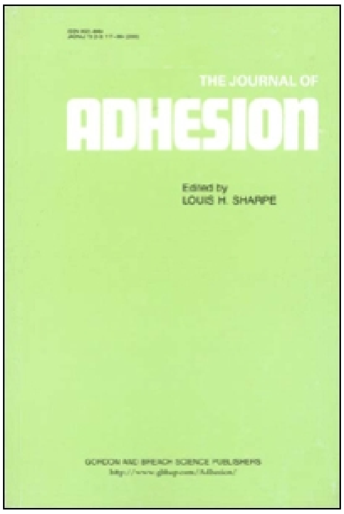

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Silane-Grafted Isotactic Polypropylene Used as a Coupling Agent on Glass. Consequences on The Interfacial Adhesion

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Silane-Grafted Isotactic Polypropylene Used as a Coupling Agent on Glass. Consequences on The Interfacial Adhesion*

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Functionalized isotactic polypropylenes have been synthetized in order to be used as coupling agents on glass fibers associated with a polypropylene matrix. This new way of interface toughening requires a grafting of such polymeric chains on the glass surface and a crystallization of these grafted chains at the same time in the same crystals as the polypropylene matrix (co-crystallization). Using a Ziegler-Natta polymerization, copolymers based on propene and two different types of dienes have been prepared. Such a synthesis allows one to change the functionality and the position of double bonds used to introduce the silane functions. A Speier hydrosilylation was used for this purpose with two kinds of silanes. Silane-functionalized oligopropenes were also prepared in order to compare the effect of the position of the silane functions on the glass/polypropylene adhesion: side chain or chain end positions. The characterization of these functionalized polypropylenes is described. Their ability to be grafted on a glass surface was checked by means of wetting measurements after extractions according to the hydrophobic nature of the polypropylene and the hydrophilic character of the glass. The co-crystallization of the pure and functionalized polypropylenes was demonstrated on blends. Two silane functionalized-PP were selected to study the glass fiber/PP adhesion by means of the microdroplet test.

KEY WORDS: Polypropylene; adhesion; glass; silane; connecting chains; grafting; coupling agents; microdroplet test; co-crystallization.

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INTRODUCTION

It is now well known that the interface plays an important role in the properties of structural composite materials such as glass fiber-based materials.[1-4] These properties do not result only from the adhesion accomplished at the fiber-matrix interface but also on the interphase properties.[5] The interfacial adhesion is generally done by means of the use of coupling agents such as organosilanes having hydrolyzable groups able to react with the silanols on the glass surface and reactive functions for reactions with the polymeric matrix.[6-7] This way works well with thermoset matrices according to the presence of functions in the reactive mixture. In the case of non-reactive matrices, the presence of such surface treatment modifies the interactions between the polymer matrix and the substrate.[8-9] Work was done by DiBenedetto[7] *et al.* on polycarbonate/glass fiber systems involving a surface treatment based on the grafting of oligomers of polycarbonate with $TiCl_4$- and $SiCl_4$-treated fibers. Using such a treatment, the OH groups of the oligomers react with the chlorine atoms leading to a grafted oligomer layer. Good adhesion was obtained with the grafted fibers, whereas, for the untreated fibers, there is poor adhesion. For semi-crystalline matrices, additional phenomena could appear according to the change in the crystallization in the vicinity of the surface. For example, a transcrystalline region can be created on the glass fiber surface as a function of the processing conditions, *i.e.*, the cooling rate, the occurence of shearing in the melt, etc.[8-11] The influence of such transcrystalline interphases on the mechanical properties of the composites is not clearly demonstrated.[12-13]

Polypropylene/glass fiber composites are now widely used in different industries according to their low cost and ease of fabrication. The hydrophobic and inert nature of the polypropylene (PP) leads to some difficulties in the wettability of hydrophilic surfaces such as glass fibers and to poor adhesion at the interface. The conventional way to improve the interfacial adhesion between a glass fiber and PP is to use a sizing combining a grafted-PP and an aminosilane in the sizing in order to create covalent bonds at the interface.[14] By this way, however, it is difficult to control the occurence of the reactions at the interface, thus, as a consequence, to control the interfacial properties. Another way consists in the modification of the glass surface with a modified-PP having functional groups able to react with the silanols and to co-crystallize with the polypropylene chains of the matrix in the bulk.[15] For this purpose, it is necessary that the modified-PP has the same structure as the PP matrix. In a previous paper,[15] the synthesis of silane-grafted isotactic polypropylenes using a Ziegler-Natta polymerization was described and the ability of such PP to co-crystallize with a pure PP was checked on 50:50 blends. Copolymers based on propene and a diene were prepared and the silane functionalization was done by means of a Speier hydrosilylation. Oligopropenes having a terminal silanated group were also considered, to obtain a series of PP having chain end and side chain silane functions. According to the Ziegler-Natta polymerization, the functionality, *i.e.*, the number of silane groups per chain, was varied by changing the amount of diene in the copolymers. Recently, Lee *et al.*[16] reported the evaluation of poly(propylene-co-1-hexen-6-ol) as an interfacial agent in polypropylene/glass laminates. The co-crystallization of these PP-OH with pure PP was also checked using DSC and reflection IR spectroscopy was used to provide direct evidence of chemical bonding between the PP-OH and the glass surface.

