Rubber toughening of polyamides with functionalized block copolymers: 2. Nylon-6,6

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The toughening of nylon-6,6 using triblock copolymers of the type styrene–(ethylene-*co*-butylene)–styrene (SEBS) and a maleic anhydride (MA) functionalized version (SEBS-*g*-MA) is examined and compared with the behaviour reported for nylon-6 in the accompanying paper. Nylon-6,6 can be made super-tough by blending with SEBS-*g*-MA, and addition of SEBS merely reduced toughness. For nylon-6 super-toughness was achieved only with certain combinations of SEBS and SEBS-*g*-MA since with just the latter the rubber particles ($\sim 0.05\ \mu m$) generated were too small for effective toughening. The SEBS served to raise particle size to within the optimal range. In contrast, blends of nylon-6,6 with SEBS-*g*-MA give rubber particles that are within the optimal size range (just less than $1\ \mu m$); however, these particles have a very complex structure. For blends containing both SEBS and SEBS-*g*-MA, there seem to be two distributions of shapes but not size. Evidence is shown that the extent of grafting to nylon-6,6 is less than that in nylon-6 for similar conditions. It is proposed that the large difference in morphology found for nylon-6,6 *versus* that for nylon-6 stems from basic chemical differences between the two polyamides rather than rheological or processing factors. Nylon-6 is monofunctional while nylon-6,6 is difunctional in their reactions with anhydride. The possible consequences of this are discussed.

(Keywords: nylon-6,6; blends; block copolymers; rubber toughening; maleic anhydride)

INTRODUCTION

The accompanying paper (part 1)[1] reported on the toughening of nylon-6 by blending with various elastomeric materials with a main focus on combinations of styrene–hydrogenated butadiene–styrene or styrene–(ethylene-*co*-butylene)–styrene triblock copolymers (SEBS) with a maleic anhydride (MA) functionalized version (SEBS-*g*-MA). Comparisons were made to blends with a typical functionalized ethylene/propylene copolymer, EPM-*g*-MA. These same elastomers were used here to form blends with nylon-6,6 as the matrix material. To our knowledge, a direct comparison of the toughening of nylon-6 and nylon-6,6 has not been made using the same materials and processing procedures. Nylon-6,6 shows some distinctly different trends than those described in the previous paper for nylon-6, which appear to be primarily a result of differences in blend morphology. The latter is proposed to be related to fundamental chemical differences between nylon-6 and nylon-6,6.

MATERIALS AND PROCEDURES

Table 1 summarizes the sources and certain information about the materials used in this study. All materials containing nylon-6,6 were dried at 80°C for at least 12 h in a vacuum oven before processing.

All processing conditions used for blends containing nylon-6,6 were identical to those used for nylon-6[1,2] except that, because of the higher melting point of the former, the processing temperature was set at 280°C rather than at 240°C used for the latter. Thus, the relative viscosity of the materials in *Table 1* is referenced to that of the nylon-6,6 at 280°C.

RHEOLOGY

As demonstrated in the previous paper[1], Brabender torque rheometry can be useful for characterizing the melt flow behaviour of the individual components of a blend and for obtaining an indication of graft reactions during blending. *Figure 1* shows torque *versus* time for nylon-6,6 at 280°C and at a rotor speed of 60 r.p.m. After several minutes of fluxing, the torque levels off at a nearly constant value about the same as that for the nylon-6 used in the previous paper at 280°C. However, the torque for the nylon-6 at 240°C (the temperature used for its melt processing) is about three-fold larger than for this nylon-6,6 at its melt processing temperature. The relative viscosity of the components under process conditions is an important parameter that affects blend morphology. As may be seen in *Table 1*, SEBS is slightly more viscous than nylon-6,6 while SEBS-*g*-MA is slightly less viscous. However, their viscosities relative to nylon-6,6 at 280°C are slightly lower than those relative to nylon-6 at 240°C. The functionalized ethylene–propylene rubber has considerably higher viscosity in comparison with nylon-6,6 than it does relative to nylon-6.

Figure 2 shows torque–time traces for blends of nylon-6,6 with SEBS-*g*-MA which are quite similar qualitatively to analogous plots for nylon-6 except that the torque levels are lower. In some cases, there is

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Table 1 Materials used

Designation used here	Material (commercial designation)	Composition	Molecular weight	Relative melt viscosity[a]	Source
Nylon-6,6	(Zytel 101)		$\bar{M}_n = 17000$ $\bar{M}_w = 35000$	1.00	E.I. DuPont Co
SEBS	Styrene/ethylene-butene/styrene (Kraton G 1652)	29% styrene	Styrene block = 7000 EB block = 37500	1.43	Shell Chemical Co.
SEBS-*g*-MA	Styrene/ethylene-butene/styrene (Kraton G 1901X)	29% styrene 1.84 wt% MA[b]	Not available	0.70	Shell Chemical Co.
SEBS-H	Styrene/ethylene-butene/styrene (Kraton G 1651)	29% styrene	Styrene block = 29000 EB block = 116000	[c]	Shell Chemical Co.
EPM-*g*-MA	Ethylene/propylene rubber grafted with maleic anhydride	1.2 wt% MA	$M_n = 40000$–50000	6.17	COPOLYMER Co.

[a] Brabender torque at 280°C and 60 r.p.m. divided by that of nylon-6,6
[b] Determined by elemental analysis after solvent/non-solvent purification
[c] Could not be characterized as explained previously[1]

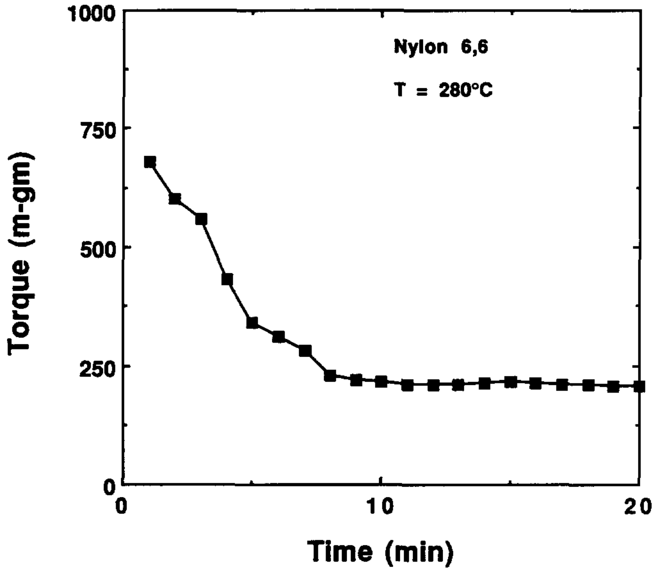


Figure 1 Brabender torque response for nylon-6,6 at 280°C and 60 r.p.m.

