

Copolymerization of Polypropylene and Functionalized Linear α -Olefin onto Glass Fibers

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ABSTRACT: This work deals with a novel glass fiber surface modification and subsequent metallocenic propylene polymerization onto it. Experimental results are presented on methylaluminoxane (MAO) fixation at the fiber surface, followed by propylene- α -olefin graft copolymerization catalyzed by $\text{EtInd}_2\text{ZrCl}_2/\text{MAO}$. First results indicate that part of the produced polymer is chemically bonded to the glass fiber. Scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray disperse energy microanalysis characterization confirm the permanence of a thin polymer layer as well as aluminum and oxygen (from the MAO) on the glass surface, even after a severe solvent extraction treatment. From these results, the copolymerization of hydroxy- α -olefin, grafted on MAO pretreated glass fiber, is foreseen as a possible way to improve fiber-matrix adhesion in glass fiber thermoplastic composites. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1266–1276, 2001

Key words: grafting; adhesion improvement; copolymerization; functionalization; hydroxyolefins

INTRODUCTION

The adhesion between matrix and fiber is an essential factor in determining the properties of thermoplastic matrix polymer composite materials.^{1–6} It is well known that weak adhesion at interfaces causes deterioration of mechanical properties, because of poor stress transfer to the fibers, and also reduces the moisture resistance of the composite. For example, Laird et al.⁷ found that the diffusion rate of water through the polymer-fiber interface is 450 times greater than through the unreinforced resin. Poor matrix-fiber adhesion generally comes from incomplete wetting of fibers by the liquid polymer, promoting the void formation at the interface. Considerable efforts have been made to improve the resin-fiber adhesion, mainly by treating the glass fiber with

coupling agents, although these are rather costly and particularly not very effective for thermoplastic resins.⁸

Most of the inorganic fillers have hydrophilic surfaces. Efforts have been underway for many years to convert hydrophilic surfaces into hydrophobic and lipophilic ones, based on their surface activity. More recent studies aim to improve the adhesion between filler and matrix by increasing the functionality of the fiber surface.^{1, 4–6, 8} It is widely known that silane-coupling agents increase strength and rigidity, whereas titanate coupling agents are very useful to improve processability and flexibility. The former agents are particularly effective for silicon-based fillers, whereas the latter can be applied to a variety of fibers. Nevertheless, the coupling mechanism of these agents has not been fully clarified yet, probably because of the complex nature of the composite phase interactions.

The chemical bonding theory states that silane undergoes a chemical reaction with the surface of inorganic substances to form Si—O—M bonds (where M is either a Si atom in glass and silica or a metallic atom). This theory was widely verified for silanes reacting with silica, where the alcoxysilanes undoubtedly formed Si—O—M bonds.⁹ Because glass consists mainly of SiO₂, silanol and siloxane groups are likely to be present at the glass fiber surface. When heated, silanol groups decompose into siloxane by releasing water. On the other hand, siloxane groups formed at moderate temperatures will rehydrate, in the presence of water, to form silanol groups.⁹ Davidov et al.¹⁰ investigated the effects of heat treatments on silanol concentration at a silica surface. They reported that water molecules, adsorbed on silanol groups in a 1:1 ratio, would remain strongly adsorbed even after degassing.¹¹ In any case, the conditions of glass surfaces depend on the environment, particularly on moisture. It can be expected that a few layers of free water (thickness in the range of the diameter of the water molecules) remain weakly adsorbed.

In unsaturated polyesters–silane-treated fiberglass composites, the interface strength depends on the reactivity of the agents to the unsaturated polyesters. This fact strongly suggests the formation of chemical bonds between the resin and the coupling agents. Instead, the coupling agents have less effect on thermoplastic resins, in particular polyolefins, for which there are no specific reactions that may involve silanes. Studies in this field include the development of aminosilane with an unsaturated bond, carboxylic acid functional silane, cationic silane, silyl peroxide, and aminimide. The esterification reaction is used most frequently to achieve composites including silica and polyesters.¹ Other chemical reactions have been attempted as well to identify functional groups on the surfaces of inorganic fillers. Some coupling agents, like chromium complexes with carboxyl ligands or alkyl ortho titanates, are useful for increasing the adhesion between glass, metals, and polymers.⁸

Few publications deal with graft polymerization onto glass fiber surfaces. It has been reported that unsaturated bonds can be introduced by the reaction between silanol groups and allyl glycidyl ether, where graft polymerization proceeds from ordinary vinyl monomers as initiator.⁴ Glass fiber treated with thionyl chloride reacts with 2-mercaptoethanol to form mercapto groups on the fiber surface. The resulting treated surface can un-

dergo radical graft polymerization with styrene or methyl methacrylate.⁵ It is possible to introduce isocyanate groups by allowing glass fiber to react with diisocyanate.⁶

The end groups of a polymer molecule can be chemically bonded to a glass surface by adsorption of an appropriate initiator and posterior polymerization from it. Several reactions have been reported for grafting polymers to an inorganic surface. Polystyrene is grown from a glass surface treated with Lewis acids.¹ Vinyl polymers are also produced on a silicic acid surface by a similar reaction in which a phenyl group is covalently attached to the silicic acid surface and decomposition of diazonium salts or derivatives, such as thioether, initiate the polymerization. Grafting of styrene, acrylic acid, or vinylpyridine could be performed by this type of reaction.¹ The reaction of the hydroxyl groups from an inorganic surface with vinyl isocyanate will produce a vinyl-substituted titanium dioxide or silicon acid. These compounds can then undergo a copolymerization reaction with styrene.⁹

