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Morphology and mechanical properties of compatibilized nylon 6/polyethylene blends

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Abstract

Blends of nylon 6 and polyethylene were investigated over a range of compositions. The polyethylenes used were grafted with maleic anhydride and, thus, have the potential to react with the amine end groups of nylon 6 during melt processing. This study focuses on the effects of the concentration, viscosity and functionality of the maleated polyethylenes (PE-g-MA) on the rheological, morphological, and mechanical properties of nylon 6/PE-g-MA blends. The impact properties of these blends are strongly influenced by the amount and type of maleated polyethylene used. A low viscosity maleated polyethylene was shown to be ineffective in toughening nylon 6; this was because of the propensity of polyethylene to become continuous even when nylon 6 was the majority component. Two higher viscosity maleated polyethylenes were able to produce blends with high impact strength and excellent low temperature toughness over a range of compositions. It was demonstrated that polyethylene materials containing a very low degree of anhydride functionality can generate blends with excellent impact properties. A brief portion of this study focused on ternary blends of nylon 6, maleated polyethylene and nonmaleated polyethylene; in general, the impact properties of these blends improved as the nylon 6 molecular weight increased and as the ratio of maleated polyethylene to nonmaleated polyethylene increased.

Keywords: Nylon 6; Polyethylene; Blends

1. Introduction

Polymer blends offer means to achieve property combinations generally not available in any single polymeric material [1,2]. However, immiscible blends often exhibit poor mechanical properties and have an unstable phase morphology during melt processing. These problems of incompatibility can generally be remedied by incorporating an appropriate block or graft copolymer which preferentially resides at the polymer–polymer interfaces [3–7]. The appropriate selection of a compatibilizer can promote a stable, fine distribution of the dispersed phase within the matrix phase by reducing the interfacial tension between the blend components [8–11] and retarding dispersed phase coalescence via steric stabilization [12–16]. Such compatibilizers may be formed in-situ during melt processing, i.e. reactive compatibilization; this also serves to physically connect the two phases through covalent bonding, which improves the interfacial adhesion between the blend components [5,17,18].

There is a body of literature describing tough polyamide blends with various hydrocarbon elastomers [8,15,19–33] and polyolefins [34–50] to which maleic anhydride was grafted; the anhydride units react readily with the amine end groups of the polyamide to form block or graft copolymers. Compatibilized polyamide/polyethylene blends are of particular interest. Polyamides generally exhibit good strength and resistance to hydrocarbon solvents, while polyethylene contributes low temperature toughness and low moisture sorption.

Several studies of compatibilization of polyamide/polyethylene blends through grafting of maleic anhydride onto the polyethylene phase were reported [34–39]. It was demonstrated that the use of maleic anhydride grafted polyethylenes can dramatically improve the impact strength and reduce the dispersed phase dimensions in these blends. The morphology and properties of these blends were shown to be a function of the ratio of reactive (maleated) to nonreactive polyethylene, the anhydride content, and the composition and viscosity of the blend components.

This paper describes the effects of the concentration, melt viscosity and functionality of a series of maleated polyethylenes (PE-g-MA) on the rheological, morphological, and mechanical properties of nylon 6/PE-g-MA blends. A

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Table 1
Nylon 6 materials used in this study

Designation	$\bar{M}_n$	End group content (μeq g^{-1})	Brabender torque[a] (N m)	Source
Ultramid B0	13 200	[COOH] = 74.2 [NH_2] = 77.0	1.8	BASF Corp.
Ultramid B2	19 400	[COOH] = 48.5 [NH_2] = 54.0	4.3	BASF Corp.
Capron 8207F	22 000	[COOH] = 43.0 [NH_2] = 47.9	7.3	AlliedSignal Inc.
Capron 8209F	29 300	[COOH] = 28.8 [NH_2] = 34.8	10.0	AlliedSignal Inc.
Ultramid B5	37 300	[COOH] = 23.8 [NH_2] = 28.1	16.2	BASF Corp.

[a] Brabender torque measured at 240°C and 60 rev min^{-1} after 10 min.

Table 2
Polyethylenes used in this study

Commercial designation	PE type	Designation used here	Melt index	Brabender torque (N m[a])	wt% MA	Source
MB110	LLDPE	L-PE(0.9% MA)	30	1.5	0.9	DuPont
MB158	LLDPE	H-PE(0.3% MA)	1.5	4.5	0.3	DuPont
MB226	LLDPE	H-PE(0.9% MA)	1.5	5.9	0.9	DuPont
14B3	LLDPE	H-PE(0%MA)	1.85	8.9	0	Novacor

[a] min^{-1} after 10 min.

portion of this work focuses on ternary blends that include nonreactive polyethylene as a third component. It is demonstrated that low melt viscosity PE-g-MA materials have a limited capacity to toughen nylon 6 resulting from the propensity of the polyethylene to become the continuous phase; whereas, higher viscosity PE-g-MA materials can generate blends with excellent low temperature toughness provided the content of the polyethylene phase is sufficient. For ternary blends, it is shown that increasing the ratio of PE-g-MA to nonreactive polyethylene and increasing the molecular weight of the nylon 6 matrix improves the impact strength of these blends.

2. Experimental

Table 1 summarizes the characteristics of the polyamide materials used in this study, each of which has nearly equivalent amounts of carboxyl and amine end groups. The nylon 6 materials with molecular weights of 22 000

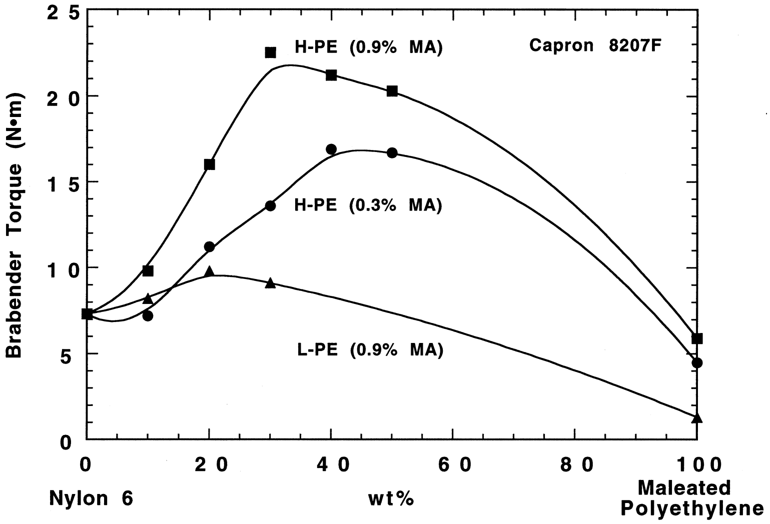


Fig. 1. Brabender torque of blends of nylon 6 (Capron 8207F) with various maleated polyethylenes. Torque readings were taken after 10 min at 240°C and 60 rev min^{-1}.

and 29 300 are commercially available and were used as the basis for most of this work. Some higher and lower molecular weight experimental grades were used for selected experiments. Prior to each processing step, all polyamide-containing materials were dried in a vacuum oven for at least 16 h at 80°C to remove sorbed water.

Pertinent information about four linear low density polyethylene, LLDPE, commercial products used here are shown in Table 2. These polyethylenes can be divided into two groups based on their melt flow characteristics; the product with low molecular weight is designated as L-PE, while those with higher molecular weights are designated as H-PE. Among the maleated LLDPE materials, L-PE(0.9%MA) and H-PE(0.9%MA) have an equivalent anhydride content but different melt flow characteristics; whereas, H-PE(0.3%MA) and H-PE(0.9%MA) have similar melt flow characteristics but different anhydride contents. Using this series of maleated polyethylenes permits independent assessment of the effects of melt viscosity and functionality on blend properties. Prior to processing, these polyethylene materials were dried in a convection oven under the same conditions as the nylon 6 materials.

Blends were prepared by simultaneously extruding all components in a Killion single screw extruder (L/D = 30, 2.54 cm diameter) at 240°C using a screw speed of 40 rpm. The extrudate was then dried in a vacuum oven and injection molded into 0.318 cm thick Izod impact (ASTM D256) and tensile (ASTM D638 type 1) specimens using an Arburg Allrounder injection molding machine. Notched Izod impact measurements were made using a TMI pendulum-type impact machine equipped with an insulated chamber for heating and cooling the specimens. Tensile testing of dry as-molded specimens was done using an Instron at a crosshead speed of 0.508 cm min^{-1} for modulus and yield strength measurements and 5.08 cm min^{-1} for elongation at break. Rheological measurements were made by melt mixing the various polymers in a Brabender torque rheometer with a 50 cm mixing head and standard rotors, operated at 240°C and 60 rpm. The dynamic mechanical properties of injection molded specimens were determined by a Polymer Laboratories DMTA operating at a frequency of 1 Hz.

Blend morphology was examined using a JEOL 200CX transmission electron microscope operating at an accelerating voltage of 120 W. Ultrathin sections (10–20 nm) were cut from Izod bars perpendicular to the flow direction using a Reichert–Jung Ultracut E microtome under cryogenic conditions (−80°C). The sections were exposed to a 2% aqueous solution of phosphotungstic acid to stain the polyamide phase. Effective particle diameters of the dispersed phase were determined from TEM photomicrographs by digital image analysis using NIH Image software.

3. Properties of nylon 6/maleated polyethylene blends

The molecular weight of nylon 6 is an important variable in determining the properties of its blends, largely affecting the viscosity and morphology of the blend, as well as elements of crystallinity and intrinsic toughness. In this section, we describe the properties of blends of nylon 6 with maleated polyethylenes. One of these materials (Capron 8207F) has a number average molecular weight of 22 000 while the other (Capron 8209F) has a number average molecular weight of 29 300. In a later section, we will explore the properties of ternary blends of nylon 6, polyethylene, and maleated polyethylene using a broad range of nylon 6 molecular weights.

