Polymer Vol. 37 No. 22, pp. 4909–4918, 1996
S0032-3861(96)00374-6
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0032-3861/96/$15.00+0.00

The role of matrix molecular weight in rubber toughened nylon 6 blends: 2. Room temperature Izod impact toughness

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(Received 21 August 1995; revised 22 January 1996)

The Izod impact strength of blends of nylon 6 with maleated and non-maleated styrene-hydrogenated butadiene-styrene triblock copolymers, SEBS, and ethylene/propylene random copolymers, EPR, is influenced by the molecular weight of the nylon 6 phase, the rubber particle size, and rubber type. The upper and lower particle size limits for super-toughening were found to be dependent on the polyamide molecular weight and rubber type. The SEBS type elastomers produce blends that have higher toughness over a broader range of rubber particle sizes than the EPR/EPR-g-MA mixtures. The effect of nylon 6 molecular weight on the room temperature Izod impact strength of these blends depends on how the comparison is made; however, generally higher levels of toughness can be obtained from the higher molecular weight nylon 6 materials. Copyright ©1996 Elsevier Science Ltd.

(Keywords: toughening; Izod impact; nylon 6)

INTRODUCTION

The mechanical behaviour of rubber-toughened plastics depends on the morphology of the blend, the characteristics of the rubber and matrix phases, and the nature of the interface between these phases[1–26]. The previous paper[27] has shown how the morphology that is generated for blends of nylon 6 with maleated and non-maleated styrene-hydrogenated butadiene-styrene triblock copolymers, SEBS, and ethylene/propylene random copolymers, EPR, can be influenced by the molecular weight of the nylon 6. The effects of nylon 6 molecular weight stem from both chemical and rheological issues. In addition to this effect on morphology, the molecular weight of nylon 6 can potentially affect the toughness of such blends in other ways. In general, the inherent ductility, or the ability to be toughened, of polymers increases with molecular weight[20,28]. For semi-crystalline matrices like nylon 6, the amount of crystallinity and crystalline texture may change with molecular weight which can influence mechanical response significantly[2,29,30].

This paper focuses on the combined effects of nylon 6 molecular weight on toughness of its blends with SEBS and EPR type elastomers. Specifically, the room temperature Izod impact strength of the blends described in the previous paper is examined to determine the separate effects of rubber particle size, polyamide molecular weight, and rubber type (SEBS or EPR) on room temperature toughness. The upper and lower critical particle sizes for toughening nylon 6 are shown to be dependent on the nylon 6 molecular weight.

EXPERIMENTAL

Table 1 shows the physical and mechanical properties of the nylon 6 materials while *Table 2* describes the various rubbers used in this study. The procedures for melt processing, morphology determination and nylon 6 characterization are given elsewhere[27,31].

Tensile and 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 by weight. The specimens were tested in the dry as moulded state using standard tensile (ASTM D638) and Izod (ASTM D256) procedures. All specimens were placed in polyethylene bags inside a dessicator immediately after being moulded. Tensile testing was done using a crosshead speed of 0.5 cm min^{-1} for the modulus and yield strength and 5 cm min^{-1} for elongation at break. Tensile properties of the various rubber toughened nylon 6 blends are presented elsewhere[31].

During room temperature Izod impact testing, many of the specimens exhibited a 'hinged-break' condition, i.e. crack growth was initiated and propagated part way through the specimen before the pendulum energy dropped below that needed to provide the critical force necessary to maintain crack growth. At this point, the pendulum either stops or the specimen deflects out of the path of the pendulum. Therefore, the total amount of energy such specimens can potentially absorb is not determined from the Izod impact test. Other impact tests can determine the energy to cause complete failure[32–37] and will be reported separately; however, the Izod impact strength is an often used indicator of toughness[7,14,32,38–41] so it is important to employ this methodology. Ductile–brittle transition temperatures using the

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Table 1 Nylon 6 materials used in this study

Supplier's designation	$\bar{M}_n$ (g mol^{-1})[a]	ΔH_{fusion} (J gm^{-1})[b]	T_m (°C)[c]	Izod impact (J m^{-1})	Young's modulus (GPa)[d]	Yield strength (MPa)[d]	Elongation at break (%)[d]	Storage modulus E' (GPa)[e]
Capron XA-1767	13 100	75.8	222	53 ± 5	2.5 ± 0.2	68 ± 1	55 ± 18	1.53
Ultramid B0	13 200	69.3	224	59 ± 8	3.2 ± 0.5	68 ± 2	44 ± 35	1.50
Ultramid B1	14 000	69.8	222	62 ± 11	2.9 ± 0.5	68 ± 2	29 ± 8	1.50
Capron 8202	16 400	73.5	219	59 ± 5	2.7 ± 0.1	62 ± 3	64 ± 8	1.53
Ultramid B3	17 500	70.5	222	59 ± 5	2.4 ± 0.2	68 ± 1	73 ± 34	1.53
Ultramid B2	19 400	69.1	223	63 ± 12	3.1 ± 0.2	64 ± 1	104 ± 25	1.51
Capron 8207F	22 000	75.3	219	43 ± 11	2.8 ± 0.2	70 ± 1	93 ± 70	1.27
Capron 8209F	29 300	64.9	222	50 ± 11	2.8 ± 0.2	70 ± 1	64 ± 56	1.42
Ultramid B5	37 300	67.1	220	63 ± 5	2.7 ± 0.2	70 ± 1	30 ± 10	1.38

