Effect of polyamide functionality on the morphology and toughness of blends with a functionalized block copolymer

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Previous work has shown that blends of a maleic anhydride functionalized triblock copolymer (with an ethylene/butene mid-block and styrene end-blocks, or SEBS-*g*-MA) with nylon-6,6 gives super-tough materials with complex-shaped rubber particles that are just below the upper critical particle size for toughening. Similar blends of SEBS-*g*-MA with nylon-6 are not toughened because the rubber particles are evidently too small, i.e. below a proposed lower critical size for toughening. It was further proposed that this difference in morphology stems from the difunctional (nylon-6,6) *versus* monofunctional (nylon-6) character of these polyamides for reaction with anhydrides. This proposal is supported here by the observation that blends of SEBS-*g*-MA with nylon-12,12 give large complex rubber particles like those in nylon-6,6 while nylon-11 and nylon-12 give smaller particles like nylon-6. Further support of this notion is provided by blending nylon-6 with other polyamides in an attempt to produce a chemically modified matrix. Addition of 10% nylon-6,6, poly(*m*-xylene adipamide) (MXD6) and nylon-12,12 to the nylon-6 matrix (under conditions that cause phase homogenization by interchange reactions) leads to rubber particle enlargement and toughening, while addition of nylon-11 or nylon-12 does not lead to either particle enlargement or toughening. Possible effects of rheological factors, extent of interchange reactions, interfacial tension and end-group contents are discussed.

(Keywords: blends; polyamides; morphology; toughening; interchange reactions; phase homogeneity; copolymers)

INTRODUCTION

Since the commercial introduction of super-tough nylon[1,2], there has been considerable scientific interest in rubber-toughened polyamides[3–20]. In most cases, the elastomer phase is grafted with a functional monomer like maleic anhydride (MA) that readily reacts with the polyamide during melt processing, thereby chemically coupling the phases and physically reducing the dispersed rubber particle size. It is well known for both nylon-6 and nylon-6,6 that the rubber particle size must be below a critical diameter of somewhat less than 1 μm to achieve super-toughness[3,4,8–11], which for most gum elastomers can only be achieved practically via the reaction scheme mentioned. It has been argued that the true critical dimension is interparticle spacing not particle diameter[11]; however, in the case of a fixed rubber content, these two dimensions are inextricably connected for particles with uniform size and distribution. For a given functionalized elastomer, the following may affect the particle size: processing method[21–23], relative viscosities of the two phases[12,23–25], interfacial tension[26,27], dilution of elastomer with its non-reactive precursor[3,4], concentration of reactive polyamide end-groups[28], etc. More recent work[3,5,29] has shown that super-toughness of nylon-6 is not achieved if the rubber particles are smaller than a critical lower limit (about 0.3 μm). For example, it has been reported that certain blends of nylon-6 with a maleated styrene-based triblock copolymer elastomer having a hydrogenated butadiene mid-block (SEBS-*g*-MA) are not super-tough because the rubber particles generated ($\sim$0.05 μm) are below the critical lower limit[3,6]. Super-toughness can be achieved by enlarging the rubber particles through dilution of the functionalized elastomer with its non-reactive precursor, SEBS[3].

A less well known effect is manifested in the fact that blends of nylon-6,6 with SEBS-*g*-MA, prepared in exactly the same way as those for nylon-6 mentioned above, do become super-tough without dilution with SEBS[4,6]. Microscopy reveals that the rubber particles in these nylon-6,6 blends have complex shapes (non-round structures with occlusions of nylon) that are about an order of magnitude larger than the relatively more simple, spherical particles in nylon-6[3,4,30]. These observations led us to consider the possibility that differences in functional symmetry of these two polyamides may give rise to this significant difference in morphology. Nylon-6 is monofunctional, in our terminology, since each chain can chemically attach only once to a maleated elastomer phase. This type of graft is efficient for lowering interfacial tension and steric stabilization against particle coalescence and should lead to small particles. Nylon-6,6 on the other hand may be difunctional, e.g. some molecules have amine groups at both ends, and can attach twice to the same particle (loops) or bridge two particles[4]. These different modes of grafting will be less effective for

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promoting drop break-up and preventing coalescence, and may encourage occlusion and complex shapes. Thus, difunctional polyamides might be expected to produce larger rubber particles than monofunctional ones. The purpose of this paper is to present a further exploration of this concept using two different approaches. First, we examine whether other monofunctional (nylon-11 and nylon-12) and difunctional (nylon-12,12) polyamides fit the suggested pattern of particle size. Secondly, we use interchange reactions to convert a monofunctional polyamide (nylon-6) into a difunctional one. Obviously, there are too many ramifications of each of these approaches to consider them all here, and further reports will address many of these in some detail.

We recently examined interchange reactions in blends of poly(*m*-xylene adipamide) (MXD6) with nylon-6[31] and other polyamides[32]. As few as five interchanges per molecule (to give a segmented block copolymer) produce a material with a single amorphous phase from MXD6 and nylon-6 that is still capable of extensive crystallization. The number of interchange reactions needed to achieve melt-phase homogenization depends on the physical interaction[31,32] or the Flory–Huggins interaction parameter, χ, between the two types of polyamide segments, which in turn depends on the molecular structure of the repeat units[33–35]. Furthermore, the opportunity for interchange reaction between two immiscible polymers depends on the extent of interfacial mixing, which is governed by the same physical interaction[32]. Thus, for two aliphatic polyamides, we may expect the extent of interchange reaction to depend on how different their repeat unit structures are for a fixed melt processing protocol, and phase homogenization may not occur if they are too dissimilar.

