

Use of Silanes and Copolymers as Adhesion Promoters in Glass Fiber/Polyethylene Composites

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ABSTRACT: Two organofunctional silanes and three functionalized copolymers were used as adhesion promoters in glass fiber/polyethylene-reinforced composites. The performance of the coupling agents was investigated by mechanical property measurements, scanning electron microscopy, and dynamic mechanical analysis. Coupling achieved with the poly(ethylene-*g*-maleic anhydride) copolymer proved to be the most successful compared with the other copolymers (ethylene/vinyl alcohol, ethylene/acrylic acid) and silane agents (γ -methacryloxypropyltrimethoxy, cationic styryl). The combined coupling performance of the silanes and copolymers examined in this study appears to be controlled by the coupling performance of the copolymer. Effective coupling was reflected in increased mechanical properties. Increased fiber/matrix adhesion is not always associated with effective coupling because structural changes occurring at the interface region can result in a deterioration of the material property. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2877–2888, 2001

Key words: polyethylene; glass fiber; silane; copolymer; adhesion

INTRODUCTION

Low density polyethylene (LDPE) is a nontoxic, recyclable polymer with excellent processibility and low cost. Because of its high elongation at break, its main application is in blown film production. The recycling of such materials is very difficult, however, because of the high degree of recycle purity required. The high cost of recycling LDPE makes its industrial use limited. LDPE could be used for applications in which recyclates of lower purity can be utilized. Even in

these applications, its use is limited because of its poor tensile strength and very low resistance to elevated temperatures. In addition, the recycling process is associated with polymer degradation, decreasing further the tensile strength and thermal stability of the material.

In the case of polyolefins, the addition of inorganic or organic additives and especially of organic fibers provides an attractive means of enhancing the mechanical and thermal properties of the polymeric matrix. Many studies have been published concerning the properties of polyethylene (PE) with glass beads,^{1,2} CaCO₃,³ talk,⁴ mica,⁵ wood fibers,^{6,7} sisal,⁸ kenaf,⁹ pineapple,¹⁰ etc. Most of the efforts, however, focus on the incorporation of short glass fibers (GFs), which

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increases the stiffness, strength, and thermal stability of PE.^{11–15} Raj et al.¹¹ found that as the amount of GF increases, there is a small increase in the tensile strength of PE up to 40 wt% fiber concentration. However, PE cannot react with GFs and does not have compatibility with the inorganic additive. This poor adhesion results in only a small increase in the tensile strength of the composite compared with the initial strength of PE. Another negative effect caused by fiber incorporation is the decrease of elongation at break and impact strength.

Good adhesion between the fibers and matrix results in efficient stress transfer from the continuous polymer matrix to the dispersed fiber reinforcement and can increase its ability to absorb energy,^{16,17} resulting in a material with increased mechanical properties. So, the importance of good adhesion between fiber and polymer matrix has been long recognized. It has been demonstrated that for some types of composites and polymer blends, the concept of adhesion is the same. For instance, graft or block polyolefin copolymers are equally effective as adhesion promoters in composites or blends containing a polyolefin component.¹⁸ In the case of PE, compatibilizers such as maleated ethylene and a few acrylic acid copolymers are reported to enhance the adhesion between the fiber and LDPE matrix.¹⁹ The carboxylic groups are grafted on the surface of the GF, followed by bonding of the polyacrylic acid macromolecules to the PE matrix by heating.²⁰

Another way to increase the compatibility between GFs and polyolefin matrix is the use of organofunctional silane compounds as GF surface modifiers.^{19,21,22} The improvement of adhesion is based on the reactivity or compatibility of the silane compounds segments with the fibers and the polymer matrix.²³ Fiber length, orientation, distribution, and diameter also play an important role in the improvement of adhesion. It has been shown that by increasing the fiber diameter, the shear strength of the composite decreases.²⁴

Therefore, it can be concluded that the development of methods for controlling the interfacial adhesion between chemically and physically different, incompatible phases has been the subject of considerable research effort. However, there is a lack of studies examining comparatively the effectiveness of silane and copolymer agents and especially their combined effect. One objective of this work was to investigate the use of different silane coupling agents containing different reactive groups, such as γ -methacryloxypropyltri-

methoxy silane (γ -MPS), cationic styryl silane, and ethylene copolymers [e.g., poly(ethylene-*g*-maleic anhydride), ethylene-*co*-vinyl alcohol, and ethylene-*co*-(vinyl acetate)]. Some of these adhesion agents were used successfully in other polymers, like polystyrene and polypropylene.^{25,26} The main purpose of this work was to study the combined effect of silanes and copolymers as adhesion promoters in PE/short GF-reinforced composites. Mechanical and dynamic mechanical measurements and scanning electron microscopy (SEM) were used for evaluating the adhesion effect of these agents on the composites.

EXPERIMENTAL

Materials

A Borealis low density polyethylene (LDPE), with a melting point of 113 °C, degree of crystallinity of 25%, and melt flow index of 2 g/10 min at 190 °C, was used as the matrix material. Short glass fibers (GF) and E-glass, with average length and diameter of 6 mm and 13 μ m, respectively, were obtained from Cristaleria Espanola (Madrid) and used as reinforcement. Silane agents were used to modify the GF surface. The fibers were classified as follows according to the surface treatment: M4 is the as-received GF that was heat-cleaned for 4 h at 500 °C, M6 is a treated M4 fiber with γ -methacryloxypropyltrimethoxy silane (γ -MPS) and cured for 12 h at 100 °C, and M8 is a treated M4 fiber with a cationic styryl silane that was cured under the same conditions. The following copolymers were used as interfacial adhesion promoters: poly(ethylene-*g*-maleic anhydride) (PE-*g*-MA), kindly supplied by Du Pont – Canada (MB-226D), with 0.9 mol% maleic anhydride content as measured by a titration technique; ethylene-*co*-(vinyl alcohol) (EVOH), with 7.5 mol% vinyl alcohol content, obtained by hydrolysis–saponification of a commercial ethylene-*co*-(vinyl acetate) (Alcudia), and with 8 mol% vinyl acetate content; ethylene/acrylic acid copolymer (Primacor 5981, Dow), containing 20 wt% acrylic acid (EAA) and with a weight-average molecular weight (M_w) of \sim 18,000 and a number-average molecular weight of \sim 7000.