3.1. Capron 8207F based blends

The influences of composition, melt viscosity, and functionality of the maleated polyethylene on properties of blends with nylon 6 having $\overline{M}_n = 22\,000$ are described here. Fig. 1 shows rheological characterization of blends

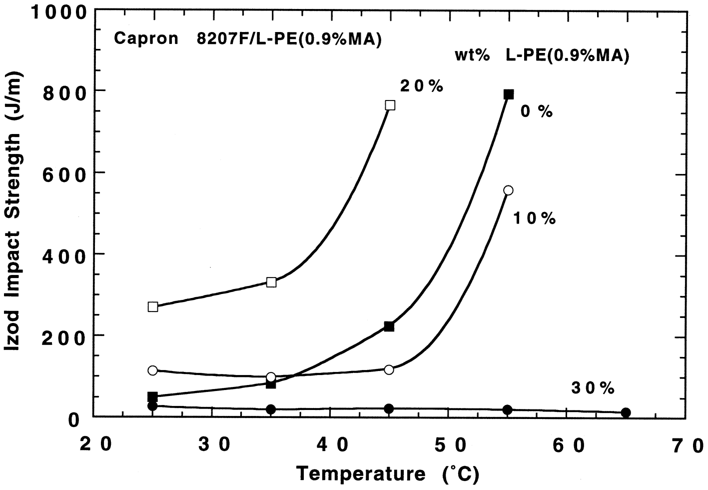
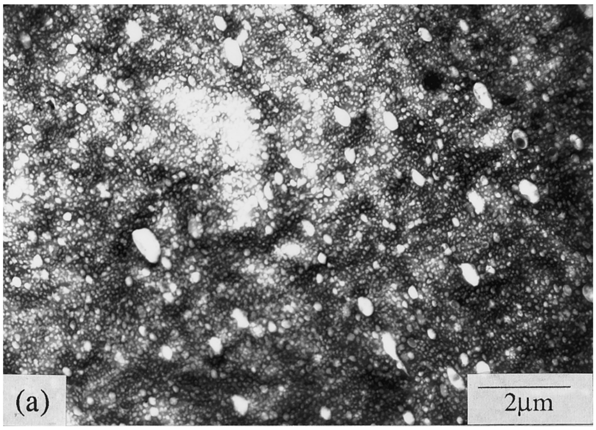
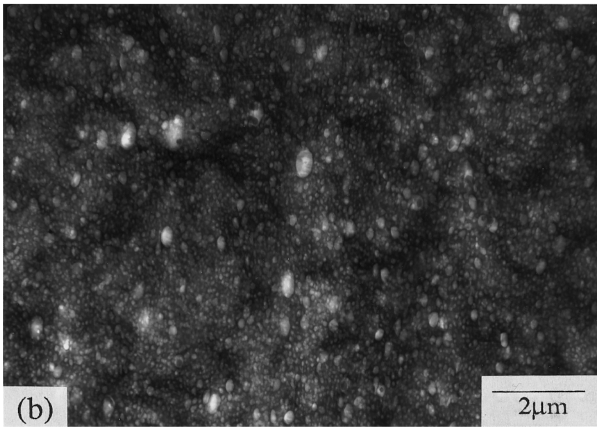


Fig. 2. Effect of temperature on the Izod impact strength of blends of Capron 8207F and L-PE(0.9%MA). This maleated linear low density polyethylene has a low melt viscosity and a high anhydride content.

90/10 Capron 8207F/L-PE(0.9%MA)



80/20 Capron 8207F/L-PE(0.9%MA)



70/30 Capron 8207F/L-PE(0.9%MA)

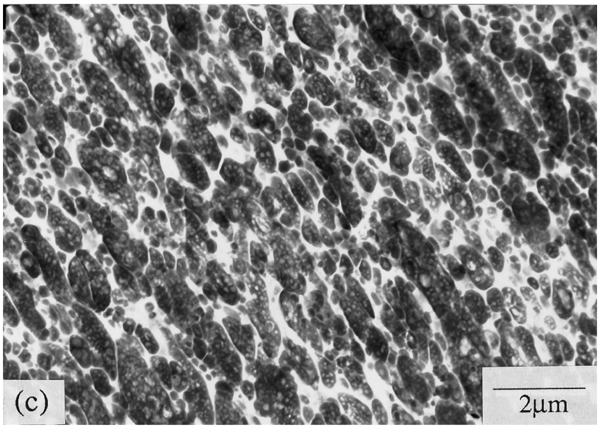


Fig. 3. TEM photomicrographs of blends of Capron 8207F and L-PE(0.9%MA) containing the following amounts of maleated linear low density polyethylene: (a) 10%; (b) 20%; and (c) 30%. The polyamide phase is stained dark by phosphotungstic acid (PTA).

of this nylon 6 with various maleated polyethylenes as a function of blend composition; each of the blends has a higher Brabender torque than either of the blend components which is evidence that grafting reactions occur. A comparison of the blends containing high viscosity polyethylenes shows that the Brabender torque is higher for blends based on the polyethylene with the higher anhydride content, i.e. the higher functionality results in a higher degree of grafting during processing. A comparison of blends based on polyethylenes with the same degree of anhydride functionality but different melt viscosities reveals a substantially larger Brabender torque for the blends containing the higher viscosity polyethylene. A somewhat larger torque is expected based on the physical consideration of mixture additivity of viscosity; however, the increment in torque is larger than can be rationalized on this basis. It is speculated that the extent of grafting is greater when the two pure phases become nearly matched in melt viscosity since this will tend, just on physical grounds, to lead to a finer dispersion or more surface area where grafting can occur.

The Izod impact strength for blends of varying L-PE(0.9%MA) content are shown in Fig. 2 as a function of temperature. The neat nylon 6 is brittle at room temperature and does not become tough until the temperature is raised above its T_g, approximately 50°C. Incorporation of 10 wt% of this polyethylene has a minor effect on impact properties; these blends have a slightly higher impact strength than the neat nylon 6 at room temperature but are less tough at higher temperatures. Blends containing 20 wt% of this maleated polyethylene have somewhat improved impact strength, but this blend is still not in the super tough range ($\backsim$800 J m^{-1}) until the temperature is raised to about 45°C. When the maleated polyethylene content is increased to 30%, the blend is brittle over the whole temperature range.

Clearly, the morphology generated during melt processing will influence the impact behavior of these blends. The TEM photomicrographs in Fig. 3 reveal that when these blends contain 10 or 20 wt% of the maleated polyethylene, the polyethylene phase is well-dispersed as small ($\backsim$0.1–0.2 μm) particles within the nylon 6 matrix. However, when the maleated polyethylene content is increased to 30%, polyethylene becomes the continuous phase with large globules of nylon 6 contained within it. This phase inversion causes the impact properties to become much poorer. It was demonstrated for other systems that the component with the lower melt viscosity tends to encapsulate the more viscous phase [42,51]; mismatch in the melt viscosities of the components can cause the minor component to become the continuous phase. This certainly appears to be the case here; Fig. 1 demonstrates the Brabender torque of the nylon 6 is more than four-fold larger than that of this maleated polyethylene. Further effects of component rheology on phase morphology are discussed in a later section.

The influence of polyethylene viscosity on blend impact properties can be explored by comparing the blends described previously with corresponding blends containing H-PE(0.9%MA); this maleated polyethylene has a higher viscosity, but the same degree of functionality, as LPE(0.9%MA). Fig. 4 shows the influence of polyethylene content on room temperature impact strength (part a) and

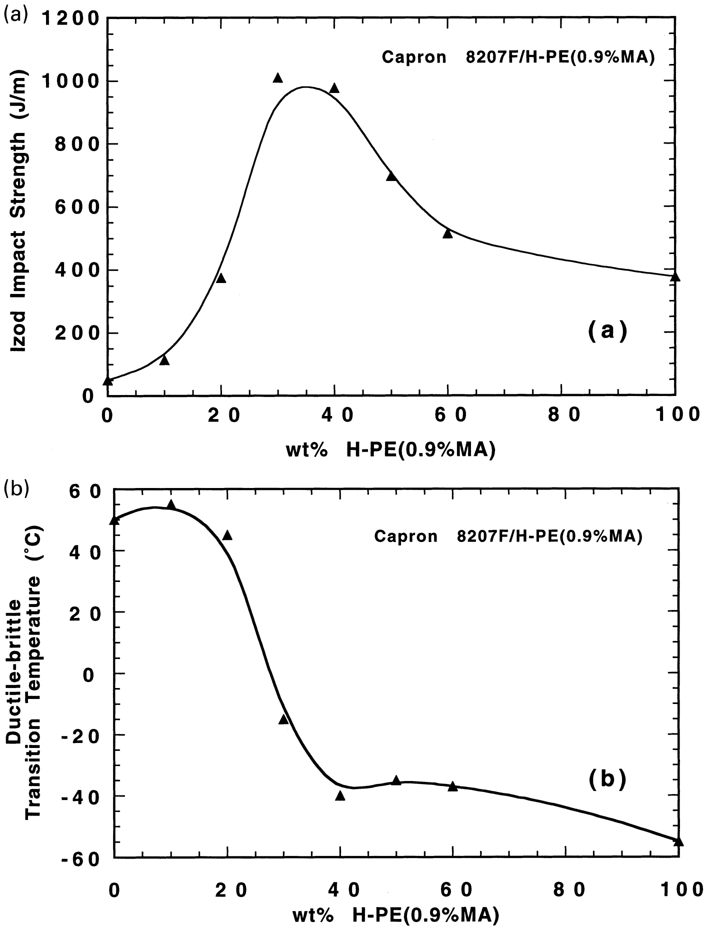
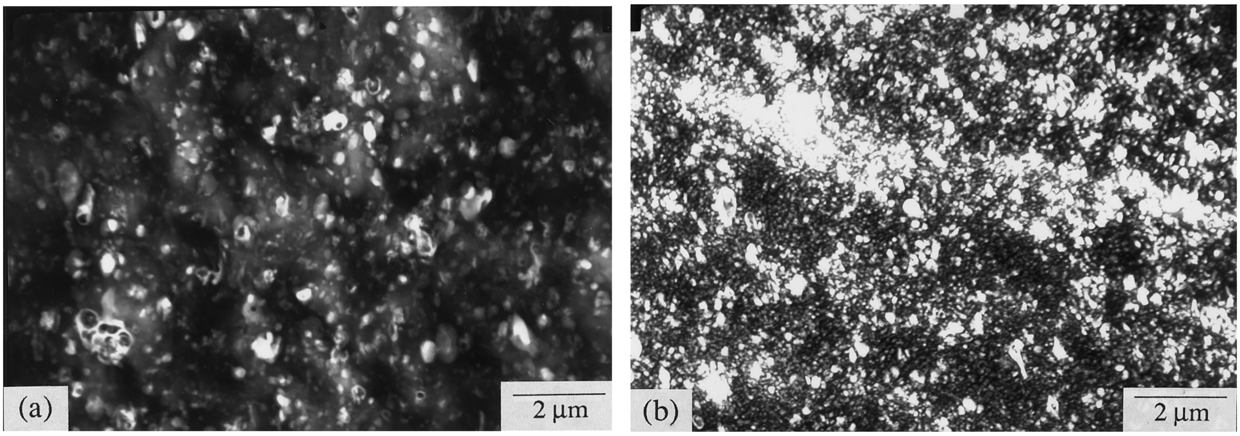


Fig. 4. Impact properties of blends of Capron 8207F and H-PE(0.9%MA): (a) Room temperature Izod impact strength; and (b) ductile–brittle transition temperature. This maleated linear low density polyethylene has a high melt viscosity and a high anhydride content.