Homo- and copolymerization of linear α -olefins, particularly hydroxyolefins, driven by Ziegler–Natta or metallocene catalysts, give homo- and copolymers with improved properties. A characteristic feature here is that oxygenated molecules poison these catalysts, so protection of their functional groups is needed. Use of aluminum alkyl compounds, for examples, trimethylaluminum (TMA) or methylaluminoxano (MAO), accomplishes this protection. However, although the OH group is protected, the copolymerization activity and the copolymer molecular weight decrease with the increase of comonomer concentration in the feed. This result was specifically reported for the system EtInd₂ZrCl₂ (EBI)/MAO both while copolymerizing ethylene–hydroxy- α -olefin¹² and polymerizing methyl methacrylate.¹³ The poly- α -olefins can be tailor made for specific applications by introducing functional groups in the hydrophobic main chain or at the chain ends. Recently, some pioneering work on α -olefin copolymerization with monomers containing functional groups has been reported. Aaltonen et al. described the copolymerization of ethylene or propylene with 10-undecen-1-ol.¹⁴ Also, organoboranes at the end of a spacer unit were incorporated into the main chain of polyolefins.¹⁵ However, because of the strong tendency of the heteroatoms to coordinate to the Lewis acidic metal center, these copolymers are very hard to obtain with a reasonable activity and high molec-

ular weight.^{16–19} Because short hydroxy- α -olefins (5-hexen-1-ol) tend to act as Lewis bases, 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.¹² Lee et al. evaluated the ability of hydroxylated polypropylenes to improve adhesion between pure polypropylene (PP) and glass laminates.²⁰ They found evidence for chemical bonding between PP—OH and glass surfaces, with a subsequent strong interfacial interaction.

Methylaluminoxane (MAO), included in metallocenic catalytic systems to alkylate the metallocene and to generate and stabilize the cationic active zirconocene, can react almost quantitatively with ROH, water, and any compound containing active hydrogen. Therefore, the reaction of MAO with the glass surface (having a low concentration of surface OH) is, in principle, feasible. Supporting the metallocene directly onto SiO₂ renders very low activity in propylene polymerization (<6 kg PP/mol Zr · h · atm). Also, the polymer formed is easily separated from the support by solvent extraction, indicating a poor adhesion between polymer and SiO₂.¹⁹

The purpose of this work is to develop a proper glass surface modification to promote chemical bonding of PP to it. This result is accomplished by initial formation of a macromonomer (hydroxyolefin—MAO) on the glass, followed by copolymerization with propylene.

EXPERIMENTAL

Materials

The metallocene EtInd₂ZrCl₂, supplied by Aldrich, was handled under N₂ atmosphere. MAO (Witco) was used at a concentration of 10 wt % in toluene, with 1.8 M total Al and 0.5 M AlMe₃. TMA (Aldrich) was diluted to 20% in isopentane. Propylene (polymerization grade) was decontaminated by passing it through a MnO/Al₂O₃, 13X molecular sieve bed to retain oxygen and water. The 9-decen-1-ol, from Aldrich, was used without further purification. Toluene (J. T. Baker HPLC purity) was dehydrated by passing it through a 13X molecular sieve bed. The fibers were commercial E-glass continuous monofilaments (10 μ m diameter). Fibers were heated at 100 °C for 12 h to eliminate weakly adsorbed water. Hexane (Aldrich) and *n*-heptane (Merck), in reactive grades, were used for soluble PP extraction.

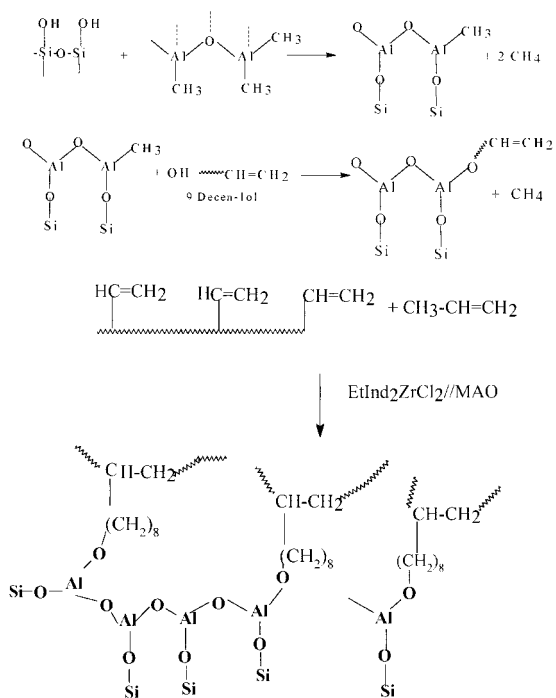


Figure 1 Reaction sequence used in this work.

Sample Preparation

The samples analyzed in this work were prepared by pretreating and modifying glass fiber surfaces. Following this step, propylene was copolymerized onto the glass fiber surface, and the physically bonded polymer was extracted from the surface by solvent extraction. Polypropylene is attached to a glass fiber surface, as it is outlined in Figure 1, by the following three-step reaction sequence.

Glass Fiber Pretreatment with MAO

Glass fibers were exposed to reaction with MAO, at 70 °C for 30 min to alkylate and stabilize the superficial sites. The reaction was then stopped by addition of an acidified ethanol solution, evolving CH₄ from the surface according to the reaction scheme. After the pretreatment, the fibers showed a bright metal appearance, which is consistent with the presence of Al₂O₃ at the surface. TMA treatment was also intended, but it was far less effective, so all the samples studied were pretreated with MAO.

Glass Surface Modification by Reaction with 9-Decen-1-ol

About 285 mg of thermally pretreated fibers (100 °C for 12 h) were contacted with 2 mL of MAO and

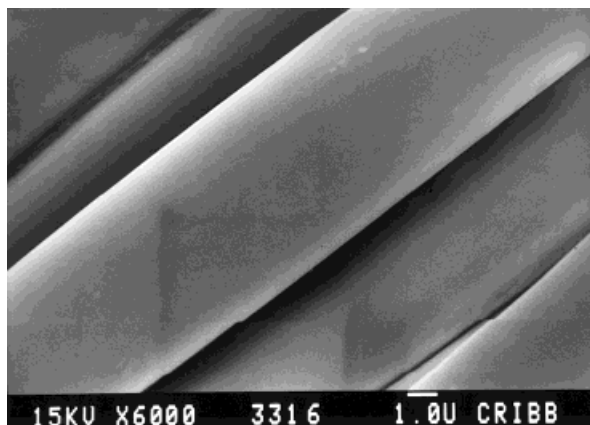


Figure 2 SEM microphotograph of MAO treated fibers (6000 \times).

