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The role of matrix molecular weight in rubber toughened nylon 6 blends:
3. Ductile–brittle transition temperature

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Izod impact strength was measured as a function of temperature for blends of nylon 6 with maleated and non-maleated styrene–hydrogenated butadiene–styrene triblock copolymers, SEBS, and ethylene/propylene random copolymers, EPR, to determine the effects of polyamide molecular weight, rubber type, and rubber particle size on the ductile–brittle transition temperature. In general, the ductile–brittle transition temperature decreases as the molecular weight of the nylon 6 matrix increases when compared at either constant maleic anhydride content of the rubber or at constant rubber particle size. Blends based on SEBS type elastomers with a standard styrene content never attain ductile–brittle transition temperatures below −20°C; whereas, blends generated with EPR type rubbers or a block copolymer of low styrene content can reach values as low as −50°C. This difference in ductile–brittle transition temperature is related to the low temperature mechanical properties of the rubber phase. Copyright © 1996 Elsevier Science Ltd.

(Keywords: toughening; molecular weight; nylon 6)

INTRODUCTION

The first two papers in this series deal with how the molecular weight of the nylon 6 matrix affects the morphology that is generated[1] and the room temperature Izod impact strength[2] of blends with maleated and non-maleated styrene–hydrogenated butadiene–styrene triblock copolymers, SEBS, and ethylene/propylene random copolymers, EPR. It was shown that the rubber particle size can be reduced by an order of magnitude by increasing the nylon 6 molecular weight over the range generally available commercially while holding all other process and material variables constant[1]. This reduction in particle size results from the large increase in the melt viscosity with this change in molecular weight in spite of the corresponding reduced number of amine chain ends available for graft reaction with the anhydride units in the rubber phase. At fixed processing conditions, a large variation in rubber particle size can be effected by varying the maleic anhydride content in the rubber phase; this allowed the determination of the upper and lower critical particle size limits for toughening of nylon 6 at room temperature[2]. For blends based on SEBS-type elastomers, the room temperature Izod impact strength was shown to increase with nylon 6 molecular weight when the weight average rubber particle size is below about 0.3 μm.

This paper focuses on the low temperature toughness of the blends of nylon 6 with the SEBS and EPR type elastomers described in previous papers. The Izod impact strength of each blend was measured as a function of temperature to determine the ductile to brittle transition temperature. Numerous studies have examined how rubber type, degree of maleation, and morphology affect the ductile–brittle transition of rubber toughened nylon[3–15]. However, very little work has been reported on how the nature of the polyamide phase or very small rubber particles (below 0.2 μm) affect low temperature toughness. This paper examines the effects of nylon 6 molecular weight, rubber type, and rubber particle size on the ductile–brittle transition temperature.

EXPERIMENTAL

Brief summaries of the nylon 6 materials (*Table 1*) and the various rubbers (*Table 2*) used are given here; more complete details are included in earlier papers[1,2]. The procedures for nylon 6 characterization, blend compounding, and morphology determination are also described elsewhere[1,16].

Izod impact specimens, 0.318 cm thick, were moulded using an Arburg Allrounder injection moulding machine for blends containing 20% rubber and 80% nylon 6. All specimens were placed inside a polyethylene bag in a desiccator immediately after being moulded. The specimens were tested in the dry as moulded state using the standard Izod procedure (ASTM D256).

Low temperature toughness was determined using a TMI Impact Tester with a thermal chamber. The temperature inside the chamber was lowered using a temperature controller connected to a CO_2 supply. Twenty to 30 specimens of a given blend (far-gate end of a standard Izod bar) were placed inside the chamber

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Table 1 Nylon 6 materials used in this study

Supplier's designation	$\bar{M}_n$ (g mol^{-1})^a	Izod impact (J m^{-1})^b	Supplier
Capron XA-1767	13 100	53 ± 5	Allied Signal Inc.
Ultramild BO	13 200	59 ± 8	BASF Corp.
Ultramild B1	14 000	62 ± 11	BASF Corp.
Capron 8202	16 400	59 ± 5	Allied signal Inc.
Ultramild B3	17 500	59 ± 5	BASF Corp.
Ultramild B2	19 400	63 ± 12	BASF Corp.
Capron 8207F	22 000	43 ± 11	Allied Signal Inc.
Capron 8209F	29 300	50 ± 11	Allied Signal Inc.
Ultramild B5	37 300	63 ± 5	BASF Corp.

[a] From intrinsic viscosity measurements using $[\eta] = 5.26 \times 10^{-4}\ \bar{M}_w^{0.745}$ assuming $\bar{M}_n = \frac{1}{2}\bar{M}_w$

[b] At room temperature (24°C)

and the temperature was reduced to 15°C. After a minimum of 5 min, the chamber was quickly opened and one specimen was tested. Another specimen was then clamped in the vice jaws, the chamber was closed and the specimen was given 1–2 min to thermally stabilize before testing. This process was repeated until three to five specimens were tested at this temperature. Typically, four or more sets of samples were placed in the chamber simultaneously allowing the specimens to remain at the desired temperature for up to 1 h. After the impact strength of each sample set was determined at 15°C, the temperature was reduced 10°C and the entire process was repeated. The temperature was reduced in 10°C increments until each sample set failed in a brittle manner at two temperatures. The ductile to brittle transition temperature was defined as the mid-point in the step-like change in Izod impact strength as the temperature was varied.

The dynamic mechanical properties of injection moulded specimens of the nylon 6 materials and rubbers were determined by a Polymer Laboratories DMTA at a frequency of 1 Hz.

EFFECT OF RUBBER TYPE ON LOW TEMPERATURE TOUGHNESS

Two types of rubber were used as toughening agents for nylon 6[1,2]. One is based on styrene–hydrogenated butadiene–styrene elastomer triblock copolymers (designated as SEBS). The amount of maleation was controlled by the amount of grafting to the rubber mid-block, SEBS-g-MA-*X*% type, or by mixing a non-maleated SEBS elastomer with a highly maleated version, i.e. SEBS/SEBS-g-MA-2%. Another maleated triblock copolymer, designated here as L-SEBS-g-MA, contains a lower styrene content and a higher rubber mid-block content than the standard SEBS material. The second type of elastomer used was an ethylene/propylene random copolymer, designated as EPR, and a maleated version, EPR-g-MA, which contains 1.14% maleic anhydride. EPR and EPR-g-MA were mixed together in a similar manner as the block copolymers to control the amount of maleation.

The weight average rubber particle size of SEBS-g-MA-*X*% and SEBS/SEBS-g-MA-2% mixtures generated in blends with nylon 6 follow similar trends as the amount of maleation is varied[1], but the former produce slightly smaller rubber particles that are less polydisperse in size distribution than the latter. Because of the similar morphological trends and the limited number of SEBS-g-MA-*X*% type elastomers available for this study, the two SEBS systems will be compared as toughening agents for nylon 6.