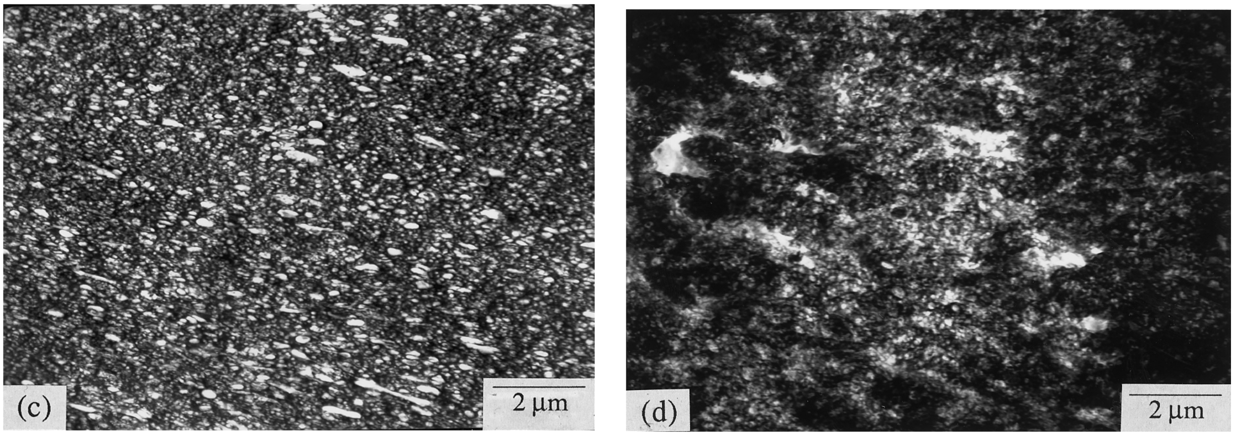
ductile–brittle transition temperature (part b) for blends of nylon 6 with H-PE(0.9%MA). Incorporation of less than 20% of this maleated polyethylene generates no significant improvement in toughness, which is similar to the trend seen with blends containing L-PE(0.9%MA). However, when the maleated polyethylene content is increased to 30%, the impact strength improves markedly and the ductile–brittle transition is reduced by more than 50°C. Further increase in the polyethylene content of the blend reduces the impact strength, while the ductile–brittle transition temperature remains relatively constant over the range of 40–60 wt% polyethylene. The influence of composition on room temperature impact strength can be explained in terms of stress–strain properties and will be described in more detail later.

Resulting from differences in polyethylene viscosity, there are significant differences in morphology between the blends represented in Fig. 2 and Fig. 4. TEM photomicrographs of the blends of nylon 6 with H-PE(0.9%MA) are shown in Fig. 5. Blends containing 10 wt% of this maleated polyethylene [see Fig. 5(a)] contain particles much more complex in shape that those of L-PE(0.9%MA). This may be attributed to the greater extent of grafting postulated earlier. The onset of high toughness appears to correspond to the point where the polyethylene phase becomes elongated in nature [see Fig. 5(c)], which marks the onset of co-continuity of this phase. As expected, the polyethylene phase tends to become more continuous as its content in the blend is increased and clearly is the continuous phase when it comprises 60 wt% of the blend. As the polyethylene phase becomes more continuous, the impact strength is reduced.

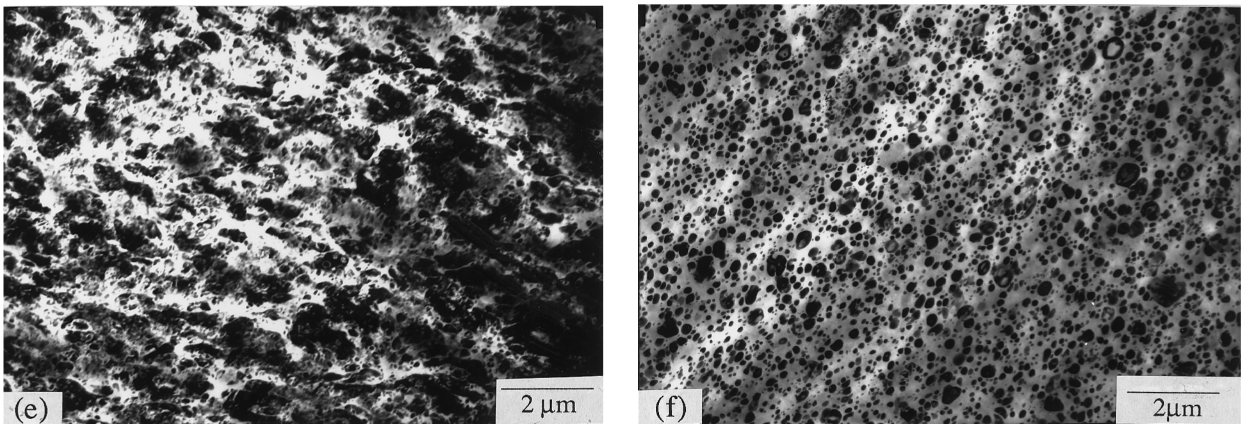
It was demonstrated earlier that the anhydride content of the polyethylene phase largely affects blend viscosity, even when the polyethylenes themselves have similar rheological characteristics. To determine whether these differences in polyethylene functionality also influence blend impact properties, blends of nylon 6 with H-PE(0.3%MA) were prepared; this maleated polyethylene has a lower degree of functionality but similar melt viscosity relative to H-PE(0.9%MA). The effects of blend composition on room temperature impact strength and ductile–brittle transition temperature of blends of nylon 6 with H-PE(0.3%MA) are shown in Fig. 6(a) and (b), respectively. These blends have low impact strengths and high ductile–brittle transition temperatures when they contain only 10 or 20 wt%


90/10 Capron 8207F/H-PE(0.9%MA)

80/20 Capron 8207F/H-PE(0.9%MA)


70/30 Capron 8207F/H-PE(0.9%MA)

60/40 Capron 8207F/H-PE(0.9%MA)


50/50 Capron 8207F/H-PE(0.9%MA)

40/60 Capron 8207F/H-PE(0.9%MA)

Fig. 5. TEM photomicrographs of blends of Capron 8207F and H-PE(0.9%MA) containing the following amounts of H-PE(0.9%MA): (a) 10%; (b) 20%; (c) 30%; (d) 40%; (e) 50%; and (f) 60%. The polyamide phase is stained dark by PTA.

maleated polyethylene. As the maleated polyethylene content is increased from 20 to 30 wt%, there is a significant improvement in impact strength at room temperature and at low temperatures; this is the same composition at which impact properties improve in the corresponding blends based on H-PE(0.9%MA). In these blends, the ductile–brittle transition temperature generally decreases with increasing H-PE(0.3%MA) content. At polyethylene contents higher than 30 wt%, the improvements in low temperature toughness are accompanied by a reduction in room temperature impact strength. These results demonstrate that a very small amount of grafted maleic anhydride

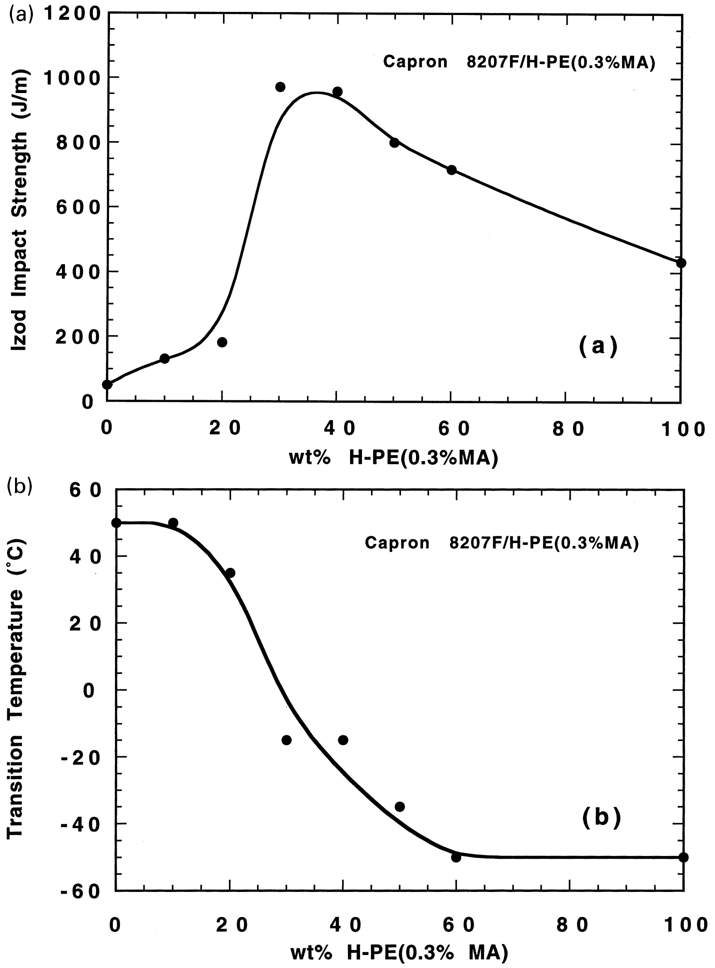


Fig. 6. Impact properties of blends of Capron 8207F and H-PE(0.3%MA): (a) Room temperature Izod impact strength; and (b) ductile–brittle transition temperature. This maleated linear low density polyethylene has a high melt viscosity and a low anhydride content.

is sufficient to generate super tough nylon 6/polyethylene blends. It is important to note that the blends shown in Fig. 6 have very similar impact properties as blends containing the more highly maleated polyethylene shown in Fig. 4, yet these blends have a much lower melt viscosity as judged by Brabender torque (see Fig. 1). This demonstrates that it is possible to obtain relatively low melt viscosities in these blend systems without a significant sacrifice in impact strength.