9-decen-1-ol in 200 mL of toluene. The reaction was carried out under propylene flux at 70 °C for 30 min in a 600-mL stainless steel reactor with stirring. Two sets of reactions, with different alcohol concentrations, were run to analyze the effect of this variable on the reaction activity. In the first set, 50 μ L of 9-decen-1-ol was used (0.4% of the total olefin concentration in the reaction medium). The second set was run with 0.5 mL of 9-decen-1-ol (\sim 4% in the reaction medium).

Propylene Copolymerization at the Modified Surface

After step 2 is completed, the temperature is reduced to near 40 °C and the copolymerization is initiated by addition of 4 mL of MAO and \sim 3 mg of EtInd₂ZrCl₂. After a reaction period of 1 h, the polymer is precipitated by acidified (HCl) ethanol.

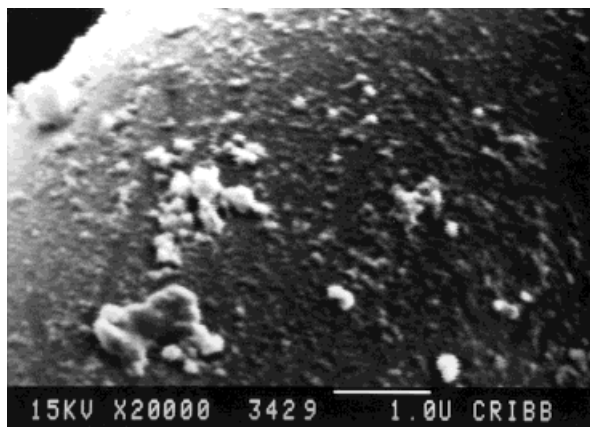


Figure 3 SEM microphotograph of IF04 sample (20,000 \times).

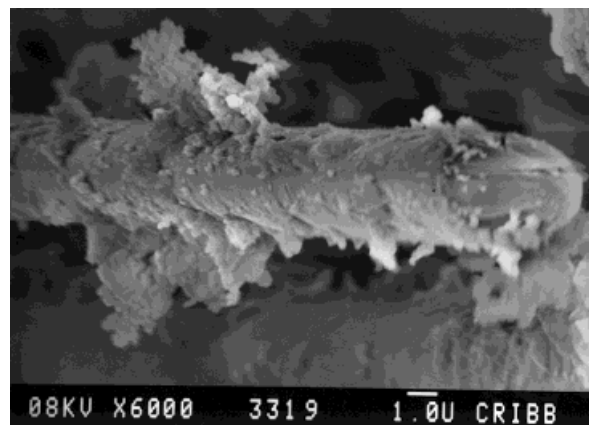


Figure 4 SEM microphotograph of IF04 sample (6000 \times).

Two sets of copolymerization runs were performed for the corresponding low and high alcohol concentration surface modifications. As expected, the activity drastically decreases with the comonomer content,^{15, 17, 21} with 15–20 g of PP being obtained from the 0.4% alcohol modification, whereas only 4 g from the 4% alcohol modification.

For simplicity, the 0.4% alcohol-modified glass fibers that are copolymerized with propylene are named IF04 samples. In the same way, the 4% alcohol-modified fibers are named IF4 samples.

Extraction of the Polymer Physically Bonded to the Surface

Polymer extraction tests under stirring, reflux, and different solvents and temperatures were carried out to remove the polymer fraction unbound to the glass surface. These tests allowed

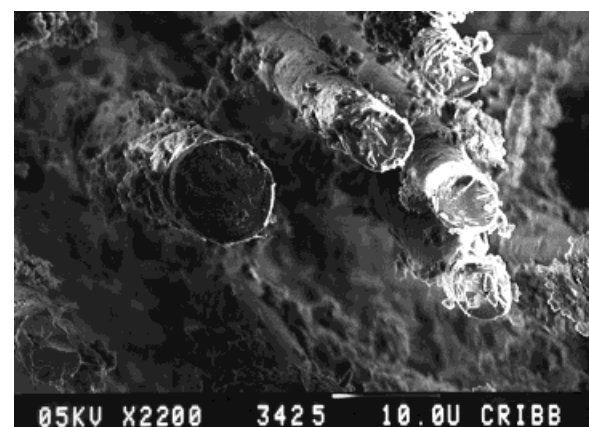


Figure 5 SEM microphotograph of IF04 sample (2200 \times).

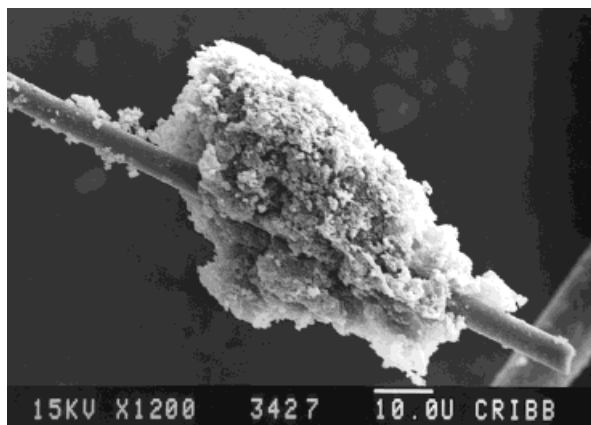


Figure 6 SEM microphotograph of IF04 sample (1200 \times).

visualization of the form and determination of the time needed for the polymer to be solubilized at each extraction condition. It was determined that complete copolymer solubilization is obtained by refluxing with *n*-heptane at 100 °C for 15 and 8 min for low and high alcohol content, respectively. Hence, the copolymerized samples were extracted at these solvent and temperature conditions for an extended period of 2 h.

