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Effect of glass fiber surface chemistry on the mechanical properties of glass fiber reinforced, rubber-toughened nylon 6

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Abstract

The mechanical properties of nylon 6 and its blends with maleated ethylene–propylene rubber (EPR-*g*-MA) plus glass fibers were examined as a function of the chemical functionality of the silane surface treatment applied to the glass fibers. Three reactive silane coupling agents, with anhydride, epoxy, or amine functionality, were used and found to have little effect on the mechanical properties when no EPR-*g*-MA is present. When 20 wt% EPR-*g*-MA is used as a rubber toughener, however, the yield strength and Izod impact strength were lowest for the amine functional silane and highest for the anhydride silane, while the epoxy silane fell in-between. These results were attributed to the differences in reactivity of the three reactive silanes. An unreactive silane (octyl groups) was used as a release agent on the glass fibers and compared with the anhydride functional silane. The octyl silane did not improve the ductility of the composite, as may have been speculated, and had poor yield strength and impact resistance when compared to the anhydride silane. Both octyl and anhydride treated glass fibers improve the heat distortion temperature such that most of the high temperature stiffness that is lost on addition of EPR-*g*-MA is regained by adding glass fibers. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Mechanical properties; Glass fibers; Polymer matrix

1. Introduction

The addition of glass fiber reinforcement is known to improve the stiffness, strength, and the high temperature performance of polymeric materials [1,2]. The mechanical properties of the resulting glass fiber reinforced composite material depend heavily on the nature of the fiber–matrix interface. A strong interface generally leads to the best composite properties, and many effective interfacial coupling agents that are capable of forming strong interface have been identified for single component polymer matrices [3]. The interfacial chemistry for multicomponent polymer matrices has received considerably less attention.

Rubber-toughening, on the other hand, is used to improve the impact properties and low temperature toughness of brittle polymers [4–6]. Unfortunately, the incorporation of soft rubber particles into a stiffer polymer matrix necessarily results in the loss of stiffness and strength. Previous papers have shown how the simultaneous use of rubber-toughening and glass fiber reinforcement can lead to an injection moldable material with a balance of stiffness/strength and toughness [7,8]. In those studies, fiber–matrix adhesion was accomplished by adding rubber to a commercially available composite of nylon 6 and glass fibers in which the fibers were already bound to the polymer matrix with a proprietary interfacial coupling agent. In this study, the glass surface is treated with different interfacial coupling agents prior to blending with nylon 6 and maleated ethylene–propylene rubber. The effect of fiber–matrix interfacial chemistry on the mechanical properties of glass fiber composites based on nylon 6 and on nylon 6/EPR-*g*-MA blends is studied.

2. Background

The need for techniques to bond glass fibers to polymer matrices was recognized since glass fibers were first used as reinforcement [3]. Silane coupling agents are widely used for this purpose today [9]. They are believed to create a bond between many inorganic substrates such as glass, and organic polymers by the scheme shown in Fig. 1 provided that an appropriate organofunctional group (R) is chosen. Appropriate organofunctional groups generally involve a moiety that reacts with the polymer resin to form a chemical bond with the glass substrate and the organic matrix or,

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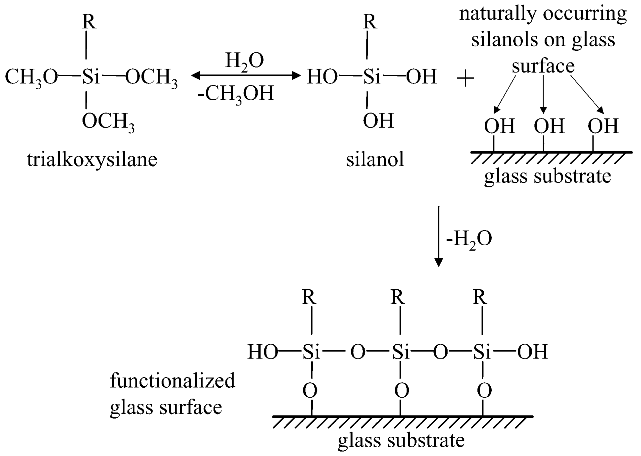
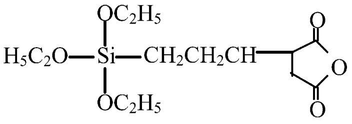
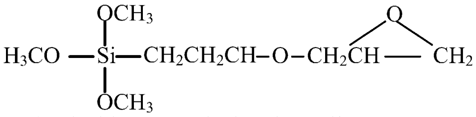
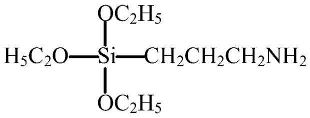
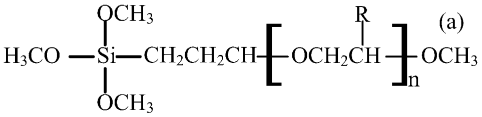
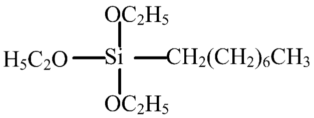


Fig. 1. Schematic of alkoxysilane reaction to produce functionalized glass fiber surface.

alternatively, a strong physical interaction. Typically, the silane coupling agent is provided as a trialkoxysilane, as shown in Fig. 1, which readily hydrolyzes in the presence of water to form the corresponding silanol, the active agent in the reaction with the glass substrate [3]. These silanol groups can undergo condensations with silanol groups naturally occurring on the glass surface to form a siloxane bond between the glass and silane coupling agent. The result is a functionalized glass surface where the organofunctional group can then react with the polymer matrix if a reactive functionality has been chosen. No doubt the simple conceptual scheme described earlier and shown in Fig. 1 may not capture all the events at the fiber–matrix interface.

In this study, the polymer matrix is nylon 6. Typically, amine functional silanes have been used as coupling agents for glass fiber reinforced polyamides [10]. In this case, the amine groups are capable of reacting with the carboxylic acid end groups of the polyamide chains. It has been demonstrated that while reaction with these end groups is an important coupling reaction, the amine groups from the silane coupling agent can also react with the amide groups along the polyamide backbone [11,12]. In addition to amine functional silanes, this study will also use epoxy and succinic anhydride functionalities to provide coupling reactions with the polyamide matrix. A complete list of the silane coupling agents used in this study is shown in Table 1. Because a nonpolar alkyl group should not interact chemically with the polyamide matrix, an octyl functional silane is employed to examine the effect of a weaker interface on toughness. The alkoxy silane shown in Table 1

Table 1
Silane coupling agents used in this study

Chemical structure/name	Manufacturer/designation	Designation in this paper
 3-(triethoxysilyl)propylsuccinicanhydride	Gelest SIT8192.6 typically for lab-scale use	Anhydride silane
 (3-glycidoxypropyl)trimethoxysilane	OSi specialties, Crompton Corp. Silquest® A-187	Epoxy silane
 3-aminopropyltriethoxysilane	OSi specialties, Crompton Corp. Silquest® A-1100	Amine silane
 γ-(polyalkylene oxide)propyltrimethoxysilane	OSi specialties, Crompton Corp. Silquest® A-1230	Alkoxy silane
 n-octyltriethoxysilane	OSi specialties, Crompton Corp. Silquest® A-137	Octyl silane

(a) R and *n* are involve proprietary formulation.

Table 2
Materials used in this study

Material designation	Source	Manufacturer's designation	Description
Nylon 6	Allied Signal	Capron B73WP	Nylon 6—$\bar{M}_n = 22\,000$; End-group content: $NH_2 = 47.9\ \mu eq\ g^{-1}$, $COOH = 43.0\ \mu eq\ g^{-1}$
EPR-*g*-MA	Exxon Chemical	Exxelor 1803	Ethylene–propylene rubber: 43 wt% ethylene; 53 wt% propylene; 1.14 wt% grafted maleic anhydride
Glass fiber	Owens–Corning		13 μm E-glass roving treated with proprietary sizing which was removed

will form a highly polar surface on the glass fibers capable of interacting with the highly polar nylon matrix, providing an intermediate fiber–matrix interfacial strength.

