Chemical anchorage of polypropylene onto glass fibers: Effect on adhesion and mechanical properties of their composites

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ABSTRACT

The objective of this work is to study the influence of the polypropylene (PP) chains, chemically anchored onto glass fibers (GFs), over the adhesion and consequently on mechanical properties of the PP/GF composites. The anchoring of glass fibers to the polymer matrix was achieved by direct metallocenic polymerization of propylene onto the fibers surface, previously treated with methylaluminoxane. With this method, homogeneous fiber coverage is obtained, drastically changing the fiber surface activity, from hydrophilic to hydrophobic.

Sandwich PP/GF/PP specimens were prepared including pre-straightened and uniaxially oriented fibers. The yield and break elongation as well as the toughness of composites having polymerized fibers were notably improved indicating clearly a much greater PP/GF adhesion. These results were corroborated by electronic microscopy analysis on the specimens after tensile tests and interpreted in terms of a phenomenological analysis of the interaction between polymerized fibers and polymer.

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1. Introduction

The tailoring of well-bonded and/or durable interfaces between matrix and reinforcement remains a critical issue in polymer composites, mainly when a thermoplastic polymer is used as a matrix. The strain-dependent mechanical properties of composites are determined by the effective load transfer between fibers and matrix. The load-transfer efficiency depends on the quality of fiber–matrix adhesion [1–4]. The stronger the interfacial bond, the greater the capacity for load-transfer. Thus, the strength and stability of the interface play a very important role in determining the composite mechanical properties.

Wu [5] postulated that the extent of molecular or local segmental diffusion across the interface determines the structure of the interfacial zone, which critically affects the mechanical strength of an adhesive bond. Negligible diffusion will give a sharp interface. In this case, high adhesive strength can be expected only when strong polar interactions or chemical bonds exist across it. On the other hand, if the interface is relatively thick and gradual as a result of extensive diffusion, a high adhesive strength will result just by the effect of dispersion forces. Poor matrix–fiber adhesion generally comes from incomplete wetting of fibers by the liquid polymer, promoting the void formation at the interface. It is the typical case where untreated inorganic fibers are embedded in a thermoplastic matrix, leading to unstable interfaces.

The strengthening of matrix-reinforcement interphases has been the goal of a great amount of research in thermoplastic composite materials. In order to improve the bonding between matrix and reinforcement, several strategies for surface modifications were proposed [6–12]. Chemical modification by coupling agents reactive with the matrix and/or the reinforcement, as well as surface physicochemical modifications of one or both constituents, had been widely used. It is known that silane-coupling agents increase ultimate mechanical properties, whereas titanate coupling agents may improve processability and flexibility [3,13–19]. However, for polypropylene (PP) and glass fiber (GF) composites, the coupling agent route has a poor cost/benefit ratio; the greatest improvement in adhesion, as reported in the literature, is about 50% with respect to untreated samples [20]. The main route to enhance PP/GF adhesion in commercial composites includes the use of maleated PP as an additive in order to obtain a product which can be advantageously used as a compatibilizing agent in the preparation of glass fiber reinforced polypropylene (GFRPP). One of the most known treatments for improving mechanical and adhesion properties of PP composites is to modify this polymer by reaction with maleic anhydride in presence of peroxide initiators [21–23]. However, the use of peroxide initiator causes byproducts formation and polymer degradation. Then the constant and repeatable composition of the compatibilizer is not guaranteed [24].

In our group [25,26], an innovative method was developed to improve the interfacial adhesion between PP and GF by direct

propylene polymerization onto the fiber surface. The chemical bonding between PP molecules and glass would assure a better anchorage than any physical coupling array. In this sense, fracture may occur by fiber or matrix failure, but not by fiber debonding.

