Evaluation of poly(propylene-*co*-1-hexen-6-ol) as an interfacial agent in polypropylene/glass laminates

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This paper evaluates an effective interfacial agent, poly(propylene-*co*-1-hexen-6-ol) (hydroxylated polypropylene, PP-OH), that improves the adhesion between polypropylene (PP) and glass. Owing to the unique brush-like microstructure of PP-OH, with flexible primary hydroxy groups and long sequences of propylene units, the hydroxy groups effectively form chemical bonds with the free silanol groups on the glass surface, and the PP segments cocrystallize with isotactic PP. The strong interfacial interactions are shown in 90° peel tests of PP/glass laminates. Both scanning electron microscopy and contact-angle studies on the fracture surfaces indicate no adhesive failure during peeling. In addition, differential scanning calorimetry studies demonstrate the cocrystallization between PP and PP-OH, and reflection infra-red results provide direct evidence of chemical bonding between PP-OH and glass surfaces.

(Keywords: hydroxylated polypropylene; polypropylene/glass laminates; interfacial adhesion)

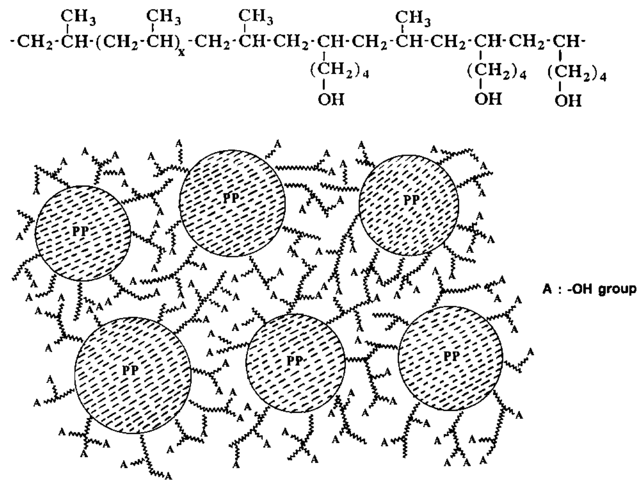
INTRODUCTION

Adhesion enhancement of polymeric resin to glass is of immense importance to many structural materials, such as glass-fibre-reinforced polymer composites and polymeric resin–glass laminates. Improvement of adhesion between glass and polymeric resin is commonly accomplished with silane coupling agents[1–5] by forming a strong covalent bond, i.e. Si–O–Si, between the two surfaces.

The poor interaction between isotactic polypropylene (PP) and glass has been a crucial problem in glass-fibre-reinforced PP materials and PP coating products. Many chemical methods, such as ionizing radiation (X-ray, γ-rays and electron beams)[6] in the presence of coupling agents and free-radical initiators to form polymeric peroxides, have been studied to improve the wettability of the PP surface, with only limited success. The inert nature of PP usually results in low functionalities and polymer chain scission[7].

In this paper, a recently developed poly(propylene-*co*-1-hexen-6-ol) copolymer (hydroxylated polypropylene, PP-OH)[8,9] is investigated as an interfacial agent between PP and glass. The PP-OH copolymer was prepared by Ziegler–Natta copolymerization with borane-containing monomer and propylene. Borane groups in copolymers were subsequently oxidized to hydroxy groups by $NaOH/H_2O_2$. Such hydroxylated copolymers not only have functional groups but also preserve most of the useful physical properties[8], such as molecular weight, crystallinity and thermostability, of isotactic polypropylene. Owing to the reactivity differences[9] between borane-containing monomer and propylene and the polymerization process, most of the borane monomers in the side chains are concentrated at the end of the polymer main chain. Consequently, the primary hydroxy groups are located close to the polymer chain end as shown in *Figure 1*.