Characterization Techniques

Scanning Electron Microscopy (SEM) and X-ray Disperse Energy Microanalysis (EDX)

The samples were observed and analyzed by SEM, with a JEOL 35 CF scanning electron microscope equipped with secondary electron detection, and by EDX (EDAX DX4 to detect elements

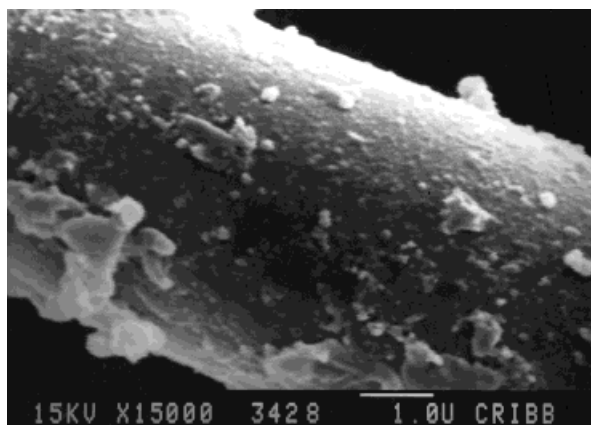


Figure 7 SEM microphotograph of IF04 sample after solvent extraction (15,000 \times).

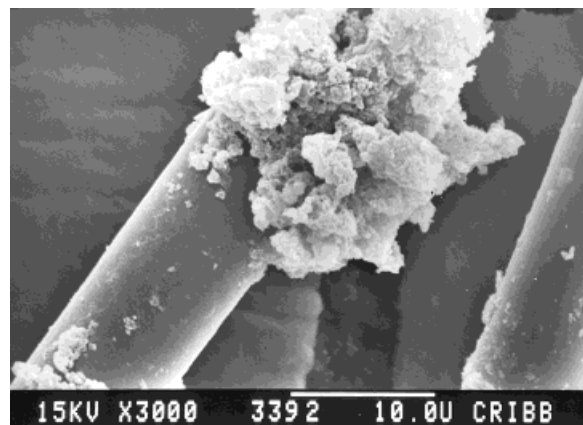


Figure 8 SEM microphotograph of IF04 sample after solvent extraction (3000 \times).

from B to U). EDX and SEM analyses were performed simultaneously on untreated and modified fibers, as well as on IF04 and IF4 samples, previously coated with Au in a vacuum chamber. The microscope was operated at 15 kV. SEM was performed at different magnifications and EDX allows a surface penetration of 1 μ m.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analyses were performed directly on the fibers before and after the surface treatments. A Nicolet 150 spectrophotometer was used. The transmittance values obtained were acceptable to detect the glass fiber modifications produced by the different treatments.

RESULTS AND DISCUSSION

As illustrated in Figure 1, Si—O—Al—O(CH₂)₈ bonds can be formed by glass surface (MAO) pretreatment and posterior reaction with the 9-decen-1-ol alcohol. Then, a copolymerization reaction follows in which propylene is attached to these groups. Finally, the reaction is stopped, by addition of acidified ethanol, and the polymer precipitates.

Part of the Al on the glass surface forms Al(OEt)_x and later Al₂O_x. It is worth noting here that the addition of acidified ethanol would produce soluble AlCl₃ if the Si—O—Al—O(CH₂)₈ bonds were either not formed or destroyed by the deactivation reaction. So, the presence of Si—O—Al and PP, on the fiber surface, will be indicative of chemical bonding between glass and polymer.

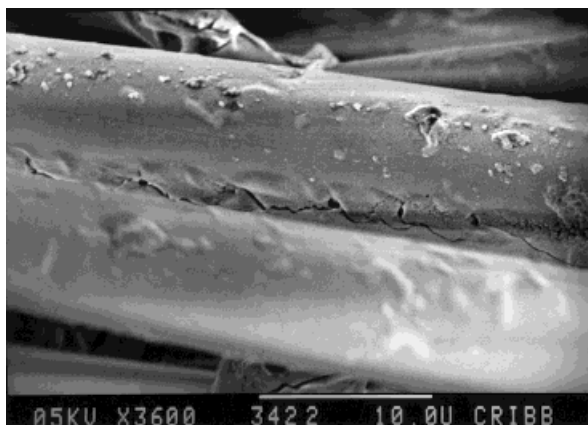


Figure 9 SEM microphotograph of IF4 sample (3600 \times).

The present work offers consistent SEM, EDAX, and FTIR evidence for glass-polymer chemical bonding after the copolymerization reaction is stopped.

SEM Characterization

MAO Pretreated Fibers

A change in fiber surface color is visible to the naked eye on fibers subjected to MAO exposure. Untreated glass fibers look white and opaque, whereas MAO pretreated ones exhibit a uniform, bright, metal-like appearance. This observation can be considered as preliminary evidence of a continuous aluminum oxide (Al_2O_3) layer formation on the surface. Also, the SEM analysis of treated and untreated fibers (Figure 2) showed clean surfaces without attached particles.

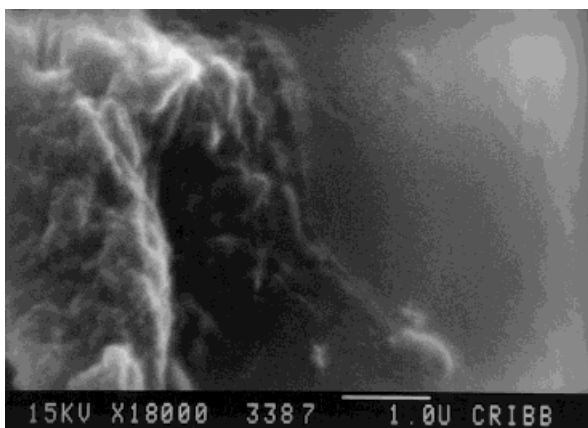


Figure 10 SEM microphotograph of IF4 sample (18,000 \times).