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

[b] From d.s.c. first heat of injection moulded specimens at 20°C min^{-1} and integrating between 150 and 250°C

[c] From d.s.c. first heat of injection moulded specimens at 20°C min^{-1}

[d] From tensile testing (ASTM D638) using a crosshead speed of 0.5 cm min^{-1} for modulus and yield strength and 5 cm min^{-1} for elongation at break
The average value of a minimum of seven specimens with '±' indicating the standard deviation

[e] From d.m.a. analysis at 1 Hz at 25°C

Table 2 Rubbers used in this study

Designation used here	Material (supplier's designation)	Composition	Molecular weight	Elastic modulus (E') (MPa)[a]	Supplier
SEBS	Kraton G 1652	29% wt styrene	Styrene block = 7000 EB block = 37 500	40	Shell Chemical Co.
SEBS-g-MA-0.5%	RP-6510	29% wt styrene 0.46% wt MA[b]	N/A	40	Shell Chemical Co.
SEBS-g-MA-1%	Kraton FG-1921X	29% wt styrene 0.96% wt MA[b]	N/A	62	Shell Chemical Co.
SEBS-g-MA-2%	Kraton FG-1901X	29% wt styrene 1.84% wt MA[b]	N/A	66	Shell Chemical Co.
L-SEBS	Kraton 1657	13% wt styrene	Styrene block = 5500 EB block = 73 000	N/A	Shell Chemical Co
L-SEBS-g-MA	RP-6509	13% wt styrene 1.4% wt MA[b]	N/A	6.7	Shell Chemical Co.
EPR	Vistalon 457	43% wt ethylene 53% wt propylene	$\bar{M}_n = 54\,000$ $\bar{M}_w/\bar{M}_n = 2$	2.5	Exxon Chemical Co.
EPR-g-MA	Exxelor 1803	43% wt ethylene 53% wt propylene 1.14% wt MA[b]	N/A	7.8	Exxon Chemical Co.

[a] From d.m.a. analysis at 1 Hz at 25°C

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

Izod configuration were also determined for these blends and will be described in the next paper in this series.

MECHANICAL PROPERTIES OF PURE NYLON 6 MATERIALS

There is extensive literature on the underlying mechanisms of toughening of blends of a rigid matrix into which a low modulus material has been dispersed[34,38,42–45]. Some criteria for toughening, based on the mechanical properties of the dispersed phase relative to those of the matrix phase, have emerged[45–48]; for example, the ratio of the shear modulus of the dispersed phase to that of the rigid matrix must be 1/10 or less to obtain the maximum stress concentration factor[47,49,50]. Borggreve *et al.* have shown experimentally that the elastic modulus and the Poisson's ratio of the rubber phase are critical parameters for achieving sufficient voiding to toughen a nylon 6 matrix[45]. These considerations are generally directed towards selection of an appropriate rubber phase for toughening a given matrix. The issue addressed here is how varying the matrix, for a fixed rubber, affects blend toughness and more specifically the case where only the molecular weight of nylon 6 is varied. This, in principle, could influence crystallinity, crystalline texture, and the mechanical properties of the neat nylon 6, all of which may subsequently affect blend toughness. *Table 1* shows the thermal and mechanical properties of the nine nylon 6 materials used in this study. All measurements were made on samples following injection moulding using a protocol similar to that employed for their blends. The melting points and the heat of fusion (which gives an indication of the amount of crystallinity) of the neat nylon 6 materials in *Table 1* show no consistent trends with molecular weight. Likewise, the Young's modulus, as measured by tensile testing and by dynamic mechanical testing (E') at 1 Hz, and the yield strength do not show appreciable differences within the limits of experimental reproducibility or any clear trends with molecular weight. The same is true of the Izod impact strength. The elongations at break for the neat nylon 6 materials suggest a maximum value for intermediate levels of molecular weight. The results in *Table 1* provide little basis to expect, or to interpret, trends in toughness of nylon 6 blends with a fixed rubber, other than those caused by how molecular weight of the polyamide influences blend morphology[20,28].

More sophisticated approaches for characterizing matrix toughness, such as fracture mechanics parameters like the critical stress intensity factor, K_{IC}; the critical energy release rate, G_{IC}; the critical crack initiation energy, J_{IC}; or crystalline texture, such as spherulite and crystallite size, tie chain content, etc.[29,33,34,36], might provide more insight about inherent toughness or toughenability of the various nylon 6 materials used in this study. However, the techniques needed to address these parameters are beyond the scope of this study.