Preparation of Composites

A series of GF/LDPE composites was produced with each of the three types of fiber (M4, M6, M8),

at a fiber content of 20wt%. Another series was also prepared in which the fiber and copolymer (PE-*g*-MA, EVOH, EAA) type was varied, with the same fiber content and the copolymer content being 10% of the fiber weight. The fibers and the polymer were mixed in a Haake Buchler Rheomixer, model 600, with roller blades and a mixing head with a volumetric capacity of 69 cm³. Prior to mixing, M4 fibers and all polymers were dried at a vacuum oven for 24 h at 75 °C. M6 and M8 fibers were also dried under vacuum for 6 h at 50 °C. The components were physically premixed before being fed into the Rheomixer. Blending was performed at 200 °C and 60 rpm for a period of 15 min. The melt temperature and torque were continuously recorded during the mixing period on a Haake Rheocord, model 5000. After preparation, the blends were immediately removed from the mixer, cooled to room temperature, and placed in tightly sealed plastic containers to prevent any moisture absorption.

Mechanical Properties

Tensile strength, Young's modulus, and elongation at break were measured on an Instron mechanical tester, model 1122, according to the ASTM D638 method. The crosshead speed was 5 mm/min. Six measurements were conducted for each sample, and the results were averaged to obtain a mean value. The specimens for mechanical property measurements were prepared by hot press molding at 200 °C for 5 min at a pressure of 250 bar.

The Izod impact measurements were performed on a Tinius Olsen instrument according to ASTM D256. Six measurements were conducted on each composite. Prior to mechanical measurements, the samples were conditioned at 50 ± 5% relative humidity for 48 h at ambient temperature in a closed chamber containing a saturated Ca(NO₃)₂ · 4H₂O solution in distilled water (ASTM E-104).

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) measurements were performed with a Rheometric Scientific Analyzer, model MKIII. The experiments were carried out using the tensile mode of the DMTA instrument over a temperature range of -120 to 100 °C, at a rate of 3 °C/min under nitrogen flow. The samples were scanned at a frequency of 1 Hz, and a strain level of 0.071%

was applied. A static force was applied to prevent buckling of the sample; its value was determined so that the experiments could be held in the area of linear viscoelastic behavior of the samples. The storage (E') and loss (E'') modulus and the loss tangent ($\tan \delta$) were recorded as a function of temperature. The testing was performed using rectangular bars with dimensions of $\sim 8 \times 5 \times 0.5$ mm. The exact dimensions of each sample were measured before the scan.

Scanning Electron Microscopy (SEM)

The impact specimens were fractured, and the exposed surfaces were observed with a scanning electron microscope (JEOL, model JSM-840A). The surfaces of the fractured specimens were coated with gold to avoid charging under the electron beam.

RESULTS AND DISCUSSION

Mechanical Properties

To study the effect of GF content on the mechanical properties of LDPE, a series of composites containing 10, 20, and 30 wt% of fibers was prepared. Two types of fibers were used: uncoated (M4) and coated fibers with γ -MPS (M6). The variation of tensile strength, elongation at break, and impact strength with GF content are presented in Figure 1. As expected, fiber incorporation in a thermoplastic matrix increased the tensile strength of the material, whereas the impact strength and elongation at break were decreased dramatically. Composites prepared with coated fibers displayed higher tensile strength values compared with those prepared with uncoated fibers. Also, the observed decrease in the impact strength was lower with coated fibers, whereas the decrease in elongation at break was not significantly influenced by the fiber type. This improvement in the tensile strength could possibly be attributed to an improved adhesion achieved between the LDPE matrix and the coated fibers. Figure 1 shows that the change in the mechanical properties is relatively small beyond a GF content of 20 wt%. This GF content was therefore chosen for the preparation of the materials investigated further in this study.

The tensile strength, modulus, elongation at break, and impact strength of GF/LDPE composites, prepared with different coupling agents and

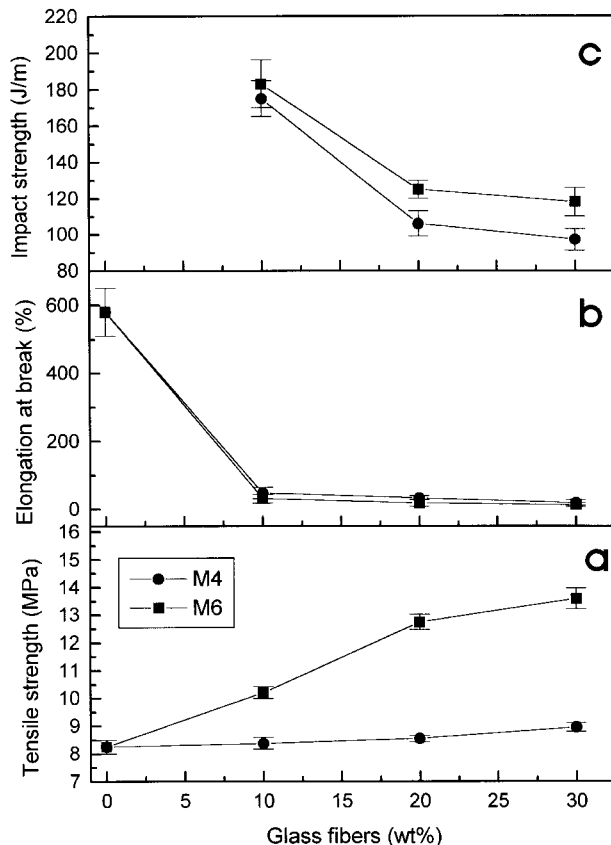


Figure 1 Variation of the mechanical properties of GF/LDPE composites with glass fiber content: (a) tensile strength, (b) elongation at break, and (c) impact strength.