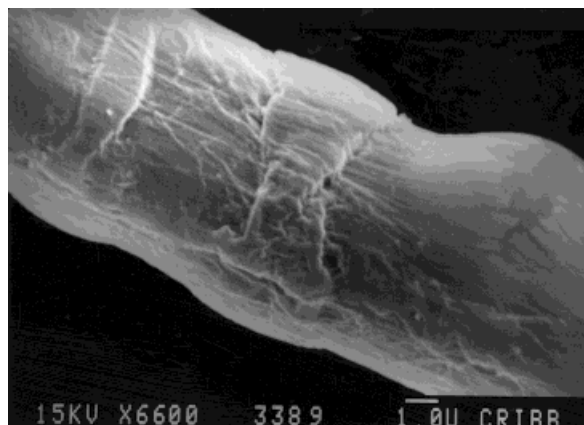


Figure 11 SEM microphotograph of IF4 sample after solvent extraction (6600 \times).

PP Copolymerized Fibers (0.4% Alcohol)

SEM micrographs of various IF04 sample locations, under different magnifications, are shown in Figures 3–6. Attached polymer to the fiber is visible in all the micrographs. A zone bearing incipient polymerization, with polymer chains growing from fairly well-distributed anchorage points on the surface, is shown in the highest magnification micrograph (Figure 3). Bonded polymer clusters of very different sizes are shown in Figure 4. The results shown in Figure 5 indicate that no matter how the cluster size formed, the whole surface is covered. Remarkably, cluster sizes of up to seven times the fiber diameter surrounding it were observed (Figure 6).

The IF04 sample surface after the solvent extraction is shown in Figures 7 and 8. It is clear from both micrographs that the grafted polymer remains attached after the extraction of physically bonded polymer. This evidence is the first of its kind for the permanence of chemically bonded polymer at the fiber surface.

PP Copolymerized Fibers (4% Alcohol)

The effect of alcohol concentration on the sample morphology is remarkable. Unlike the “cluster” type morphology found for 0.4% alcohol (Figures 3–8), the polymer looks like a coating layer on the surface when high alcohol fraction is used in the copolymerization (Figures 9–11). Moreover, the fibers appear linked to each other by the polymer layer (Figure 9), with this “connected” appearance observed through the entire sample. The IF4 sample surface after solvent extraction is shown in Figure 11. It is clear that polymer remains at-

tached to the surface as fairly homogeneous layers surrounding the fibers.

The PP copolymerization onto modified glass fibers gives rise to strikingly different polymer morphologies, “cluster” or “layer”, according to the surface treatment conditions used. The “cluster” type morphology, as observed by SEM, seems to grow from a small number of non-uniformly grouped anchorage points on the surface, whereas the “layer” type may develop from a well-distributed large number of sites. A primary analysis indicates that the prevalence of one or the other type of morphology is probably controlled by the alcohol concentration used during the glass surface modification step.

As was observed (Figure 2), the MAO pretreated fibers exhibit a uniform bright metal surface appearance, which is a reasonable indication of complete alumina coverage. Then, taking into account that anchorage points for copolymerization are created by reaction of an alcohol molecule with a surface-attached MAO (Figure 1), the number of them should be proportional to the alcohol concentration. Thus, a large number of

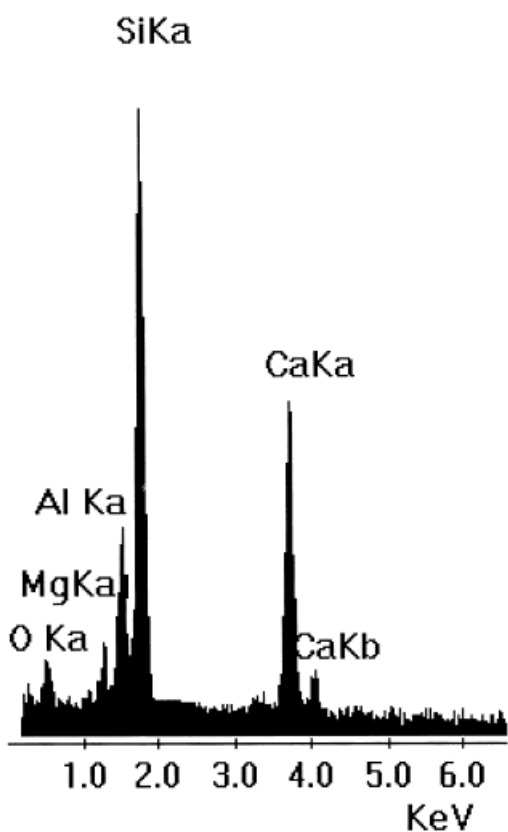


Figure 12 EDX spectra of glass fiber surface without treatments (full scale: 1000).

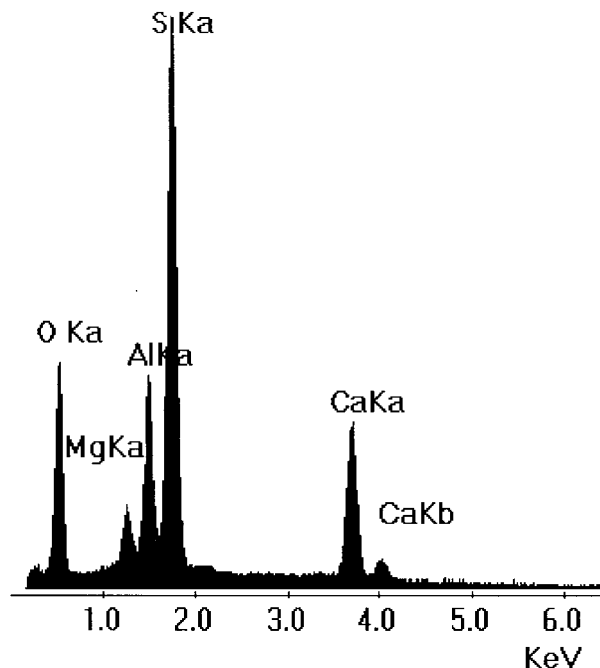


Figure 13 EDX spectra of MAO treated fiber from Figure 2 (full scale: 6000).

sites can be expected to form from high alcohol concentration and conversely, developing “layer” or “cluster” morphologies, respectively.