3. Experimental

The materials used in this study are described in Table 2. The nylon 6 used in this study is Capron B73WP, a commercial product having $\bar{M}_n = 22,000$. The ethylene–propylene rubber (EPR-*g*-MA) has 1.14 wt% grafted maleic anhydride capable of reacting with the amine end groups of nylon 6. This rubber has been employed successfully in the formation of 'super-tough' nylon blends [13–16]. The glass fibers are E-glass roving (fiber diameter = 13 μm) provided by Owens–Corning.

As received from the manufacturer, the glass fiber is coated with a proprietary sizing not intended for use in polyamide matrices. This sizing was burned off in a furnace for 30 min at 500 °C. Once this sizing has been removed, the silane coupling agents shown in Table 1 can be applied. The amine, epoxy, and alkoxy silanes were applied by first dissolving them in deionized water to form a 0.67 wt% solution. Adjusting the solution to pH 5 with acetic acid catalyzed the epoxy and alkoxy silane reactions. Amine silanes are basic, and therefore self-catalyzed, and would react with acid if it were used; therefore, no acid was used in solutions of amine silanes. Because the anhydride and octyl silanes are not water soluble, they were dissolved in a solution of 10 wt% water in ethanol. The octyl silane was catalyzed with acetic acid and the anhydride silane was left uncatalyzed because of the possibility of reaction between acetic acid and the anhydride group. After dissolution of the siloxanes, it is kept for 5 min to form the silanol according to the first step of the reaction in Fig. 1.

After this, the silane solutions were then applied to the glass fibers and allowed to react for 1 h. The solution was then removed and the glass fibers are washed with either water or ethanol, depending on the solubility of the coupling agent. The fibers are then allowed to air dry. A small sample of the dry, treated glass was weighed and placed in a furnace to remove any organic chemicals from the glass surface. After removal from the furnace, the samples were again weighed to determine the amount of silane coupling agent that had been burned off in the furnace. The results of this burnoff indicated that the silane treated glass fiber roving has approximately 0.5 wt% silane coupling agent on the surface.

In order to incorporate the glass fibers into the nylon matrix, chopped fibers are needed, but are impractical to handle in the coating process outlined earlier. To solve this problem, the treated glass fiber roving was coated with nylon 6 in a wire-coating, pultrusion type die. The polyamide coated glass roving strand was then chopped in a conventional polymer pelletizer without the additional equipment typically associated with handling and chopping glass fiber roving. The pellets produced contained a core of glass fiber surrounded by an annulus of nylon 6 and exposed to air at either end of the pellet. The purpose of this process was to produce chopped glass for use in extrusion and injection molding steps. Pellets containing 40 wt% or more of glass fibers could be produced by this method. These glass fiber/nylon 6 pellets were dried using the procedure for drying nylon 6 described later. The fiber dispersion in injection molded specimens produced by this method was generally good; however, in some cases a small percentage of the total fiber content formed poorly dispersed bundles. In order to minimize the effects of this phenomenon, Izod and Dynatup impact test specimens were selected such that these bundles did not cross the fracture surface. This was not possible in tensile tests, but the mechanical properties of these materials compare favorably with materials produced in this lab that did not contain such bundles [7].

All nylon 6 containing materials were dried for 24 h in a vacuum oven at 80 °C. The reinforced materials were compounded in a Killion single-screw extruder ($L/D = 30$, $D = 2.54$ cm), equipped with an intensive mixing head, at 240 °C using a screw speed of 40 rpm. Most of the materials were formulated by introducing all the components simultaneously into the hopper of the extruder during a single processing step. Other mixing protocols were investigated and are described in a later section along with the results obtained. Following extrusion, the materials were again dried and molded in an Arburg Allrounder injection molding machine operating at an injection pressure of 70 bar and holding pressure of 35 bar. The temperature of the feed zone of the injection molder was set at 240 °C, then ramped up to 270 °C at the nozzle, while the mold was held at 80 °C. Screw speed was maintained at 150 rpm. Izod bars, thickness = 6.35 or 3.18 mm and width = 12.7 mm, were molded for impact testing, and ASTM D638 type I dogbone bars were molded for tensile testing. Tensile testing was performed on an Instron 1127 testing frame, upgraded to allow for computerized data acquisition, at a rate of 5.08 mm min^{-1}.

Two types of impact tests were performed. Notched Izod impact tests were performed on 3.18 mm thick specimens according to ASTM D256. In addition, a Dynatup drop tower model 8200 was used for instrumented impact testing of 6.35 mm thick, three-point bend specimens notched with a fresh razor blade. Testing was performed at 3.5 m s^{-1} with a falling mass of 14 kg. The data were analyzed in terms of the impact fracture model outlined by Mai and coworkers [17–20], based on Broberg's unified fracture theory [21,22]. According to this model, which has been slightly modified here, the total fracture energy, U, per unit of fracture surface area, A, is given by

$$\frac{U}{A} = u_0 + u_d \ell \qquad (1)$$

where u_0 is the limiting specific fracture energy and u_d is the dissipative energy density. Because the specimen geometry and testing speed are different than those used by Mai in the development of the essential work of fracture (EWF) model, the parameters in Eq. (1) are considered phenomenological in nature and may not represent material parameters. The model as applied to these testing conditions is considered in detail elsewhere [8,23,24].

To examine the fiber surfaces, scanning electron microscopy was performed using a LEO 1530 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). SEM specimens were sputter-coated with gold. Morphology was examined using a transmission electron microscopy (TEM). Samples were first cryogenically microtomed to 15 nm sections at −40 °C with a diamond knife. The sections were stained using a 2% aqueous solution of phosphotungstic acid for 30 min and imaged using a JEOL 200CX transmission electron microscope at an accelerating voltage of 120 kV.

In order to determine thermal characteristics, a Rheometric Scientific dynamic mechanical thermal analyzer (DMTA) Mark III was used to measure modulus while increasing temperature from −100 to 220 °C at a rate of 2 °C min^{-1}. This apparatus measures the components of the complex modulus across a broad temperature range. Scobbo [25] has developed a method to relate the storage modulus data from DMTA experiments to the heat distortion temperature (HDT). The HDT is the temperature at which a stated deformation takes place under a specified load. This method translates this standardized load and deformation into a modulus assuming approximately linear stress–strain behavior for the small loads and deformations typically specified in the standards. There are two common stresses specified in the standards, 0.46 and 1.82 MPa; the HDT is defined as the temperature at which a 0.25 mm deflection occurs under one of these stresses. The storage modulus from DMTA experiments is typically plotted in the form of log(modulus), where the modulus is in Pa units. For the displacement of 0.25 mm and two loads of 0.46 or 1.82 MPa, this translates into log(modulus) = 8.9 or 8.3, respectively.

