Chemical Grafting of Metallocene-Catalyzed Functional Polypropylene Copolymer on Glass Substrates Through Surface Modification

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ABSTRACT: This work deals with surface modification of soda-lime glass slides which, by itself, does not have hydroxyl groups at the surface. So, a glass surface pretreatment is needed, to create hydroxyl groups onto it, before carrying out the polypropylene (PP) grafting reaction. Different acid/base pretreatments were performed to develop an adequate concentration of superficial hydroxyl groups. Subsequently, a metallocenic polymerization (propylene-α olefin graft reaction, catalyzed by $EtInd_2ZrCl_2$/methylaluminoxane), was carried out to provide graft-PP chains chemically linked to the glass surface. The surface so modified can be further functionalized and tailored for different applications, including polymer composites. The pretreatment conditions that best preserved homogeneity and caused less damage to the glass surface resulted from a step of contact with dilute HF/NH_4F buffer, a washing step with distilled water, and a final exposure to KOH. After the propylene copolymerization was performed, part of the graft copolymer formed remained chemically bonded to the glass slide surface. The presence of grafted PP at the surface was confirmed by SEM, FTIR, and EDAX characterization, even after the physically adsorbed polymer was excluded by a severe solvent extraction treatment. From these results, the copolymerization of a hydroxy α-olefin, grafted on a MAO-pretreated glass slide, is foreseen as a possible way to graft polymers onto inorganic solids. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2815–2822, 2008

Key words: polypropylene-glass grafting; metallocene polymerization; glass surface modification; *in situ* polymerization; surface treatments

INTRODUCTION

The application of the surface treatment concept to a range of materials and processing technologies appears functional to improve final material properties as well as to bring about innovative transformation techniques. Materials with tailored surface properties are useful for diverse applications, two examples of potential benefit from using modified glass surfaces are: (1) Thermoplastic matrix composites exhibit potential important advantages as compared with the traditional thermoset ones: greater tenacity, formability, weldability, recyclability, vibration dampening, and low cost.[1,2] However, poor matrix-fiber adhesion, even using coupling agents, as well as the high viscosity of the molten matrix, makes it difficult to take full advantage of the properties and processing capabilities of these composites. The interfacial adhesion can be greatly improved by a proper modification of the inorganic filler surfaces. (2) In the field of absorption and/or covalent immobilization of bio molecules (nucleic acids, proteins, etc.) a key factor is to prepare a reactive surface for stable binding of bio-macromolecules on the support.[3] Once the molecule is attached, the surface must keep away other biomolecules to reduce interference.[4]

The most popular glass modifications are aminosilane or polylysine coatings, which allow electrostatic interactions between polar substrates and the surface. Also, glass surfaces can be modified by silane chemistry to introduce specific functions such as amino, epoxy, carboxylic acid, or aldehyde groups.[5] However, other glass modifications were recently reported, based on the use of polypropylene (PP) and polyethylene as grafting polymers.[6–10]

In a previous work, we reported the occurrence of PP grafting onto glass fibers.[10] A chemical link between glass and PP was obtained by grafting methylaluminoxane (MAO) directly on the glass. Then, this MAO-treated glass was functionalized with a hydroxyolefin (9-decen-1-ol), and finally copolymerized with propylene via metallocene catalyst. It was also proved that the OH groups at the glass fiber surface were the reaction site between MAO and 9-decen-1-ol.

This work deals with surface modification of soda-lime glass slides which, by itself, does not have hydroxyl groups at the surface. So, a glass surface pretreatment is needed, to create OH groups onto it,

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before carrying out the PP grafting reaction. Hydrofluoric acid is a well-known etchant of glass; see for example Binkowski et al.[11] The reactivity and reaction product of hydrofluoric acid (HF) with glass was first described in a scientific journal in 1771 by Scheele,[12] and considerable amount of research was devoted to it since then. However, due to the intricacies of this reaction, a complete understanding of the process was not achieved up today.[13–15] In the Integrated Circuit manufacturing, for example, one of the most basic step is masking the wafer with SiO_2. Subsequent removal of all (or part) of this oxide layer is critical to device fabrication.[16–18] This industry frequently resorts to aqueous HF solutions as SiO_2 etchants. A buffered NH_4F is commonly used as a diluent. Solutions of equvimolar NH_4F and HF concentration were reported to cause the optimal etching rate.[17,18]

The purpose of this work is to create anchoring points onto the glass surface to chemically bond different modifiers. In this regard, different acid/base pretreatments are proposed to generate the sufficient amount of OH groups on the surface. The methodology designed to carry out these pretreatments aims to preserve the superficial homogeneity and to minimize the weakness in mechanical properties of the glass. The resulting hydrophobic surface, chemically linked to the glass, could then be further functionalized or tailored to meet different applications. In this work, a metallocenic polymerization is performed to graft PP molecules onto the modified glass surface.