The 'brush-like' molecular microstructure[9] results in consecutive sequences of propylene units in the polymer backbone, which can crystallize by themselves or cocrystallize with pure isotactic polypropylene (as will be discussed later). The hydroxy groups are expelled to the surfaces of crystalline phases and located in the



$$-CH_2-\overset{CH_3}{CH}-(CH_2-\overset{CH_3}{CH})_x-CH_2-\overset{CH_3}{CH}-CH_2-\underset{OH}{\underset{(CH_2)_4}{CH}}-CH_2-\overset{CH_3}{CH}-CH_2-\underset{OH}{\underset{(CH_2)_4}{CH}}-CH_2-\underset{OH}{\underset{(CH_2)_4}{CH}}-$$

Figure 1 Schematic perspective of the chain arrangements in the 'brush-like' poly(propylene-*co*-1-hexen-6-ol)

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amorphous phases, which are very accessible even under solid-state conditions. In fact, the hydroxy groups have been used as the anchor sites for the immobilization of homogeneous catalysts[10,11]. It is logical to expect that the flexible hydroxy group in the side chain may offer some processing advantages in the interaction with substrates.

EXPERIMENTAL

Instruments and measurements

The 90° peel test (ASTM D 773-47) was performed on an Instron 4201 Tensile Tester at a rate of 1 cm min^{-1}, by peeling PP backing materials from PP-OH coated matrices. Peel strengths were measured on 1 inch × 3 inch (~2.5 cm × 7.5 cm) specimens, which were clamped to the supports as shown in *Figure 2*. The peel strength was calculated from peel force/width of test specimen. Five samples were measured to obtain the average peel strength. The contact angle was measured directly on the sessile drop of distilled water on each sample with the help of a Rame Hart telescope goniometer. The sessile drop has a diameter of at least 4 mm in order to eliminate the size influence on the contact angle[12,13]. The contact angles were obtained from the average of 10 points on each sample surface. The ISI 40X scanning electron microscope (SEM) was used to examine the features of the specimens obtained from the peel strength tests. Specimens were lightly coated with gold by sputtering. Differential scanning calorimetry (d.s.c.) was measured on a Perkin–Elmer DSC-7 with TAC-7 instrument controller. The d.s.c. scans were measured from −30 to +200°C at a heating rate of 20°C min^{-1}.

In order to evaluate the reactivity of PP-OH on silica glass surfaces, reflectance infra-red spectroscopic measurements of the adsorbates were made, which were taken by using a Digilab model FTS 60 spectrometer. The sample was prepared by coating PP-OH (0.25% by weight in xylene) solution onto the silica glass surface. For high reflection sensitivity, a thin layer (60 Å) of silica glass was deposited on the gold surface by the sol–gel process[14]. The sol–gel process involved tetraethylorthosilicate/aluminium butoxide solution and spin coating on a vapour-deposited gold surface. After the thermal treatment of coated PP-OH film at 140°C for 2 h, the excess PP-OH was removed by rinsing with pure solvent. A uniform PP-OH film with thickness about 1000 Å was coated on the silica surface. Thickness of both PP-OH and silica films was determined by an ellipsometer operating at a wavelength of 632.8 nm and an incident angle of 70°.

