Effect of the Length of Tethered Chains and the Interphase Structure on Adhesion between Glass and Polyethylene

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ABSTRACT: The adhesion between glass and polyethylene (high-density polyethylene (HDPE) or low-density polyethylene (LDPE)) was improved by means of polyethylene chains grafted on the glass surface. Chlorosilane-terminated polyethylene (PE) with different molar masses were synthesized in order to obtain (i) semicrystalline polymers able or not to crystallize with the free chains of the polyethylenes matrices and (ii) polymer chains which could react with the silanol groups from the glass surface. The grafting of alkylchlorosilanes (alkyl chain length varying from C_4H_9 to $C_{30}H_{61}$) was considered in comparison to the polymer chains. The adhesion developed at the polyethylene/glass interface was studied as a function of the molar mass of functionalized-polyethylene grafted on the glass surface. For that purpose, the asymmetric double cantilever beam test was used to determine the fracture energy, G_i, of the interface. On both high-density and low-density polyethylene/glass joints, the fracture energy of the interface, G_i, was found to increase with the length of the interfacial connecting chains. The locus of the failure was studied by means of wettability measurements and atomic force microscopy analysis of the surfaces after separation. The higher values of the fracture energy of the interface with HDPE can be explained by a better compatibility of the tethered-PE chains with the free chains of the PE matrix which are more linear than LDPE. It was demonstrated that for the shortest chains (alkylchlorosilanes), the connectors were extracted from the bulk PE (LDPE or HDPE) whereas for the polymeric chains, a cohesive failure occurred for the glass/HDPE interfaces. Such a study can be used to design the connecting polymeric chains for improving the adhesion between glass and a semicrystalline polymer.

Introduction

The enhancement of the interfacial adhesion between semicrystalline thermoplastic polymers, such as polyethylene or polypropylene, and a glass surface is of a great importance in many structural materials (glass fibers-based composites or multilayered materials). The low adhesion level results from the poor interaction existing between the hydrophilic surface of glass and the hydrophobic polyolefin one. The enhancement of the adhesion is commonly achieved by using silane coupling agents.[2] According to the nonreactive nature of such polymers, the organosilane-based surface treatments are efficient for improving the wettability of the glass surface but the resulting interfacial adhesion remains low. The chemical modification of polyolefins[3] is an alternative way for increasing the interactions between a pretreated glass surface, which could be treated previously, and the polyolefin matrix. Nevertheless, these treatments lower the molar mass of the polymer by chain scissions, decreasing the mechanical properties.[4] Commonly, blends of pure and modified polyolefin are used as matrixes. In such a way, the efficiency is driven by the diffusion of the functionalized polymers to the free surface.[5,6] Recently, to obtain highly filled polyolefins, different authors proposed to synthesize by a catalysis polymerization the polymer from the filler surface by adsorbing the Ziegler−Natta catalyst on the filler.[7,8] Nevertheless, even if a better adhesion was noticed from the observance of fractured surfaces of filled polymers, the interactions between the filler and the polyolefin remains low and the method cannot be used in most of the cases.

A new way was developed for modifying the glass/semicrystalline polymer interface by grafting connecting polymer chains having the same chemical nature as the matrix.[9,10] According to the compatibility between the tethered chains (connectors) and the polymer used as matrix, the tethered chains can diffuse into the bulk matrix (free polymer chains). The enhancement of the interfacial adhesion is achieved by the segmental interactions and by the creation of entanglements. Penn et al.[11,12] applied this method for improving the toughness of glass fiber/polystyrene (or polysulfone) interface. The interfacial shear strength of the glass fiber/poly-(phenylene sulfide) (PPS) was also enhanced using such a method.[13] Carboxy-functionalized PPS were grafted on aminosilane-treated glass fibers, and it was demonstrated that a large increase of the interfacial shear strength can be reached by controlling the molar mass of the grafted-PPS chain, the amount, and the position of the functional groups. In this case, according to the crystallizable nature of the grafted chains, a cocrystallization of the tethered chains and the free chains of the matrix is expected.

This concept of connecting chains is well-known for improving the adhesion between two immiscible polymers by means of block copolymers.[14,15] Recently, this method was used for improving the adhesion between semicrystalline polymers, i.e., polypropylene and poly-

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amide-6.[16] In this case, it was suggested that the blocks of the copolymer formed at the interface can cocrystallize with the corresponding polymer. In addition, during the past decade, theoretical works [17] were done to describe the effect of the area density at the interface, Σ, and the length of the connectors, N (number of monomer units). The conclusions from these modelings were verified on different polymer–polymer systems, especially those involving polystyrene.[18,19] For example, for an interface formed from two amorphous thermoplastics such as PS, PMMA, or PVP depending on length and the grafting density of connectors, three failure mechanisms were identified. The interface fails either by pull out, by chain scission, or by chain disentanglement. For short connectors with a molar mass smaller than the average molar mass between entanglements, M_e, of the matrix and for a low areal density, pull-out of the connecting chains occurs during the interfacial debonding leading to rather weak energies of fracture ($G_i = 1-6 \text{ J·m}^{-2}$). For long connectors with a low areal density, chain scission of the connectors occurs during interfacial debonding. For chains which are not enough long to form entanglements with the free polymer chains used as matrix and for a high grafting area density, crazes, involving chain disentanglements, can be formed close to the crack tip. In both former regimes, the G_i value increases linearly with the areal density of connectors, Σ, and varies as the square of the extracted length (i.e., $G_i \sim \Sigma N^2$).[20,21] In the crazing regime, G_i was found to vary as Σ^2.[22]

In the present work, the polyethylene/glass adhesion is enhanced by grafting chlorosilane-terminated polyethylene chains on the glass surface. According to the reactivity and the structure of the tethered chains, a continuum of bonding is expected from the glass surface (reaction of the chlorosilane group with the silanols of the glass surface) to the bulk of the polyethylene (PE) (entanglements of the grafted PE with the free PE chains). The adhesion between the bulk polymer and the grafted monolayer will be achieved only by segmental interactions, cocrystallization, or entanglements as the grafted chains are nonreactive. Two types of silane-terminated PE were synthesized: linear homopolyethylenes with low molar masses and a high molar mass copolymer from ethylene and hexene in order to study both the effect of the chain length and the ability of the connecting chains to cocrystallize with the free PE used to form the glass/PE interface. As a consequence, different types of interface/interphase can be considered: (i) an interface resulting from regular polymers with a low thickness which could display a crystalline ordering; (ii) a thicker and amorphous interface.

Short connectors were also considered as references by preparing glass surfaces grafted with alkylchlorosilanes. The effect of the length (i.e., the molar mass) of the connectors on the fracture energy of the interface measured by the asymmetric double cantilever beam test was discussed.