SEBS-g-MA-X% and SEBS/SEBS-g-MA-2%

Izod impact strength was measured at various temperatures for blends of each nylon 6 shown in *Table 1* as a function of maleic anhydride content of the SEBS rubber phase over the full range of compositions that available materials permitted. *Figure 1* shows representative plots of Izod impact strength vs. temperature for blends based on low, medium, and high molecular weight nylon 6 materials. For blends based on SEBS/SEBS-g-MA-2% mixtures, data are only shown for the following rubber phase compositions 0%, 25%, 50%, 75%, and 100% SEBS-g-MA-2% in the interest of clarity; data for other compositions can be found elsewhere[16]. Similar plots for nylon 6 blends with EPR/EPR-g-MA mixtures are shown in *Figure 2*. As found previously[2], *Figure 1* shows that an increase in

Table 2 Rubbers used in this study

Designation used here	Material (supplier's designation)	Composition	Molecular weight	Supplier
SEBS	Kraton G 1652	29wt% styrene	Styrene block = 7 000 EB block = 37 500	Shell Chemical Co.
SEBS-g-MA-0.5%	RP-6510	29wt% styrene 0.46wt% MA	N/A	Shell Chemical Co.
SEBS-g-MA-1%	Kraton FG-1921X	29wt% styrene 0.96wt% MA	N/A	Shell Chemical Co.
SEBS-g-MA-2%	Kraton FG-1901X	29wt% styrene 1.84wt% MA	N/A	Shell Chemical Co.
L-SEBS	Kraton 1657	13wt% styrene	Styrene block = 5 500 EB block = 73 000	Shell Chemical Co.
L-SEBS-g-MA	RP-6509	13wt% styrene 1.4wt%, MA	N?A	Shell chemical Co.
EPR	Vistalon 457	43wt% ethylene 53wt% propylene	$\bar{M}_n = 54\,000$ $\bar{M}_w/\bar{M}_n = 2$	Exxon Chemical Co.
EPR-g-MA	Exxelor 1803	43wt% ethylene 53wt% propylene 1.14wt% MA	N/A	Exxon Chemical Co.

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

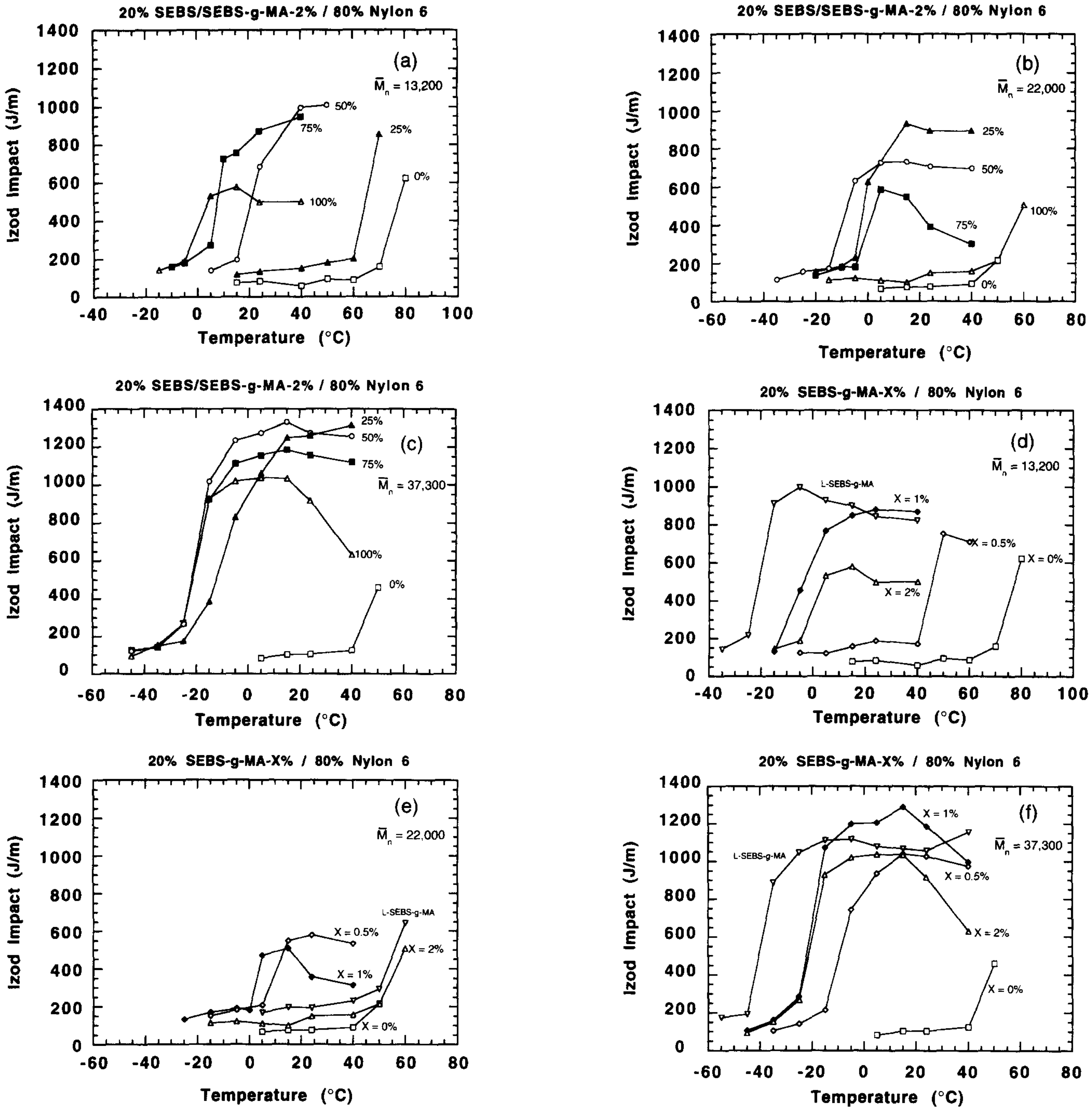

Figure 1 Effect of rubber phase maleic anhydride content and nylon 6 molecular weight on Izod impact strength vs. temperature relationship for blends of SEBS/SEBS-g-MA-2% (a–c), and SEBS-g-MA-X% (d–f) with nylon 6 in the ratio of 20% rubber/80% nylon 6. Data are shown here only for selected rubber mixtures and three representative nylon 6 molecular weights: $\bar{M}_n$ = 13 200 (low), $\bar{M}_n$ = 22 000 (medium), and $\bar{M}_n$ = 37 300 (high). More complete data are available elsewhere[16]. Parts d–f compare the L-SEBS-g-MA and SEBS-g-MA-X% elastomers as toughening agents for nylon 6

maleic anhydride content does not ensure an increase in toughness above the ductile–brittle transition temperature. Below the ductile–brittle transition temperature, impact strength is relatively constant regardless of maleic anhydride content or nylon 6 molecular weight. It must be emphasized that in general a high room temperature Izod impact strength does not ensure a low ductile–brittle transition temperature.

Figure 1 shows that for certain blends the Izod impact strength reaches a maximum just above the ductile–brittle transition temperature and then decreases as the temperature is raised further. Such behaviour has been observed for a variety of toughened nylon 6 blends[8,9,11] using various specimen thicknesses and testing geometries[17]. From the current results it appears that this occurs when the rubber particle size is below a certain limit. *Figure 3* shows this limit on plots of room temperature impact strength vs. rubber particle size; the symbols used to distinguish the various compositions in *Figures 1* and *3* are identical with the exception of the additional compositions in *Figure 3* which are included to aid the construction of the curves. Blends having rubber particles smaller than those within the optimal range for toughness, see the vertical lines drawn in *Figure 3*, show this behaviour[16]. A future paper will examine this phenomenon in more detail using other techniques for characterizing the fracture process[17].