Strong interfacial interactions were shown in 90° peel tests of PP/glass laminates. According to the thick PP-OH layer (20 to 25 μm) deposited on the glass surface, an interpenetrated PP-OH/PP layer was formed by the interdiffusion and co-crystallization between the PP-OH and PP segments.

In this paper, silane-functionalized isotactic poly(propylene-co-diene) materials synthesized using a Ziegler-Natta polymerization are considered. These have silane functions in side chain positions and the amount of such silane groups can be varied by changing the percentage of the diene in the copolymer. Silane-grafted oligopropene is also considered in order to compare the effect of the position of the silane groups: chain end and side chain positions for the oligopropenes and poly(propylene-co-diene), respectively. The silane groups on the modified-PP are able to react with the silanols of the glass surface to form anchor sites. In addition, with such a treatment, the nature of the glass surface changes from hydrophilic to hydrophobic, improving the wettability of the substrate with the PP melt. The grafting of the functionalized-PP is checked using wetting measurements after extraction of the ungrafted PP with various solvents. In fact, in opposition to the work done by Lee *et al.*, only one grafted monolayer is required. The second requirement for improved adhesion between pure PP and the glass surface through the grafted PP is that the co-crystallization between the pure PP and modified-PP segments occurs. This fact is studied on pure PP/modified-PP blends. Two of the silane-modified PP are selected from these requirements and used as polymeric coupling agents on glass fibers. The interfacial adhesion between glass fiber and PP is studied using the microdroplet test and comparisons are done with untreated and organosilane-treated glass fibers.

EXPERIMENTAL

Reagents and Synthesis of Isotactic Functionalized PP

The synthesis of the silane-functionalized isotactic polypropylenes from diene-propene copolymers is briefly described in Figures 1 a and b. The details of the synthesis were reported in a previous paper.[15] The synthesis proceeds from a polymerization, with an heterogeneous Ziegler-Natta catalyst, between propene and 7-methyl-1,6-octadiene or 1,9-decadiene. The obtained copolymers are very stereoregular with a comb structure and molar masses, $\bar{M}w$, of about 200,000 g·mol^{-1}. The molar percentage of double bonds determined from the polymerization conditions (*i.e.*, the relative amount of diene monomer) can be varied from 1.9 to 13.5 for the poly(propene-co-7-methyl-1,6-octadiene) and from 0.65 to 1.7 for the poly(propene-co-1,9-decadiene).

A series of oligopropenes (provided by R. Mülhaupt) prepared from an homogeneous Ziegler-Natta catalyst using a stereo rigid zirconocene system were also considered. These have a linear structure with a degree of polymerization between 50 and 250 (Fig. 1). The characteristics of all the oligopropenes and copolymers are reported in Table I.

A Speier hydrosilylation method was used to graft a chlorosilane or a triethoxysilane on the polypropylene chain (copolymers or oligopropenes) using the double bonds. A solution of hexachloroplatinic acid (1% wt.) in 2-propanol was used as the catalyst.

An isotactic polypropylene from Exxon, denoted "pure PP", was used as the matrix for the microcomposites (see Table I).

Physico-chemical Measurements (DSC, FT-IR)

DSC measurements were done on a Perkin-Elmer DSC7 calorimeter on pure polypropylene, functionalized-PP, and blends of functionalized-PP/pure PP (50:50 wt.). A thermal treatment of 5 minutes at 200 °C was done on all the samples to destroy the thermal history. Thermograms were obtained in an anisotherm (dynamic) mode (20 K.min^{-1}) for cooling and heating. The melting and crystallization temperatures (denoted T_m and T_c, respectively) and the enthalpies (denoted ΔH_m and ΔH_c) were determined.

FT-IR spectra were recorded using a Nicolet SX2 spectrometer in a transmission mode on thin films made by molding at 200 °C for 5 minutes.

Grafting Glass Plates and Fibers

Glass float plates were used to verify the grafting of the functionalized polypropylenes. The glass plates were initially washed with a sulfochromic solution. The grafting was performed by dipping the glass plate in a xylene solution (5% wt.) of the functionalized