4. Effect of interfacial chemistry on tensile and Izod properties

4.1. Summary for all silane coupling agents

The mechanical properties of materials containing 15 wt% glass fiber with different silane coupling agents and 0 and 20 wt% EPR-*g*-MA are shown in Table 3. Anhydride, epoxy, and amine functional silanes are all capable of chemical reaction with the nylon 6 matrix. In the absence of rubber, there is no significant difference in the mechanical properties of the materials containing these three reactive coupling agents; however, there are significant differences in the case of nonreactive coupling agents. The composite using the octyl coupling agent has the lowest

Table 3
Mechanical properties of Nylon 6 with 15 wt% glass fibers

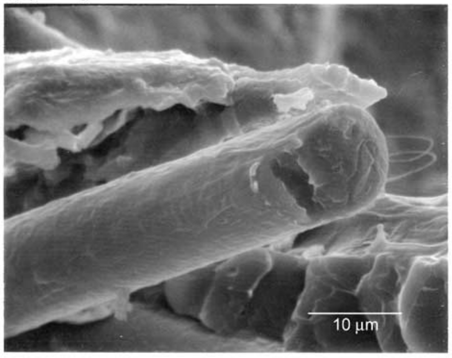
Silane coupling agent	Tensile modulus (GPa)	Yield strength (MPa)	Elongation at break (%)	Notched Izod impact strength (J m^{-1})	Tensile modulus (GPa)	Yield strength (MPa)	Elongation at break (%)	Notched Izod impact strength (J m^{-1})
	No EPR-g-MA				*20 wt% EPR-g-MA*			
Anhydride	5.6	117	4.2	60	4.0	80.5	4.3	292
Epoxy	5.5	110	4.5	59	4.1	79.8	3.9	265
Amine	5.7	114	4.3	58	4.2	73.7	4.3	225
Polyalkoxy	5.3	92	4.0	47	4.3	72.5	3.9	196
Octyl	5.3	81	3.4	45	4.1	53.4	2.6	148
Unreinforced materials	*Neat nylon 6*				*Nylon 6/EPR-g-MA (80/20)*			
	2.8	70	73	52	1.9	47.0	73	617

yield strength, elongation at break, and notched Izod impact strength, while the modulus is only slightly lower than that of reactive coupling agents. The alkoxy silane also has a similar modulus but intermediate values for yield strength, elongation at break, and notched Izod impact strength. Modulus is defined in the limit of zero strain and is not expected to differ based on interfacial strength unless there is significant slippage at the fiber–matrix interface. In fact, models of composite stiffness do not generally include consideration of the nature of the interface [1,2]. All of the current materials have virtually the same tensile modulus.

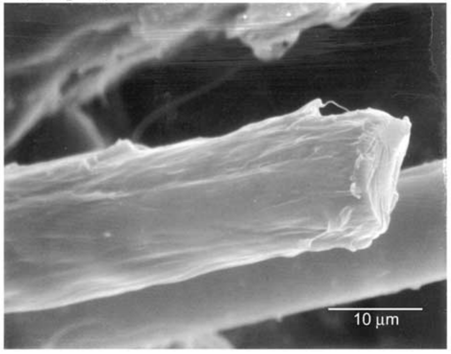
Yield strength is highly dependent on interfacial strength [1,26]; therefore, the octyl silane should produce the lowest value of yield strength since it has no strong interaction with the nylon 6 matrix. The alkoxy silane is polar and capable of forming physical interactions with the polyamide matrix; however, these interactions are not expected to lead to adhesion as strong as that resulting from the chemical bonds formed by the reactive coupling agents, hence intermediate values of yield strength are expected. When there is good chemical bonding between the glass fibers and the polymer matrix, the effective interfacial strength becomes the shear strength of the matrix. Examining the fibers at the fracture surface after specimen failure demonstrates this fact because the fibers will be coated with a sheath of matrix material when the interfacial shear strength is stronger than the shear strength of the polymer matrix. SEM micrographs of fibers from the fracture surfaces of the materials from Table 3 that do not contain rubber are shown in Fig. 2. Indeed, for every reactive coupling agent, failure occurs in the polymer matrix as opposed to the fiber–matrix interface, and mechanical properties are independent of the type of reactive silane coupling used. Since the interface is stronger than the matrix, failure occurs in the matrix in an identical manner for all three reactive silane coupling agents. This explains why the mechanical properties of composites based on the three reactive coupling agents are the same in the absence of EPR-*g*-MA. The two unreactive coupling agents have no sheath of polymer around them. In this case, failure occurs at the interface and mechanical properties are dependent on the nature of the interface.

Tensile stress–strain behavior for these specimens is shown in Fig. 3. The materials in Fig. 3(a) contain no EPR-*g*-MA. The reactive coupling agent shown here, anhydride silane, behaves as expected, providing significant increases in strength and modulus relative to the unreinforced nylon 6 which is accompanied by a large loss in ductility. The other reactive silanes, amine and anhydride, have nearly identical responses, and their curves would fall directly on top of this one. The octyl sizing provides a similar increase in modulus and a modest increase in yield strength; however, there is no improvement in ductility over the reactive silane coupling agents. Fig. 3(b) shows the results of these tests for materials containing 20 wt% EPR-*g*-MA. The material reinforced with glass treated with reactive anhydride silane provides large increases in stiffness and strength relative to the nylon

(a) anhydride silane



(b) epoxy silane



(c) amine silane

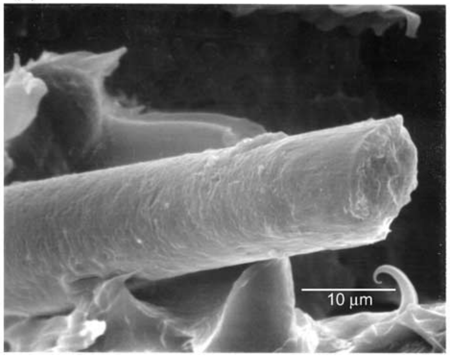


Fig. 2. SEM micrographs of glass fibers taken from the fracture surfaces of Izod impact test specimens showing a thin layer of nylon 6 matrix on the fibers. Fibers are from nylon 6 reinforced with 15 wt% glass fibers treated with (a) anhydride silane, (b) epoxy silane, and (c) amine silane.

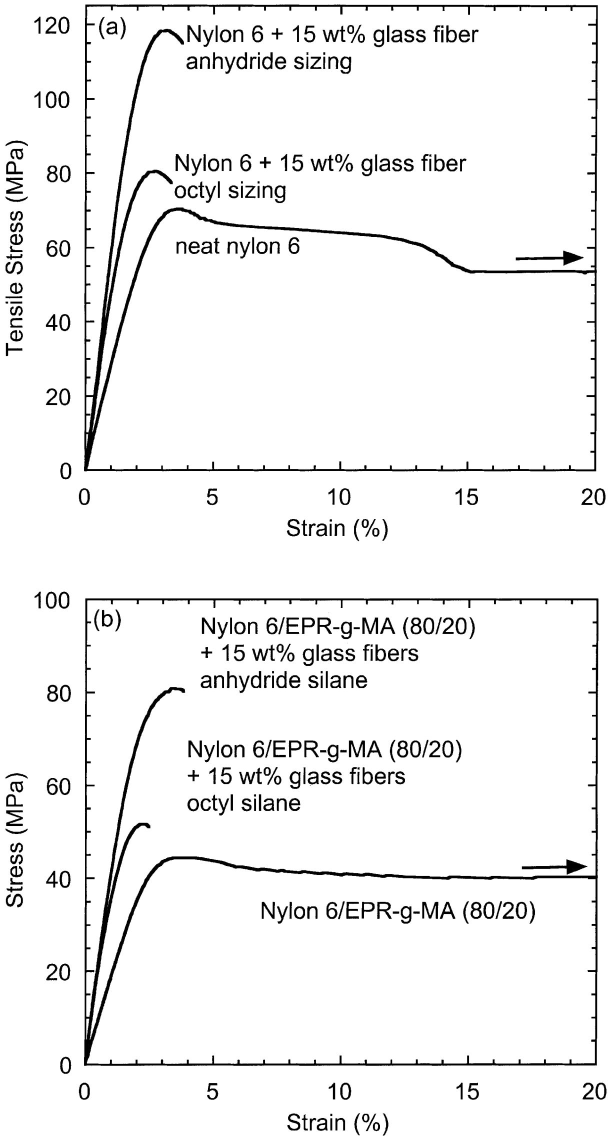


Fig. 3. Stress–strain behavior in tension for (a) nylon 6 and (b) nylon 6/EPR-*g*-MA (80/20) blend reinforced with 15 wt% glass fibers treated with anhydride and octyl silanes.

6/EPR-*g*-MA (80/20) blend and a very large decrease in ductility. The glass treated with unreactive octyl silane provides a similar increase in stiffness and a smaller increase in strength; it is even less ductile than the anhydride silane treated material. Previous work has shown a loss in ductility to be the main cause of decreased toughness in glass fiber reinforced, rubber-toughened polyamide compared to their unreinforced counterparts. The octyl silane was chosen in this study to act as a release agent, so that the ductile matrix material would not be tightly bound to the brittle fiber reinforcement, thereby improving composite ductility at the expense of yield strength. Since there was no improvement in ductility, rubber-toughened materials reinforced by glass fibers treated with the octyl sizing are unlikely to show any improvement in toughness.

