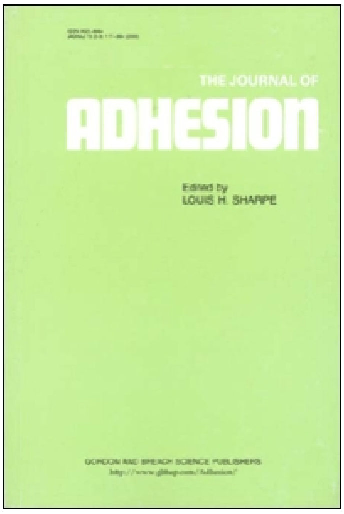

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New Coupling Agents as Adhesion Promoters at the Poly(Phenylene Sulfide)/Glass Interface – Studies with Micro and Macro Composites

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Carboxy-functionalized poly(phenylene sulfide) having different molar masses and amount of the functional group were prepared in order to be used with γ-aminopropyltriethoxysilane as surface treatment of E-glass fibers. These grafted polymer chains act as connecting chains in order to improve the interfacial shear strength of the PPS-glass interface. According to their chemical nature, which is the same as the PPS matrix, and their ability to crystallize in the same crystalline form as the pure PPS, a continuum of bonding from the fiber surface to the bulk matrix is achieved. A chemical linkage is established at the glass surface by means of hydrolyzed ethoxysilane groups of the γ-APS and from the formation of amide units resulting from the reaction of amine functions of the silane and the carboxylic groups of the modified PPS. A "physical" linkage is expected between the grafted PPS and the PPS chains by means of entanglements and co-crystallization. A large improvement of the interfacial shear strength measured from the microdroplet test is observed when a modified-PPS having a medium molar mass and a low amount of functional groups is used in comparison with untreated or silane-treated glass fibers. This improvement is also observed for short glass fibers/PPS composite materials. In fact, a large improvement is obtained on mechanical properties such as the tensile, flexural, and impact strengths.

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Keywords: Poly(phenylene sulfide); grafting; connecting chains; glass fiber sizing; interface; interphase; microbond test; short glass fiber composites

INTRODUCTION

Fiber reinforced polymer composites are multiphase systems in which the fiber-matrix interface plays an important role [1, 2]. In most cases, it is necessary to consider the interfacial regions (interphase) instead of the interface to define the various phenomena involved in the vicinity of the fiber surface (surface chemistry, physical interactions, adsorption, etc.) [3, 4]. Thus, numerous works have been done to characterize and to modify the interphase in fiber-based composites, especially in the case of glass-fiber-reinforced thermosets [5, 6]. In fact, with such fibers and reactive polymeric systems, the interphase can be modified by changing the chemical nature of the sizing (nature of the polymer film former and/or chemical structure of the organosilane) [7, 8]. In contrast, the case of the thermoplastic polymer/glass interface is not so well documented according to the non-reactive character of the matrix. In fact, for such matrices, no covalent link can be ensured between the matrix and the coupling agent by means of the organofunctional group of the organosilane, as for the reactive polymer matrices, but only physical interactions can be established [9–11].

In the common composite materials made by mixing a thermoplastic polymer and short glass fibers using an extrusion-injection process, a functionalized polymer is added during the processing [12, 13]. For example, a maleic anhydride grafted polypropylene is considered in the case of short glass fiber–polypropylene composite materials. This method supposes that the functionalized thermoplastic diffuses and then reacts with the fiber surface. In the previous example, it would be expected that the anhydride groups react with the amine functions from the γ-aminopropyltriethoxysilane used as coupling agent in the sizing formulation. Such a diffusion to the fiber surface which is dependent on the surface effects and the processing conditions was not clearly evidenced. In addition, in all cases, the glass fibers need to be sized before any handling and processing. Thus, chemical reactions of the grafted polymer with the sizing and/or diffusion of the sizing from the fiber surface to the bulk could occur, leading to non-well-defined interphases.

Most of the thermoplastic matrices used for composite materials, such as polypropylene or polyamide, are semicrystalline polymers. It is well known that such polymers exhibit a different type of crystallization in the vicinity of a surface than in the bulk [14–17]. This surface-induced crystallization, called transcrystallinity, is very sensitive to the processing conditions (thermal history, shearing) and remains a controversial phenomenon. Especially, the effect of the presence of such transcrystalline interlayers on the interfacial shear strength of the interface is poorly understood [18].

In order to *a priori* control the structure of the interphases in semicrystalline thermoplastic/glass fiber composites, a concept of connecting chains grafted on the fiber surface during the surface treatment or sizing was developed [19, 20]. These connecting chains, of the same chemical nature as the semi-crystalline matrix, are able to diffuse and co-crystallize with the polymer matrix leading to a continuum of bonding from the glass fiber surface to the bulk matrix. Covalent bonding is established at the interface by means of the reactive functions introduced as side chains or as chain ends of the functionalized polymer. "Physical bonding" is ensured between the grafted chain and the matrix by means of a co-crystallization of these polymers [21]. This way for modifying the glass-polypropylene interface was reported previously [22]. Isotactic poly(propene-co-diene) copolymers and oligopropenes were synthetized and hydrosilylated to obtain chlorosilane or triethoxysilane-functionalized polypropylenes. The ability of such polymers to be grafted on a float glass surface and to co-crystallize with a commercial isotactic polypropylene was demonstrated from wetting and calorimetric measurements [23]. The same kind of concept of connecting chains which are able to co-crystallize was also used for improving the adhesion between two semi-crystalline polymers by means of block copolymers [24].

This paper is devoted to composite materials based on poly(phenylene sulfide) (PPS) and short glass fibers. PPS displays high temperature and high strength properties and the common ease of processing of the thermoplastics [25–27]. Numerous papers were published on the reinforcement of PPS with carbon or glass fibers [28–29]. The crystallization kinetics of the PPS in the presence of fibers was also studied [30–32]. The occurrence of transcrystalline interphases depends on the nature of the fiber, the molar mass of the PPS, and on the cooling rate.