In another paper[36], we examined the rubber toughening of phase homogenized mixtures of nylon-6 and MXD6 using SEBS-*g*-MA. Ternary blends of nylon-6 with SEBS-*g*-MA containing MXD6 led to super-tough materials (see *Figure 2*). By reaction with MXD6, nylon-6 becomes difunctional and the rubber particle size increased, which we proposed[4] is the cause for increased toughening. By this reasoning, addition of nylon-11 or nylon-12 to nylon-6 should not toughen its mixtures with SEBS-*g*-MA, whereas addition of nylon-6,6 or nylon-12,12 should lead to toughening. We explore this hypothesis here.

EXPERIMENTAL

The various polyamides and the maleated rubber (i.e. SEBS-*g*-MA) used in this work are described in *Table 1*. The homopolyamides were blended with SEBS-*g*-MA by a single pass through a Killion single-screw extruder ($L/D = 30$, 2.54 cm diameter) at 280°C for nylon-6,6 and at 260°C for the other polyamides. Nylon-6 was melt mixed with other polyamides by one pass through a single-screw extruder at 290°C to promote interchange reaction and phase homogenization except as noted in the text. These polyamide mixtures were then blended with SEBS-*g*-MA by single-pass extrusion at 260°C. Extruded blends were moulded into Izod bars (ASTM D256, 0.318 cm thick) using an Arburg Allrounder screw injection moulding machine with the mould temperature set at 80°C. All samples were dried in a vacuum oven at 80°C for at least 12 h before each melt processing operation.

Notched Izod impact strengths of dry as-moulded samples were measured at room temperature. Melt rheological characterization consisted of the Brabender Plasti-Corder torque after 10 min of fluxing with a rotor speed of 60 rev min^{-1} at 280°C or 260°C.

Blend morphology was determined using an NEC transmission electron microscope (JEM-2000FX). Samples were microtomed from Izod bars perpendicular to the flow direction and stained with RuO_4. Weight-average diameters of rubber particles were measured from TEM microphotographs. In the case of complex shapes of the rubber phase, the diameter assigned to each particle (including any occluded polyamide) was the average of its longest dimension and its dimension perpendicular to this major axis[36].

Table 1 Polymers used in this study

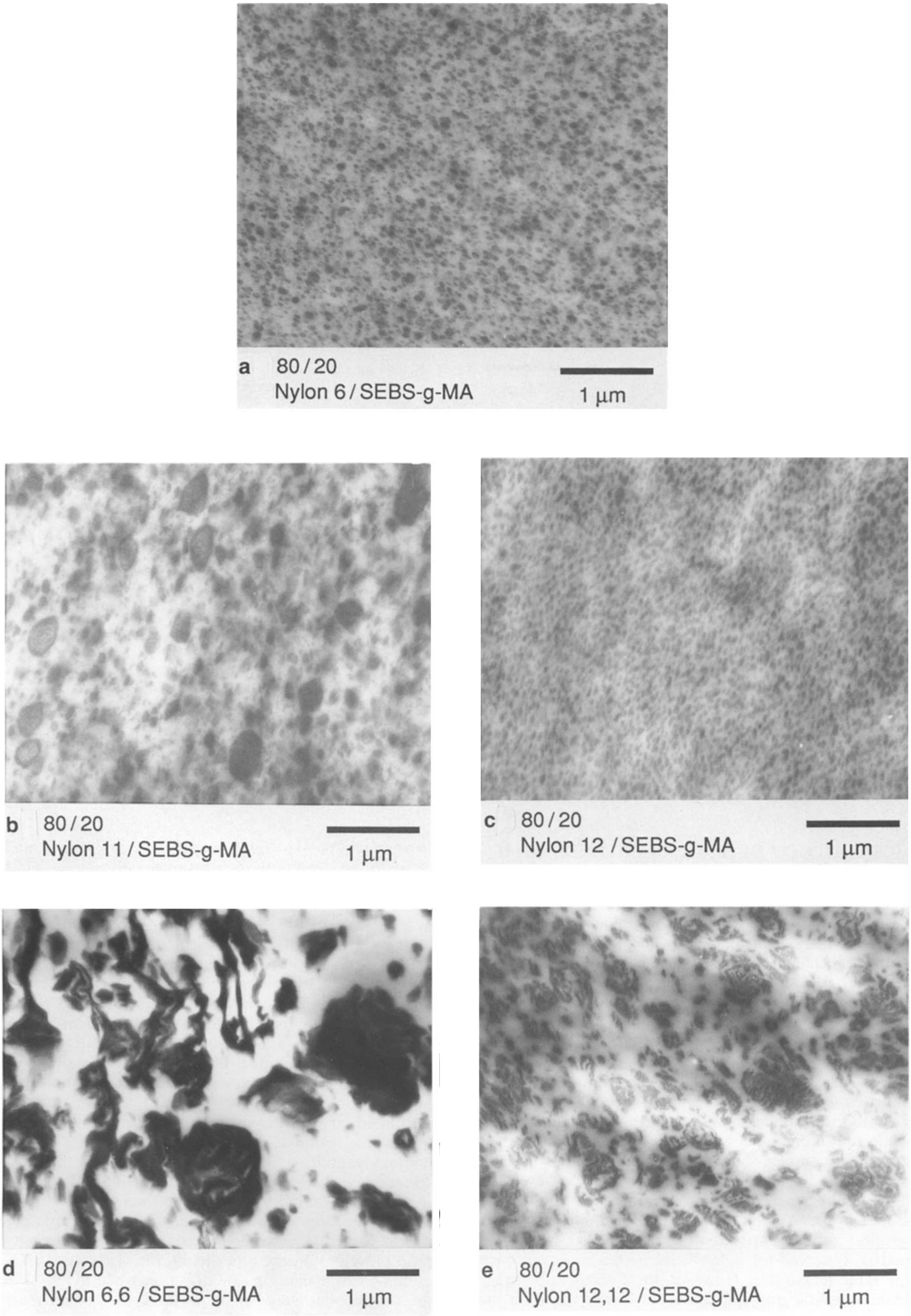
			End-group content (μeq g^{-1})			
Polymer	Description	$\bar{M}_n$	NH_2	COOH	Relative melt viscosity[a]	Source
Nylon-6	Capron 8207F	25 000	40	40	1.0	Allied Signal Inc.
Nylon-11	BMNO TL	n.a.[b]	n.a.	n.a.	0.4	Atochem Inc.
Nylon-12	AESNO TL	n.a.	n.a.	n.a.	1.7	Atochem Inc.
Nylon-6,6	Zytel 101	n.a.	n.a.	n.a.	1.1[c]	E. I. du Pont Co.
Nylon-12,12	Zytel 40-401	n.a.	n.a.	n.a.	0.7	E. I. du Pont Co.
Poly(*m*-xylene adipamide)						Mitsubishi Gas Chemical Co.
	MXD6 6001	14 700	38	98	0.3	
	MXD6 6007	25 300	12	67	0.4	
	MXD6 6121	40 000	20	30	2.4	
Styrene–(ethylene–butene)–styrene grafted with 1.84% maleic anhydride[d]	SEBS-*g*-MA	n.a.	–	–	0.8	Shell Chemical Co.