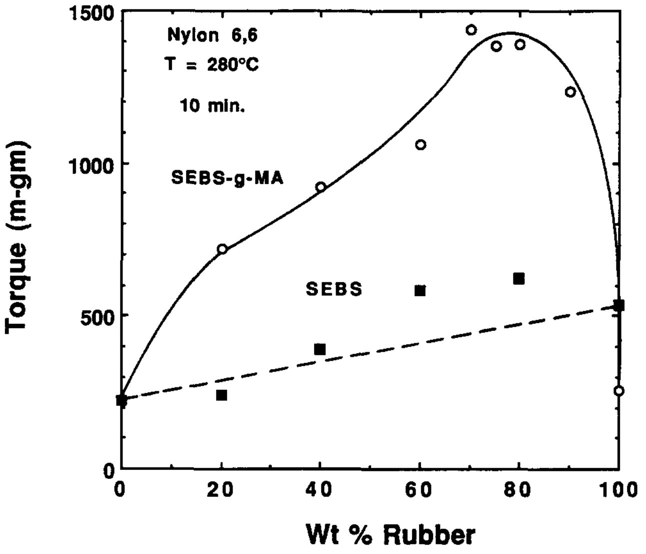


Figure 3 Brabender torque for blends of nylon-6,6 with SEBS and with SEBS-*g*-MA after 10 min at 280°C and 60 r.p.m.

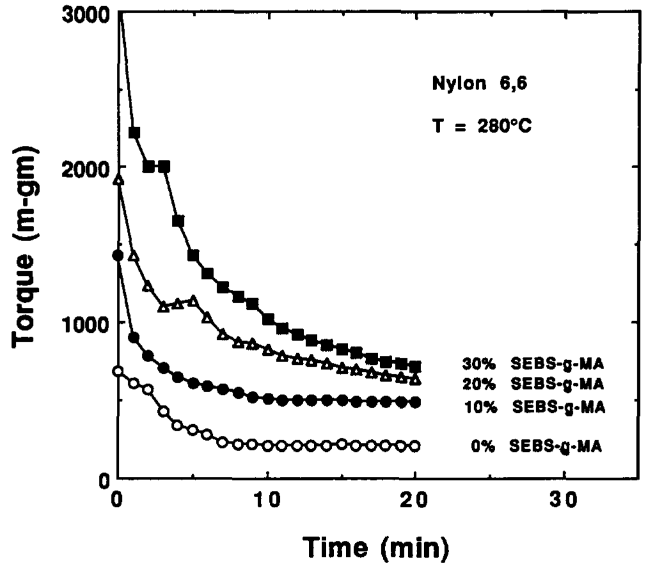


Figure 2 Brabender torque response for SEBS-*g*-MA blends with nylon-6,6 at 280°C and 60 r.p.m.

evidence for a 'bump' in the torque curves at the end of fluxing. *Figure 3* shows the torque at 10 min for the entire spectrum of blend compositions. Blends of nylon-6,6 with SEBS show nearly additive behaviour as expected[1–3], but for blends with SEBS-*g*-MA there is a strong maximum in torque at about 80% rubber. Nylon-6 showed similar behaviour but the maximum occurred at about 30% rubber in that case. The relative increase in torque caused by reaction with SEBS-*g*-MA was somewhat larger for nylon-6 than observed for nylon-6,6. Thus, there appears to be some rather basic differences in the grafting response of nylon-6,6 compared with that of nylon-6. Other indications of this difference will be discusssed later.

Figure 4 shows torque–time curves for blends of nylon-6,6 with the EPM-*g*-MA elastomer. Note the much higher viscosity of EPM-*g*-MA compared with nylon-6,6. Blends with 30% functional rubber have steady-state torques lower than that of the rubber in contrast to what was found for nylon-6. The melt viscosity of the EPM-*g*-MA decreases very little with time compared with the changes observed for the block copolymers or the nylons. Its high viscosity apparently makes this

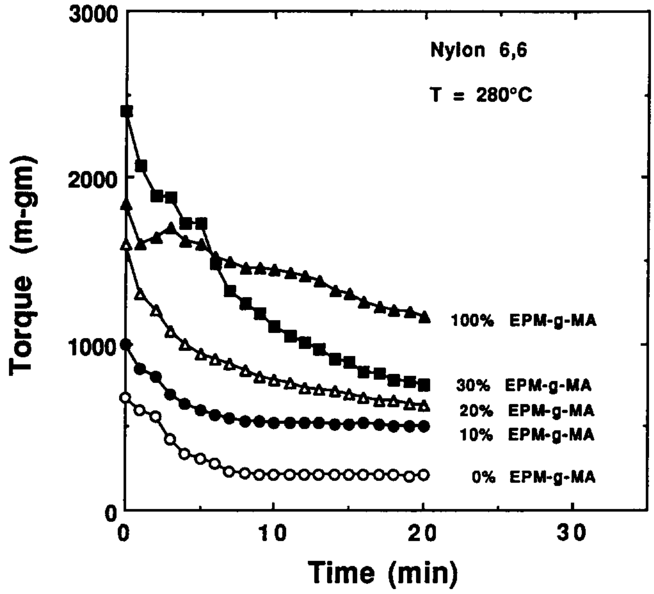


Figure 4 Brabender torque response for EPM-*g*-MA blends with nylon-6,6 at 280°C and 60 r.p.m.

material harder to disperse and may limit the extent of grafting. The Weissenberg-type effect that was quite prominent for its blends with nylon-6 was less so for blends with nylon-6,6 probably because of less graft formation.

MECHANICAL PROPERTIES

Blends of nylon-6,6 with varying levels of SEBS and SEBS-*g*-MA were made using two passes through a single-screw extruder followed by injection moulding into test specimens as described previously for nylon-6 blends[1,2]. Impact and tensile properties are shown in *Figures 5–7*. As expected, addition of SEBS leads to very little toughening of nylon-6,6. In contrast to the case for nylon-6, addition of SEBS-*g*-MA alone to levels of 20% or more leads to super-tough materials. At 20% SEBS-*g*-MA, the nylon-6,6 blend has an Izod impact strength about four times that of the nylon-6 blend. Modic *et al.*[4–6] found a similar result. The modulus and yield strength of nylon-6,6 blends with SEBS-*g*-MA are much lower than for blends with SEBS. For nylon-6, the differences between the two elastomers were not so great.