Especially, for the glass fibers, the results are sometimes contradictory [28, 31]. The sizing of the glass fibers is also an important parameter governing the glass transition temperature of the composite materials [33]. As for the other glass/thermoplastic interfaces, the effect of the presence of a transcrystalline interphase for PPS/glass interface is not clearly evidenced. To improve the mechanical properties and the hydrothermal stability of PPS-glass composites, sulfur-based silane coupling agents can be used [34]. The efficiency of such a silane coupling agent supposes that at high temperatue radical reactions occur with the PPS. In this paper, we describe another way for modifying the interface in order to control the chemical mechanisms by the use of a functionalized-PPS/γ-aminopropyltriethoxysilane mixture for the surface treatment of glass fibers. Using such a treatment, PPS chains are grafted on the fiber surface and, during the melting of the PPS matrix, these chains can diffuse and co-crystallise with the PPS matrix. The present paper describes the surface treatment process of E-glass fibers with carboxy-modified PPS of different molar masses and having different amounts of functional groups. The effect of such treatments on the interfacial adhesion measured by the microdroplet test and on the mechanical properties of short glass fiber/PPS composite materials is discussed as a function of the characteristics of the grafted PPS chains.

EXPERIMENTAL

Chemical Products

Three different carboxy-terminated polymeric co-coupling agents from Solvay Co. were considered in this study to be used as coatings for E-glass fibers. These polymers differ in their molar mass and functionality (amount of functional group). These carboxy-functionalized poly(phenylene sulfide)s were obtained from the copolymerization of paradichlorobenzene and an halogenated derivative carrying the carboxylic group. The synthesis of such polymers will be detailed in another paper [35]. The first one, denoted LW/HF, has a low molar mass and a high degree of functionalization, whereas the second one, denoted HW/LF, has a higher molar mass (close to that of the matrix) and a low amount of carboxylic functions. The last one, denoted MW/LF, has an intermediate molar mass (Tab. I). The molar masses

TABLE I Physico-chemical properties of the polymeric co-coupling agents

Name	*LW/HF*	*MW/LF*	*HW/LF*
Intrinsic viscosity (dl.g^{-1})	0.08	0.18	0.25
Molar mass (g.mol^{-1})	13,600	32,400	46,000
Theoretical amount of reactive functions (%)	11	<1	<1
Melting temperature (°C) (20 K.min^{-1})	267	282	280
Crystallization temperature (°C) (−20 K.min^{-1})	233	240	201

were determined from the intrinsic viscosity and the Mark-Houwink relation [36]. The amount of functional groups reported in the Table I corresponds to the initial molar amount of comonomer introduced for the synthesis in comparison with that of the paradichlorobenzene. FT-IR spectroscopy was used in the DRIFT mode to visualize the carboxylic groups but the sensitivity of this technique is not sufficient to quantify the amount of functional groups in the modified-PPS (except for LW/HF). The same problem was noted for ^{13}C-NMR CP/MAS analysis.

A poly(phenylene sulfide) (PPS) was used as the matrix for the microcomposites and for the short fiber based composite materials. The molar mass of this PPS matrix is 53,000 g.mol^{-1} as determined from its intrinsic viscosity and application of the Mark-Houwinck equation [36]. Its melting temperature is 280°C.

Microcomposites and Composite Materials

E-glass fibers from Owens-Corning Fiberglas were used for making the microcomposites. These fibers have an average diameter of 19 μm. Untreated and γ-aminopropyl triethoxysilane (γ-APS)-treated fibers were considered as references (supplied by OCF Co.).

$$(CH_3-CH_2-O)_3-Si-(CH_2)_3-NH_2 \qquad (\gamma\text{-APS})$$

The polymeric co-coupling agents were deposited on previously γ-APS treated glass fibers using a solvent process. Toluene was used as solvent (1% wt. of functionalized PPS). The modified-PPS was dispersed for 4 hours at 50°C using ultra-sonic stirring under nitrogen. The fibers previously γ-APS-treated were dipped into the toluene dispersion for 1.5 h and then dried for 12 hours at 100°C.

Microdroplets (microcomposites) were prepared according to the procedure proposed by Miller *et al.* [37] from a PPS film (100 μm-thick) (Fig. 1a). The heating cycle used to prepare these samples consists of 30 minutes at 330°C followed by 30 minutes at 200°C (annealing) (cooling $1^\circ\ \mathrm{min}^{-1}$) according to a previous study on the crystallization kinetics [32, 38].

The composite materials were prepared from fibers treated with sizings combining the different co-coupling agents and the γ-APS in the industrial process for E-glass fibers. Glass fibers treated with a conventional sizing were also considered (denoted commercially treated glass fibers from Vetrotex Co.). These two types of E-glass fibers have a diameter of 14 μm. The shear strength of the interface studied by the microdebonding method for the commercially treated fiber/PPS interface can not be directly compared with that obtained with the different treatment, because of the different diameters [49]. Composites with various volume fractions (from 0 to 45%) of short E-glass fibers were prepared using a twin-screw extruder (ZSK25 from Werner & Pleiderer) and an injection machine (Battenfeld 35T). Specimens for tensile, flexural, and impact tests were prepared. For all the specimens, the mean fiber length was the same (4.5 mm).

Microbond Test

The micromechanical tests were performed on a two-parallel-blade device at a speed of $100\ \mu\mathrm{m.min}^{-1}$ on an Adhamel-Lhomargy tensile machine equipped with a 5N-load cell.