EXPERIMENTAL

Materials

Microscope (borosilicate) glass slides from Marienfeld GmbH and Co. KG 97922 Lauda Königshofen, (Germany) were used as glass substrate. The slides, of $76 \times 26 \times 1$ mm, were carefully selected from the commercial stock to assure thickness differences of less than ± 0.01 mm.

HF (Fluka) p.a. quality and ammonium fluoride (Sigma-Aldrich), 99.99+ % (metals basis) were used as buffer. Potassium hydroxide, from Sigma-Aldrich, with purity ≥85% was used for the alkaline treatment. The metallocene catalyst, $EtInd_2ZrCl_2$ was supplied by Aldrich. The cocatalyst MAO, from Witco, was used at a concentration of 10 wt % in toluene, with 1.8M total Al and 0.5M $Al(CH_3)_3$. Propylene (polymerization grade) was dehydrated and deoxygenated by passing it through a MnO/Al_2O_3–13× molecular sieve bed. The reactive grade 9-decen-1-ol, from Aldrich, was used without further purification. Toluene (J. T. Baker, HPLC grade) was also dehydrated by passing it through a 13× molecular sieve bed. N-heptane (Merck, reactive grade) was used for soluble PP extraction.

Glass surface pretreatments

The generation of hydroxyl groups on the glass surface includes a strong acid attack aiming to create anchor sites at the surface, followed by several washes with distilled water, stove drying (60 min at 100°C), and finally an alkaline attack with a concentrated base to provide the OH groups. Two kinds of pretreatments were performed. First, screening experiments using HF and KOH (acid pretreatment) were done by the following routine: Sample exposure to HF 0.08M, temperatures 30°C, 50°C, 70°C, and times 30, 120, and 210 min. The samples were then exposed to two different KOH concentrations (2.5N and 5.0N). The contact time was 5 h and the temperature 95°C. Finally, they were washed with distilled water for 24 h. These samples were named $A_{OHconc.}$-time-temperature (i.e., $A_{2.5}$-30-50 means acid treated slide, for 30 min at 50°C followed by KOH treatment of 2.5N).

A second set of experiments, using a HF/NH_4F buffer solution (buffer pretreatment) was carried out. In this case, two solution concentrations, with pH 5, were used: low, HF (0.32M)/NH_4F (1.79M) and high, HF (0.65M)/NH_4F (3.58M). In both cases, the experiments were performed at different temperatures (30 and 50°C) and exposure times (5 and 10 min). The samples were then exposed to 5.0N KOH for 5 h and 95°C. These samples were named $B_{buffer\ conc.}$-time-temperature.

To analyze thickness variations due to the pretreatments, the glass slide thicknesses were measured with a digital micrometer (precision of 0.001 mm). The thickness was determined at 10 points distributed along the slide surface and a set of 10 slides were measured after each treatment. On the other side, the glass surface topology, before and after pretreatments, was characterized by optical and scanning electron microscopy in a Zeiss Phomi III POL and a JEOL 35 CF instruments, respectively.

Propylene polymerization

Optimization of the hydroxyolefin concentration in the reaction media

A series of polymerization reaction was done, without slides, to select the best conditions. MAO (2.5 mL), 1 mg of metallocene catalyst, and different concentrations of 9-decen-1-ol were added to 150 mL of toluene contained in the reactor. The reaction was carried out at 70°C, for 30 min, under propylene flux and agitation. The reaction activity was tested by running three sets of experiments with alcohol concentrations corresponding to 1.0, 1.5, and 2.0% of polar olefin content, as calculated by considering the concentration of propylene in toluene at the reaction temperature and 1 atm of total pressure.[19]

Although the toluene used in the reaction was HPLC grade, the concentration of MAO was high enough to assure the solvent purity, eliminating potential reaction contaminants that could arise from toluene purifiers like CaH$_2$, Na, Zeolites, etc. Propylene (instead of an inert gas) was used as purge to simplify the subsequent steps in the polymerization procedure. In this way, a constant concentration of pure propylene is guaranteed at the reaction start (MAO injection).

Propylene polymerization onto pretreated slides

The polymerization technique followed in this work is similar to the previously reported by our Group on metallocene catalyzed propylene polymerization.[10] It was carried out at different Al/Zr molar ratios and varying the cocatalyst to catalyst ratio. The reaction conditions were optimized for maximum amount of propylene polymerized, which corresponds to a cocatalyst to catalyst ratio of 1700.