Fig. 7 shows TEM photomicrographs of the blends whose properties are depicted in Fig. 6. At low H-PE(0.3%MA) contents, the polyethylene particles appear to be larger than in corresponding blends containing H-PE(0.9%MA). These larger polyethylene particles are a consequence of the low functionality of H-PE(0.3%MA). At higher H-PE(0.3%MA) concentrations, the relationship between blend morphology and impact strength is quite similar to that of blends of nylon 6 with H-PE(0.9%MA) described earlier; i.e. the impact strength reaches a maximum when the polyethylene domains are elongated and “fiberlike” in appearance, then declines as the polyethylene phase becomes more continuous. In comparing the micrographs in Fig. 5 and Fig. 7, it is evident that blends based on H-PE(0.3%MA) tend to have polyethylene as the continuous phase at lower polyethylene contents than blends containing H-PE(0.9%MA). This may be attributed to the slightly lower melt viscosity of H-PE(0.3%MA).

Each blend series described in this section shows a continuous decrease in modulus and yield strength as the polyethylene content is increased, see Table 3, the change becomes more dramatic at the point of phase inversion. Some blends based on the high melt viscosity polyethylenes are quite ductile, as indicated by large elongation at break values, when nylon 6 is the continuous phase. For these materials, the extensive plastic deformation leads to high fracture energies despite the low stresses during fracture that result from the low modulus and yield stress. As the polyethylene phase becomes more continuous, the elongation at break decreases as well as the modulus and yield strength, and this combination leads to much reduced impact strength as more polyethylene is incorporated.

3.2. Capron 8209F Based Blends

Many of the same issues described in the previous section

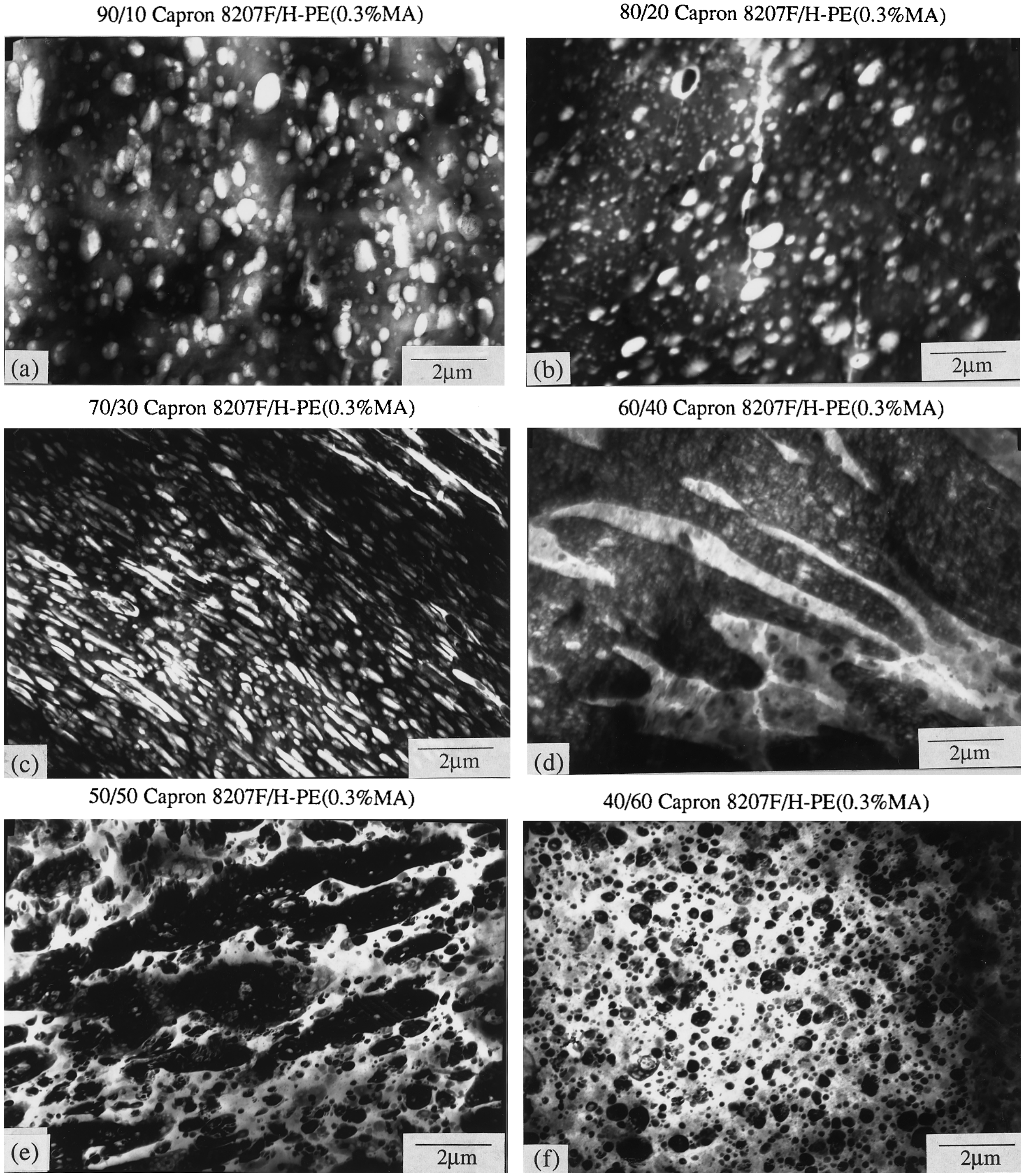


Fig. 7. TEM photomicrographs of blends of Capron 8207F and H-PE(0.3%MA) containing the following amounts of H-PE(0.3%MA): (a) 10%; (b) 20%; (c) 30%; (d) 40%; (e) 50%; and (f) 60%. The polyamide phase is stained dark by PTA.

are explored here for blends of a higher molecular weight nylon 6 ($\overline{M}_n = 29\,300$) with the maleated polyethylenes. The Brabender torque for these blends are shown as a function of composition in Fig. 8. In certain cases, the torque values for blends containing the low viscosity polyethylene L-PE(0.9%MA) are higher than those for corresponding blends using the higher viscosity polyethylene H-PE(0.3%MA). Clearly, the blend melt viscosity is influenced by both the viscosity and functionality of the polyethylene phase; at 10 or 20 wt% polyethylene, the higher functionality of the low viscosity polyethylene increases the melt viscosity to levels higher than that of blends containing a higher viscosity polyethylene with lower functionality.

The neat nylon 6 material described in this section is

Table 3
Tensile properties of nylon 6 (Capron 8207F)/maleated polyethylene blends[a]

Nylon 6/PE blend (wt/wt)	Tensile modulus (GPa)	Yield strength (MPa)	Elongation at break
Capron 8207F/L-PE(0.90%MA)			
100/0	2.59	75.3	31
90/10	1.86	50.8	12
80/20	1.81	50.1	25
70/30	0.67	20.1	3
0/100	0.45	10.0	93
Capron 8207F/H-PE(0.3%MA)			
90/10	2.25	55.4	22
80/20	1.70	50.6	30
70/30	1.49	42.3	122
60/40	1.43	34.5	189
50/50	1.11	28.3	160
40/60	0.78	19.0	113
0/100	0.33	8.8	no break
Capron 8207F/H-PE(0.9%MA)			
90/10	2.29	52.6	75
80/20	2.14	48.4	157
70/30	1.86	41.0	220
60/40	1.43	34.3	81
50/50	0.92	24.5	46
40/60	0.49	15.4	39
0/100	0.25	6.9	no break

[a] min^{-1} for tensile modulus and yield strength, and 5.08 cm min^{-1} for elongation at break.

brittle until its temperature is raised above 50°C. While addition of 10 wt% of L-PE(0.9%MA) leads to a slight improvement in impact properties, the blend is still brittle at room temperature, as seen in Fig. 9. Incorporation of 20 wt% of this maleated polyethylene significantly improves impact strength at room temperature. However, when the polyethylene content is increased to 30% the blends are brittle at all temperatures.

In light of the morphological nature of blends of Capron 8207F with this maleated polyethylene described in the previous section, one could expect similar morphological issues to come into play for the blends described here. The TEM photomicrographs shown in Fig. 10(a) and (b) demonstrate that there are two different populations of polyethylene particles in the blends containing 10 and 20 wt% L-PE(0.9%MA), respectively. Several issues influence morphology generation, e.g. extent of reaction, relative melt viscosity and elasticity of the two phases, processing conditions, etc.; however, the fact that the melt viscosity of this nylon 6 is near seven-fold larger than that of

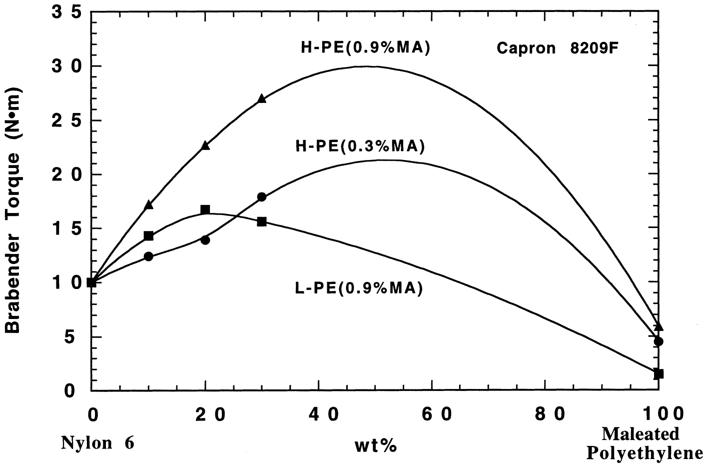


Fig. 8. Brabender torque of blends of nylon 6 (Capron 8209F) with various maleated polyethylenes. Torque readings were taken after 10 min at 24°C and 60 rev min^{-1}.