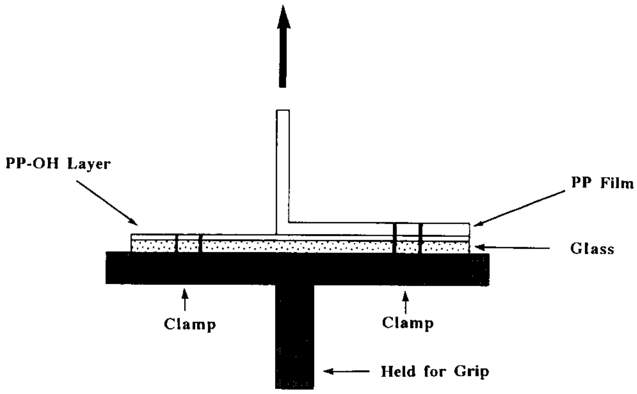

Figure 2 Schematic diagram of the 90° peel test

Materials

Poly(propylene-*co*-1-hexen-6-ol) copolymers were prepared by a continuous copolymerization process shown in the previous paper[9]. The polypropylene (PP) used was a pellet-type product of Shell Development Co. (denoted 5C08) and extruded as a film of thickness 0.9 mm. It has a density of 0.903 g cm^{-3} and a melt flow index of 2.9. Drawn PP film with high modules and high strength was produced via the continuous hot nip drawing technique[15]. PP film was drawn at a constant rate, and a neck produced in the hot nip zone. The final draw ratio of drawn PP film used in this study was 8, and the resulting film had modulus and tensile strength of ≈4.5 GPa and ≈400 MPa, respectively. Undrawn PP film was prepared by the hot press process at 180°C for 30 min with 10 000 psi (≈70 MPa) pressure, followed by cooling under pressure for 2 h. Both drawn and undrawn PP film were used as backing materials. For control experiments, some PP films were also chemically etched in a mixed solution of $Na_2Cr_2O_7/H_2SO_4/H_2O$ (1/1/30 by weight) at 70°C for 5 min, followed by rinsing with distilled water, then dried in a vacuum oven at 40°C for more than 5 h.

Microscope E-glass and quartz slides (3 inch × 1 inch in length and breadth and 0.047 inch in thickness (~75 mm × 25 mm × 1.2 mm)) were purchased from VWR Scientific Inc. and Chemglass Inc., respectively. E-glass is a calcium boroaluminosilicate glass of nominal composition 56% SiO_2, 14% Al_2O_3, 22% CaO, 6% B_2O_3 and fractional percentages of Na_2O, MgO, TiO_2 and Fe_2O_3 (by weight). To enhance adhesion, the surface treatment of E-glass was carried out using various methods. Some of the E-glass slides were cleaned in acetone, rinsed in distilled water and dried in an oven at 170°C for 15 min. The E-glass slides were also chemically etched in a hydrochloric acid solution (25 vol% of HCl in H_2O) at 70°C for 24 h, followed by rinsing with distilled water and then dried in a vacuum oven at 40°C until use.

Lamination procedures

A PP-OH layer was coated on the glass surface using one of two methods, namely solution casting and hot press processes. In solution casting, a hot PP-OH solution (1% by weight in xylene) at 140°C was spread on glass (plain E-glass, acid-etched E-glass and quartz slides) to form a complete coating layer. The solvent was then allowed to evaporate under room temperature and humidity. After the selected evaporation time, the films that had formed were placed in a vacuum oven at 50°C for 24 h to remove any residual solvent remaining in the film, prior to bonding with backing materials. Usually, the PP-OH layer is approximately 20 μm in thickness measured from SEM micrographs.

In the hot press process, PP-OH powder was spread on a glass surface and was melted between a pair of Teflon-coated aluminium plates at 180°C. After waiting at least 20 min to ensure complete melting, the sample was pressed at minimum applied pressure for 25 min. During this procedure, the hydroxy groups of PP-OH react with silanol groups on the glass surface. The melt was then cooled to induce solidification of the PP-OH.

The resultant layer has an approximately 25 μm thickness estimated from SEM micrographs.

PP/glass laminates, PP film on top of PP-OH coated glass, were prepared in a Carber hot press. Laminates were held at 180°C for 25 min under minimum applied pressure and then slowly cooled down under pressure for 5 h. The resulting laminates were able to retain most of the original dimensions of PP films based on SEM micrographs. Usually, both undrawn PP and drawn PP backing materials after lamination have 170–180 μm thickness.