[a] Brabender torque at 260°C and 60 rev min^{-1} after 10 min divided by that of nylon-6

[b] Not available

[c] Brabender torque at 280°C and 60 rev min^{-1} after 10 min divided by that of nylon-6

[d] Determined by elemental analysis after solvent/non-solvent purification


a 80/20
Nylon 6/SEBS-g-MA
1 µm
b 80/20
Nylon 11/SEBS-g-MA
1 µm
c 80/20
Nylon 12/SEBS-g-MA
1 µm
d 80/20
Nylon 6,6/SEBS-g-MA
1 µm
e 80/20
Nylon 12,12/SEBS-g-MA
1 µm

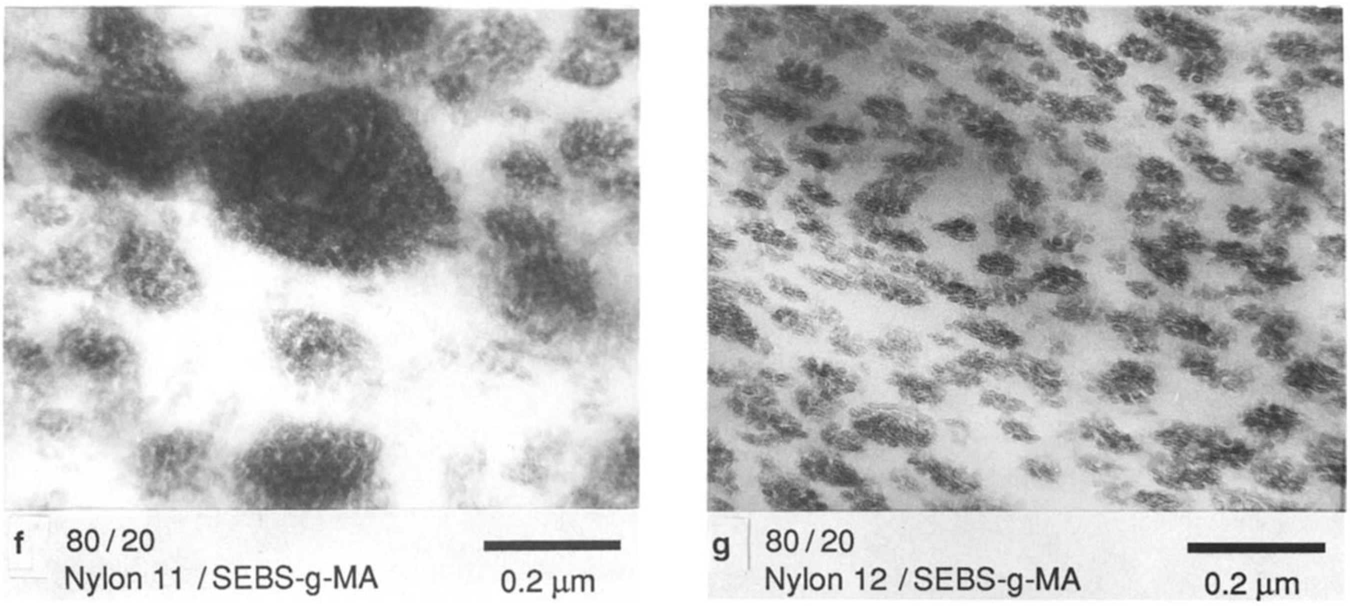


Figure 1 TEM photomicrographs of 80/20 homopolyamide/SEBS-*g*-MA blends: (a) nylon-6, (b) nylon-11, (c) nylon-12, (d) nylon-6,6 and (e) nylon-12,12; (f) and (g) show higher magnifications of (b) and (c)

Table 2 Rubber particle size and relative melt viscosity for polyamide blends

	Rubber particle size, $\bar{d}_w$ (μm)		Melt viscosity of SEBS-*g*-MA relative to[c]	
Polyamide	Homopolyamide[a]	Modified nylon-6[b]	Homopolyamide	Modified nylon-6
Nylon-6	0.06	–	0.8	–
Nylon-11	0.21	0.07	2.0	1.3
Nylon-12	0.06	0.06	0.5	1.0
Nylon-6,6	0.98	0.33	1.4[d]	1.2
Nylon-12,12	0.32	0.11	1.1	1.1

