

Glass Fiber-Reinforced Polyamide Composites Toughened with ABS and EPR-*g*-MA

JAE WHAN CHO, D. R. PAUL

Department of Chemical Engineering and Texas Material Institute, University of Texas at Austin, Austin, Texas 78712

Received 7 March 2000; accepted 30 June 2000

ABSTRACT: A series of glass fiber-reinforced rubber-toughened nylon 6 composites was prepared. The mechanical properties and morphology of the composites toughened with ABS were investigated and compared with composites toughened with EPR-*g*-MA. A study of the mechanical properties showed that the balance of the impact strength and stiffness for both types of systems can be significantly improved by proper incorporation of glass fibers into toughened nylon 6. The differences between these two types of rubber-toughened composites are significant at a high rubber content. However, the ductility of both composites toughened with rubber was significantly lower than that of blends without glass fiber. The relationships between rubber content, nylon 6 molecular weight, compatibilizer, processing, and mechanical properties are discussed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 484–497, 2001

Key words: nylon; rubber-toughened; glass fiber-reinforced

INTRODUCTION

Polyamides like nylon 6 are widely used as engineering plastics because of their desirable properties such as high strength, stiffness, and resistance to nonpolar solvents.¹ However, nylon 6 has some other characteristics that limit its use in many applications; for example, it has poor low-temperature toughness and is quite notch- and moisture-sensitive.² To solve the latter problems, nylon 6 is often blended with a suitable rubber or rubber-containing material with chemical functionality that can react with polyamide chain ends.^{3–16} Such formulations can be “supertough,” that is, having an Izod impact strength higher than 800 J/m. However, incorporation of a rubber phase in nylon 6 reduces the strength and stiff-

ness relative to neat nylon 6. On the other hand, glass fibers are often incorporated into polymer matrices specifically for the purpose of increasing the strength and stiffness; usually, this sacrifices the toughness and ductility.^{17,18} Composites with a superior balance of strength, stiffness, toughness, and ductility may be achieved by the proper combination of glass fiber and rubber toughening. However, the literature on combined reinforcement and rubber toughening is quite sparse.^{19–29} Our laboratory has recently initiated a program to explore the limits of the possibilities for making engineering thermoplastics simultaneously stiffer/stronger and tougher by combining these two approaches.³⁰

The purpose of this article was to report on nylon 6 compositions containing glass fibers for reinforcement and an ABS phase (plus reactive compatibilizer) for toughening. The effectiveness of ABS as a toughener was evaluated by comparison with formulations containing maleated ethylene/propylene rubber.

Correspondence to: D. R. Paul.

Contract grant sponsor: Texas Advanced Technology Program; contract grant numbers: 003658-0017; 0067.

Journal of Applied Polymer Science, Vol. 80, 484–497 (2001)
© 2001 John Wiley & Sons, Inc.

Table I Material Used in This Study

Material	Grade	Composition	Average Molecular Weight (g/mol)	Supplier
Polyamide 6	Capron 8200	Nylon 6	$\bar{M}_n = 14,950^a$	Allied Signal (Morristown, NJ)
	Capron 8202		$\bar{M}_n = 16,400$	
	Capron 8207F ^b		$\bar{M}_n = 22,000$	
	Capron 8209F ^c		$\bar{M}_n = 29,300$	
N6/GF 70/30	Durethan BKV30	Glass fiber-reinforced nylon 6 30 wt % well-bonded discontinuous glass fibers		Bayer Corp. (Pittsburgh, PA)
ABS	Starex (SAN-g)	45% rubber 25% AN in SAN particle size: 0.3 μm	$\bar{M}_n = 35,000$ $\bar{M}_w = 90,000$	Cheil Industries (Kyungki-Do, Korea)
EPR-g-MA	Exxelor 1803	Ethylene-propylene rubber 53 wt % propylene 1.14 wt % grafted maleic anhydride		Exxon Chemical (Baytown, TX)
Imidized acrylic (IA) polymer	EXL 4140	55.7% methyl glutamide 41.0% methyl methacrylate 2.18% methacrylic acid 1.08% glutaric anhydride	$\bar{M}_w = 95,000$	Rohm & Haas (Philadelphia, PA)
SANMA	—	65.7% styrene 33.0% acrylonitrile 1.3% maleic anhydride	$\bar{M}_n = 56,600$ $\bar{M}_w = 119,400$	Bayer Corp. (Springfield, MA)

^a Calculated from \bar{M}_w , assuming $\bar{M}_n = \frac{1}{2}\bar{M}_w$.

^b The designation of this material was recently changed to B73WP.

^c The designation of this material was recently changed to B135WP.

EXPERIMENTAL

Table I summarizes pertinent information about the various materials used. Most of this work was done with the nylon 6 designated as Capron 8207F (currently denoted as B73WP); however, for comparison, other commercial grades of nylon 6 materials from Allied-Signal that differ only in molecular weight were also used in this study. BKV 30 is a glass fiber-reinforced nylon 6 composite containing 30 wt % discontinuous glass fiber, diameter = 13 μm .³⁰ The ABS material, designated as ABS-45-a in our prior publications, is a high rubber, emulsion-made product from Cheil Industries (their designation is SAN-g) that has proven to be especially effective for giving good low-temperature toughness of blends with nylon 6.^{14–16} Two compatibilizers for blends with ABS were used: an imidized acrylic (IA) polymer from Rohm and Haas Co., which contains methyl methacrylate, glutarimide, methacrylic acid, and anhydride units, and SANMA from Bayer Corp., which is a terpolymer of styrene, acrylonitrile, and maleic anhydride (MA); both have been described in detail elsewhere.¹⁵ The maleated eth-

ylene/propylene rubber from Exxon Chemical Co., EPR-g-MA, contains 1.14% MA by weight.

The majority of the toughened nylon 6 glass fiber composites were prepared by compounding a rubber-toughened nylon 6 blend with BKV 30, which contains 30 wt % glass fiber, in a injection-molding machine. In certain cases, mixtures were made in a Haake 30-mm intermeshing corotating twin-screw extruder operated at a barrel temperature of 240°C and screw speed of 180 rpm. All rubber-toughened nylon 6 blends were prepared in a Killion single-screw extruder ($L/D = 30$, $D = 25.4$ mm diameter) outfitted with a high-intensity mixing screw at 240°C using a screw speed of 40 rev min⁻¹. Before all melt-processing steps, the polyamide materials were predried for 16 h at 80°C in a vacuum oven to remove absorbed water. The different rubbers and compatibilizers were dried in a convection oven under the same conditions as for nylon 6. Each polymeric component in a given formulation were dry-mixed and then simultaneously fed to the hopper of the extruder.