EFFECT OF RUBBER TYPE ON ROOM TEMPERATURE BLEND TOUGHNESS

Two different types of rubber were used as impact modifiers for nylon 6 in this work[27]. One type was styrene–hydrogenated butadiene–styrene triblock copolymers commonly designated as SEBS or SEBS-g-MA for maleated versions. The amount of maleation of the latter was controlled by the extent of grafting to the rubber mid-block, denoted by SEBS-g-MA-*X*%, or by mixing a non-maleated SEBS elastomer with a highly maleated triblock copolymer, e.g. SEBS/SEBS-g-MA-2%. One such material with a lower styrene content and higher rubber mid-block, designated here as L-SEBS-g-MA, than the standard material used in prior work[21,22,27] designated as SEBS was also used. The second type of elastomer system was an ethylene/propylene random copolymer, designated as EPR, and a maleated version, EPR-g-MA, containing 1.14% maleic anhydride. The two were mixed together in a similar manner as the SEBS/SEBS-g-MA-2% system to vary the level of maleic anhydride in the rubber phase.

All blends were prepared by simultaneously extruding 20% rubber with 80% nylon 6. The previous paper[27] showed that the weight average rubber particle size of SEBS-g-MA-*X*% and the SEBS/SEBS-g-MA-2% mixtures blended with nylon 6 in a single screw extruder at fixed processing conditions follow the same trends with respect to the amount of maleation of the rubber phase. Generally, the SEBS/SEBS-g-MA-2% mixtures produced slightly larger rubber particles that are more polydisperse in size distribution than found for the SEBS-g-MA-*X*% elastomers of the same maleic anhydride content. Because of the limited number of the SEBS-g-MA-*X*% type materials and the similarity in the morphological trends of the two SEBS rubber systems, the SEBS-g-MA-*X*% and SEBS/SEBS-g-MA-2% systems will be compared together as toughening agents for nylon 6.

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

Room temperature Izod impact strength was measured for blends of each rubber system with the nylon 6 materials (20% rubber by weight) shown in *Table 1* as a function of maleic anhydride content of the rubber over the full range of compositions possible with the available materials. *Figure 1* shows representative plots of impact strength *versus* maleic anhydride content of the triblock copolymer elastomer phase of blends with high, low, and medium molecular weight nylon 6 materials; similar plots for nylon 6 blends with EPR/EPR-g-MA mixtures are shown in *Figure 2*. In every case, the impact strength goes through a maximum and then declines as the level of maleation of the SEBS-type rubber is increased. The shape of the curve, however, depends very much on the molecular weight of the nylon 6 used in the blend. Blends based on nylon 6 materials having molecular weights between 16 000 and 22 000 show a sharp peak in toughness at relatively low levels of maleation and then rapidly decline with further increases in maleic anhydride content, see *Figure 1b*. At the extremes in nylon 6 molecular weight the curves are much broader and the decrease in toughness at the highest levels of maleation is more modest, see *Figures 1a* and *c*.