Experimental Section

Materials. Polyethylene Matrixes Used as Pure Polymers for Forming the Interface. High-density and low-density polyethylenes (from Fina Chemicals) were used as matrixes for processing PE/glass joints. PE films were prepared under a hot press at 180 °C for 1 min and were cooled with a cooling rate of 5 °C·min^{-1}.

The physicochemical characteristics of the neat PE are reported in Table 1.

Table 1. Characteristics of Chain Connecting and Pure PE

	$\overline{M_n}$ (g·mol^{-1})	$\overline{M_w}$ (g·mol^{-1})	IP	T_m (°C)	X (%)
C$_{30}$-Cl		515.42		>60	
C$_{18}$-Cl		347.10		27.0	
C$_8$-Cl		206.83		$< T_{RT}$	
C$_4$-Cl		150.72		$< T_{RT}$	
PE1,200-Cl^a	1 194	5 230	4.4	121.0	49
PE3,700-Cl^a	3 710	16 000	4.3	139.0	69
EH32,500-Cl^a	32 500	65 000	2.0	91.5	17
HDPE	13 050	213 100	16.0	126.0	45.5
LDPE	19 350	106 700	5.5	112.0	32.0

^{a} For functionalized and pure polymer. The characteristics are measured by SEC and DSC.

Chart 1

Linear polyethylene with low molar masses

Poly(ethylene-co-hexene) Compound
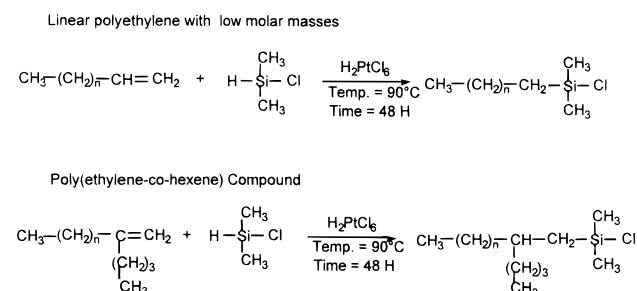
Connecting Chains. Short-Chain Connectors: Alkylchlorosilanes. Alkyldimethylchlorosilanes of general formula $CH_3-(CH_2)_n(CH_3)_2-Si-Cl$, with $n = 3, 7, 17$, and 29, from Roth Sochiel were used as received. These are denoted C_i-Cl, where i is the number of carbon atoms in the alkyl chain.

Polymer Connectors: Chlorosilane-Functionalized Polyethylenes. The functionalized polyethylenes were produced from polymerization with a metallocene catalyst in heptane. Two types of polymers were prepared: (i) linear polyethylenes (denoted PE1,200 and PE3,700) and (ii) an ethylene-*co*-hexene copolymer (EH32,500). The hexene-1 comonomer was used, with 6.6% molar ratio, to reduce the regularity of the chain, and as a consequence, the crystallinity of the resulting polymer. Their synthesis was detailed elsewhere.[23]

These polymers were endcapped by a dimethylchlorosilane unit by hydrosilylation at 90 °C using a Speier hexachloroplatinic acid catalyst in xylene with chlorodimethylsilane (used as received from ABCR Products). The hydrosilylation can be described as shown in Chart 1.

The disappearance of the double bonds ($-CH=CH_2-$) and the existence of the silane functions were checked by FT-IR spectroscopy.[23]

The physicochemical characteristics of the chlorosilane-terminated PE are reported in Table 1.

Grafting of Connecting Chains. Float glass slides were used as substrates for making the polyethylene/glass joints whereas oxidized silicon wafers were considered for studying the ability of the silane-terminated polyethylenes to be grafted on a silica surface.[1,24]

A solvent method was used for grafting the PE connectors on the glass surfaces. The experimental conditions used in this study have been previously optimized in another study.[1] The cleaned glass slides (acetone washing followed by a treatment with a "Pirhana" solution (70% vol H$_2$SO$_4$ + 30% vol H$_2$O$_2$) and an exposition under UV) were dipped in the silane or silane-terminated PE solution. For short silanes, CCl$_4$ was used as solvent (2% mol) for 15 min at room temperature under nitrogen atmosphere (for the C$_{30}$-Cl silane, the reaction took place at 60 °C). The grafting of the functionalized polymers was done in xylene at 145 °C for 2 h under an argon atmosphere. The dimers resulting from the self-condensation of two molecules and/or the physisorbed molecules were removed by a Soxhlet extractions using THF or xylene.
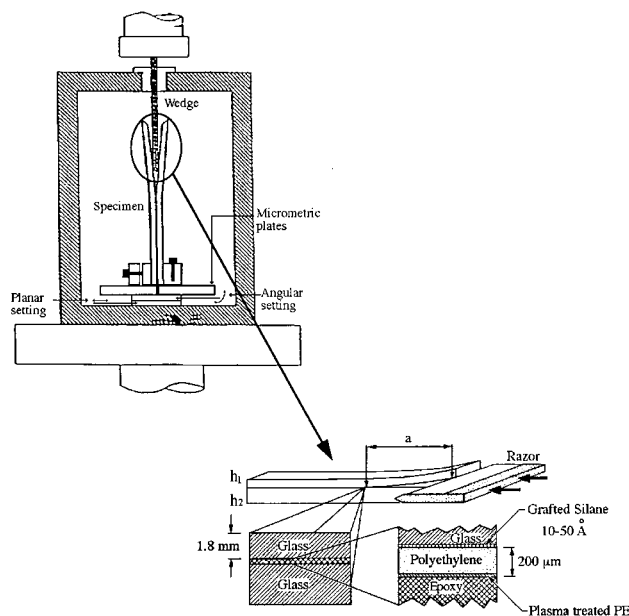
Figure 1. Testing device and specimen geometry for the asymmetric double cantilever beam test (ACDB).

Processing of the PE/Glass Interfaces. The double cantilever beam specimen used in the PE/glass experiments was prepared from two glass beams ($50 \times 15 \times 2$ mm³). Each slide was cleaned with a "Pirahna" solution at 120 °C, rinsed in deionized water, and further dried in nitrogen. On one slide, the connecting chains were grafted as detailed previously. The thickness of the grafted monolayer was from 10 to 55 Å for the C_4-Cl and the polyethylene with the lower molar mass (PE1,200), respectively.[1,23]

This grafted slide was joined to a pure 200 μm thick PE film (HDPE or LDPE). A second glass slide was required to stiffen the PE film and to reduce the dissipative phenomena during the fracture test. Without modification, the PE/epoxy adhesion was too low due to the lack of polar surface groups on the PE surface. To obtain sufficient PE/epoxy adhesion level, the PE surface was subjected to an oxygen plasma with a postdischarge. The exposure time was 10 min at 300 W with an oxygen flow of 100 standard cm³·min⁻¹. The formation of polar groups on the PE surface was confirmed by the large decrease of the contact angle with water from 104.0 ± 1.9° to 24.1 ± 1.0° (sessile droplet method). An epoxy resin was used as adhesive between the PE film and the glass slide used as stiffner. The epoxy resin was cured for 3 h at 50 °C under 6 kPa pressure. Figure 1 illustrates the structure of the specimen.