The pretreated slides were reacted with MAO and 9-decen-1-ol in a 300 mL stainless steel reactor having 260 mL of toluene. The reactor was flushed out with propylene for 30 min and then 1.5 mL of MAO and 1 mg of metallocene were added. During reaction, a propylene pressure of 1.8 bar was maintained. The mixture was kept at 85°C for 15 min and 0.075 mL of 9-decen-1-ol was then added by syringe technique. The polymerization reaction was allowed to proceed during 1 h at 60°C.

Characterization

To determine the presence of chemically bonded PP to the glass surface, the samples were extracted with heptane at 80°C during 2 h to eliminate the physically adhered PP. Then, they were washed with ethanol (96%) and finally with distilled water.

The surface characterization was performed in a SEM with an on line X-ray Dispersive Energy Microanalyzer (EDAX-4), the effectiveness of PP bonding was assessed by following the C/Si peak ratio before and after treatment and extraction. Also, A Nexus FTIR spectrometer, equipped with an optical microscope was used to study the surface modification after polymerization. The resolution was 4 cm^{-1}. Each spectrum is the result of 50 scans in the 650–4000 cm^{-1} range.

RESULTS AND DISCUSSIONS

Glass surface pretreatment

Acid pretreatment: The reaction between silica and HF is

$$4HF + SiO_2 \leftrightarrow SiF_4 + 2H_2O \qquad (1)$$
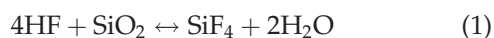
and in presence of aqueous HF

$$SiO_2 + 6HF \leftrightarrow H_2SiF_6 + 2H_2O \qquad (2)$$

where H$_2$SiF$_6$ is water-soluble and SiF$_4$ is in gas state. This simplified scheme represents the reaction stoichiometry. Mechanistically, the reaction of HF with a silica surface requires an initial insertion of water into a silicon oxygen bond. Such insertion hydrates the silica, providing a readily exchangeable group to further react with the HF. This reaction step is controlled by the activities of the hydronium ion and the silica surface. As the silica is hydrated, the hydroxyl groups present on its surface are replaced by fluoride ions in a highly exothermic reaction. The reaction rate depends upon the balance of a wide variety of species among the reactants as well as the products. Because of the complexity of the reaction, there have been few or no definitive studies of the reaction of HF with siliceous materials in spite of the great interest and long time elapsed since the discovery of the reaction.[14,15] The complete acid/base pretreatment results in an initial severe silica lattice attack by the acid, followed by the substitution of F for OH from the subsequent basic hydrolysis.

Figure 1 show the time and temperature effects of 0.08M HF treatment on the slide thickness. As expected, the greater the exposure time and temperature the greater the thickness decrease; although the temperature influence seems to be greater. It is also noted that at room temperature, there is not appreciable variation in thickness during the first 30 min of treatment.

Figure 2(a,b) show SEM micrographs of the slides with no surface pretreatment (2a), and pretreated sample A$_{2.5}$-30-50 (2b), respectively. Several surface inhomogeneities are observed, including holes of up to about 1 μm diameter in the pretreated sample, similar results were obtained for any treatment con-
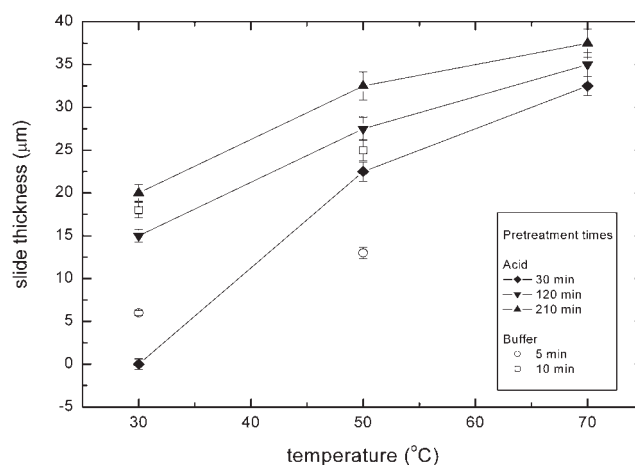

