Toughening of Nylon 6 with Grafted Rubber Impact Modifiers

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SYNOPSIS

Recent work has shown that nylon 6/acrylonitrile–butadiene–styrene (ABS) blends can be made tough by the addition of some polymer additives that are chemically reactive with nylon 6 and physically compatible with the styrene-acrylonitrile copolymer (SAN) phase of ABS. Imidized acrylic polymers (IA) represent a successful example of such additives that improve the dispersion of ABS in the nylon 6 matrix and render the blends tough. This article examines the possibility of toughening nylon 6 with ethylene/propylene/diene elastomer grafted with SAN copolymer (EPDM-g-SAN). This EPDM-g-SAN consists of 50% rubber and 50% SAN by weight. However, it was found that the same IA that works well to disperse ABS materials of similar rubber content is not as effective for EPDM-g-SAN, primarily because the EPDM forms the continuous phase, not SAN, and, thus, interfaces with nylon 6 during melt blending. Maleated elastomers like maleic anhydride grafted ethylene–propylene copolymer (EPR-g-MA) and styrene–(ethylene-co-butylene)–styrene triblock copolymer (SEBS-g-MA) were more effective for dispersing EPDM-g-SAN in the nylon 6 matrix than IA. Various mechanisms that improve the dispersion are discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

There is an extensive literature[1-8] on blends of polyamides with various rubbery materials that demonstrate some of the requirements to achieve toughening,[3,4] viz., an appropriate range of rubber particle size and some level of interfacial adhesion between these phases. Blends of polyamides and unfunctionalized rubbers are not tough because the rubber particles formed during melt blending are too large and adhesion may not be adequate. A practical solution is to graft maleic anhydride (MA) to the rubber prior to blending with the polyamide.[3,4,8-17] MA grafted ethylene–propylene copolymer (EPR-g-MA) and styrene–(ethylene-co-butylene)–styrene triblock copolymer (SEBS-g-MA)[4,6,17] are successful examples of such rubbers that are useful for toughening nylons. The MA units can react with the amine end groups of the polyamide to form in

situ graft copolymers at the rubber–matrix interface that decrease the interfacial tension and retard particle coalescence during mixing, resulting in uniformly distributed rubber particles in the polyamide matrix of sizes within the useful range for effective toughening. The graft copolymer also enhances interfacial adhesion. For nonfunctional rubber, addition of a third component that acts as a dispersant for the rubber in the polyamide phase is an interesting alternative.[18,19]

Blends of acrylonitrile–butadiene–styrene (ABS) materials with polyamides are attractive, provided they are tough, for a variety of reasons, including the reduced moisture absorption caused by the dilution of the polyamide with a hydrophobic material. However, simple blends of ABS and nylon 6 have poor mechanical properties because the styrene-acrylonitrile copolymer (SAN) matrix of ABS does not interact well enough with the polyamide to achieve an adequate dispersion of the components[20] and the interface between these phases appears to be weak.[21] Compatibilization of nylon 6/ABS blends has been achieved by either grafting the ABS with

MA[22-24] or by adding a reactive compatibilizer that is miscible with SAN that can also react with the polyamide.[25,26] Imidized acrylic polymers (IA)[21,25-27] that have anhydride and free acid groups meet these requirements as a reactive compatibilizer for this system.

A major limitation of butadiene-based rubbers for toughening plastics is their propensity for thermooxidative degradation, typical of materials with a high degree of unsaturation. This is especially a problem for materials that require processing temperatures approaching 300°C. Accordingly, there is a strong need to employ saturated elastomers for this purpose. An ethylene/propylene/diene elastomer grafted with styrene/acrylonitrile copolymer, EPDM-g-SAN, has become commercially available, and it has been claimed to be useful for toughening polymers such as SAN, polycarbonate, polyester/polycarbonate alloys, and polyvinylchloride (PVC).[28] An issue of interest here is whether such a material can be useful for toughening nylon 6. Of course, some dispersant or compatibilizer will certainly be needed. In principle, the IA mentioned above could be useful for this purpose owing to their reactivity with nylon 6 and miscibility with the grafted SAN. This proposal is explored. In addition, other third components will also be considered. These include as examples the EPR-g-MA and SEBS-g-MA materials mentioned earlier. These materials may have some physical affinity for the rubber phase of EPDM-g-SAN, in addition to their reactivity with the polyamide, and, hence, some ability to act as a compatibilizer. They may also function as co-impact modifiers by forming a separate, third phase. In some cases, the EPDM-g-SAN is replaced with an ABS material in these ternary blends for comparison.

EXPERIMENTAL

Table I summarizes pertinent information about the various materials used. The ABS is an emulsion-made material with a high rubber content (50%) that has been used in several previous investigations.[21,25-27,29] The rubber phase has a glass transition temperature, T_g, of −60°C measured by dynamic mechanical analysis at 1 Hz. The rubber particles have a broad distribution of sizes as shown in Figure 1(a) where rubber particles are stained dark by OsO$_4$. The SAN component has been estimated to contain 24% AN by weight.[26] The EPDM-g-SAN material contains 50% EPDM and 50% SAN (25% AN by weight); the degree of grafting is unknown.[28]

The glass transition temperature of the rubber phase is −30°C. As shown in Figure 1(b), the SAN copolymer forms the dispersed phase, appearing as small dark particles stained by RuO$_4$. Further details about this material are given elsewhere.[28] The IA obtained from Rohm & Haas Co. contains methyl methacrylate, glutarimide, methacrylic acid, and anhydride units. This polymer has been shown to be miscible with SAN25 and the anhydride or acid units are capable of reacting with polyamides, presumably via the amine end groups.[26] The SEBS-g-MA contains 1.84% MA by weight and has a rubber phase T_g of −35°C. The EPR-g-MA contains 1.14% MA by weight with the rubber T_g = −40°C. Both SEBS-g-MA and EPR-g-MA have been extensively studied as impact modifiers for polyamides.[6-8,17]

Rheological characteristics of the components were assessed using a Brabender Plasticorder with a 60-mL mixing head and standard rotors operated at 60 rpm and 240°C. All blends were prepared in a Killion single screw extruder (L/D = 30, 2.54 cm screw diameter) at 40 rpm and 240°C and then injection molded into test bars using an Arburg All-Rounder molding machine. These process conditions[6] have proved effective for forming reactive blends based on nylon 6, and to aid comparisons among a variety of formulations, have not been varied in this study. All materials were dried at 80–100°C for at least 12 h in a vacuum oven prior to each melt processing step.

Test specimens were sealed in plastic bags and stored in a dessicator and subsequently tested dry as molded. Tensile testing was done using an Instron machine in accordance with ASTM D638 at a crosshead speed of 5.08 cm/min. An extensometer strain gauge with a 5.08-cm gauge section was used to obtain the modulus and yield stress; all values reported are averages of at least five determinations that generally are reproducible to better than ±5%. Notched Izod impact tests were conducted according to ASTM D256 using 0.318-cm thick specimens; reported values are averages of at least six determinations with reproducibility generally better than ±10%.

The morphology of selected blends was examined by transmission electron microscopy (TEM) using a JEOL JEM 200CX. Ultrathin samples were obtained by microtoming molded specimens using a Reichert–Jung ultramicrotome at −40°C and stained by OsO$_4$ (2% solution in water) for at least 1 h and/or RuO$_4$ (vapor) for a maximum of 15 min.