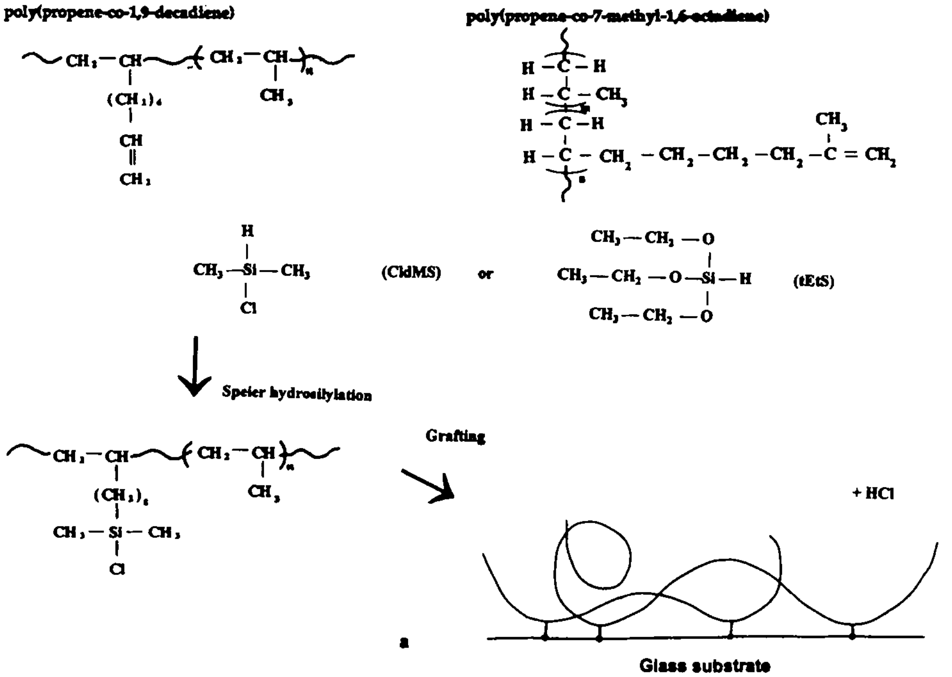

FIGURE 1 Schematic synthesis of the silane-functionalized polypropylenes (hydrosilylation using CldMS): a. side chain silane-grafted poly(propene-co-diene), b. chain end silane-grafted oligopropene.

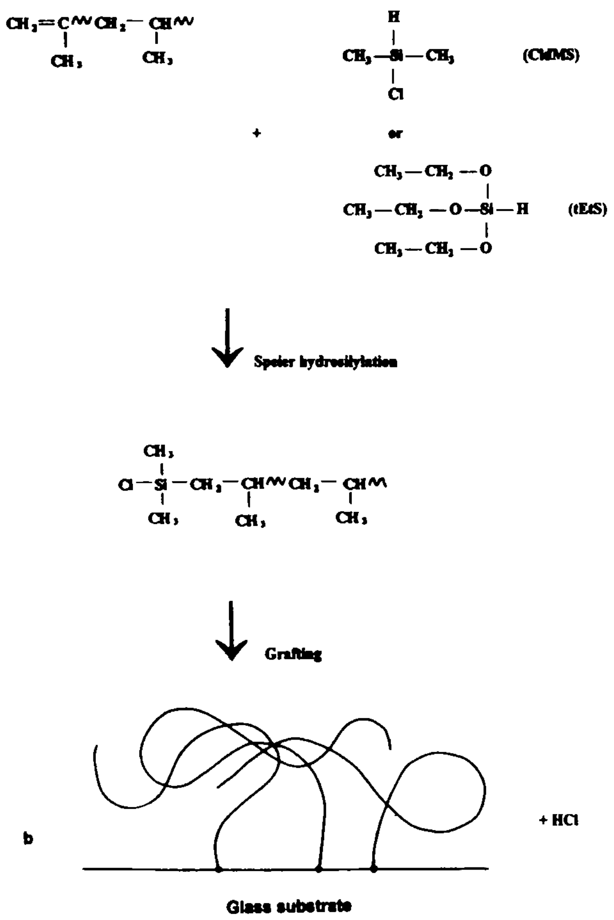

FIGURE 1 (*Continued*).

polymer for 5 minutes at 140 °C. The glass plates were dried at 100 °C for one hour under vaccum. Successive extractions were done before wetting measurements to remove the polymer which is not grafted to the glass surface: 5 hours with methanol, followed by 5 hours with tetrachloroethane, and 5 hours with xylene. Glass float plates were also treated using dodecyl triethoxy silane to compare with a surface grafted with short alkyl chains.

Untreated E-glass fibers having a mean diameter of 19 μm (from Owens-Corning Fiberglass) were treated using the same procedure.

Wetting Measurements

Wetting measurements were done by means of the sessile droplet method using home-made equipment at room temperature. The contact angle was measured using a video system. The video signal was digitized and the contact angle was determined

TABLE I
Characteristics of the considered polypropylenes: pure PP used as a matrix and silane-functionalized ones