Figure 1 Slide thickness variation as a function of the time and temperature for acid and buffer treatments.
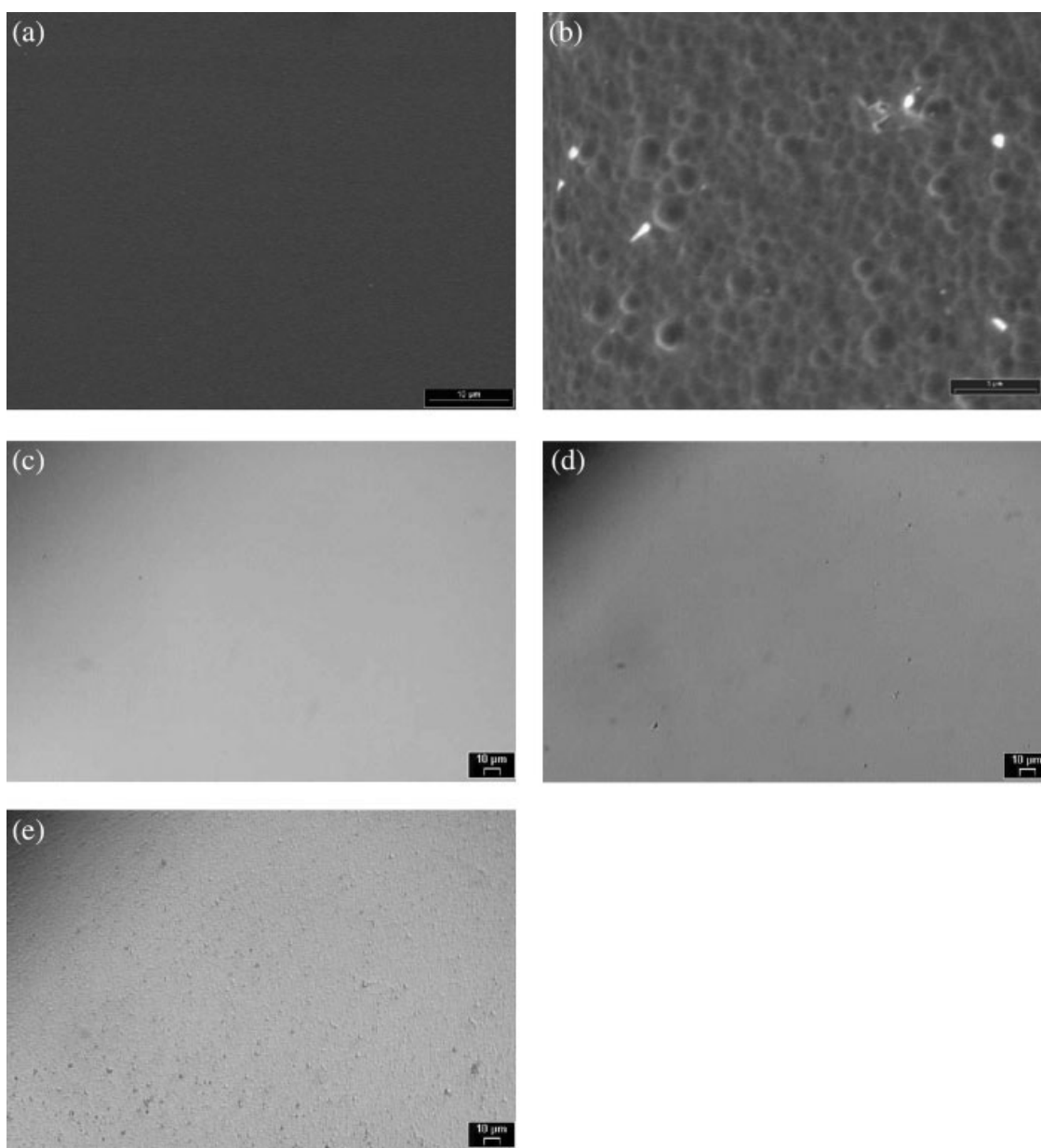
Figure 2 Slide surface previous and after acid pretreatment. (a) SEM micrograph of untreated sample (2000×), (b) SEM micrograph (4000×) of sample treated at 50°C during 30 min ($A_{2.5}$-30-50), (c) Optical micrograph (25×) of untreated sample, (d) Optical micrograph (25×) of $A_{2.5}$-30-30, and (e) Optical micrograph (25×) of $A_{2.5}$-30-70.