For nylon-6, it was found that the mechanical properties of ternary blends involving combinations of the two elastomers, SEBS and SEBS-*g*-MA, did not depend on mixing order. We did not repeat the complete sequence of order of mixing experiments for nylon-6,6 because of the need to contain the scope of this work. For comparison with the previous blends with nylon-6, all ternary blends involving nylon-6,6 were prepared by the simple protocol of simultaneous addition of all components to the extruder. The mechanical properties of these ternary blends are shown in *Figures 8–11*. The most interesting result here is that the Izod impact strength (*Figure 8*) does not go through any maximum like it did for nylon-6 as the SEBS/SEBS-*g*-MA ratio varies at constant total rubber level. For nylon-6,6, there is a continuous increase in toughness as the amount of functional rubber is increased. For the higher rubber levels, super-tough materials are achieved for a range of SEBS-*g*-MA content. As seen in *Figures 9* and *10* the

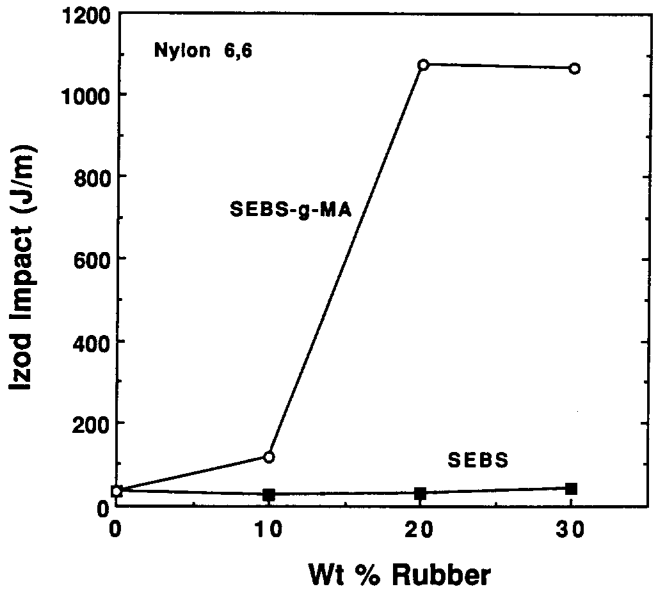


Figure 5 Notched Izod impact strength of nylon-6,6 blends with SEBS and with SEBS-*g*-MA

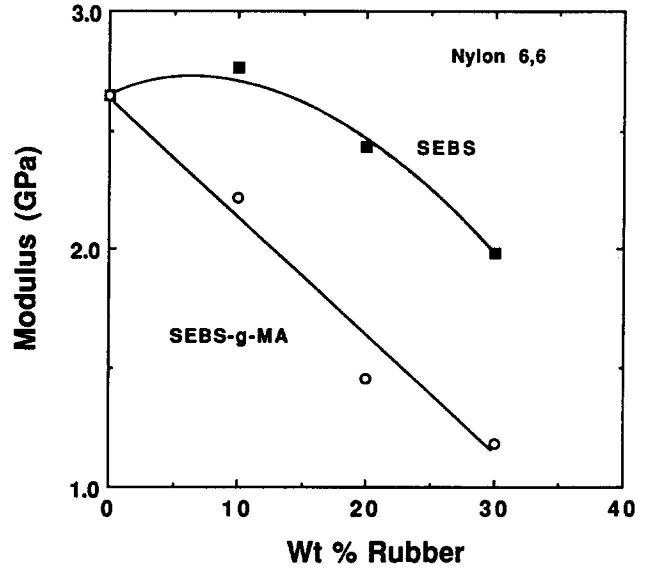


Figure 6 Tensile modulus of nylon-6,6 blends with SEBS and with SEBS-*g*-MA

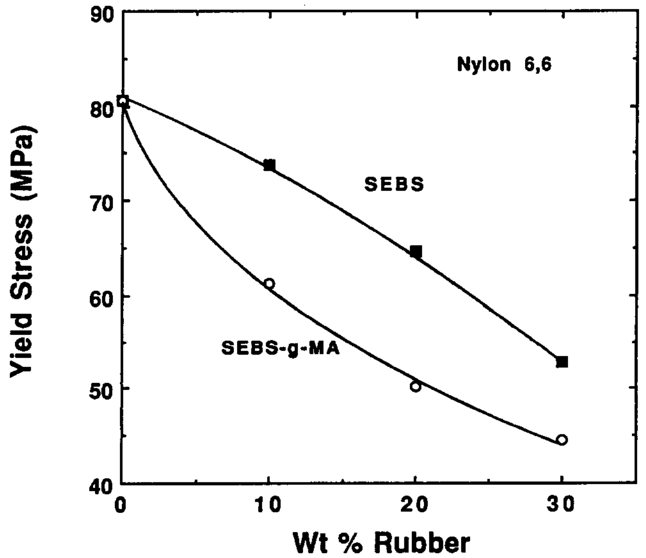


Figure 7 Tensile yield stress of nylon-6,6 blends with SEBS and with SEBS-*g*-MA

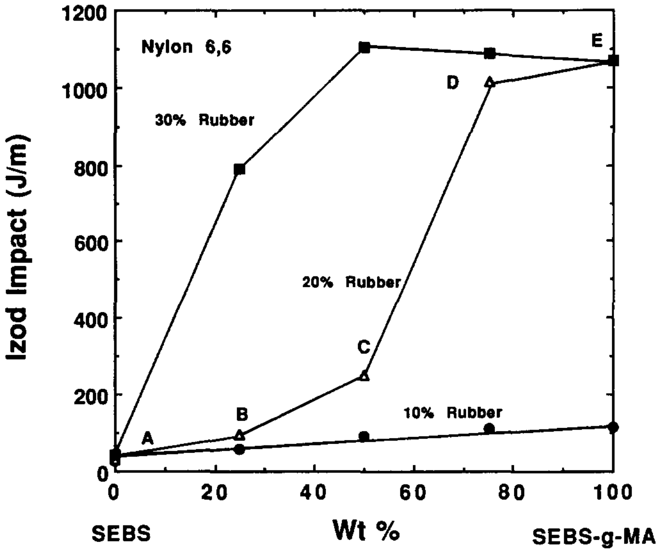


Figure 8 Notched Izod impact strength for 10, 20 and 30% rubber/nylon-6,6 blends as a function of SEBS/SEBS-*g*-MA ratio

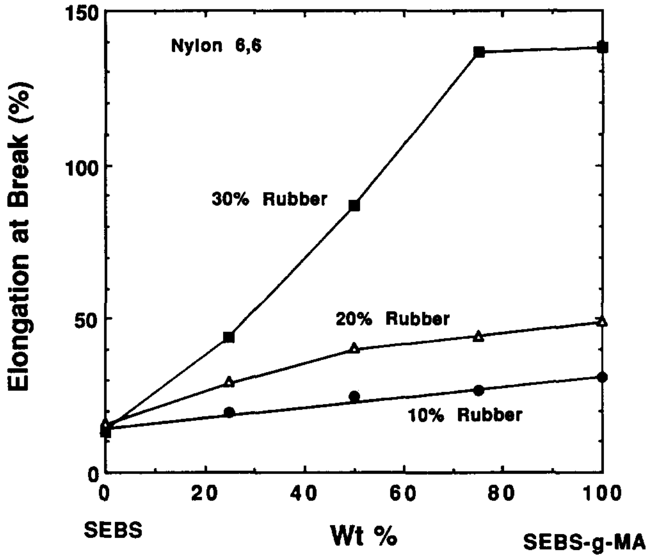


Figure 11 Elongation at break for 10, 20 and 30% rubber/nylon-6,6 blends as a function of SEBS/SEBS-*g*-MA ratio