The interfacial shear strength, $\bar{\tau}$, between the PPS droplet and the glass fiber was estimated using the following formula [39–40].

$$\bar{\tau} = F_d / \pi D L_e$$

where F_d is the debonding force, D the fiber diameter, and L_e the embedded length. It was demonstrated in a previous paper [41] that

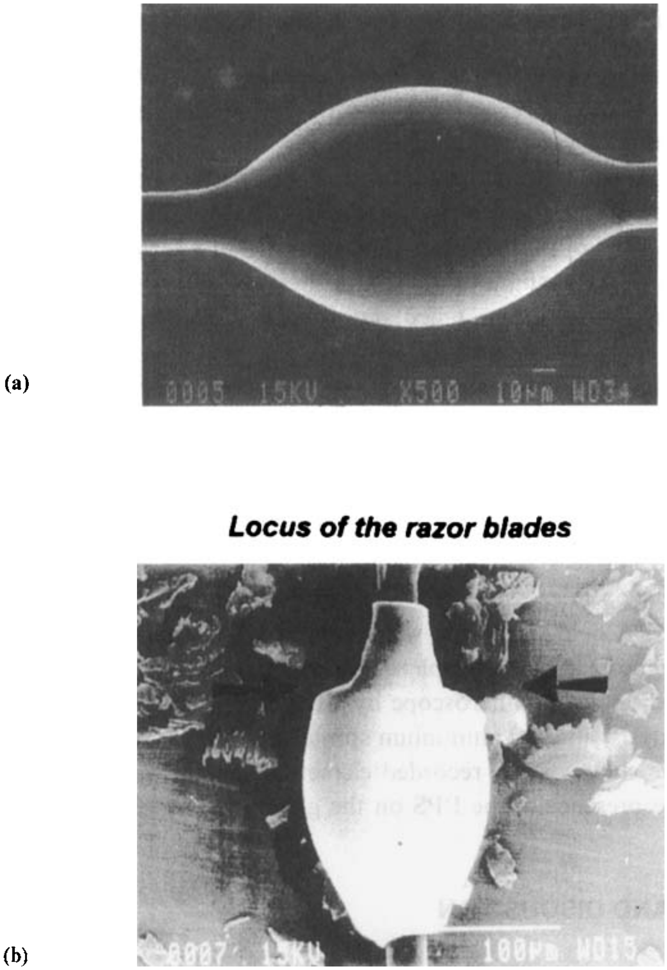


FIGURE 1 PPS microdroplet formed on a E-glass fiber: (a) before debonding; (b) after debonding.

plastic flow of the PPS matrix occurs during the debonding of the microdroplet (Fig. 1b). In such a case, one could assume a constant shear stress along the interface as supposed in the given equation. The various micromechanical models developed in the literature for this test were reported and applied to the PPS/glass fiber system in a previous paper [41].

Mechanical Characterization of the Composites

The tensile strength of the composite materials was determined by tensile tests performed on an Instron 4204 tensile machine operating at 1 mm.min^{-1} on ISO6 dogbone specimens.

The flexural strength of the composites was determined using the same machine on parallelepipedic specimens ($10 \times 4 \times 120$ mm^3) using a crosshead speed of 2 mm.min^{-1}. The span distance was 60 mm.

The Izod impact strength of the composites was determined using a Frank B1 apparatus on unnotched and notched specimens ($120 \times 12.7 \times 4$ mm^3).

All the mechanical tests were performed at room temperature and at a relative humidity of 50% (50% HR).

Scanning Electron Microscopy

The fracture surfaces of the broken specimens were observed by scanning electron microscopy (SEM) (Jeol 840 A microscope) operating at 15 kV. A gold sputtering was done before examination.

For the debonded microdroplets, the embedded area of the fiber was analyzed under the microscope by EDAX (X-Rays Electron Diffraction Analysis) after an aluminium sputtering. The occurence of the K_α ray of the sulfur on the recorded elemental spectra was used as a probe for the presence of the PPS on the glass fiber surface.

RESULTS AND DISCUSSION

Interfacial Shear Strength

The characteristics of the polymeric co-coupling agents are given in Table I. Before using the functionalized polymers as co-coupling agents, the presence of the functional groups is checked by means of FT-IR spectroscopy. The amount of reactive groups (carboxylic) are given as theoretical because of the difficulty of a quantitative determination. The carboxylic groups can react with the amine functions of the γ-aminopropyl triethoxysilane (γ-APS) to form amide units leading to covalent bonding of the modified polymeric chain to the glass surface (Fig. 2).

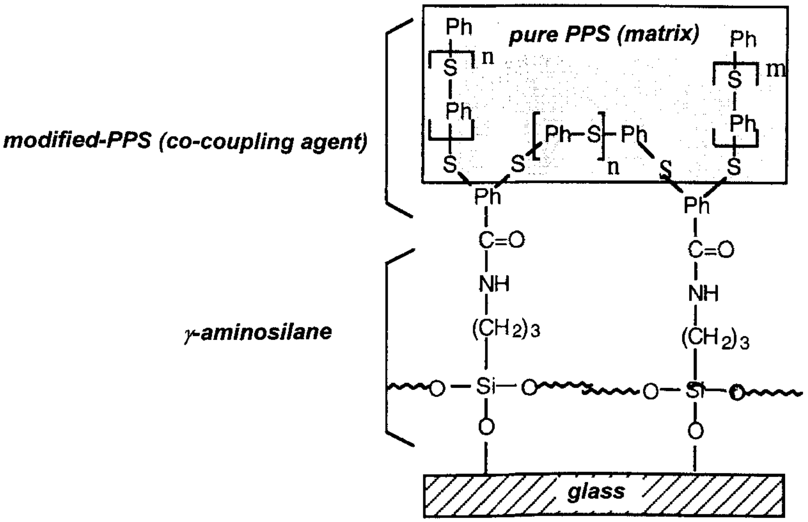
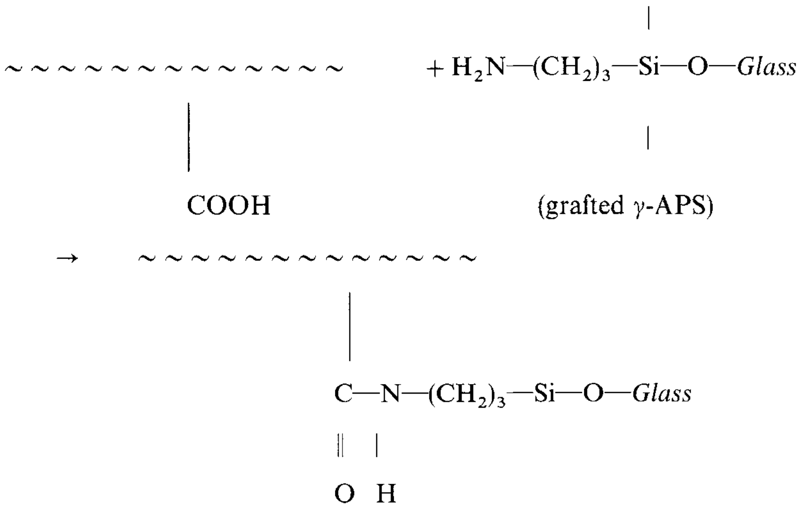