dition. For a wide appreciation of the acid attack characteristics, optical micrographs of samples, $A_{2.5}$-30-30 and $A_{2.5}$-30-70 [Fig. 2(d,e), respectively] were included and compared with untreated ones [Fig. 2(c)]. For the same exposure time, the temperature effect is clear from Figure 2(d,e). The sample pretreated at 70°C resulted entirely harmed, as compared to the one treated at 30°C which presents few scattered sites of attack. Moreover, it seems that the deterioration develops by appearing of successive corrosion spots rather than by a smooth and simultaneous attack over the whole sample surface. These appreciations are in agreement with the fact that sili-

con fluoride is a gas and take up almost 840 times more volume than the oxides. The SiF_4 causes gas "eruptions," which remove some SiO_2 from the surface, leaving round holes on it. The gaseous nature of the reaction products provides for rapid mass transport of the products from the reaction site. Additionally, the reaction creates heat in the forward direction, contributing to the force of the eruption. The escaped fluoride gases, in the presence of water, are in equilibrium with SiO_3H_2 and HF. This is essentially the reverse reaction, proceeding from the protonation point at the glass surface. The SiO_2 precipitates as a silica gel when the water around it
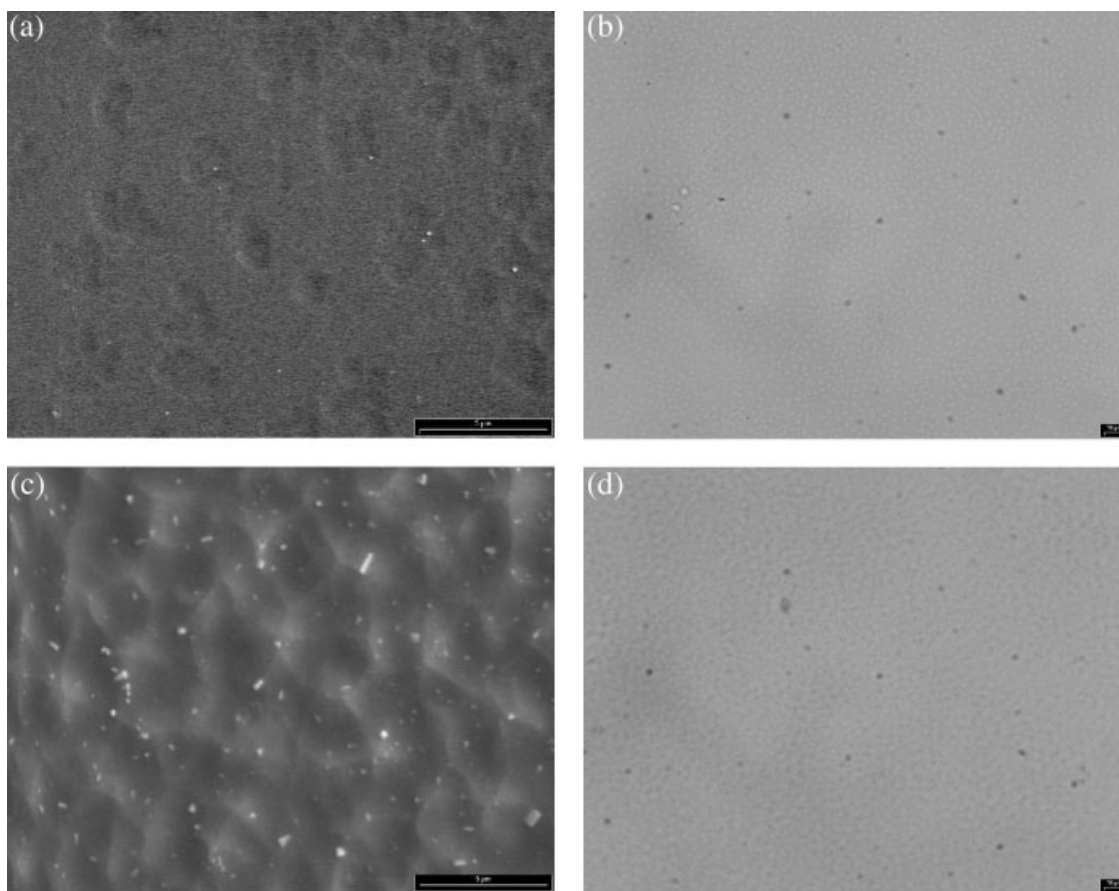
Figure 3 Slide surface after buffer pretreatment. (a) SEM micrograph (4000×) of B_{LC}-5-30, (b) Optical micrograph (25×) of B_{LC}-5-30, (c) SEM micrograph (4000×) of B_{HC}10-50, and (d) Optical micrograph (25×) of B_{HC}10-50.

evaporates, giving rise to spherical shapes surrounding the hole. These spheres are silica in a hydrated state, but not vitreous glass.[14] The above explanation gives a reason for the holes founded at the glass slides surface and their growing number as the temperature and time of acid exposure increase. It is noted that these silica spheres are not visible in Figure 2 as the samples were washed with distilled water after the pretreatment.

