the polarity

A finely powdered suspension of the material was mixed with an excess of methyl glycol chitosan (MGCh; Wako Chemical GMBH, Neuss, Germany) as a cationic reagent.¹⁷ The excess of MGCh was titrated with a solution of potassium polyvinyl sulfate, blue of *o*-toluidine being used as an indicator. The polarity values are expressed as microequivalents of MGCh per gram of the material.

Water-uptake behavior

The processed composites were soaked in distilled water at 23°C for different periods, and the water

uptake was determined. The kinetics of water absorption were evaluated with eq. (2) or its linearized version [eq. (3)], which was obtained from Fickian theory:

$$\left(\frac{M_t}{M_\infty}\right) = kt^n \tag{2}$$

$$\log\left(\frac{M_t}{M_{\infty}}\right) = \log k + n \cdot \log t \tag{3}$$

where M_t is the moisture content at time t, M_{∞} is the moisture content at the equilibrium state, and k and n are constants.

Interface characterization

The fracture area of the specimens for tensile tests was observed with scanning electron microscopy (SEM). The samples were metalized with gold and observed with a Zeiss DMS 960 microscope (Oberkochen, Germany).

RESULTS AND DISCUSSION

Mechanical properties

The addition of natural fibers to polymer matrices for improving mechanical properties, such as the strength and stiffness, is a very well known technique applied for several decades. Several resources have been used for obtaining natural fibers to be added to polymers for composite fabrication. In this work, the cellulose resource was softwood derived from pine (P. radiata) and isolated by mechanical methodologies to produce GWP. This reinforcement was added to the PP matrix in the range of 20–50 wt %, giving rise to mechanical properties under tensile, flexural, and impact assays that are summarized in Table II. In the case of the tensile and flexural tests, a large improvement in the Young's and flexural moduli was achieved because of a stiffening effect derived from the decrease in the mobility of the polymer chains of the matrix by the presence of reinforcements. This usual effect and progression with the increase in the GWP content gave rise to



Figure 1 SEM microphotograph of the breaking area of a tensile specimen of the GWP40 formulation.

values of the Young's and flexural moduli up to 2.3 and 2.9 times higher than those of plain PP, respectively, for the GWP50 formulation. Related to this increase in the moduli, a decrease in the strain at break was observed. Under experimental conditions of 23°C ant 50% humidity, the strain at break of plain PP was higher than 20%. The addition of increasing quantities of GWP produced a continuous decrease in this property because of the stiffening of the material. The impact strength followed the same trend as the strain at break, decreasing with the increase in the GWP content. The capacity to absorb the impact of the prepared composites was decreased by the addition of GWP. The low compatibility between the fibers and the matrix led to tensioned areas at the interface between both components that avoided the correct transference of stresses from the polymer to the fiber.

The ultimate tensile strength was observed to decrease slightly because of the addition of GWP. The decrease in this property was attributed to the different chemical natures of the two components. Cellulose-based fibers present hydroxyl groups on their surface that award a hydrophilic character with a high capacity to interact with water by hydrogen bonding. On the other hand, the PP matrix is an aliphatic polymer based on C-H and C-C bonds with an acutely hydrophobic character. Both natures, hydrophilic and hydrophobic, were confirmed by colloidal titration, which yielded values of 4.6 and 27.3 µequiv of MGCh/g of substrate for PP and GWP, respectively. MGCh is a cationic polymer that interacts mainly with polar surfaces. This high difference in the polarity produces an ineffective interaction between both components of the composite, leading to a decrease in the ultimate tensile strength.

The limitation in the capacity to support high tensile stresses can be corroborated by the SEM evaluation of the breaking area of tensile specimens after testing. Figure 1 shows such an area of GWP40 formulation. There is not good adhesion between the polymer matrix and reinforcement because of the existence of voids in both components. This effect is also related to the low wettability of the polymer matrix on the surface of the natural fibers due to the low compatibility derived from the different chemical structures. The sum of all of these phenomena produces an inefficient transfer of stresses from the polymer matrix to the reinforcement, with a corresponding detriment in the mechanical properties.