The general experimental route for this in-situ polymerization involves an initial contact with methylaluminoxane (MAO) and hydroxy-α-olefin to generate the reaction locations on the fiber surface, followed by propylene polymerization catalyzed by metallocene/MAO. During the polymerization reaction, PP chains grow straight from the glass fiber surface, creating strong anchorage points between phases (Fig. 1). The hydroxy-α-olefin addition supplies the necessary vinyl-bonds to initiate the propylene polymerization. It was demonstrated that short hydroxy-α-olefins (5-hexen-1-ol) tend to act as Lewis bases; however, the use of long-chain hydroxy-α-olefins (9-decen-1-ol, 10-undecen-1-ol) is preferred to assure a low level of poisoning. Then, a copolymerization reaction can be initiated from these macrocomonomers [27]. The propylene molecules are attached via metallocenic catalytic polymerization using rac-ethylenebis(1-indenyl)zirconium dichloride (EtInd$_2$ZrCl$_2$)/MAO. The MAO is included in the metallocenic catalyst to alkylate the metallocene, and to generate and stabilize the cationic active zirconocene [27]. As a result, PP chains grow by copolymerization of propylene with the vinyl group of the Al–O(CH$_2$)$_n$–CH=CH$_2$, remaining chemically bonded to the glass. The reaction scheme followed to graft PP molecules onto a glass surface is shown in Fig. 1.
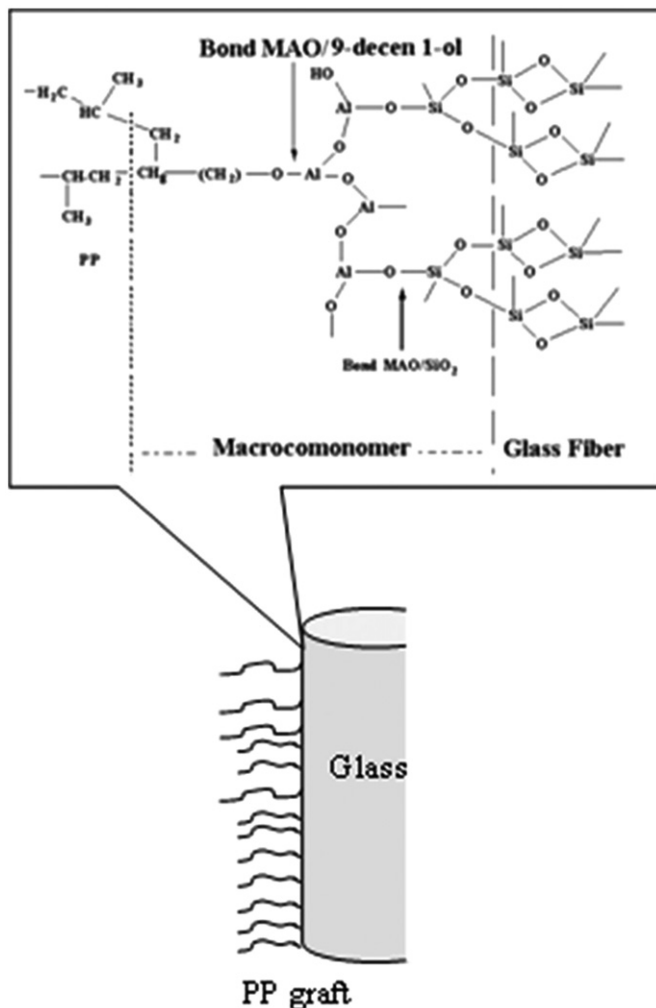

Fig. 1. PP graft molecules onto GF surface. General scheme of the reaction.

Initially, a set of screening experiments was performed to prove the occurrence of a surface polymerization reaction [25]. Two sets of copolymerization runs were performed (0.4% and 4%) for the corresponding low and high hydroxy-α-olefins concentration surface modifications. In both cases, PP chains remained grafted onto the glass surface, even after the physically bonded polymer was eliminated by a solvent extraction treatment. Different morphologies of the grafted polymer resulted at low or high 9 decen-1-ol concentrations.

A systematic study of the influence of hydroxy-α-olefins concentration was performed in order to optimize the hydroxy-α-olefins concentration that maximizes the PP/GF adhesion. In this way, several hydroxy-α-olefin concentrations, within the original range, were studied. By an accurate morphological analysis an optimal coverage grade and maximum PP amount in the bulk were obtained with 1% of hydroxy-α-olefin. This optimal point could be explained in terms of a competition between the length of the growing PP chains and the number of anchorage points generated on the fiber surface by the reaction used. The higher the amount of hydroxy-α-olefin, the higher the number of anchorage points and the lower the PP chain length. The presence of hydroxy-α-olefin (a polar compound) results in a decrease of the catalyst's activity. It is important to note that with this concentration, the best improvements in the interfacial shear strength of PP/GF composites, measured by the fragmentation test, were obtained [28].