Attempts to identify superficial OH on slides by diffuse reflection infrared spectroscopy (DRIFTS), after the treatment with HF and KOH, were unsuccessful. However, the presence of superficial OH was verified, as will be explained below, by chemical linkage of PP molecules to the glass after *in situ* polymerization.

Acid/buffer pretreatment: Figure 1 also shows the effect of buffered HF treatment on slide thickness. Two different concentrations of buffer solutions were tested but keeping the same molar ratio to maintain the pH constant ($\sim$ 5). It is known that addition of buffer solutions retard the HF attack as it maintains and moderate the pH, resulting in a more homogeneous etching by disfavoring the eruption of fluoride gases and displacing the equilibrium

of reaction 1.[15–17] Moreover, taking into account that the HF concentration in the buffered solutions are 4 and 8 times greater than in the plain acid pretreatment, a much greater amount of OH groups can be expected to be bonded to the surface.

Our results show that the samples treated at 30°C during 5 min present a slight change in thickness for the two buffer concentrations used. Instead, significant thickness reductions were observed on samples treated at 50°C during 10 min. In particular, for high buffer concentration (0.65M), the slide thickness decreased significantly. Figure 3 show the surface of the buffer treated slides at the two extreme conditions, B_{LC}-5-30 [3(a,b)] and B_{HC}10-50 [3(c,d)]. The etching marks in B_{LC}-5-30 are detectable only by SEM, while the marks in B_{HC}10-50 can be observed by the naked eye. Moreover, these samples are about 3% thinner. Figure 3 also show the surface of these two samples viewed by optical microscopy. The buffer attack is evident at weak conditions (low concentration, temperature, and time) by some holes in SEM micrographs. On the other hand, the sample subjected to severe conditions seems to be more homogenously etched; they present a ''constant''
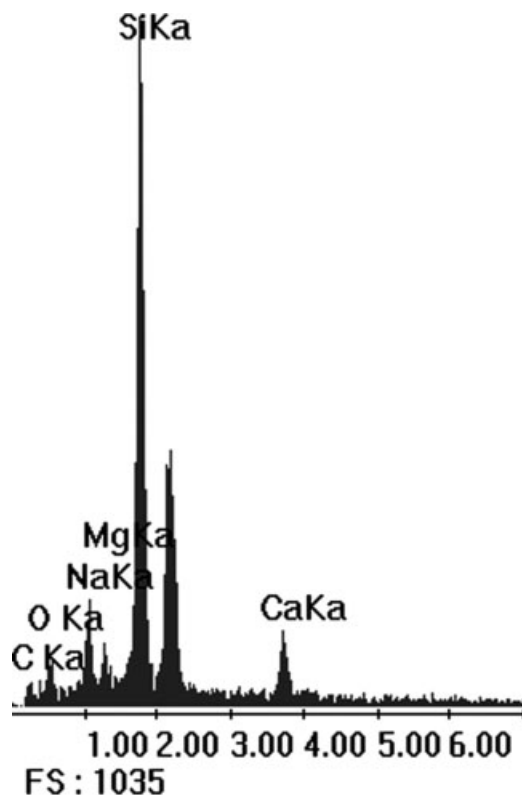
Figure 4 EDX spectrum of glass slides without treatment [from surface on Fig. 2(a)].

pattern without holes in SEM micrographs. Optical images [Fig. 3(b,d)] are very similar each other, they do not show localized attack and the surface homogeneity is preserved, although the resulting roughness is different in any condition. In any case the surface of buffered pretreated slides appears more homogeneous than for acid pretreated ones, as expected.

PP polymerization onto glass slides

To confirm the presence of OH groups on the glass surface, a metallocenic PP polymerization onto the pretreated glass slides was performed. It was demonstrated elsewhere that this reaction occurs from OH at the glass surface.[10] For further comparisons during characterization, untreated glass slides of the same kind were used as reference. Figure 4 shows the reference glass EDX spectra. Peaks from Si, Ca, C, Mg, O, and Na are present. The peak without denomination corresponds to Au from the sample coating to make it conductive. From EDX semi quantitative analysis, the peak ratios can be obtained. In this case, increments in C/Si ratio are expected whenever polymer grows from the glass surface. The C/Si ratio from untreated glass slide is 0.021. Also, peaks from Al should appear because of the MAO reaction.