Ductile–brittle transition temperatures as defined

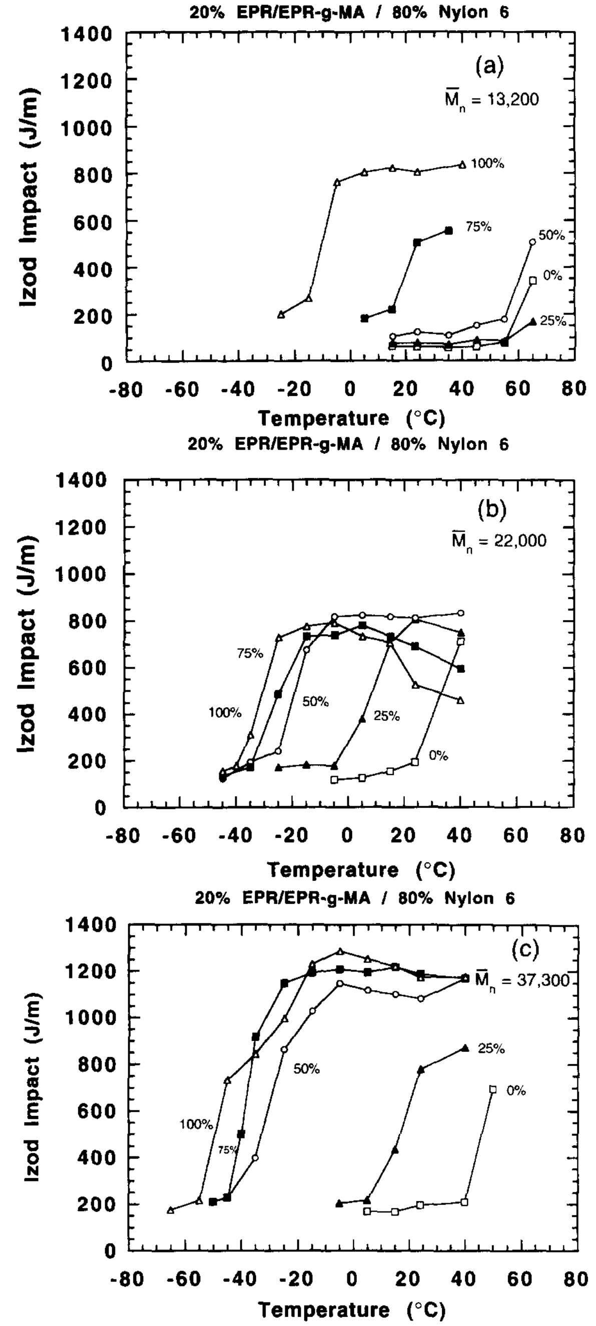

Figure 2 Effect of rubber phase maleic anhydride content and nylon 6 molecular weight on Izod impact strength vs. temperature for blends of EPR/EPR-g-MA with nylon 6 in the ratio of 20% rubber/80% nylon 6. Data are shown here only for selected rubber mixtures and these representative nylon 6 molecular weights: (a) $\bar{M}_n = 13\,200$, (b) $\bar{M}_n = 22\,000$ and (c) $\bar{M}_n = 37\,300$

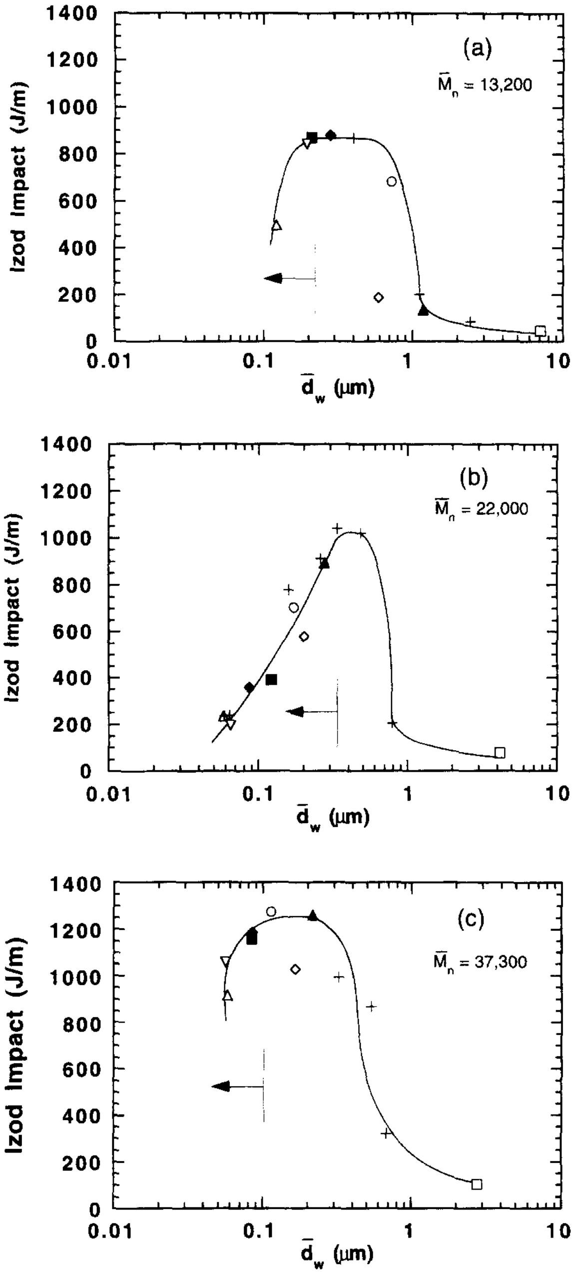

Figure 3 Effect of weight average rubber particle diameter on room temperature Izod impact strength for blends of SEBS/SEBS-g-MA-2% and SEBS-g-MA-X% with a low (a), medium (b) and high (c) molecular weight nylon 6, all in the ratio of 20% rubber/80% nylon 6. The symbols correspond to the blend compositions in *Figure 1*. When the particle size is below the limit shown by the vertical line, Izod impact strength decreases with temperature above the ductile–brittle transition temperature

earlier, deducted from plots like those in *Figure 1* are shown in *Figure 4* as a function of the maleic anhydride content in the rubber phase. For blends based on either SEBS-g-MA-X% or SEBS/SEBS-g-MA-2% mixtures with nylon 6 materials having low or high molecular weight (see *Figures 4a* and *c*), the ductile–brittle transition temperature monotonically decreases with increasing maleic anhydride content of the rubber phase eventually reaching a plateau region that is dependent on the nylon 6 molecular weight. As the molecular weight of the matrix phase increases, the amount of maleic anhydride required to reach the plateau decreases and the value of the ductile–brittle transition temperature in the plateau region decreases with increasing nylon 6 molecular weight. For nylon 6 materials of intermediate molecular weight, viz., $\bar{M}_n = 17\,500$ and 22 000, the ductile–brittle transition temperature goes through a minimum and then increases when the maleic anhydride content exceeds about 1.5%. Blends based on SEBS-g-MA-X% and SEBS/SEBS-g-MA-2% rubber systems have identical ductile–brittle transition temperatures when the molecular weight of nylon 6 is greater than 22 000. When the $\bar{M}_n$ is in the range of 13 100–16 400, SEBS-g-MA-X% type elastomers have lower ductile–brittle transition temperatures; however, when the matrix molecular weight is between 17 500 and 22 000 the SEBS/SEBS-g-MA-2% mixture leads to better low temperature toughness[16]. It is significant to note that none of the blends based on