In the present work, a study of the influence of the anchorage PP chains on GF on the mechanical properties of the PP/GF composites is performed. For that matter, sandwich PP/GF/PP specimens were prepared including pre-straightened and uniaxially oriented fibers. Simultaneously, a phenomenological analysis was performed in order to understand the interaction between polymerized fibers and polymer chains. Morphological adhesion analyses, before and after mechanical test, were carried out and related with GF surface activity and the mechanical properties variation.

2. Experimental

2.1. Materials

The in-situ polypropylene polymerization was performed using propylene (polymerization grade) kindly supplied by Petroquímica Cuyo. The metallocene catalyst (EtInd$_2$ZrCl$_2$), and the cocatalyst, 9 decen-1-ol were supplied by Sigma-Aldrich. The MAO was furnished by Witco. The reaction was carried out directly on glass fibers, using toluene (HPLC purity) from J.T. Baker as solvent. E-glass fibers ($\rho = 2.54$ g/cm^3, $D_f = 25$ μm) were supplied by Vetrotex Argentina.

For composite sample preparation, commercial PP film, supplied by MG Lavorazioni Materie Plastiche (Vicenza, Italy), was used as matrix. This film, of 78 μm nominal thickness, was obtained from a polypropylene co-ethylene random copolymer (Moplen RP348T from Basell) with ethylene content lower than 4% (Mw = 198900 g/mol and polydispersity 2.71).

2.2. In situ polymerization reaction

Reactions were performed in a stainless steel stirred reactor. GFs were aligned parallel to each other and supported on a special glass frame, in order to expose their entire surface to reagents. As a result of this reaction, PP chains grow by copolymerization of propylene from the olefin anchored to the GF surface [28–30]. Fig. 2 shows a photograph of GF after polymerization reaction. The relative amount of hydroxy-α-olefin/propylene used corresponds to 1 mol%
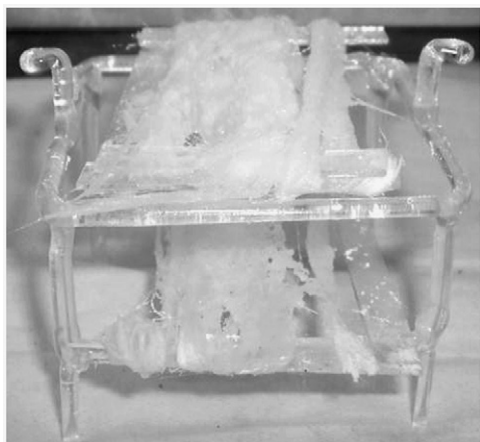
Fig. 2. GF in the glass frame, after polymerization reaction.

Table 1
Mechanical properties of PP and GF.

	E (MPa)	σ_u (MPa)	ε_b (%)
PP	685 ± 69.6	25.7 ± 1.7	412 ± 92
GF	17600 ± 2015	234 ± 31.3	2.6 ± 0.9

Table 2
Mechanical properties of the PP/GF/PP composites prepared.

	E (MPa)	σ_u (MPa)	ε_b (%)	Toughness (J)
PP/GF/PP	8125 ± 1060	101.6 ± 14.1	14.1 ± 8.3	12654 ± 1100
PP/MAO-GF/PP	8491 ± 1029	103.4 ± 12.3	16.56 ± 6.4	12054 ± 512
PP/COP-GF/PP	8852 ± 1017	104.7 ± 11.1	35 ± 7.2	38579 ± 1600

of hydroxyl content, and is calculated by considering the concentration of propylene in toluene, at the reaction temperature and 1 atm of total pressure [31]. The polymerization time and temperature were 45 min and 65 °C respectively. To ensure an excess of MAO in the reactor, the MAO/9 decen-1-ol ratio was about 100/1 by volume. After reaction occurrence, a mixture of ethanol/hydrochloric acid was added to precipitate the polymer from the solution. The fibers were washed with distilled water and separated from the frame. More details about the reaction technique are reported elsewhere [26,27].