[a] For 80/20 homopolyamide/SEBS-*g*-MA blends determined from *Figure 1*
[b] For 72/8/20 nylon-6/polyamide/SEBS-*g*-MA blends determined from *Figure 8*
[c] Brabender torque of SEBS-*g*-MA divided by that of the polyamide matrix phase (all at 260°C and 60 rev min^{-1} after 10 min)
[d] Brabender torque of SEBS-*g*-MA divided by that of the nylon-6,6 matrix phase (all at 280°C and 60 rev min^{-1} after 10 min)

MORPHOLOGY OF SEBS-*g*-MA BLENDS WITH HOMOPOLYAMIDES

The question of the correlation between morphology and the functionality type of the polyamide phase for the homopolymers was examined by TEM. Thorough studies of their mechanical properties are provided elsewhere[37]. *Figure 1* shows TEM photomicrographs of blends containing 80% pure polyamide and 20% SEBS-*g*-MA blends. *Figures 1a* (nylon-6), *1b* (nylon-11) and *1c* (nylon-12) show the morphology for monofunctional polyamide matrices, while *Figures 1d* (nylon-6,6) and *1e* (nylon-12,12) give results for two difunctional polyamide matrices. Quantitatively, the monofunctional polyamides seem to form smaller spherical particles of SEBS-*g*-MA, while the difunctional polyamides tend to form larger and more complex-shaped particles of SEBS-*g*-MA, as may be seen from the summary in *Table 2*. However, the largest rubber particles in a monofunctional polyamide matrix, observed for nylon-11 ($\sim$0.2 μm), and the smallest rubber particles in a difunctional polyamide matrix, observed for nylon-12,12 ($\sim$0.3 μm), approach the same magnitude. However, there seem to be other basic morphological differences for blends based on the two types of polyamides. Spherical rubber particles tend to be formed in the monofunctional polyamides, while rubber particles of more complex shape tend to be formed in the difunctional polyamides. This trend was proposed in a recent paper[4], and these TEM photomicrographs strongly support this hypothesis.

In addition to the functionality type of the polyamide, we can expect the observed rubber particle size to be quantitatively affected by the viscosity of SEBS-*g*-MA relative to the polyamide, the polyamide–rubber interfacial tension, and possibly the end-group type and content of the polyamide. The rubber particles observed in the nylon-11 matrix are somewhat larger than those in nylon-6 or nylon-12 (see *Table 2*), and this may be attributed, at least in part, to the low melt viscosity of nylon-11. Nylon-11 is the least viscous of the homopolyamides used here, while nylon-12 is the most viscous (see *Table 1*). The dispersed SEBS-*g*-MA phase is a factor of 2.0 more viscous than the nylon-11 matrix phase (see *Table 2*), which would tend to cause larger rubber particles[12,25] compared to the case of a viscosity ratio of unity. On the other hand, the viscosity ratio is mismatched in the opposite direction when nylon-12 is the matrix, but very small particles ($\sim$0.06 μm) are

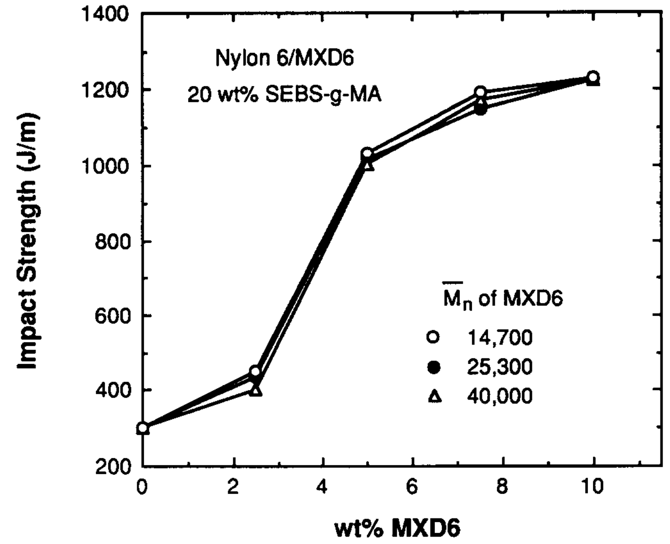


Figure 2 Impact strength of 80/20 (nylon-6/MXD6)/SEBS-*g*-MA blends as a function of the MXD6 content in the polyamide matrix

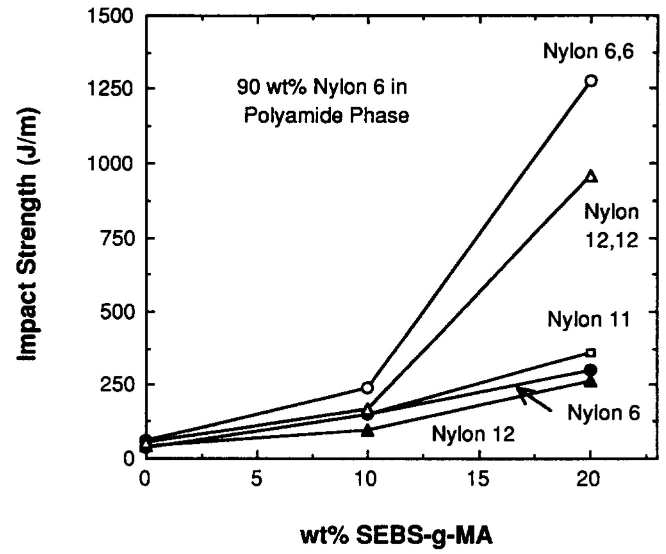


Figure 3 Impact strength of modified nylon-6/SEBS-*g*-MA blends as a function of the SEBS-*g*-MA content. Nylon-6 is modified by 10% of various polyamides