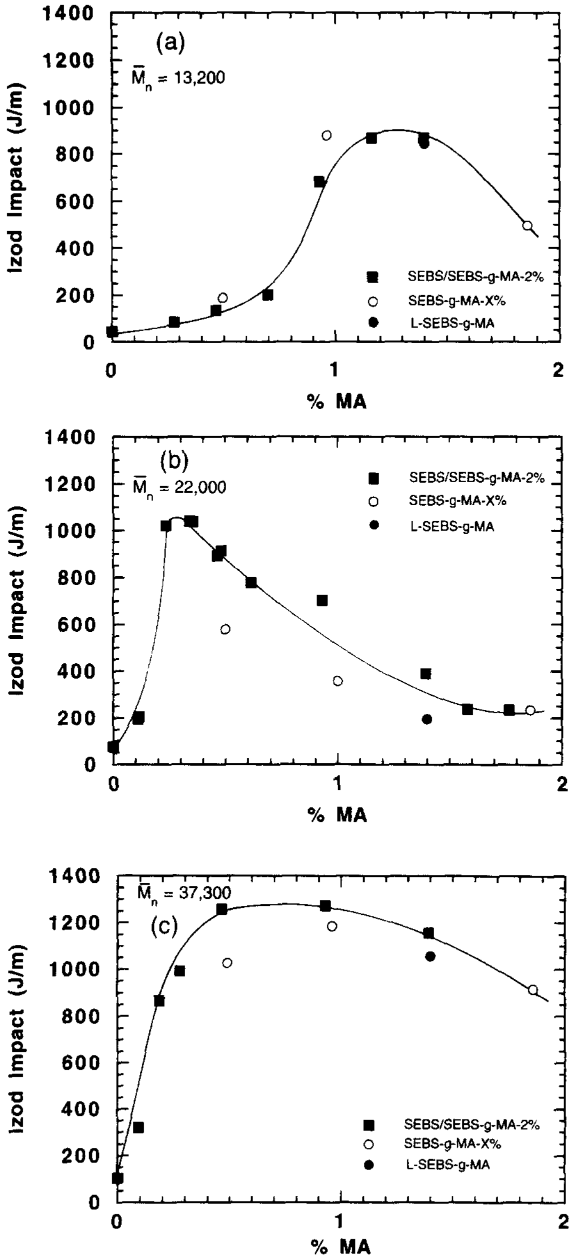

Figure 1 Effect of maleic anhydride content in rubber on room temperature Izod impact strength for blends of SEBS/SEBS-g-MA-2%, SEBS-g-MA-*X*%, and L-SEBS-g-MA with nylon 6, all in the ratio of 20% rubber/80% nylon 6. The nylon 6 molecular weight in each graph is as follows: (a) $\bar{M}_n$ = 13 200, (b) $\bar{M}_n$ = 22 000, and (c) $\bar{M}_n$ = 37 300

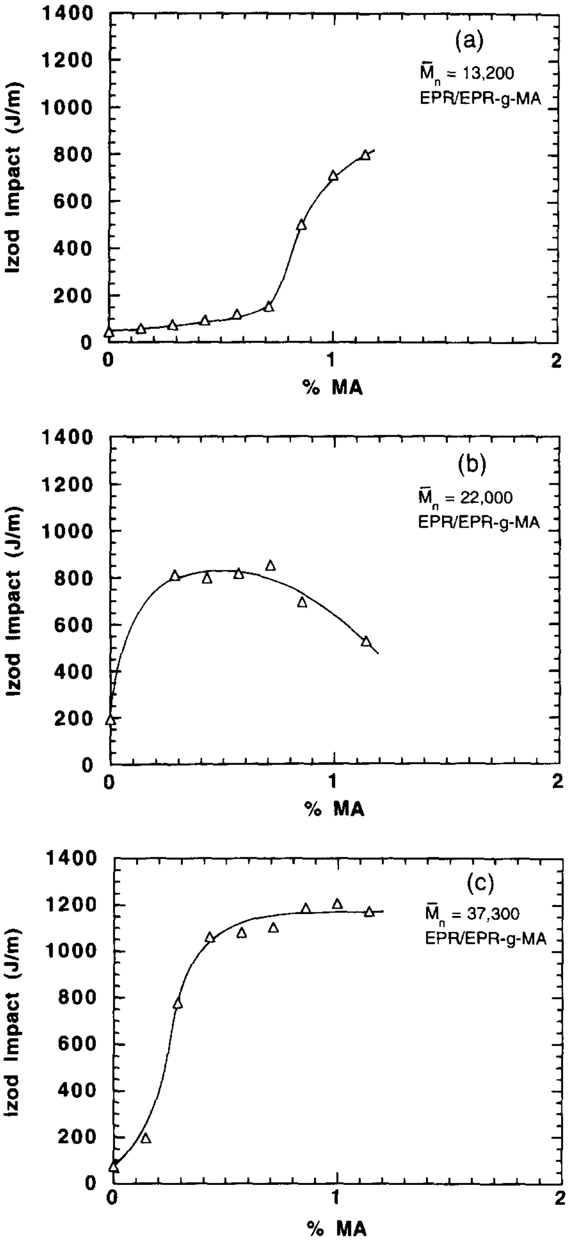

Figure 2 Effect of maleic anhydride content in rubber on room temperature Izod impact strength for blends of EPR/EPR-g-MA with nylon 6, all in the ratio of 20% rubber/80% nylon 6. The nylon 6 molecular weight in each graph is as follows: (a) $\bar{M}_n = 13200$, (b) $\bar{M}_n = 22000$, and (c) $\bar{M}_n = 37300$