their combination with copolymers, are presented in Table 1. Use of untreated fibers, M4, resulted in a slight increase in the tensile strength of PE from 8.14 to 8.54 MPa, whereas the modulus increased from 180 to 469 MPa. Fiber incorporation was associated with a significant decrease in the elongation at break (from 600 to 33.5%) and material embrittlement, as seen in the low impact strength value of 106 J/m. The significant reinforcing capability of the fibers could only be realized in materials containing a silane or a copolymer coupling agent. Stronger, stiffer, and tougher materials were produced with silane-modified fibers. The tensile strength, modulus, and impact strength of the composites increased when treated fibers (M6, M8) were used, the best result being observed with M6 fiber. For the M6 fiber composite, the tensile strength increased to 12.74 MPa compared with 8.54 MPa for the untreated M4 fiber (49% improvement), whereas the modulus increased from 469 to 707 MPa (51% improve-

ment). Increased modulus for both treated fibers was associated with decreased elongation at break, whereas the impact strength increased from 106 (M4) to 125 (M6) to 128 J/m (M8).

The increase in the mechanical properties of treated-fiber composites can apparently be attributed to the improved interfacial adhesion achieved between fiber and matrix due to the coupling effect of the silane compounds. PE cannot react with and does not exhibit any compatibility with the GF. The hydrophilic nature of GF, due to its surface hydroxyl groups, adversely affects the adhesion to hydrophobic thermoplastic matrix and, as a result, fiber/matrix adhesion is poor. So, to promote adhesion, the fiber should be treated with a coupling agent containing functional groups that can bridge the interface between resin and reinforcement. Organofunctional silanes contain hydroxyl and R groups (methacrylate, cationic styryl, etc.); the former bond to the mineral, whereas the latter can form covalent bonds with the resin or, in the case of a nonreactive resin such as PE, promote adhesion through the formation of a pseudo-interpenetrating polymer network at the interface region.²⁷ Because of the hydrophobic character imparted to fiber surface by silane compounds, a treated fiber can wet out more readily in the polymeric matrix, resulting in an improved interfacial adhesion. Furthermore, silanes may have the tendency to reduce fiber agglomeration, improving the distribution within the polymer matrix and thus resulting in improved mechanical properties. Untreated fibers tend to form clusters.²⁸

Micrographs of fracture surfaces of GF/LDPE composites made of untreated and treated fibers are presented in Figure 2. Figure 2a shows that in composites prepared with M4 fiber, failure occurs at the fiber/matrix interface as a result of the poor interfacial adhesion existing between fiber and matrix. Comparing the fracture surface of M6 fiber (Figure 2b) with that of the untreated glass fiber, it can be seen that failure increasingly occurs within the matrix, whereas adhesive failure at the interface decreases. This result suggests that fiber/matrix interfacial adhesion was improved with γ -MPS treatment. The micrograph in Figure 2c shows that composites prepared with M8 fiber displayed failure within the matrix. This failure occurs to a lesser extent for the materials prepared with the M6 fiber, reflecting the lower interfacial adhesion achieved with the cationic styryl silane. The extent of interfacial adhesion is also reflected in the mechanical properties of the

Table I Mechanical Properties of Polyethylene Composites

LDPE				
Composite	Impact (J/m)	PE-g-MA	PE-co-OH	PE-co-COOH
LDPE	—	—	—	—
M4	106	170	139	94
M6	125	170	146	96
M8	128	155	134	102
Composite	Tensile (MPa)	PE-g-MA	PE-co-OH	PE-co-COOH
LDPE	8.14	—	—	—
M4	8.54	14.46	9.86	9.26
M6	12.74	12.81	9.49	9.36
M8	9.01	11.71	8.92	9.21
Composite	Young (MPa)	PE-g-MA	PE-co-OH	PE-co-COOH
LDPE	180	—	—	—
M4	469	1290	550	557
M6	707	719	568	572
M8	586	616	482	548
Composite	Elongation (%)	PE-g-MA	PE-co-OH	PE-co-COOH
LDPE	600	—	—	—
M4	33.5	17	22	24
M6	18	23	24	27
M8	25	28	25	26

material. These results suggest that γ -MPS exhibits a higher performance as coupling agent compared with the cationic styryl silane.

Interfacial adhesion is associated with energy-absorbing mechanisms in addition to increasing the strength of the composite because stress transfer from matrix to fiber becomes more effective. Such mechanisms include fiber debonding and failure within the matrix, which lead to increased toughness and impact strength. It is worth noting that unlike γ -MPS treatment, which raises both the tensile and impact strength of the material, treatment with the cationic styryl silane has a significant influence only on the impact strength. It would appear that although the GF/silane matrix bridging system formed by the cationic styryl silane is not very efficient at transferring stress but is effective in consuming energy, which results in increased impact strength.

Use of the maleated copolymer PE-g-MA as coupling agent in composites prepared with each of the three fibers (M4, M6 and M8) resulted in

increased mechanical properties independently of surface treatment. A significant increase is noted in the mechanical properties for composites prepared with the untreated fiber M4, demonstrating the high compatibility of PE-g-MA with both phases of the material (i.e., polyethylene and the inorganic fiber). The tensile strength, modulus, and impact strength of the composite increased from 8.54 MPa, 469 MPa, and 106 J/m, respectively, to 14.46 MPa (69%), 1290 MPa (175%) and 170 J/m (60%), respectively (Table 1), reflecting the strong interfacial adhesion achieved with PE-g-MA. The excellent performance of PE-g-MA as coupling agent in GF/PE composites could be attributed to the following two factors: (a) the ability of the maleic anhydride groups to react with the hydroxyls of the glass fiber, and (b) the great compatibility of the grafted copolymer PE chains with the main PE phase. However, the performance of PE-g-MA as coupling agent seems to be reduced in the presence of silanes. Although composites made of M6 and M8 fibers exhibit higher mechanical properties compared with those not