FIGURE 2 Schematic representation of the chemical structure of the interphase between the glass fiber surface and the PPS matrix resulting from a sizing based on a coupling agent and a polymeric PPS co-coupling agent (functional groups in side-chain position).



$$\underset{\substack{|\\ \text{COOH}}}{\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim} \quad + H_2N\text{—}(CH_2)_3\text{—}\overset{|}{\underset{|}{Si}}\text{—}O\text{—}\mathit{Glass} \quad (\text{grafted } \gamma\text{-APS})$$

$$\rightarrow \quad \underset{\substack{|\\ \underset{\substack{\| \\ O}}{C}\text{—}\underset{\substack{| \\ H}}{N}\text{—}(CH_2)_3\text{—}Si\text{—}O\text{—}\mathit{Glass}}}{\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim}$$

These functionalized polymers are semi-crystalline and can crystallize in the same orthorhombic system as the PPS matrix as demonstrated by WAXS (Wide Angle X-Ray Spectroscopy) [35]. The compatibility with the PPS matrix is required and demonstrated by scanning calorimetry. In fact, only one endotherm is observed on the DSC recording of a blend based on the PPS matrix and the co-coupling agent (50 : 50 by wt.). In addition, the same blends were found to be homogeneous by scanning electron microscopy. Thus, it can be concluded that these functionalized polymers are able to co-crystallize with the PPS matrix (*i.e.*, the chains are able to crystallize together in the same crystalline form and at the same time). This concept was also developped for the modification of the glass fiber/isotactic polypropylene interface [22]. In this case, it was found that the efficiency of the modified polypropylenes to co-crystallize with the pure polypropylene depends on the degree of functionalization and the molar mass. Because of the high temperature processing of the PPS composites, the thermostability of the co-coupling agents is also required and this was checked by thermogravimetric analysis. The details on the synthesis and characterization of these functionalized materials will be given in a future paper [35].

Because of the ability of the functionalized polymers to co-crystallize with the poly(phenylene sulfide) used as the matrix and to react with the aminosilane grafted on the glass fiber, these polymers can be used as a co-coupling agent with a conventional coupling agent such as the γ-APS. These polymers are expected to establish a continuum of bonding from the glass surface (chemical bonding with the γ-APS) to the bulk matrix (co-crystallization with the PPS matrix).

γ-APS sized E-glass fibers were coated with these three functionalized polymers using a solvent process in order to test their efficiency for the improvement of the interfacial shear strength of the PPS/glass interface. The amount of deposit was determined by thermogravimetric analysis and was found to be about 2% by weight. The amount of γ-APS measured on the initial fibers was about 0.3%.

The interfacial shear strength of the PPS/glass fiber interface as a function of the surface treament of the E-glass fiber measured by means of the microbond test is reported in Figure 3. τ is found to be twice as high for the γ-APS treated fiber as for the untreated one. Different crystallization phenomena for the two types of microcomposites cannot be involved since no difference was noted between the two surface treatments by polarized light optical microscopy. As for Desio *et al.* [31], no transcrystalline interphases were observed with glass fibers. The higher value of the interfacial shear strength for the aminosilane