RESULTS AND DISCUSSION

The brush-like microstructure of PP-OH copolymers may offer several advantages as an adhesion promoter between PP and glass. In addition to good thermal stability, an important requirement in processing, the clear phase separation between PP segments in the crystalline phase and hydroxy groups in the amorphous phase may enhance the interactions to both PP and glass surfaces. In the ideal case, the functional groups can have chemical or physical interactions to the glass surface, and the propylene segments in PP-OH copolymer penetrate into PP homopolymer and form a highly crystalline structure as shown in *Figure 3.*

Ideally, a defect-free monolayer of PP-OH should be enough to secure the interaction between PP and glass, which actually involves two interfaces PP/PP-OH and PP-OH/glass. The mobility of functional groups in PP-OH offers processing advantages* to find the anchor sites on the glass surface. It will be thermodynamically favourable for the hydrophobic polypropylene segments to move away from the hydrophilic interface and form crystalline structures with pure isotactic PP.

D.s.c. cocrystallization studies

The cocrystallization of PP and PP-OH was revealed by d.s.c. analysis[15]. A drawn PP film and PP-OH copolymer were melted together and the d.s.c. endotherm was observed over the normal melting range of these two components. Upon cooling, crystallization occurred at a temperature of approximately 110–130°C, and peak shape and location seem to be the net result of individual PP and PP-OH crystallization. However, when the sample was reheated after cooling, cocrystallization of PP and PP-OH was shown by the presence of a single melting peak below the melting region of PP as shown in *Figure 4b.*

The other study directly used a laminated sample containing PP and PP-OH layers. As shown in *Figure 4c,* the melting endotherm of the PP/PP-OH laminate sample consists of three peaks. The peak in the middle is at approximately the same position as the previously identified cocrystallization peak in *Figure 4b,* whereas the other two peaks are indicative of pure PP and PP-OH. Accordingly, cocrystallization occurs at the PP/PP-OH interface in the laminate. The results offer an experimental basis for the postulated PP/PP-OH interaction in *Figure 3.* The chemical interaction between PP-OH and glass surfaces will be discussed later.

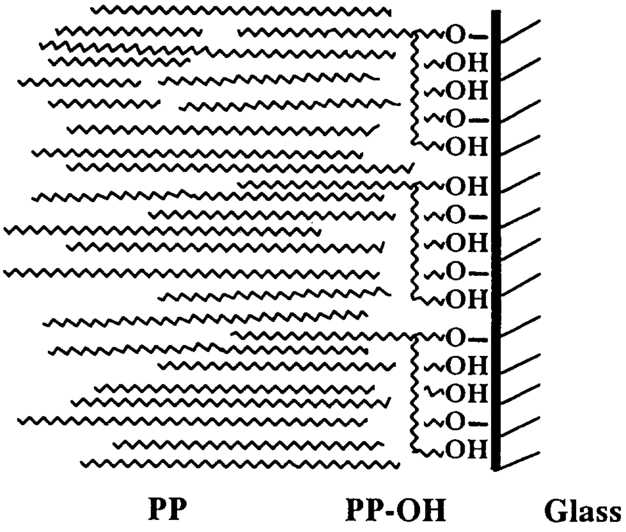

Figure 3 The molecular arrangement in an ideal PP/glass laminate bonded by PP-OH

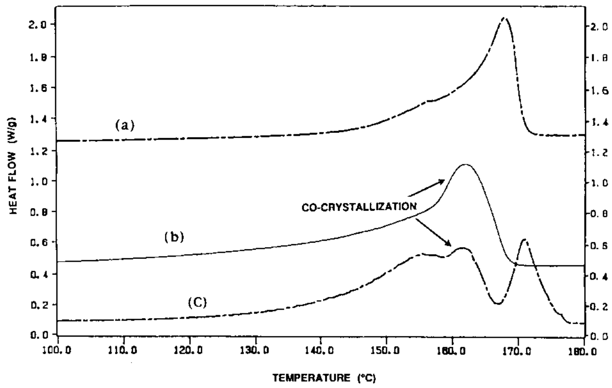

Figure 4 D.s.c. curves of (a) PP, (b) PP/PP-OH blend and (c) PP/PP-OH laminate

PP/glass laminates

The first step in the preparation of PP/glass laminates involves the coating of PP-OH onto the glass surface. Both solution casting and hot press processes were monitored by contact-angle measurements. For optimum adhesion[16,17], the glass surfaces were cleaned or converted to a suitable condition before bonding. Chemical etching increases the hydrophilicity of E-glass surface and changes the contact angle of a water drop from 39° ± 1° to 17° ± 2°, as shown in *Table 1.*