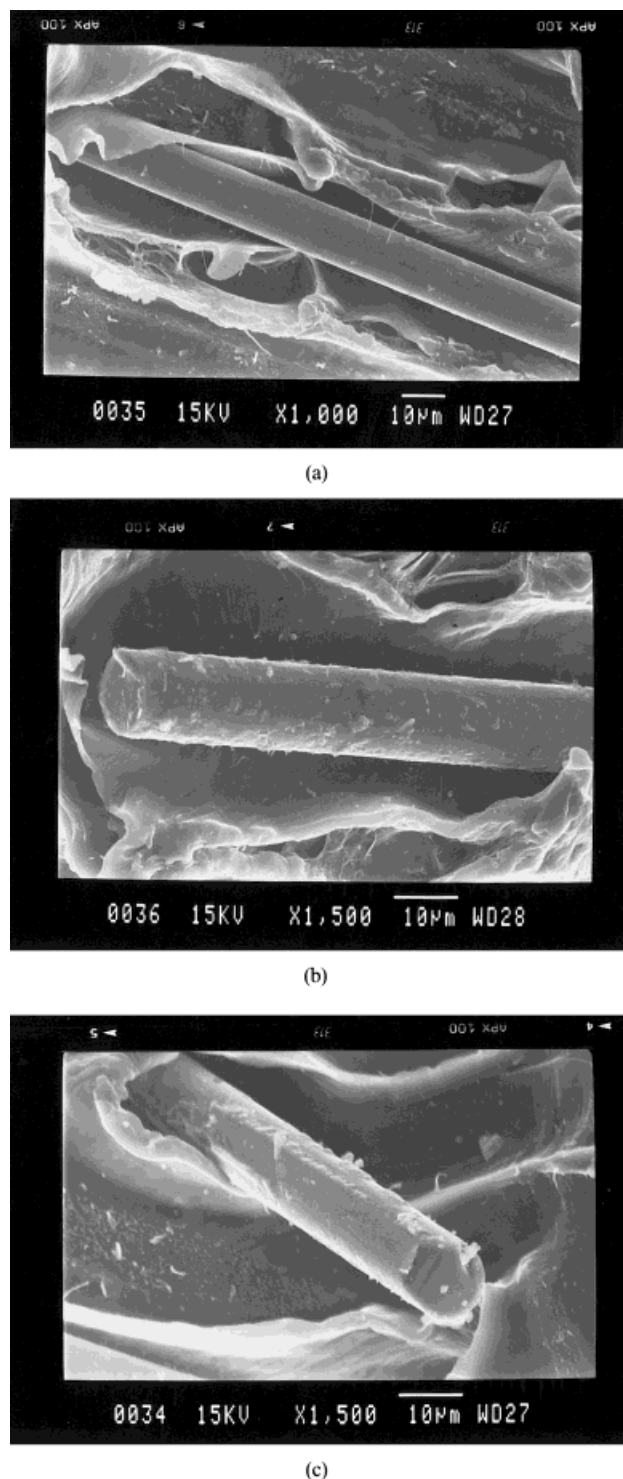


Figure 2 SEM micrographs of fracture surfaces of GF/LDPE composites containing different types of fibers: (a) M4, (b) M6, and (c) M8 fibers.

containing PE-g-MA, these properties are still lower than those achieved with M4 fiber and PE-g-MA.

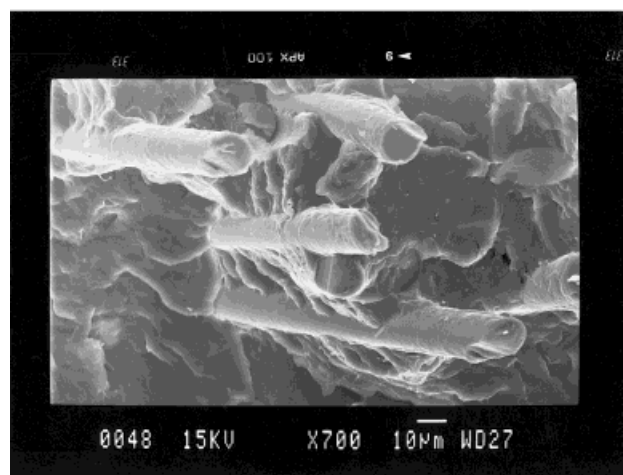
SEM images of fracture surfaces from composites containing PE-g-MA are shown in Figure 3. Figure 3a (M4 fiber) shows that there is a large contact area between the matrix and the fiber surface. It is interesting to note that the adhered matrix usually ends in quite long strips of material. This result suggests that the polymer network formed between the grafted PE and main PE phase through solubility/interdiffusion²⁷ not only affects a few polymeric chains but a considerable part of the matrix resin. Comparing the fracture surfaces shown in Figures 3b (M6 fiber) and 3c (M8 fiber) with the corresponding surfaces of Figures 2b and 2c, indicates that improved interfacial adhesion occurs in the presence of PE-g-MA. However, despite the presence of improved interfacial adhesion, the performance of PE-g-MA is reduced in the presence of silane agents. This reduction could probably be attributed to the limited ability of the maleic anhydride groups to react with the hydroxyls of the glass fiber because they have been covered with hydrophobic groups. Another reason may be that the silanes are impeding the contact between the hydroxyl groups and the anhydride. However, the increased amount of polymer adhering to the surface of the fibers suggests that a small percentage of the anhydride groups must have reacted. Such considerations could probably explain the lower improvement in the mechanical properties of the composites coupled with silanes and PE-g-MA.

The effect of EVOH on the mechanical properties of composites prepared with each of the three fibers (M4, M6, and M8) differs from that of PE-g-MA. The best, although moderate, result was achieved when untreated fibers (M4) were used. There was an increase in the tensile strength, modulus, and impact strength of the material from 8.54 MPa, 469 MPa, 106 J/m, respectively, to 9.86 MPa (15%), 550 MPa (17%) and 139 J/m (31%), respectively. Comparison of the fracture surfaces presented in Figures 2a and 4a shows that a relatively small improved interfacial adhesion is achieved with EVOH, as suggested by the small parts of matrix remaining on the fiber surface. This result is in agreement with the observed increase in the mechanical properties and may be due to the hydrogen bonds formed between the —OH groups of the fiber and those of the copolymer. However, the low amount of —OH groups in the copolymer (7.5 mol%) limits the extensive formation of such bonds.