The PE/glass joints were made at the melting temperature of the considered PE for 3 h in order to ensure the interdiffusion of grafted chains in the molten PE matrix.

Fracture Energy Measurements. Fracture toughness of the interface was measured using the asymmetric double cantilever beam (ADCB) test, according to the fact that it is a reliable test for polymer–polymer[16] or glass–polymer interfaces.[19] The efficiency of the connectors was evaluated in terms of the fracture energy of the interface, G_i, required to create an increment of new surface as a razor blade was propagated along the interface.

The ADCB test yields reliable values of G_i if some test conditions are obeyed. First, the samples must be asymmetric (that is $h_1/h_2 \neq 1$). According to the different stiffnesses of the two polymers, a propagation of the crack can be done out of the interface plane into one of the two layers. It is known that varying the ratio of thicknesses changes the balance between the two modes (I and II) in the fracture process and that if the fracture tends to deviate into the more compliant material (PE in our case) the measured energy release rate can be overestimated leading to substantial errors in the evaluation of G_i. Smith[19] demonstrated that, for a glass/

polymer joint as in the present case, by choosing a thickness ratio $h_1/(h_1 + h_2)$ varying between 0.41 and 0.49, the effects of mixed modes are lowered (h_1 being the thickness of the grafted glass slide and h_2 the thickness of PE/epoxy/glass slide). As a consequence, all samples in this study were therefore made according to a ratio $h_1/(h_1 + h_2)$ equal to 0.47 ± 0.01. Above the upper limit, the specimen failed by cohesive fracture occurring in the thicker material, and below the lower one, the thinner glass beam breaks.

On the other side, the critical energy release rate must be calculated in the proper limit. It is assumed that all of the energy relased during fracture is dissipated locally close to the crack tip in an interface zone which is small compared to the thickness of the outer glass beams.

This assumption allows the fracture toughness, G_i, to the energy release rate, G, of the beam sample to be obtained using a simple relationship derived from beam theory

$$G_i = \frac{3}{8} \frac{\Delta^2}{a^4} \frac{E_1 h_1^3 E_2 h_2^3}{E_1 h_1^3 + E_2 h_2^3} \qquad (1)$$

where the subscripts 1 and 2 refer to the top and bottom glass beams. a is the crack length as shown in Figure 1, E is the Young's modulus of the glass, h is the thickness of the beam sections, and Δ is the opening displacement which is assumed to be the thickness of the razor blade (0.1 mm).

While the approximation given by eq 1 is sufficient for weak interfaces with long cracks, for shorter cracks typical of the stronger interfaces measured in this investigation, the relationship overestimates G and G_i. On the basis of calculations done by Kanninen,[25] the main assumption is that the finite elasticity of the material ahead of the crack tip required correction factors for small crack lengths, and a more accurate approximation for G_i was obtained. This approximation is valid as the crack length to beam thickness ratio is large and the length of the nonfractured interface ahead of the crack tip is also large as compared with the beam thickness. According to this model G_i is found to be

$$G_i = \left(\frac{3E_1 E_2 h_1^3 h_2^3 \Delta^2}{8a^4}\right)\left[\frac{C_2^2 E_1 h_1^3 + C_1^2 E_2 h_2^3}{(C_2^3 E_1 h_1^3 + C_1^3 E_2 h_2^3)^2}\right] \qquad (2)$$

where

$$C_1 = \left(1 + 0.64 \frac{h_1}{a}\right)$$

$$C_2 = \left(1 + 0.64 \frac{h_2}{a}\right)$$

Equation 2 was used to calculate the interfacial fracture energy for the PE/glass adhesion experiments. It should be noted that this model is based on an elastic behavior of the beams and does not take into account the plastic deformation which could occur. To respect the assumptions of the mechanical modeling, the glass/polyethylene interface cannot be tested directly and the specimens was modified by a second glass layer as detailed previously. Nevertheless, this test is reliable for studying this type of interface, as it was used for polymers having similar mechanical behavior such as polypropylene.[16]

The ACBD device was mounted on a Adamel Lhomargy DY25 tensile machine (see Figure 1). A 0.1 mm thickness wedge cleaved the specimen at a low speed (3 μm/s) in order to assume that the measured energy release rate is equal to G_i, the critical energy release rate at a zero velocity.

The crack length ahead of the wedge was measured during a stable propagation step using a videocamera. A minimum of 10 values of crack lengths were obtained and the mean value was used to calculate the fracture toughness. The deviation in measurements was about 5%. The accuracy of the measured energy of adhesion (G_i) was estimated to be about 10%.

Experimental Techniques. The crystallization studies were carried out on pure polymers and on blends made from the double-bond terminated and pure polyethylenes (50:50 wt). It has been assumed in this part that the polymers used as precursors had the same behavior during crystallization as the functionalized ones. In fact, as the temperature increased, the silane-terminated PE can condense together and modify the crystallization behavior. The blends were realized by swelling the polymers at 140 °C in xylene separately and by coprecipitation in methanol at room temperature. The blends were subsequently dried under vacuum at 100 °C. Thermograms were obtained using a Perkin-Elmer DSC7 thermal analyzer under nitrogen atmosphere. All the samples were considered after the following cycle: heating at 40 °C·min^{-1}, followed by a stage at 150 °C during 5 min, cooling at 10 °C·min^{-1}, a second stage at 50 °C during 5 min, and final heating to 200 °C at 10 °C·min^{-1}. The theoretical melting enthalpy value of a PE monocrystal, ΔH_o, was taken as being equal to 280 J/g[26] to compute the rate of crystallinity, X (in %). This value needs to be considered only as a relative value (especially in the case of ethylene-*co*-hexene copolymer).

Wide angle X-ray spectroscopy (WAXS) spectra were obtained with a Siemens D500 diffractometer with a back monochromator and a Cu anticathode.

The sessile drop method was used to characterize the surface energy of the grafted glass and PE films before and after cleavage. A homemade image analysis allowed measurement of the contact angle from the shape of the droplet. From the contact angles with distilled water and diiodomethane, the characteristics of the surface energy were determined using Fowkes' equation.[27]

From the atomic percentage of carbon determined on nanometer-size silica (Degussa 200) treated with the same silane or silane-terminated PE solutions, the grafting density, Σ, can be calculated using the following equation:

$$\Sigma_{AE} = \frac{1}{A} \frac{10^6 P_c}{(1200 n_c) - P_c(\overline{M_w} - 1)} \text{ silane molecules·nm}^{-2}$$

where A is the specific area of the bare silica and n_c is the number of carbon atoms. $\overline{M_w}$ is the molar mass of the grafted compound, and P_c is the percentage of carbon for the grafted silica.