Slides pretreated with HF

Figure 5 shows the localized FTIR spectra from the surface of the $A_{2.5}$-30-30 sample before and after the reaction. Before the polymerization no bands in the 2750–3000 cm^{-1} range appear. However, after reaction, four bands appear in this zone: 2950, 2920, 2860, and 2840 cm^{-1}. These bands are assignable to vs and va corresponding to CH_2/CH_3 in PP and are confirmatory of polymer presence on the surface.

The optical and SEM microscopy demonstrate the presence of PP, before and after the extraction procedure. Figure 6(a,b), shows optical micrographs of the reacted slide (from $A_{2.5}$-30-30) before and after PP extraction with heptane. The chemically bonded PP onto the slide can be assessed by comparison of Figure 6(a,b) with Figure 2(d), corresponding to the unreacted slide. To perform a more accurate analysis, SEM studies of the same samples were done. Figure 6(c) shows the SEM micrographs for this sample before extraction. The presence of polymer onto glass is indicated by the typical spheres resulting from PP polymerization. The corresponding SEM micrograph for the extracted sample is shown in Figure 6(d). The particles remain bonded to the surface, although in lower concentration due to the removal of physically attached PP by the extraction process.

Slides pretreated with HF/NH$_4$F

The results of the polymerization onto samples B_{HC}10-50 before and after extraction are shown in the Figure 7 through SEM micrographs and the corresponding EDAX spectra. The SEM micrographs show the presence of a great amount of PP linked to the surface before and after the extraction procedure [Fig. 7(a,b)]. The observed peaks, corresponding to C, O, and Al, confirm the occurrence of the metallo-
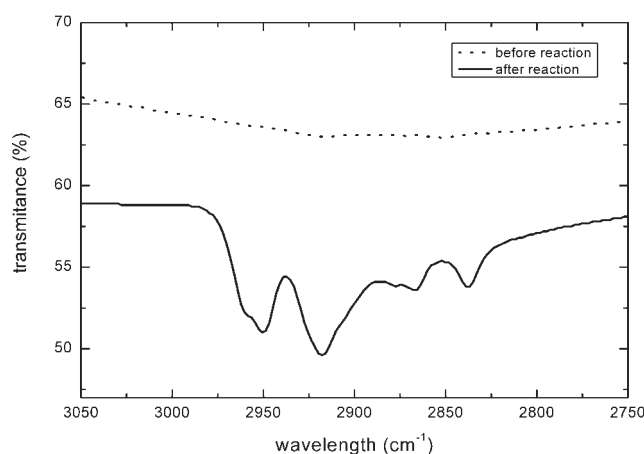

Figure 5 FTIR spectra of the slide surface of $A_{2.5}$-30-30 before and after polymerization reaction.
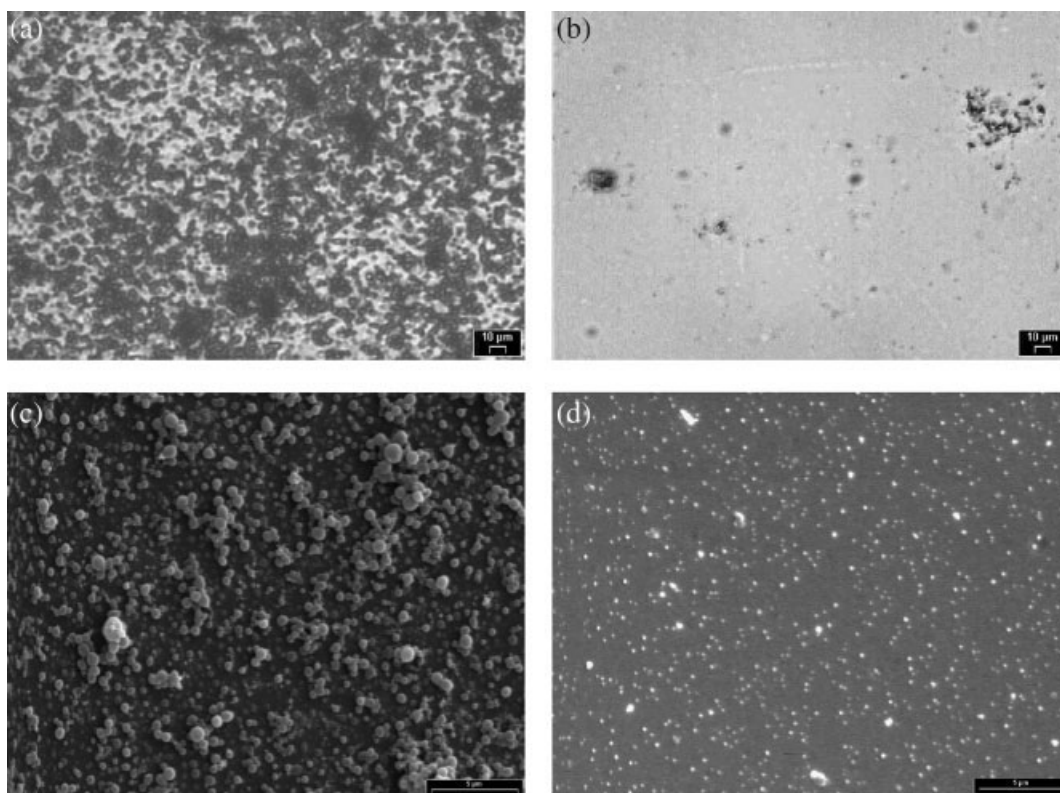
Figure 6 Surface of reacted samples from acid pretreated slide A$_{2.5}$-30-30. Optical micrograph (25×): (a) before extraction, (b) after extraction. SEM micrograph (4000×): (c) before extraction, (d) after extraction.