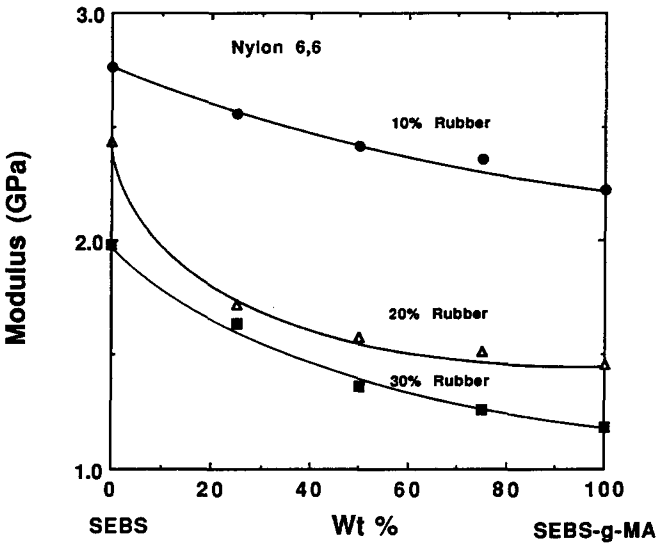


Figure 9 Tensile modulus for 10, 20 and 30% rubber/nylon-6,6 blends as a function of SEBS/SEBS-*g*-MA ratio

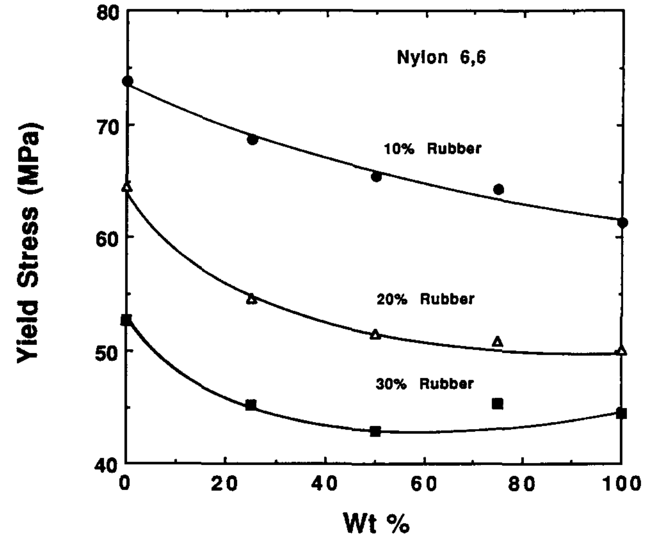


Figure 10 Tensile yield stress for 10, 20 and 30% rubber/nylon-6,6 blends as a function of SEBS/SEBS-*g*-MA ratio

modulus and yield strength decrease continuously as the fraction of functionalized rubber increases for each total rubber level. The elongation at break (*Figure 11*) shows the opposite trend. The latter in some sense parallels the Izod impact behaviour except for the fact that there is a large difference in the elongation at break between blends having 20% and 30% total rubber at high contents of SEBS-*g*-MA, whereas the impact strengths of these materials are about the same, i.e. super-tough.

A main physical difference between the nylon-6,6 blends described here and the nylon-6 blends discussed in the previous paper is that the former were made at 280°C while the latter were made at 240°C. To ascertain whether this significantly affects properties, e.g. owing to differences in reaction rates, blends of SEBS-*g*-MA and nylon-6 were made at 280°C. The mechanical properties of the blends made at 280°C were essentially the same as those made at 240°C.

For some ternary blends based on nylon-6,6, the non-functional rubber SEBS was replaced with its higher-molecular-weight counterpart SEBS-H. At all levels examined, inclusion of SEBS-H reduced blend toughness, as may be seen in *Figure 12*. This is also in contrast with what was found for nylon-6.

Figure 13 compares the effectiveness of a functionalized ethylene/propylene rubber, EPM-*g*-MA, with SEBS-*g*-MA for toughening nylon-6,6. Again, contrary to what was found for nylon-6 EPM-*g*-MA does not lead to super-tough blends at 20% rubber whereas SEGS-*g*-MA does.

INTERFACIAL ADHESION

A limited number of lap shear experiments were performed on laminated specimens to investigate the interfacial adhesion of SEBS-*g*-MA to nylon-6,6. Samples failed cohesively in the polyamide phase, indicating that the adhesion to nylon-6,6 is as good as or better than that to nylon-6.

MORPHOLOGY

As in the case of nylon-6 in the previous paper[1], a

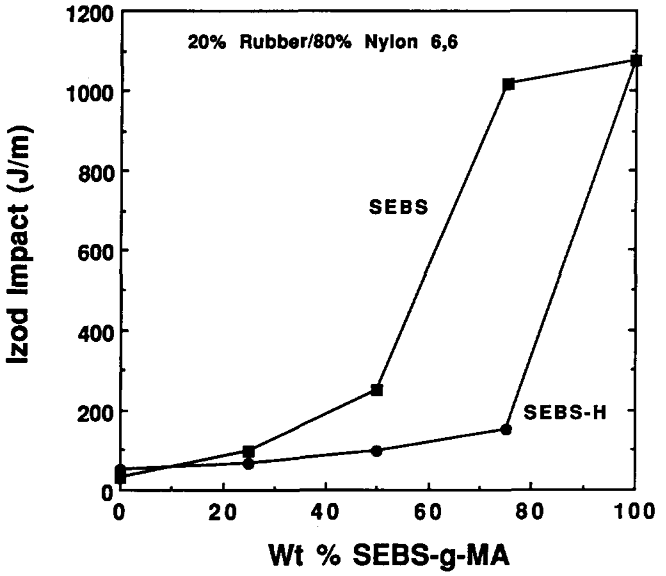


Figure 12 Notched Izod impact strength for 20% rubber/80% nylon-6,6 blends as a function of the ratio of SEBS or SEBS-H non-functionalized rubber to SEBS-*g*-MA

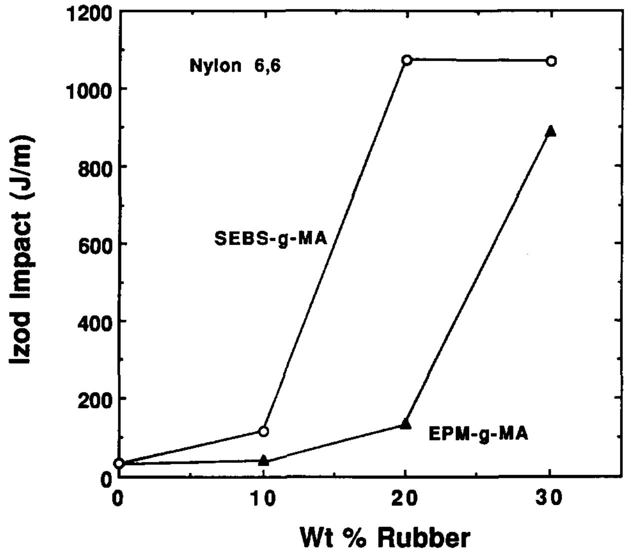


Figure 13 Notched Izod impact strength of nylon-6,6 blends with SEBS-*g*-MA and with EPM-*g*-MA