EDX Characterization

The EDX spectra of glass fiber surfaces (naked, modified, and bearing PP copolymerization) are shown in Figures 12–17. For simplicity, the characteristic peak of the gold layer was subtracted in all of these figures. The untreated fibers (Figure 12) show clear aluminum and oxygen peaks corresponding to the glass composition, whereas in MAO pretreated fibers (Figure 13), these peaks come up higher because the Al_2O_3 layer formation at surface. As can be expected, in neither of these samples is a carbon peak present.

The EDX spectra of IF04 sample are shown in Figure 14, in correspondence to the locations reported in the microphotographs of Figures 3 (Figure 14a) and 6 (Figure 14b). Carbon peaks are detected in these spectra, in contrast to the spectra for treated and untreated fibers, confirming the presence of polymer on the surface.

The carbon peak is significantly higher in Figure 14b than in Figure 14a, which is consistent with the greater amount of polymer observed for the sample location corresponding to Figure 6. The presence of elements from the fiber structure

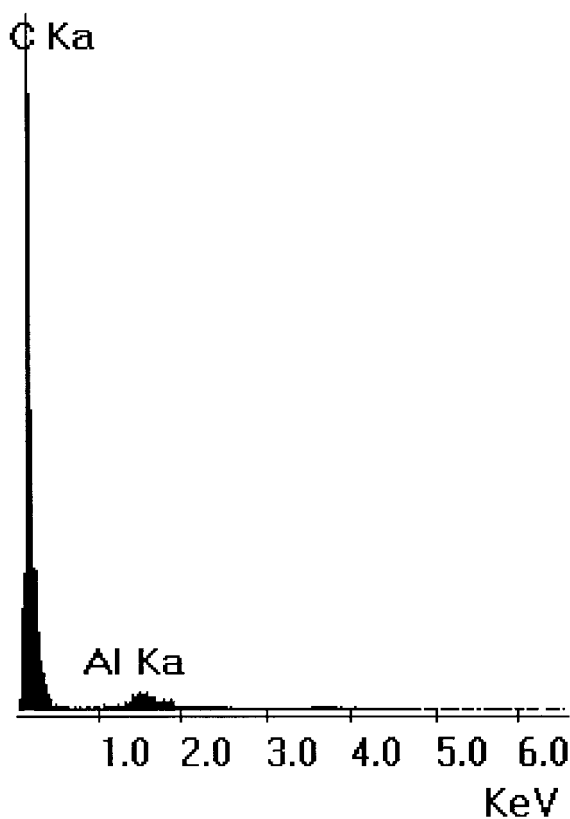
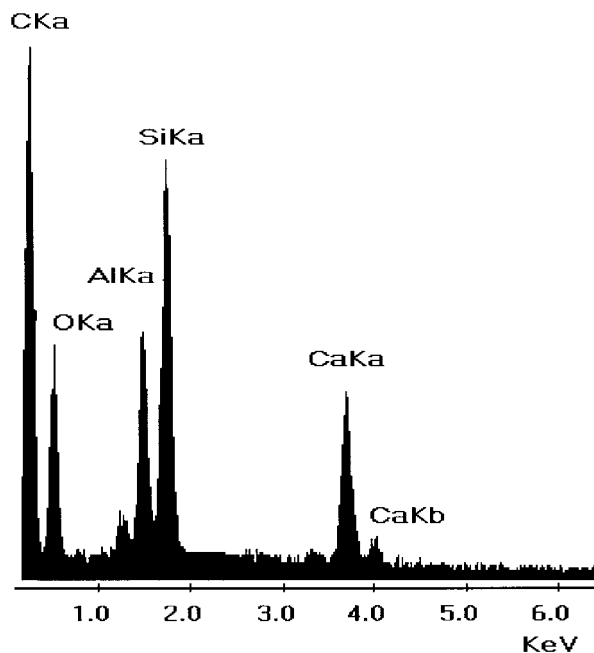


Figure 14 EDX spectra on IF04 sample (a) from the surface shown in Figure 3 (full scale: 6000) and (b) from the surface shown in Figure 6 (full scale: 3000).

(O, Al, Si, and Ca), which appear in Figure 14a, can be explained by the EDX analysis penetration ($\sim 1\mu\text{m}$) beneath the surface. Here, the very thin

clusters of polymer coating the surface, shown in Figure 3, are of the order of $1\mu\text{m}$ thick. Instead, only C and Al peaks are detected in Figure 13b, corresponding to "cluster" type morphology. This small Al peak probably corresponds to soluble AlCl_3 , which may remain occluded into the polymer as explained next.

The EDX spectra of IF4 samples exhibit similar C and O peaks as the spectra of IF04 (Figure 15). However, a distinct chlorine peak is detected in the former, which probably results from the polymer precipitation step. As already described, the copolymerization is stopped by addition of a mixture of ethanol, toluene, and hydrochloric acid. Here, the solubilized MAO reacts with HCl to produce AlCl_3 that remains in the alcoholic solution, so that the precipitating polymer molecules tend to occlude the alcohol (and the solubilized AlCl_3). Then, on solvent evaporation, the AlCl_3 may remain with the polymer.

The EDX spectra of IF04 and IF4 samples after extraction with solvents are shown in Figures 16 and 17, respectively. The presence of large C peaks on both samples denote the permanence of attached copolymer to the glass surface, in agreement with the SEM observations shown in Figures 7 and 11.