cenic polymerization on the glass slides and the incorporation of MAO at the surface.

The C peak in Figure 7(b), although small, is higher than in the unreacted slide (Fig. 4) and comes from the very thin polymer layer that remains chemically bonded to the surface after the extraction. The calculated ratio C/Si is 0.095, increased 4 times respect to the starting slide. The observed increase in the O peak, as well as the appearance of an Al peak, shows that the bond Si—O—Al (due to MAO) is effective. These results confirm the ability of the buffer surface pretreatment in promoting the propylene polymerization on the glass slides surface.

By observation of the reacted samples, after extraction from acid and buffer pretreatments [Figs. 6(d) and 7(b), respectively], is clear that the amount of anchoring points, resulting for the buffered treated samples, is much greater. This is consistent with the higher acid concentration and pH constancy of the buffered solutions.

CONCLUSIONS

The surface treatment concept was applied to soda-lime glass plates to create superficial hydroxyl groups. Subsequent metallocenic copolymerization
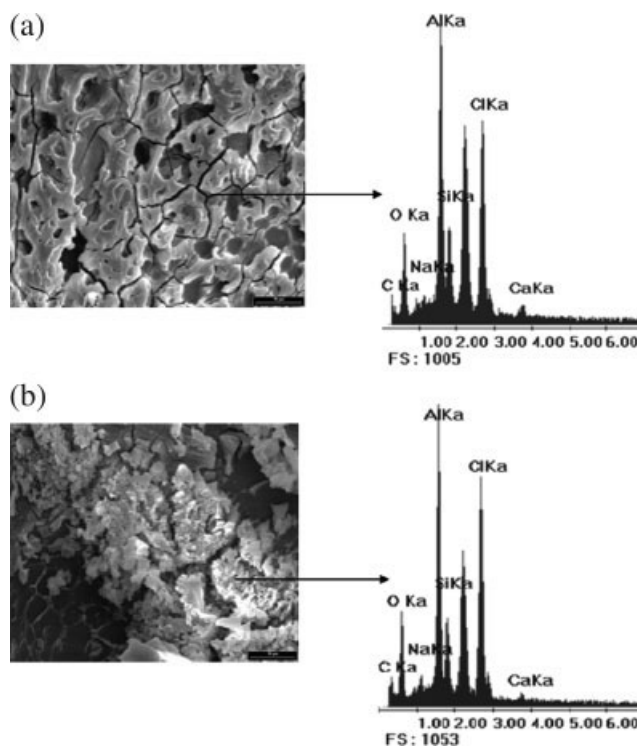

Figure 7 Surface of reacted samples from buffer pretreated slide B$_{HC}$10-50. SEM micrographs (2000×) and EDX spectrum of the sample (a) before extraction and (b) after extraction.

was carried out onto the modified glass surface to confirm the chemical nature of the hydroxyl groups bonding by the presence of grafted PP molecules adhered to the surface.

The acid/base pretreatment proposed is able to create anchoring points on the glass slides through the chemical bonding of hydroxyl groups onto the silica lattice. Either the acid or the buffer pretreatments produce a sufficient amount of OH groups to allow the subsequent PP grafting onto the surface. However, the buffered solutions cause less glass damage, bring a more homogeneous surface and create a much larger number of OH groups bonded to the surface.

This procedure allows the generation of a chemical linkage between the glass slide and PP. The generation of chemically bonded OH on the glass surface would allow the distribution of molecular probes by further reaction/adsorption processes. Besides, the grafted PP and the possibility of subsequent functionalization, opens the door to a wide range of practical applications in the adhesion field.

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