Polypropylene	Silane funct.	Double bonds(*) (% mol.)	$\overline{Mn}$ ($g.mol^{-1}$)	$\overline{Mw}$ ($g.mol^{-1}$)
Pure PP	–	–	38,000	260,000
Oligopropene 6,200	CldMS Chain end	1.0	6,200	–
Oligopropene 10,000	CldMS Chain end	1.1	10,000	20,000
Oligopropene 10,000	tEtS Chain end	1.1	10,000	20,000
Poly(propene-co-1.9% 7-methyl-1,6-octadiene)	CldMS Side chain	1.9	60,000	200,000
Poly(propene-co-8.5% 7-methyl-1,6-octadiene)	CldMS Side chain	8.5	–	–
Poly(propene-co-13.5% 7-methyl-1,6-octadiene)	CldMS Side chain	13.5	39,000	170,000
Poly(propene-co-0.65% 1,9-decadiene)	CldMS Side chain	0.65	38,000	201,000
Poly(propene-co-0.65% 1,9-decadiene)	tEtS Side chain	0.65	38,000	201,000
Poly(propene-co-1.7% 1,9-decadiene)	CldMS Side chain	1.7	–	–
Poly(propene-co-1.7% 1,9-decadiene)	tEtS Side chain	1.7	–	–

*The number of double bonds is determined from the amount of diene considered in the copolymer synthesis.

using an image analyzer from Nachet after the image capture. In this paper, only the contact angle, θ, with distilled water is considered. The contact angles used were the initial (0.5 s) ones.

Microdroplet Adhesion Test

Microdroplets having diameters from 100 to 500 μm were formed from the melting of pure polypropylene film at 165 °C for 35 minutes and quenching at room temperature (Fig. 2). Adhesion experiments were carried out using the microdroplet test in order to determine the average interfacial shear strength, $\bar{\tau}$. This was calculated considering a constant shear stress along the interface.[17] Thus, the following formula was used:

$$\bar{\tau} = F_d / 2 \Pi r_f L$$

where F_d is the debonding load, r_f the radius of the fiber, and L the embedded length. About 50 microdroplets were considered for the determination of $\bar{\tau}$.

The fragmentation test performed on single filament composites cannot be done on this polypropylene/glass fiber system because of the low strain at break of the polypropylene matrix. In fact, for such an experiment, the matrix needs to display a strain at break three times as high as that of the fiber. The microbond test was prefered to the pull-out test because of the easiness of making the specimens.

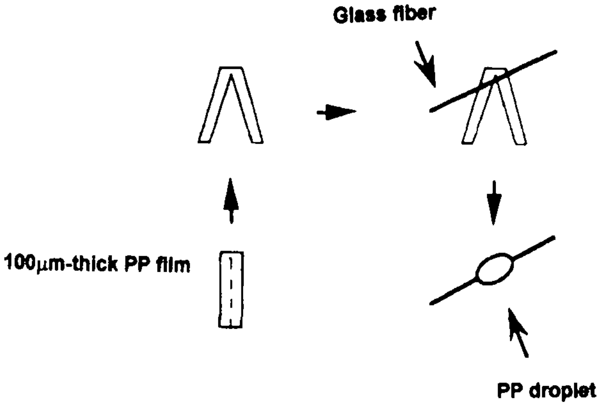

FIGURE 2 Processing of polypropylene microdroplets on E-glass fibers.

RESULTS AND DISCUSSION

These polymeric precursors, *i.e.*, the isotactic polypropylenes, are functionalized by hydrosilylation using hexachloroplatinic[18-20] or triphenyl phosphine chlororhodium[21-22] acid catalysis on the double bonds. The functionalization can be done using chlorodimethylsilane -denoted CldMS- or triethoxysilane -denoted tEtS-(Figs. 1a and b). In the case of CldMS, the functionality of each grafted group is 1, whereas for tEtS, the functionality is 3 (Fig. 1). The presence of silane groups in the functionalized polymers is checked by ^{1}H-NMR and FT-IR after the hydrosilylation step. The evidence can be gathered for the polymers having the higher concentration of double bonds. For example, on the FT-IR spectrum of the oligopropene 10,000 functionalized with the tEtS, the double bond band initially located at 885 cm^{-1} disappears (Fig. 3). On the spectrum, Si-O-(1102 and 1044 cm^{-1}) and Si-OC$_2$H$_5$ bands (1084 cm^{-1}) (or Si-CH$_3$ at 1258 cm^{-1} when the CldMS is used) are clearly evidenced indicating that the silane functionalization occurs. A quantitative determination of the conversion of the double bonds by ^{1}H-NMR is difficult because of their low amount. It can be noted that the hydrosilylation of the poly(propene-co-13.5%-7-methyl-1,6-octadiene) takes place in a two-step mechanism. First, the double bond needs to move into a terminal position and, second, the silylation occurs. According to the NMR measurements, it seems that 10% of the double bonds move to an internal position (–CH=CH–), 80% return to their initial place (–CH=C(CH$_3$)$_2$), and only 10% move to the favorable position for functionalization (–CH(CH$_3$)=CH$_2$). This determination was done only for the poly(propene-co-13.5%-7-methyl-1,6-octadiene), *i.e.*, for the highest amount of diene. Thus, in this case, only a low amount of the copolymer is functionalized by the silane. As a consequence, the amount of double bonds reported in Table 1 is given by the amount of diene considered for the copolymer synthesis.