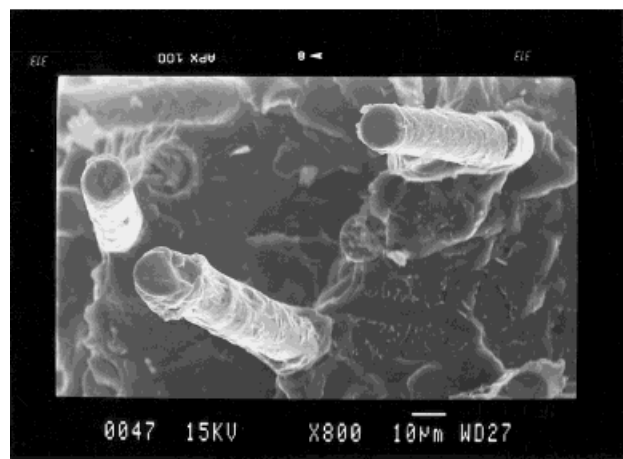
The use of EVOH with γ -MPS modified fibers (M6) caused a decrease in the tensile strength



(a)

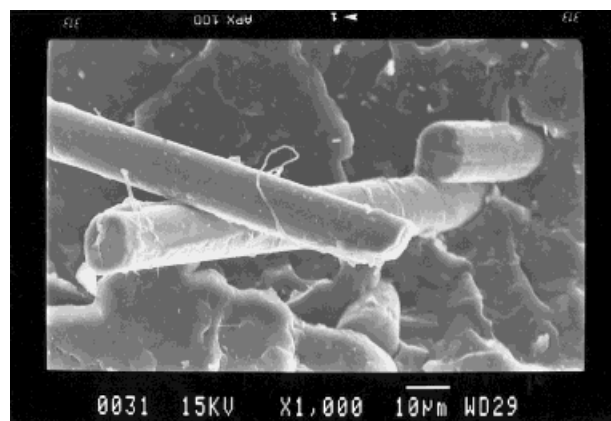


(b)

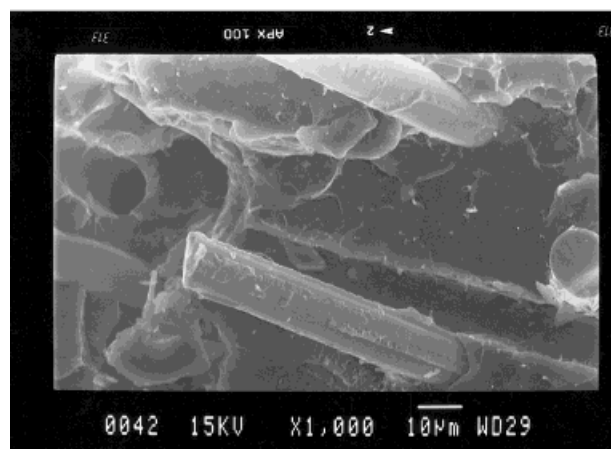


(c)

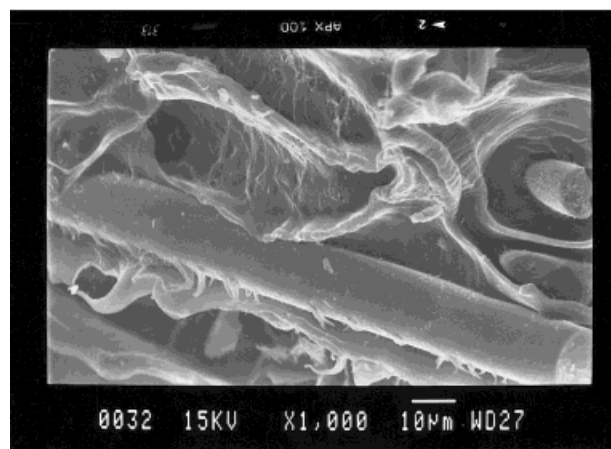
Figure 3 SEM micrographs of fracture surfaces of GF/LDPE composites containing PE-g-MA and different types of fiber: (a) M4, (b) M6, and (c) M8 fibers.



(a)



(b)



(c)

Figure 4 SEM micrographs of fracture surfaces of GF/LDPE composites containing EVOH and different types of fiber: (a) M4, (b) M6, and (c) M8 fibers.

and modulus of the composite from 12.74 and 707 MPa to 9.49 (−26%) and 568 MPa (−20%), respectively, whereas the impact strength increased from 125 to 146 J/m (17%). But, looking at the

micrographs in Figures 2b and 4b, it can be seen that there is no deterioration of interfacial adhesion with the addition of EVOH, as indicated by the amount of matrix adhering to the fiber surface. The decrease in the tensile strength might be related to the tensile strength of EVOH (6.73 MPa), which is considerably lower than that of LDPE (8.14 MPa). The increase in the impact strength might contribute to the high compatibility of the PE chains of EVOH with the main PE phase and the possible formation of hydrogen bonds between the —OH groups of the copolymer and those of the fiber. This hydrogen bonding as well as the formed polymer network between the PE chains of EVOH and main phase could be contributing to additional energy-absorbing mechanisms. Similar considerations could also explain the change in the mechanical properties of composites made with the cationic styryl silane-modified fibers (M8) and the addition of EVOH.

Using an EAA copolymer as an adhesion promoter was not very successful, as indicated by the mechanical properties (Table 1). Use of M4 and M8 fiber led to a very small increase in the tensile strength of the material, whereas a decrease was observed with the M6 fiber. The elongation at break for these materials remained similar to that recorded for the previous composites, whereas the impact strength decreased. In untreated fibers, the hydroxyl groups of the fiber can form ester or hydrogen bonds with the carboxyl groups of EAA. This result is evidenced by the significant parts of polymer matrix remaining on the fiber surfaces (Figure 5a). In general, the effect of EAA on the mechanical properties of the composite was similar to that of EVOH except for the impact strength.