formed in this case. In addition, interfacial tension between the polyamide and SEBS-*g*-MA may also affect the rubber particle size and the extent of reaction at the interface. The SEBS-*g*-MA particles in blends with nylon-6,6 are larger than for blends with nylon-12,12. This may relate to the differences in the physical interaction, and hence the interfacial tension, of SEBS-*g*-MA with the two polyamides. Nylon-12,12 has a greater hydrocarbon character, like the rubber, than nylon-6,6. Information about end-group contents of these polyamides was not available, so the influence of this factor cannot be assessed at this time.

BLENDS OF SEBS-*g*-MA WITH NYLON-6 MODIFIED BY OTHER POLYAMIDES

Mixtures of nylon-6 and three different molecular-weight grades of MXD6 (see *Table 1*) were extruded at 290°C to give melt-phase homogenized materials (transparent in the melt, one T_g) with varying contents of each MXD6. These materials were in turn melt blended with 20% SEBS-*g*-MA and moulded into test specimens. As shown in *Figure 2*, incorporation of as little as 5% MXD6 into a predominantly nylon-6 matrix leads to super-toughening. Interestingly, the type of MXD6, either molecular weight or end-group content, apparently has no influence on the results. Incorporation of MXD6 into nylon-6 significantly increases rubber particle size to beyond the lower critical diameter as shown previously[36] (presumably because of the increased difunctional character) and, therefore, increases toughness.

Now we examine the question of what happens when nylon-6 is modified with other difunctional (nylon-6,6 and nylon-12,12) and monofunctional (nylon-11 and nylon-12) polyamides. In each case, the amount of the modifying polyamides was limited to 10% by weight or less in order to preserve the mechanical characteristics of nylon-6 as nearly as possible. An issue here is the extent to which interchange reactions occur between these polyamides and nylon-6 and whether phase homogenization is achieved or not.

Whether a monofunctional or a difunctional polymer is used to modify nylon-6 has a very significant effect on the impact strength of blends with SEBS-*g*-MA. *Figure 3* shows the impact strength as a function of the SEBS-*g*-MA content for nylon-6 matrices modified with 10% of the various polyamides. Blends of nylon-6 modified by the difunctional polyamides have a dramatically higher impact strength at 20% of SEBS-*g*-MA than those modified by monofunctional polyamides. *Figure 4* shows the impact strength of 80/20 modified nylon-6/SEBS-*g*-MA blends as a function of the content of the modifying polyamide in the polyamide phase. Again, blends modified with monofunctional polyamides show lower impact strength than those modified by difunctional polyamides. Nylon-6,6 increases the impact strength more effectively than does nylon-12,12. *Figure 5* shows the Brabender torque of the blends in *Figure 4* after melt mixing at 280°C (note that the melting point of nylon-6,6 is 260°C). Blends of higher impact strength tend to have lower viscosity. In a previous paper[4], it was shown that the viscosity of blends

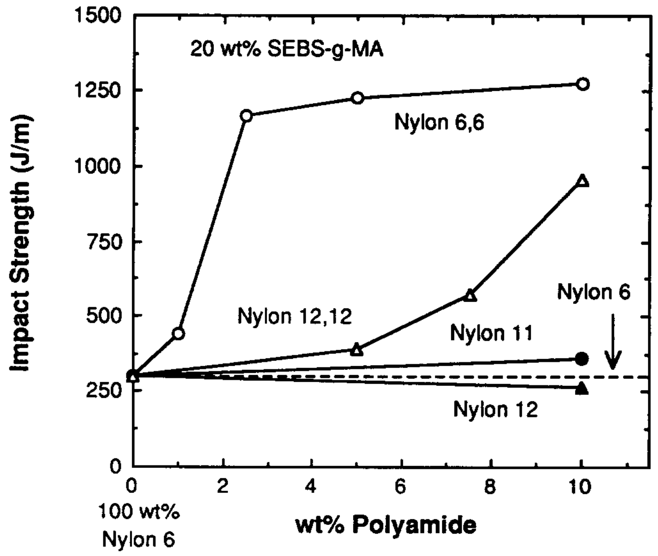


Figure 4 Impact strength of 80/20 modified nylon-6/SEBS-*g*-MA blends as a function of the content of modifying polyamide in the polyamide matrix

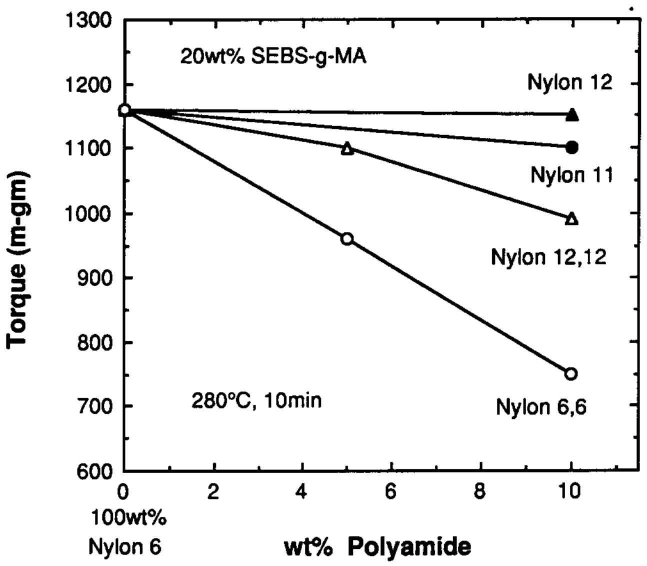


Figure 5 Brabender torque at 280°C of 80/20 modified nylon-6/SEBS-*g*-MA blends as a function of the content of modifying polyamide in the polyamide matrix

of SEBS-*g*-MA with nylon-6,6 are less than those with nylon-6. The blends that have the larger particles (and are therefore toughened) have less surface area for grafting between the phases and, thus, have lower melt viscosity.