The thermal characteristics of the pure polypropylene and of the functionalized polypropenes, *i.e.*, the oligopropenes and the copolymers based polymers, are given in Table II. As reported, the oligopropenes with the lower molar masses have a low

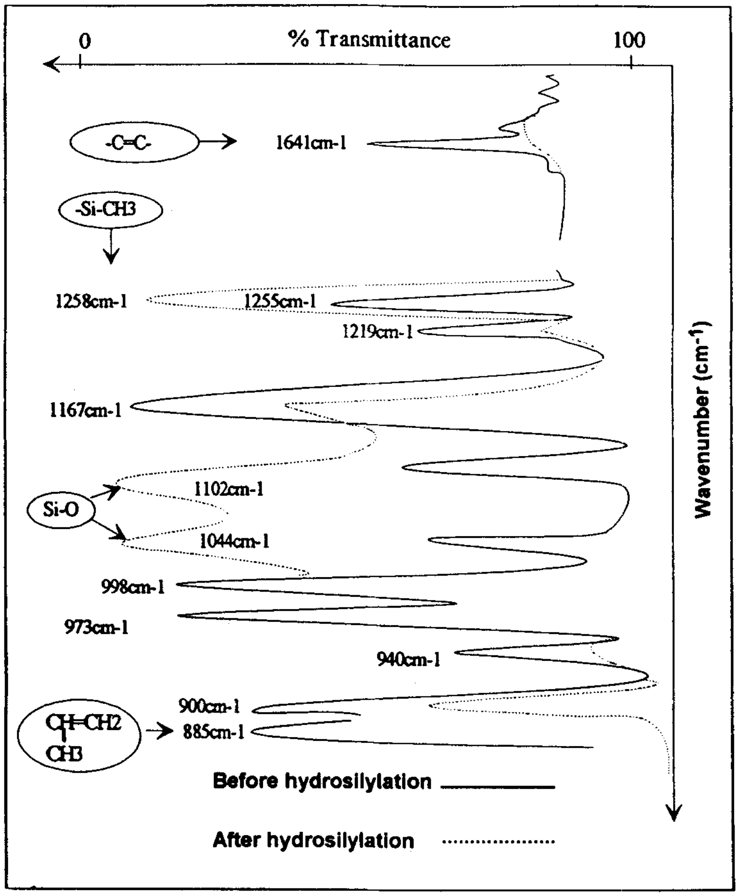

FIGURE 3 FT-IR spectrum of the oligopropene 10,000 functionalized by the chlorodimethylsilane.

melting temperature but, for a molar mass of 10,000, T_m is close to that of the pure PP. In comparison with the poly(propene-co-diene)s, the oligopropene 10,000 displays the highest crystallinity with respect to the amount of defects. The defects in these polymers include the chain ends and the insertions of the comonomer in the polypropylene chains. In fact, it is well known that for the same molar mass, a large amount of defects leads to a decrease of the degree of crystallinity of the polymer. It was demonstrated that the degree of crystallinity decreases to under 40% for more than 3% of defects in the copolymers and for more than 5% for the oligopropenes.[15] The copolymers display melting temperatures close to the pure PP (10° lower than for the commercial PP). The poly(propene-co-7-methyl-1,6-octadiene) copolymers having 8.5 and 13.5% mol. of diene display two melting and crystallization peaks. The same behavior is observed for the crystallization of the poly(propene-co-1.7% 1,9-decadiene). This effect could be attributed to the presence of different types of crystallites having different thicknesses. Nevertheless, it was demonstrated by WAXS that all the products (pure PP, functional-

TABLE II
Thermal characterization of the pure PP and the functionalized polymers (heating rate 20° K.min^{-1} and cooling rate −20° K.min^{-1})

Polypropylene	Tm (°C)	ΔHm (cal·g^{-1})	Tc (°C)	ΔHc (cal·g^{-1})	X (%)
Pure PP	165.5	22	101.5	21	61.5
Oligopropene 6,200	129	15	88.5	14.5	40
Oligopropene 10,000	152	24	111	23.5	66
Poly(propene-co-1.9% 7-methyl-1,6-octadiene)	152	12.5	95.5	14.5	40
Poly(propene-co-8.5% 7-methyl-1,6-octadiene)	105.7 152	0.5 2	59 97	2 3.5	15
Poly(propene-co-13.5% 7-methyl-1,6-octadiene)	56 154	2.5 3	54 84.5	0.5 3	10
Poly(propene-co-0.65% 1,9-decadiene)	154	18.2	103	17	47
Poly(propene-co-1.7% 1,9-decadiene)	151	13	54.5 106	0.5 13	37

ized-PP) have the same X-ray diffraction patterns, thus the same crystallographic structure.[23] The ability of the copolymers to crystallize and to co-crystallize with the pure polypropylene as a function of the number of defects is detailed in another paper.[15] It is well-known that high melting temperatures can be reached for high molar masses and low amounts of defects in the macromolecular chains. On the contrary, high molar mass reduces the mobility and, as the consequence, leads to a lower crystalline rate for the same amount of defects. Thus, the introduction of the diene sequence in the polypropylene chain decreases the ability of the copolymers to crystallize. Only few studies have been done to determine the shortest length of the crystallizable sequence in poly(propene-co-diene) copolymers.[24–25] A value of 9 units was proposed for the polypropylene from dilatometric measurements.[26] A Monte-Carlo simulation taking into account the molar mass, the defect ratio, and the chain mobility was developed.[27] Comparison of the simulated and experimental values shows that the minimal length of the crystallizable sequence is in between 24 and 30 units. Nevertheless, it was suggested that a distinction can be made between the shortest sequence length to initiate crystallization (germination) and to take part in the crystal growth. In the first case, 27 units are necessary, whereas a length of 10 units is sufficient in the second case. Thus, for use as polymeric coupling agents able to crystallize, the choice is limited to copolymers with a low amount of diene, *i.e.*, a low amount of defects.