The topography before and after cleavage was analyzed by atomic force microscopy, AFM (Park Instrument), in contact mode with a scanning frequency of 2 Hz.[23]

Results and Discussion

Grafting Density of the Connectors. The first step in the processing of PE/glass joints involves the grafting of connecting chains onto the glass surface. The control of this interface was well-detailed in a previous work [1]. The covalent grafting was demonstrated by means of ^{29}Si NMR cross polarization magic angle spinning and wetting measurements.[1-23] The contact angles with water and the hysteresis ($\Delta\theta = \theta^M - \theta^D$) determined on the grafted glass surfaces are reported in Table 2.

The hydrophobicity of the grafted surface increases with the molar mass of the connectors. It should be noted that the contact angle measured on the pure PE film is close to the value of the EH32,500-g-glass surface.

The grafting density, Σ, determined by atomic analysis on nanometer-size silica, is found to decrease as the molar mass of the connectors increases (Table 3). Thus, the length (i.e., the size) of the connector has an effect on the ability of such reactive functional ends to reach to the surface and to react with the reactive sites on the silica surface.

Table 2. Water Contact Angle and Hysteresis Measured on Untreated Glass, Connector Grafted Glass, and Pure PE Films

surfaces	Θ_{water}^M (deg)	$\Theta_{water}^M - \Theta_{water}^D$ (deg)
untreated glass	12.6 ± 1.9	*a*
C$_4$Cl-g-glass	78.0 ± 1.7	7.9 ± 4.3
C$_8$Cl-g-glass	88.3 ± 2.2	3.5 ± 3.5
C$_{18}$Cl-g-lass	98.7 ± 1.7	1.4 ± 3.4
C$_{30}$Cl-g-glass	95.7 ± 0.9	8.6 ± 3.2
PE1,200Cl-g-glass	85.6 ± 4.4	41.5 ± 7.6
PE3,700Cl-g-glass	86.5 ± 2.1	35.4 ± 3.8
EH32,500Cl-g-glass	99.6 ± 0.9	19.7 ± 2.1
HDPE	96.3 ± 2.6	33.3 ± 4.9
LDPE	96.3 ± 1.9	30.3 ± 4.3

a Because of the hydrophilic character of glass, it is difficult to measure the water contact angle for dewetting.

Table 3. Grafting Density of Chain Connecting Determined by Elemental Analysis on Divided Silica (Aerosil200)

grafted surface	Σ (nm^{-2})
C$_4$Cl-g-glass	1.46 ± 0.04
C$_8$Cl-g-glass	1.39 ± 0.04
C$_{18}$Cl-g-glass	0.96 ± 0.06
C$_{30}$Cl-g-glass	0.98 ± 0.05
PE1,200Cl-g-glass	0.02
EH32,500Cl-g-glass	0.001

From the thicknesses of the grafted monolayer determined by ellipsometry and atomic force microscopy and in agreement with the wettability behavior, the conformations of the tethered chains were proposed.[23,24] For the shortest alkylchlorosilanes, dense and well-ordered monolayers are obtained, whereas in the case of the C$_{30}$-Cl and for the PE polymers, the monolayers are more disordered. For the grafted polyethylene, as the molar mass increases, the chains display a brush-like to a mushroom-like structure whereas the chains spread out on the surface for the highest molar mass.

In the present work, the influence of the characteristics of the graft monolayers (i.e., the grafting ratio, Σ, the length molar mass, regularity, and organization) on the fracture energy measured for interfaces between PE and glass grafted with silane and PE connectors can be evidenced. The ability of the connecting chains to interdiffuse and form entanglements with the free chains of the pure PE matrix is the main parameter for improving the interfacial toughness. In the ideal case, the tethered PE chains penetrate into the bulk PE matrix forming during cooling to a highly crystalline interphase. By choosing two types of polymer connectors: an amorphous one (EH32,500) and a semicrystalline one (PE1,200 or PE3,700), the effect of the cocrystallization on the fracture energy can be estimated. As pointed out by various papers, the spreading phenomenon of polymeric films on similar brush-covered surfaces is governed by the length of the grafted chains compared to that of the free ones.[30,31] In fact, the wetting is expected when the mixing entropy is large enough to lead to the interpenetration. It depends on the variations in the molar mass ratio between the brush and free chains and to a lesser degree by the changes of the brush surface density. Nevertheless, the main conclusions from these papers concern the spreading of polymeric films and not the effects on the interfacial adhesion.

Cocrystallization of the Tethered PE-Connectors with the Free PE Chains. The same crystalline
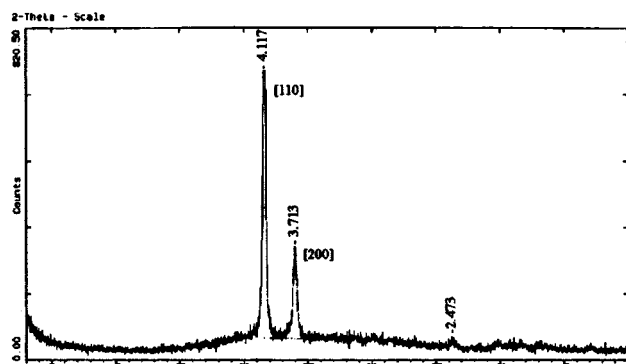
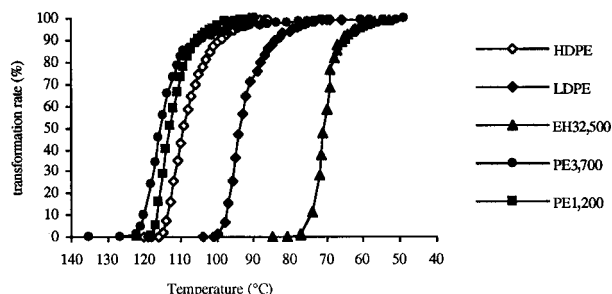**Figure 2.** X-ray diffraction profile obtained of a double-bond-terminated PE precursor (PE3,700).

Figure 3. Crystallization kinetics determined by DSC analysis for the double-bond-terminated PE and the pure PE (HDPE and LDPE).