A semiautomatic digital image analysis was used for determining the EPDM-g-SAN domain size from TEM photomicrographs using software from the

Table I Material Used

Study Designation	Commercial Designation	Composition	T_g (°C)	Relative Melt Viscosity[a]	Source
Nylon 6	Capron 8207F	Polyamide 6	50[b]	1.00	Allied Signal Inc.
ABS	BL-65	50% SAN (24% AN) and 50% butadiene rubber (40% of SAN grafted to rubber)	-60[b] (rubber phase)	3.97	Sumitomo Naugatuck Co.
EPDM-g-SAN	Tuf372	50% EPDM rubber and 50% SAN (%25 AN) grafted to rubber	-30[b] (rubber phase)	2.88	Uniroyal Co.
Imidized acrylic polymer, IA	Paraloid EXL4140	55.7% Methyl glutarimide 40.3% Methyl methacrylate 2.8% Methacrylic acid 1.25% Glutaric anhydride	134[c]	1.56	Rohm and Haas Co.
SEBS-g-MA	Kraton G 1901X	Styrene–(ethylene-co-butylene)–styrene 29% styrene and 1.84% maleic anhydride	-35[b]	0.96	Shell Chemical Co.
EPR-g-MA	Exxelor 1803	Ethylene-propylene rubber grafted with 1.14% maleic anhydride	-40[b]	1.46	Exxon Chemical Co.

[a] Brabender torque after 5 min of mixing at 240°C and 60 rpm relative to that of nylon 6.
[b] Determined by dynamic mechanical thermal analysis at 1 Hz and a scan rate of 5°C/min.
[c] Determined by differential scanning calorimetry at a scan rate of 20°C/min.
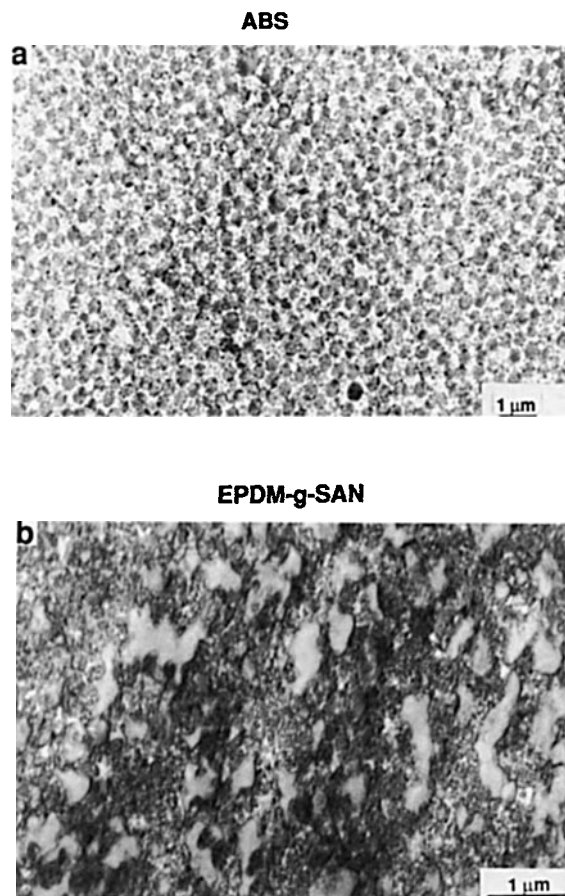
ABS

EPDM-g-SAN

Figure 1 TEM photomicrographs of (a) ABS and (b) EPDM-g-SAN. Both samples were cryogenically microtomed from injection-molded bars; ABS sample was stained by OsO_4 and EPDM-g-SAN was stained by RuO_4.

National Institutes of Health. For nonspherical shapes, the diameter was defined as the average of the major and minor dimensions of each particle. Of course, microtoming cuts through particles at random and only rarely does this correspond to the maximum dimension; hence, in TEM photomicrographs, the particles appear to be smaller and more broadly distributed in size than they really are. No attempt was made to correct for this effect. Apparent weight average particle diameters were calculated from measurements on more than 100 particles.

RESULTS AND DISCUSSION

Binary Blends

The mechanical properties of various pure components and some binary blends are of interest for comparison with the subsequent data for ternary blends, and these results are included in Tables II–V. It has been shown that at least 15–20% rubber is needed for effective toughening of nylon 6.[6,18] Here we compare various blends at 22.5% rubber content. The 55/45 nylon 6/ABS (Table II) and nylon 6/ EPDM-g-SAN (Table III) blends have lower modulus and yield strength than pure nylon 6 (Table II) due to the presence of the rubbery component. Their elongation at break is significantly lower than that of nylon 6, suggesting poor compatibility of the dispersed phase with the matrix. There is marginal improvement of the notched Izod impact strength on addition of ABS or EPDM-g-SAN to nylon 6. TEM photomicrographs to be described in subsequent sections show that the minor component is poorly dispersed in the nylon 6 matrix in the form of large domains that have some tendency toward cocontinuity. The binary blends of nylon 6 with the two functional rubbers, EPR-g-MA (Table IV) and SEBS-g-MA (Table V) on the other hand show much better mechanical properties. These blends exhibit excellent elongations at break that exceed that of pure nylon 6. The nylon 6/EPR-g-MA blend is supertough while the nylon 6/SEBS-g-MA blend

Table II   Room Temperature Mechanical Properties of Nylon 6/IA/ABS Blends

Composition (%)			Yield Stress (MPa)	Modulus (GPa)	Break Strain (%)	Izod Impact (J/m)	Ductile–Brittle Transition Temperature (°C)
Nylon 6	IA	ABS					
100	0	0	72.0	2.61	145	50	
82	18	0	81.4	3.13	105	45	
55	0	45	39.6	1.74	25	90	60
53	2	45	42.7	1.80	230	1050	10
50	5	45	44.0	1.80	270	1020	0
45	10	45	44.7	1.91	140	940	-10
40	15	45	47.2	1.83	110	880	-12
0	0	100	18.4	0.77	100	500	

Table III   Room Temperature Mechanical Properties of Nylon 6/IA/EPDM-*g*-SAN Blends

Composition (%)			Yield Stress (MPa)	Modulus (GPa)	Break Strain (%)	Izod Impact (J/m)	Ductile–Brittle Transition Temperature (°C)
Nylon 6	IA	EPDM-*g*-SAN					
55	0	45	31.8	1.30	25	80	60
53	2	45	34.8	1.49	50	760	20
50	5	45	38.3	1.60	30	820	20
45	10	45	38.7	1.64	10	660	20
40	15	45	42.3	1.79	10	250	35
0	0	100	11.3	0.37	20	405	

is about five times tougher than virgin nylon 6. As reported previously,[6] the nylon 6/SEBS-*g*-MA blends only achieve moderate improvements in toughness because the rubber particles (about 0.05 μm in diameter, as shown subsequently) are below the reported lower critical limit for toughening this nylon 6. The rubber particles in the nylon 6/EPR-*g*-MA blends have a broad distribution of sizes, but the average lies below the upper critical limit, ca. 1 μm, for toughening this nylon 6 (see later).