The extruded pellets were injection-molded into dog-bone-shaped tensile (ASTM D638 type I) and standard Izod bars using an Arburg All-

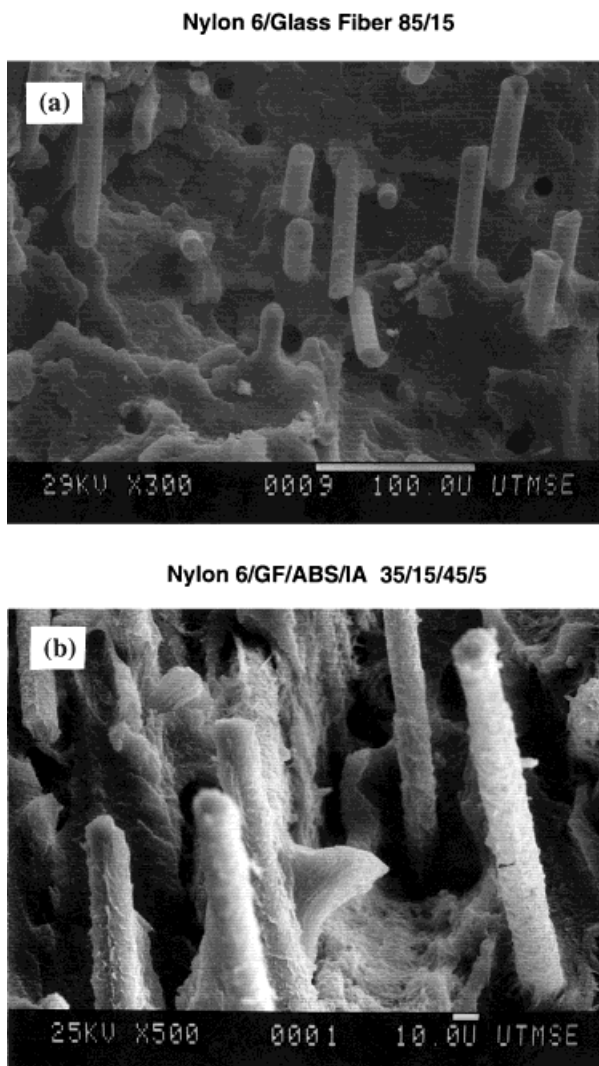


Figure 1 Scanning electron photomicrographs of the fracture surfaces of nylon 6 formulations containing 15% glass fibers and (a) no ABS and (b) 45% ABS plus 5% IA compatibilizer.

rounder injection-molding machine set at a melt temperature of 260°C and a mold temperature of 80°C. Molded test specimens were 3.18 or 6.35 mm thick and sealed in plastic bags and stored under a vacuum in a desiccator prior to testing. Therefore, all mechanical properties were determined for samples in the dry as-molded condition.

Standard notched Izod impact tests were conducted according to ASTM D256 using a TMI pendulum-type impact tester equipped with an insulated chamber for heating and cooling the specimen. At least five samples each from the gate and far ends of the Izod bars were tested at room temperature and in the temperature region of the ductile–brittle transition. The ductile–brittle transition temperature was taken as the midpoint of the jump in Izod impact strength versus temperature.

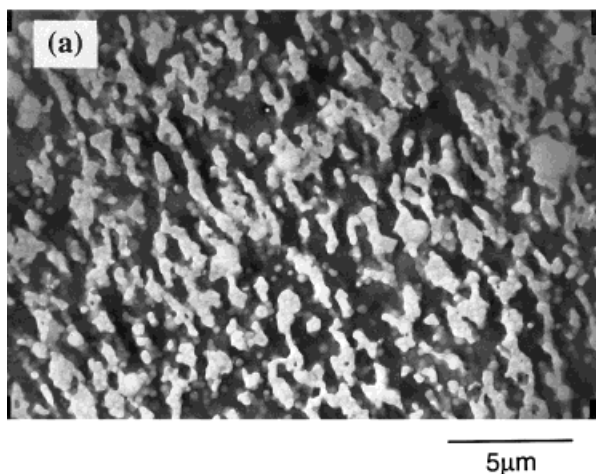
An Instron Model 1137 was used for determining the modulus, yield strength, and elongation at break in accordance with ASTM D638. Most tests were carried out at a crosshead speed of 0.51 cm/min. Elongation at break for noncomposite materials was measured at a crosshead speed of 5.08 cm/min. An extensometer strain gauge was used in the determination of the modulus.

A JSM 35C scanning electron microscope (SEM) operated at 25 kV was used to view the fracture surfaces of Izod bars to assess the nature of the glass fiber–matrix bond. Fiber lengths were measured by a typical burnout test. The composite sample was kept in a furnace at 500°C until the matrix material had burned off. The residual glass fibers were then immersed in a 10 wt % solution of polystyrene in methyl ethyl ketone and cast onto a glass plate. After evaporating the solvent, the remaining glass fibers were photo-

Table II Dispersed-phase Domain Size in Nylon 6/GF/ABS/IA Composites

N6	Composition			Rubber Content (wt %)	ABS Domains			Weight-average Fiber Length (μm)
	GF	ABS	IA		\bar{d}_w	Aspect Ratio	Polydispersity (\bar{d}_w/\bar{d}_n)	
90	0	10	0	4.5	1.72	1.30	1.36	—
85	0	10	5	4.5	0.43	1.30	1.11	—
75	15	10	0	4.5	1.78	1.55	1.31	358
70	15	10	5	4.5	0.33	1.40	1.25	360
80	0	20	0	9	2.65	1.53	1.53	—
65	15	20	0	9	2.17	1.62	1.52	374
60	0	40	0	18	3.35	1.56	1.49	—

Nylon 6/ABS/IA 49/49/2



Nylon 6/GF/ABS/IA 49/15/49/2

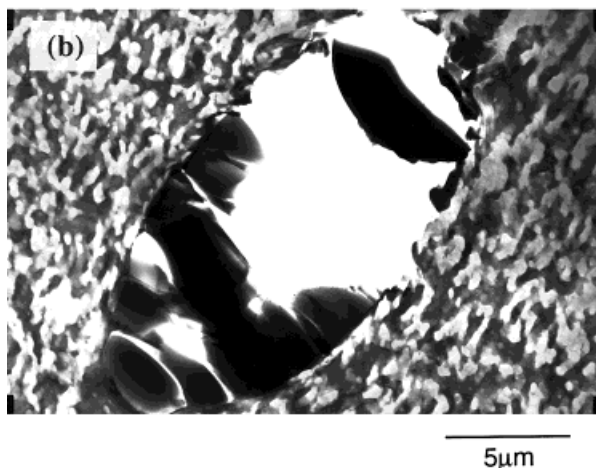


Figure 2 Transmission electron photomicrographs for (a) nylon 6/ABS/IA 49/49/02 blend and (b) nylon 6/GF/ABS/IA 49/15/49/02 composite (the nylon 6 phase is stained with PTA).

graphed and characterized using an optical microscope.

A JEOL JEM 200CX transmission electron microscope (TEM) operated at an accelerating voltage of 120 kV was used to observe the blend morphology. Ultrathin samples were obtained from Izod bars by microtoming perpendicular to the flow direction using a Reichert–Jung ultramicrotome with a diamond knife at -50°C . Thin samples were exposed to a 2% phosphotungstic acid (PTA) aqueous solution for a period of 30 min at room temperature to stain the polyamide phase. Quantitative analysis of the dispersed phase size from TEM photographs was carried

out with a semiautomatic digital image analysis technique using NIH Image[®] software. For nonspherical shapes, the diameter was assigned as the average of the major and minor dimensions of each dispersed phase.

Fracture analysis was carried out in the single-notch, three-point bend configuration (SN3PB) using an instrumented Dynatup Drop Tower Model 8200. Izod bars of thickness 6.35 mm were cut into two 54-mm sections with a band saw. Each specimen was notched at the center point by the band saw to give various ligament lengths; sharp notches were introduced by tapping a fresh razor blade into the saw cut. All tests were made by dropping a 10-kg weight at a speed of 3.5 m/s at the point contact with the specimen.

BLENDS TOUGHENED BY ABS

Morphology

Figure 1 shows typical SEM photomicrographs of the fracture surface of glass fiber-reinforced nylon 6 composites and those rubber-toughened by addition of ABS. Smooth fiber surfaces were observed for the composite without the ABS material [see Fig. 1(a)]. However, when the matrix is a blend with ABS [see Fig. 1(b)], there appears to be some matrix material adhering to the fiber surface and the amount adhering seems to be proportional to the rubber content.