2.3. Composite sample preparation

PP/GF composites samples consist of continuous parallel fiber lamina. They were prepared by compression molding in a hydraulic press at 165 °C. The fibers were carefully aligned and compounded by sandwiching about 1800 GFs within two PP sheets [29]. Samples were pressed for 3 min at 20 kg cm^{-2} and then cooled at room temperature.

Three kinds of samples were prepared by using no-pretreated, in situ polymerized and just MAO treated surface glass fibers, and the same matrix. These composites were named PP/GF/PP, PP/COP-GF/PP and PP/MAO-GF/PP, respectively. Lamina thickness was about 150–170 µm for all cases.

Rectangular specimens (40 × 5 mm) for tensile tests were obtained by carefully cutting with a sharp blade in order to have net edges and minimize errors during experimental tensile measurements.

In order to analyze the GF/PP adhesion by electronic microscopy, special samples of sandwich composites containing one fiber were prepared following the steps explained above. These samples were analyzed in order to enhance the cryogenic fracture and to study the GF/PP interaction during it.

2.4. Characterization

2.4.1. Determination of fiber concentration in composite samples
The fiber concentration of tensile specimens was measured by weight difference before and after ashing them in a convection oven at 500 °C for 5 h. This determination was repeated 10 times for all samples.

2.4.2. Fiber coating coverage evaluation
The polymer coverage efficacy after in-situ polymerization, and previous to composite preparation, was qualitatively determined by a hydrophilic/hydrophobic test. This technique includes the immersion of fibers in a mixture of two immiscible liquids

with different polarity and density. A mixture of 50% v/v hexane/water was used in these tests. The densities at 20 °C are hexane—0.675 g/cm^3 and water—1 g/cm^3. The fraction of covered surface was assessed by the treated fiber's relative floatability.

2.4.3. Morphological analysis
The morphological aspects were studied by scanning electron microscopy (SEM) using a JEOL 35 CF microscope, equipped with secondary electron detection. All the specimens were previously coated with Au in a vacuum chamber. The microscope was operated at 15 kV. SEM was performed at different magnifications which allows a surface penetration of 1 µm. Different samples were analyzed. GFs, the surface cryogenic fractured (under liquid nitrogen) one fiber composites and the composites subjected to mechanical tests.

2.5. Mechanical tests

Tensile tests were carried out on GF, PP and composite rectangular specimens in an Instron 3369 mechanical spectrometer. All the samples were run at room temperature (25 °C) and crosshead speed of 5 mm/min, using a 1 kN load cell. The specimen length within the jaws was 20 mm. Tensile properties were acquired and calculated using the Blue Hill software. Twenty specimens were measured for each sample set. Tables 1 and 2 summarize the mechanical properties of the PP and fibers, and composites respectively.