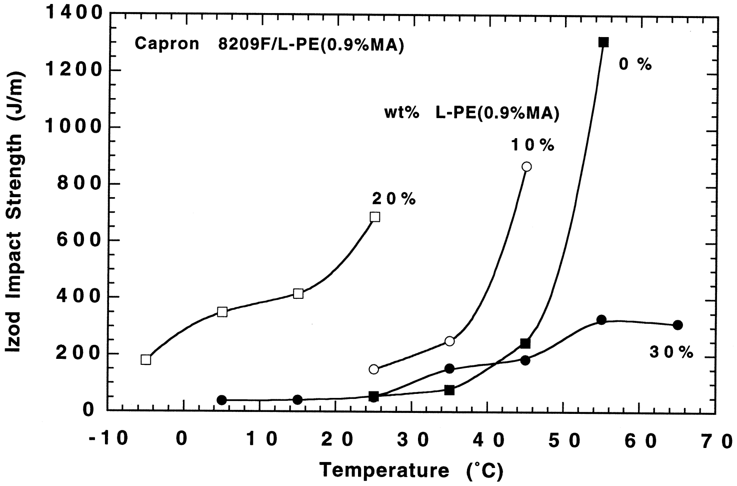


Fig. 9. Effect of temperature on the Izod impact strength of blends of Capron 8209F and L-PE(0.9%MA). This maleated linear low density polyethylene has a low melt viscosity and a high anhydride content.

L-PE(0.9%MA) is a major factor that drives the polyethylene phase to become continuous and to exist in the form of large particles.

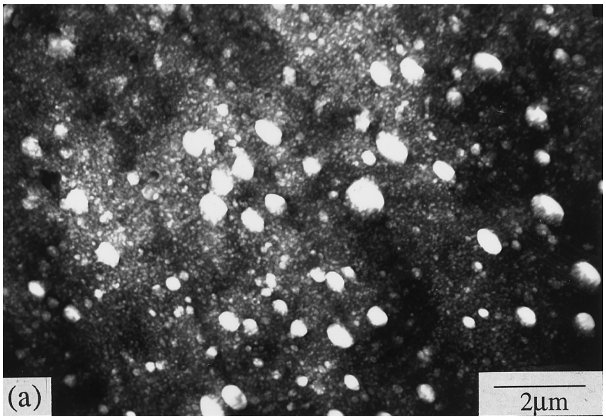
Comparison of the photomicrographs in Fig. 2(a) and (b) and Fig. 10(a) and (b) clearly shows that the polyethylene particles become larger as the nylon 6 melt viscosity is increased. The dispersed phase particles can become either larger or smaller with increasing matrix melt viscosity, depending on how close the blend system is to the point of phase inversion. Normally, one could expect the dispersed polyethylene particles to become smaller with increasing molecular weight of the polyamide matrix resulting from increased rheological stresses on the dispersed phase; this will be demonstrated in a later section. However, in this case, these blends are near the point of phase inversion, and the dispersed phase particles become larger with increasing matrix melt viscosity. At the level of 10 or 20 wt% polyethylene, just prior to the point of phase inversion, this mismatch in viscosity between the two phases causes the polyethylene to form large domains; when the maleated polyethylene content is increased to 30%, polyethylene becomes the continuous phase and the impact properties decrease dramatically.

In blends of nylon 6 with H-PE(0.9%MA), incorporation of the maleated polyethylene leads to an increase in impact strength and improvement of low temperature toughness, as seen in Fig. 11. When 10 wt% maleated polyethylene is added, the ductile–brittle transition is shifted to near room temperature; addition of more polyethylene results in blends which are tough at temperatures below 0°C. The TEM photomicrographs in Fig. 12 demonstrate that the polyethylene forms small, well-dispersed particles in each of these blends. These polyethylene particles are smaller than those in blends based on the corresponding low melt viscosity material, L-PE(0.9%MA). This finer dispersion is no doubt a consequence of the more evenly matched viscosities of these blend components, i.e. the H-PE(0.9%MA) particles have less tendency to become continuous and to form large particles like those shown in Fig. 10(a) and (b).

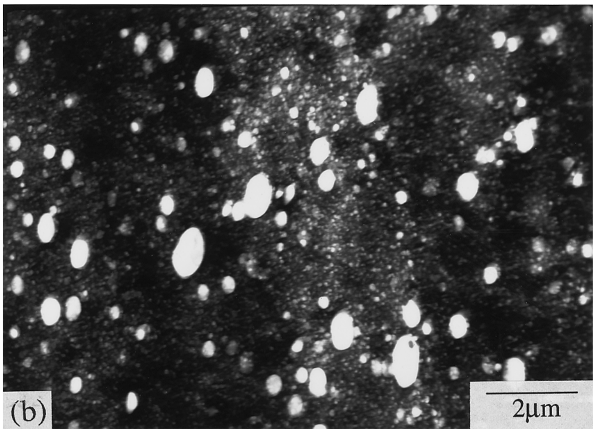
Although these particles are still finely dispersed when the maleated polyethylene content is increased to 30%, the high viscosity of this blend precluded using standard processing conditions; thus the extrusion temperature was increased to 270°C. Since changes in processing temperature affect the rheological character of the blend components and the kinetics of grafting reactions during melt processing, one must compare the morphology of this blend [Fig. 12(c)] to the blends in Fig. 12(a) and (b) with caution.

The high viscosity of blends of this nylon 6 with H-PE(0.9%MA) is certainly unfavorable for ease of processing by injection molding. In the previous section, it was demonstrated that incorporation of a polyethylene with low anhydride functionality, H-PE(0.3%MA), can produce blends with a lower melt viscosity than those based on H-PE(0.9%MA), while achieving similar improvements in impact properties. Here we explore whether blends of the higher molecular weight nylon 6 with H-PE(0.3%MA) can improve toughness to the same extent as the corresponding blends based on H-PE(0.9%MA). The Izod impact strength of blends of nylon 6 with H-PE(0.3%MA) is shown as a function of temperature in Fig. 13. Over the range of blend compositions shown, the changes in impact properties are qualitatively similar to those of the corresponding blends containing H-PE(0.9%MA); as the polyethylene content is increased, the room temperature impact strength increases and the ductile to brittle transition is steadily reduced. However, a comparison of Figs. 11 and 13 demonstrates that this improvement in impact properties is not as large as in blends containing the more highly functional polyethylene. TEM photomicrographs of blends of nylon 6 with H-PE(0.3%MA), shown in Fig. 14, clearly indicate that the reduction in particle size is not as great as in the

90/10 Capron 8209F/L-PE(0.9%MA)



80/20 Capron 8209F/L-PE(0.9%MA)



70/30 Capron 8209F/L-PE(0.9%MA)

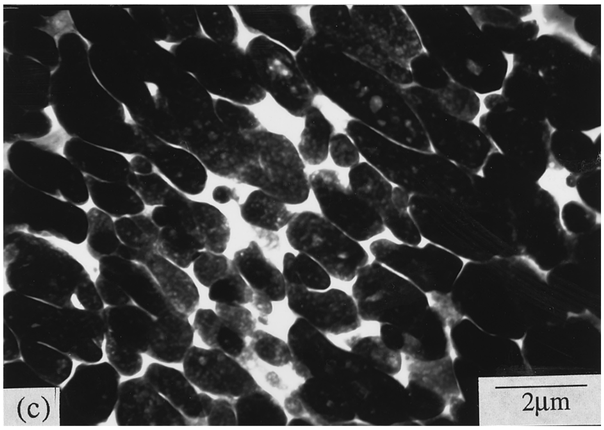


Fig. 10. TEM photomicrographs of blends of Capron 8209F and L-PE(0.9%MA) containing the following amounts of maleated linear low density polyethylene: (a) 10%; (b) 20%; and (c) 30%. The polyamide phase is stained dark by PTA.

corresponding blends containing H-PE(0.9%MA). One would expect a less efficient reduction in particle size based on the lower degree of functionality in H-PE(0.3%MA). When the maleated polyethylene content is 30%, some of the polyethylene domains become large and elongated, showing a tendency toward co-continuity.

4. Effect of viscosity on blend morphology

The mechanical properties of polymer blends are largely governed by which material forms the continuous phase and which is dispersed. The volume and viscosity ratios of the blend components are two important factors which control the phase continuity. Other things being equal, the component which occupies the most space is expected to be continuous. However, based on energetic considerations, the component with the lower viscosity tends to envelope the more viscous phase [52]. The morphological analysis in the previous section emphasized that both the relative volume and viscosity of the blend components must be considered in achieving a desired phase arrangement. In this section, our purpose is to compare the experimentally observed phase arrangement (polyamide-continuous, co-continuous, or polyethylene-continuous) with that predicted by theory in a quantitative manner.

Simple quantitative relationships for phase continuity were developed in terms of the viscosity and volume ratios of the blend components for identifying the region where phase inversion occurs [51,53,54]. Jordhamo et al. suggested that the point of phase inversion for non-reactive systems is given by the following relationship

$$\frac{\eta_1 \phi_2}{\eta_2 \phi_1} = 1$$

where ϕ_i is the volume fraction and η_i is the melt viscosity of phase i [51]. According to this model, phase 1 forms the continuous phase when this ratio is less than 1, whereas phase 2 will be continuous if the ratio is greater than 1. While this model strictly defines the point of phase inversion, in reality one would expect to observe zones of co-continuity when the ratio is close to unity [52]. Such an analysis can be extended to the present system if we neglect changes in viscosity resulting from grafting reactions and replace viscosities of the pure components with Brabender torque values [42]. The current data are analysed in terms of this model in Table 4 and compared to the actual morphology as observed by TEM. It is evident that the predicted and actual morphologies do not agree in all cases. In some blends based on Capron 8207F, the low molecular weight nylon 6, the left hand side of the equation is slightly above unity. These blends have co-continuous morphologies, which could be interpreted as consistent with the model. In general, the model predicts polyethylene to be the continuous phase at lower polyethylene contents than actually observed. However, the model qualitatively illustrates the tendency of the lower viscosity phase to become continuous even when it is the minority component. Obviously, the reactions that occur during melt processing to form graft copolymers at the nylon 6 polyethylene interface influence the interfacial tension, particle coalescence, and melt viscoelasticity. It is clear that these factors must influence the morphology formed; we make no attempt to explain how these complicated factors govern phase continuity. The

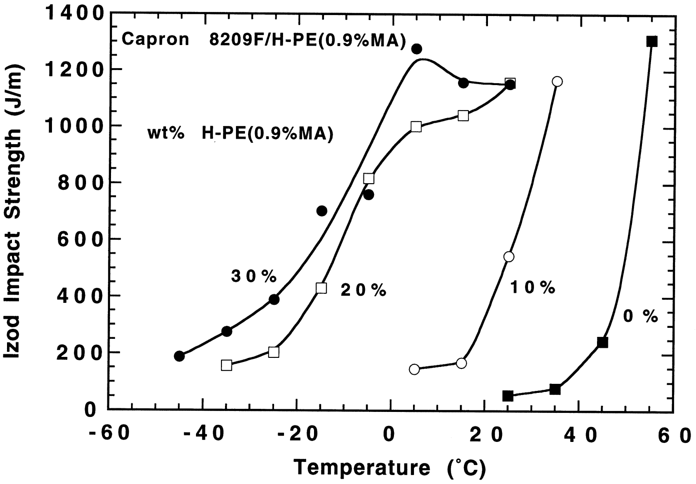


Fig. 11. Effect of temperature on the Izod impact strength of blends of Capron 8209F and H-PE(0.9%MA). This maleated linear low density polyethylene has a high melt viscosity and a high anhydride content.

influence of reactions on phase continuity for other blend systems was discussed in recent papers [53,55].