To devise a solution to this impediment, a coupling agent was added to the composite to improve the interaction between PP and GWP. MAH-PP was added to the composite during the mixing process. MAH-PP is an agent¹⁸ used for compatibilizing surfaces of materials with different polarities. The mechanism of compatibilization of this agent, establishing covalent bonding^{7,8} between grafted maleic anhydride and polar groups such as hydroxyl and amine groups, is very well known. On the other hand, the long aliphatic PP-based chain can interact with macromolecules of the polymer matrix, mainly PP, by an entanglement mechanism. Both effects produce an efficient transfer of loads, and an improvement in the mechanical properties is expected. To determine the influence of the MAH-PP content, different formulations were prepared by the addition of 4, 6, 8 and 10 wt % MAH-PP with respect to the GWP content, and later, they were evaluated under tensile testing. The evolution of the ultimate tensile strength of the formulation reinforced with 40 wt % GWP (GWP40) after the addition of different amounts of MAH-PP is shown in Figure 2. The addition of MAH-PP induced an important



Figure 2 Dependence of the ultimate tensile strength (σ_t) of the GWP40 formulation modified with different amounts of MAH–PP.

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Figure 3 Tensile mechanical properties of different GWP-reinforced composites coupled with 6 wt % MAH–PP: (A) ultimate tensile strength (σ_t), (B) Young's modulus (E_t), and (C) elongation at break (ε_t).

increment in the values of this property. By the addition of 4 wt % MAH-PP to GWP40 to obtain formulation GWP40-MP4, the ultimate tensile strength jumped from 25.9 to 50.9 MPa. This effect is related to the establishment of ester bonds at the interface. The addition of larger amounts of MAH-PP also increased the value of the property, providing a maximum value for the formulation GWP40–MP6 (6 wt % MAH–PP). Once this coupling agent concentration is exceeded, the ultimate tensile strength suffers a very slight decrease. This effect is attributed to the increment in the number of polymer chains with a molecular weight (from MAH-PP) lower than that of the polymer matrix (PP), acting as a plasticizer.^{12,19} The same result was found by Mutjé et al.¹³ for PP-based composites reinforced with hemp strands, the phenomenon in this case being acuter. With this argument, the formulations compatibilized by 6 wt % MAH-PP were chosen for developing a deeper study of the influence of MAH–PP in composites.

A mechanical study was carried out with PP-based composites reinforced with GWP in the range of 20–50 wt % and coupled with 6 wt % MAH–PP. The results of the tensile tests are summarized in Figure 3, in which the ultimate tensile strength, Young's modulus, and strain at break are shown in different graphs. The dependence of the values of the properties for each formulation followed the same trend, being independ-

ent of the formulations being coupled or uncoupled, except for the ultimate tensile strength. The addition of MAH-PP induced a very important improvement in the ultimate tensile strength that was progressive with the GWP content. Thus, for instance, the addition of 6 wt % MAH-PP to GWP50 to obtain GWP50-MP6 gave rise to a value of the ultimate tensile strength 2.2 times higher than that of GWP50. The increments for the formulations with 20, 30, and 40 wt % GWP were also important, the values of the ultimate tensile strength being 1.3–2.0 times higher than those of the corresponding uncoupled formulations. In the case of the Young's modulus, the addition of MAH-PP as a coupling agent did not produce significant modifications, leading to values for the coupled formulations very close to those of uncoupled ones. This effect corroborates the theory that the improvement of the quality of the interface between the components of the composite did not affect substantially the stiffness of the material.^{10,11} The values of the strain at break followed the same trend, with a slight improvement due to a better capacity for being deformed.

On the other hand, mechanical testing under flexural conditions was also carried out, and the results are shown in Figure 4. As in the case of the tensile testing, the ultimate strength under flexural conditions was increased, the formulation GWP50–MP6 again showing the greatest improvement in comparison A

o, (MPa)

C

6, (%)

0

PF



GWP content (wt%) Figure 4 Flexural and impact mechanical properties of different GWP-reinforced composites coupled with 6 wt % MAH–PP: (A) flexural strength (σ_f), (B) flexural modulus (E_f), (C) elongation at break (ε_f), and (D) impact strength (I).