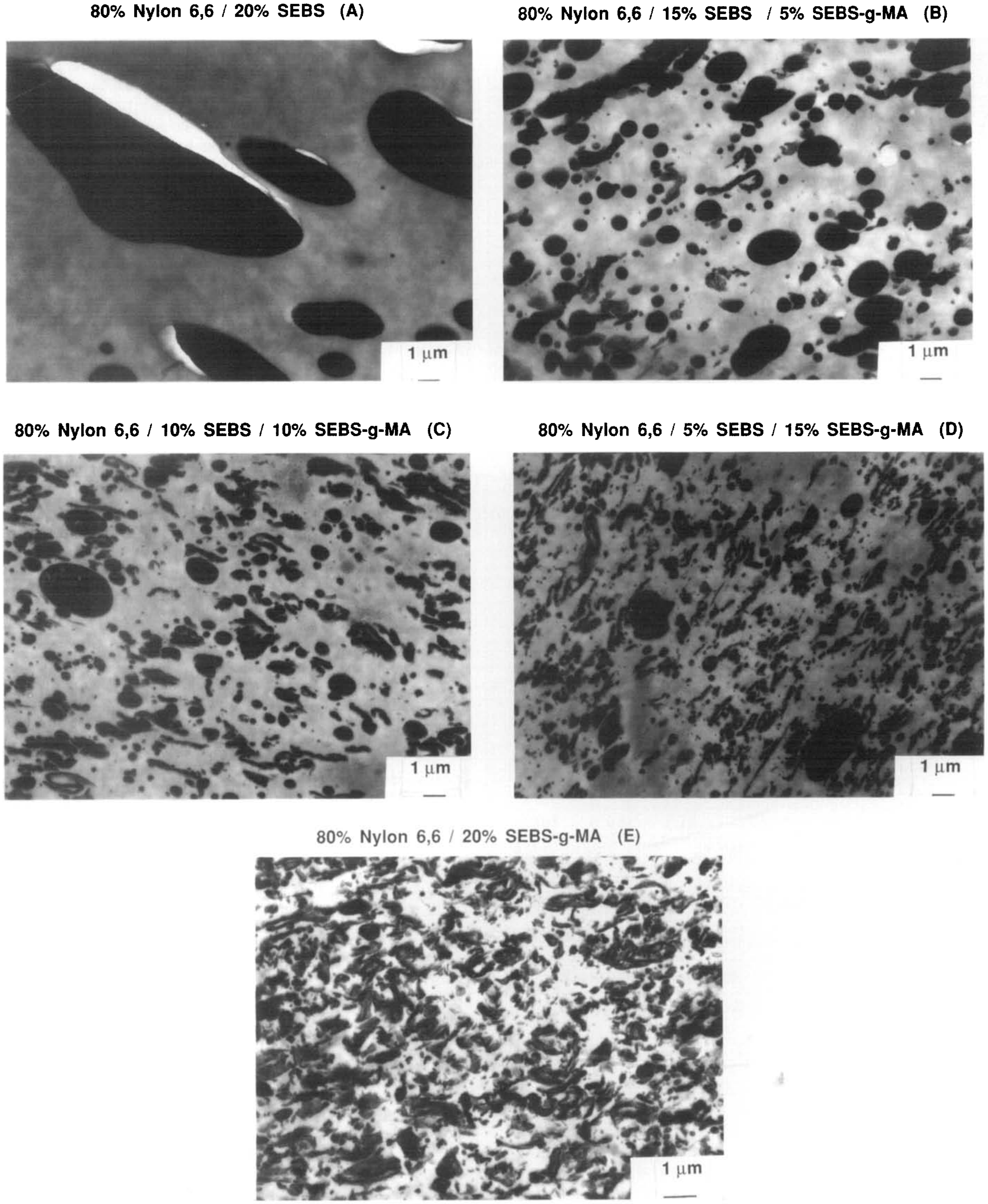
carefully selected series of blends were examined by transmission electron microscopy (TEM). Each blend contained 20% total rubber while the ratio of SEBS-*g*-MA to SEBS was varied. The photomicrographs in *Figure 14* compare the morphology of this series at the same magnification. The letters A–E correspond to the compositions so designated in *Figure 8*.

For SEBS alone (*Figure 14A*), the rubber particles are very large (greater than 6 μm in effective diameter) and somewhat oblong in nature, and they obviously do not adhere well to the matrix. Thus, the situation for nylon-6,6 is virtually the same as that found for nylon-6 in this case. However, for SEBS-*g*-MA alone, the morphology for nylon-6,6 blends is very different from those based on nylon-6. For the latter, the rubber particles appeared to be essentialy spherical and were very small (~ 0.05 μm). As may be seen in *Figure 14E* for nylon-6,6 as the matrix, the particles are definitely not spherical and are much larger. The particle structure is very complex, with evidence that they contain some nylon-6,6 within their rather ill-defined external boundaries. Others[7] have noted for blends with functionalized ethylene/propylene rubber that the rubber particles may have significant amounts of occluded nylon-6,6. To our knowledge, the literature on similar blends using nylon-6 does not report such occluded material although this probably would not be detected using the scanning electron microscopy (SEM) techniques commonly employed. However, in the previous paper[1] we found only minor occlusion of nylon-6, if any, using TEM techniques. That nylon-6,6 tends to become occluded but nylon-6 does not explains at least part of the reason why rubber particles are larger in nylon-6,6 blends. Careful examination of most published TEM photomicrographs reveals some tendency for complex rubber particle shapes in the case of nylon-6,6. Based on solvent extraction tests, Modic *et al.*[4–6] suggested that blends based on nylon-6,6 have a more continuous rubber phase than do those based on nylon-6.

Leaving the issue of complex shapes aside for the moment, we can now see why 20% SEBS-*g*-MA in nylon-6,6 gives a super-tough material, whereas the comparable blend based on nylon-6 is not so tough. For the latter, the rubber particles (~ 0.5 μm) are too small for effective toughening as discussed before, while for nylon-6,6 the particles (~ 0.5 μm) are not too small nor are they too large for effective toughening[8–15] as in the case of SEBS. The obvious question we are now left with is why the rubber particle sizes are so different in the two polyamides. There seems to be no explanation for this in terms of rheological or processing factors; however, as proposed later, chemical differences may be the root cause of this very fundamental difference.

For ternary blends that contain both SEBS and SEBS-*g*-MA, the rubber particles exhibit varying levels of complexity and sizes as seen in *Figures 14B–D*. For composition D, there are many spheroidal-type particles, but there are some elongated or stringy types as well. As the blend includes more SEBS-*g*-MA, the proportion of spheroidal particles decreases while that of the more complex ones increases. *Figure 15* shows a more highly magnified view of some particles for composition D. Here we see some small and essentially spherical-type particles, some stringy particles, and a larger one near the centre that clearly contains occluded nylon-6,6. However, the latter particle looks as if, in reality, it might be an agglomeration of stringy particles or an elongated one that folded onto itself encapsulating some nylon-6,6 in the process.