3. Results and discussion

The polymer fiber coverage efficacy was determined by a simple hydrophilicity/hydrophobicity qualitative test. The results are interpreted in terms of surface energy (or activity) changes due to the attached material to GF. The GF surface behaves, initially, as hydrophilic since its superficial hydroxyl groups tend to form hydrogen bonds with water. However, such hydrophilicity should disappear as a consequence of the surface copolymerization and the resulting "polypropylene coverage". The different morphologies exhibited by the fiber surface before and after copolymerization with 1% of hydroxyl-α-olefin, is shown in Fig. 3. The complete PP coverage onto the GF is apparent from comparison of Fig. 3a and b. This is consistent with possible surface activity variations that occurred by the polymerization onto the fibers. Untreated GFs, which have surface hydroxyl groups [18], are hydrophilic and sink in water, as their density is 2.5 times greater. However, propylene copolymerized fibers remain at the water–hexane interphase. Since the "coating" is non-polar, fibers become more compatible with the organic
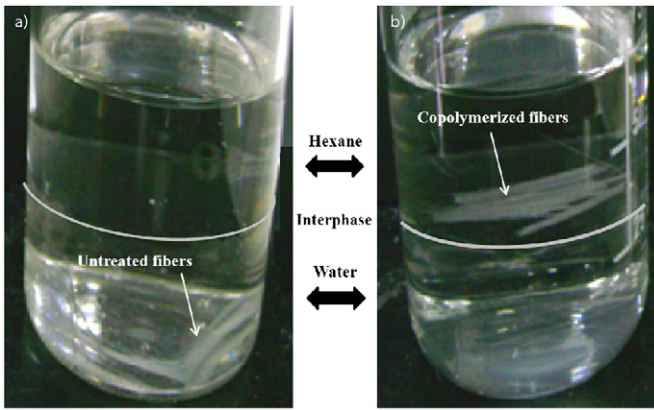
Fig. 3. Photographs of hydrophobicity test of (a) untreated fibers and (b) copolymerized fibers.
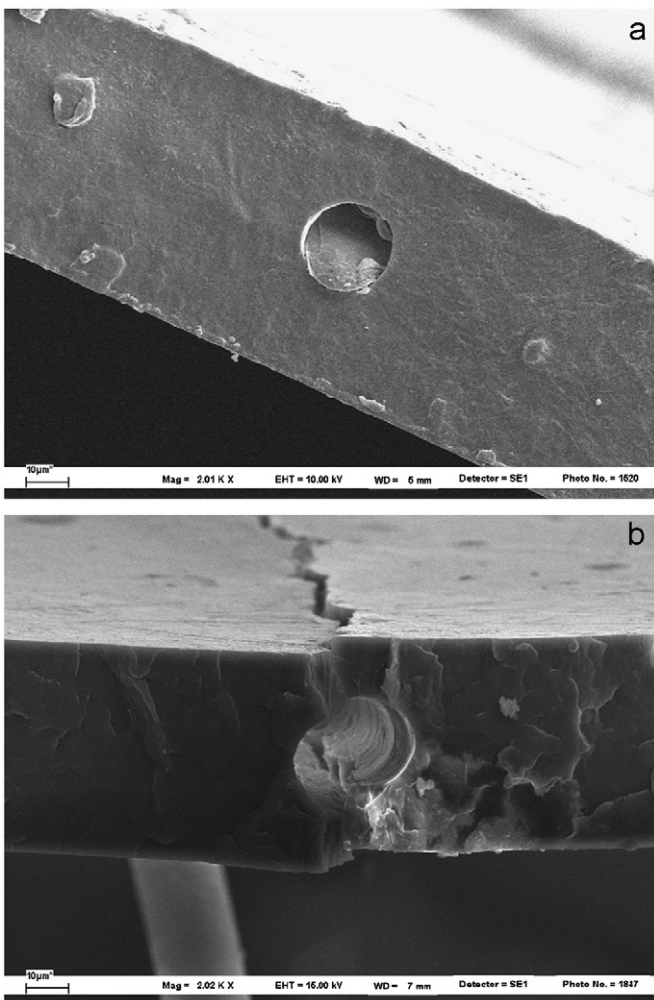

Fig. 4. SEM micrograph of composites (2000×) after fracture with different magnifications: (a) PP/untreated GF/PP, and (b) PP/COP-GF/PP.

phase. Then, it is clear from Fig. 3, that the "attraction forces" of the organic phase are greater than the gravity effect, showing that the GF surface energy radically changed. This simple test gives a qualitative but strong indication of the surface change that occurred to the fibers by the copolymerization treatment.

Taking into account that the surface activity strongly changes with the PP in-situ polymerization, a simple study was performed in order to perform a preliminary adhesion analysis. In this sense, samples of one-fiber composites were prepared with polymerized and untreated fibers. Each sample was fractured under liquid nitrogen and both fracture and overall film surface were observed by SEM. Fig. 4 shows the micrographs obtained. In the case of composites prepared with untreated fibers, both fiber and PP seem to fracture in the same plane. No influence on the PP matrix is observed. There are no fracture lines evidencing that PP/untreated GFs are so weak and each one fractures itself. However, opposite behavior is observed in Fig. 4b, for the fracture of one fiber composite done with the best polymerization condition. An overall film fracture is observed in the fiber axial direction, as well as lots of fracture lines beginning in the GF/PP interface. This behavior can be interpreted in terms of the adhesion improvement by in situ polymerization. GFs have chemically anchored PP molecules. During composite preparation in molten state, these molecules diffuse into the bulk PP molecules and entangle with them. As a consequence, the fiber drags the PP matrix, fracturing it in its axis direction.