Compatibilization of ABS and EPDM-g-SAN Blends with Nylon 6 Using an IA

IAs can be effective compatibilizers for nylon 6 and ABS blends because of their reactivity with nylon 6 and miscibility with the SAN matrix of ABS[21] as demonstrated in Figure 2. A blend of nylon 6 and ABS without such a compatibilizer is not tough, at least in part because the ABS phase is not well dispersed in the nylon 6 as shown in Figure 3(a). Addition of 10% of the IA causes the ABS to be more finely and uniformly dispersed as shown in Figure 3(b). As seen in Figure 2, even the addition of 2% IA increases the room temperature notched Izod impact strength of nylon 6/ABS blends to above 1000 J/m. Further addition of compatibilizer, up to 15% IA, reduces the ductile–brittle transition temperature significantly without much effect on the room temperature impact strength. At 15% IA, the ductile–brittle transition temperature is −12°C. Table II summarizes room temperature mechanical properties of nylon 6/IA/ABS blends; the addition of the compatibilizer generally improves the tensile properties. Compared to the nylon 6/ABS binary blend, the addition of the IA compatibilizer leads to improved elongation at break.

As expected, binary blends of nylon 6 with EPDM-*g*-SAN are brittle due to the poor dispersion of the rubber phase in the nylon 6 matrix. Figure 4 shows that addition of small amounts of IA to such

blends does improve room temperature impact strength; however, toughness is decreased when more than 5% IA is added to these blends. Furthermore, even the toughest of these blends become brittle just slightly below room temperature. The ductile–brittle transition temperature is only reduced to about 20°C in the optimal case. Table III summarizes other mechanical properties of these blends. The elongation at break was not enhanced substantially by the addition of the IA polymer. These observations are in sharp contrast to the case for ABS-based blends (see Fig. 2, Table II). The IA should be miscible with the SAN phase of the EPDM-*g*-SAN material just as it is miscible with the SAN phase of ABS. We believe that the much lower effectiveness of the compatibilization by the IA additive seen in Figure 4 compared to Figure 2 lies in the structures of the EPDM-*g*-SAN and ABS materials shown in Figure 1. For ABS, the SAN is the continuous phase and it is easy for the IA compatibilizer to reach this phase and form an in situ graft copolymer with nylon 6 at the interface. However, the SAN forms a dispersed phase in a continuous EPDM matrix in EPDM-*g*-SAN. The IA may be somewhat hindered from reaching the SAN phase because of this morphology. Furthermore, when EPDM-*g*-SAN is blended with nylon 6, the EPDM matrix not the SAN phase tends to form interfaces with the polyamide. Both factors tend to limit the usefulness of the IA as a dispersant or compatibilizer in such blends. Nevertheless, Figure 5(b) shows that the addition of the IA does aid the breaking up of the large EPDM-*g*-SAN domains shown in Figure 5(a). Clearly some SAN domains may form interfaces with the polyamide allowing the IA to function as a reactive compatibilizer for the blend. However, it is important to point out that, at least in part, the cause for the improved dispersion may be rheological in origin.[30] The reaction between the IA and nylon 6 during melt blending can increase the matrix melt viscosity substantially, and this also will tend to aid

Table IV   Room Temperature Mechanical Properties of Nylon 6 + EPR-g-MA/EPDM-g-SAN Blends

Composition			% EPR-g-MA of Total Rubber	Yield Stress (MPa)	Modulus (GPa)	Break Strain (%)	Izod Impact (J/m)	Ductile–Brittle Transition Temperature (°C)
Nylon 6	EPR-g-MA	EPDM-g-SAN						
55	0	45	0	31.8	1.30	25	80	60
57.5	2.5	40	11.1	35.9	1.27	20	90	50
62.5	7.5	30	33.3	35.8	1.31	30	230	30
67.5	12.5	20	55.6	38.7	1.43	40	990	-20
70	15	15	66.7	40.2	1.45	40	970	-30
72.5	17.5	10	77.8	41.7	1.46	150	910	-32
75	20	5	88.9	43.7	1.55	130	800	-40
77.5	22.5	0	100	40.3	1.48	230	840	-40

EPDM-g-SAN was mixed with EPR-g-MA first followed by blending with nylon 6 in a second extrusion step as indicated by the + sign.

the breaking up of the EPDM-g-SAN domains. While the EPDM-g-SAN domains in this blend are smaller than in the binary blend without the IA polymer, the average size of these domains ($\bar{d}_w$ = 0.94 μm), is quite close to the upper size limit for toughening nylon 6 with conventional maleated elastomers, ca. 1 μm, as reported by numerous investigators.[3,4,6,9]

Blends Containing Maleated Elastomers as a Third Component

In view of the failure of the IA to provide effective compatibilization of nylon 6/EPDM-g-SAN blends, alternative approaches were explored. One potentially useful strategy is to select a third component that can chemically react with nylon 6 but physically interact with the EPDM continuous phase of the EPDM-g-SAN; materials like EPR-g-MA and SEBS-g-MA are potential candidates for this purpose. These hydrocarbon-based materials may be physically compatible, if not miscible, with the EPDM continuous phase of EPDM-g-SAN. Of course, both elastomers can react with the nylon 6 via their grafted MA units.

Both EPR-g-MA and SEBS-g-MA can be successfully used for toughening polyamides.[4,9–12] Typically, EPR-g-MA based blends give lower ductile–brittle transition temperatures than those based on SEBS-g-MA, and the reasons for this are currently being investigated. We explore here whether these materials can be used successfully in conjunction with EPDM-g-SAN to produce tough nylon 6 alloys. They may function in such blends either as a co-impact modifier, an interfacial agent (or a compatibilizer), or some combination thereof. To give the greatest opportunity for interaction of the rubber phases, EPDM-g-SAN was first mixed with the maleated elastomers, EPR-g-MA or SEBS-g-MA, before blending with nylon 6 in a second extrusion. Because EPR-g-MA and SEBS-g-MA are rubbery materials themselves, it is most useful to compare blends at a fixed total rubber content. The sum of the EPDM portion (50%) of EPDM-g-SAN plus all of the EPR-g-MA or SEBS-g-MA has been fixed at 22.5% by weight for these ternary blends. Note that SEBS-g-MA contains about 29% by weight of the styrene-based hard phase; but because this is present in the form of very small microdomains, we treat this material as all rubber in this definition.