The similarity between the impact strength of the composites with unfunctionalized fibers (106 J/m) and those containing EAA (94, 96, and 102 J/m) would suggest that the absorption of energy to fracture in these materials is similar despite the presence of increased interfacial adhesion in the compatibilized materials (Figures 2a and 5). However, interfacial adhesion in fiber-reinforced tough thermoplastics can have various effects on the impact strength of the material. Good bonding between fiber and matrix inhibits the flow of the ductile matrix and hence promotes brittle fracture. On the other hand, mechanisms such as fiber debonding and failure within the matrix can increase the fracture energy of the material.²⁹

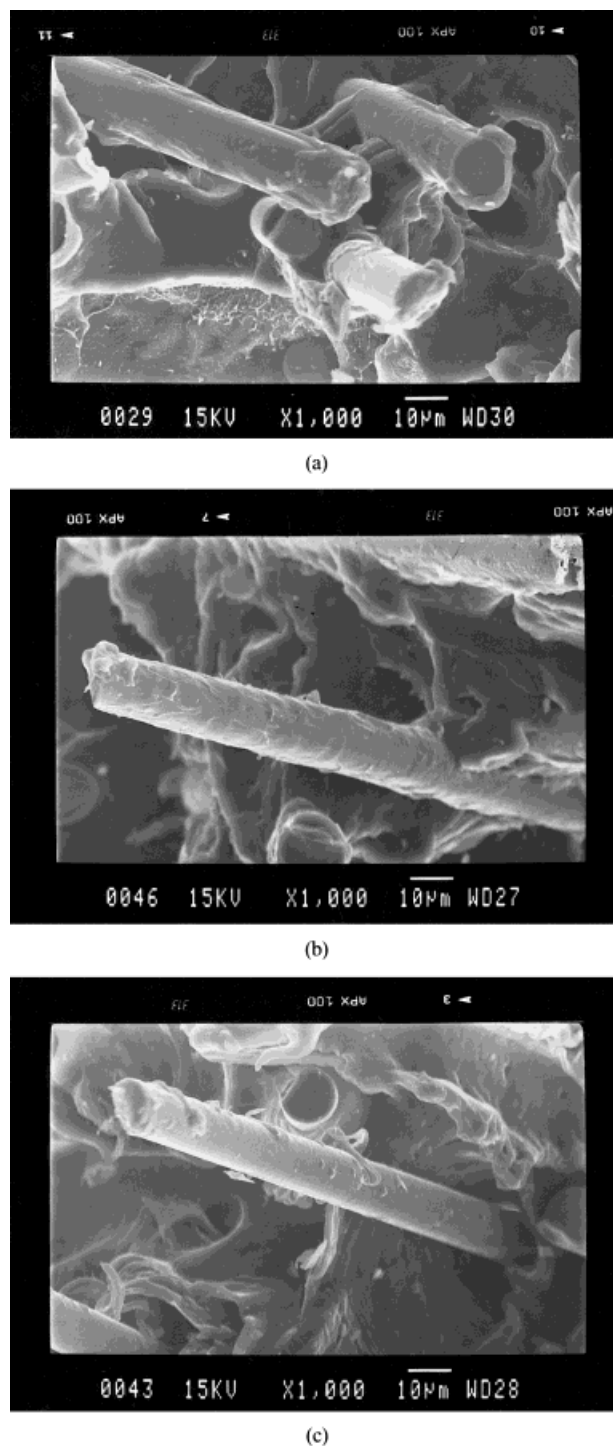


Figure 5 SEM micrographs of fracture surfaces of GF/LDPE composites containing EAA and different types of fibers: (a) M4, (b) M6, and (c) M8 fibers.

The impact strength of the material is therefore controlled by balancing these two mechanisms.

It would appear that the main factor controlling the impact behavior of the prepared compos-

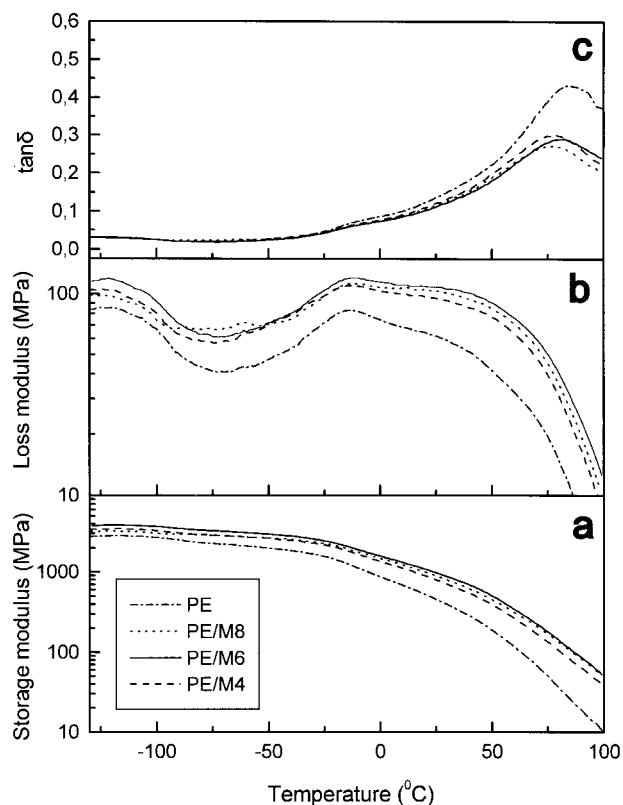


Figure 6 DMTA thermographs of GF/LDPE composites made with M4, M6, and M8 fibers: (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$.

ites is lack of energy absorption. The matrix is embrittled with the addition of EAA, which leads to a decrease in impact strength. Matrix embrittlement caused by the presence of carboxyl groups has also been observed by other researchers.³⁰ Polypropylene/elastomer/short GF composites prepared with an acrylated ethylene-propylene elastomer exhibited a lower impact strength than those containing the unfunctionalized component. Furthermore, EAA is a low molecular weight copolymer ($M_w = 18,000$), and the ability of its chains to form an effective polymer network, as postulated by the interpenetration theory,²⁷ and thus provide the material with a new fracture energy absorption mechanism is lower compared with that of PE-*g*-MA and EVOH.