The concluding analysis in order to evaluate adhesion improvements in composite materials is to perform a comparative study of mechanical properties. Strain-dependent properties have a strong sensibility to adhesion changes, mainly elongation at break.

Mechanical properties were measured on sandwich PP/GF/PP specimens, prepared as explained in the experimental section. This kind of sample was selected in order to minimize the number of variables affecting the composite mechanical properties. This approach entails the following assumptions: (a) fibers uniformly distributed throughout the matrix, (b) perfect bonding between fibers and matrix, (c) matrix free of voids, (d) applied loads parallel to the fiber direction, (e) no residual stresses, and (f) both fibers and matrix behave as linearly elastic materials [32,33].

In order to perform a systematic study that allows avoiding variables involved in mechanical behavior, comparative measurements were done on different composites. Three types of laminated composites were prepared, containing untreated fibers, fibers treated only with MAO and copolymerized fibers at the optimal polymerization condition.

The possible occurrence of fiber damage, caused by MAO attack, was studied in a previous work [28], in which tensile stress–strain tests on both untreated and MAO treated single glass fibers were reported. The strength data, statistically treated according to the Weibull distribution, showed that MAO induced only a slight decrease in the fiber tensile strength, indicating that very small fiber damage could occur by the presence of MAO.

The fiber concentration was measured in all the composites prepared and tested. The weight fraction average values for PP/GF/PP, PP/MAO-GF/PP and PP/COP-GF/PP are 76.4 ± 4.3, 74.2 ± 3.7 and 70.8 ± 4.6 respectively. However, for the comparison of mechanical properties, only samples with fiber concentrations as close each other as possible (around 75% w/w) were used.

Fig. 5 shows tensile stress–strain curves and the final aspect of the fractured sample for all the composites tested, PP/GF/PP, PP/MAO-GF/PP and PP/COP-GF/PP. The corresponding properties are summarized in Table 2. It is important to note that in all of the experiments performed, the specimen failure does not occur in or at the junction of the jaws, validating our data. As expected, the modulus variation is not significant because it is an initial property not depending on the PP/GF adhesion. Also, no significant variation is observed in strength value but it is reached at different deformation values. From the strain-dependent tensile behavior, it is observed that the strength of PP/GF/PP and PP/MAO-GF/PP composites is reached at 1–3% deformation. This trend confirms that the MAO treatment does not significantly change the mechanical behavior of the composites, in accordance with previous results [28].

However for PP/COP-GF/PP, the deformation is close to 7%, three times larger. This is related to the composite fracture mechanism. In the first two, the whole composite fracture occurs by fiber breakage, at $\varepsilon < 3\%$, without any matrix contribution to resistance due to the low matrix–fiber adhesion. On the other hand, for copolymerized fiber composites, the fibers start breaking at about 2% strain (Fig. 5), according to the main break strain of GF. However, material strength increases up to a strain value of 7%, which can be attributed to a greater matrix/fiber adhesion. In a previous work [24], fragmentation tests were carried out on
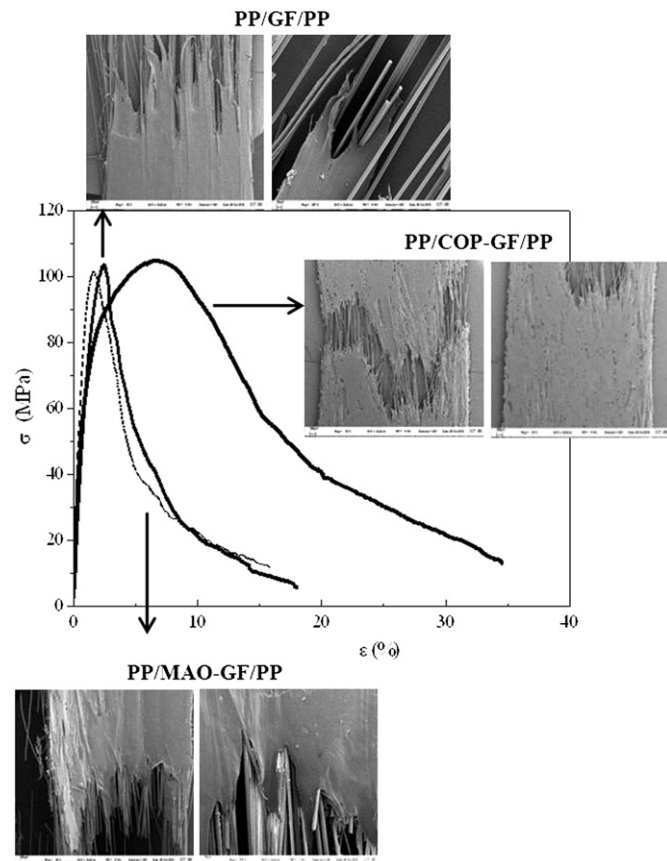