After PP-OH coating to a thickness of 20–25 μm, the surface completely changes from hydrophilic to hydrophobic. The contact angles of a water drop on PP-OH/glass surfaces are 83° ± 6° and 108° ± 4° for solvent casting and hot press processes, respectively. It is interesting to note that the hot press method offers almost identical contact angle as that (111° ± 3°) of pure isotactic polypropylene film. This may indicate a better processing condition to obtain PP-OH/glass structure. The hot press process offers some favourable conditions, such as heat, pressure and density, in producing good interfacial interaction between PP-OH and glass. In fact, the adhesion study (discussed later) shows a better peel strength by using the hot press process.

Commercial drawn and undrawn PP films were then laminated with PP-OH/glass to form a sandwich

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* PP-OH copolymer, containing 5 mol% of hydroxy groups, has been found to be a useful compatibilizer in PP/PP-OH/poly(ethylene glycol) blends. The results indicate the excellent mobility of functional groups, which diffuse to the interface under similar processing conditions

Table 1 Contact angles of sample surfaces

Sample surfaces	Contact angle (deg)
E-glass	
Cleaned by acetone and hydrated	39±1
Acid etched	17±2
Quartz	
Cleaned by acetone and hydrated	23±1
PP-OH (on the acid-etched E-glass)	
Solvent casting	83±6
Hot press	108±4[a]

[a] The contact angle of polypropylene is 111°±3°

structure as shown in *Figure 2*. To enhance the cocrystallization between PP and PP-OH, the laminates were held at 180°C (slightly above the melting point of PP) for 25 min and then slowly cooled down to room temperature under pressure for 5 h. The final PP films were about 170–180 μm in thickness.

Peel tests and SEM studies

Table 2 shows the 90° peel test results of several PP/glass laminates, including both undrawn and drawn PP samples with various glass surfaces. Most of the specimens have strong peel strength. Especially, the drawn PP/acid-etched E-glass laminates, with PP-OH interfacial agent and hot press process, have very high peel strength (about 1200 to 1500 N m^{-1}). For comparison, a control experiment by laminating acid-etched PP film with acid-etched E-glass, without the use of PP-OH, only shows very low adhesion (too low to get any significant number in the 90° peel test). This result indicated the important role of PP-OH layer as an interfacial agent between glass and PP film. In detail, the acid-etched glasses show significantly better adhesion than the simple solvent-cleaned ones. It is known that acid etching can increase both the concentration of free Si–OH groups and the roughness of the glass surface. Although a rough glass surface can enhance the mechanical interlocks with the interfacial agent, it is believed that the strong adhesion is primarily due to the chemical bonding between PP-OH and the glass surface. The experimental evidence for the chemical reaction between free Si–OH groups on the glass surface and PP–OH will be discussed in the reflection i.r. studies.

In general, the peel strengths of PP/glass laminates by hot press process are greater than those by solution casting process. This result may be attributed to the deleterious effects of solvent and the cohesive energy of PP-OH layer after solution casting. The favourable effects of heat and pressure in hot press process enhance the interaction between silanol groups on the glass surface and hydroxy groups in PP-OH and better interpenetration of PP-OH into PP layer with high overall density.