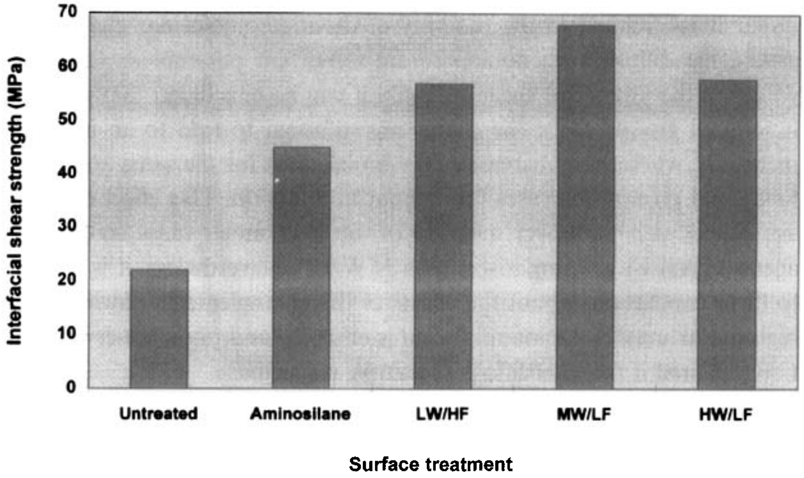


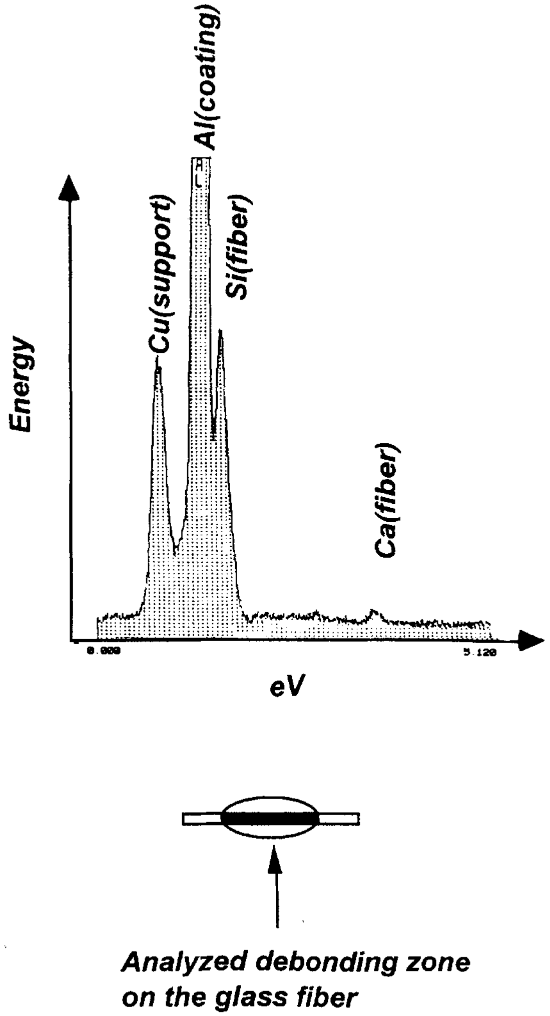
FIGURE 3 Dependence of the interfacial shear strength on the surface treatment of the glass fiber surface.

can be associated with the better wettability of the silane-treated glass fiber with the melted PPS than for the untreated one. Nevertheless, the interfacial shear strength can be improved by using the functionalized polymers as co-coupling agents. The highest value for $\bar{\tau}$ is obtained for the polymer having the intermediate molar mass and a low amount of functional groups (MW/LF). It was also demonstrated that the interfacial adhesion in the case of the glass/PPS interface can be divided in two components:

- the physico-chemical interactions developed at the interface
- the mechanical adhesion associated with the frictional forces developed at the interface during the processing, especially during the crystallization process.

Because of the fact that the same thermal cycle was used for all the surface treatments, the changes in the value of the interfacial shear strength can be associated only with the interactions created at the interface. The magnitude of these changes is related to the two parameters which could be varied: i) the number of covalent bonds between the amine and carboxylic groups and ii) the interdiffusion of the grafted polymeric chains in the PPS matrix followed by a co-crystallization process. Thus, the degree of functionalization and the molar mass (related to the mobility of the macromolecular chains governing the diffusion phenomenon) are important parameters. From the values of the interfacial shear strength, it can be concluded that only few functional groups along the chains are sufficient to lead to an improvement of $\bar{\tau}$, whereas an increase of the molar mass for the same amount of functional groups decreases the interfacial adhesion. This effect could be associated with the lower mobility of the high molar mass co-coupling agent (HW/LF) in comparison with MW/LF. Nevertheless, it is difficult to form conclusions about the effects of the entanglements (favored by a high molar mass if the interdiffusion is ensured) and of the co-crystallization (ensured if the interdiffusion occurs), respectively.

Elemental analysis performed in the scanning electron microscope on the embedded zone of the glass fiber after debonding (Fig. 4) shows a cohesive failure for the LW/HF-treated fiber, whereas an adhesive failure is observed for the MW/LF and HW/LF-treated fibers. The nature of the failure is determined from the presence of the K_α-ray of sulfur on the EDAX spectrum (Fig. 4b). Thus, the locus of the failure for the LW/HF-treated fiber is between the grafted polymer (co-coupling agent) and the PPS matrix (Fig. 5a). In fact, the low molar mass and the high number of defects in the chain (introduced by the functional groups) reduce the ability to form entanglements and to co-crystallize with the pure PPS, respectively. For the co-coupling agents having a low amount of functional groups (MW/LF and HW/LF), thus forming few covalent bonds, the failure occurs in the interphase between the grafted polymer chains and the aminosilane or the glass surface. In fact, in this case, the higher molar masses lead to entanglements and/or a co-crystallization with the bulk PPS matrix. For these surface treatments, the critical links are the covalent bonds (amide units) established from the reaction of amine and carboxylic functions (Fig. 5b). Because of the low amount of covalent bonds which could be created at the interface, the evidence of amide bonds can not easily done. Thus, the formation of physical interactions such as hydrogen bonds at the interface between the aminosilane-treated glass surface and the carboxy-terminated PPS can be supposed. Therefore, the lower interfacial shear strength of the interface for the highest molar mass coupling agent can be explained by the formation of physical interactions instead of covalent bonds. This phenomenon can result from the lower reactivity of the functionalized-PPS as the molar mass increases.



(a)

FIGURE 4 Elemental analysis performed on the embedded area after debonding the PPS droplet for different surface treatments:(a) untreated fiber, (b) polymer LW/HF deposited on a γ-APS treated fiber.

Short E-glass Fiber Based Composites

A mixture of the γ-aminopropyltriethoxysilane and the co-coupling agent, denoted MW/LF (leading to the highest value of the interfacial shear strength), was considered as a sizing for glass fibers in on-line