Figure 4. DSC traces of pure PE, precursor PE1,200, and blends based on pure PE and PE1,200 for the two types of pure PE (HDPE and LDPE) (heating rate, 10 K·min^{-1}).

structure and the same crystallization rate are required for such a cocrystallization between the PE-connecting chains and the free PE chains occur. The first condition was obeyed since WAXS analysis displays the same crystalline structure for both modified polyethylenes and the HDPE matrix (Figure 2). On the other way, the crystallization kinetics of homo-polyethylenes (PE1,200 and PE3,700) and of HDPE matrix are quite close to favor cocrystallization. Because of their branched structure, the LDPE matrix and the poly(ethylene-*co*-hexene) exhibit crystallization kinetics which are very different from the other silane-terminated polyethylenes (Figure 3). As a consequence, cocrystallization between the copolymer and free HDPE chains or between free LDPE and the grafted PE chains cannot be obtained.

In fact, differential scanning calorimetry (DSC) analysis confirms these hypothesis. The cocrystallization of HDPE and PE1,200 is evidenced by the presence of a single melting peak on HDPE/PE1,200 blends (Figure 4). Moreover, the crystalline rate ($X = 58.3\%$) of this blend is higher than those of the initial polymers crystallized in the same conditions (49% and 45.5% for PE1,200 and HDPE, rspectively). In the opposite, the LDPE/PE1200 blend displays two melting peaks on the DSC trace corresponding to those of LDPE and PE1,200. The same phenomenon is observed with the blends based on the PE3,700 polymer and confirms that these polymers in the blends crystallize separately.

The blends based on the EH32,500 copolymer do not evidence any cocrystallization between this modified polyethylene and the pure PE matrixes (Figure 5). For the blend based on the HDPE matrix, the single melting temperature corresponds to the pure PE. As the polymer chains of HDPE matrix begin to crystallize, the copolymer chains are thrown in the amorphous parts. Although the rate of crystallinity ($X = 17\%$) of the pure copolymer is already low, it becomes insignificant in the
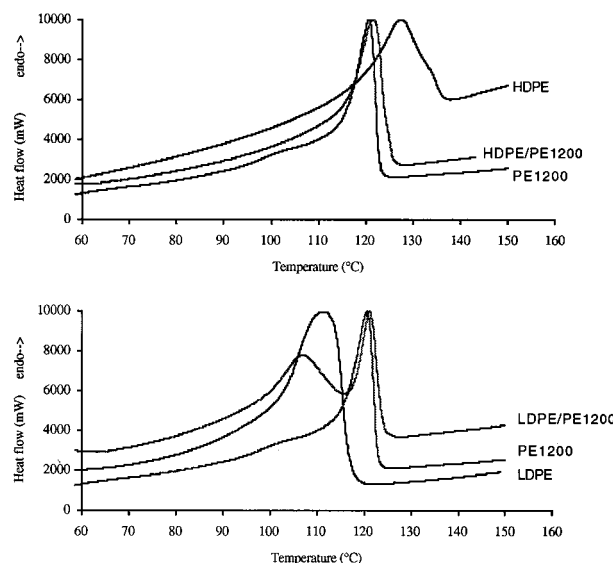
blend. The nonregular structure of the copolymer decreases drastically the rate of crystallinity of the HDPE matrix as the rate of crystallinity of the blend is only 16% compared to 45.4% for the pure matrix crystallized in the same conditions. For the blend EH32,500/LDPE, even if the presence of a single melting peak suggests a possible cocrystallization, the crystallinity rate remains limited. Thus, the nonregular structure of copolymer hinders the crystallization of the blend ($X = 8\%$, resulting rate of crystallinity).

It results from these analysis that a cocrystallization can occur between the HDPE matrix and modified polymers having a regular structure (PE1,200 and PE3,700). On the opposite, as expected, the insertion of the hexene units in the polyethylene chains (i.e., copolymer EH32,500) reduces the ability of its cocrystallization with the pure PE chains.

As a consequence, it can be possible to correlate the morphology of the resulting interphases with the fracture properties measured by the asymmetric double cantilever beam test. Does the cocrystallization between matrix and precursor polymer toughen or weaken the interface?

Fracture Energy of the Interface as a Function of the Length of the Connecting Chains and Matrix Morphology in the Vicinity of the Interface. The grafting of the connectors at the glass surface compared to the case of an unmodified glass/PE interface enhances the fracture toughness of the interface. Figure 6 gives the fracture energy of the interface measured from the double cantilever beam test versus the length of the connectors (expressed as $\overline{M_w}$).

The unmodified interface is very weak with a low fracture energy of about 1 J·m^{-2}. This value is similar to that measured at the PS/glass interface by Smith and Kramer.[16] However, without connecting chains, the measured fracture energy is 10 times higher than the reversible thermodynamic work of adhesion, W_a, between glass and polyethylene (about 70 mJ·m^{-2}). This result shows that the test speed was probably too high to neglect the dissipative phenomena in the material and/or that the polyethylene film surface could be oxidized during processing leading to additional interactions with the glass surface.
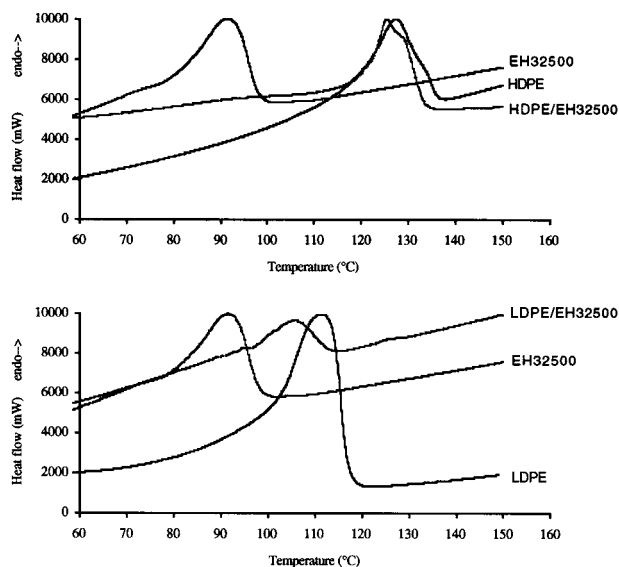
Figure 5. DSC traces of pure PE, precursor EH32,500, and blends based on pure PE and EH32500 for the two types of matrixes (HDPE and LDPE) (heating rate, 10 K·min⁻¹).
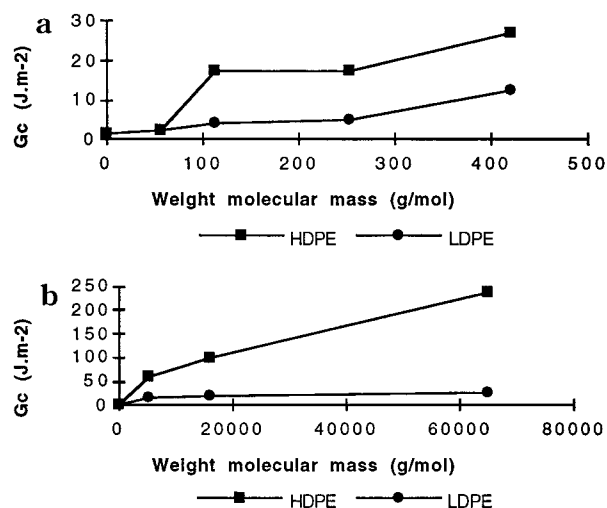

Figure 6. Fracture energy, G_i, of a PE/glass interface modified with connectors as a function of the molar mass of the connecting chains: (a) alkylsilanes; (b) functionalized PE.