With regard to the data for rubber-containing materials in Table 3, there are some interesting trends. For reasons discussed earlier, the tensile moduli of the different materials are nearly the same; however, important differences in other mechanical properties exist. Unlike the case when no rubber is present, the yield strength of the materials based on reactive silanes, which incorporate 20 wt% EPR-*g*-MA, is highest for the anhydride silane and lowest for the amine silane, with the epoxy silane falling in-between but nearly equal to that of the anhydride-based material. The yield strengths of the unreactive silanes are still lower, as expected for the same reasons given earlier for materials with no rubber. Previous work has also shown that

Table 4
Mechanical properties of nylon 6 reinforced with 30 wt% glass fibers

Silane coupling agent	Tensile modulus (GPa)	Yield strength (MPa)	Notched Izod impact strength (J m^{-1})	Tensile modulus (GPa)	Yield strength (MPa)	Notched Izod impact strength (J m^{-1})
	No EPR-g-MA			*20 wt% EPR-g-MA*		
Amine	9.7	155	147	6.6	73.2	173
Epoxy	9.6	153	135	7.2	102	269
Anhydride	9.6	159	163	7.7	109	306

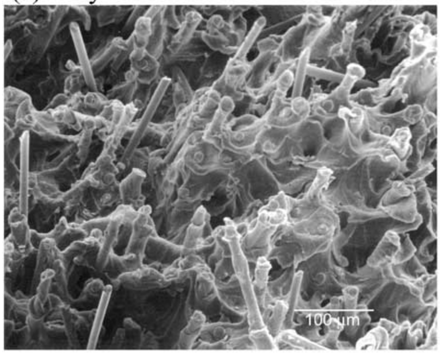
composite strength and toughness are directly related for this system. It is then not surprising that the notched Izod impact strengths of these materials follows the same trend as the yield strength.

4.2. Reactive silane coupling agents

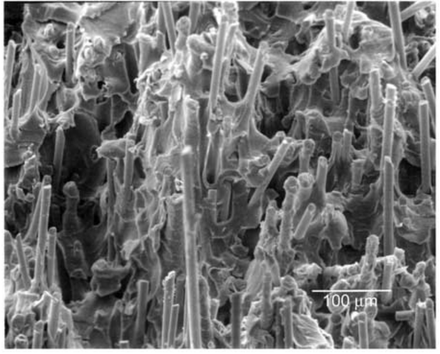
Table 4 shows the mechanical properties of composites containing 30 wt% of glass fibers treated with the three reactive silanes, anhydride, epoxy, and amine. Once again the mechanical properties for the reactive silanes are the same in the absence of rubber; however, when 20 wt% EPR-*g*-MA is present there are some marked differences. In this instance, the amine silane treated glass produces a significantly lower modulus. The yield strength and impact toughness follow a similar trend as the materials in Table 3. The yield strength values for the reactive silanes should be nearly equal for these three reactive silanes provided that two conditions are met. First, the surface treatment must react with the polymer matrix to form a strong chemical bond between the polymer matrix and the glass fibers. Second, it is necessary that the nature of the matrix in the vicinity of the glass fibers be the same in each case. As discussed earlier, if the first condition is met in a single component matrix, then it is unlikely that there will be any difference in mechanical properties. This picture is complicated somewhat by the fact that the polymer matrix here consists of nylon 6 and EPR-*g*-MA phases. If the silane coupling agent used is capable of reacting preferentially with the low strength dispersed polymer component, EPR-*g*-MA in this case, the yield strength of the polymer matrix in the vicinity of the glass fibers would be lower. This would decrease the composite tensile strength and possibly toughness. Given the high reactivity of amines with anhydrides, it is highly possible that the amine silane would react with the anhydride of the EPR-*g*-MA phase. Indeed, this amine–anhydride coupling reaction is integral to the reactive compatibilization of the nylon 6/EPR-*g*-MA blend used for the matrix. Another possibility is that the glass fibers are not bound to the same degree for every silane. This would obviously cause a weak interface and affect mechanical properties.

In order to investigate these possibilities, SEM photomicrographs of postmortem fracture surfaces from nylon 6/EPR-*g*-MA (80/20) specimens reinforced with 30 wt% glass fibers are shown in Fig. 4. Only the three reactive silanes are considered here. Most of the glass fibers treated with the anhydride silane in Fig. 4(a) broke off near the surface. Of those that are not broken off, most are coated in a sheath of the polymer blend that comprises the matrix. There are also some fibers that appear to be bare, having no polymer on them at all. It should be noted that a fiber which is not bound to the polymer matrix is much more likely to pull out during fracture, as opposed to breaking off at the fracture surface, thereby making them more visible. These fibers are in fact a small minority of the population of fibers

(a) anhydride silane



(b) epoxy silane



(c) amine silane

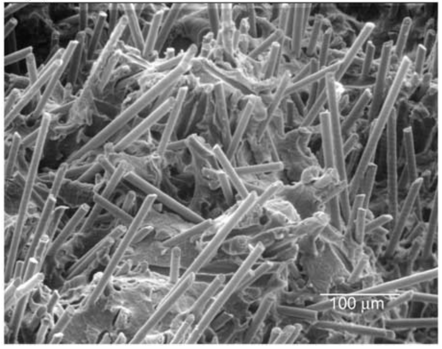


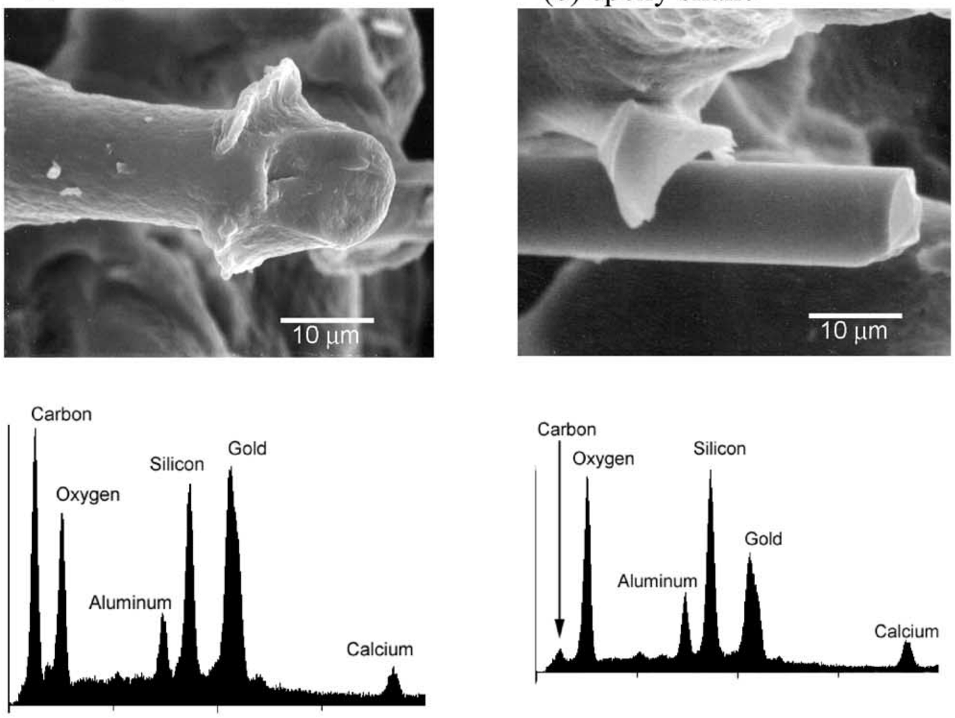
Fig. 4. SEM photomicrographs of fracture surfaces from Izod impact specimens of nylon 6/EPR-*g*-MA (80/20) reinforced with 30 wt% glass fibers treated with (a) anhydride silane, (b) epoxy silane, and (c) amine silane.

for this material. The glass fibers treated with the epoxy silane are shown in Fig. 4(b). Here, there is a greater proportion of what appear to be uncoated fibers. The vast majority of fibers treated with the amine silane, shown in Fig. 4(c), appear to be completely clean. Typically, glass fibers treated with amine functional silanes have been used to reinforce polyamide matrices. These results suggest that use of this amine functional silane coupling agent may not be effective for reinforcement of such a rubber-toughened polyamide material.