Image analysis of transmission electron photomicrographs was used to determine the ABS phase domain size, shape, and distribution in blends compatibilized by the IA polymer and reinforced by glass fiber [see Table II]. Figure 2 shows general TEM photomicrographs of nylon 6 containing ABS, the compatibilizer, and glass fiber reinforcement. The blends were stained with a PTA solution so that the nylon 6 phase appears dark. The glass fiber shown in Figure 2(b) broke during microtoming. Clearly, the domains of the polymer phase are orders of magnitude smaller than is the diameter of the glass fibers ($\sim 13\ \mu\text{m}$).

Generally, the ABS domains become larger as the ABS content is increased. The size of the ABS domains is significantly reduced by adding the IA polymer as shown in other work.^{11,14,31} The size of the ABS domains and the other features of the blend morphology were not changed by addition of the glass fibers. Composites without a rubber phase in the matrix show slightly lower values of

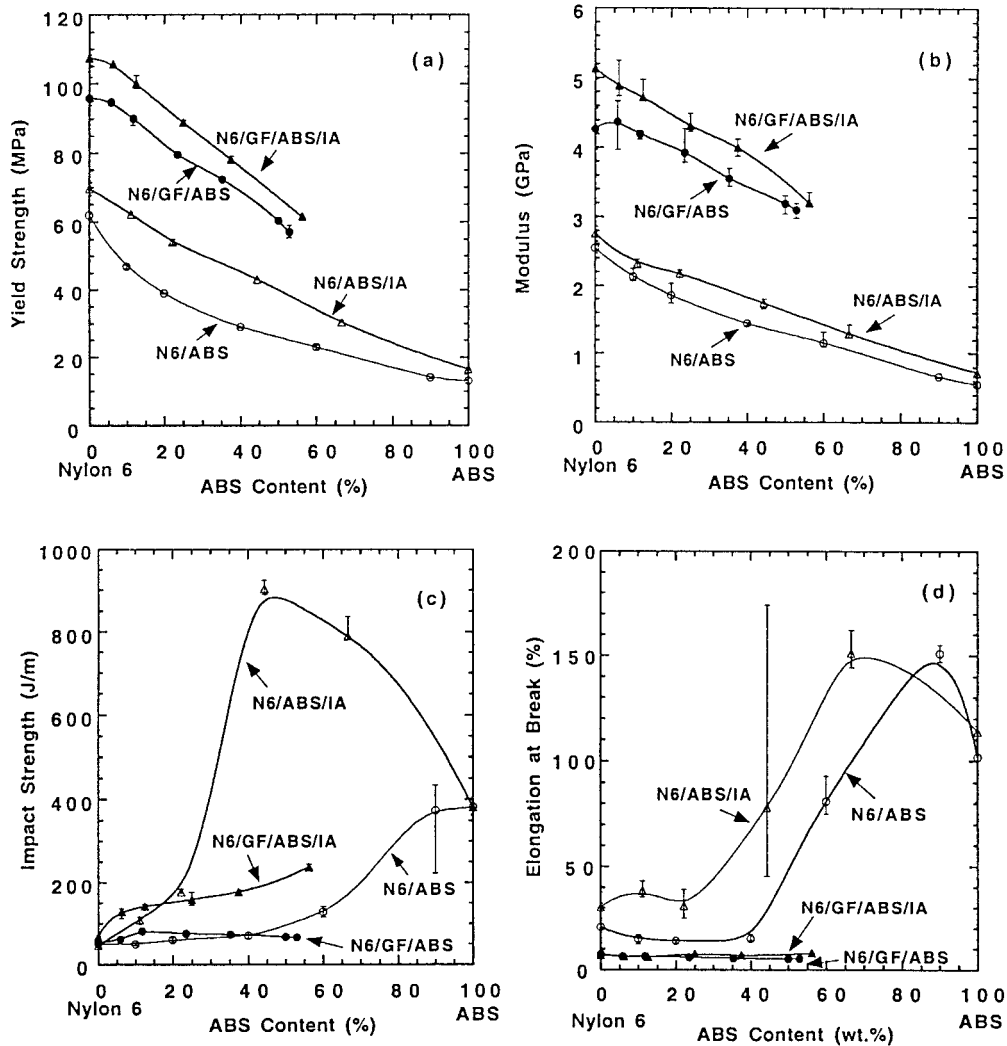


Figure 3 Mechanical properties of nylon 6/GF/ABS/IA composites as a function of ABS content: (a) yield strength; (b) modulus; (c) Izod impact strength; (d) elongation at break.

weight-average fiber length than when the matrix contains a higher amount of rubber.

Mechanical Properties

Blends of nylon 6 with varying levels of ABS were prepared and tested; the impact and tensile properties are shown in Figure 3 as a function of the ABS content. For the unreinforced material, as expected, there is a continuous increase in toughness with the ABS content since this increases the amount of rubber in the material. In the absence of the IA compatibilizer, addition of ABS leads to only minor toughening, whereas with compatibilization, there is significant toughening. For the materials containing 15 wt % glass fiber,

compatibilized blends show a continuous increase in toughness as ABS is added; however, the extent of toughening at high ABS contents is well below that achieved without reinforcement. For blends without compatibilization, the Izod values remain at levels comparable to neat nylon 6. Figure 3 also shows the tensile properties of these materials as a function of the ABS content. Generally, the stiffness is decreased by adding ABS. As expected, addition of glass fibers substantially increases the stiffness of all these materials. Blends, with or without reinforcement, have a slightly higher modulus when the compatibilizer is present. For unreinforced blends, the elongation at break increases substantially; however,

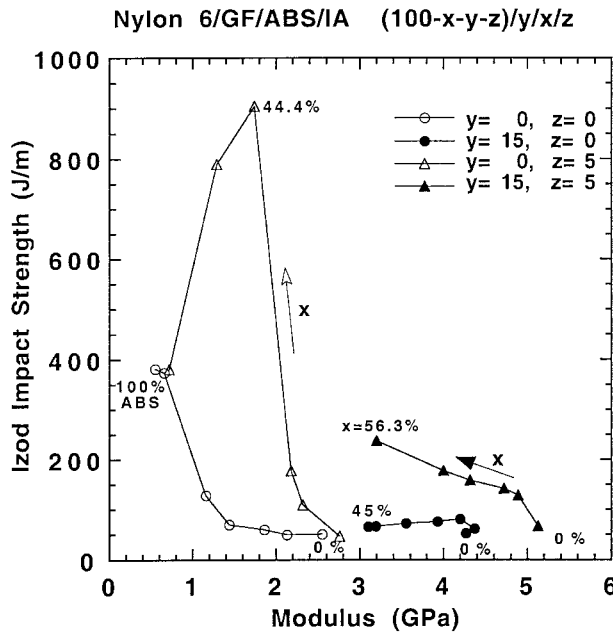


Figure 4 Izod impact strength versus modulus for nylon 6/GF/ABS/IA composites.

the compatibilized blends generally have higher levels of ductility. In any case, addition of glass fibers greatly reduces the elongation at break.

Figure 4 shows the trade-off relationship between toughness as measured by the Izod test versus stiffness for these materials. The open symbols represent unreinforced blends while the closed symbols indicate those reinforced with 15 wt % glass fibers. Impact strength is increased by addition of ABS but stiffness is decreased. The compatibilized blends containing in 40–70% ABS are supertough, but their modulus is lower than that of neat nylon 6.

Addition of only 15% glass fibers by weight increases the modulus of these polymer systems by twofold or more; however, the very high levels of impact resistance achieved for some compositions is sacrificed to a significant degree. Nevertheless, reinforcement of properly compatibilized blends of nylon 6 with ABS leads to some attractive combinations of stiffness and fracture energy as noted previously for toughened reinforced systems.³⁰ For example, moduli greater than 4 GPa are possible for materials having Izod values of 150 J/m or more. However, a proper processing formulation is essential to achieve these performance levels.