It can be noticed that an enhancement of the fracture energy can be obtained even by grafting the glass surface with short connectors (in comparison with the untreated glass) (Figure 6a). The fracture energy of the LDPE/glass interface modified with C_{30}-Cl is about 10 times higher than that of the PE/untreated glass interface. This effect can be attributed to a better wettability of the glass substrates with the molten polyethylene as the glass surface is more and more hydrophobic. Large values of G_i are reached in the presence of polymer chains as connectors and a continuous increase is observed as the molar mass of the connecting chains increases (Figure 6b). This effect can be related to the creation of entanglements between the tethered chains and free chains of the PE matrix.

The very large values of the fracture energies obtained with the high-density polyethylene can be explained by a better compatibility of the linear grafted chains with the pure HDPE according to its linear structure in comparison with the low-density polyethylene. The difference between the moduli of the two types of polyethylenes cannot be responsible of the large

Table 4. Water Contact Angles and Hysteresis Measured on Grafted Glass Slides after Joining

grafted glass from organosilane/HDPE joint	Θ_{water}^{M} (deg)	$\Theta_{water}^{M} - \Theta_{water}^{D}$ (deg)
C_4Cl-g-glass	80.3 ± 2.8	18.5 ± 5.6
C_8Cl-g-glass	87.6 ± 1.0	5.1 ± 2.4
C_{18}Cl-g-glass	93.6 ± 1.6	5.1 ± 3.7
C_{30}Cl-g-glass	92.8 ± 1.5	7.7 ± 4.2

a)
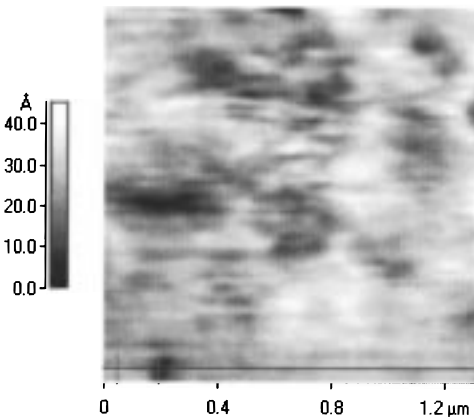
b)

Figure 7. Topography of grafted glass surface from a C30-HDPE system after separation: (a) AFM image; (b) height profile

differences between the fracture energies of the HDPE- and LDPE-based interfaces. The fracture energy measured on a glass/HDPE joint is about 240 J·m⁻² and can be compared to a value of 30 J·m⁻² for a glass/LDPE interface. The effect of the compatibility was demonstrated previously from DSC experiments performed on PE/functionalized-PE blends. In addition, by studying the crystallization phenomena close to the surface of the grafted glass by means of X-ray diffraction measurements, it was demonstrated that only the shortest polyethylene grafted chains (i.e., PE1,200-Cl and PE3,700-Cl) are able to cocrystallize with the HDPE.[28] This phenomenon is confirmed by the DSC analysis (endotherm peaks analysis and crystallization kinetics of neat PE/functionalized-PE) reported previously.

Analysis of Separated Surfaces. For a better understanding of the molecular mechanisms involved at the interface during the separation, the fractured surfaces were studied by wettability measurements and atomic force microscopy.

For the interfaces prepared from HDPE and glass surfaces grafted with short chains (C_4-Cl to C_{30}-Cl), the contact angles with water are close to the initial values obtained on the treated glass before joining (Table 4). The small decrease of water contact angle in addition to a higher hysteresis after cleavage results from the presence of holes in the grafted monolayer and the debonding of connectors by chain scissions. In fact, the AFM observations (Figure 7) performed on the C_{30}-Cl grafted-glass slide after fracture demonstrate the pres-

Table 5. Water Contact Angles and Hysteresis Measured on Grafted Glass Slides after Joining

grafted glass from polymer/HDPE joint	Θ_{water}^{M} (deg)	$\Theta_{water}^{M} - \Theta_{water}^{D}$ (deg)
PE1,200Cl-g-glass	95.8 ± 3.3	46.4 ± 7.6
PE3,700Cl-g-glass	94.5 ± 1.9	42.5 ± 4.5
EH32,500Cl-g-glass	99.8 ± 1.0	30.1 ± 2.9

**Table 6. Water Contact Angles and Hysteresis Measured on Grafted Glass Slides after Joining**

grafted glass from connector/LDPE joints	Θ_{water}^{M} (deg)	$\Theta_{water}^{M} - \Theta_{water}^{D}$ (deg)
C_4Cl-g-glass	80.8 ± 2.6	16.8 ± 4.2
C_8Cl-g-glass	84.0 ± 2.4	10.8 ± 5.4
C_{18}Cl-g-glass	95.9 ± 1.7	1.9 ± 3.7
C_{30}Cl-g-glass	88.9 ± 2.0	13.2 ± 4.9
PE1,200Cl-g-glass	90.0 ± 2.0	33.7 ± 3.7
PE3,700Cl-g-glass	81.9 ± 3.7	27.3 ± 6.6
EH32,500Cl-g-glass	99.7 ± 0.8	14.7 ± 2.5
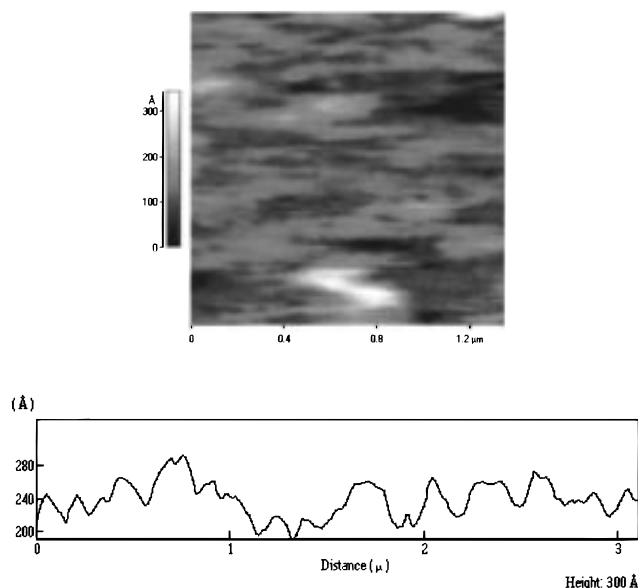
Figure 8. Topography of grafted glass surface from a PE3,700/HDPE system after separation: (a) AFM image; (b) height profile.

ence of holes with a depth corresponding to a 30 carbon atom monolayer. As a conclusion, it can be said that the connecting chains are pulled out from the PE matrix (extraction process).