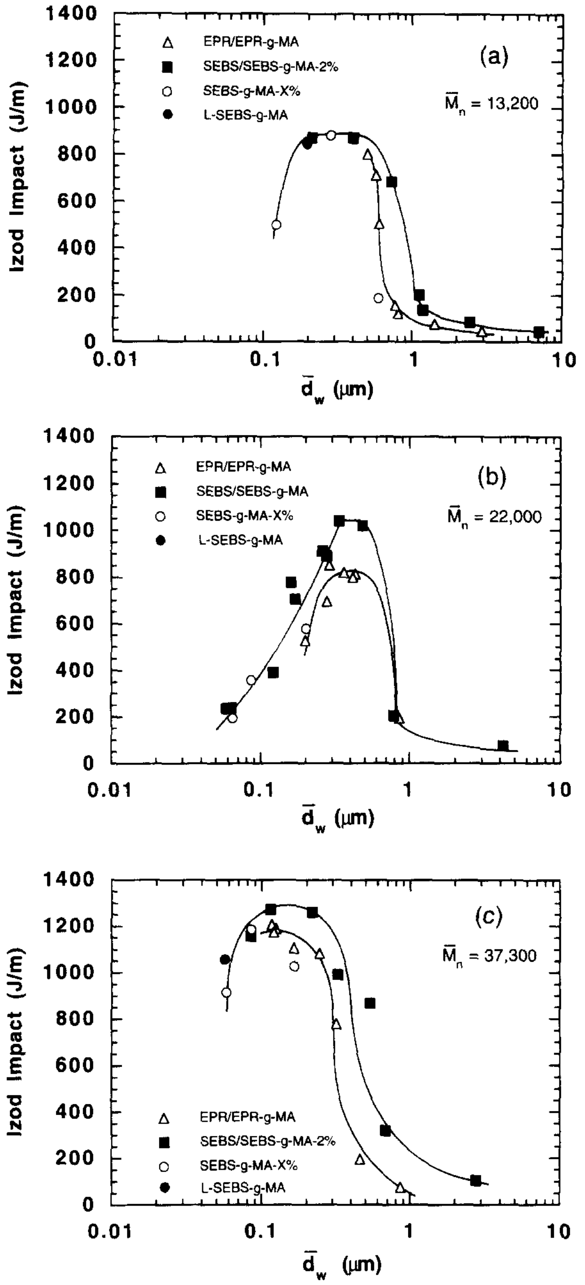

Figure 3 Effect of weight average rubber particle diameter on Izod impact strength for blends of EPR/EPR-g-MA, SEBS/SEBS-g-MA-2%, SEBS-g-MA-X%, and L-SEBS-g-MA with nylon 6, all in the ratio of 20% rubber/80% nylon 6. The nylon 6 molecular weight in each graph is as follows: (a) $\bar{M}_n = 13200$, (b) $\bar{M}_n = 22000$, and (c) $\bar{M}_n = 37300$

In addition, the maximum Izod impact strength and the amount of maleic anhydride needed to produce this optimum toughness are influenced by the molecular weight of the nylon 6 used in the blend.

When the nylon 6 molecular weight is below 16000, the Izod impact strength for all the SEBS rubber systems have nearly identical values at the same level of maleic anhydride, see *Figure 1a*. However, as the molecular weight increases beyond this, the impact strength of the blends based on SEBS-g-MA-X% type elastomers, see open circles in *Figure 1*, fall below the curve established by blends based on the SEBS/SEBS-g-MA-2% mixtures.

Plots like those in *Figure 1* (or *Figure 2*) are useful from the point of view of establishing an optimum chemical formulation but do not lead to much understanding of the causes that underlie the very interesting trends shown. For example, the literature teaches[4,7,14,38,39,51] that rubber particle size, or interparticle distance as suggested by Wu[14], is a key factor in toughening polyamides. On this basis, the data in *Figure 1* are replotted as a function of weight average particle size, using data from the first paper in this series[27], in *Figure 3*. Assuming rubber particle size is the key variable, *Figure 3* clearly shows an upper and lower size limit for toughening of nylon 6.

The results shown in *Figure 3* indicate that blends based on SEBS-g-MA-X% and SEBS/SEBS-g-MA-2% rubber systems have identical values of Izod impact when compared at constant rubber particle size if the maleic anhydride content is 1% or greater. However, blends based on SEBS-g-MA-0.5% always have somewhat lower room temperature impact strength than (see open circle below the curves drawn in *Figure 3*) SEBS/SEBS-g-MA-2% mixtures with an equivalent rubber particle size[31]. The difference in Izod impact strength between blends based on SEBS/SEBS-g-MA-2% mixtures and SEBS-g-MA-X% materials diminishes as the molecular weight of the polyamide phase increases. When the nylon 6 molecular weight is below 16 000, blends with SEBS-g-MA-0.5% are brittle while the blend based on the SEBS/SEBS-g-MA-2% mixture with an equivalent rubber particle size are super-tough. As the molecular weight of the nylon 6 phase increases, the blends based on SEBS-g-MA-0.5% become super-tough but not to the levels attained by the blends based on SEBS/SEBS-g-MA-2% mixtures with an equivalent weight average rubber particle size. In general, the room temperature Izod impact strength and the ductile–brittle transition temperature of blends of the SEBS-g-MA-0.5% elastomer are poorer than corresponding blends containing SEBS/SEBS-g-MA-2% mixtures that give an equivalent weight average rubber particle size. This suggests the SEBS-g-MA-X% elastomers may have a toughness curve (of the type shown in *Figure 3*) that is different from the SEBS/SEBS-g-MA-2% curve, specifically at rubber particle sizes greater than 0.5 μm or at lower maleic anhydride contents.