Fig. 5 shows close-ups of the fibers from Fig. 4, along with EDS data for these fibers. The peaks from these graphs for the anhydride treated glass are consistent with a blend of a nylon 6/EPR-*g*-MA existing in a sheath around the glass fiber. Most notably, there is a large carbon peak, consistent with the obvious sheath of polymer around this fiber. For the epoxy silane treated glass, some fibers were coated with a sheath of polymer and some appeared bare. A fiber that appears bare was chosen in this case for the purpose of comparison with the amine treated glass fibers. The EDS scans for the amine silane and epoxy silane treated glass indicate no organic material. A small carbon peak occurs in both cases but the scan is more consistent with background noise than a hydrocarbon sheath on the glass fiber. Since there is no expected reaction between EPR-*g*-MA and the epoxy silane, it is reasonable to conclude that this fiber is indeed bare. Since the EDS graphs for both the epoxy treated and amine treated glass fiber are very similar, these results indicate that there is no hydrocarbon rubber or nylon 6/EPR-*g*-MA blend on the surface of the apparently smooth glass fibers from these postmortem fracture surfaces. If the amine silane had formed chemical bonds with EPR-*g*-MA, a material rich in EPR-*g*-MA would be expected in the vicinity of these glass fibers prior to fracture. As a result of the higher content of low strength EPR-*g*-MA, the shear strength of the matrix would be lower in the area near the glass and would be expected to result in a sheath of hydrocarbon-rich polymer after fracture. Since this sheath was not present after fracture, it would indicate that this proposed reaction did not occur; nevertheless, there is the possibility, however, unlikely, that this material was removed naturally during the fracture process. Fig. 6 shows examples of amine and anhydride treated fiber microtomed from a (nylon 6/EPR-*g*-MA)/glass fiber [(80/20)/15] blend. There is no evidence of any preference of the EPR-*g*-MA rubber particles to bond with the amine treated glass, or any difference in rubber composition between the fiber surface and the bulk polymer blend. The anhydride treated glass fiber has the same appearance in Fig. 6(b). This representative example fiber, and all others like it, indicates that the possible adherence of EPR-*g*-MA to the amine treated glass does not occur under these experimental conditions.

The above results suggest that a reduction in bonding reactions between the glass and polymer matrix leads to lower toughness and tensile strength for the amine and epoxy silane treated glass fibers for these reinforced polymer blends of (nylon 6/EPR-*g*-MA)/glass fiber [(80/20)/15 or 30]. There seems to be no evidence for reaction between the maleated rubber and the silane coupling agent. Because interfacial adhesion has such an important effect on mechanical properties, it is important to understand why addition of 20 wt% EPR-*g*-MA to the nylon 6 matrix does not lead to the same bonding for all three coupling agents, since all three lead to essentially the same result in the absence of the rubber.

Fig. 7 shows the Brabender (an internal mixer) torque versus time for molten nylon 6 and 30 wt% of glass fibers treated with silane coupling agents. The resulting torque



(a) anhydride silane

(b) epoxy silane

(c) amine silane

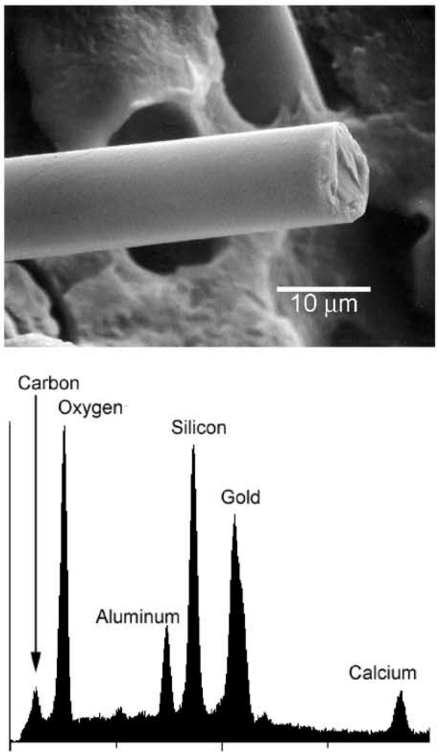


Fig. 5. SEM close-ups of the fibers from Fig. 4, plus EDS scans of the same fibers treated with (a) anhydride silane, (b) epoxy silane, and (c) amine silane.

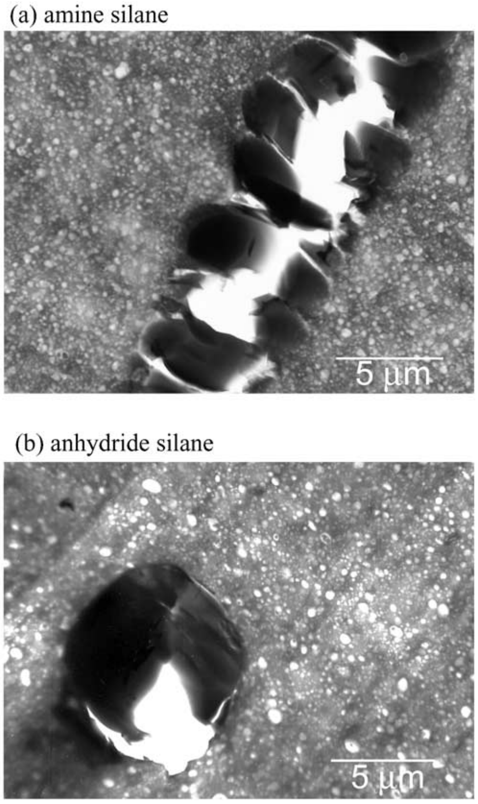


Fig. 6. TEM photomicrograph of (a) amine treated fiber and (b) anhydride treated fiber microtomed from a (nylon 6/EPR-*g*-MA)/glass fiber [(80/20)/15] blend. The glass fibers were shattered in the microtoming process. Phosphotungstic acid (PTA) was used to stain the nylon 6 phases making it dark. The rubber phase appears as small particles within the polymer matrix.

curves indicate that the anhydride treated glass leads to a greater extent of reaction than do the others. The extent of reaction for the reactive silanes follows the same order as the yield strength of the rubber-toughened composites. Since the yield strength is related to the fiber adhesion to the matrix, there is some reason to expect that the differences in adhesion may be due to differences in the extent of reaction or reaction rate. Experiments on mixing protocol may shed light on this proposal.

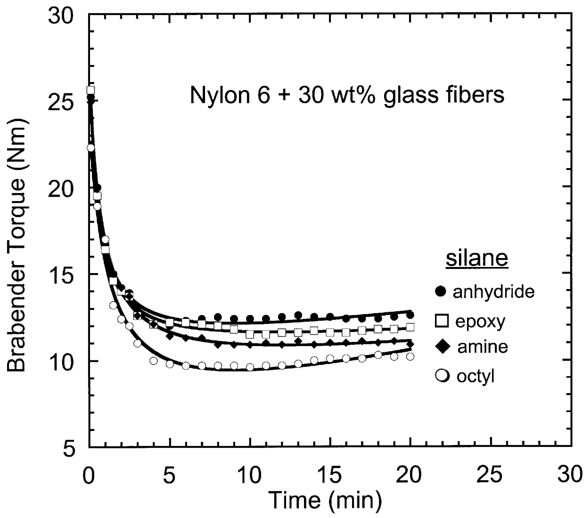


Fig. 7. Brabender internal mixer torque versus time for molten nylon 6 containing 30 wt% of glass fibers treated with anhydride, epoxy, and amine silane coupling agents.