Matrix embrittlement at the fiber/matrix interfacial region could also account for the low tensile strength values observed for all three composites (M4, M6, and M8) coupled with EAA. During the fracture of such materials, cracks can be formed at the embrittled fiber/matrix interface³⁰ as fiber debonding or pull-out occurs, and their propaga-

tion into the main matrix could lead to failure at lower tensile strength.

The addition of EEA, as was the case with EVOH, confirmed that factors such as the molecular weight, the mechanical properties, as well as the effect on the matrix of the adhesion promoter can influence the coupling performance.

Dynamic Mechanical Analysis

The temperature dependence on the dynamic mechanical properties for materials investigated in this study is presented in Figures 6–8.

Figure 6 shows data for the storage (E') and loss (E'') modulus and damping factor ($\tan \delta$) of PE and composites prepared with M4, M6, and M8 fibers as a function of temperature. As expected, the $\tan \delta$ curve of PE (Figure 6c) exhibits three relaxations located in the vicinity of -120°C (γ), 0°C (β), and 80°C (α). The nature of these relaxations has been reviewed by McCrum and

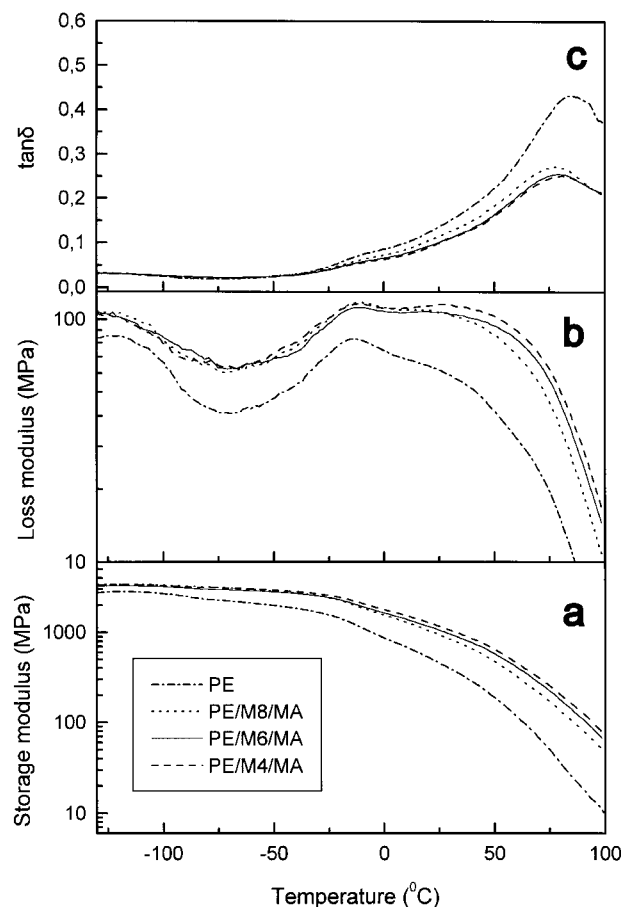


Figure 7 DMTA thermographs of GF/LDPE composites made with M4, M6, and M8 fibers containing PE-*g*-MA: (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$.

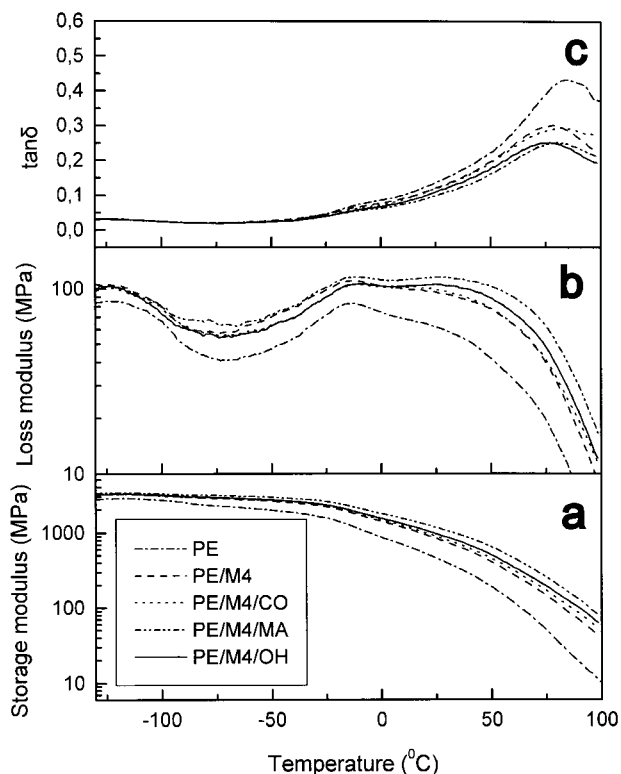


Figure 8 DMTA thermographs of GF/LDPE composites made with M4 fiber containing each of the three copolymers (PE-*g*-MA, EVOH, EAA): (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$.

co-workers.³¹ The γ -peak is assigned to chain relaxation in the amorphous phase. The β -peak, almost absent in the unbranched material,³² has been associated with the relaxations of side groups or short branch points. The α -relaxation was first described as vibrational and reorientational motion within the crystals. Later, this relaxation has also been interpreted as relaxation of the constrained molecules with reduced mobility located near the crystallites.^{33,34}

Concerning the glass transition temperature (T_g) of LDPE, both the γ - and β -relaxations are quoted to have the properties of the glass-rubber transition. When the alkylidene content is low, the γ -peak is more prominent, whereas β -relaxation is the dominant mechanism at high alkylidene content. The higher modulus drop occurs in the vicinity of 0 °C rather than at -120 °C, which would suggest that β -relaxation is the dominant mechanism in the PE used in this study (Figures 6a and 6c). At relaxation temperatures, E' decreases (Figure 6a), whereas both E'' (Figure 6b) and $\tan \delta$ (Figure 6c) pass through a maximum.