The reason for this difference in toughening response for the two SEBS rubber systems may be related to differences in polydispersity effects, the methods used for controlling the maleic anhydride content, or differences in the mechanical properties of the rubbers. In the previous paper[27], blends of nylon 6 having molecular weights below 16000 with SEBS/SEBS-g-MA-2% mixtures where the maleic anhydride content is less than 0.5% were observed to have a broad distribution of rubber particle sizes and appeared in some cases to be bimodal. However, comparison of the polydispersity ratios, $\bar{d}_v/\bar{d}_n$ and $\bar{d}_w/\bar{d}_n$, rubber particles formed from SEBS-g-MA-0.5% and the corresponding SEBS/SEBS-g-MA-2% mixture when blended with the various molecular weight nylon 6 materials showed no correlation to the differences seen in room temperature Izod impact strength[31]. This is in contrast to the studies by Dijkstra[19] who showed blends of nylon 6 and polybutadiene with different rubber particle size distributions having the same fracture toughness values, but different ductile to brittle transition temperatures.

It is useful to point out the chemical differences in the structure of the rubber-polyamide graft copolymers formed in the two systems. In the case of SEBS-g-MA-X% type elastomers, every rubber molecule is presumably grafted with maleic anhydride and can potentially form a graft copolymer with a number of polyamides appendages to the rubber backbone. However, for SEBS/SEBS-g-MA-2% mixtures of the same maleic anhydride content only the SEBS-g-MA-2% fraction of the elastomer mixture is maleated. The previous paper showed that the extent of reaction with nylon 6 amine chain ends is the same for the two rubber systems[27]. Thus, the SEBS/SEBS-g-MA mixture leads to the same number of nylon 6 chains grafted to a smaller number of rubber backbones than in the case of SEBS-g-MA-X% materials. The mixture approach leads to similar blend morphology; however, in general the average rubber particles formed in blends with nylon 6 are usually somewhat larger with a slightly broader distribution in size. Whether this difference in the number of rubber chains participating in the grafting reactions affects the toughness cannot be answered; however, the polydispersity differences do not appear to be enough to cause such an effect. At this time, it is unclear what factors influence the difference in toughness between the two SEBS rubber systems; this warrants further investigation.

EPR/EPR-g-MA

Mixtures of non-maleated EPR and a maleated EPR rubber containing 1.14% maleic anhydride were blended only with the nylon 6 materials designated as B0, 8207F, and B5, which represent low, medium, and high molecular weight grades. However, binary blends of EPR-g-MA and all the nylon 6 materials shown in *Table 1* were generated for comparative purposes with a similarly maleated SEBS type elastomer, SEBS-g-MA-1%. Details of the preparation of these blends are given in the first paper of this series[27]. *Figure 2* shows the room temperature Izod impact strength of blends based on the EPR/EPR-g-MA mixtures as a function of the maleic anhydride content of the rubber phase. The trends for the EPR/EPR-g-MA mixtures (*Figure 2*) are similar to those for the SEBS type elastomers (*Figure 1*), except that for the lowest molecular weight nylon 6, $\bar{M}_n = 13\,200$, it appears that a maximum toughness has not been reached at the highest maleic anhydride content possible for the EPR/EPR-g-MA rubber system. The shapes of the curves depend on the nylon 6 molecular weight; the maximum toughness achieved and the amount of maleic anhydride needed to produce this optimum toughness varies from *Figure 2a* to *c*.

Figure 3 shows these data replotted as a function of weight average rubber particle size, $\bar{d}_w$. It is clear that the trends are similar to those for blends with the block copolymer elastomers. However, nylon 6 blends with the SEBS type elastomers generally have higher room temperature Izod impact strength than similar blends with EPR/EPR-g-MA mixtures; this is especially pronounced when the nylon 6 molecular weight is above 17 000[31]. A future paper will examine this phenomenon in more detail using other techniques for characterizing the fracture process[37].

Figure 3 shows that the upper rubber particle size limit for effective toughening nylon 6 is smaller for EPR/EPR-g-MA mixtures than for SEBS type elastomers. Because of the relatively low maleic anhydride content of EPR-g-MA material used here, it was not possible to generate the extremely small rubber particles that can be made with the SEBS-g-MA-2% material. Thus, it was not possible to probe the lower limit on particle size for this system in every case. However, if *Figure 3b*, for nylon 6 with $\bar{M}_n = 22\,000$, is a representative curve, the lower limit for EPR/EPR-g-MA mixtures may be larger than that for SEBS/SEBS-g-MA-2% mixtures. Therefore, the effective particle size range for super-toughening nylon 6 with EPR/EPR-g-MA mixtures seems to be smaller than for SEBS type elastomers.

L-SEBS-g-MA

The triblock elastomer in *Table 2* designated as L-SEBS-g-MA has a smaller styrene content (shorter end blocks and a larger rubber mid-block molecular weight) than the SEBS-type materials described above. In *Figure 1*, the room temperature toughness of L-SEBS-g-MA (closed circle) can be compared with the other SEBS rubber systems of similar maleic anhydride content. The room temperature Izod impact strength of L-SEBS-g-MA is identical to the other SEBS elastomer systems until the nylon 6 molecular weight becomes greater than 15 000, then the L-SEBS-g-MA rubber falls below the curve established for SEBS/SEBS-g-MA-2% mixtures[31]. Blends based on the L-SEBS-g-MA material have identical room temperature toughness as the SEBS-g-MA-X% and SEBS/SEBS-g-MA-2% rubber systems when compared at the same weight average particle size as seen in *Figure 3*.