The physical interaction of nylon-6 with the added polyamide affects the extent of interchange reaction achieved and whether melt-phase homogenization occurs or not[32]. The reactions with SEBS-*g*-MA will obviously proceed differently depending on whether the polyamide phase is homogeneous or heterogeneous[36]. Furthermore, immiscibility of the two polyamides creates a weak interface that will diminish mechanical behaviour. Based on available evidence[31,32,38–40], nylon-6 is either miscible or nearly miscible with nylon-6,6, not miscible with MXD6 but the interaction is only weakly unfavourable, and definitely immiscible with nylon-11, nylon-12 and nylon-12,12 (i.e. strongly unfavourable interaction). As the physical polyamide–polyamide interaction becomes more unfavourable for mixing of the segments, the opportunities for interchange reaction (and any subsequent phase homogenization) at the interface become more limited[32]. It was observed that melt extrusion of nylon-6 at 290°C with nylon-6,6 and MXD6 yielded transparent melts and solids with a single T_g (phase homogenization), but similarly prepared mixtures of nylon-6 with the other polyamides did not lead to transparent melts. It is for this reason, we believe, that addition of nylon-6,6 and MXD6 to nylon-6 increases the impact strength of their blends with SEBS-*g*-MA more effectively than addition of nylon-12,12. To support this point of view, the effect of the extent of interchange reactions between nylon-6 and nylon-12,12 on impact strength of blends with SEBS-*g*-MA was examined more fully. *Figure 6* shows how the initial melt mixing of nylon-6/nylon-12,12 affects the impact strength of subsequent blends with 20% of SEBS-*g*-MA. Nylon-6 was premixed with various amounts of nylon-12,12 for the following extrusion conditions: single pass at 240°C, single pass at 290°C and double pass at 290°C. Each modified nylon-6 was opaque in the molten state; however, the samples with more high-temperature mixing history for the polyamide phase have higher impact strength. *Figure 7* also shows the impact strength of nylon-6/nylon-12,12/SEBS-*g*-MA blends as a function of the number of extrusion passes in the melt mixing at 240°C of the 90/10 nylon-6/nylon-12,12 polyamide matrix phase. Again, the modified nylon-6 melt was opaque irrespective of the number of extrusion passes; however, the impact strength of the blends of these matrix materials with SEBS-*g*-MA increases continuously with the number of extrusion passes. Even though nylon-6 and nylon-12,12 remain phase-separated in the melt state (based on lack of melt transparency), the mechanical properties of their blends with SEBS-*g*-MA improve as the opportunity for more interchange reaction between these polyamides increases.

Finally, we examine the morphology of blends of SEBS-*g*-MA (20%) with the nylon-6 matrices modified by the various polyamides (at 10% of the polyamide phase). TEM photomicrographs shown in *Figure 8* were

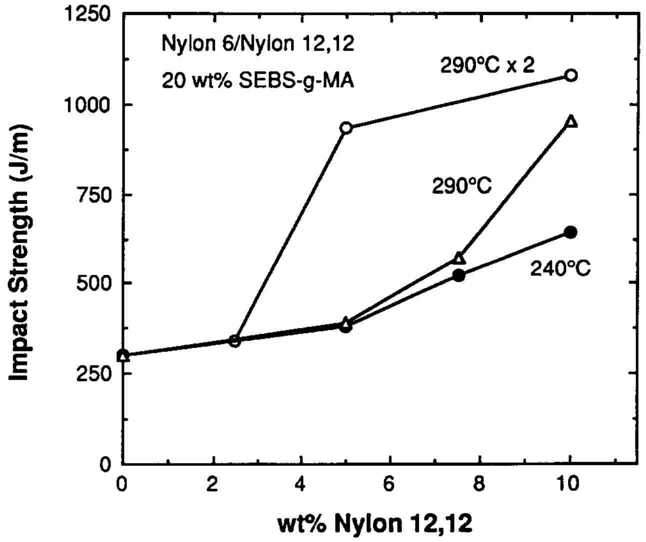


Figure 6 Impact strength of 80/20 (nylon-6/nylon-12,12)/SEBS-*g*-MA blends as a function of the nylon-12,12 content in the polyamide matrix prepared by various extrusion conditions for the nylon-6 modification