5. Mechanical properties of ternary blends

There was recent interest in ternary blends of nylon 6 with maleated and nonmaleated polyolefins and with maleated and nonmaleated elastomers as a method of adjusting the dispersed phase particle size [20–22,24,31,42]. Altering the ratio of the maleated to nonmaleated material provides a powerful means to control the dispersed phase morphology, and consequently, blend properties. In this section, the mechanical properties of ternary blends of nylon 6, H-PE(0%MA), and H-PE(0.9%MA) are investigated. The nylon 6 content is fixed at 80 wt% while the ratio of H-PE(0.9%MA) to H-PE(0.0%MA) and nylon 6 molecular weight are varied.

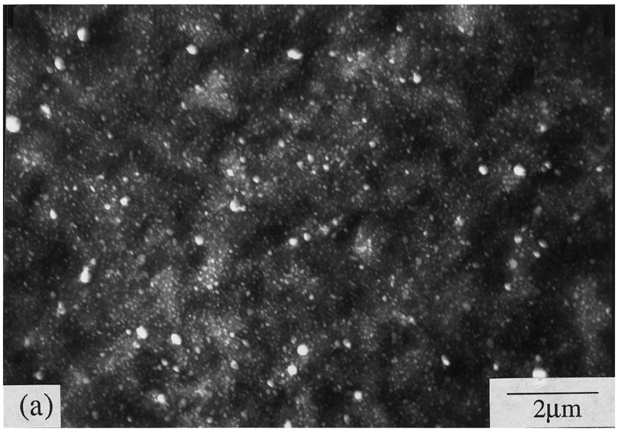
The impact properties of these ternary blends are expected to be a function of the relative amounts of maleated and nonmaleated polyethylene incorporated. Fig. 15 demonstrates that the room temperature impact strength of these blends generally improves as the ratio of H-PE(0.9%MA) to H-PE(0.0%MA) is increased. The lowest molecular weight nylon 6 is insensitive to the composition of the polyethylene phase and is brittle at all compositions shown; it is likely that a higher amount of polyethylene is required to toughen these blends. An increase in the amount of reactive functionality would be expected to reduce the dispersed phase particle size, which can improve impact properties if the particles were originally too large for effective toughening [24,56]. Increasing the polyethylene functionality should improve the interfacial adhesion between the blend components, decrease the dispersed phase particle size, and generate a more stable morphology, all of which potentially could contribute to improved mechanical properties.

For a fixed composition, the impact strength of these blends improves with increasing molecular weight of the nylon 6 matrix, except for blends based on the nylon 6 with $\overline{M}_n = 22\,000$. Blends containing the highest molecular weight nylon 6 ($\overline{M}_n = 37\,300$) are super tough ($> 800\ \mathrm{J\ m^{-1}}$) over a range of compositions; these levels of toughness can only be achieved at higher amounts of H-PE(0.9%MA) for the lower molecular weight nylon 6 materials. Generally, the ability to be toughened increases with molecular weight [33,57,58]. It was shown that higher levels of toughness can be achieved in polyamide–rubber blends when the molecular weight of the polyamide is increased [58]. The effects of nylon 6 molecular weight on the mechanical property response of its blends were attributed to both chemical and rheological factors [58,59], as well as the crystallinity and crystalline texture of the nylon 6 matrix [60–62].

In order to assess the influence of the degree of reactive functionality on the dispersed phase dimensions, certain ternary blends were selected for particle size analysis. Fig. 16 shows the dispersed phase particle size as a function of the relative amounts of H-PE(0.9%MA) and H-PE(0%MA) for blends based on the nylon 6 with $\overline{M}_n = 22\,000$. The binary blend of nylon 6 and the nonmaleated polyethylene contains large particles; however, only a small amount of H-PE(0.9%MA) is required to significantly reduce the dispersed phase dimensions. Although these particles become smaller as the ratio of maleated to nonmaleated polyethylene increases, the reductions in particle size are not very dramatic once the H-PE(0.9%MA) content is above a certain level.

The results in Fig. 16 are for blends based on the nylon 6 with $\overline{M}_n = 22\,000$. These blends are the exception to the trend of increasing toughness with increasing nylon 6 molecular weight, as mentioned earlier. They are clearly not as tough as those based on nylon 6 with $\overline{M}_n = 19\,400$ when the H-PE(0.9%MA) content is high (see Fig. 15). Previous work

90/10 Capron 8209F/H-PE(0.9%MA)



80/20 Capron 8209F/H-PE(0.9%MA)

70/30 Capron 8209F/H-PE(0.9%MA)

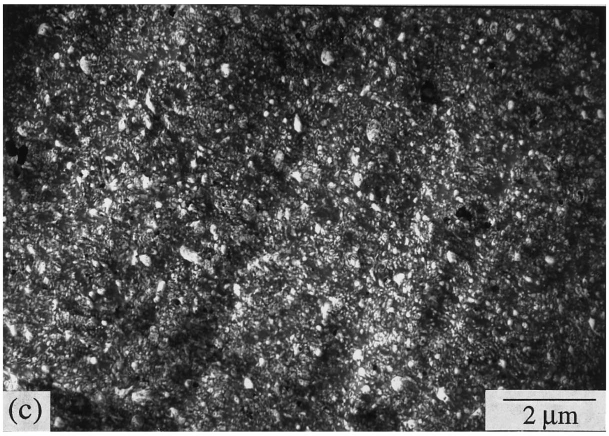


Fig. 12. TEM photomicrographs of blends of Capron 8209F and H-PE(0.9%MA) blends containing the following amounts of maleated linear low density polyethylene: (a) 10%; (b) 20%; and (c) 30%. The polyamide phase is stained dark by PTA.

by Oshinski et al. has demonstrated that this particular nylon 6, with $\overline{M}_\mathrm{n} = 22\,000$, is more difficult to toughen than other nylon 6 materials with either lower or higher molecular weight for producing rubber toughened blends because of the relationship of the size of the rubber particles generated in this matrix during processing relative to the particle size limits for toughening [58]. It was proposed that this matrix produces rubber particles that are too small for toughening. Lower molecular weight matrices generate larger particles that are above the lower limit for toughening, while higher molecular weight matrices can be toughened by a broader range of particle sizes, thus both are able to develop tough blends.

To investigate these issues further, the dispersed phase particle size was determined as a function of nylon 6 molecular weight for binary nylon 6/H-PE(0.9%MA) blends. Fig. 17 shows that the weight average particle size decreases as the nylon 6 molecular weight increases; this is no doubt a consequence of the higher rheological stresses transmitted to the polyethylene particles resulting from the higher melt viscosity of the polyamide matrix. The blends containing the two highest molecular weight nylon 6 materials contain extremely small polyethylene particles (<0.1 μm). This demonstrates that very small particles can effectively toughen high molecular weight nylon 6 matrices and suggests that the lower particle size limits for toughening these materials may be below 0.05 μm. The super tough binary blend containing nylon 6 with $\overline{M}_\mathrm{n} = 19\,400$ has a larger dispersed phase particle size than the corresponding blend with $\overline{M}_\mathrm{n} = 22\,000$, which is not very tough. It is tempting to propose, based on the work of Oshinski [58], that the polyethylene particles generated in the binary blend based on the nylon 6 with $\overline{M}_\mathrm{n} = 22\,000$ are too small for toughening this matrix. If this were the case, one could expect to generate tough blends by "fattening" these dispersed phase particles with nonmaleated polyethylene. However, none of the ternary blends based on this particular nylon 6 are tough, despite the fact that the dispersed phase particle size can be enlarged by increasing the ratio of nonmaleated to maleated polyethylene as shown in Fig. 16. At this point, it is unclear what the factors are that lead to the inability of this particular nylon 6 to be toughened by polyethylene relative to other nylon 6 materials; the dispersed phase domain size is evidently only one of the issues involved.

It was demonstrated here that the room temperature impact strength of these ternary blends is affected by the relative proportions of maleated and nonmaleated polyethylene and the molecular weight of the nylon 6 matrix. The ductile–brittle transition temperature of these blends is also significantly influenced by these factors; Fig. 18 shows that the ductile–brittle transition generally decreases as the ratio of H-PE(0.9%MA) to H-PE(0%MA) increases and as the nylon 6 molecular weight increases. Within this series, blends that have good room temperature toughness also have good low temperature toughness (compare Figs. 15 and 18). Once again, blends based on the nylon 6 with $\overline{M}_\mathrm{n} = 22\,000$ are the exception to the trend of improved impact properties with increasing nylon 6 molecular weight; these blends have a higher ductile–brittle transition temperature than blends containing nylon 6 with $\overline{M}_\mathrm{n} = 19\,400$ over nearly the entire composition range observed. This is

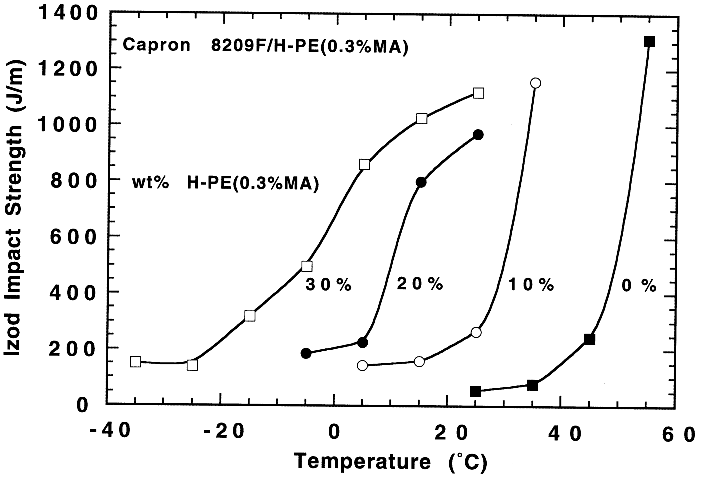


Fig. 13. Effect of temperature on the Izod impact strength of blends of Capron 8209F and H-PE(0.3%MA). This maleated linear low density polyethylene has a high melt viscosity and a low anhydride content.