The room temperature mechanical properties of the nylon 6/EPDM-g-SAN blends containing EPR-g-MA as the third component are summarized in Table IV. Figure 6 shows a distinct transition from

Table V Room Temperature Mechanical Properties of Nylon 6 + SEBS-g-MA/EPDM-g-SAN Blends

Composition			% SEBS-g-MA of Total Rubber	Yield Stress (MPa)	Modulus (GPa)	Break Strain (%)	Izod Impact (J/m)	Ductile–Brittle Transition Temperature (°C)
Nylon 6	SEBS-g-MA	EPDM-g-SAN						
55	0	45	0	31.8	1.30	25	80	60
57.5	2.5	40	11.1	36.1	1.51	45	570	25
62.5	7.5	30	33.3	40.6	1.72	170	1100	−5
67.5	12.5	20	55.6	43.3	1.75	180	1080	−20
70	15	15	66.7	43.6	1.79	200	1000	−15
72.5	17.5	10	77.8	44.7	1.76	190	710	−10
75	20	5	88.9	44.7	1.76	145	490	0
77.5	22.5	0	100	46.9	1.86	190	290	40

EPDM-g-SAN was mixed with SEBS-g-MA first followed by blending with nylon 6 in a second extrusion step as indicated by the + sign.

brittle to ductile fracture when the fraction of EPR-g-MA in the total rubber goes from 33 to 56% in such blends. The ductile–brittle transition temperature changes rather continuously from about 60°C when the rubber comes entirely from EPDM-g-SAN to about −40°C when EPR-g-MA is the only rubber present. This appears to be the result of changes in morphology caused by addition of the maleated elastomer. As noted earlier, EPDM-g-SAN forms large domains [see Fig. 5(a), typical domain dimensions ~ 5 μm] in binary blends with nylon 6 that tend to be cocontinuous with the polyamide. As seen in Figure 7(a) the EPR-g-MA phase is well dispersed in binary blends with nylon 6 (weight average diameter = 0.34 μm). When both types of rubber are present, two populations of dispersed particles can be identified as shown in Figure 7(b,c). The EPDM-g-SAN particles are stained by RuO_4 and appear dark while the EPR-g-MA particles are not stained and appear light. Figure 7(b,c) shows that the use of EPR-g-MA as a third component does contribute to a better dispersion of EPDM-g-SAN in the nylon 6 matrix. A rough particle size analysis (see Fig. 8) indicates that addition of EPR-g-MA results in a substantial reduction in EPDM-g-SAN domain size while the size of the EPR-g-MA domains seems to remain more or less constant. It is not possible to be more precise about these trends because of the difficulties associated with image analysis of such complicated structures. Figure 7(c) shows that some EPDM-g-SAN domains are encapsulated by the EPR-g-MA phase while the rest of the EPR-g-MA appears to form separate phases without much interaction with EPDM-g-SAN. This suggests that EPR-g-MA tends to act as a dispersant for the EPDM-g-SAN in the nylon 6 matrix. However, because the reaction of EPR-g-MA with nylon 6 increases the melt viscosity, there is potentially some rheological component to the improved EPDM-g-SAN dispersion as proposed earlier. In addition to improving the dispersion of the EPDM-g-SAN phase by possibly some combinations of these two mechanisms, the EPR-g-MA clearly acts as a co-impact modifier because alone it provides excellent toughness of nylon 6.

Table V and Figure 9 show corresponding mechanical property results for ternary blends when the maleated elastomer is SEBS-g-MA. The most obvious difference here is that binary blends of this nylon 6 and this SEBS-g-MA are not tough. The reason for this is that this particular maleated elastomer forms extremely small particles [see Fig. 10(a), $\bar{d}_w$ ~ 0.05 μm] that do not toughen this polyamide as established earlier.[6] The EPR-g-MA particles [see
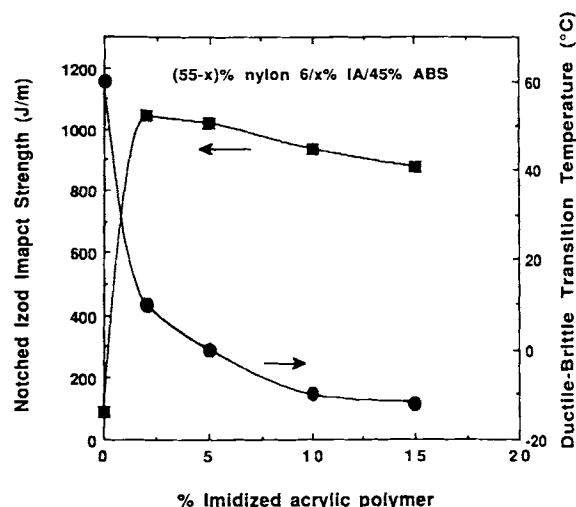
Figure 2 Effect of imidized acrylic polymer content on room temperature notched Izod impact strength and the ductile–brittle temperature for nylon 6 blends containing 45% ABS.

Fig. 7(a)] are larger than the lower limit for toughening. This difference in particle size stems primarily from the higher MA content of the SEBS-g-MA (see Table I). Figure 10(b) shows that incorporation of this maleated elastomer also tends to reduce the size of the EPDM-g-SAN domains. However, in this case it is difficult to distinguish the two types of rubber because both contain styrene and are stained to about the same extent by RuO$_4$. Nevertheless, we may assume that the large particles are EPDM-g-SAN and the tiny particles are SEBS-g-MA based on the morphologies of their binary blends with nylon 6. Figure 11 shows an approximate analysis of the particle sizes that is quite analogous to that in Figure 10 except for the much smaller particles formed by this maleated elastomer. Despite the fact that SEBS-g-MA does not toughen this polyamide, combinations with EPDM-g-SAN lead to super-tough ternary blends with ductile–brittle transition temperatures as low as $-20°C$, as seen in Figure 9. This toughening evidently stems from the fact that the average rubber particle size is within an effective range for these compositions.

It could be argued that the benefits of adding these maleated elastomers to nylon 6/EPDM-g-SAN blends are due simply to their role as co-impact modifiers. If this were true, then one might expect similar benefits to occur by adding them to nylon 6/ABS blends. This possibility is examined next. For proper comparison, the mixing protocol was the same as before, that is, ABS was first mixed with the MA modified rubber, followed by an a second extrusion

with nylon 6. The total rubber concentration was fixed at 22.5%. The effect of adding EPR-g-MA on the toughness characteristics of ABS blends with nylon 6 are summarized in Figure 12. Table VI summarizes other mechanical properties of these ternary blends; note that all of the ternary blends have poor elongation at break. The response of impact strength to the addition of the maleated elastomer seen in Figure 12 is rather different from that in Figure 6 for EPDM-g-SAN based blends. Toughness is not significantly improved until the maleated material becomes the dominant rubber phase. Figure 13 shows that the dispersion of ABS is not improved by the addition of EPR-g-MA. The EPR-g-MA is not stained by either RuO$_4$ or OsO$_4$ so it appears light in these TEM photomicrographs. These EPR-g-MA particles are actually somewhat larger than those in binary nylon 6/EPR-g-MA blends [see Fig. 7(a)]; the reasons for this are not evident.