50

40

30

PP

with GWP50 (1.9 times higher). This improvement confirmed again the strength gain of the material due to the establishment of covalent interactions.¹¹ As expected, the flexural modulus did not experience any significant change, although the strain at break and impact strength were improved. GWP50–MP6 gave

20



Figure 5 SEM microphotograph of the breaking area of a tensile specimen of the GWP40–MP6 formulation.

rise to a value of the impact strength 70% higher than that of GWP50, although this value is still quite low compared with that of plain PP. This improvement is related to an increase in the capacity of the coupled composites to be deformed. The establishment of matrix-reinforcement covalent interactions allows the material to absorb a greater amount of energy, dispersing it through the coupled material.

30

20

40

50

This improvement in the mechanical properties can be justified by an optimization of the interface. Figure 5 shows a microphotograph of GWP40–MP6, in which



Figure 6 FTIR spectra of GWP fibers and GWP fibers modified with PI.

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Lengin and Diameter Measurements of GWI Tibers							
Composite	GWP (wt %)	MAH-PP (wt %) ^b	Length (µm)	Diameter (µm)	Length/diameter		
GWP ^a	_	_	856 (20)	31 (15)	27.6		
GWP20	20	0	208 (10)	31 (15)	6.7		
GWP30	30	0	215 (10)	31 (15)	6.9		
GWP40	40	0	197 (8)	31 (15)	6.3		
GWP20-MP6	20	6	225 (10)	31 (15)	7.3		
GWP30-MP6	30	6	220 (9)	31 (15)	7.1		
GWP40-MP6	40	6	200 (10)	31 (15)	6.4		

TABLE III Length and Diameter Measurements of GWP Fibers

The standard deviations are shown in parentheses.

^a Before its addition to the composite.

^b With respect to the GWP content.

no spaces between the two components can be observed. This improvement produced better adhesion, giving rise to a better transfer of stresses from the polymer matrix to the reinforcement.

Another effect related to the addition of MAH–PP, which contributes to better matrix–fiber adhesion, is the increase in the melt flow index of the polymer matrix. This effect is due to the lower molecular weight of MAH–PP compared with that of PP. The melt flow index of PP can be enhanced up to 6–7% by the addition of 5.3 wt % MAH–PP,²⁰ which improves the mixing process with the fibers, promoting their dispersion within the polymer matrix.

Composite preparation with modified GWP fibers

Taking into account that the —OH group is the responsible functionality of GWP that interacts with maleic groups of MAH–PP, we believe that its absence on the fiber surface should produce a decrease in the ultimate tensile strength. In this sense, GWP was modified with PI to decrease the population of —OH groups on the surface of the reinforcement. The decrease in the number of —OH groups on the fiber surface was confirmed by FTIR, and the corresponding spectra are shown in Figure 6. The spectra of GWP and GWP modified by PI were normalized with the C-O-C signal at 1027 cm⁻¹, which was expected to be constant after the PI modification. It is easy to observe that the signal related to the O-H bond (3332 cm⁻¹) decayed after the reaction with PI, and this produced a decrease in the population of -OH groups on the surface of the fiber. Under these conditions, this modified GWP had a lower number of -OH groups to interact with MAH-PP. This hypothesis was confirmed because the ultimate tensile strength of the formulation GWP20-MP6, using modified GWP as a reinforcement, suffered a decrease in the ultimate tensile strength from 38.6 to 34.5 MPa (10%). This decrease was related to the lower number of ester bonds generated by a reaction between the -OH groups from GWP and the maleic anhydride groups from MAH-PP. This result confirms the covalent nature of the interaction between GWP and MAH-PP.

Fiber length/diameter ratio

The fiber length of the GWP fibers was measured under optical techniques, and the results are summarized in Table III. The fiber length was deeply diminished by compounding and processing. This decrease is related to the high shear forces that take place inside



Figure 7 Water-uptake behavior of formulations of composites reinforced with GWP: (A) uncoupled and (B) coupled with 6 wt % MAH–PP.