The first requirement for the modified-PP is to co-crystallize with the pure PP. In order to check that such a co-crystallization could occur, DSC measurements were carried out on 50:50 (by wt.) pure-PP/modified-PP blends (thus, before the hydrosilylation) (Table III). The same results are obtained on pure PP/copolymers (or oligopropenes) and pure-PP/silylated-copolymers (or silylated-oligopropenes) blends. The theoretical melting temperatures and crystallinity rates computed from the rule of mixtures ($T_{m\ \mathrm{average}}$ and X_{average}, respectively) are also reported (Table III). In most of the

TABLE III
Thermal characterization of the 50:50 (by wt). blends based on pure-PP and functionalized-PP (heating rate 20° $K.min^{-1}$) (The functionalized-PP in the thermal characterization of blends refer to the copolymers and the oligopropenes before grafting the silane group)

Blends	X (%)	Tm (°C)	$X_{average}$ (%) (a)	$T_{m\ average}$(°C) (a)
Pure PP	61	165.5	–	–
Oligopropene 6,200/pure PP	42	161.5	50	146.3
Oligopropene 10,000/pure PP	63.5	157	62.5	159
Poly(propene-co-1.9% 7-methyl-1,6-octadiene)/pure PP	51	160	50.5	159
Poly(propene-co-8.5% 7-methyl-1,6-octadiene)/pure PP	46.5	161.5	38	159
Poly(propene-co-13.5% 7-methyl-1,6-octadiene)/pure PP	47	160.5	35.5	160
Poly(propene-co-0.65% 1,9-decadiene)/pure PP	54	161	54	160
Poly(propene-co-1.7% 1,9-decadiene)/pure PP	46	158	49	158

(a) Computed from the rule of mixtures

cases, the melting temperature of the blend is higher than the theoretical value (computed from the rule of mixtures); thus, the changes of the melting temperatures are governed by the pure-polypropylene behavior. No second exotherm is observed for the copolymers/pure-PP blends, suggesting that a good miscibility exists between the pure and modified PP (Fig. 4). Thus, for the copolymers displaying a complex crystallization behavior (two melting or crystallization peaks), the presence of the pure-PP has a homogeneization effect. The presence of a single crystalline phase in the X-ray spectrum similar to the pure-PP suggests that a co-crystallization occurs between the modified-PP and the pure-PP. The oligopropenes, close to their maximum of crystallinity, do not increase the total crystallinity of the blend. For the copolymers, quite far from their maximum of crystallinity, the units which have not crystallized in the pure copolymer seem to be included in the polypropylene crystals and lead to an increase of the crystallinity of the blend. This effect can be explained by the initiating crystallization effect of the polypropylene on the copolymers confirmed by the crystallization kinetics.[15] These preliminary studies suggest that only three modified-PP have suitable characteristics to co-crystallize with the pure-PP (Table III):

- oligopropene 10,000
- poly(propene-co-1.9% methyl-1,6-octadiene)
- poly(propene-co-0.65% 1,9-decadiene)

According to the required characteristics for the polymeric coupling agents, three silane-grafted polypropylene were selected for grafting on the glass surface: silane (chlorodimethylsilane CldMS)-grafted (oligopropene 10,000, poly(propene-co-1.9% methyl-1,6-octadiene), and poly(propene-co-0.65% 1,9-decadiene). The grafting of the float glass plates is described in the experimental section and the evidence of such a grafting is obtained indirectly by means of wetting measurements with distilled water