Figure 14 shows that combinations of SEBS-g-MA and ABS can also lead to tough blends with nylon 6 with a ductile–brittle transition temperature

nylon 6/ABS (55/45)

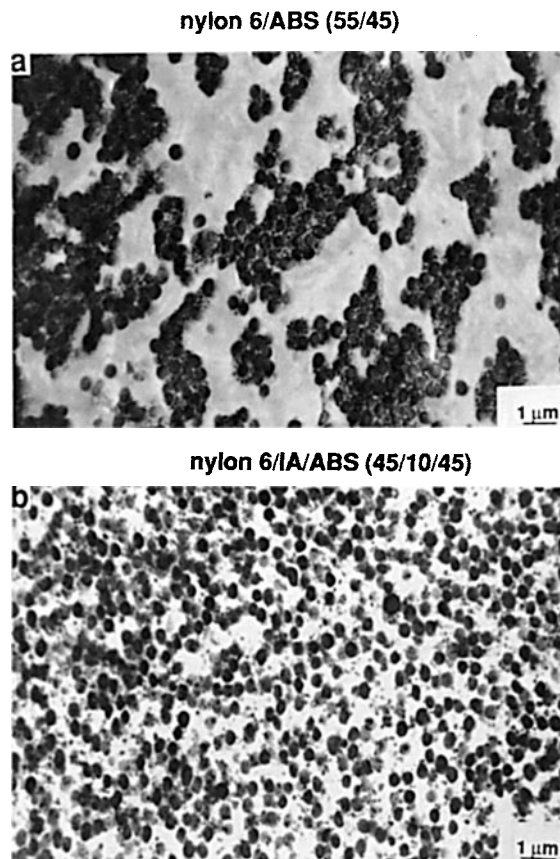**nylon 6/IA/ABS (45/10/45)**

Figure 3 TEM photomicrographs of nylon 6 blends containing 45% ABS (a) without and (b) with 10% imidized acrylic polymer. Both samples were stained by OsO$_4$.
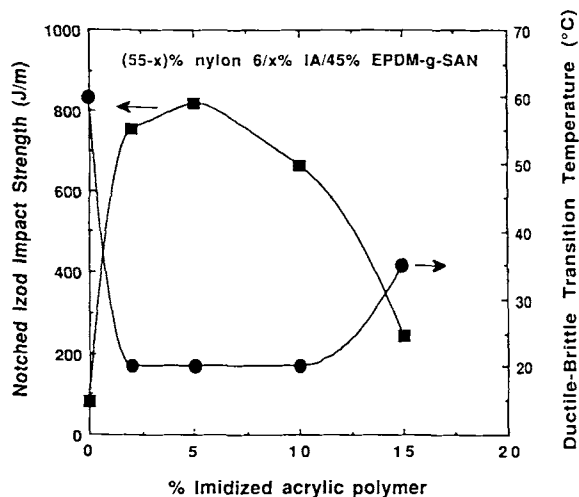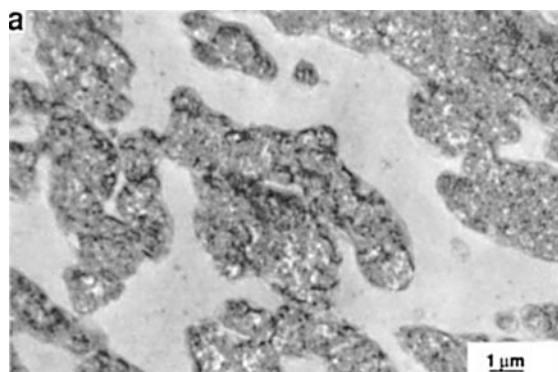
Figure 4 Effect of imidized acrylic polymer content on room temperature notched Izod impact strength and the ductile–brittle transition temperature for nylon 6 blends containing 45% EPDM-g-SAN.

nylon 6/EPDM-g-SAN (55/45)
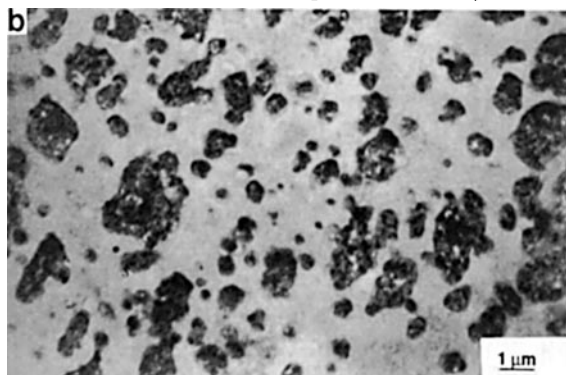

nylon 6/IA/EPDM-g-SAN (50/5/45)

Figure 5 TEM photomicrographs of nylon 6 blends containing 45% EPDM-g-SAN (a) without and (b) with 5% imidized acrylic polymer. Both samples were stained by RuO_4.
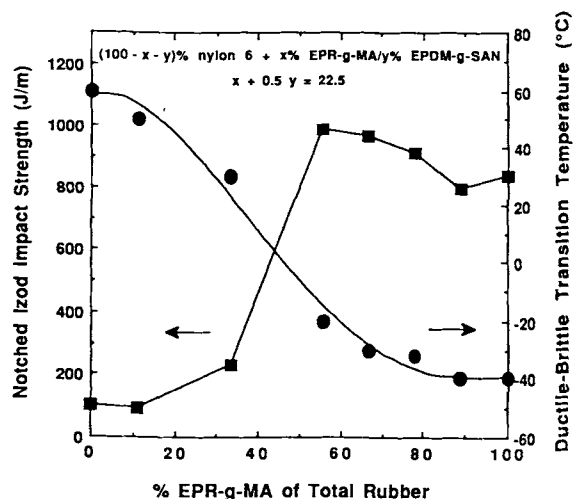

Figure 6 Effect of EPR-g-MA fraction of total rubber on room temperature notched Izod impact strength and the ductile–brittle transition temperature for $(100 - x - y)\%$ nylon 6 + $x\%$ EPR-g-MA/$y\%$ EPDM-g-SAN blends. The total rubber content is constant at 22.5%, i.e., $x + 0.5 y = 22.5$.

as low as $-12°C$, over a narrow composition region where SEBS-g-MA comprises about 60–90% of the total rubber. Table VI summarizes other mechanical properties of the blends. The dispersion of ABS was not improved by addition of SEBS-g-MA until it comprised about two-thirds of the total rubber (see Fig. 15); this improvement could be the result of the increased melt matrix viscosity due to the graft reaction as mentioned earlier. When the particle size distribution of the ABS and SEBS-g-MA domains falls within the useful range for toughening nylon 6, the blends tend to be toughened. These results show that these maleated elastomers can have some limited ability to lead to toughened nylon 6/ABS compositions even though there is no obvious interfacial compatibilization involved. These materials most likely are acting as co-impact modifiers and dispersants through rheological mechanisms.