The effect of temperature on the toughness of the nylon 6/GF/ABS/IA composites is shown in Figure 5. As the ABS concentration is increased,

toughness is effectively increased at all temperatures. The reinforced blends do not exhibit the very low subambient ductile–brittle transition temperatures that are possible for unreinforced nylon 6/ABS blends.¹⁴

Compatibilizer Type

Kudva et al.¹⁵ compared the properties of nylon 6/ABS blends compatibilized by the IA polymer discussed above with those compatibilized by a styrene/acrylonitrile/maleic anhydride terpolymer (SANMA); blends based on either exhibited supertough behavior at room temperature. However, they found after multiple extrusions that blends with high IA content show higher ductile–brittle transition temperatures than those of analogous blends based on the SANMA terpolymer. They indicated that the main differences between these two compatibilizers is their reactive nature. The nylon 6 amine end groups can react with both the acid and anhydride functionalities of the IA polymer, whereas SANMA contains only the anhydride functionality. In general, SANMA appears to be the preferred compatibilizer. As part of this work, a limited study of the influence of type and content of the compatibilizer on the morphology and mechanical properties of glass fiber-reinforced composites for nylon 6/ABS blends was carried out.

Figure 6 show typical TEM photomicrographs of reinforced blends containing equal parts of ny-

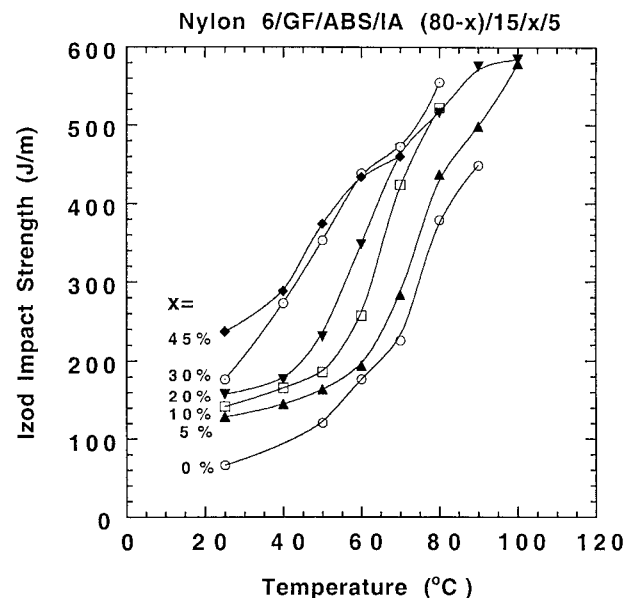


Figure 5 Effect of temperature on the Izod impact strength of nylon 6/GF/ABS/IA composites.

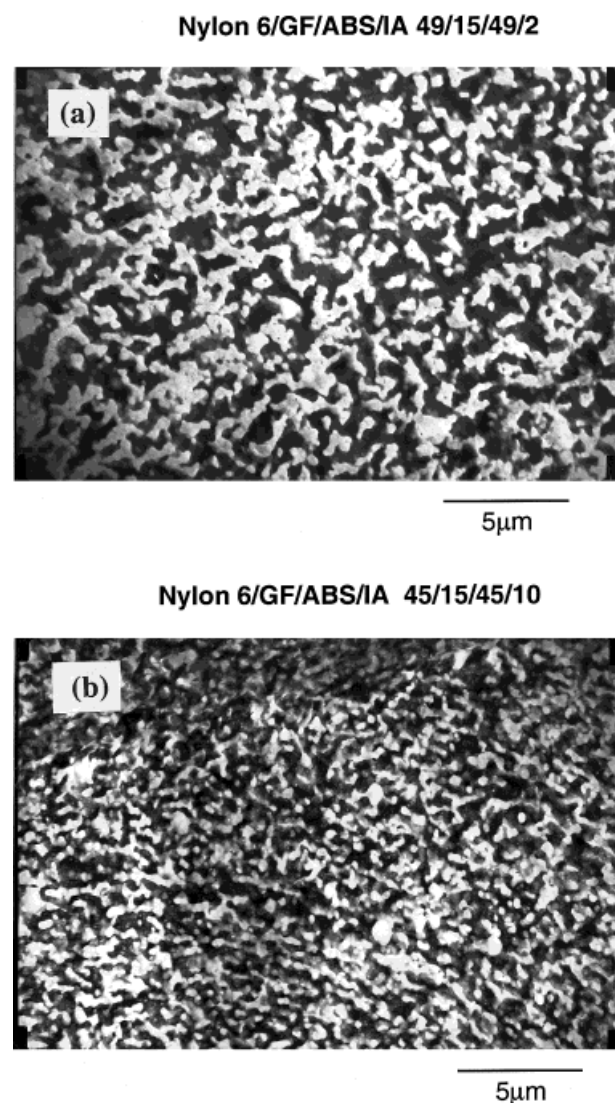


Figure 6 TEM photomicrographs of nylon 6/GF/ABS/IA composites containing (a) 2 wt % of IA and (b) 10 wt % of IA.

Table III Mechanical Properties of Nylon 6/GF/ABS/IA Composites: Effect of Compatibilizer

N6	Composition			Rubber Content (wt %)	Yield Strength (MPa)	Modulus (GPa)	Elongation (%)	Izod Impact Strength (J/m)	ABS Phase Size (μm)
	GF	ABS	IA						
49	0	49	2	22.1	36.3	1.54	244	968	1.36
49	15	49	2	22.1	63	3.37	7	167	1.12
45	0	45	10	18.0	40	1.65	96	875	0.81
45	15	45	10	18.0	60	3.35	8	216	0.76
N6	GF	ABS	SANMA						
49	0	49	2	22.1	34.9	1.45	214	967	1.44
49	15	49	2	22.1	61	3.04	8	213	1.13
45	0	45	10	18.0	40.8	1.68	152	916	0.78
45	15	45	10	18.0	68	3.21	8	235	0.77

lon 6 and ABS at two levels of the IA compatibilizer; note that no glass fibers are visible in the fields of view shown. Regardless of the type (or amount) of the compatibilizer or the incorporation of glass fibers, these blends have a cocontinuous nylon 6/ABS phase morphology. As the amount of the compatibilizer is increased or as glass fibers are added, the ABS phase becomes more efficiently dispersed and the nylon 6 phase becomes more continuous in character.

Table III compares the mechanical properties and dispersed-phase size of blends with and without glass fibers based on these two types of compatibilizers. As expected, the room-temperature toughness of nylon 6/ABS blends with low contents of either compatibilizer are quite similar. On the other hand, blends with a high content of SANMA tend to have higher impact strength and elongation at break. The addition of glass fiber to these blend systems reduces their impact strength and ductility. Figure 7 compares the Izod impact strength versus temperature relationship for the nylon 6/ABS blends compatibilized by 2% IA versus those compatibilized by 2% SANMA. The blends without glass fiber exhibit very low ductile–brittle transition temperatures while the addition of glass fibers increases the transition temperature and lowers the overall fracture energy. In both cases, there is a slightly lower ductile–brittle transition when SANMA is used as the compatibilizer.