4.3. Effect of mixing protocol

Three mixing protocols were investigated here. In mixing protocol A, all materials are placed into the hopper of the extruder simultaneously and blended in a single extrusion step. This is the mixing protocol used earlier. In mixing protocol B, the glass fibers were blended with nylon 6 in one extruder pass, and EPR-*g*-MA was added in a subsequent extrusion. This protocol was investigated to produce a material where the silane treated glass fiber was able to react with the polyamide matrix before any EPR-*g*-MA was present in an attempt to prevent the rubber from interfering, in whatever way, with the reaction between the glass and the polymer matrix. In mixing protocol C, on the other hand, the nylon 6 and EPR-*g*-MA were blended in the first extrusion step, and glass fiber was added in the second step. As discussed in Section 3, the process used prevents the formation of pellets containing more than 40 wt% glass fibers. Because the glass fibers are always introduced into the extruder in this pellet form, not as loose chopped fiber, material balance constraints preclude making nylon 6/EPR-*g*-MA blends reinforced with 30 wt% glass fibers by mixing protocol C.

Table 5 shows the mechanical properties obtained for materials prepared by these three different mixing protocols based on nylon 6/EPR-*g*-MA (80/20) blends reinforced with 15 and 30 wt% of glass fibers treated with amine or anhydride silanes. For the anhydride sizing, mixing the glass fiber and nylon 6 in a first pass and adding EPR-*g*-MA in a second pass (mixing protocol B) produces results similar to mixing protocol A. This occurs despite a decrease in fiber aspect ratio (length/diameter) from 26 to 20, where the loss of aspect ratio is attributed to the fact that the glass fibers undergo further breakage in the second extrusion. For the amine silane having 30 wt% glass fibers, protocol A gives a significantly higher yield strength and toughness than protocol B despite the same drop in fiber aspect ratio from 26 to 20. This difference is not as prevalent for the material having 15 wt% glass fibers. By mixing the nylon 6 and EPR-*g*-MA in the first pass and adding glass fiber in a second pass (mixing protocol C), there is a lower yield strength when either the amine and anhydride silanes are used. There is also a corresponding lower impact strength. Protocol C produces the poorest mechanical properties for both coupling agents.

During melt blending of systems containing three or more components there are a number of competitive processes occurring at once which complicates understanding how these systems work. Other studies have shown the importance of mixing protocol for these systems and its

Table 5
Mechanical properties of nylon 6 blended by different mixing protocols for amine and anhydride sizings

Glass fiber content (wt%)	Mixing protocol	Amine silane				Anhydride silane			
		Tensile modulus (GPa)	Yield strength (MPa)	Elongation at break (%)	Notched Izod impact strength ($J m^{-1}$)	Tensile modulus (GPa)	Yield strength (MPa)	Elongation at break (%)	Notched Izod impact strength ($J m^{-1}$)
15	A	4.2	73.7	4.3	225	4.0	80.5	4.3	292
	B	4.0	74.6	5.7	269	4.2	81.0	4.6	298
	C	4.2	63.6	2.5	173	4.2	73.9	4.9	258
30	A	6.6	73.2	2.6	173	7.7	109.0	3.3	303
	B	6.3	89.2	4.3	258	7.0	107.0	4.6	329

A: All materials added to extrusion hopper at the same time; B: This mixing protocol involves two extrusions. In the first extrusion, glass fibers are melt blended with nylon 6. In the second extrusion, EPR-*g*-MA is blended with the nylon 6/glass fiber composite from the first step; C: This mixing protocol involves two extrusions. In the first extrusion, EPR-*g*-MA is melt blended with nylon 6. In the second extrusion, glass fibers are blended with the nylon 6/EPR-*g*-MA blend from the first step.

usefulness in understanding the competitive processes [27,28]. One possible explanation of the results seen here has to do with reaction rates. Compared to the anhydride reaction, the amine reaction with the polyamide matrix is much slower. When the amine treated glass is allowed to react with the polyamide matrix without EPR-*g*-MA (protocol B), a strong bond is formed. If EPR-*g*-MA is added in a subsequent step, the best mechanical properties result. If the EPR-*g*-MA is added in the first step (protocol C) or all components are added simultaneously (protocol A), there is an increase in viscosity and a competition with maleic anhydride for reactive species in the polyamide matrix. The amine is likely to lose this competition because it is much less reactive. Both of these effects may slow the reaction of the amine treated glass fibers and impede the bonding of the glass fibers to the polyamide matrix. The maleic anhydride in the rubber phase does not appear to react with the amine on the glass fiber surface. This may be due to a lack of affinity of the nonpolar rubber for the polar amine treated surface, the competition with the amine end groups of the polyamide phase, and the fact that the rubber particles are very small compared to the glass fibers and are embedded in the nylon 6 matrix. The anhydride silane appears to react much more quickly and compete more effectively for the amine end groups, thus forming a strong fiber–matrix interface.

5. Comparison of weak and strong interfaces

5.1. Tensile and Izod properties

It was found in prior work [7,8] that the reduction in fracture energy that results from incorporating glass fibers in this rubber-toughened material was due, primarily, to a loss in ductility. The octyl silane shown in Table 1 was

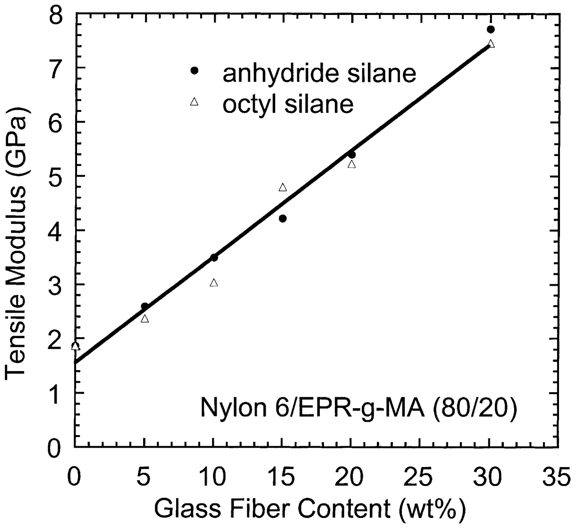


Fig. 8. The effect of glass fiber content on tensile modulus for fibers treated with octyl and anhydride silanes in a nylon 6/EPR-*g*-MA blend.

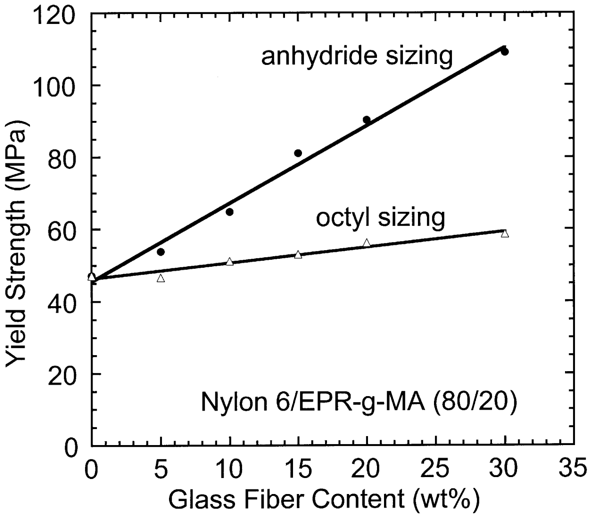


Fig. 9. The effect of glass fiber content on tensile strength for fibers treated with octyl and anhydride silanes in a nylon 6/EPR-*g*-MA blend.

employed to act as a release agent between fiber and matrix on the premise it would alleviate at least some of the ductility loss. In the remainder of this work, this release agent is compared with the anhydride silane that was shown to produce strong chemical bonds to the nylon 6/EPR-*g*-MA (80/20) matrix. Fig. 8 shows the effect of glass fiber content on tensile modulus for fibers treated with octyl and anhydride silanes. The moduli of these materials are nearly the same at all fiber loadings. As discussed earlier, modulus is determined at very small strains and is not so sensitive to the nature of the interface. This may be useful in the formation of materials with balanced mechanical properties because modulus will not necessarily have to be sacrificed to improve other properties.