Because of the complex shapes of the rubber particles in *Figure 14*, it is somewhat difficult to characterize their size quantitatively. However, we attempted to do this manually by analysing the photomicrographs shown. The entire field of view was used for A and B while only a fraction of the field was used for C to E. Non-round particles were assigned the diameter of a circle of equivalent area. No corrections were attempted to convert these apparent particle diameters into true sizes since these methods[16–20] are not applicable for such complex particle shapes. The particle size histograms constructed in this way[2] showed much broader particle size distributions than found earlier for nylon-6; however, we must re-emphasize the difficulties associated with a detailed analysis of such complex particles. Nevertheless,


80% Nylon 6,6 / 20% SEBS (A)

80% Nylon 6,6 / 15% SEBS / 5% SEBS-g-MA (B)

80% Nylon 6,6 / 10% SEBS / 10% SEBS-g-MA (C)

80% Nylon 6,6 / 5% SEBS / 15% SEBS-g-MA (D)

80% Nylon 6,6 / 20% SEBS-g-MA (E)

Figure 14 TEM photomicrographs of 20% rubber/80% nylon-6,6 blends at various ratios of SEBS/SEBS-*g*-MA rubber. Samples were cryogenically microtomed from injection-moulded bars and stained with RuO_4

this information was used to estimate average particle sizes, and the results are shown in *Figure 16*. There is a sharp drop in rubber particle size in going from pure SEBS to the next composition where one-quarter of the rubber is SEBS-*g*-MA. Further increases in SEBS-*g*-MA content reduce the average size by modest amounts compared with that observed for nylon-6. If we now replot the impact strength from *Figure 8 versus* the particle size from *Figure 16*, we get the result shown in *Figure 17*, which looks quite similar in both form and detail to results published by Wu[8,10] for nylon-6,6 blends with functionalized ethylene/propylene rubber.

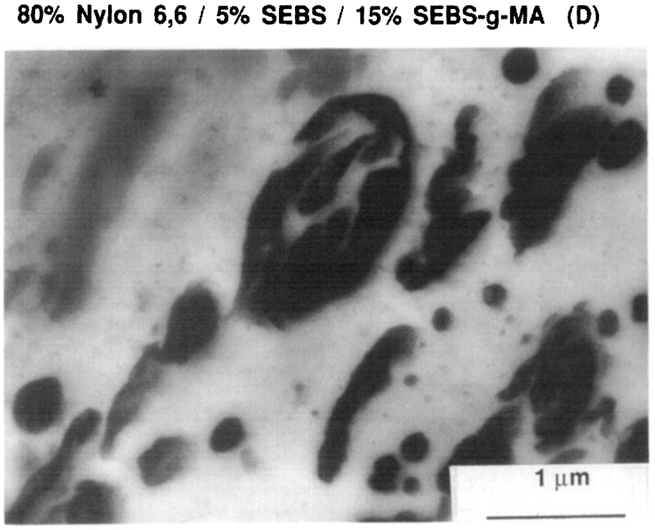


Figure 15 TEM photomicrograph of composition D (5% SEBS/15% SEBS-*g*-MA/80% nylon-6,6)

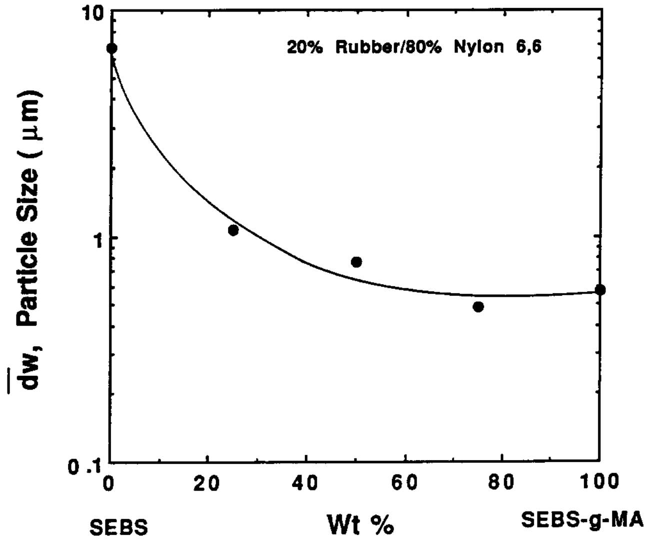


Figure 16 Variation in particle size with SEBS-*g*-MA level for 20% rubber/80% nylon-6,6 blends

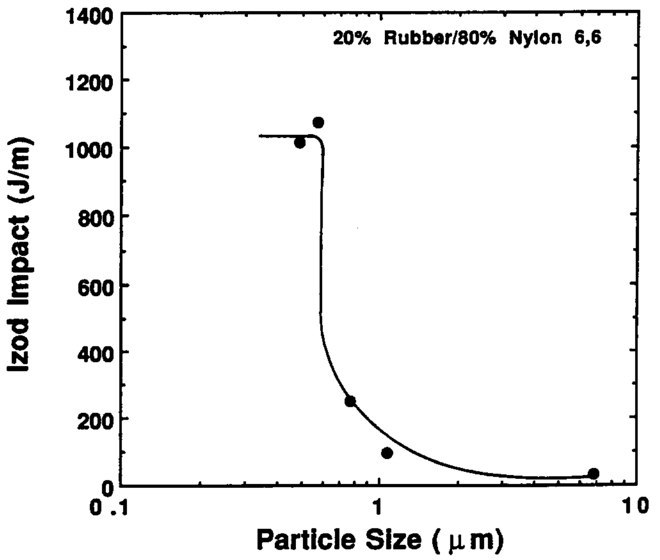


Figure 17 Notched Izod impact strength of 20% rubber/80% nylon-6,6 blends as a function of particle size

Whether SEBS and SEBS-*g*-MA are effectively mixed in the rubber particles, as we believe is nearly the case for nylon-6 ternary blends, is much less clear cut for nylon-6,6. For blends containing any SEBS-*g*-MA, it is clear that there are no really large particles like those seen in *Figure 14A* for pure SEBS. In general, the particles tend to be smaller the more SEBS-*g*-MA there is, and though the size distributions are broad there is no evidence for two distinct populations of size. Such facts imply some degree of co-mingling of the two elastomers. However, for the ternary blends, there are clearly at least two classes of shapes as mentioned above. We are not able to give a definitive explanation for this at the present time, but it may mean some significant differences in chemical nature for the particles with different shapes.

THERMAL AND DYNAMIC MECHANICAL ANALYSIS

Thermal and dynamic mechanical analyses for the series of blends A to E in *Figure 8* were made to assess the extent that graft reactions change the characteristics of the semicrystalline matrix and the elastomer phase. The results will be compared with those for the similar series of blends based on nylon-6 as the matrix.

Figure 18 shows the ratio of the heat of fusion for nylon-6,6 in the blend relative to that of pure nylon-6,6 after identical processing and thermal analysis protocols. A ratio of 0.8 would indicate that the nylon-6,6 in the blend has the same crystallinity as that for nylon-6,6 that has not been blended. In *Figure 18*, first heat values are just above this limit while second heat values are slightly below it regardless of SEBS-*g*-MA to SEBS ratio. For nylon-6, there was a consistent trend to lower crystallinity of the blend matrix as the amount of SEBS-*g*-MA increased. In contrast, it appears that the presence of the reactive elastomer has little influence on the crystallinity of nylon-6,6.