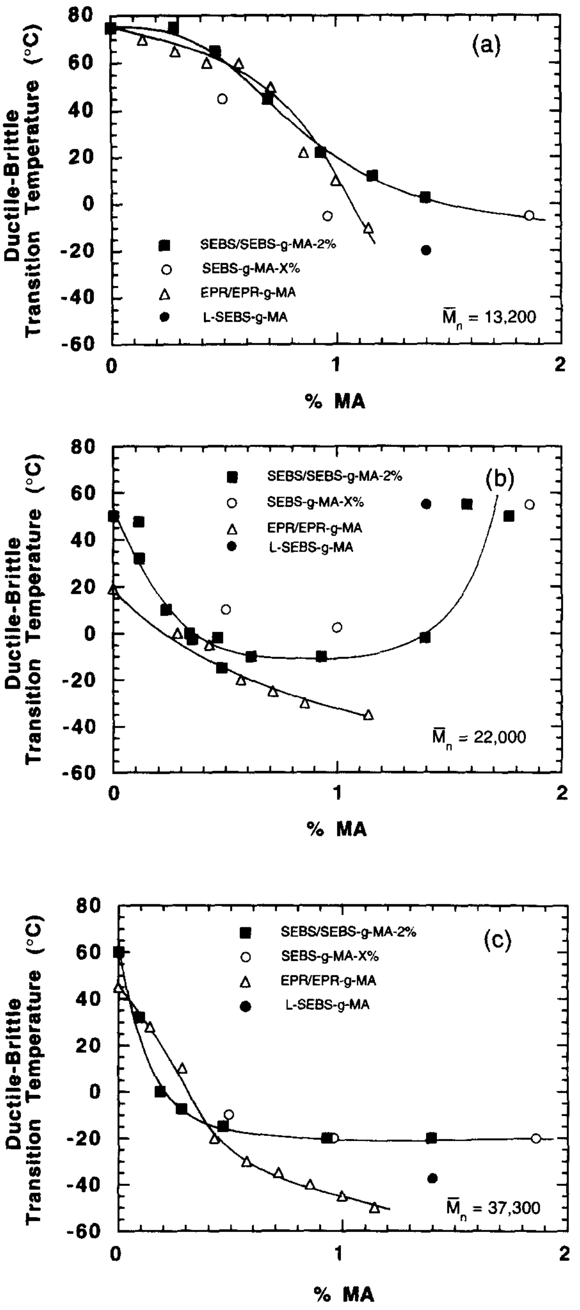

Figure 4 Effect of rubber phase maleic anhydride content on the ductile–brittle transition temperature for blends of SEBS/SEBS-g-MA-2%, SEBS-g-MA-*X*%, L-SEBS-g-MA, and EPR/EPR-g-Ma with a low (a), medium (b) and high (c) molecular weight nylon 6, all in the ratio of 20% rubber/80% nylon 6

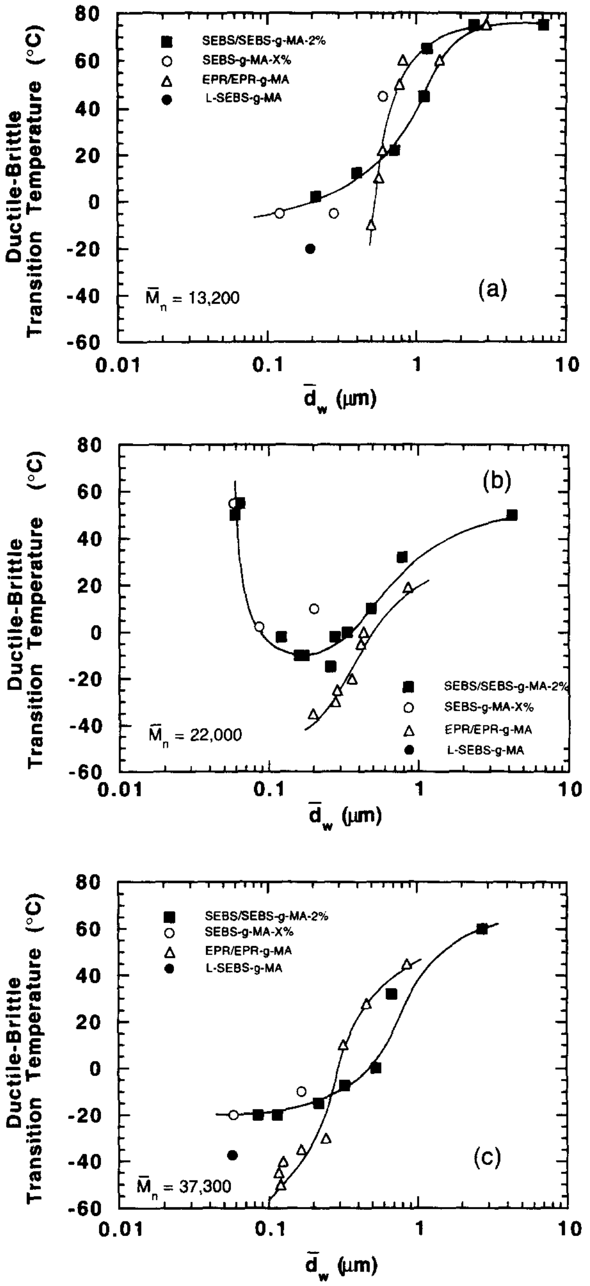

Figure 5 Effect of weight average rubber particle diameter on the ductile–brittle transition temperature for blends of SEBS/SEBS-g-MA-2%, SEBS-g-MA-*X*%, L-SEBS-g-MA, and EPR/EPR-g-MA with a low (a), medium (b) and high (c) molecular weight nylon 6, all in the ratio of 20% rubber/80% nylon 6

20% of these SEBS type rubbers have ductile–brittle transition temperatures below −20°C.

The above discussion has focused on parameters which appear to be important from a formulation point of view but do not provide insight into the fundamental issues underlying the trends seen in *Figures 1* and *4*. Previous studies[3,4,14,18,19] have shown the importance of the rubber particle size, or interparticle distance, as a key factor in toughening polyamides. In this study the rubber fraction has been held constant; thus, ideal interparticle distance calculated in the usual way[14] is dependent only on the rubber particle size. The data from *Figure 4* are shown in *Figure 5* as a function of the weight average rubber particle size using information from Part 1[1].

The ductile–brittle transition temperature decreases as the weight average rubber particle size decreases and reaches a plateau for both SEBS rubber systems. However, for blends based on nylon 6 with $\bar{M}_n = 22\,000$, there is a sharp increase in the ductile–brittle transition temperature when the rubber particle size is less than 0.1 μm. One other nylon 6 material, $\bar{M}_n = 15\,500$, exhibits similar behaviour but to a lesser degree[16]. Oostenbrink[11] has also shown a rise in the ductile–brittle transition temperature for blends of nylon 6 ($\bar{M}_n = 15\,000$) and maleated EPR rubber for particle sizes less than 0.2 μm. It has been shown that extremely small rubber particles are not effective for toughening[11,18,20–22], but the size range where this becomes critical appears to be affected by the nylon 6 molecular weight and the rubber type[2,11].

The results in *Figure 5* indicate that SEBS-g-MA-*X*% and SEBS/SEBS-g-MA-2% rubber systems having a maleic anhydride content of 1% or greater lead to similar values of ductile–brittle transition temperatures when compared at equivalent rubber particle sizes. However, blends based on SEBS-g-MA-0.5% always have higher ductile–brittle transition temperatures than those based on SEBS/SEBS-g-MA-2% mixtures of an equivalent rubber particle size; a similar trend was observed for the room temperature Izod impact strength[2]. The disparity between the ductile–brittle transition temperatures of blends based on SEBS/SEBS-g-MA-2% vs. SEBS-g-MA-0.5% elastomers increases as the nylon 6 molecular weight decreases. Differences in polydispersity of rubber particle size between the two SEBS rubber systems could be a contributing factor. For low molecular weight nylon 6 materials, blends with SEBS/SEBS-g-MA-2% mixtures having maleic anhydride contents less than 0.5% were observed to have much broader distributions of rubber particle sizes (almost bimodal in some cases) compared to blends based on SEBS-g-MA-0.5%. On the other hand, Dijkstra[9] claims that narrower particle size distributions lead to lower ductile–brittle transition temperatures for blends of nylon 6 and polybutadiene.

EPR/EPR-g-MA

Mixtures of maleated ethylene/propylene rubber and its precursor, designated here as EPR-g-MA and EPR, respectively, were blended only with nylon 6 materials of low, medium, and high molecular weight using procedures described previously[1]. On the other hand, binary blends of EPR-g-MA, which contains 1.14% maleic anhydride, were made with all the nylon 6 materials shown in *Table 1* for comparison with SEBS-type rubbers of similar maleic anhydride contents. *Figure 2* shows Izod impact strength vs. temperature for blends based on various EPR/EPR-g-MA mixtures. For clarity, only the compositions containing 0%, 25%, 50%, 75% and 100% EPR-g-MA are shown; data for additional compositions are reported elsewhere[16]. *Figure 2* shows that blends with EPR/EPR-g-MA mixtures generally have lower room temperature Izod impact strength than similar blends with SEBS-type rubber systems[2].