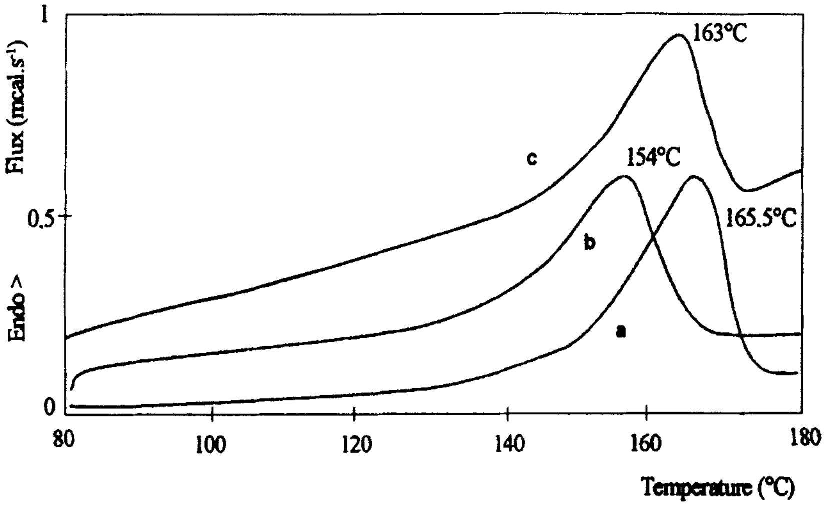

FIGURE 4 DSC recordings of pure PP (a); poly(propene-co-0.7% 1,9 decadiene) (b); and 50:50 (by wt.) blend based on pure PP and poly(propene-co-0.7% 1,9 decadiene) (c) (heating rate: 20°.min^{-1}).

after solvent extractions. The neat surface after rinsing and washing using the same solvents (methanol, xylene, and carbon tetrachloride) displays a contact angle close to 22°–25° (Table IV). Using different solvents for the successive extractions, all of the ungrafted polymer and/or polymerized material (from the reaction between the silane groups) is removed from the surface. A hydrophobic character (corresponding to a contact angle of water close to 100°) is obtained with dodecyl triethoxysilane. In addition, the contact angle is not changed after the different steps of solvent extraction and the dispersion is low, indicating good bonding to the surface. With such a silane, the grafting density is high because of the functionality of the silane (3 per Si atom instead of 1 for the chlorosilane-modified PP) and the grafted layer is homogeneous and dense. In the case of the modified-PP (copolymer and oligopropene), intermediate values of contact angle are obtained (Table IV). It can be seen that, during the different extractions, chlorosilane-grafted oligopropene 10,000 is partly removed from the glass surface, whereas the chlorosilane-modified poly(propene-co-0.65% 1,9-decadiene) seems to be well grafted. This effect could be explained by a higher steric hindrance of the SiCl function for the silane-modified oligopropene in comparison with the modified-copolymer. For the CldMS-modified poly(propene-co-0.65% 1,9-decadiene), the decrease of the contact angle from 90° to 70° after the xylene extraction can be explained by the insertion of the solvent (xylene) onto the free glass surface (ungrafted). A contact angle of 90° is retrieved after a further extraction with carbon tetrachloride as a solvent.

In addition, the silane groups as side chains lead to a more covered surface than for the oligopropene having a silane as chain end. In all the cases, the conformation of the first polypropylene chains bonded to the glass surface limit the accessibility of the others to the unreacted silanol groups of the surface. As a consequence, the grafting density is lower for the grafted polypropylene than for the short alkyl chlorosilanes.[28]

TABLE IV
Contact angles with distilled water of float glass plates treated with silane-modified polypropylenes and dodecyltriethoxysilane after various successive solvent extractions

Treatment after coating	Untreated glass	Glass treated with CldMS-modified poly(propene-co-0.65% 1,9-decadiene)	Glass treated with CldMS modified oligopropene 10,000	Glass treated with dodecyl triethoxy silane
No extraction	< 10°			
Extraction # 1				
Rising with water	25° ± 4	90° ± 6	85° ± 4	99° ± 5
Extraction # 2				
With methanol for 5 hours	25° ± 4	90° ± 6	85° ± 4	99° ± 5
Extraction # 3				
With xylene for 5 hrs.	22° ± 4	70° ± 6	50° ± 8	103° ± 2
Extraction # 4				
With carbon tetrachloride for 5 hours	23° ± 4	90° ± 8	50° ± 8	102° ± 2

In addition, the resulting grafted polypropylene layer is more heterogeneous. The same behavior is observed on silane-modified polyethylene and alkyl chlorosilanes grafted on oxidized silicon wafers.[28]

The results of the values of the interfacial shear strength, $\bar{\tau}$, obtained from the microdroplet adhesion test are reported on Figure 5. The values are in agreement with those reported in the literature[29–31] and the same trends between the τ values for the various surface treatments are observed using the Greszczuk and Penn & Lee models. These approaches use a stress criterion and assume an elastic behavior of the matrix. Thus, as a consequence, the parameters used to fit the experimental data and related to the interphase have no physical meaning. According to the ability of the polypropylene to be deformed plastically, a constant shear stress along the interface can be considered. Assuming this fact, the average shear stress can be calculated from the equation given in the experimental section. A slight difference is obtained between all of the surface treatments. This effect could be explained by the fact that the increasing adhesion using such grafted polypropenes can be accomplished only if a co-crystallization occurs between the grafted chains and the pure-PP used as matrix. The co-crystallization can occur only if good interdiffusion between the grafted chains and matrix is ensured in the melt. The interdiffusion is time- and temperature-dependent. In this case, the mobility of the grafted chains is restricted in comparison with the ungrafted polypropylene, thus it is difficult to compare the crystallization of the modified-PP/pure-PP blends and at the glass surface. The thermal process for making the droplets consists of 45 minutes, then a heating up to 175 °C with a heating rate of 20 °C min^{-1}. The holding time at 175 °C was 17 minutes followed by a cooling to 40 °C (cooling rate: -40 °C min^{-1}). For these thermal conditions, the time and temperature to ensure the interdiffusion of the grafted chains in the bulk polypropylene are probably not sufficient. The processing of the microdroplets obtained from melting the film needs to be at a temperature for which the viscosity is not too low. As a consequence, the interdiffusion of the grafted chains needs long times. In fact, the ability of the chain to interdiffuse in the bulk