FTIR Characterization

MAO Pretreated Fibers

The FTIR transmission spectrum of the original commercial fibers (Figure 18a) shows OH

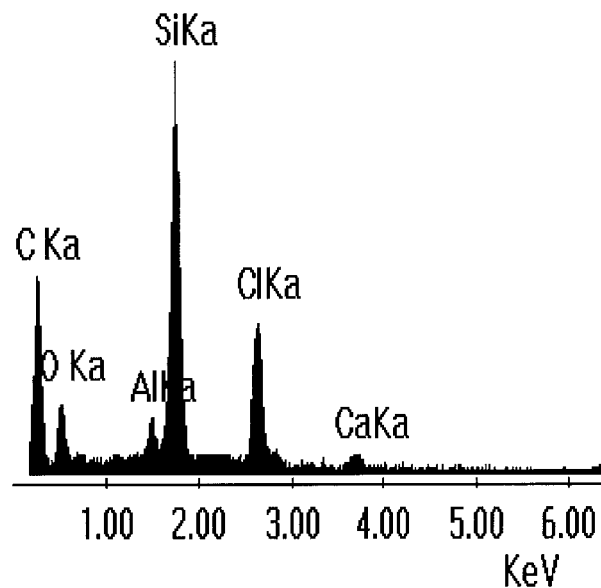


Figure 15 EDX on IF4 surface from Figure 9 (full scale: 1000).

group bands in the $3300\text{--}3600\text{ cm}^{-1}$ region, corresponding to bonded water.²² The band at 1880 cm^{-1} is assigned to vibration of the Si—O net. The FTIR spectrum of the MAO pretreated fibers, shown in Figure 18b, exhibits bands at 868, 750, 706 and 610 cm^{-1} . The first two are assigned to Al—O—Si and Al—O vibrations, respectively, and the last two can be assigned to Al—CH_x.²³ The Al—O—Si vibration can originate in the chemical bond between MAO and the glass fiber surface. The bond is produced by reaction between a methyl group from MAO and a terminal OH group from the glass fiber surface, eliminating a CH₄ molecule per each connection. Our previous work on metallocenes heterogenization onto SiO₂ surfaces offers both theoretical and experimental confirmation of this mechanism.^{23,24} Additional evidence comes from the FTIR spectrum of E-glass (which contains $\sim 14\%$ Al₂O₃ in its for-

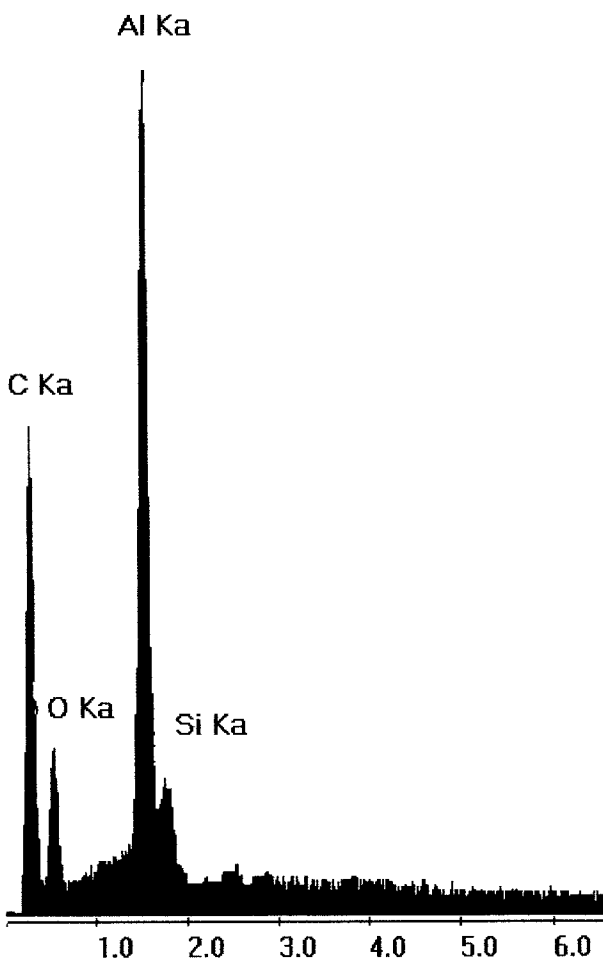


Figure 16 EDX spectra of IF04 sample after solvent extraction, from the surface shown in Figure 8 (full scale: 1000).

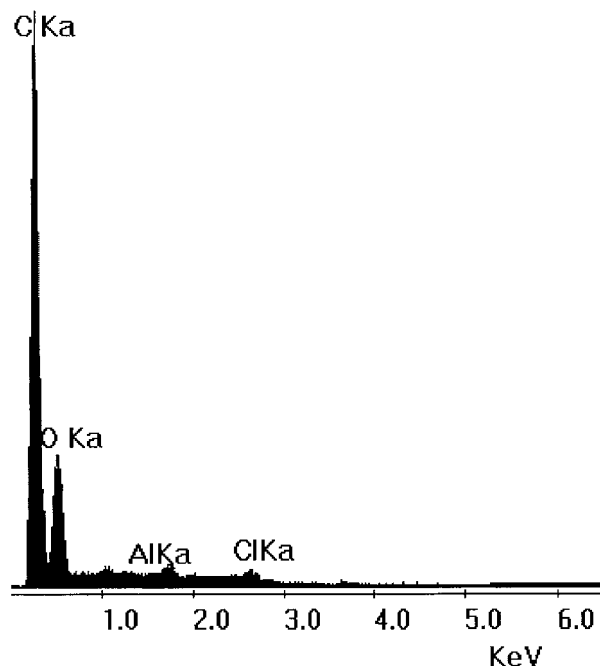


Figure 17 EDX spectra of IF4 sample after solvent extraction, from the surface shown in Figure 11 (full scale: 9000).

mulation). As shown in Figure 18c, the bands assigned to Al—O—Si and Al—O vibrations are also present.

PP Copolymerized Fibers

The fiber modification produced by the copolymerization procedure proposed here is shown in Figure 19. The FTIR spectra from IF04 and IF4 samples show that the broad band in the $3300\text{--}3600\text{ cm}^{-1}$ zone (OH band) remains present, although reduced in intensity, compared with the original fiber. The band at $1700\text{--}1800\text{ cm}^{-1}$ is identical to that observed for the original fiber (Si—O net). The IF04 samples, before the extraction treatment, show bands in the $2800\text{--}3100\text{ cm}^{-1}$ zone and at 1400 cm^{-1} . These bands are assigned to CH₃/CH₂ and are typical of PP (see Figures 19a and 19b). In contrast, the IF4 samples show a different pattern in which the CH₃/CH₂ bands appear either considerably reduced in intensity ($2800\text{--}3100\text{ cm}^{-1}$) or vanished (1400 cm^{-1}).