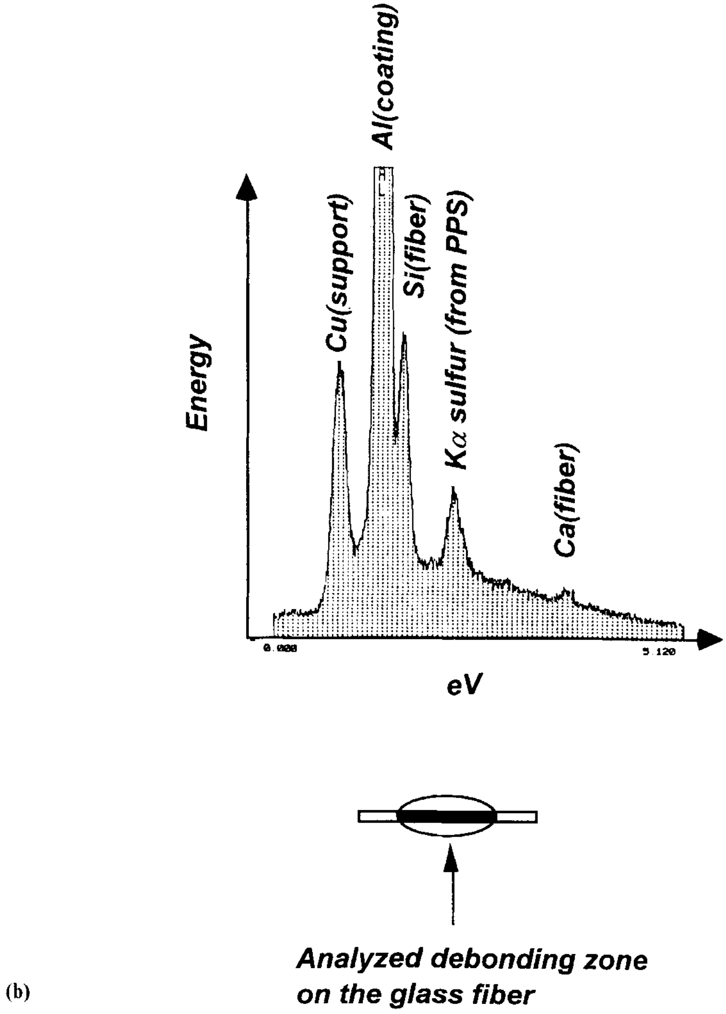


FIGURE 4 (Continued).

industrial glass fiber manufacturing. Commercially treated glass fibers from Vetrotex Co. were also considered as a reference. These glass fibers were used to prepare composite materials with different volume fractions of glass (from 0-pure PPS-to 45%). This study was done in order to verify the increase of the interfacial shear strength reported for microcomposites on real composite materials. All the composite

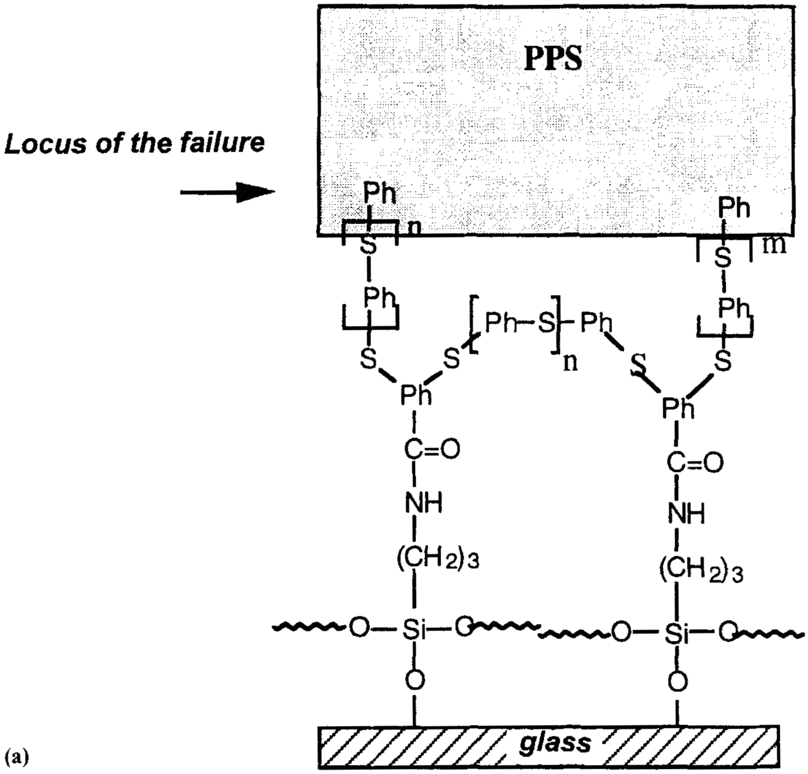


FIGURE 5 Schematic representation of the locus of the failure in the case of a γ-APS treated fiber coated with the co-coupling agent LW/HF (Fig. 5a) and with the co-coupling agents MW/LF and LW/LF (Fig. 5b).

materials have about the same average fiber length (Tab. II). The average fiber length slightly decreases as the volume fraction of the glass fibers increases. This effect could be attributed to the increase of the viscosity of the filled PPS. The increase of the shear stresses in the extrusion process induces the breakage of glass fibers [42]. In addition, using DSC, it was found that the PPS has the same amount of crystallinity (48%) for all the volume fractions and surface treatments of the fibers.

For all the composite materials considered, the average fiber length is lower than the critical length, l_c [43]. In fact, if the fiber length is higher than the critical length, fiber break occurs, whereas, in the

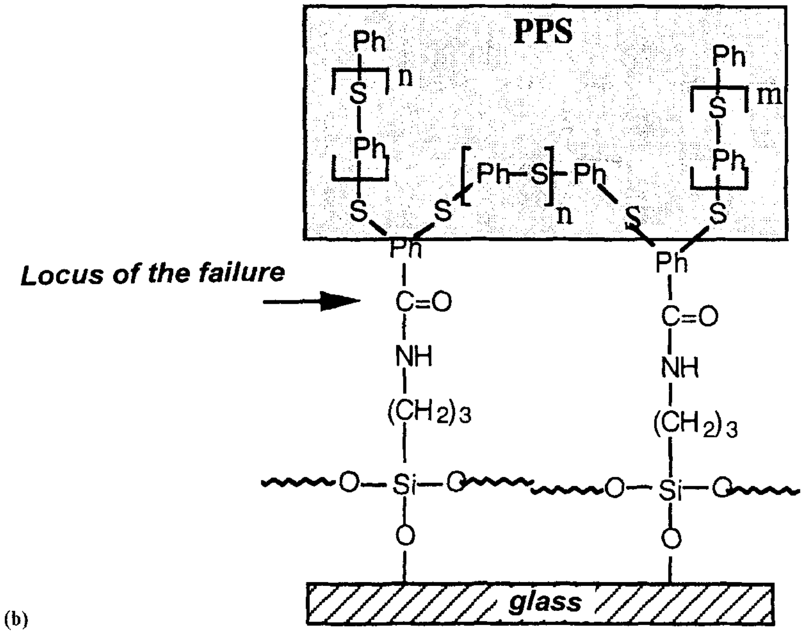


FIGURE 5 (Continued).

opposite, the interface debonds. The critical length can be estimated from the interfacial shear strength, $\bar{\tau}$, measured using the microbond test. For $\bar{\tau}$ equal to 20 and 100 MPa, the critical lengths are 5.9 and 1.2 mm, respectively [44]. As a consequence, for all the composites considered in this study, the fracture mechanism is the same, *i.e.*, the interface debonds.