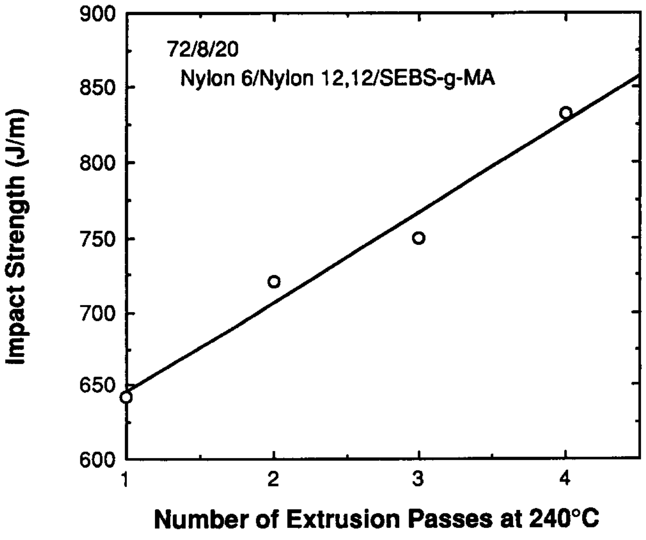
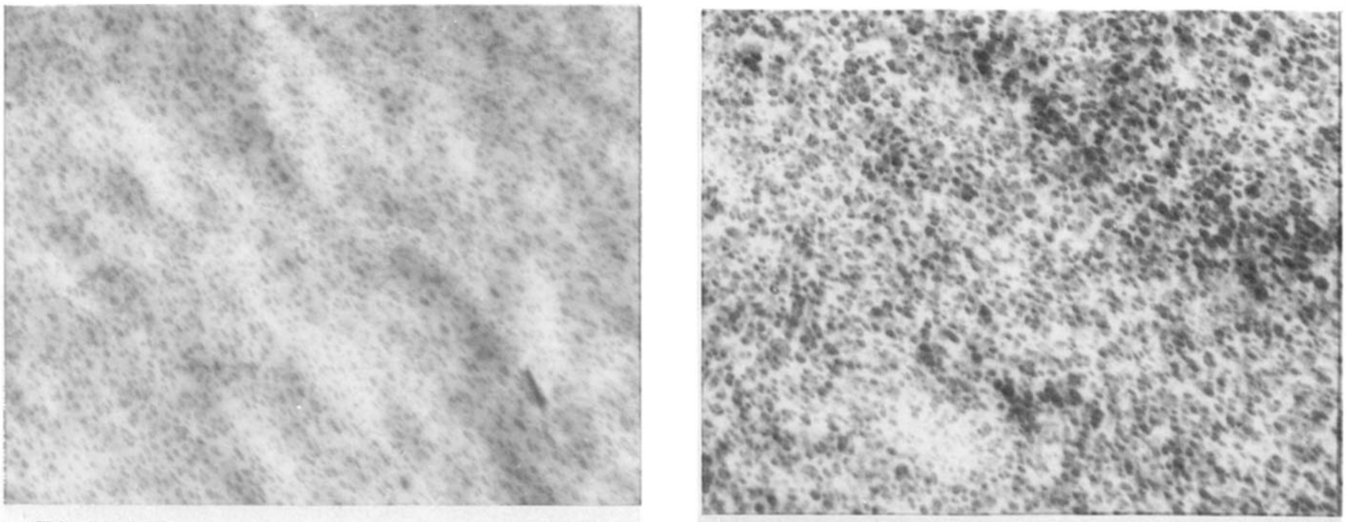
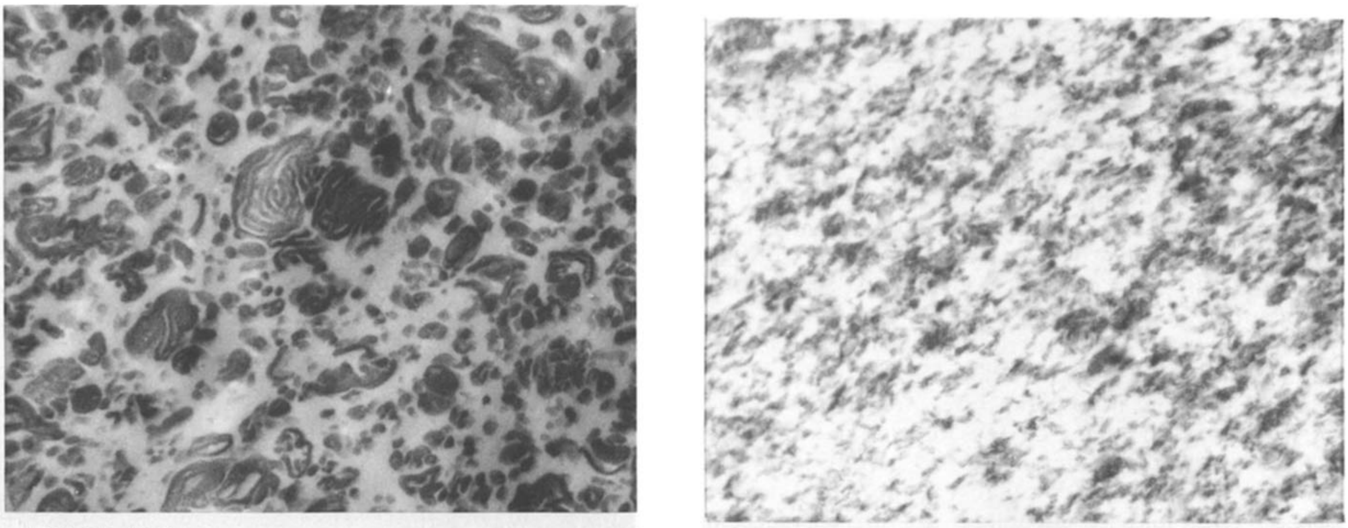


Figure 7 Impact strength of 72/8/20 nylon-6/nylon-12,12/SEBS-*g*-MA blends as a function of the number of extrusion passes at 240°C for the nylon-6 modification with nylon-12,12



a 72 /8 /20
Nylon 6 / Nylon 11 / SEBS-g-MA

b 72 /8 /20
Nylon 6 / Nylon 12 / SEBS-g-MA



c 72 /8 /20
Nylon 6 / Nylon 6,6 / SEBS-g-MA

d 72 /8 /20
Nylon 6 / Nylon 12,12 / SEBS-g-MA

e 72 /8 /20
Nylon 6 / Nylon 12,12 / SEBS-g-MA

Figure 8 TEM photomicrographs for 80/20 modified nylon-6/SEBS-*g*-MA blends. The nylon-6 matrix is modified by 10% of the following polyamides: (a) nylon-11, (b) nylon-12, (c) nylon-6,6 and (d) nylon-12,12; (e) shows a higher magnification of (d)