Fig. 5. Stress–strain curves of all composites tested and SEM micrograph of composites after tensile break with different magnifications: PP/GF/PP at 53× and 270×, PP/MAO-GF/PP at 53× and 270×, and PP/COP-GF/PP at 53×.

single fiber composites. It was reported there that for the same strength, the copolymerized fiber breaks into much smaller segments than samples having untreated fibers. Then, although the first fracture occurs at the same strain for both treated and untreated fibers, the treated ones keep breaking as the deformation increases over this strain. This is due to the more effective matrix/fiber load transfer that requires greater energy consumption to fracture. In composites with polymerized fibers, GF/PP interface resists essentially by chemical anchorage. The observed increase in strength deformation, once the fibers fracture, can be assigned to the greater stability of the glass–PP interface, as compared to PP–PP entanglement resistance. Then, the overall fracture occurs in the PP region around the fibers, in agreement with the results reported in [28]. Another point to be remarked is that the toughness in PP/COP-GF/PP samples triplicate the PP/GF/PP and PP/MAO-GF/PP ones. This behavior agrees with the above observations.

The results obtained could be explained by the following sequence of fracture events. The composite initially contains continuous and aligned fibers. However, as the fiber fracture occurs, the sample could be considered as a short fiber composite. Average fiber length is the length around the critical fiber [28]. The fiber fragments remain aligned with the load direction and well attached to the matrix. As the strain increases, each fiber fragment bears a growing stress up to its rupture limit. The rate at which the load is transferred to the fibers decreases as voids begin to form and grow at the fiber tips. It is clear that fibers always break at their fracture limit; however, the mechanism for crack propagation, and consequently the composite mechanical strength, will be quite dependent on the fiber/matrix adhesion. When adhesion is low (composites with untreated fiber) the crack propagates mainly by fiber debonding. It results in fewer and relatively longer fiber segments. Instead, when polymerized (treated) fibers are used, cracks spread radially, preventing the fiber pullout. In this case, the propagating crack finds a greater amount of bonded fiber fragments in its way; so more energy is needed to break (or evade) them and allow the crack to grow. Therefore, when a large amount of short and well adhered fiber segments are present, a considerable barrier to crack propagation is set, essentially by increment of the fissure path tortuosity. The proposed mechanism justifies the increment in elongation at break (more than twice for polymerized fiber samples as compared to PP/GF/PP and PP/MAO-GF/PP), as it is shown in Fig. 5. Also, the toughness, calculated as the composite energy to break from the area under the stress–deformation curve, resulted to be three times greater for the treated fiber samples (see Table 2).
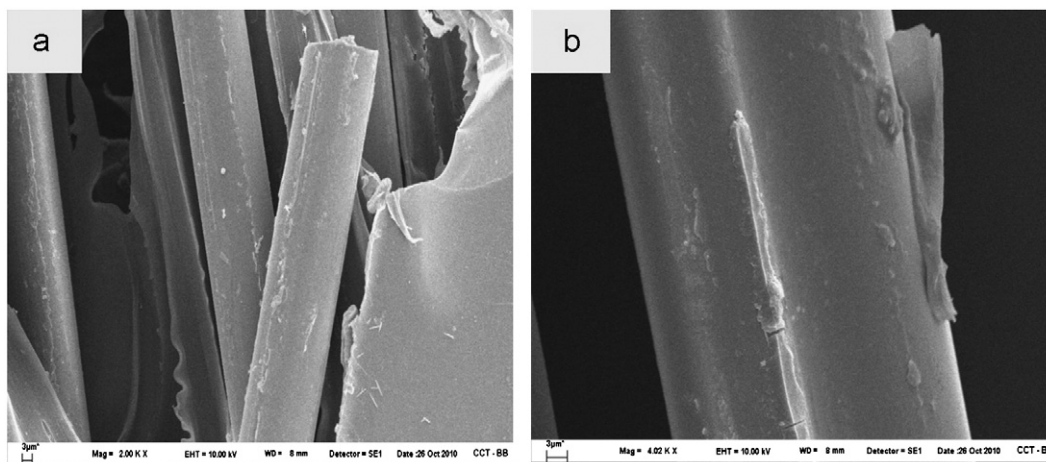