GWP (wt %)	n	k	Water uptake at equilibrium (wt %)	Diffusion coefficient $(10^{12} \text{ m}^2/\text{s})$
0 wt % MAH–PP				
20	0.41	0.065	1.41 (0.08)	1.17
30	0.50	0.038	3.20 (0.10)	1.17
40	0.48.	0.046	8.07 (0.42)	1.00
50	0.44	0.063	8.37 (0.21)	1.47
6 wt % MAH-PP				
20	0.44	0.052	1.29 (0.03)	1.01
30	0.47	0.046	1.79 (0.10)	1.0
40	0.49	0.043	3.84 (0.02)	0.93
50	0.57	0.023	6.88 (1.09)	0.54

 TABLE IV

 Fick Coefficients (n and k), Water Uptake at Equilibrium, and Diffusion Coefficients of Coupled and Uncoupled PP-Based Composites Reinforced with GWP

The standard deviations are shown in parentheses.

the chamber of the internal mixer used to carry out the dispersion process of the fibers within the polymer matrix. This process decreases the fiber length, keeping constant the value of the diameter and leaving the value of the length/diameter ratio dependent only on the fiber length. This length/diameter ratio is a very important parameter for considering the fibers as reinforcing or filler agents. To consider a fiber as a reinforcing agent, this fiber must have a mean length longer than l_{cr} which is determined by eq. (1).¹⁶ In the case of GWP fibers, σ_t^{f} has a value in the range of 125– 150 MPa.²¹ According to the Pigot model,²² τ_i represents half of the value of the tensile strength of the polymer matrix in the elastic limit (superior strength limit without permanent deformations), and for PP, this value was 14.20 MPa. Taking into account the average of σ'_t (137.5 MPa), we found the value of l_c to be approximately 300 μ m, which indicates that all the composites prepared in this work (coupled and uncoupled) had a fiber length lower than l_c . This calculus obligates us to accept that when the material is not coupled, GWP fibers work like fillers instead of reinforcements, giving rise to a lower value of the ultimate tensile strength. However, the addition of MAH-PP improves the quality of the interface, and GWP fibers act as reinforcements through the establishment of covalent bonding with PP.

Water-uptake behavior

Because of the hydrophilic nature of the surface of the GWP fibers, the composites with more of that reinforcement showed higher sensitivity to water absorption, as can be observed in Figure 7. The presence of MAH–PP produced a decrease in the maximum absorbed water content, which was reached at the equilibrium state. Linked to this effect, the immersion time to achieve such an equilibrium state was delayed for the materials formulated with MAH–PP. For

instance, formulation GWP50 reached 80% of the maximum water uptake after 11 days, but in the case of GWP50–MP6, this level was reached after 25 days. This delay is indicative of the lower capacity of the coupled composite to interact with water due to the lower number of available hydroxyl groups on the surface of the GWP fibers.

From the point of view of water diffusion, PP-based composites reinforced with GWP fibers showed Fickian behavior (the *n* coefficient was close to 0.5), as can be observed in Table IV. On the basis of this behavior, the diffusion coefficients were evaluated.²³ Formulations made of MAH–PP showed lower diffusion coefficients than uncoupled formulations. This decrease is indicative of the lower capacity of water to diffuse from the outer part to the inner part of the composites due to the improvement of the wettability and adhesion between the composite components. This is another confirmation of the better compatibility achieved in PP-based composites reinforced with GWP fibers due to the presence of an agent that links their components.

CONCLUSIONS

In this study, an evaluation of the viability of GWP fibers as reinforcing agents of PP was carried out. The addition of GWP in the range of 20–50 wt % produced a stiffening effect of the material, increasing the Young's modulus of the formulations, without any improvement in the ultimate tensile strength. This effect was attributed to the different polarities of the components and a fiber length lower than l_c . This situation forced the coupling of the matrix and reinforcement by the incorporation of MAH–PP. The addition of 6 wt % MAH–PP, with respect to the GWP content, improved the mechanical resistance of the composites as well as the water sensitivity. In the presence of MAH–PP, the mechanical properties were improved,

compared with those of noncoupled composites, even for similar fiber lengths, and this indicated that an extra interaction between the matrix and reinforcement was established. The decrease in the number of hydroxyl groups on the surface, due to the reaction with PI, diminished the ultimate tensile strength of the materials, even in the presence of MAH–PP. This modification corroborates the establishment of covalent bonds between those groups of the fibers and maleic anhydride groups of MAH–PP. With all these results, GWP can be considered a reinforcing agent for polyolefins when the system is compatibilized with coupling agents.

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