Fig. 9 shows the effect of glass fiber content on tensile strength for fibers treated with octyl and anhydride silanes. The tensile strength of materials based on the octyl silane is much lower than those based on the anhydride silane. This difference is much greater at higher fiber loading. There is some increase in yield strength for the blends containing fibers with the octyl silane treatment relative to the unreinforced, rubber-toughened matrix, but even at 30 wt% glass fibers the tensile strength is still lower than that of neat nylon 6. At 5 wt% glass fibers, the composite formed from the octyl silane treated material exhibits significant necking (~ 15% elongation at break) unlike most glass fiber reinforced materials. At higher glass fiber content, however, the octyl treated material fails at lower strains than for the anhydride silane treated material. The notched Izod impact strength of these materials is shown in Fig. 10. In every case, the impact strength is lower for materials containing octyl silane treated glass fibers, even at very low fiber loading where increased ductility was found in tension tests. As the glass fiber composition is increased, the impact strength for the octyl treated material actually decreases.

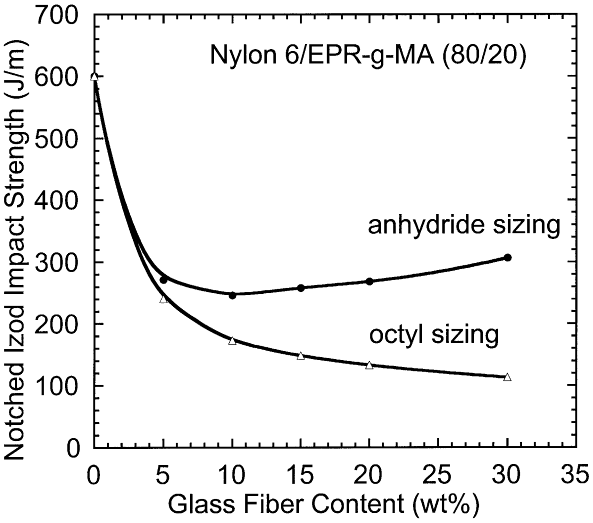


Fig. 10. The effect of glass fiber content on notched Izod impact strength for fibers treated with octyl and anhydride silanes in a nylon 6/EPR-*g*-MA blend.

5.2. Impact fracture tests

Fig. 11 shows the results of the Dynatup fracture tests for nylon 6/EPR-*g*-MA (80/20) blends reinforced with glass fibers treated with octyl and anhydride silane coupling agents. The lines are the best fit of the data to Eq. (1). The EWF theory, on which this analysis is based [17–22], indicates that the slopes of these lines, referred to here as the dissipative energy density, are related to the amount of fracture energy dissipated in a volume of material away from the fracture surface. This analysis indicates that lowering the interfacial coupling between the pseudoductile matrix and the brittle fibers does not lead to an increase in dissipative energy density for the composite.

Earlier work showed that the incorporation of well-bonded

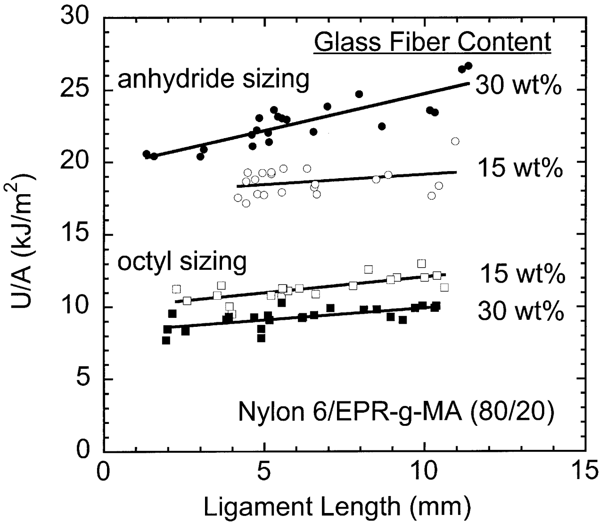


Fig. 11. Total impact energy per unit fracture surface area (U/A) versus ligament length (ℓ) for nylon 6/EPR-*g*-MA (80/20) blends reinforced with glass fibers treated with octyl and anhydride silanes.

glass fibers into nylon 6/EPR-*g*-MA blends led to a dramatic decrease in the dissipative energy density due to a loss in ductility [8]. In this EWF analysis, the loss of ductility manifested itself in the form of lower dissipative energy density. Typically, composite research has focused on creating strong bonds between the polymer matrix and the reinforcing fibers to improve material strength; however, there has been significant speculation on the question of what type of polymer–fiber interfacial bond, strong or weak, will lead to the highest fracture energy in fiber reinforced composites [29–32]. The octyl silane was used here to prevent the ductile polymer matrix from being bound tightly to the brittle glass fibers in an effort to allow greater matrix deformation. Force–displacement diagrams from impact tests (see Fig. 12 for example) provide interesting insights about the fracture process. Compared to the material treated with the anhydride silane, the material reinforced with glass fibers treated with the octyl silane does not reach nearly as high a load and is less ductile, i.e. the tup displacement at specimen failure is less. The result is a much lower total fracture energy. Using the octyl silane as a release agent did not lead to an increase in ductility or dissipative energy density. Lower values of limiting specific fracture energy, u_0, also resulted from the loss in composite strength.

Force–displacement diagrams for a nylon 6/EPR-*g*-MA (80/20) blend reinforced with 15 and 30 wt% glass fibers treated with octyl silane reveals that the composite with more glass fibers reaches a higher but does not deform as much prior to specimen failure. The net result is significantly lower total fracture energy for the material containing 30 wt% glass fibers. When a strong interfacial coupling agent is used, increasing the glass fiber content from 15 to 30 wt% leads to much higher loads and a more modest decrease in ductility. This results in significant increases in fracture energy at higher glass fiber content. When octyl silane treated glass is used, on the other hand, there is a reduction in fracture energy at higher glass fiber content. Fig. 12 shows force–displacement diagrams for a nylon 6/EPR-*g*-MA (80/20) blend reinforced with 30 wt% glass fibers treated with either the octyl or anhydride silane. The anhydride treatment leads to both higher load and a greater displacement before specimen failure. In this case, the anhydride treatment has more than twice the fracture energy of the octyl treated material.

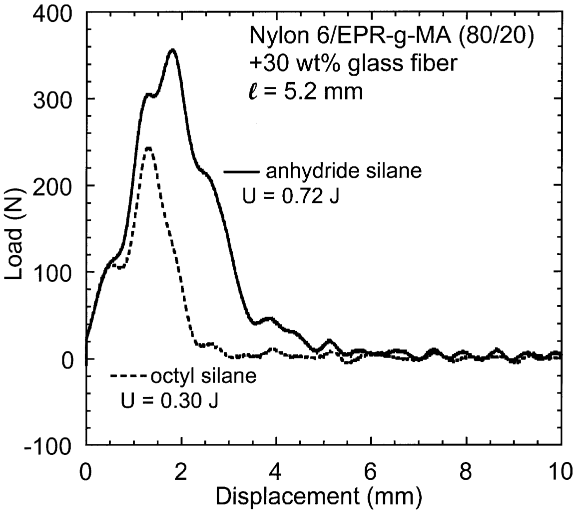
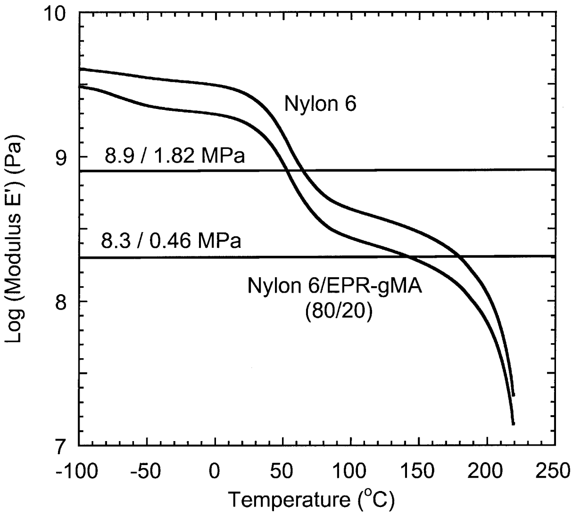


Fig. 12. Force versus displacement for nylon 6/EPR-*g*-MA (80/20) blends reinforced with 30 wt% glass fibers treated with either octyl or anhydride silane. Curves are for single-edge notched, three-point bend (SEN3PB) specimens during impact tests with total fracture energy (U) given.