Nylon 6 Molecular Weight

The nylon 6 molecular weight may influence the mechanical properties of neat nylon 6 via issues of intrinsic ductility and rubber-toughened blends

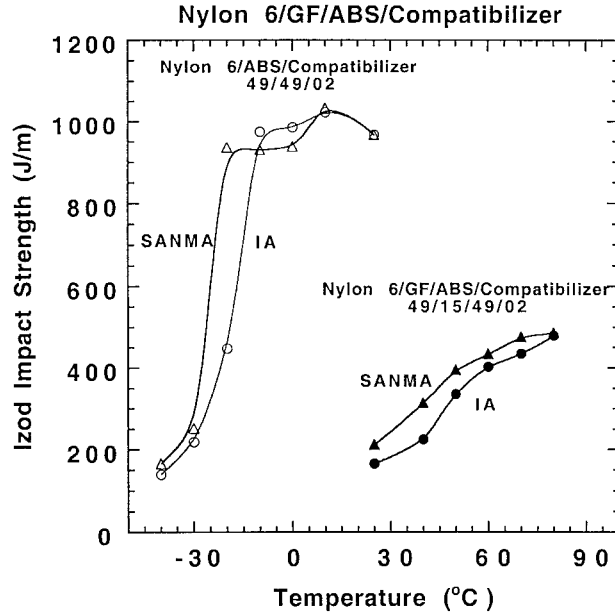


Figure 7 Effect of temperature on the Izod impact strength for nylon 6/ABS blend and nylon 6/GF/ABS composites with different compatibilizers.

through the additional effects of how melt viscosity influences the morphology.^{13,32} For glass fiber-reinforced rubber-toughened composites, one may expect all these mechanisms plus issues of fiber distribution, orientation, and damage to affect performance. A preliminary assessment of these possibilities was explored for the current system at selected glass fiber, compatibilizer, and ABS

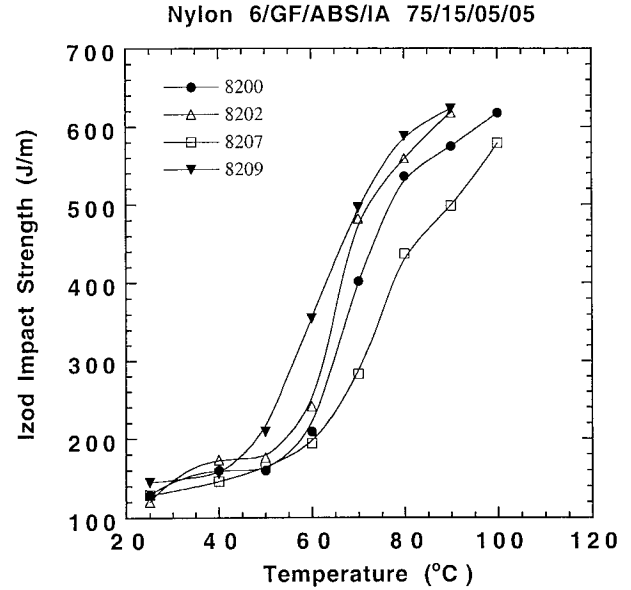


Figure 8 Effect of temperature on the Izod impact strength of nylon 6/GF/ABS/IA composites based on different molecular weight grades of nylon 6.

contents using a series of nylon 6 materials with a range of molecular weights. The results are summarized in Table IV; essentially, the effect of the nylon 6 molecular weight on the mechanical properties is very slight. However, the nylon 6 with the lowest molecular weight (Capron 8200) has slightly lower values of impact strength and elongation to break. The nylon 6 with the highest molecular weight (Capron 8209F) is toughened

Table IV Mechanical Properties of Nylon 6/GF/ABS/IA Composites: Effect of Nylon 6 Molecular Weight

Grade	Composition (wt %)				Yield Strength (MPa)	Modulus (GPa)	Elongation at Break (%)	Izod Impact Strength (J/m)
	N6	GF	ABS	IA				
Capron 8200	100	0	0	0	69.1	2.65	40	36
	80	0	10	10	62.2	2.58	25	163
	75	15	5	5	99.3	4.82	8	130
Capron 8202	100	0	0	0	56.8	2.34	92	58
	80	0	10	10	60.7	2.4	25	129
	75	15	5	5	101.1	4.64	6	120
Capron 8207F	100	0	0	0	70.6	2.58	60	58
	80	0	10	10	62.4	2.32	38	109
	75	15	5	5	105.8	4.89	7	129
Capron 8209F	100	0	0	0	66.9	2.62	83	51
	80	0	10	10	59.3	2.66	111	205
	75	15	5	5	96.6	4.59	8	145

Table V Mechanical Properties of Nylon 6/GF/ABS/IA Composites: Effect of Compounding History

Compounding History	Composition (wt %)				Yield Strength (MPa)	Modulus (GPa)	Elongation at Break (%)	Izod Impact Strength (J/m)	Weight-average Fiber Length (μm)
	N6	GF	ABS	IA					
Method I	85	15	0	0	107	5.13	7	67	354
	42.5	15	42.5	0	60.4	3.19	5	67	384
	75	15	5	5	96.6	4.59	8	145	356
Method II	85	15	0	0	108	4.9	6	58	338
	42.5	15	42.5	0	56.7	3.24	6	66	360
	75	15	5	5	95	4.35	9	139	346
Method III	85	15	0	0	97.0	4.58	9	50	265

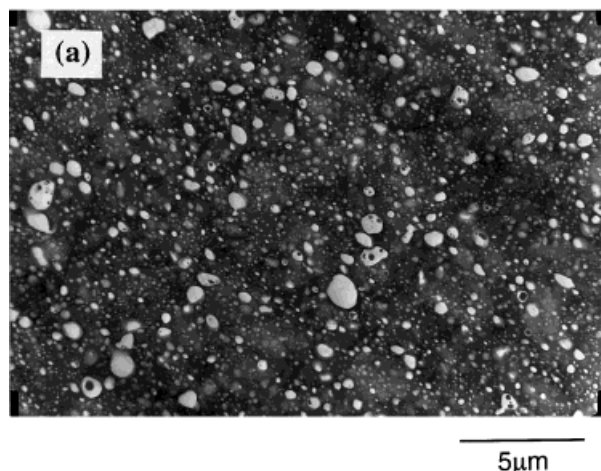
Method I: Injection molding. Method II: Compounding with single-screw extruder before injection molding. Method III: Compounding with twin-screw extruder before injection molding.

more effectively with ABS/IA. Figure 8 shows the Izod impact strength as a function of temperature for the glass fiber-reinforced composites of nylon 6/ABS/IA blends based on this series of nylon 6 materials. In general, the ductile–brittle transition temperature is lower the higher is the molecular weight of the nylon 6 phase. However, there seems to be no relationship with the nylon 6 molecular weight for glass fiber-reinforced composites. Additional work will be required to separate all of the effects mentioned above.

Compounding History

Blending or compounding history may be an important factor affecting the resulting performance of blends or composites. Clearly, the length distribution of the fibers in the composite is a key factor determining the mechanical properties. The effects of the compounding history and matrix nature on fiber degradation and mechanical properties were assessed by processing these formulations in two different extruders prior to injection molding. As shown in Table V, composites obtained directly from the injection molding of the dry-mixed mother blend and pellets of BKV 30 (Mixing Method I) show the least fiber damage and the best mechanical properties. The mechanical properties of composites processed in the twin-screw extruder prior to injection molding (Mixing Method III) were much poorer, primarily due to the severe length reduction of the glass fibers. Fiber degradation also depends on the matrix polymer. Composites without a rubber phase in the matrix show slightly lower values of weight-average fiber length than those of a matrix with a larger amount of rubber.

Nylon 6/EPR-g-MA 78/22



Nylon 6/GF/EPR-g-MA 78/15/22

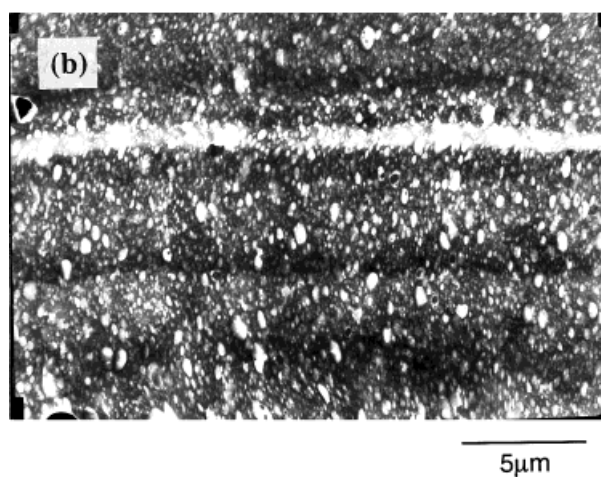


Figure 9 TEM photomicrographs for (a) nylon 6/EPR-*g*-MA 78/22 blend and (b) nylon 6/GF/EPR-*g*-MA 78/15/22 composite (the nylon 6 phase is stained with PTA).