As expected, the ultimate mechanical properties (tensile and flexural strengths) are improved when short glass fibers are introduced into the

TABLE II Average fiber lengths in the injected short-glass-fiber/PPS composites

Surface treatment of glass fibers	*Vol. fraction of glass (%)*	*Fiber length (μm)*	*Rate of crystallinity (%)*
Commercial	12	131	49
	24	119	47
	43	112	48
γ-APS + MW/LF PPS	11	147	49
	25	124	46
	42	125	49

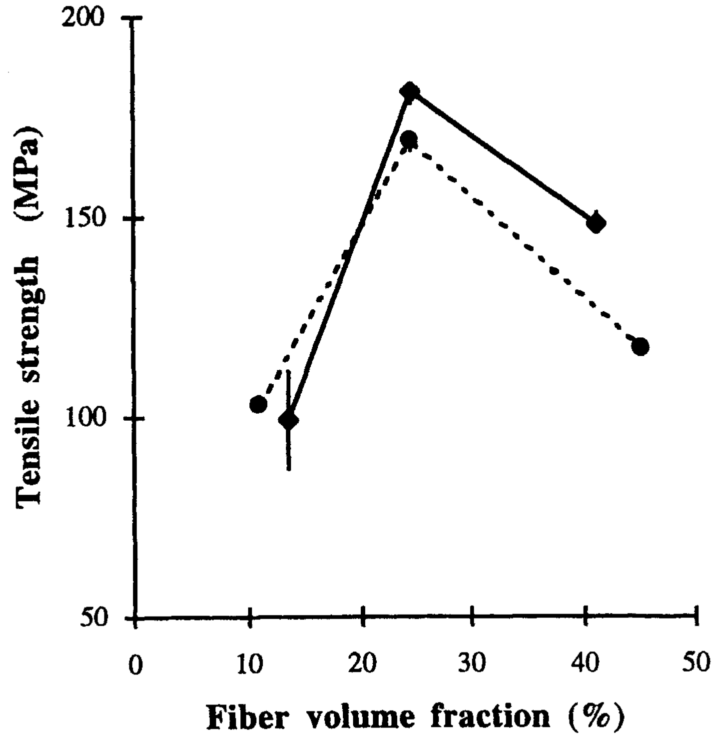


FIGURE 6 Tensile strength of the short-glass-fiber-based composites as a function of the volume fraction of glass:
(●): composites based on glass fibers commercially treated
(◆): composites based on γ-APS treated fibers coated with the polymer MW/LF.

PPS matrix (Figs. 6 and 7). The ultimate tensile and flexural strengths pass through maxima with the volume fraction of glass. The same trend was already observed for carbon fiber reinforced PPS [44]. The short fibers increase the fracture properties by reducing the propagation of microcracks through the debonding phenomena. In another way, the fibers lead to microdefects at the fiber ends acting as zones of stress concentrations. As a consequence, the effects of fiber ends are the main phenomena for the highest values of volume fractions of glass fibers.

The use of a functionalized polymer as a co-coupling agent increases the ultimate tensile and flexural strengths for all the volume fractions of fibers (Figs. 6 and 7). The effect is more pronounced for the bending tests than for the tensile test because of the fact that the

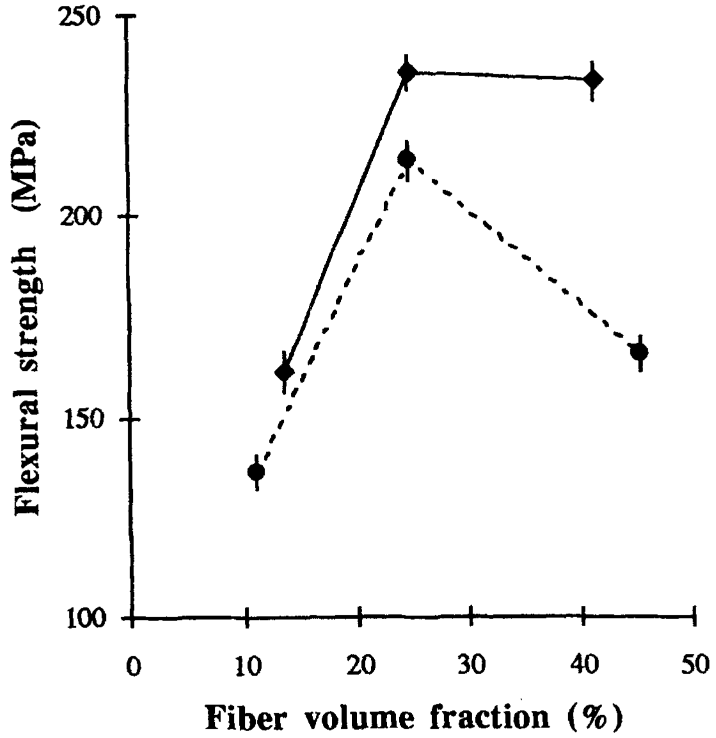


FIGURE 7 Flexural strength of the short-glass-fiber-based composites as a function of the volume fraction of glass:
(●): composites based on glass fiber commercially treated
(♦): composites based on γ-APS treated fibers coated with the polymer MW/LF.