EFFECT OF POLYAMIDE MOLECULAR WEIGHT ON ROOM TEMPERATURE BLEND TOUGHNESS

Maleic anhydride limits

Cross comparisons of the individual plots in *Figures 1–3* reveal that the nylon 6 molecular weight influences room temperature Izod impact strength of its blends with EPR/EPR-g-MA and the three SEBS type elastomer systems. This is more conveniently demonstrated by examining how polyamide molecular weight affects the range of maleic anhydride content in the rubber phase needed to produce high levels of toughness and the value of the room temperature Izod impact strength within this optimum composition range for SEBS/SEBS-g-MA-2% (see *Figure 4*) and EPR/EPR-g-MA (see *Figure 5*) mixtures. In *Figures 4a* and *5a*, boundaries are drawn, as a function of $\bar{M}_n$ of the nylon 6 matrix, to indicate the maleic anhydride contents above (open circles) or below (closed circles) which the Izod impact strength is less than 700 J m^{-1}. Setting the limit at 700 J m^{-1} is somewhat arbitrary but near this value there is a steep transition between brittle and super-tough behaviour as particle size changes over a small range. Arrows on three of the points in *Figure 4a* indicate that higher levels of maleic anhydride than 1.84% would be needed to cause the Izod values to drop below 700 J m^{-1}. The trends for the EPR/EPR-g-MA mixtures are similar to those for the SEBS type elastomers but are not as well defined since only three of the nylon 6 materials in *Table 1* were blended with the former. An upper limit on maleic anhydride level for the EPR/EPR-g-MA system was reached for only one nylon 6 material of intermediate molecular weight; the dashed line shown in *Figure 5a* has been drawn to be consistent with available information in *Figure 2*. The general picture that emerges for blends based on either rubber system is that the minimum amount of maleic anhydride in the rubber phase needed to produce super-tough blends (i.e. Izod >700 J m^{-1}) decreases monotonically with nylon 6 molecular weight before reaching a plateau beyond $\bar{M}_n \sim 20\,000$, see *Figures 4a* and *5a*. However, the upper maleic anhydride boundary appears to reach a minimum at $\bar{M}_n \sim 22\,000$; beyond this, the upper maleic anhydride limit is greater than that of the available materials as indicated by the dashed lines for both the SEBS and EPR type elastomers.

The maximum room temperature Izod impact strength, within the optimum maleic anhydride range,

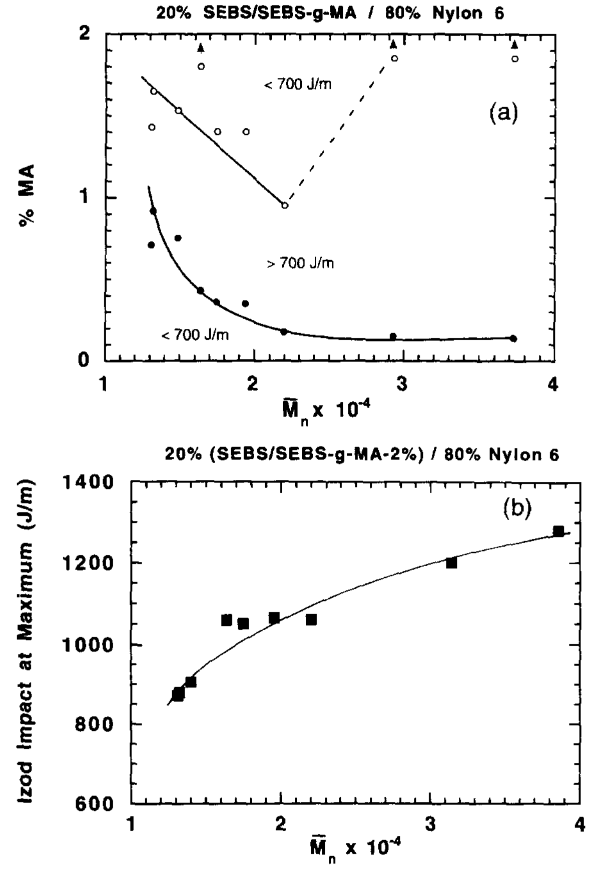

Figure 4 Effect of nylon 6 molecular weight for blends of 20% SEBS/SEBS-g-MA-2%/80% nylon 6 on: (a) the maleic anhydride content required in the rubber to produce blends with Izod impact strength values above 700 J m^{-1} and (b) the maximum Izod impact strength within the optimal maleic anhydride range