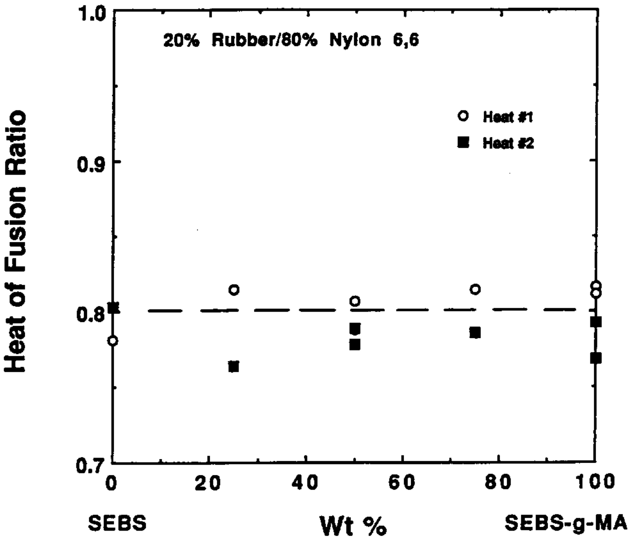


Figure 18 Heat of fusion ratio for injection-moulded 20% rubber/80% nylon-6,6 blends from d.s.c. Heats of fusion from the first heat for these blends were divided by first heat values of twice extruded nylon-6,6 ($\Delta H = 63.37\ \mathrm{J\ g^{-1}}$) and heats of fusion from the second heat were divided by second heat values of twice extruded nylon-6,6 ($\Delta H = 75.99\ \mathrm{J\ g^{-1}}$)

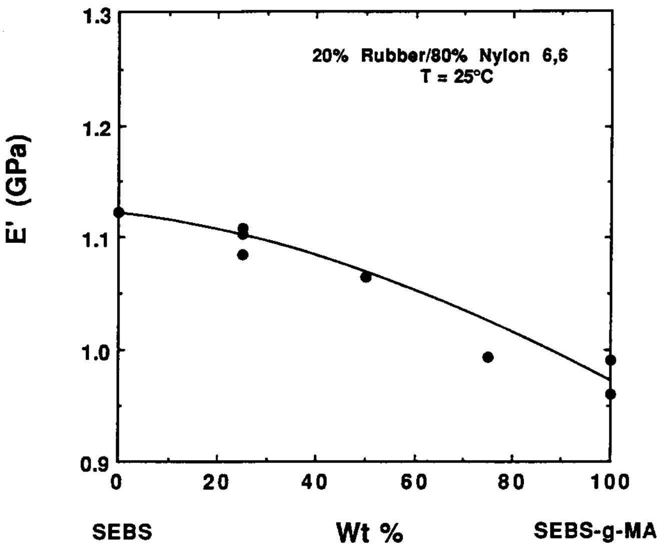


Figure 19 Storage modulus of 20% rubber/80% nylon-6,6 blends as a function of the amount of SEGS-g-MA in the rubber phase

The storage modulus E' at 25°C is plotted against the fraction of SEBS-g-MA in the rubber phase in *Figure 19*. As in the case of nylon-6, E' decreases as the fraction of reactive rubber increases; however, for nylon-6,6 the change is not nearly as large as that seen for nylon-6.

The maximum value of tan δ at the glass transition for nylon-6,6 in these blends is plotted in *Figure 20*. For nylon-6 blends, there was a significant increase in the size of this peak as the SEBS-g-MA fraction increased consistent with a reduction in crystallinity and possible alterations in texture caused by increased grafting reaction. For nylon-6,6 there is also an increase in tan δ at the matrix glass transition as the SEBS-g-MA fraction increases, but the effect is considerably smaller than that seen in nylon-6.

Figure 21 shows the maximum tan δ for the rubber phase glass transition. For nylon-6 as the matrix, there was a sizeable reduction in this peak as the fraction of SEBS-g-MA in the blend increased consistent with decreased damping of the rubber as the amount of grafting increased. On the contrary, *Figure 21* shows very little change in the size of the rubber peak as the fraction of functional rubber increases.

One interpretation of the above results is that nylon-6,6 does not react as extensively with the anhydride groups of SEBS-g-MA as does nylon-6. This is quite reasonable since there is more external surface of the rubber particles exposed to the matrix for blends of nylon-6 that contain SEBS-g-MA compared with nylon-6,6; however, chemical analyses that quantify the extent of reaction are needed to be certain. If there is less reaction for nylon-6,6, the question is whether this is the cause for its larger rubber particles or are the larger particles (low surface area) the cause for the low extent of reaction.

CONCLUSIONS

Nylon-6,6 may be made super-tough by blending with SEBS-g-MA alone, whereas for nylon-6 such toughness levels could be achieved only by using a combination of SEBS-g-MA and SEBS[1,2]. Melt blending of SEBS-g-MA alone with nylon-6 produces rubber particles (~0.05 μm) that are too small for effective toughening, and dilution of the rubber phase with the non-reactive SEBS increases particle size to within the optimal range[8–15]. On the other hand, melt blending of SEBS-g-MA with nylon-6,6 results in particles that are already within the optimal size range for toughening, i.e. much larger than for SEBS-g-MA in nylon-6 and smaller than those for SEBS in nylon-6 or nylon-6,6. The SEBS-g-MA rubber particles in nylon-6,6 blends have very complex, often elongated, shapes and show evidence for considerable occlusion of matrix material. The interfaces between the rubber and matrix are somewhat diffuse, and the surfaces do not have the uniform curvature expected for two-phase mixtures where interfacial tension forces govern. Use of mixtures of SEBS and SEBS-g-MA in nylon-6,6 results in a continuous variation of particle size with no evidence for two size distributions as would be expected if the two rubbers formed separate, non-interacting particles. However, there are definitely two or more populations

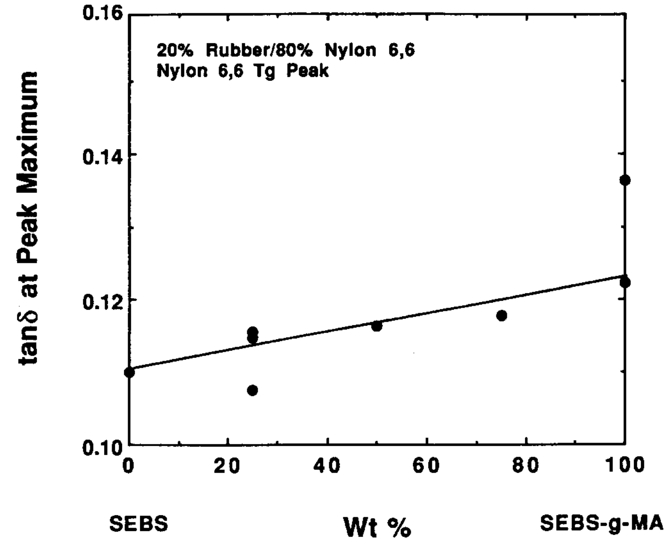


Figure 20 Tan δ at the nylon-6,6 glass transition peak maximum for 20% rubber/80% nylon-6,6 blends as a function of SEBS-g-MA in the rubber phase