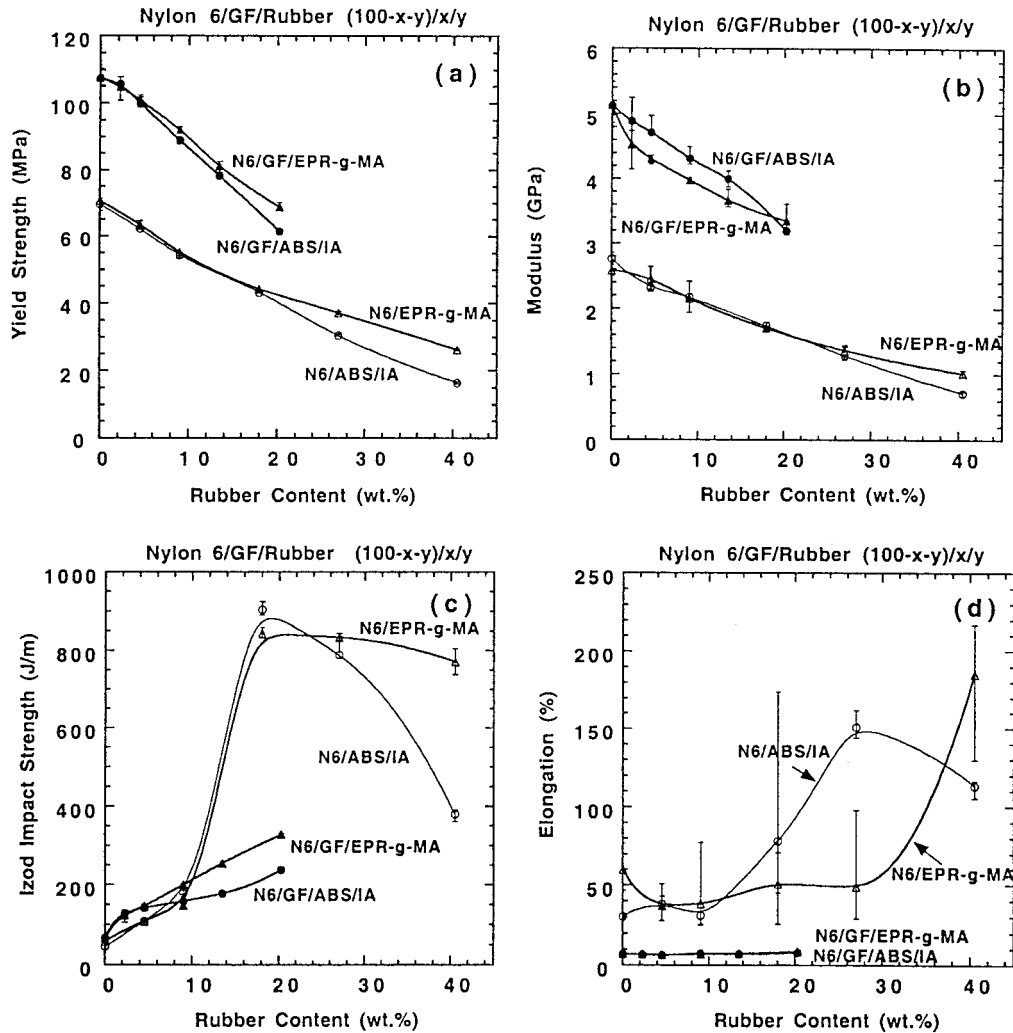


Figure 10 Mechanical properties of nylon 6/GF/ABS/IA and nylon 6/GF/EPR-*g*-MA composites as a function of rubber content: (a) yield strength; (b) modulus; (c) Izod impact strength; (d) elongation at break.

BLENDS TOUGHENED BY EPR-G-MA

In this section, nylon 6 glass fiber composites toughened with EPR-*g*-MA are compared with those toughened by ABS. Figure 9 shows TEM photomicrographs of a nylon 6 blend containing 22 wt % EPR-*g*-MA and a composite based on this blend containing 15 wt % glass fiber. Image analysis of these photomicrographs reveals that the weight-average particle size of EPR-*g*-MA decreases slightly with incorporation of glass fiber (0.23 versus 0.19 μm). On the other hand, there is no significant increase in the rubber particle size with increased rubber content. This is in good agreement with other recent work from this laboratory.³⁰

Figure 10 shows the effect of the rubber content on the mechanical properties of the glass fiber-reinforced nylon 6 toughened with EPR-*g*-MA and with ABS for comparison. Regardless of the rubber type, the yield strength and modulus decrease as the rubber content increases, as expected. Below about 20 wt % rubber content, the yield strength and modulus for these two types of unreinforced rubber blends are nearly identical. When glass fibers are introduced, the ABS-based system shows higher values of the modulus. At high rubber contents, the EPR-*g*-MA blend system shows better properties. However, the differences between these two types of rubber-toughened composites are not great. The effect of toughness and ductility are shown in Figure 10(c,d). As

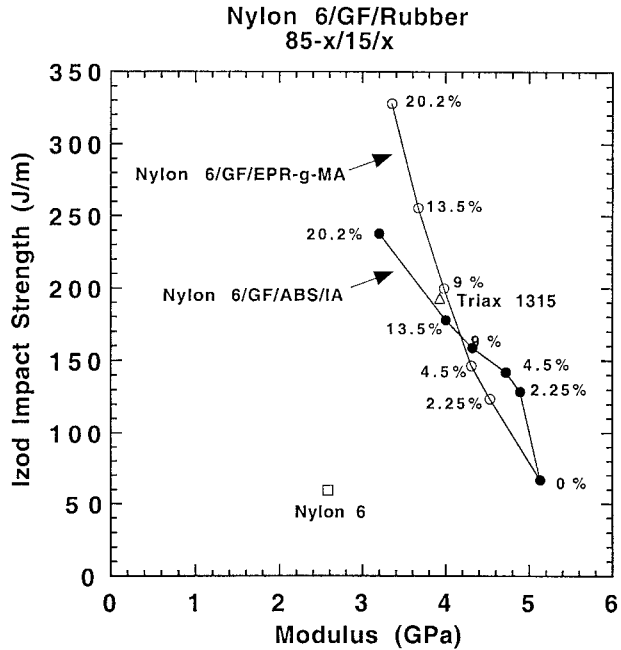


Figure 11 Izod impact strength versus modulus of toughened, glass fiber-reinforced nylon 6 composites with varying rubber content.

expected, the impact strength increases as the rubber content is increased, but these values are substantially decreased by incorporation of the glass fiber. The elongation at break for the ABS system begins to increase beyond about 10% rubber, but the EPR-g-MA system shows an essentially constant value until the material contains about 25% of rubber. Regardless of rubber type, incorporation of glass fibers leads to greatly reduced ductility.

Figure 11 shows the stiffness versus toughness balance for these two rubber types. A data point is also shown for Triax[®]1315, which is a commercial nylon 6 composite from Bayer Corp. containing 15 wt % of glass fiber toughened with ABS, but the exact composition of this material has not been disclosed. Figure 12 shows the Izod impact strength as a function of temperature for glass fiber-reinforced composites toughened with various contents of EPR-g-MA. In general, the ductile–brittle transition temperature of these composites is lower the more EPR-g-MA there is in the material. The composites toughened with EPR-g-MA show higher values of room-temperature impact strength and lower ductile–brittle transition temperatures than those of comparable ABS-based materials (Fig. 13).