CONCLUSION

Proper dispersion of impact modifiers in nylon 6, and other polymers, is critical for toughening. Most impact modifiers lack adequate physical interaction with nylon 6 to achieve the desired dispersion and, hence, require chemical modification (e.g., grafted MA) or use of a third component. Usually, this third component is a compatibilizer that is needed only in relatively small quantities. Such compatibilizers are often block or graft copolymers that locate at
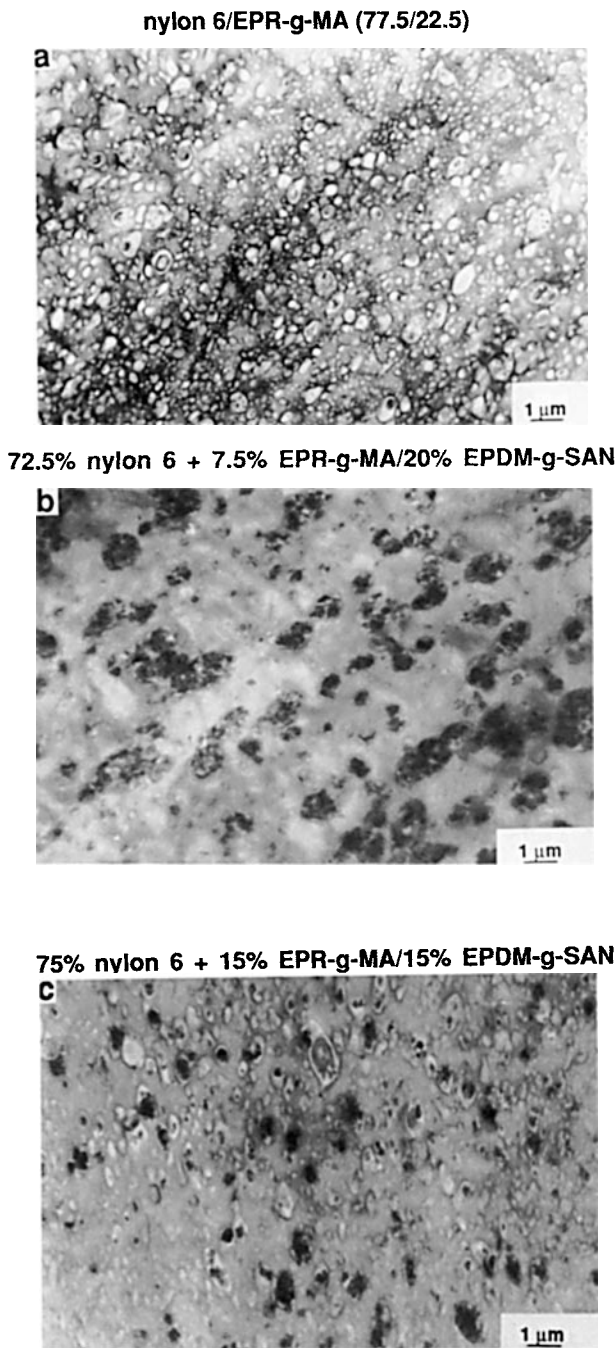
nylon 6/EPR-g-MA (77.5/22.5)

72.5% nylon 6 + 7.5% EPR-g-MA/20% EPDM-g-SAN

75% nylon 6 + 15% EPR-g-MA/15% EPDM-g-SAN

Figure 7 TEM photomicrographs of nylon 6 blends containing 22.5% rubber: (a) 77.5% nylon 6/22.5% EPR-g-MA; (b) 72.5% nylon 6 + 7.5% EPR-g-MA/17.5% EPDM-g-SAN; (c) 75% nylon 6 + 15% EPR-g-MA/15% EPDM-g-SAN. All samples were stained by RuO_4.

the interface between phases, owing to the miscibility of their different segments with these components, that assists the dispersion of the rubber phase and strengthens the interface. It is useful to call this "interfacial compatibilization" as sche-
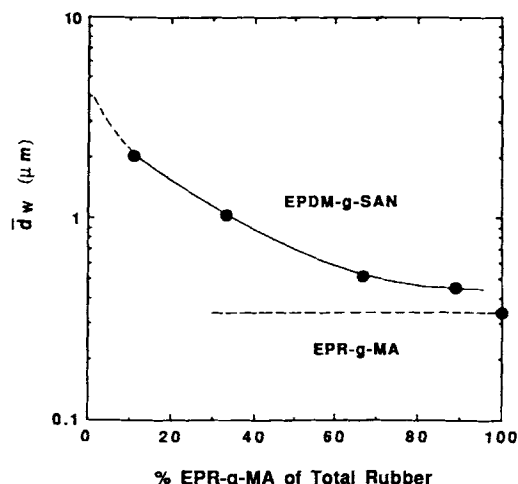
Figure 8 Effect of EPR-g-MA fraction of total rubber on particle size in $(100 - x - y)\%$ nylon 6 + $x\%$ EPR-g-MA/$y\%$ EPDM-g-SAN blends. When % EPR-g-MA approaches zero, the EPDM-g-SAN phase tends to be co-continuous with the nylon 6 phase with a domain dimension of about 5 μm.

matically illustrated in Figure 16(a). Sometimes, a third component may produce similar results without functioning by this interfacial mechanism. Here, we have considered combinations of materials, in blends with nylon 6, where both additives contain rubber phases and might be regarded as impact modifiers. In principle, the two materials could have no interaction with each other when blended with
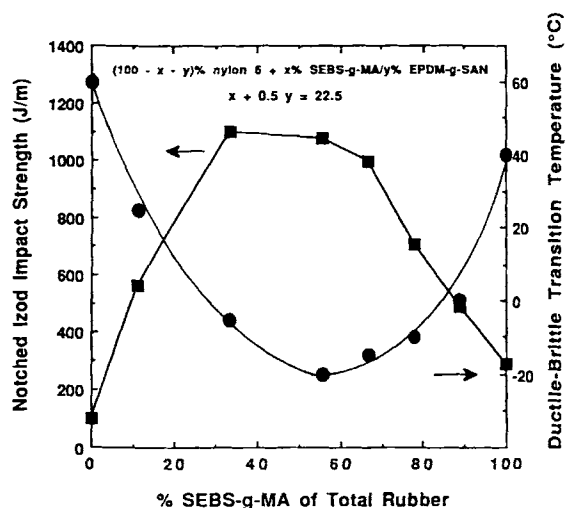

Figure 9 Effect of SEBS-g-MA fraction of total rubber on room temperature notched Izod impact strength and the ductile–brittle transition temperature for $(100 - x - y)\%$ nylon 6 + $x\%$ SEBS-g-MA/$y\%$ EPDM-g-SAN blends. The total rubber content is constant at 22.5%, i.e., $x + 0.5y = 22.5$.
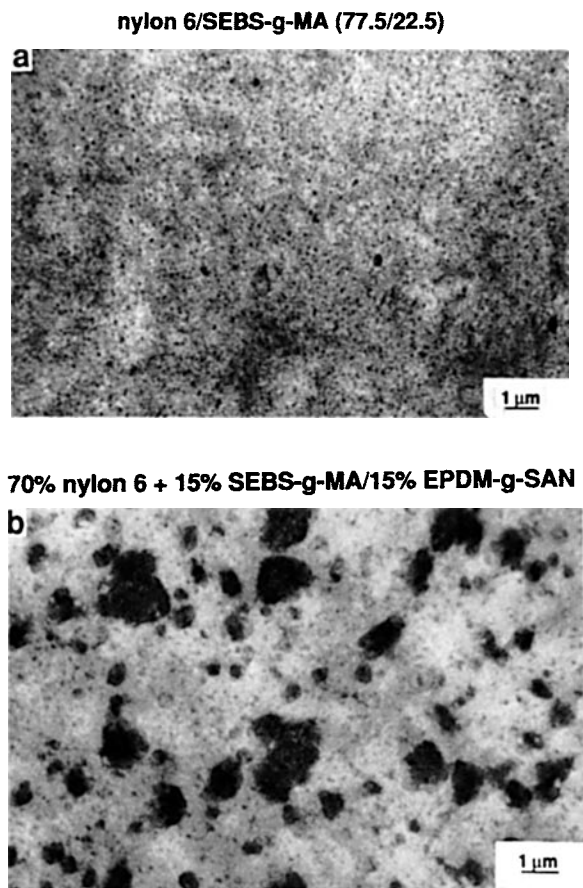
nylon 6/SEBS-g-MA (77.5/22.5)

70% nylon 6 + 15% SEBS-g-MA/15% EPDM-g-SAN

Figure 10 TEM photomicrographs of nylon 6 blends containing 22.5% rubber: (a) 77.5% nylon 6/22.5% SEBS-g-MA; (b) 70% nylon 6 + 15% SEBS-g-MA/15% EPDM-g-SAN. Both samples were stained by RuO_4.