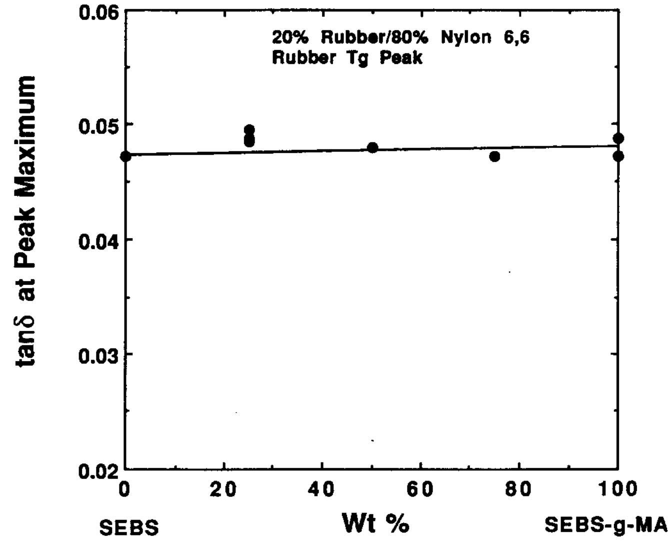


Figure 21 Tan δ at the rubber glass transition peak maximum for 20% rubber/80% nylon-6,6 blends as a function of SEBS-g-MA in the rubber phase

of particle shapes (complex with irregular surfaces and spheroidal with smooth surfaces) that vary in proportion with the ratio of SEBS-*g*-MA to SEBS content.

Limited lap shear measurements indicated that graft reactions at SEBS-*g*-MA/nylon-6,6 interfaces result in strong adhesion that appears to be at least equivalent to that for nylon-6. However, thermal and dynamic mechanical measurements suggest that the extent of graft reaction in blends with nylon-6,6 is significantly less than that in comparable blends with nylon-6. Torque rheometry comparisons between nylon-6 and nylon-6,6 systems reveal differences that can also be interpreted as less grafting in nylon-6,6 blends. This proposal needs to be examined more carefully by direct chemical analyses that can accurately assess the extent of graft reaction in such cases. At first sight, lower extent of reaction for nylon-6,6 could easily be understood given the larger size of the rubber particles observed and, therefore, the lower exterior surface area contact between the phases. However, because of the irregularity of the rubber particle surfaces and the occluded matrix material within these particles in the case of nylon-6,6 the extent of actual surface contact between phases is difficult to assess. Another interesting observation relates to differences in power consumption (current to extruder motor) during processing. For nylon-6 blends, the power consumption during the second extrusion was higher than in the first extrusion, indicating that the reaction continues with increased melt residence time. For nylon-6,6 blends the power consumption in the second extrusion was about the same as that in the first.

The differences in mechanical behaviour of blends based on nylon-6 and nylon-6,6 appear to be well explained in terms of morphological factors. The obvious question then is why the two polyamides generate such different rubber particle morphologies when blended with SEBS-*g*-MA. Do similar differences develop for other functionalized elastomers? No other detailed comparisons of nylon-6 *versus* nylon-6,6 like that given here have appeared, to our knowledge. We believe that these differences are not due to simple rheological or processing factors but that they relate to differences in the fundamental chemical nature of these polyamides. We present here the basic issues of this proposal without attempting to give a detailed description of how rubber particles evolve during reactive blending. Nylon-6, like its open ring monomer, is always monofunctional in each of the two types of functional units, $-NH_2$ or $-COOH$. On the other hand nylon-6,6, also like its monomers, can be difunctional with respect to either $-NH_2$ or $-COOH$. That is, some nylon-6,6 molecules have two amine ends while others may have only one or none. This leads to fundamentally different ways that the two polyamides can react with maleic anhydride units at the interface of a rubber particle, as schematically suggested in *Figure 22*. It is often assumed[11,21–23] that the dominant reaction is an amine end with an anhydride unit to give an imide linkage; however, the basic chemical difference between nylon-6 and nylon-6,6 remains the same even for the alternative of interchange reactions with amide linkages rather than reaction of amine chain ends. Thus, nylon-6 can only undergo simple grafting reactions that involve one point of attachment per polyamide chain as suggested in *Figure 22*. In the classical view of compatibilization[24–27], this leads to a decrease in interfacial tension and some stabilization against coalescence. In addition, the graft chains may transmit extra rheological forces to the particles beyond those envisioned by continuum mechanics. On the other hand, nylon-6,6 can have up to two particle attachments per chain because of its difunctionality to anhydrides or 'crosslinking' type effects. As shown in *Figure 22*, nylon-6,6 may form loops or bridges between particles when they approach each other closely enough. Such chain connections can act to prevent particle break-up or separation, encourage coalescence and provide a mechanism for occlusion of matrix material into the rubber particles. If the dominant reaction involves amine ends, then a certain fraction of chains will not participate at all since statistically they can have acid units at both ends. We believe that these fundamental chemical differences play some role in the physical differences observed for blends of nylon-6 *versus* nylon-6,6. Further work is required to define the mechanisms better and whether other factors also play any role.

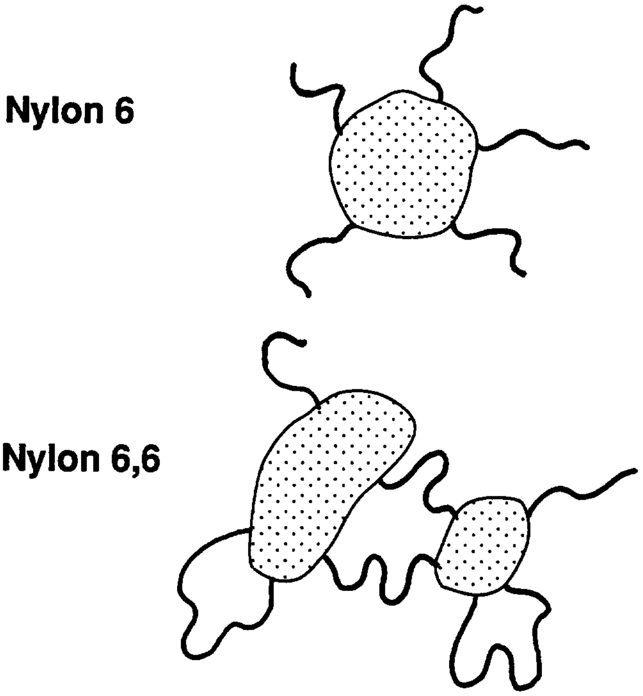


Figure 22 Schematic representation of possible grafting reactions for nylon-6 and nylon-6,6 with elastomeric phase

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