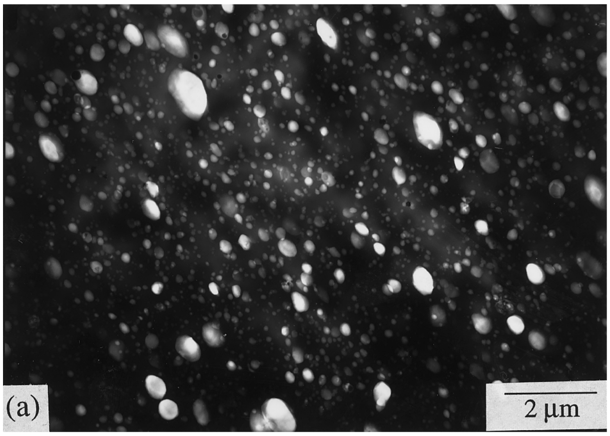
consistent with results obtained by Oshinski et al., who observed that nylon 6/rubber blends containing nylon 6 with $\overline{M}_n = 22\,000$ generally had higher ductile–brittle transition temperatures than nylon 6 materials with lower or higher molecular weights [59].

It is evident that nylon 6 can be toughened when the molecular weight of the matrix and the anhydride content of the dispersed phase are above a certain level. However, a comparison of the current ternary blends to previously studied blends containing combinations of maleated and nonmaleated rubbers, such as styrene-hydrogenated butadiene–styrene triblock copolymers (SEBS/SEBS-g-MA) and ethylene–propylene random copolymers (EPR/EPR-g-MA), demonstrates that polyethylene is generally not as effective, especially at low temperatures, for toughening nylon 6 as these rubbers. The toughness of blends of the nylon 6 materials used here with SEBS/SEBS-g-MA and EPR/EPR-g-MA mixtures was investigated as a function of nylon 6 molecular weight, maleic anhydride content, and dispersed phase particle size [58,59,63], regardless of the basis of comparison, these rubber-based blends generally have higher impact strengths and lower ductile–brittle transition temperatures than the ternary blends described here. This difference in the ability to toughen nylon 6 no doubt stems from differences in the mechanical properties of polyethylene compared to these rubbers.

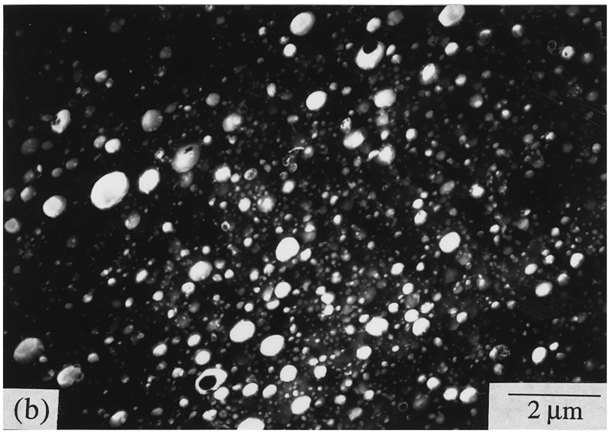
There was considerable interest in understanding the role of dispersed phase particles in the toughening process. The early literature describes stress concentration caused by the incorporation of low modulus particles dispersed in a rigid matrix [64,65]. It was suggested that the dispersed phase will act as an effective stress concentrator when its modulus is lower than that of the matrix by a factor of ten or more [66,67]. More recently, cavitation of the dispersed phase particles was proposed as the trigger that permits ductile shear yielding of the matrix [68–70]. Cavitation of the dispersed phase particles becomes more difficult as their modulus increases, just as the stress concentration factor in the matrix decreases with increasing modulus of the dispersed phase. Thus, it is useful to examine how the modulus of the dispersed phase (relative to nylon 6) changes with temperature.

Here, we explore the dynamic mechanical properties of the maleated polyethylene described in this section versus maleated elastomers previously studied by Oshinski et al. The elastic component of the dynamic modulus (E') of nylon 6 (Capron 8207F), the maleated elastomers reported by Oshinski et al. (SEBS-g-MA and EPR-g-MA), and the maleated polyethylene described in this section, H-PE(0.9%MA), are shown as a function of temperature in Fig. 19. It is evident that the moduli of the rubbery SEBS-g-MA and EPR-g-MA materials are significantly lower than that of H-PE(0.9%MA) over the entire temperature range shown. Fig. 20 shows the ratio of the modulus of the nylon 6 matrix to each of the dispersed phase materials shown in Fig. 19. Both of the rubbery materials have moduli that are low enough such that the ratio $E'_{\text{nylon 6}}/E'_{\text{dispersed phase}} = 10$ at temperatures well below room temperature. It was demonstrated earlier that the temperature at which the modulus ratio reaches this critical point corresponds quite closely to the lowest ductile–brittle transition temperatures for blends based on these rubbers [59]. The modulus of H-PE(0.9%MA) is such that the ratio $E'_{\text{nylon 6}}/E'_{\text{dispersed phase}}$ is significantly lower than 10 over the entire temperature range observed here. It is interesting to note that the ratio of the modulus of nylon 6 relative to that of H-PE(0.9%MA) is slightly above 10 at room temperature when measured by tensile testing (see Table 3). This discrepancy between the dynamic mechanical and tensile property results stems from the strong sensitivity of the polyethylene modulus to differences in loading configurations and testing rates (i.e. their viscoelastic nature) employed by these two types of methods; on the other hand, the modulus of the rigid polyamide phase is relatively independent of these differences. In light

90/10 Capron 8209F/H-PE(0.3%MA)



80/20 Capron 8209F/H-PE(0.3%MA)



70/30 Capron 8209F/H-PE(0.3%MA)

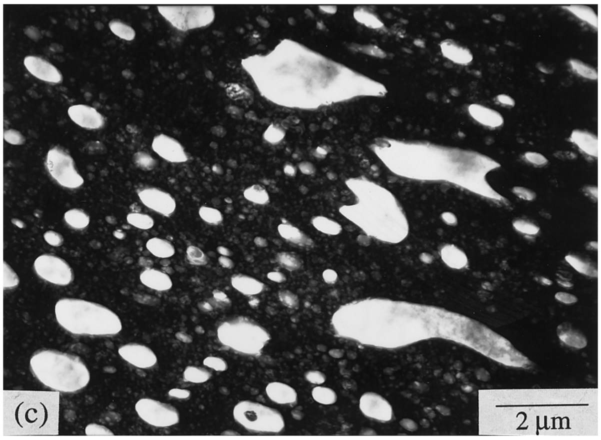


Fig. 14. TEM photomicrographs of blends of Capron 8209F and H-PE(0.3%MA) containing the following amounts of maleated linear low density polyethylene: (a) 10%; (b) 20%; and (c) 30%. The polyamide phase is stained dark by PTA.

of the sensitivity of the present modulus comparisons to the method of testing, one must interpret these results with caution.

The ability of dispersed particles to toughen nylon 6 appears to be significantly affected by the mechanical properties of the dispersed phase. The maleated elastomers, SEBS-g-MA and EPR-g-MA, are more effective for toughening nylon 6 [58,59] than the maleated polyethylene, H-PE(0.9%MA), described earlier. The significantly lower modulus of the maleated elastomers relative to the maleated polyethylene appears to make them more attractive for toughening nylon 6.

However, the higher modulus and lower cost of maleated polyethylene can potentially make nylon 6/maleated polyethylene blends more favorable in applications which do not require extremely low temperature ductility, but have stiffness or cost requirements that cannot be provided by blends containing maleated elastomers. It is important to note that there are numerous factors associated with the dispersed phase which play a role in toughening, i.e. melt viscosity and elasticity, morphology, degree of maleation, etc. A more detailed analysis is required to gain a more complete understanding of the role of the dispersed phase in the toughening process.

6. Conclusions

The effects of the concentration, melt viscosity, and functionality of maleated polyethylenes on the properties of their blends with nylon 6 were investigated. The morphology and mechanical properties of these blends are dependent on the nature of the maleated polyethylene used. A low viscosity maleated polyethylene was found to be ineffective for toughening two nylon 6 materials of different molecular weights resulting from the large mismatch in the melt viscosity of the blend components; the low viscosity polyethylene phase tended to become continuous even when it was the minority component. High viscosity polyethylenes with both low (0.3%) and high (0.9%) anhydride contents were able to produce tough blends, provided the polyethylene concentration was high enough. In certain cases, blends containing polyethylene with a low degree of functionality can generate levels of toughness comparable to blends containing a more highly functional polyethylene, while maintaining a lower melt viscosity. The impact properties of ternary blends of nylon 6, polyethylene, and maleated polyethylene were influenced by the molecular weight of the nylon 6 matrix and the relative amounts of maleated and nonmaleated polyethylene. In general, increasing the nylon 6 molecular weight and the ratio of maleated to nonmaleated polyethylene resulted in improved room temperature impact strength and lower ductile–brittle transition temperatures. While these combinations of maleated and nonmaleated polyethylene can toughen nylon 6 in certain cases, these materials are generally not as effective for toughening nylon 6 as mixtures of maleated and nonmaleated elastomers. This appears to be related to the mechanical properties of these rubbers relative to those of polyethylene.