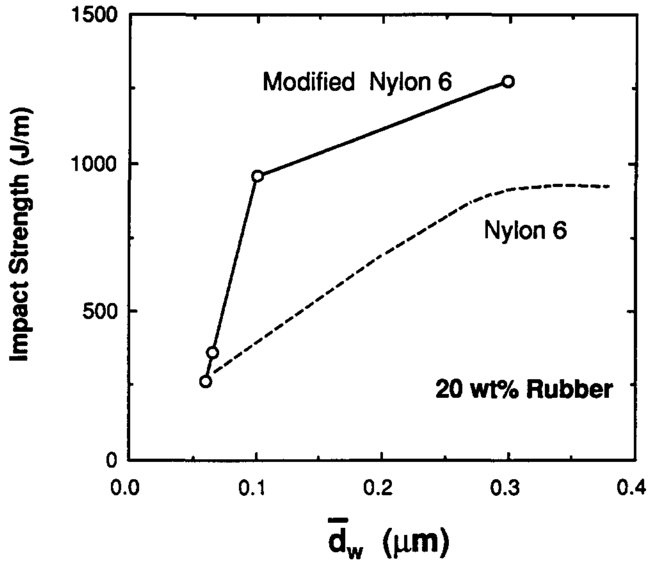


Figure 9 Impact strength of 80/20 modified nylon-6/SEBS-*g*-MA blends as a function of the rubber particle size taken from *Figure 8*. The broken curve shows the data for nylon-6/SEBS-*g*-MA/SEBS blends reported by Oshinski *et al.*[3]

obtained using samples prepared in the same manner as those used to obtain the mechanical properties shown in *Figures 3* and *4*. Particle size information from these TEM photomicrographs is summarized in *Table 2*. Modification by the monofunctional polyamides, nylon-11 (*Figure 8a*) and nylon-12 (*Figure 8b*), does not make noticeable changes in the morphology compared to the nylon-6/SEBS-*g*-MA control. On the other hand, the difunctional polyamides, nylon-6,6 (*Figure 8c*) and nylon-12,12 (*Figure 8d*) tend to generate larger and more complex rubber particles like those seen in *Figure 1* for blends based on pure difunctional polyamides. The enlargement effect is more obvious for nylon-6,6 modified blends than is the case for nylon-12,12 modified blends (see expanded TEM photomicrograph in *Figure 8e*).

These morphological differences are directly reflected in the impact strength (see *Figure 4*) via the rubber particle size effect. This is shown directly in *Figure 9*, where impact strength is plotted *versus* rubber particle size at 20% SEBS-*g*-MA and 10% polyamide modifier in the matrix phase taken from data in *Figures 3* or *4*. The impact strength increases with rubber particle size monotonically over the limits of this experiment. The broken curve represents previously reported data for nylon-6/SEBS-*g*-MA/SEBS blends[3]. Nylon-6-containing difunctional polyamides are toughened more than nylon-6/SEBS-*g*-MA/SEBS blends since the occluded polyamide in the rubber particles for the former increases apparent rubber volume[41,42].

SUMMARY

The effect of polyamide functionality for reaction with anhydrides (number of amine groups per molecule) on the morphology and toughness of their blends with the functionalized elastomer SEBS-*g*-MA has been examined in two different ways.

First, homopolyamides of the monofunctional type (nylon-6, nylon-11 and nylon-12) and the difunctional type (nylon-6,6 and nylon-12,12) were used as the matrix. In general, the types that have only one amine per chain yield rubber particles that are simple in shape and substantially smaller in size than the polyamides that may have two amines on some molecules. The latter tend to yield particles of complex shape with occlusions. Further work detailing the effects of melt viscosity and end-group content balance on rubber particle size is needed; nevertheless, the current results support the hypothesis that polyamide functionality is a key factor in morphology generation in blends with the maleated elastomer. A more detailed investigation of the toughening of these various polyamides will be reported subsequently[37].

Secondly, nylon-6 has been mixed with other polyamides in an attempt to use interchange reactions to alter the functionality of the polyamide matrix phase. Nylon-6 alone is not significantly toughened by blending with SEBS-*g*-MA since the rubber particles are too small. A nylon-6 phase homogenized with a difunctional polyamide becomes difunctional in character and particle size and toughness should increase. This is exactly what was observed when only 10% nylon-6,6, MXD6 or nylon-12,12 were used to modify the nylon-6 matrix. The effect for nylon-12,12 was less dramatic than that for nylon-6,6 or MXD6 since its more unfavourable physical interaction with nylon-6 limits the ability to achieve a phase homogenized matrix by interchange reaction. On the other hand, modification of nylon-6 with other monofunctional polyamides does not change the functionality of the polyamide matrix phase; hence, no increase in particle size or toughness should be expected. This is exactly what was observed when 10% of nylon-11 and nylon-12 was used to modify the nylon-6 matrix. The opportunity for these polyamides to undergo phase homogenization with nylon-6 is limited as in the case of nylon-12,12; however, the latter did lead to some enhancement of particle size and toughness for blends with SEBS-*g*-MA while the former did not. Thus, the approach also supports the proposed effect of polyamide functionality on morphology generation[4].

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