The ductile–brittle transition temperatures deduced from the curves in *Figure 2*, see *Figure 4*, decrease rapidly as the maleic anhydride content of the rubber phase increases. Blends based on EPR/EPR-g-MA mixtures (open triangles) do not appear to reach a plateau over the limited maleic anhydride contents available. For higher molecular weight nylon 6 materials, ductile–brittle transition temperatures as low as −50°C are observed. The ultimate possible limit may be lower but could not be reached with the highest level of maleic anhydride available, i.e. pure EPR-g-MA.

EPR/EPR-g-MA mixtures provide better low temperature toughening than the SEBS-g-MA-*X*% and SEBS/SEBS-g-MA-2% rubber systems for nylon 6 materials with $\bar{M}_n > 13\,200$ and when the maleic anhydride content is greater than 0.5%[16]. Comparing binary blends of two rubber types with similar levels of maleation, i.e. EPR-g-MA (%MA = 1.14) and SEBS-g-MA-1%, with the various nylon 6 materials indicates that the molecular weight of the latter must be greater than 16400 before the ductile–brittle transition temperature of the EPR-g-MA blends become lower than that of the SEBS-g-MA-1% elastomer[16].

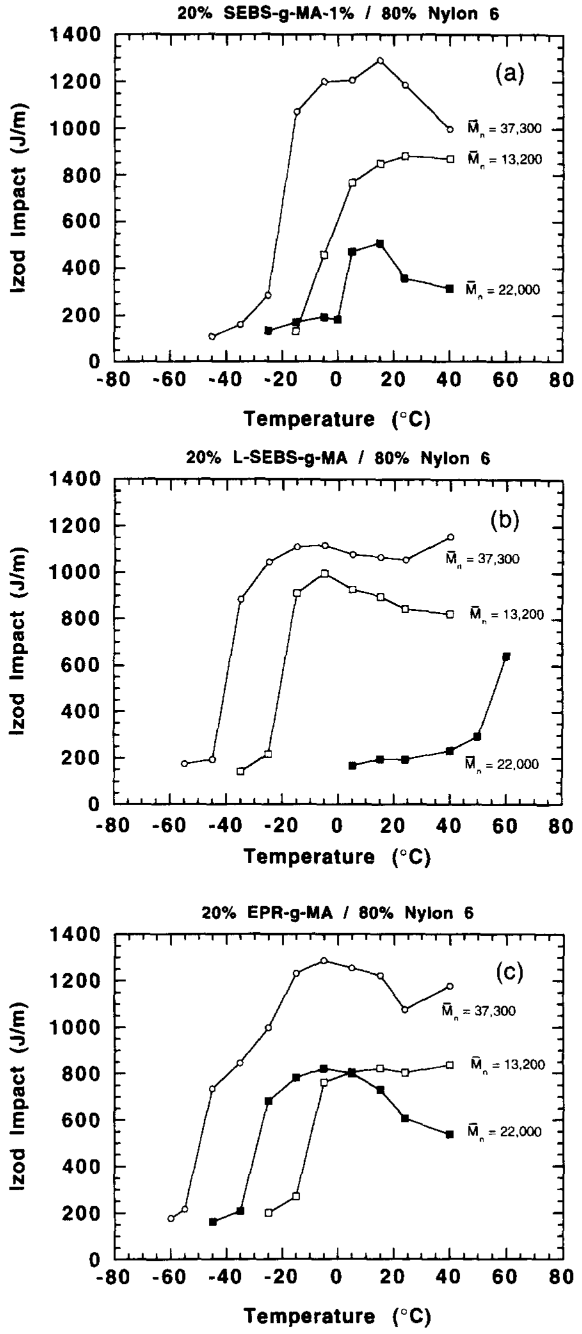

Figure 6 Effect of nylon 6 molecular weight on the Izod impact strength vs. temperature relationship for blends of 20% rubber/80% nylon 6 ($\bar{M}_n$ = 13 200, 22 000, and 37 300) with the following rubbers; (a) SEBS-g-MA-1%, (b) L-SEBS-g-MA, and (c) EPR-g-MA

Figure 5 shows the ductile brittle transition temperature of the blends from *Figure 4* plotted vs. the weight average rubber particle size (see Part 1). The ductile–brittle transition temperature for the EPR/EPR-g-MA system shows a rapid decrease over a small range of rubber particle sizes compared to the gradual reduction over a broad range of rubber particle sizes for the SEBS-based systems. In general, EPR-based rubber leads to better low temperature toughness than SEBS-based rubber only when the particle size is below a certain limit that varies with nylon 6 molecular weight. In all cases, binary blends of EPR-g-MA with the nine nylon 6 materials used in this study have lower ductile–brittle transition temperatures than blends based on SEBS-g-MA-*X*% or SEBS/SEBS-g-MA-2% when compared at the same rubber particle size[16].

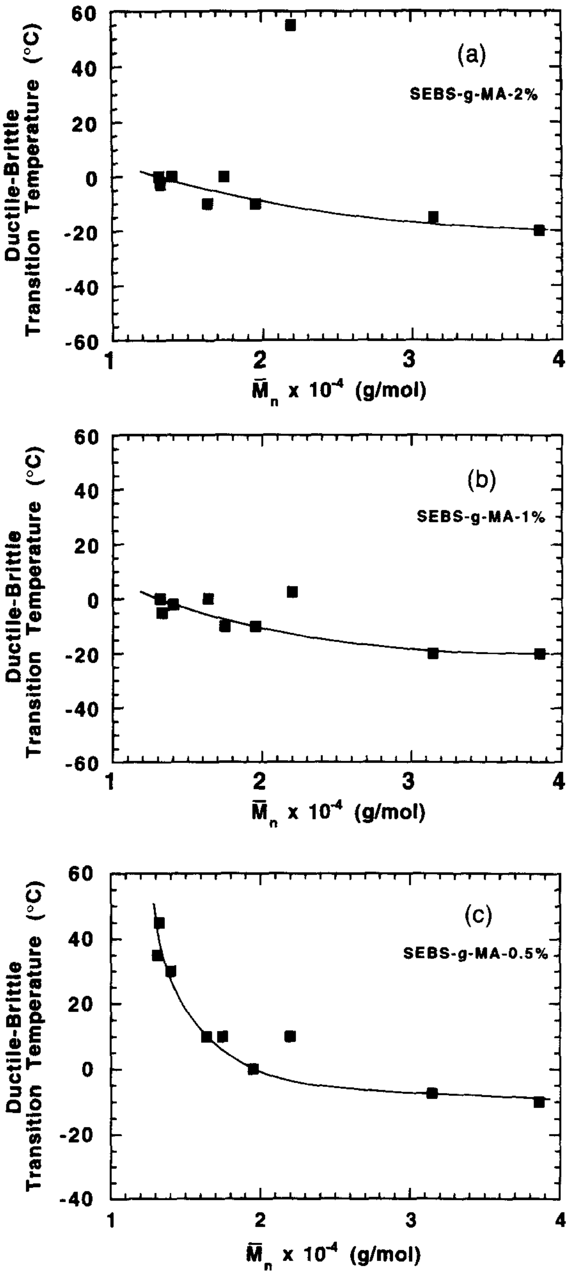

Figure 7 Effect of nylon 6 molecular weight on the ductile–brittle transition temperature for blends of 20% SEBS-g-MA-X%/80% nylon 6 as a function of X: (a) $X = 2\%$, (b) $X = 1\%$, and (c) $X = 0.5\%$

L-SEBS-g-MA

A triblock elastomer designated as L-SEBS-g-MA in *Table 2* has lower molecular weight styrene end blocks and a greater rubbery mid-block molecular weight than the SEBS-type materials described above. In *Figure 1*, the Izod impact strength of its blends with nylon 6 can be compared with the other SEBS-type rubber systems as a function of the temperature. From the ductile–brittle transition temperatures determined from *Figure 1*, the blends based on L-SEBS-g-MA generally have lower ductile–brittle transition temperatures than SEBS-g-MA-X% or SEBS/SEBS-g-MA-2% mixtures when compared at similar maleic anhydride contents (see *Figure 4*) or at the same weight average rubber particle size as seen in *Figure 5*. However, blends of L-SEBS-g-MA with nylon 6 $\bar{M}_n = 17\,500$ and 22 000 are exceptions. The weight average rubber particle size of these blends is less than 0.1 μm which apparently is too small to effectively toughen the blends since the ductile–brittle transition temperature is above room temperature for both materials.