Fig. 6. SEM micrographs of PP/COP-GF/PP at (a) 2000× and (b) 4000×.

Furthermore, the elongation at yield (related to the energy required to generate cracks) indicates that PP/COP-GF/PP needs 5% more elongation than composites with non-copolymerized fibers to initiate cracks. Table 2 also shows the tensile modulus from non-polymerized and polymerized samples. As it is expected, no appreciable variation is observed since this is a zero strain property and neither fiber nor matrix modulus changed after treatment [24].

Either the tensile data or the micrographs included in Fig. 5 further validate our interpretation of the explanations given above. SEM micrographs show sample specimens after tensile fracture of PP/GF/PP, PP/MAO-GF/PP and PP/COP-GF/PP. It is clear that untreated and MAO treated composites break mainly by fiber debonding; hence polypropylene matrix remains "unchanged". On the other side, in PP/COP-GF/PP samples, the polypropylene presents a lot of holes evenly distributed through the sample, indicating that fibers pull the matrix before composite fracture. This is consistent with the greater resistance of chemical anchorage relative to PP molecular entanglements. Moreover, the less regular overall fracture is consistent with a greater resistance to breakage. Also, PP patches remain adhered to the fiber surface after the composite fracture (see Fig. 6). Here the interphase presents a micro-damage mode of debonding accompanied by matrix cracks and promotes a stronger adhesion between matrix and fibers. The result is better resistance to development of damage and thus higher normal tensile stress. The interface debonding can reduce the effect of the matrix crack. The breakage (instead of debonding) of several small fiber bundles triggers larger matrix cracks, causing their propagation along the longitudinal direction.

Other authors [29–31] found similar behavior, but attributed it to the ability of coupling agents to change the matrix nature, which could act as an impediment to crack propagation. These authors did not report an increase in the strain at which the maximum stress occurs, but proposed just an increase of matrix ductility by the coupling agent use as the main cause of improvement.

From our results it is clear that the in situ polymerization technique improves the compatibility between phases allowing for more ductile composite materials without affecting their rigidity.

4. Conclusions

The glass fiber modification by in situ metallocenic polymerization of propylene onto their surface is a suitable route to increase the mechanical properties of PP/GF composites. From the experimental data presented and discussed in this work, the following conclusions are achieved:

– The PP fiber coverage obtained by the proposed technique is homogeneous and drastically changes the activity of GF surface, from hydrophilic to hydrophobic.
– Uniaxial composites PP–copolymerized GF present considerably higher ductility and toughness without detriment of strength, with respect to the composites prepared with untreated fibers. These improved properties are assigned only to the increased adhesion caused by molecular entanglements between the PP–grafted glass fiber and PP matrix.
– The MAO pretreatment does not change the PP/GF mechanical properties since both the adhesion and fiber properties remain unchanged.
– This treatment strongly modifies the composite fracture behavior. The interface fiber debonding is the main mechanism for

untreated fiber composites, while PP disentanglement accounts for the breakage of polymerized fiber composites.

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