Figure 11 Effect of SEBS-g-MA fraction of total rubber on particle size in $(100 - x - y)\%$ nylon 6 + $x\%$ SEBS-g-MA/$y\%$ EPDM-g-SAN blends. When % SEBS-g-MA approaches zero, the EPDM-g-SAN phase tends to be cocontinuous with the nylon 6 phase with a domain dimension of about 5 μm.

The IA serves as a very effective interfacial compatibilizer for nylon 6/ABS blends because it is miscible with SAN and reacts with nylon 6. However, it is not very effective for dispersing EPDM-g-SAN into nylon 6 or for achieving toughened materials. The free and grafted SAN copolymer chains form the continuous phase in ABS that allows IA chains dissolved in the SAN phase to have good ac-

the matrix and perform as independent impact modifiers as suggested by Figure 16(b). However, the two impact modifiers can influence the phase morphology of each other by at least three different mechanisms. First, physical interactions between the two dispersed phases can occur that amount to the same type of compatibilization suggested in Figure 16(a). Second, one of the additives, particularly when it reacts with the matrix, can increase the effective melt viscosity thereby raising the stresses, during processing, on the other dispersed phase leading to an increased rate of drop break-up.[30] Finally, this component may retard the process of coalescence[31,32] of particles of the other phase by reducing the frequency of collision of particles of the same type with each other during processing. The net result in all cases can be beneficial improvements in dispersion. As a result, different morphologies may result when the two impact modifiers are combined as suggested in Figure 16(c).
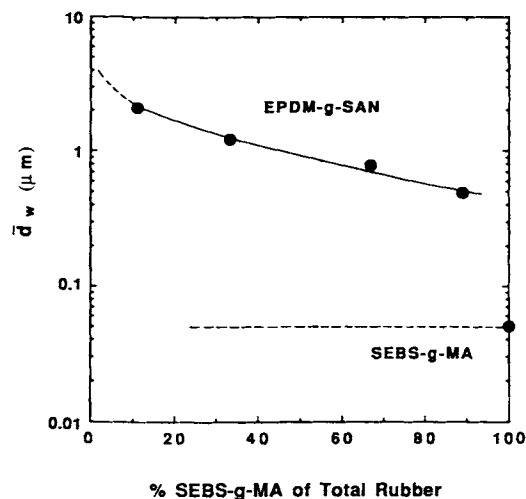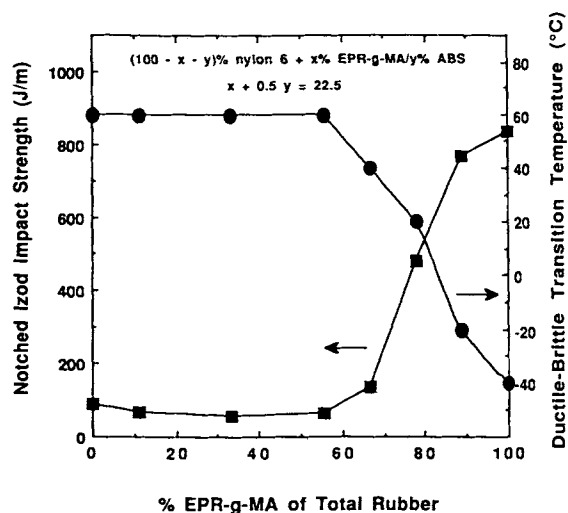

Figure 12 Effect of EPR-g-MA fraction of total rubber on room temperature notched Izod impact strength and ductile-brittle transition temperature for $(100 - x - y)\%$ nylon 6 + $x\%$ EPR-g-MA/$y\%$ ABS blends. The total rubber content is constant at 22.5%.

Table VI   Room Temperature Mechanical Properties of Nylon 6 + EPR-*g*-MA/ABS Blends

Composition			% EPR-*g*-MA of Total Rubber	Yield Stress (MPa)	Modulus (GPa)	Break Strain (%)	Izod Impact (J/m)	Ductile–Brittle Transition Temperature (°C)
Nylon 6	EPR-*g*-MA	ABS						
55	0	45	0	39.6	1.74	25	90	60
57.5	2.5	40	11.1	35.3	1.51	10	70	60
62.5	7.5	30	33.3	40.1	1.74	20	60	60
67.5	12.5	20	55.6	41.2	1.75	10	70	60
70	15	15	66.7	40.0	1.72	20	140	40
72.5	17.5	10	77.8	42.5	1.82	20	480	20
75	20	5	88.9	44.7	1.88	30	770	−20
77.5	22.5	0	100	40.3	1.48	230	840	−40

ABS was mixed with EPR-*g*-MA first followed by blending with nylon 6 in a second extrusion step as indicated by the + sign.

cess to react with nylon 6 at the polyamide–ABS interface. On the other hand, the EPDM is the continuous phase in EPDM-*g*-SAN that makes it more difficult for IA to reach the dispersed SAN phase or

to react with nylon 6 at the polyamide/EPDM-*g*-SAN interface, even if it is dissolved in the SAN phase. Thus, the effectiveness of the IA as a compatibilizer for EPDM-*g*-SAN/nylon 6 blends is limited as demonstrated by the poor low temperature toughness obtained.

Because the continuous EPDM phase in EPDM-*g*-SAN will tend to form interfaces with nylon 6 during blending rather than the SAN, a third component that can react with nylon 6 but physically interact with the EPDM phase was considered. Both EPR-*g*-MA and SEBS-*g*-MA have hydrocarbon segments that are similar to the EPDM phase of EPDM-*g*-SAN, which may provide some degree of
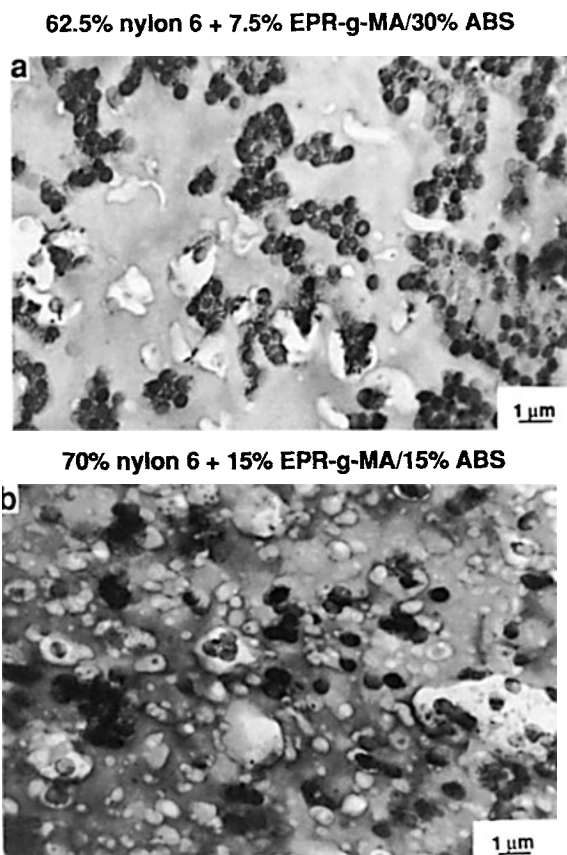
62.5% nylon 6 + 7.5% EPR-g-MA/30% ABS