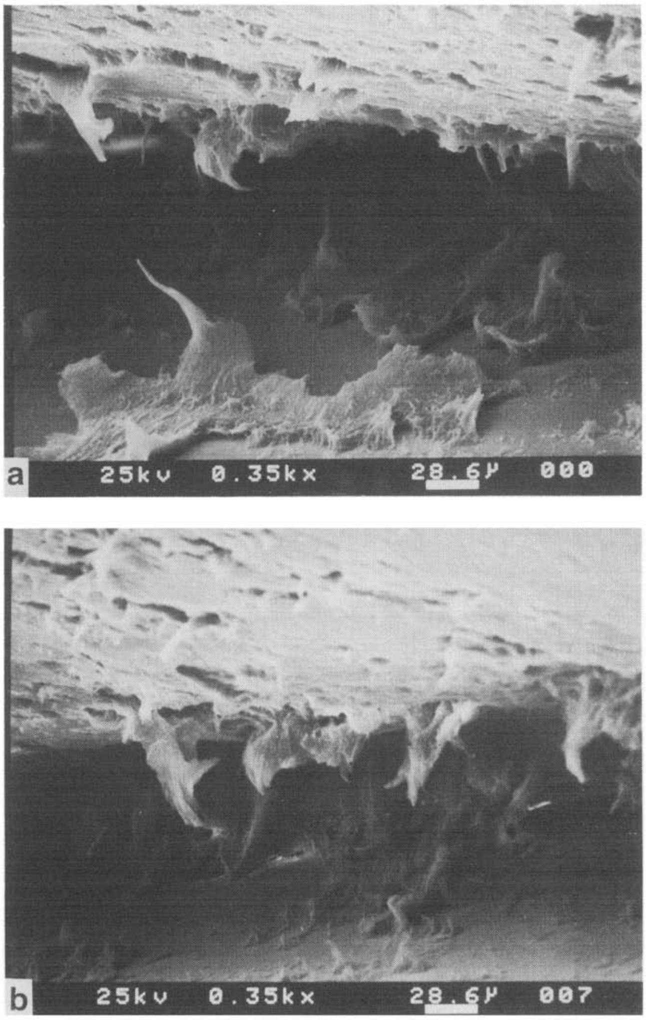

Figure 5 SEM micrographs of peeled surfaces of (a) drawn PP/acid-etched E-glass and (b) undrawn PP/acid-etched E-glass laminates bonded by PP-OH via hot press process

Figure 5 shows the SEM results of the peeled surfaces of two laminates, drawn PP/acid-etched E-glass and

Table 2 The peel strength of PP/glass laminates

Glass surfaces	Peel strength (N m^{-1}) Undrawn PP (a)	Undrawn PP (b)	Drawn PP (a)	Drawn PP (b)
E-glass				
Cleaned by acetone and hydrated	223±26	327±23	297±28	415±61
Acid etched	416±77	1092±141	520±83	1373±18
Quartz				
Cleaned by acetone and hydrated	362±30	529±78	488±42	672±86

(a) Solution casting method with 20 μm PP-OH thickness
(b) Hot press process with 25 μm PP-OH thickness

Table 3 Contact angles of fracture surfaces of PP/glass laminates[a]

	Contact angle (deg)	
Sample surfaces	Undrawn PP	Drawn PP
Peeled PP	103±5	107±7
Peeled glass[b]	110±11	106±8
Split PP interior	112±8	110±6