contribution of the interphase is more important in this mode. In fact, a large part of the short fibers are lined up in the injection direction. In addition, the effect of the surface treatment is more pronounced for the highest volume fractions of fibers, as the distance between fibers is lower [45]. Because of the phenomena involved in the improvement of short-fiber-based composite materials, it can be concluded that the glass fiber/PPS interface is improved by using the functionalized polymer as co-coupling agent with γ-APS. This effect is also confirmed by the observation of the fracture surfaces by scanning electron microscopy (Fig. 9). For the commercially treated fibers, the failure seems to occur in the vicinity of the glass surface through debonding along the interface (Fig. 9a). For the MW/LF treated fibers, some PPS matrix remains attached to the glass fiber (cohesive failure) (Fig. 9b). The same trend is observed for the impact properties of the composite materials, especially for the unotched specimens (Fig. 8). The fracture mechanisms of poly(phenylene sulfide)/glass fiber composites have been studied by Karger-Kocsis *et al.* [46]. These authors demonstrated the large influence of the testing rate and of the temperature on the fracture energy and the modulus. The ability of the fibers to toughen the PPS matrix is especially important as the matrix displays a brittle behaviour, *i.e.*, for a low temperature and for a low speed of testing. These conclusions could explain the larger difference observed between the composites based on commercially treated fibers and those based on MW/LF treated fibers for the ultimate tensile and/or flexural strengths than for the impact strength. In fact, the testing speeds are 1 mm.min^{-1} for the tensile test (2 mm.min^{-1} for the flexural test) and about 4 m.s^{-1} for the impact strength. In addition, the slight difference observed for the notched specimens is in agreement with the results reported in the literature

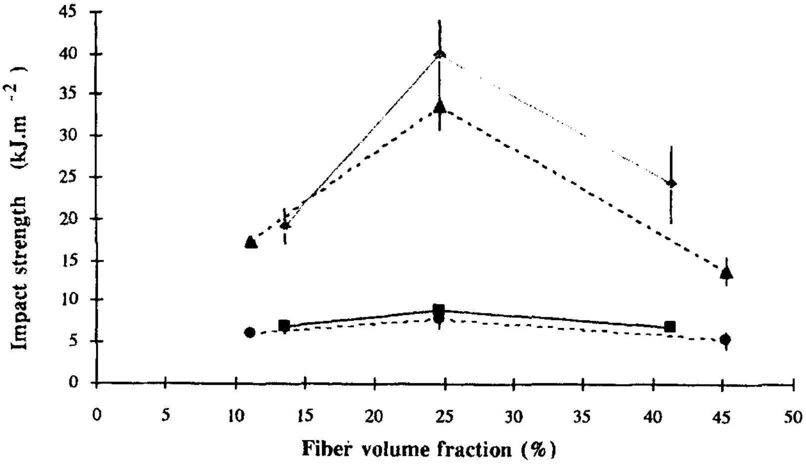


FIGURE 8 Impact strength of the short-glass-fiber-based composites as a function of the volume fraction of glass:
composites based on glass fibers commercially treated
(●): notched; (△): unnotched
composites based on γ-APS treated fibers coated with the polymer MW/LF
(■): notched; (◆): unnotched.

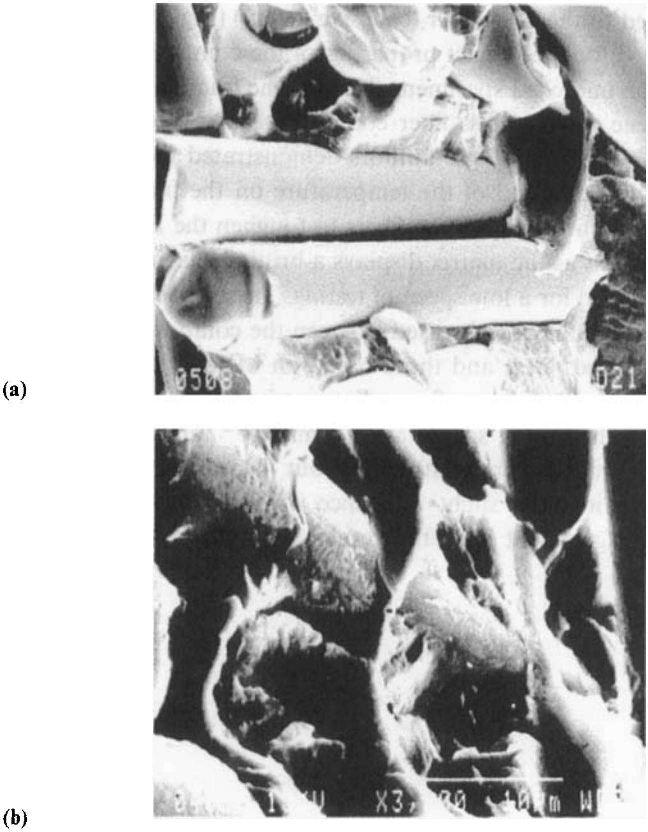


FIGURE 9 SEM micrograph of the fracture surface of the composite materials based on commercially sized fibers (Fig. 9a) and on γ-APS treated fibers coated with the polymer MW/LF (Fig. 9b) (volume fraction of glass fibers: 25%).

[47]. In this work, a PPS matrix was reinforced with glass fibers treated with silylated epoxy resins in comparison with γ-APS treated fibers. They reported a large improvement of ultimate tensile and flexural strengths and impact properties determined on unnotched specimens, whereas for the notched ones the values are similar. A comparison between these results and our work is difficult because of the fact that the exact chemical natures of the sizings are not given.

Thus, the increase of the interfacial shear strength measured by the microbond test (microcomposites) is confirmed for the ultimate mechanical properties of composite materials.

CONCLUSION

By using carboxy-functionalized poly(phenylene sulfide) in addition to γ-aminopropyltriethoxysilane for the surface treatment of E-glass fibers, it is possible to improve the shear strength of the glass/PPS interface. The same trend is observed on the mechanical properties of short-glass-fiber reinforced PPS in comparison with commercialy treated glass fibers. This effect can be explained by the concept of grafted connecting polymeric chains on the glass surface which are able to be entangle and to crystallize with the pure PPS chains of the matrix. This way of modifying the interface of semi-crystalline polymers can be applied with various substrates [48].

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