On the other hand for the HDPE/polymer treated glass, the contact angles are close to those obtained for the pure polyethylene matrix indicating that some chains from the HDPE matrix remain anchored on the glass surface after separation (Table 5). Moreover, the thickness and the roughness measured by AFM on the grafted glass after separation are very different from those determined on the monolayer before joining (Figure 8). The height profile reveals the damaged fracture pattern with a medium height value indicating indirectly but clearly that the layer thickness results from the matrix decohesion. In this later case, the fracture occurs thus in the bulk of the HDPE film (cohesive failure).

In the joints prepared from LDPE, the pull-out of the connectors occurs whatever the length of the connector is. For the LDPE/treated glass systems, the contact angles with water on the separated surfaces are very close to those before forming the interface (Table 6). Moreover, the same topography observed on the grafted
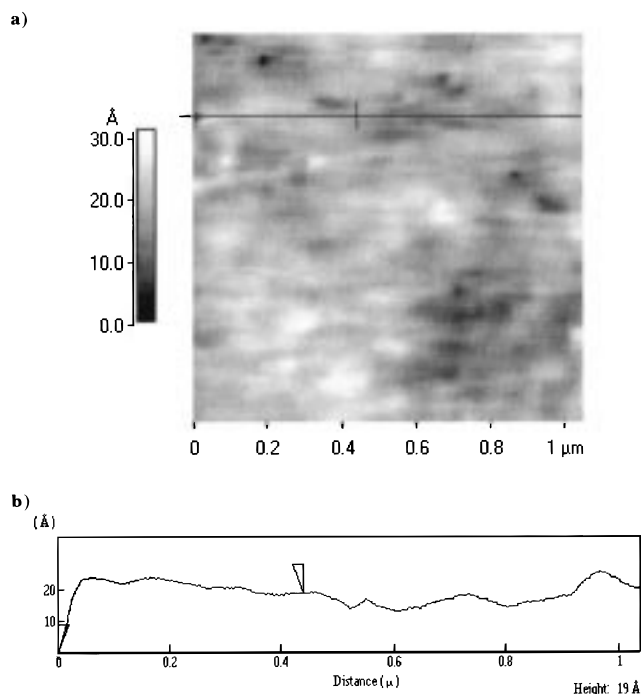
Figure 9. Topography of grafted glass surface from a C18/LDPE system after separation: (a) AFM image; (b) height profile.
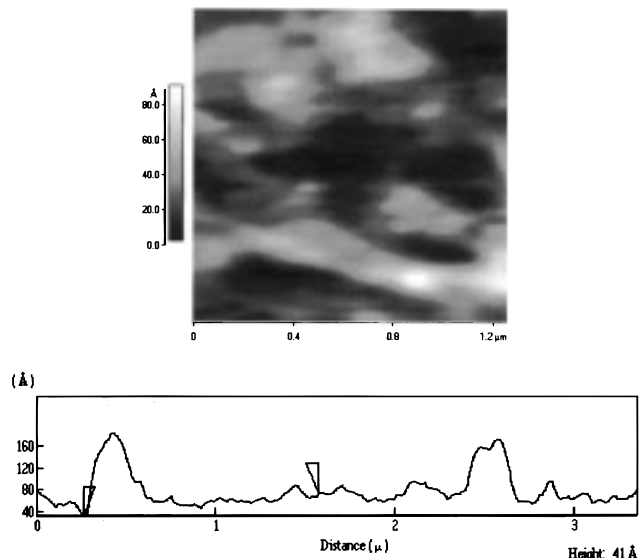
Figure 10. Topography of grafted glass surface from a PE3,700/LDPE system after separation: (a) AFM image; (b) height profile.

glass before and after separating confirms this phenomenon (Figure 9).

In the case of polymer-grafted glass/LDPE interfaces, the failure is almost interfacial, but it should be noticed that this designation is not completely correct since polymer residues are still present on the separated surfaces as it is shown on the height profile of the glass surface (Figure 10).

Relationship between G_i and Σ. Studies devoted to the interface between incompatible glassy polymers modified with diblock copolymers reported two general relationships between the energy of fracture, G_i, and the areal density of copolymers chains at the interface, Σ. De Gennes[19] demonstrated that if the fracture mechanism involved is the pull-out or scission of the
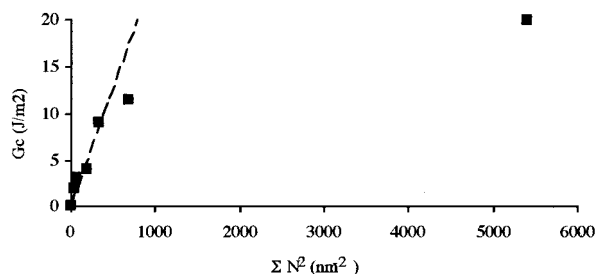
Figure 11. Fracture energy, G_i, of a LDPE/glass interface modified with connectors as a function of the product of the grafting density, Σ, and the number of monomer units, N, of the connecting chains at the interface.

connecting chains from the matrix, G_i increases linearly with the areal density of connectors at the interface and varies as the square of the extracted length, N (i.e., $G_i \approx \Sigma N^2$). In the opposite, as one of the polymers crazes during separation, Brown[21] showed that the energy of fracture increases with the square of the density of connectors (i.e., $G_i \approx \Sigma^2$).

For the interface between LDPE and glass surfaces modified with connectors which breaks with a pull out of the connecting chains, the former relationship is verified as demonstrated in Figure 11 by plotting of the fracture energy of the interface measured versus ΣN^2. The linear relationship is well verified with the connectors with a short length (from 4 to 30 carbons) whereas the fracture energy of the interface involving functionalized polyethylenes cannot be describe with such a relation. Two hypothesis can be evocated.

(i) The first one concerns the determination of N. It is not clear at all that the distribution of molar masses of precursor polymers determined before grafting remains the same for the chains grafted on the glass surface. In fact, the shortest chains react preferentially with the silanol groups on the glass surface whereas the functionalized chains with high molar masses are less reactive. Of course, this effect is more pronounced with the connecting chains having the high molar masses. As a consequence, the N value is over estimated for the grafted chains of the monolayer. This phenomenon could explain the difference between the expected values of G_i from the model and the experimental data.

(ii) The second hypothesis refers to the measure of the grafting density, Σ. In fact, Σ was determined on the particulate silica and cannot be exactly the same as the grafting ratio obtained on float glass. In addition, all the connecting chains do not participate in the interdiffusion process into the free PE.