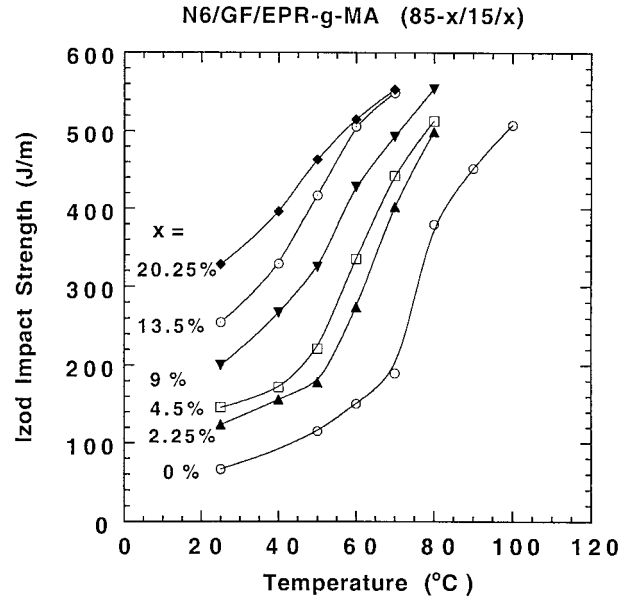


Figure 12 Effect of temperature on the Izod impact strength of nylon 6/GF/EPR-g-MA composites with various nylon 6 formulations.

ESSENTIAL WORK OF FRACTURE (EWF)

The Izod impact strength is not a very complete indicator of the toughness or fracture resistance of most materials; therefore, it is imperative to employ other methods to obtain a more complete picture. The fracture behavior of the glass fiber-

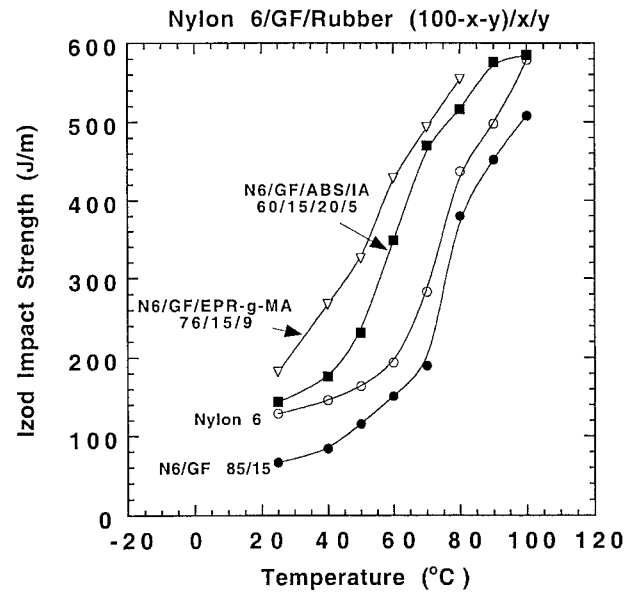


Figure 13 Effect of temperature on the Izod impact strength of various nylon 6 formulations.

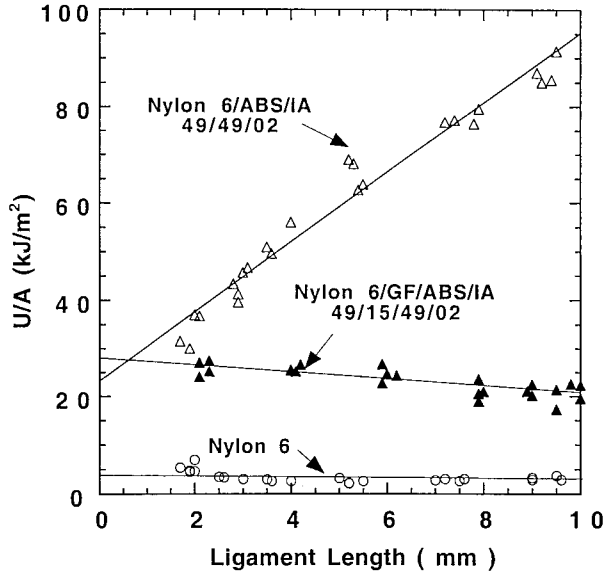


Figure 14 Specific fracture energy as a function of ligament length for neat nylon 6, nylon 6/ABS/IA 49/49/02 blend, and nylon 6/GF/ABS/IA 49/15/49/02 composite.

reinforced/rubber-toughened nylon 6 materials developed here were further investigated by using a single-notch three-point bend (SN3PB) instrumented Dynatup test. The fracture energy, U , was measured as a function of the unbroken ligament length, l , using specimens of thickness $t = 6.35$ mm. The specific fracture energy, U/A (where $A = tl$), is plotted versus the ligament length as suggested by the essential work of fracture (EWF) methodology described extensively in the recent literature.^{16,33–43} Blends toughened by both ABS and EPR-*g*-MA containing a fixed amount of rubber (22 wt %) were compared to each other and the blend containing no glass fiber.

Figure 14 shows results for neat nylon 6, the nylon 6/ABS blend compatibilized with IA, and the glass fiber-reinforced, compatibilized nylon 6/ABS blend. As expected, the specific fracture energy is much higher at all ligament lengths for the compatibilized blend than for neat nylon 6. The large positive slope is indicative of a larger zone of energy dissipation by plastic deformation about the fracture plane. In addition, the presence of ABS increases the intercept at $l = 0$ or the specific limiting fracture energy (essential work of fracture). The slope or the dissipative energy density (nonessential work of fracture) is reduced to zero or perhaps even a negative value by addition of glass fibers to the compatibilized blend system. However, the spe-

cific limiting fracture energy for the toughened composite is comparable to that of the blend without glass fibers and much higher than that of neat nylon 6. The fracture behavior for the nylon 6/EPR-*g*-MA blend system is qualitatively similar to that of the nylon 6/ABS blend system.

Figure 15 shows the fracture energy per unit area for unreinforced rubber-toughened blends which have the same rubber content. This implies that there is no significant difference between these two types of rubber or the two different compatibilizers. Figure 16 compares the fracture energy per unit area for glass fiber-reinforced composites with two different rubber types and Triax® 1315. As shown, these composites are brittle and the fracture responses are independent of ligament length. However, the specific limiting fracture energy for composites prepared in our laboratory have a slightly higher value than that of Triax® 1315. This suggests that more energy is required to initiate fracture.

CONCLUSIONS

The mechanical properties of glass fiber-reinforced nylon 6 composites toughened with ABS were investigated and compared with composites toughened with EPR-*g*-MA. The addition of rubber particles into nylon 6 enhances the toughness and ductility but reduces the modulus and yield

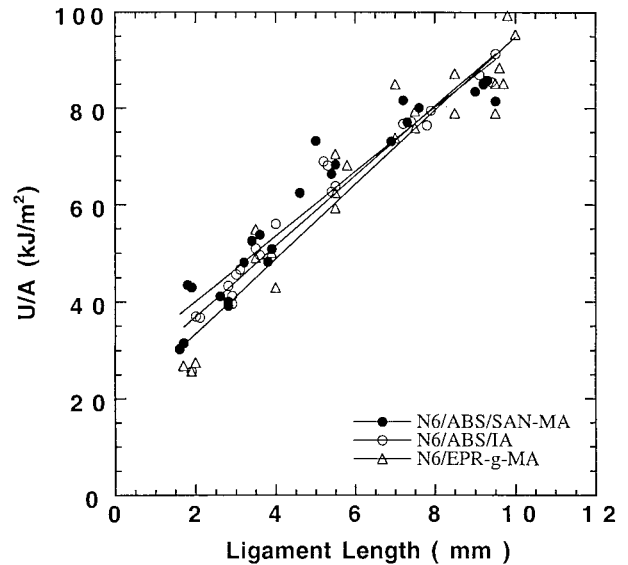


Figure 15 Specific fracture energy as a function of ligament length for rubber-toughened nylon 6 blends without glass fiber.