[a] The laminates are prepared by hot press process
[b] Acid-etched E-glass

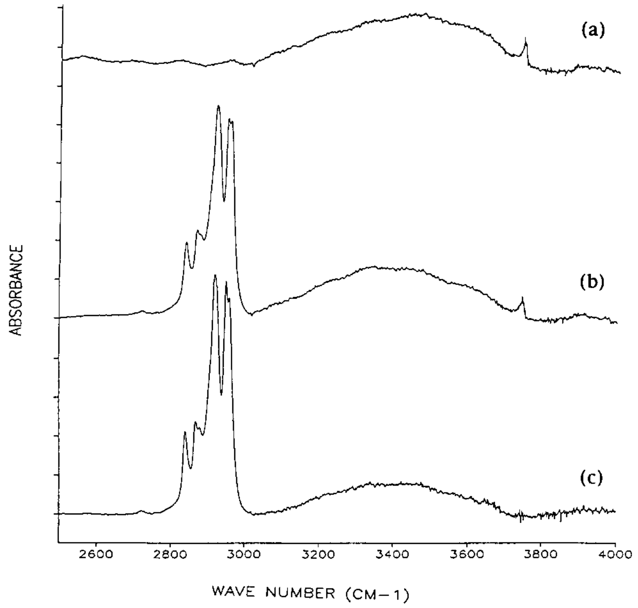

Figure 6 Reflection i.r. spectra of (a) glass surface, (b) PP-OH (thickness about 1000 Å) coated on glass and (c) PP-OH/glass after thermal treatment

undrawn PP/acid-etched E-glass laminates bonded by PP-OH via hot press process. Micrographs of both peeled surfaces of undrawn and drawn PP films show about the same morphology. Both are very rough, with many fracture structures different from the flat surfaces of the original PP and glass. It is apparent that failure was not due to the adhesive failure at the PP-OH/glass interface. The cohesive energy in PP/PP-OH matrix was responsible for both drawn and undrawn cases. In fact, the contact angles of water drops on the peeled surfaces of acid-etched E-glass and PP shown in *Table 3* have similar numbers and indicated hydrophobic properties. Large deviation in contact-angle value was due to roughness of the peeled surface. So the contact-angle data of peeled surfaces were average values of major trend.

Reflection i.r. spectra

The energy required to break the interfacial interaction is greater than that required to break the PP/PP-OH matrix, which helps to explain the persistently lower peel strength in the undrawn PP cases, owing to the lower cohesive energy in undrawn PP/PP-OH matrix. Similar experimental results were repeated at various test rates and temperatures. It is fundamentally interesting to know the nature of adhesion between PP-OH and glass. The reflection i.r. technique was used to reveal the chemical bonding of PP-OH to a silica glass surface. *Figure 6* compares the i.r. spectra of three samples, silica glass surface and coated PP-OH/glass before and after thermal treatment.

The i.r. absorption of the glass surface in *Figure 6a* shows two absorptions, a broad band between 3000 and 3700 cm^{-1} due to H_2O and vicinal Si–OH absorption modes[18,19] and a small peak at 3745 cm^{-1} corresponding to the free Si–OH groups on the surface. After PP-OH coating with thickness of about 1000 Å, several additional absorption peaks between 3000 and 2800 cm^{-1}, corresponding to saturated hydrocarbon, appear in *Figure 6b*. At this stage, the PP-OH thin film is mostly in physical interaction with the glass surface and can be redissolved in xylene solvent at elevated temperature. After the thermal temperature of PP-OH/glass at 140°C for 2 h, the peak intensity at 3745 cm^{-1} is almost completely diminished as shown in *Figure 6c*. In addition, the PP-OH thin film becomes completely insoluble in xylene even up to 150°C. The combination of both results strongly suggests the effective chemical reaction of free silanol groups and primary hydroxy groups to form –Si–O–C– bonds, to which may be attributed the high adhesion at PP-OH/glass interface.

CONCLUSIONS

The objective of this study is the development of a strong interfacial agent between glass and polypropylene. Great improvement of adhesion between glass and PP film was accomplished by the newly developed PP-OH interfacial agent with the combination of glass surface treatment and hot press process. The interfacial agent formed a strong chemical bond in PP-OH/glass layer and an interpenetrated PP-OH/PP layer by interdiffusion and cocrystallization between PP-OH and PP segments. Extremely high peel strength, more than 1100–1500 N m^{-1}, was obtained from drawn PP/acid-treated E-glass laminates by hot press process.

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