Table 4
Comparison of predicted and actual morphologies

Nylon 6/PE blend (wt/wt)	$\frac{\{T_1\}}{\{T_2\}}$ [a]	$\frac{\{T_1\}}{\{T_2\}}\frac{\{\phi_2\}}{\{\phi_1\}}$ [b]	Predicted continuous phase	Observed continuous phase
Capron 8207F/L-PE(0.9%MA)				
90/10	4.86	0.67	Nylon	Nylon
80/20	4.86	1.51	PE	Nylon
70/30	4.86	2.58	PE	PE
Capron 8207F/H-PE(0.3%MA)				
90/10	1.62	0.22	Nylon	Nylon
80/20	1.62	0.50	Nylon	Nylon
70/30	1.62	0.86	Nylon	Nylon
60/40	1.62	1.34	PE	Co-continuous
50/50	1.62	2.01	PE	PE
40/60	1.62	3.01	PE	PE
Capron 8207F/H-PE(0.9%MA)				
90/10	1.24	0.17	Nylon	Nylon
80/20	1,24	0.38	Nylon	Nylon
70/30	1.24	0.66	Nylon	Nylon
60/40	1.24	1.02	PE	Co-continuous
50/50	1.24	1.53	PE	Co-continuous
40/60	1.24	2.30	PE	PE
Capron 8209F/L-PE(0.9%MA)				
90/10	6.67	0.92	Nylon	Nylon
80/20	6.67	2.06	PE	Nylon
70/30	6.67	3.54	PE	PE
Capron 8209F/H-PE(0.3%MA)				
90/10	2.22	0.31	Nylon	Nylon
80/20	2.22	0.69	Nylon	Nylon
70/30	2.22	1.18	PE	Nylon
Capron 8209F/H-PE(0.9%MA)				
90/10	1.69	0.23	Nylon	Nylon
80/20	1.69	0.52	Nylon	Nylon
70/30	1.69	0.90	Nylon	Nylon

[a] Torque ratio of nylon 6 (phase 1) to PE (phase 2). Torques measured by Brabender at 240°C 60 min $^{-1}$ after 10 min. Viscosity changes due to reaction are neglected.

[b] Volume fractions were calculated based on the following melt density estimates at 240°C: 0.99 g cm^3 for nylon 6 and 0.80 g cm^{-3} for PE.

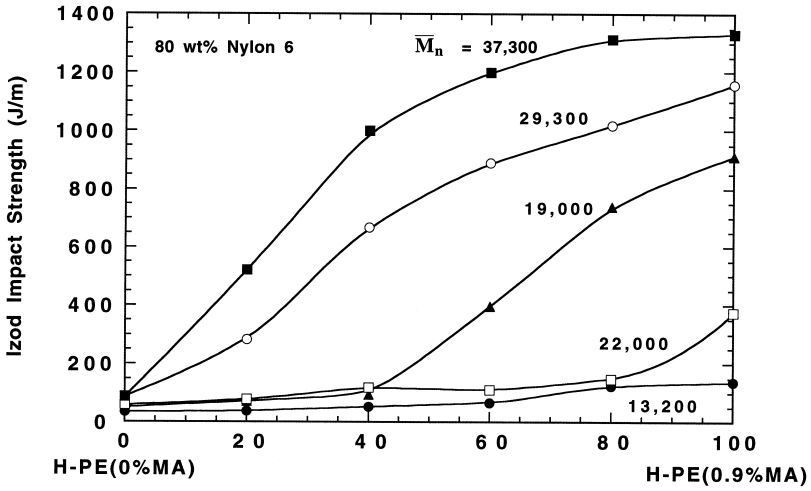


Fig. 15. Izod impact strength of ternary blends of nylon 6, H-PE(0%MA), and H-PE(0.9%MA) as a function of nylon 6 molecular weight and ratio of H-PE(0.9%MA)/H-PE(0%MA). The nylon 6 content is fixed at 80 wt%.

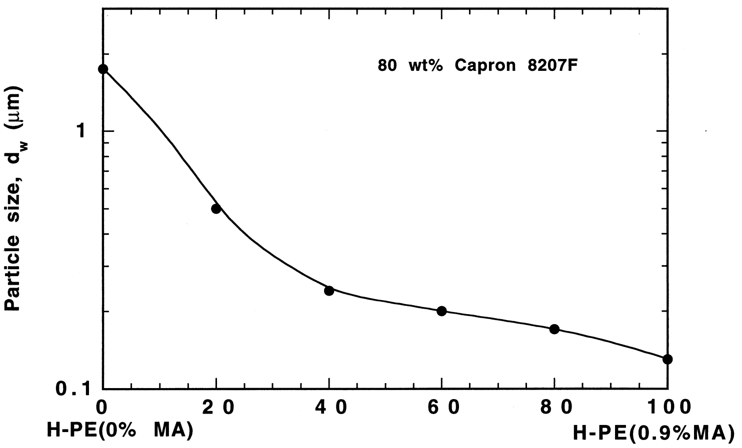


Fig. 16. Effect of ratio of maleated polyethylene to nonmaleated polyethylene, H-PE(0.9%MA)/H-PE(0%MA), on the weight average particle size of the dispersed phase for ternary blends of Capron 8207F, H-PE(0%MA), and H-PE(0.9%MA). The Capron 8207F content is fixed at 80 wt%.

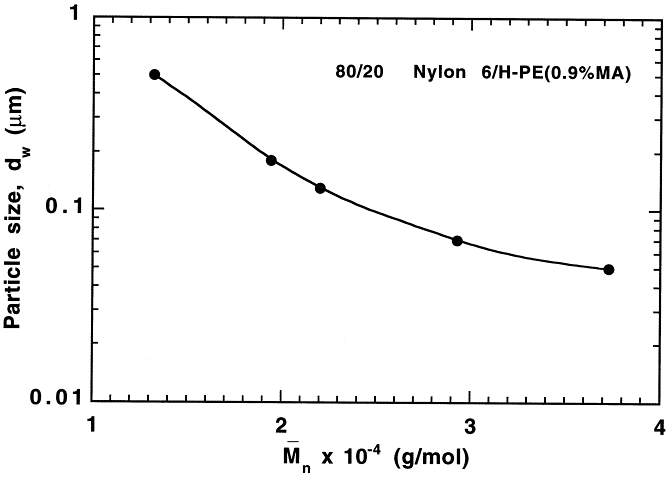


Fig. 17. Effect of nylon 6 molecular weight on the weight average particle diameter of the dispersed phase for binary blends of nylon 6 and H-PE(0.9%MA). The nylon 6 content is fixed at 80 wt%.

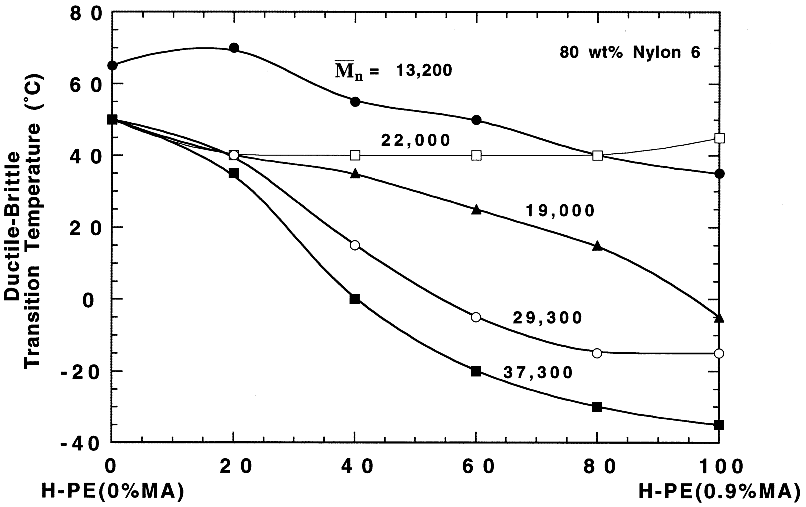


Fig. 18. Ductile–brittle transition temperature of ternary blends of nylon 6, H-PE(0%MA), and H-PE(0.9%MA) as a function of nylon 6 molecular weight and ratio of H-PE(0.9%MA)/H-PE(0%MA). The nylon 6 content is fixed at 80 wt%.

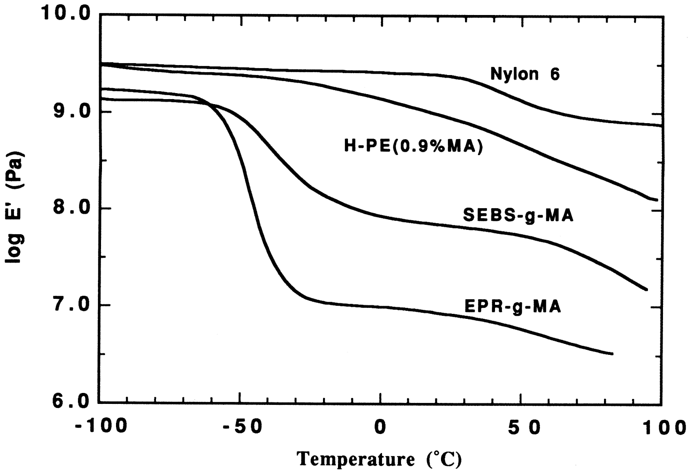


Fig. 19. Elastic modulus (*E*) as a function of temperature for nylon 6 (Capron 8207F), H-PE(0.9%MA), and maleated elastomers SEBS-g-MA and EPR-g-MA. SEBS-g-MA and EPR-g-MA contain 2 and 1.14 wt% maleic anhydride, respectively.

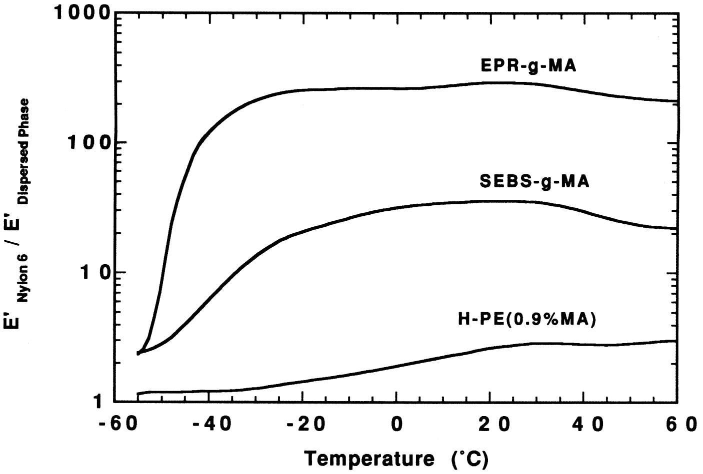


Fig. 20. Matrix to dispersed phase modulus ratio, $E'_{\text{nylon 6}}/E'_{\text{dispersed phase}}$ as a function of temperature for the dispersed phases H-PE(0.9%MA), SEBS-g-MA, and EPR-g-MA.

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