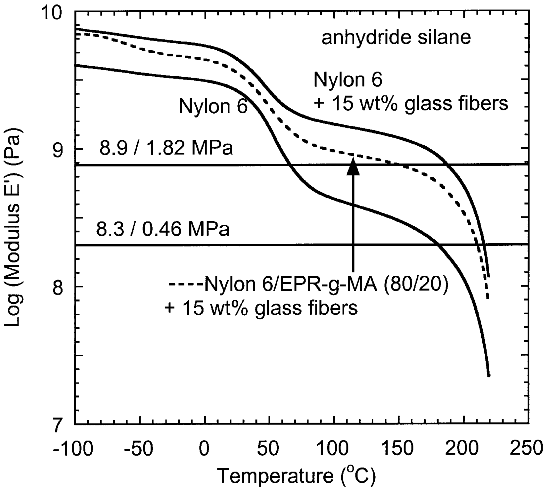
Heat Distortion Temperature (HDT)

material	HDT@0.46 MPa	HDT@1.82 MPa
nylon 6	182 °C	61 °C
nylon 6/EPR-g-MA (80/20)	144 °C	53 °C

Fig. 13. log(modulus E') versus temperature from DMTA for nylon 6 and a nylon 6/EPR-*g*-MA (80/20) blend. The HDT is shown in tabular form.

5.3. Dynamic mechanical thermal analysis

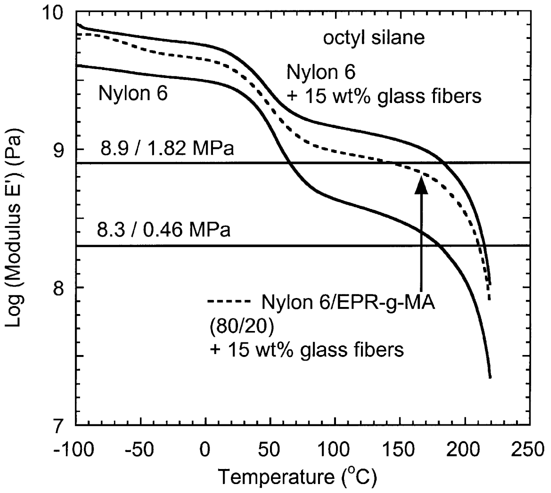
As mentioned earlier, dynamic thermal mechanical analysis (DMTA) can be used to determine HDT for plastics [25]. Results for nylon 6 and a nylon 6/EPR-*g*-MA (80/20) blend are shown in Fig. 13. For both materials the higher stress HDT (1.82 MPa) occurs near the glass transition temperature of nylon 6. The blend containing EPR-*g*-MA loses modulus much more rapidly at higher temperatures leading to a difference of about 40 °C in the low stress HDT (0.46 MPa). Fig. 14 shows log(modulus) versus temperature for materials reinforced with 15 wt% glass fibers treated with the anhydride silane where nylon 6 is shown for comparison. Adding 15 wt% glass fibers to nylon 6 significantly increases both the high stress and low stress HDT. Even when 20 wt% EPR-*g*-MA is present in the nylon matrix, both HDTs are well above the glass transition temperature of nylon 6. The same holds true if the octyl silane is used to treat the glass fibers, as seen in Fig. 15. These curves, and the HDTs, are nearly identical to those for



Heat Distortion Temperature (HDT)

material	HDT@0.46 MPa	HDT@1.82 MPa
nylon 6	182 °C	61 °C
nylon 6 + 15 wt% glass fibers	215 °C	190 °C
nylon 6/EPR-g-MA (80/20) + 15 wt% glass fibers	211 °C	144 °C

Fig. 14. log(modulus E') versus temperature from DMTA for neat nylon 6 and nylon 6/EPR-*g*-MA (80/20) blend with 15 wt% glass fibers. The HDT is shown in tabular form. Glass fibers were treated with anhydride silane.



Heat Distortion Temperature (HDT)

material	HDT@0.46 MPa	HDT@1.82 MPa
nylon 6	182 °C	61 °C
nylon 6 + 15 wt% glass fibers	215 °C	192 °C
nylon 6/EPR-g-MA (80/20) + 15 wt% glass fibers	208 °C	143 °C

Fig. 15. log(modulus E') versus temperature from DMTA for neat nylon 6, nylon 6/EPR-*g*-MA (80/20) blend reinforced with 15 wt% glass fibers, and nylon 6 reinforced with 15 wt% glass fibers. The HDT is given in tabular form. Glass fibers were treated with octyl silane.

the materials in Fig. 14. In this method, HDT is determined based on the specimen's modulus. As discussed earlier, the modulus is relatively independent of the type of treatment applied to the glass. For this reason there is little difference in HDT between the octyl and anhydride silanes.

6. Conclusions

The effects of interfacial chemistry on the mechanical properties of glass fiber reinforced nylon 6 and nylon 6/EPR-*g*-MA (80/20) blends were studied. Tensile modulus is relatively independent of the type of silane treatment applied to the glass fibers. Yield strength and Izod impact strength depend on the nature of silane treatment used. In the absence of EPR-*g*-MA, all three reactive silane coupling agents produce nearly identical mechanical property values. The octyl silane treatment produces the lowest yield strength and Izod impact strength values, which is attributed to the dissimilar natures of the nonpolar octyl group and the polar polyamide matrix. The polyalkoxy treatment produces higher yield strength due to its highly polar nature.

When 20 wt% EPR-*g*-MA is added to the polymer matrix, there are some significant differences in the mechanical property behavior of the three reactive silanes. The anhydride silane produces the highest values of yield strength and impact strength and the amine silane produces the lowest. The epoxy silane leads to strength intermediate between these two. These differences in yield strength and impact strength appear to be caused by a difference in the amount of adhesion between the glass fiber and the polymer matrix. Nearly all the fibers treated with the anhydride silane appear to be bound to the polymer matrix. Many fibers treated with the epoxy silane are unbound to the rubber-toughened polymer matrix while most of the fibers treated with the amine silane are unbound. The extent of reaction of these fibers followed the same trends as the yield and impact strength. Brabender and mixing protocol experiments indicated that the lack of reaction of the amine or epoxy treated glass with the polyamide matrix was attributed to increased viscosity and competitive reactions during the blending process, while the anhydride treatment, being much more reactive, was able to overcome much of this competition.

It has been proposed that a weak interface might produce greater toughness in composite materials [29–32]. The gains in fracture energy would naturally be offset by a loss in yield strength. The octyl silane was used here to test this proposal. The use of this octyl silane produces much lower yield strength and fracture energies than the anhydride silane, which was shown to produce strong interfaces. At low fiber content, the octyl silane treated material was more ductile than the anhydride treated material, but at higher glass fiber content the octyl treated material is less ductile. The loss of strength and ductility lead to much lower fracture energies. The increase in modulus typically associated with glass fiber reinforcement was retained when the octyl silane treated glass was used, as well as improved thermal properties. Either octyl or anhydride treatment produces improved HDTs relative to either nylon 6 or nylon 6/EPR-*g*-MA (80/20) blends. Future work will investigate variables involving the rubber phase of these glass fiber reinforced rubber-toughened polymer blends.

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