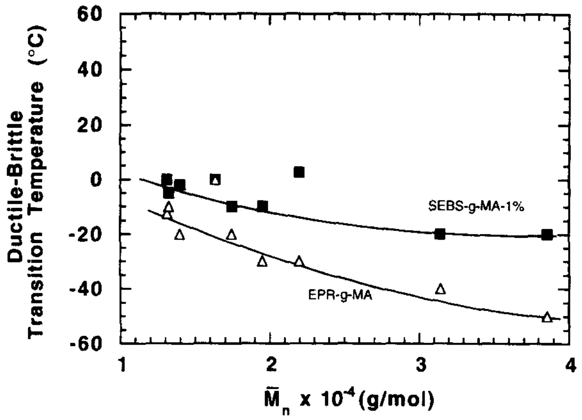

Figure 8 Effect of nylon 6 molecular weight on the ductile–brittle transition temperature for blends with 20% SEBS-g-MA-1% and 20% EPR-g-MA. These two elastomers have similar maleic anhydride contents

EFFECT OF POLYAMIDE MOLECULAR WEIGHT ON LOW TEMPERATURE BLEND TOUGHNESS

The effect of nylon 6 molecular weight on the ductile–brittle transition temperature of blends with the various rubber systems is examined below for fixed maleic anhydride levels in the rubber phase and then for fixed rubber particle size.

Fixed maleic anhydride content

Figure 6 shows the Izod impact strength as a function of temperature for blend based on SEBS-g-MA-1%, L-SEBS-g-MA, and EPR-g-MA with low, medium, and high molecular weight nylon 6 materials. The ductile–brittle transition temperature of SEBS-g-MA-X% type blends, deduced from plots like those in *Figure 6a*, are shown as a function of nylon 6 molecular weight in *Figure 7* for all the materials listed in *Table 1*. In general, the ductile–brittle transition temperature is lower the higher the molecular weight of the nylon 6 phase; the same trend is seen with all maleated rubbers used in this study[16]. The nylon 6 material with $\bar{M}_n = 22\,000$ is a clear exception to this trend; the ductile–brittle transition temperature lies well above the curve and the difference intensifies the higher the maleic anhydride content (see *Figures 7a* to *c*). This same nylon 6 material also has lower room temperature Izod impact strength than the other nylon 6 grades as seen in Part 2 of this series and in *Figures 1* and *6*[2]. The reason for the lower ductile–brittle transition temperature and room temperature impact strength is related to the rubber particle size of the blend with respect to the limits of super-toughening, i.e. the particle size is too small for effective toughening to occur[2]. Limited studies were also conducted using a nylon 6 with $\bar{M}_n = 20\,500$ from another supplier[16]; the trends in the room temperature Izod impact strength and ductile–brittle transition temperature for this nylon 6 were nearly identical with that for the nylon 6 with $\bar{M}_n = 22\,000$. This suggests such behaviour is generally characteristic of nylon 6 in this intermediate molecular weight range.

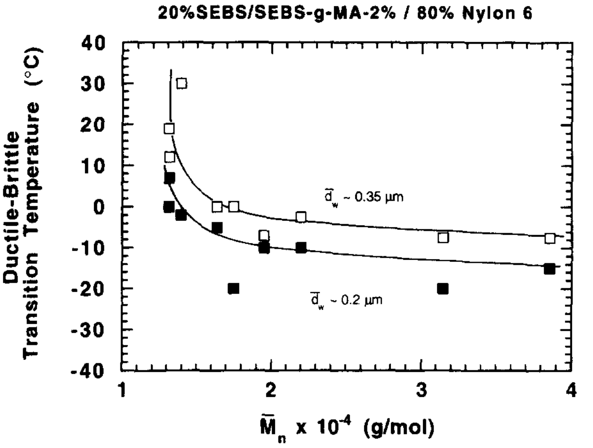

Figure 9 Effect of nylon 6 molecular weight on the ductile–brittle transition temperature for two fixed weight average rubber particle sizes ($\bar{d}_w \sim 0.2 \pm 0.05\,\mu$m and $0.35 \pm 0.05\,\mu$m) for blends of 20% SEBS/SEBS-g-MA-2%/80% nylon 6

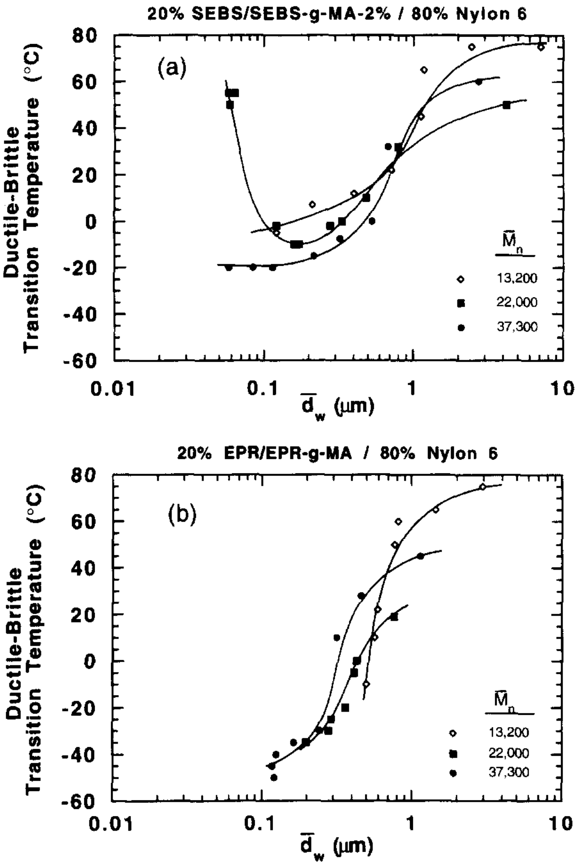

Figure 10 Effect of weight average rubber particle diameter on the ductile–brittle transition temperature for blends of 20% rubber/80% nylon 6 ($\bar{M}_n$ = 13 200, 22 000, and 37 300) with the following rubbers: (a) SEBS/SEBS-g-MA-2% and (b) EPR/EPR-g-MA

Figure 8 shows the ductile–brittle transition temperature of blends based on EPR-g-MA (1.14% MA) as a function of nylon 6 molecular weight. Results for SEBS-g-MA-1% based blends are shown for comparison; the maleic anhydride contents of these two rubbers are very similar. In both cases, the ductile–brittle transition temperature decreases with nylon 6 molecular weight; however, blends based on EPR-g-MA approach a lower limit of −50°C while SEBS-g-MA-1% based blend plateau at −20°C. As will be discussed in a later section, these differences in low temperature toughness are related mainly to the mechanical properties of the rubber phase at low temperatures (< −10°C). It is important to recognize, however, that the rubber particle size varies significantly with polyamide molecular weight and is smaller for blends based on SEBS-g-MA-1% than those based on EPR-g-MA.