70% nylon 6 + 15% EPR-g-MA/15% ABS

Figure 13   TEM photomicrographs of nylon 6 blends containing 22.5% rubber: (a) 62.5% nylon 6 + 7.5% EPR-*g*-MA/30% ABS; (b) 70% nylon 6 + 15% EPR-*g*-MA/15% ABS. Both samples were double stained by RuO₄ and OsO₄.
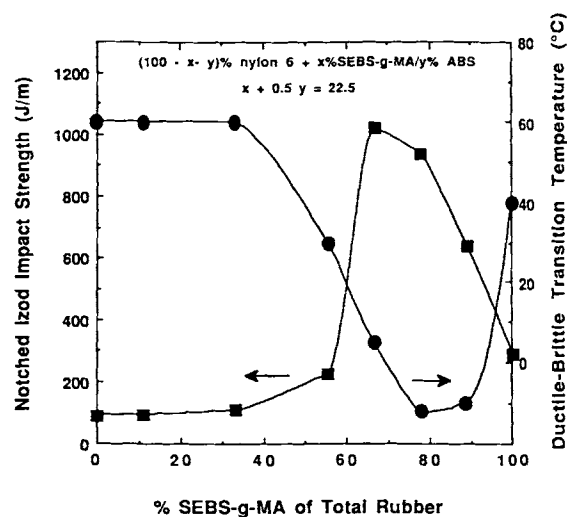

Figure 14   Effect of SEBS-*g*-MA fraction of total rubber on room temperature notched Izod impact strength and the ductile–brittle transition temperature for (100 − *x* − *y*)% nylon 6 + *x*% SEBS-*g*-MA/*y*% ABS blends. The total rubber content is constant at 22.5%.

Table VII   Room Temperature Mechanical Properties of Nylon 6 + SEBS-_g_-MA/ABS Blends

Composition			% SEBS-_g_-MA of Total Rubber	Yield Stress (MPa)	Modulus (GPa)	Break Strain (%)	Izod Impact (J/m)	Ductile–Brittle Transition Temperature (°C)
Nylon 6	SEBS-_g_-MA	ABS						
55	0	45	0	39.6	1.74	25	90	60
57.5	2.5	40	11.1	35.0	1.52	30	95	60
62.5	7.5	30	33.3	39.6	1.70	60	110	60
67.5	12.5	20	55.6	40.5	1.65	240	230	30
70	15	15	66.7	41.4	1.72	250	1020	5
72.5	17.5	10	77.8	44.3	1.82	250	940	−12
75	20	5	88.9	44.0	1.82	220	640	−10
77.5	22.5	0	100	46.9	1.86	190	290	40

ABS was mixed with SEBS-_g_-MA first followed by blending with nylon 6 in a second extrusion step as indicated by the + sign.

compatibility. The addition of EPR-_g_-MA or SEBS-_g_-MA to nylon 6/EPDM-_g_-SAN blends significantly improved toughness even at relatively low

62.5% nylon 6 + 7.5% SEBS-g-MA/30% ABS

70% nylon 6 + 15% SEBS-g-MA/15% ABS

Figure 15   TEM photomicrographs of nylon 6 blends containing 22.5% rubber: (a) 62.5% nylon 6 + 7.5% SEBS-_g_-MA/30% ABS; (b) 70% nylon 6 + 15% SEBS-_g_-MA/15% ABS. Both samples were stained by RuO₄.

temperatures. While the EPR-_g_-MA and SEBS-_g_-MA can be regarded as co-impact modifiers, they also serve to substantially improve the dispersion of EPDM-_g_-SAN in the nylon 6 matrix. These maleated elastomers did not produce equally beneficial results for nylon 6/ABS blends because the SAN
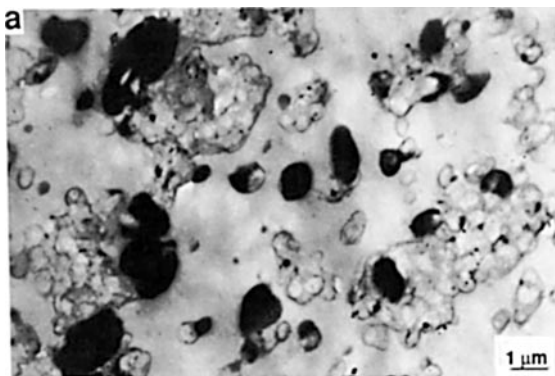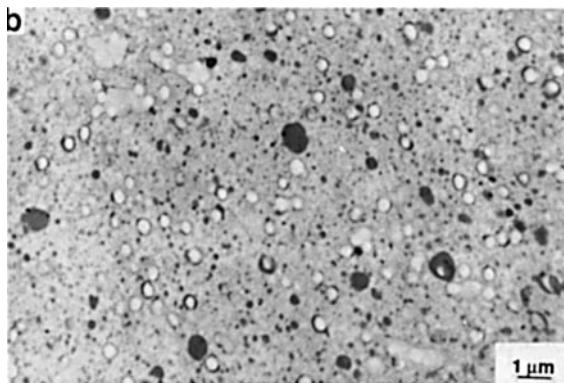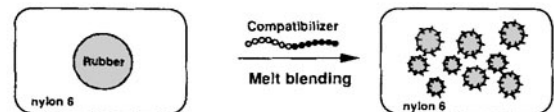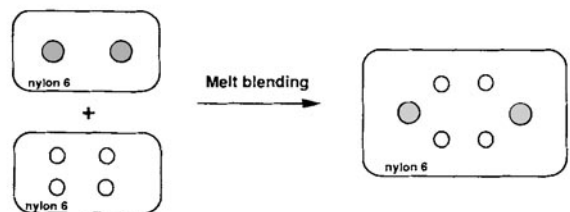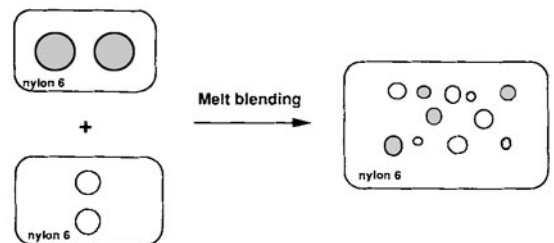

Figure 16   Schematic illustration of three modes of dispersing elastomer phases in a nylon 6 matrix: (a) interfacial compatibilization; (b) independent co-impact modifiers; (c) dual impact modifiers with morphological interaction.

forms the continuous phase in ABS and it has poor physical compatibility with EPR-g-MA or SEBS-g-MA so that interfacial compatibilization is unlikely. However, the presence of these maleated elastomers do have some effect on the degree of ABS dispersion due to a rheological mechanism [see Fig. 16(c)].

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