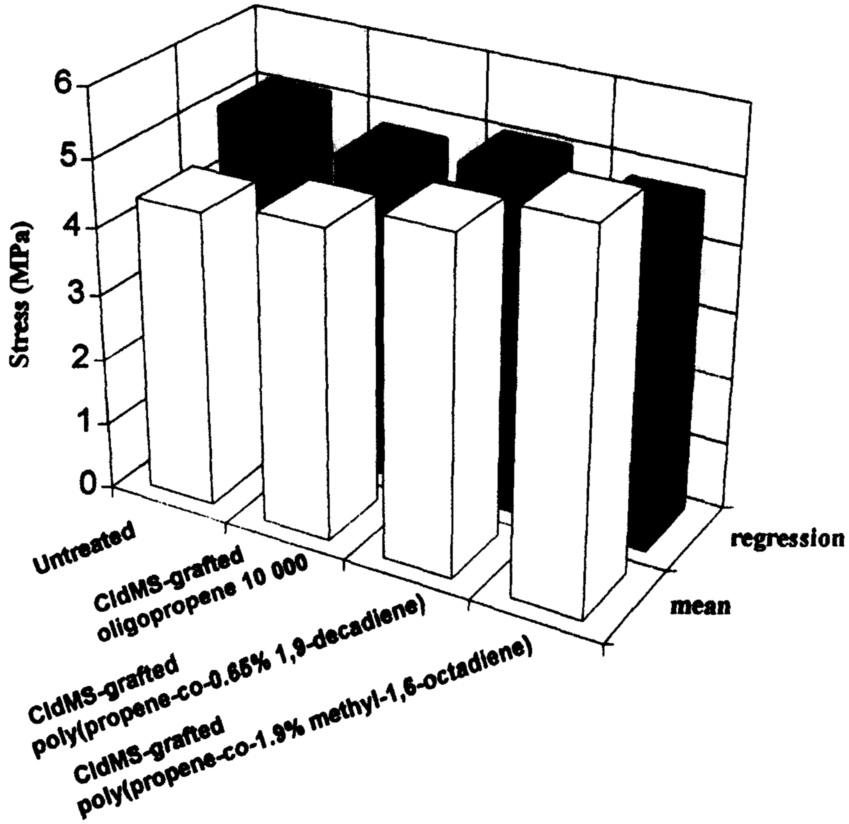

FIGURE 5 Interfacial shear strength of the E-glass fiber/pure PP interface as a function of the surface treatment of the fiber using the microdroplet test (mean value and regression).

polymer and the further co-crystallization with the PP is reduced by the anchoring on the glass surface. The same concept was used for the polyphenylene sulfide (PPS)/glass fiber interface.[32] In this case, the interfacial shear strength of the interface was greatly enhanced by the use of side-chain-modified PPS in comparison with chain-end-modified PPS. The slight differences observed for the PP/glass fiber can be also attributed to the deformation of the PP droplet. In fact, a high level ot stress is reached at the contacts between the knifes and the droplet[33] leading to a shear yielding of the polypropylene droplet. Thus, the interfacial shear strength of the interface cannot be determined by the microdroplet test. The micromechanical interpretation of the microdroplet test in this case will be detailed in another paper.[34]

CONCLUSIONS

The glass/polypropylene interface can be modified by grafting the glass surface with silane-modified polypropylenes which are able to co-crystallize with the pure polypropylene in the bulk. A continuity of bonding from the glass surface to the bulk matrix can be obtained in this way. These silane modified isotactic polypropylenes can be prepared from poly(propene-co-diene)s obtained by Ziegler-Natta polymerization and Speier hydrosilylation. According to the synthesis, the amount of silane functions along the chain can be varied by changing the amount of diene in the copolymer. Oligopropenes prepared from homogeneous polymerization are also considered in order to compare the effect of the position of the silane group (side chain position for the copolymer *vs.* chain end position for the oligopropene). The ability of the silane-grafted polypropylenes is verified on 50:50 modified-PP/pure-PP blends and the grafting on the glass surface is checked indirectly by means of wetting measurements. From the requirements (co-crystallization and grafting on the glass surface), silane-modified PP are selected and tested as coupling agents on glass fibers. The interfacial shear strength is evaluated using the microdroplet test but yielding of the polypropylene occurs leading to similar values of $\bar{\tau}$ for all the surface treatments. Studies are in progress in order to measure the changes in adhesion when the glass surface is modified by these grafted polypropylenes.

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