Fixed rubber particle size

As described above, both rubber particle size and nylon 6 molecular weight influence the low temperature toughness of these blends. It would be informative to examine the effect of nylon 6 molecular weight on the ductile–brittle transition temperature while holding rubber particle size fixed. This is feasible for the SEBS/SEBS-g-MA-2% rubber system where a wide range of rubber particle sizes can be generated by varying the ratio of maleated to non-maleated rubber in blends with each nylon 6 material in *Table 1*. For this system, comparisons can be made at certain rubber particle sizes (within $\pm 0.05\,\mu$m); e.g., rubber particles with $\bar{d}_w \sim 0.2\,\mu$m and $\sim 0.35\,\mu$m were generated for each of the nylon 6 materials in *Table 1*. *Figure 9* shows that the ductile–brittle transition temperature decreases with increasing nylon 6 molecular weight for these fixed particle sizes.

The trend seen in *Figure 9*, however, only applies over a limited range of particle sizes as may be seen in *Figure 10*. Here, the ductile–brittle transition temperature is shown as a function of weight average rubber particle size for blends based on low, medium, and high molecular weight nylon 6 materials. The effect of molecular weight on the ductile–brittle transition temperature at a fixed rubber particle size can be seen by construction of vertical lines that intersect the curves representing a fixed nylon 6 molecular weight. In the size range $0.1 < \bar{d}_w < 0.6\,\mu$m, the ductile–brittle transition temperature decreases as the molecular weight of the nylon 6 phase increases as shown in *Figure 9*. When $\bar{d}_w > 0.6\,\mu$m, the low temperature toughness is poor regardless of the molecular weight of the nylon 6 matrix. For blends based on certain nylon 6 materials of intermediate molecular weight, e.g. $\bar{M}_n = 22\,000$ and to a limited extent $\bar{M}_n = 17\,500$, the ductile–brittle transition temperature increases to values above room temperature when the rubber particle size is less than 0.1 μm[11].

The data available for blends based on EPR/EPR-g-MA mixtures is much more sparse; no common particle size could be generated for all levels of nylon 6 molecular weight. However, the limited results in *Figure 10b* suggest similar conclusions as those described above for the SEBS based system; i.e., in the optimum size range for toughening, higher molecular weights lead to lower ductile–brittle transition temperatures. Particles smaller than 0.1 μm could not be generated for this system.

THE EFFECT OF RUBBER TYPE ON LOW TEMPERATURE TOUGHNESS

From *Figures 4* and *5* it is clear that in addition to rubber particle size and nylon 6 molecular weight, low temperature toughness is also influenced by the nature of the rubber. Of particular interest here is that blends based on the SEBS-g-MA-*X*% and SEBS/SEBS-g-MA-2% rubber systems never exhibit a ductile–brittle transition temperature lower than −20°C, regardless of

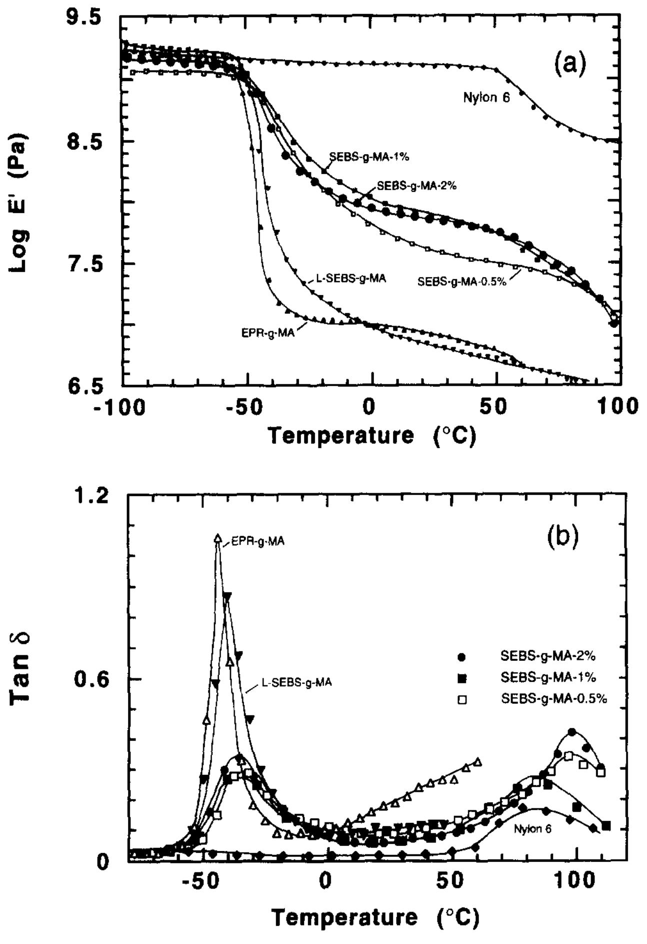

Figure 11 Dynamic mechanical properties of SEBS-g-MA-X%, L-SEBS-g-MA, EPR-g-MA, and nylon at a frequency of 1 Hz: (a) elastic modulus (E′) and (b) tan δ

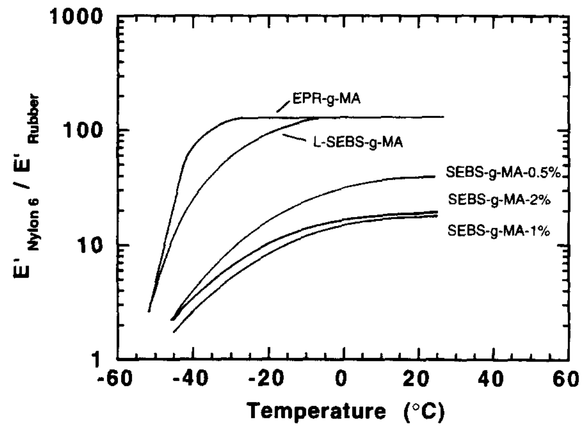

Figure 12 Matrix to rubber modulus ratio, $E'_{\text{nylon 6}}/E'_{\text{rubber}}$, as a function of temperature for the rubbers SEBS-g-MA-X%, L-SEBS-g-MA and EPR-g-MA

rubber particle size or nylon 6 molecular weight; whereas, blends based on certain EPR/EPR-g-MA mixtures and L-SEBS-g-MA have ductile–brittle transition temperatures much lower than this. To understand how physical and mechanical properties of the rubber phase affects the toughness of the blend[5,14,23–26] requires some knowledge of the role of the rubber particle in the toughening process. The early literature focuses on the stress concentration caused by the presence of low modulus particles dispersed in a more rigid matrix[27,28]. More recently the role of rubber particle cavitation in the relief of triaxial stress, which permits subsequent shear yielding of psuedo-ductile matrices, has been stressed[20,29,30]. Cavitation of rubber particles depends on numerous structural parameters, e.g. crosslink density or the block copolymer microdomain structure; however, just as the stress concentration factor in the matrix decreases with increasing modulus of the rubber phase, the relative ease of rubber particle cavitation is also expected to decrease as the rubber becomes stiffer. Thus, as a first approximation, it is useful to examine how the modulus of these rubber systems change with temperature relative to that of nylon 6. Theoretical solutions for the stress concentration factor resulting from a spherical particle in a rigid matrix have been developed in terms of the ratio of the moduli of the two phases[27,28]. The dispersed phase will act as an effective stress concentrator when its modulus is one tenth or less than that of the matrix. This criterion has been invoked in patents on rubber toughening of polyamides[31,32].