The introduction of GF in the PE matrix has profound effects on the dynamic mechanical properties of the material. Both, the stiffness and heat resistance of the composite increase over the whole temperature range, whereas the damping factor decreases. Figure 6a shows that the drop in modulus on passing through α - and β -relaxation temperatures, is comparatively less for reinforced materials than for PE alone. In other words, the effect of GF on modulus is larger at temperatures >0 °C (β -relaxation) than below it. A material with a relatively higher modulus at higher temperatures is produced. This higher modulus is probably the result incorporation of GF that reduces the flexibility of the material by introducing constraints on the segmental mobility of polymeric molecules at relaxation temperatures,³⁵ a phenomenon that is more pronounced at higher temperatures.

The plot of loss modulus as a function of temperature (Figure 6b) shows that the most pronounced effect of GF reinforcement is the broadening of the relaxation regions, especially at temperatures >0 °C (β -relaxation). Change in the physical state of the matrix surrounding the GFs^{35,36} hinders molecular motion, which may be one of the factors causing the observed broadening of relaxation peaks. A comparison of the $\tan \delta$ curves presented in Figure 6c further supports that GF incorporation leads to a reduction in magnitude of peak intensity for the β - and especially for the α -relaxation. The position of the peaks practically remains unchanged. This result suggests that GF incorporation does not significantly influence the crystallization or percentage of crystallinity because such processes are related to peak location change.³⁷ Existence of interfacial adhesion results in a material with an increased storage modulus, resistance to elevated temperatures, decreased damping, and broader peaks. The best results were observed with γ -MPS-treated fibers (M6) and are in agreement with both the tensile strength results and microscopic evidence. It appears that the presence of interfacial adhesion hinders further molecular motion, leading to a stiffer, stronger, and tougher material.

Data for the storage (E') and loss modulus (E'') and damping factor ($\tan \delta$) as a function of temperature for PE and composites prepared with the three types of fiber (M4, M6, and M8) and use of the coupling agent PE-*g*-MA is shown in Figure 7. Existence of increased interfacial adhesion, in addition to improving the mechanical properties of

the material is also reflected in improved thermo-mechanical properties (i.e., increased storage modulus and decreased damping factor). The best result is achieved for the composite made with the untreated fiber M4, which is in agreement with mechanical property results and microscopic evidence. The ability of the maleic anhydride groups to react with the hydroxyls groups of the GF and the compatibility of the grafted PE chains with the main PE phase translate to better composite properties.

Comparison of the DMTA traces (Figure 8) for composites made with M4 fiber and each of the three copolymers, as well as no coupling agent, show that the effect of adhesion on the thermo-mechanical properties of the material is in agreement with that on the mechanical properties. Use of the copolymers, PE-*g*-MA and EVOH, result in increased storage modulus (E') and lower damping factor. The best result is achieved for the composite containing PE-*g*-MA. EAA does not improve the thermomechanical properties of the composite, despite the promotion of interfacial adhesion (Figure 5a). Use of EAA improved only slightly the storage modulus (Figure 8a), whereas the damping factor remained practically the same (Figure 8c). It would appear then that improved interfacial adhesion does not always translate to improved thermomechanical properties.

Although coupling agents are primarily materials that improve the adhesive bond of dissimilar surfaces by reacting to form bridges, they may also modify the organic and inorganic boundary layers of the interface region.^{27,30} Processes associated with the action of a coupling agent, such as structural changes, matrix embrittlement, and differences in the expansion coefficients of the different structures, could possibly explain the observed behavior with the EAA. Ethylene/acrylic acid copolymer is a low molecular weight compound and is probably more readily diffusible onto the fiber surface. The EAA can therefore form a relatively high crosslink density at the fiber surface, which in turn can lead to a higher than expected stiffness level at the fiber/matrix interface. Matrix weakening due to the effect of steric stress^{30,38} is another factor related to the action of EAA. Such considerations can possibly explain the behavior of EAA.

CONCLUSIONS

Glass fiber-reinforced PE composites can be effectively coupled by standard organofunctional si-

lane coupling agents. Silane compounds impart a hydrophobic character to the fiber surface, and coupling is achieved through compatibility of their R groups with PE, whereas the hydroxyl groups bond to the mineral. Increased interfacial adhesion results in a material with increased mechanical properties. Materials coupled with the methacrylate silane showed improved properties compared with those coupled with the cationic styryl silane, implying that methacrylate groups exhibit a higher degree of compatibility with PE than cationic styryl groups. Another reason for this result may be that methacrylate groups hinder the hydroxyl reaction less than the styryl due to their smaller size.

Functionalized copolymers may be successfully used as adhesion promoters in thermoplastic composites. Of all materials investigated in this study, the best mechanical properties were exhibited by composites coupled with PE-*g*-MA. The excellent compatibility of the grafted PE copolymer chains with the main PE phase and the ability of the maleic anhydride groups to react with the hydroxyl groups of the mineral can explain the superior coupling performance of PE-*g*-MA. EVOH was proved to be a less effective coupling agent than PE-*g*-MA. Increased interfacial adhesion is not always reflected in increased material properties. Although EAA displayed increased interfacial adhesion, there was a deterioration in the impact strength of the material and only a slight increase in its tensile strength. It would appear that parameters associated with the action of a coupling agent, such as structural changes, matrix embrittlement at the interfacial region, and difference in the thermal expansion coefficients of the different structures, could possibly account for this discrepancy.

The combination of silane agents with copolymers had various effects on the mechanical properties of the coupled materials. A moderate increase in the material properties was observed only with the PE-*g*-MA; EVOH and EAA were not as efficient. It would appear that the combined coupling performance of silanes and copolymers is significantly influenced by the coupling performance of the copolymer.

Interfacial adhesion, in addition to affecting the mechanical properties of the composites, affected similarly their viscoelastic behavior. In general, improved interfacial adhesion in GF composites meant an increase in the storage modulus and a lowering of the damping factor.

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