It is important to note from Figures 19 that the Si—O—Al peak at 868 cm^{-1} is present in both the IF04 and IF4 spectra. As already stated, this result is a clear indication that Si—O—Al remained after the copolymerization reaction.

CONCLUSIONS

A novel method to chemically attach PP to glass fibers is reported. It involves the creation of alcohol functionalized olefin sites, chemically bonded to a MAO-modified glass surface, and posterior metallocenic propylene copolymerization onto them. The following conclusions arise from this work. Results of SEM observation and EDX analysis reveal that PP copolymers remain grafted onto the glass surface even after the physically bonded polymer was eliminated by a very strong solvent extraction treatment (*n*-heptane, 100 °C, 2 h). Because the MAO pretreatment provides continuous Al₂O₃ surface coverage, the amount of grafting anchorage points and its distribution uniformity appear to be controlled by the func-

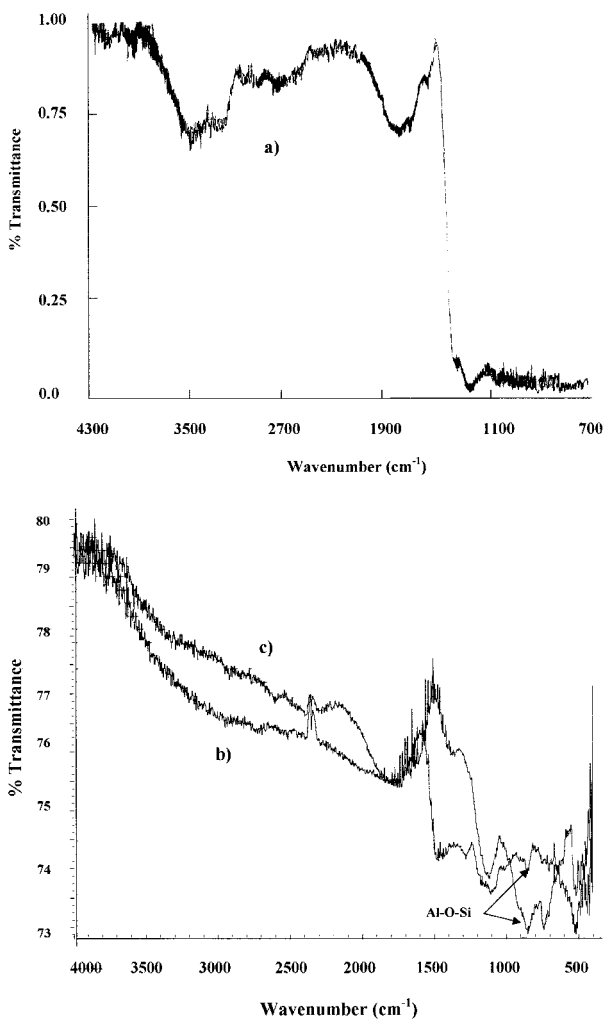


Figure 18 Transmission FTIR spectra of (a) bore/silicate fiber, (b) E-glass fiber, and (c) MAO-treated fiber.

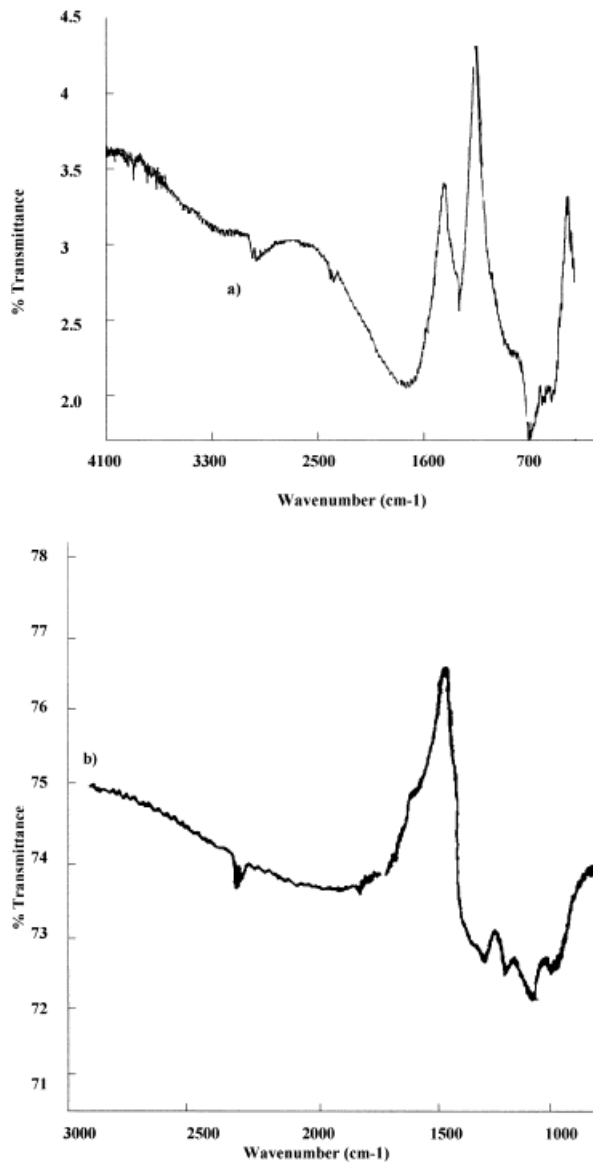


Figure 19 Transmission FTIR spectra of (a) IF04 sample and (b) IF4 sample.

tionalizing alcohol concentration. Different morphologies of the grafted polymer, “cluster” or “layer” type, result according to the use of low or high alcohol concentration, respectively. FTIR and SEM evidence of glass–polymer chemical bonding is provided, even for samples subjected to severe extraction conditions.

This route for polymer grafting onto a glass surface can be suitable for technological applications to improve the fiber–matrix adhesion in glass fiber thermoplastic composites.

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