Effect of the Crystallization at the Interface. The data reported previously allow us to determine the characteristics of silane-functionalized polyethylene (molar mass, grafting ratio, ...) to be used as interfacial connectors in order to improve the glass/polyethylene interface.

As the chains are short (from 4 to 30 carbons) and well grafted (30 to 50% of sites grafted), the fracture energy remains low (from 2 to 13 J·m^{-2} for the glass/LDPE interface and from 2 to 27 J·m^{-2} for the glass/HDPE interface) and the failure occurs from the pull-out of the grafted connecting chains.

As the molecular mass of connecting chains increases and the grafting density decreases, the glass/HDPE interface is so tough that the failure occurs in the bulk of the matrix. The highest fracture energy is obtained
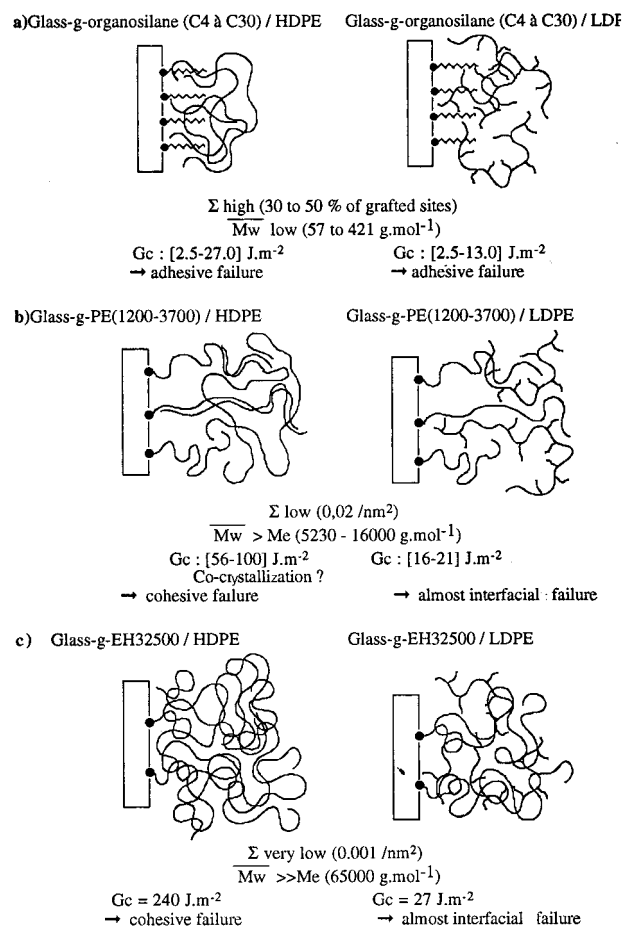

Figure 12. Modeling of the different types of interphases resulting from the diffrent tyeps of connecting chains and nature of the pure PE.

by the grafting of the EH32,500 copolymer at the interface ($G_i = 240$ J·m^{-2}). The different features of the fracture process are summarized in Figure 12.

From these results, three characteristics are required to obtain a large enhancement of the fracture energy of the interface by means of grafting connecting chains: a molar mass of the connecting chains much higher than the mass between entanglements of the matrix (for EH32,500:65,000 $\gg$ 900 g·mol^{-1}); a low grafting density ($\Sigma = 0.001$ nm^{-2}); a low ability of the grafted chains to crystallize ($X = 17\%$ for the precursor copolymer denoted EH32,500) and as a consequence for a cocrystallization ($X = 16\%$ for the blend EH32,500/HDPE)

Thus, an amorphous interphase leads to an increase of the fracture toughness of glass/PE systems. However, it must be noticed that G_i of the glass/HDPE interface modified with connectors is higher than for the corresponding LDPE/glass whatever the connector length used. The higher values of the fracture energy of the interface with HDPE can be explained by a better compatibility of the tethered-PE chains with the free chains of the PE film which are more linear than the LDPE ones. Furthermore, Boucher,[16] by studying the interface between two semicrystalline polymers modified by the in-situ formation of a block copolymer at the interface, demonstrated that if the fracture mechanisms are similar to those observed at the interface between glassy polymers, the local crystal organization of the chains governs the dissipation efficiency and the fracture toughness of the interface. Thus, for the shortest connecting chains (from 4 to 30 carbons), as the ability

for crystallizing with the HDPE matrix is high, the toughness of such interfaces could be explained by a crystallization in the vicinity of the surface. As a consequence, the mechanical properties of the interphase are changed. Nevertheless, this hypothesis remains qualitative and is difficult to verify experimentally. As the connecting chain is long enough and has a linear structure, a cocrystallization between the linear functionalized polyethylenes (PE1,200 and PE3,700) and the HDPE matrix can explain the higher value of G_i. As evidence of the interphase morphology, the crystallization of blends based on double-bond-terminated and pure polyethylenes (50:50 wt) demonstrate a possible cocrystallization between the linear polyethylenes (PE1,200 or PE3,700) and HDPE. Gent demonstrated that the cocrystallization at the interface can greatly enhance the intrinsically small level of adhesion obtained with polyethylene, probably by energy dissipation in local yielding processes.[29] However, the higher fracture energy is obtained with the less crystallizable connecting chains which proves that the cocrystallization alone cannot explain the entirely the involved adhesion mechanisms. In fact, the longest chains are the most effective to interdiffuse into the bulk and to form entanglements with the more linear matrix. A thicker and amorphous interphase provides a more effective enhancement of interfacial toughness than a thinner and crystalline interphase.

Conclusion

The adhesion between HDPE or LDPE and glass can be improved by the use of grafted connecting chains having different lengths (i.e., molar masses). Large improvements of the fracture energy of the interface measured by the asymmetric double cantilever beam test are obtained by controlling the molar mass, i.e., the length of the connectors. It appears that larger chains are more effective than shorter chains. The toughness is enhanced by the presence of some tethered chains, but a too high surface grafting density does not necessarily improve the fracture energy. The crystallization between the tethered and the free chains seems to play a minor role in the toughening mechanisms of the interface. Thus, the chlorosilane-terminated polyethylenes are able to form entanglements with the pure polyethylenes used as matrixes and more particularly with the more linear matrix. It would be interesting to control the polydispersity of the connecting chains in order to study their effect on mechanical performance of PE/glass systems. It was shown, theoretically[16] and experimentally[10] that polydisperse tethered chains were found to be more effective than monodisperse tethered chains. This work should be continued by considering independently the chain length and the effect of grafting density on the adhesion.

This preliminary study allows nevertheless to define the components which could be used in glass fiber sizings for composite materials based on a semicrystalline matrix. Especially, the connecting chains could be designed for controlling the level of the interfacial adhesion.

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