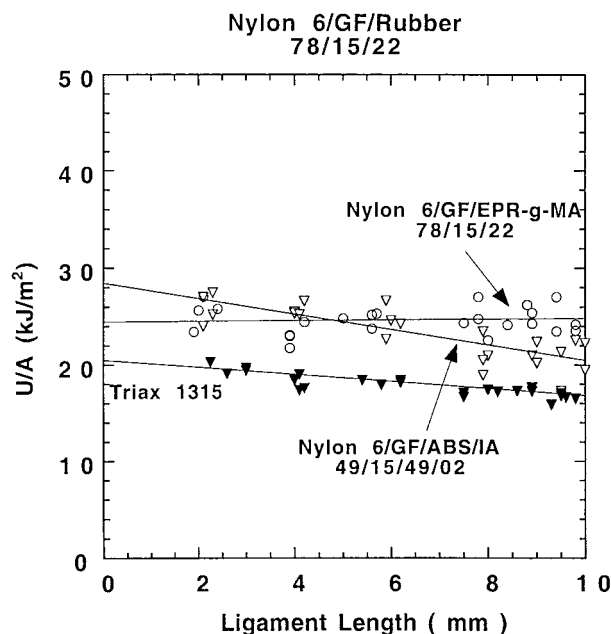


Figure 16 Specific fracture energy as a function of ligament length for toughened, glass fiber-reinforced nylon 6 composites.

strength, as expected. The incorporation of glass fibers into toughened nylon 6 blends substantially improves the stiffness and strength but sacrifices the toughness and ductility of the blend. Composites with a balance of strength/stiffness and toughness can be achieved by the proper combination of glass fiber and rubber content. For example, the incorporation of 15 wt % glass fiber and 45 wt % ABS into nylon 6 improved the modulus by 24% and the impact strength by 300% relative to neat nylon 6. As expected, the ductile–brittle transition temperature of the composites was lowered by increasing the rubber content. The EPR-*g*-MA-toughened materials tend to have higher impact strength than that of those toughened with ABS. Future work will be concentrated on composites with EPR-*g*-MA toughening in an effort to better characterize fracture toughness and understand the deformation processes involved.

This material is based, in part, upon work supported by the Texas Advanced Technology Program under Grant Numbers 003658-0017 and 0067.

REFERENCES

1. Kohan, M. I. *Nylon Plastics Handbook*; Hanser: New York, 1995; Chapter 10.

2. Bragaw, C. G. *Mod Plast* 1956, 33, 199.
3. Wu, S. *Polymer* 1985, 26, 1855.
4. Oshinski, A. J.; Keskkula, H.; Paul, D. R. *Polymer* 1992, 33, 268.
5. Oshinski, A. J.; Keskkula, H.; Paul, D. R. *J Appl Polym Sci* 1996, 61, 623.
6. Oshinski, A. J.; Keskkula, H.; Paul, D. R. *Polymer* 1996, 37, 4909.
7. Oshinski, A. J.; Keskkula, H.; Paul, D. R. *Polymer* 1996, 37, 4919.
8. Baer, M. U.S. Patent 4 584 344. 1986 (to Monsanto).
9. Lavengood, R. E.; Silver, F. M. *Soc Plast Eng ANTEC* 1987, 45, 1369.
10. Lavengood, R. E.; Padwa, A. R.; Harris, A. F. U.S. Patent 4 713 415, 1987 (to Monsanto).
11. Majumdar, B.; Keskkula, H.; Paul, D. R. *Polymer* 1994, 35, 3164.
12. Majumdar, B.; Keskkula, H.; Paul, D. R. *Polymer* 1994, 35, 5453.
13. Majumdar, B.; Keskkula, H.; Paul, D. R. *Polymer* 1994, 35, 5468.
14. Kudva, R. A.; Keskkula, H.; Paul, D. R. *Polymer* 2000, 41, 225.
15. Kudva, R. A.; Keskkula, H.; Paul, D. R. *Polymer* 2000, 41, 239.
16. Kudva, R. A.; Keskkula, H.; Paul, D. R. *Polymer* 2000, 41, 335.
17. Lowrie, R. E. In *Modern Composite Materials*; Broutman, L. J., Ed.; Addison-Wesley: Reading, MA, 1967; pp 270–323.
18. Scheetz, H. A. In *Nylon Plastics Handbook*; Kohan, M. I., Ed.; Hanser: New York, 1995; pp 387–413.
19. Bailey, R. S.; Bader, M. G. In *Proceedings of the 5th International Conference on Composite Materials*, San Diego, 1985 (Metallurgical Society, 1985); p 947.
20. Kinloch, A. J.; Maxwell, D. L.; Young, R. J. *J Mater Sci* 1985, 20, 4169.
21. Kelnar, I. *Angew Makromol Chem* 1991, 189, 207.
22. Nair, S. V.; Shiao, M. L.; Garrett, P. D. *J Mater Sci* 1992, 27, 1085.
23. Pecorini, T. J.; Hertzberg, R. W. *Polym Compos* 1994, 15, 174.
24. Shiao, M. L.; Nair, S. V.; Garrett, P. D.; Pollard, R. E. *Polymer* 1994, 35, 306.
25. Azari, A.; Boss, F. *Soc Plast Eng ANTEC* 1996, 54, 3022.
26. Din, K. J.; Hashemi, S. *J Mater Sci* 1997, 32, 375.
27. Nair, S. V.; Wong, S. C.; Goettler, L. A. *J Mater Sci* 1997, 32, 5335.
28. Nair, S. V.; Subramaniam, A.; Goettler, L. A. *J Mater Sci* 1997, 32, 5347.
29. Nair, S. V.; Subramaniam, A.; Goettler, L. A. *J Mater Sci* 1998, 33, 3455.

30. Laura, D. M.; Keskkula, H.; Barlow, J. W.; Paul D. R., *Polymer* 2000, 41, 7165.
31. Lu, M.; Keskkula, H.; Paul, D. R. *J Appl Polym Sci* 1995, 58, 1175.
32. Lu, M.; Keskkula, H.; Paul, D. R. *J Appl Polym Sci* 1996, 59, 1467.
33. Mai, Y.; Williams, J. G. *J Mater Sci* 1977, 12, 1376.
34. Mai, Y. *Polym Commun* 1989, 30, 330.
35. Mai, Y. *Int J Mech Sci* 1993, 35, 995.
36. Vu-Khanh, T. *Polymer* 1988, 29, 1979.
37. Vu-Khanh, T. *Theor Appl Fract* 1994, 21, 83.
38. Mamat, A.; Vu-Khanh, T.; Favis B. D. *J Polym Sci* 1997, 35, 2583.
39. Kayano, Y.; Keskkula, H.; Paul, D. R. *Polymer* 1997, 38, 1885.
40. Kayano, Y.; Keskkula, H.; Paul, D. R. *Polymer* 1998, 39, 821.
41. Kayano, Y.; Keskkula, H.; Paul, D. R. *Polymer* 1998, 39, 2835.
42. Hale, W.; H. Keskkula, H.; Paul, D. R. *Polymer* 1999, 40, 3353.
43. Wildes, G.; Keskkula, H.; Paul, D. R. *Polymer* 1999, 40, 7089.