The ductile–brittle transition temperature observed here can be examined in terms of this criterion using the dynamic mechanical property information shown in *Figure 11*. The elastic component, E', of the dynamic moduli for the EPR-g-MA and L-SEBS-g-MA materials are much lower than that of SEBS-type elastomers above the rubber T_g. The former also show substantially larger $\tan\delta$ peaks at the rubber T_g. The microdomains formed by the styrene segments of the block copolymers act both as physical crosslinks and as a reinforcing filler[33]. Thus, the materials with the higher styrene content have higher levels of modulus above the rubber phase T_g than does L-SEBS-g-MA; of course, EPR-g-MA has the lowest apparent modulus in the rubbery state since it has no hard domains and is not chemically crosslinked. Interestingly, the SEBS-g-MA materials become stiffer, above the rubber phase T_g, the higher the degree of maleation. This effect is no doubt present for all the maleated elastomers and probably reflects increased interchain cohesion and intrachain stiffening caused by grafting of maleic anhydride to the backbone. *Figure 12* shows the ratio of the modulus of the polyamide matrix to that of the pure elastomer phase as a function of temperature for each maleated rubber used here. At room temperature, the ratio $E'_{\text{nylon 6}}/E'_{\text{rubber}}$ varies considerably among the different rubbers; however, there is no correlation between room temperature toughness and this ratio. As expected, the $E'_{\text{nylon 6}}/E'_{\text{rubber}}$ ratio decreases as the temperature is lowered and approaches the order of unity near the rubber phase T_g. However, the rate of decline of this ratio varies significantly among the different rubber types. If we use the criterion $E'_{\text{nylon 6}}/E'_{\text{rubber}} = 10$, we see that EPR-g-MA and L-SEBS-g-MA reach this limit at −48 to −46°C while the SEBS-g-MA-X% materials do so at −13 to −26°C. These temperatures correspond rather closely to the lowest ductile–brittle transition temperatures achieved for blends (i.e., optimum rubber particle size and polyamide matrix molecular weight) based on these rubber types. The glass transition of the rubber phase is often regarded as a lower limit of the ductile–brittle transition that can be achieved by toughening; however, for complex elastomers, like block copolymers, it appears that a more detailed consideration of how the magnitude of the modulus of the elastomer (relative to that of the matrix) changes with temperature is in order.

CONCLUSIONS

The effect of nylon 6 molecular weight on the ductile–brittle transition temperature of its blends with maleated elastomers has been investigated. The ductile–brittle transition temperature also depends on rubber particle size and the type of rubber used. For example, as the rubber particle size is reduced for SEBS base blends, the ductile–brittle transition temperature decreases but levels off at about −20°C. Blends based on EPR/g-MA mixtures show a monotonic decrease in the ductile–brittle transition temperatures and obtain values as low as −50°C. In part the difference in the low temperature toughness produced by these two rubber types is related to their mechanical properties below −10°C.

For a given elastomer of fixed maleic anhydride content, the ductile–brittle transition temperature of the blend decreases with increasing nylon 6 molecular weight. However, as seen in Part 1 of this series, the size of the rubber particles generated decreases as the nylon 6 molecular weight increases owing to the increased matrix melt viscosity. When compared at a fixed rubber particle size, within the size range for toughening, the ductile–brittle transition temperature continues to show lower values as the nylon 6 molecular weight increases. Thus, in general, better toughness at both ambient conditions and at low temperatures can be achieved for blends based on nylon 6 with high molecular weight. While this trend is intuitively expected, a detailed understanding of how matrix molecular weight influences toughening is not yet available.

For certain blends examined in this study, the Izod impact strength reaches a maximum value above the ductile–brittle temperature and then decreases as the temperature is increased further. This behaviour seems to occur only when rubber particle size of the blend is below a certain limit. For blends based on nylon 6 with $\bar{M}_n$ in the range of 20 000 to 22 000, the ductile–brittle transition temperature exceeds room temperature when the rubber particle size is reduced to less than 0.1 μm.

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REFERENCES

1 Oshinski, A. J., Keskula, H. and Paul, D. R. *Polymer* 1996, **37**, 4891
2 Oshinski, A. J., Keskkula, H. and Paul, D. R. *Polymer* 1996, **37**, 4909
3 Majumdar, B., Keskkula, H. and Paul, D. R. *Polymer* 1994, **35**, 1386
4 Borggreve, R. J. M., Gayumans, R. J., Schuijer, J. and Ingen Housz, J. F. *Polymer* 1987, **28**, 1489
5 Borggreve, R. J. M., Gaymans, R. J. and Schuijer, J. *Polymer* 1989, **30**, 71
6 Borggeve, R. J. M. and Gaymans, R. J. *Polymer* 1989, **30**, 63
7 Borggreve, R. J. M., Gaymans, R. J. and Eichenwald, H. M. *Polymer* 1989, **30**, 78
8 Dijkstra, K., ter Laak, J. and Gaymans, R. J. *Polymer* 1994, **35**, 315
9 Dijkstra, K., Wevers, H. H. and Gaymans, R. J. *Polymer* 1994, **35**, 323
10 Dijkstra, K. and Gaymans, R. J. *Polymer* 1994, **35**, 332
11 Oostenbrink, A. J., Molenaar, L. J. and Gaymans, R. J. 'Polyamide–Rubber Blends: Influence of Very Small Rubber Particle Sizes on Impact Strength', Poster given at 6th Annual Meeting of Polymer Processing Society, Nice, France, 18–20, April 1990
12 Flexman, E. A. *Polym. Eng. Sci.* 1979, **19**, 564
13 Wu, S. J. *Polym. Sci., Polym. Phys. End.* 1983, **21**, 699
14 Wu, S. *Polymer* 1985, **26**, 1855
15 Lawson, D. F., Hergenrother, W. L. and Matlock, M. G. J. *Appl. Polym. Sci.* 1990, **39**, 2331
16 Oshinski, A. J. Ph.D. Thesis, University of Texas at Austin, 1995
17 Kayano, Y., Keskkula, H. and Paul, D. R. *Polymer* in press
18 Oshinski, A. J., Keskkula, H. and Paul, D. R. *Polymer* 1992, **33**, 268
19 Oshinski, A. J., Keskkula, H. and Paul, D. R. *Polymer* 1992, **33**, 284
20 Bucknall, C. B., Karpodinis, A. and Shang, X. C. *J. Mater. Sci.* 1994, **29**, 3377
21 Modic, M. J., Gilmore, D. W. and Kirkpatrick, J. P. 'Proc. First Int. Cong. on Compatibilization and Reactive Polymer Alloying (Compalloy '89)', New Orleans, LA, 1989, p. 197
22 Gelles, B.M., Modic, M. and Kirkpatrick, J. *Soc. Plast. Eng., ANTEC* 1988, **34**, 513
23 Parker, D. S., Sue, H-J, Huang, J. and Yee, A. F. *Polymer* 1990, **31**, 2266
24 Kinloch, A. J. and Young, R. J. 'Fracture Behaviour of Polymers', Elsevier Applied Science, London, 2nd Edn., 1985
25 Williams, J. G. 'Fracture Mechanisms of Polymers', J. Wiley and Sons, New York, 1985
26 van der Sanden, M. C. M., de Kok, J. M. M. and Meijer, H. E. H. *Polymer* 1994, **34**, 2995
27 Goodier, J. N. *Trans. Am. Soc. Eng.* 1993, **55**, 39
28 Oxborough, R. J. and Bowden, P. B. *Phil. Mag.* 1974, **30**, 171
29 Bucknall, C. B. and Lazzeri, A. *J. Mater. Sci.* 1993, **28**, 6799
30 Dompas, D. and Groeninckx, G *Polymer* 1994, **35**, 4743
31 Epstein, B. N., *U.S. Patent 4,174,358* (to E.I. DuPont), 1979
32 Epstein, B. N., *U.S. Patent 4,172,859* (to E.I. DuPont), 1979
33 Paul, D. R. in 'Thermoplastic Elastomers: Research and Development' (Eds N. R. Legge, H. Schroeder and G. Holden), Hanser Verlag, Munich, 1987, Ch. 12, Sec. 6