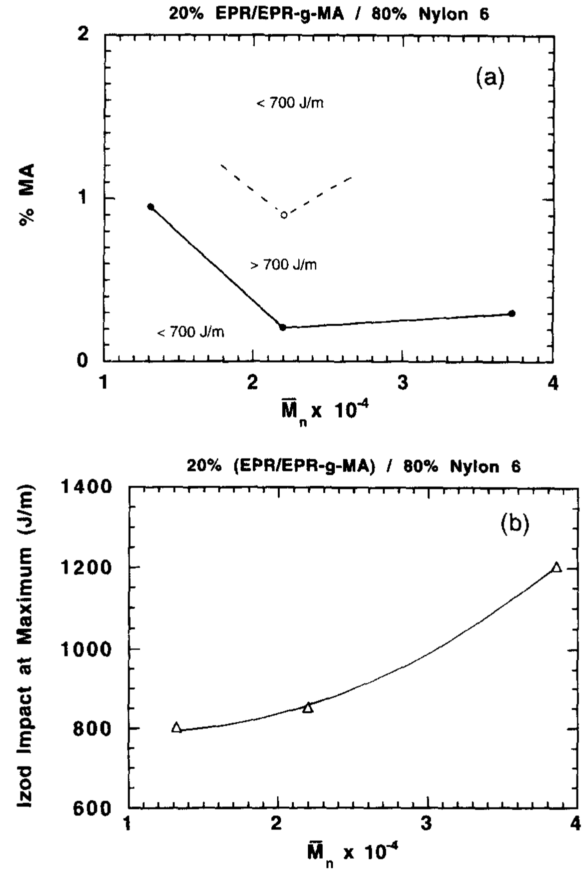

Figure 5 Effect of nylon 6 molecular weight for blends of 20% EPR/EPR-g-MA/80% nylon 6 on: (a) the maleic anhydride content in the rubber required to produce blends with Izod impact strength values above 700 J m^{-1} and (b) the maximum Izod impact strength within the optimal maleic anhydride range

increases as the molecular weight of the nylon 6 matrix increases, for both rubber types, as seen in *Figures 4b* and *5b*. The maximum impact strengths for the EPR/EPR-g-MA mixtures are lower than those for the SEBS/SEBS-g-MA-2% mixtures. More detailed studies in progress will explore possible reasons for this.

Particle size limits

From *Figure 3* it is clear that there are upper and lower rubber particle size limits for both EPR and SEBS type elastomers for effectively toughening nylon 6, and these limits are affected by the molecular weight of the polyamide phase. The limits are defined here as the rubber particle size above or below which Izod impact strength is less than 700 J m^{-1}. The upper and lower rubber particle size limits for the blends based on the SEBS/SEBS-g-MA-2% mixtures are shown as a function of polyamide molecular weight in *Figure 6*. The upper limit is below 1 μm, which has been well documented[8,9,14,21,22,26,38,39,51], and it appears to be relatively independent of the nylon 6 molecular weight. Conversely, the lower rubber particle size limit is strongly affected by the polyamide molecular weight which causes the rubber particle size range associated with effective toughening of nylon 6, i.e. the difference between the upper and lower curves, to increase with the matrix molecular weight. Therefore, blends of SEBS/SEBS-g-MA-2% with the highest molecular weight nylon 6 material are generally super-tough, even for rubber particle sizes below 0.1 μm.

At fixed processing conditions, small EPR/EPR-g-MA rubber particles could not be produced to fully define the toughness curves in *Figures 3a* and *c*. Therefore, only the upper rubber particle size limit could be determined. *Figure 3* shows that the EPR rubber system must have significantly smaller rubber particles than SEBS type elastomers before super-toughening begins. This may be related to physical or mechanical property differences between the two rubber types which affect the deformation mechanisms in the nylon 6 matrix.

Fixed maleic anhydride content

Figure 7 shows the room temperature Izod impact strength for blends based on SEBS-g-MA-X% materials as a function of the nylon 6 molecular weight (note that rubber particle size varies considerably from point to point). Broadly speaking a minimum in toughness occurs at a nylon 6 molecular weight of approximately 22 000 for each of the SEBS-g-MA-X% elastomers, and for all maleated rubber systems used in this study[31]. The lines in *Figures 7a–c* were drawn to highlight this trend. There are some clear exceptions. For SEBS-g-MA-0.5%, Izod impact strength falls even lower than the suggested minimum for nylon 6 with molecular weights in the range of 13 100 to 16 400. For SEBS-g-MA-2% the impact strength for the blend based on nylon 6 with $\bar{M}_n$ = 16 400 falls well above the line drawn. The indicated minimum in Izod impact strength is the result of the relationship between the rubber particle size produced in these blends and the lower limit for effective toughening as nylon 6 molecular weight is varied. This can be understood by the type of plot shown in *Figure 8*. As the molecular weight of nylon 6 is increased, the size of the SEBS-g-MA-X% rubber particles generated decreases monotonically until approximately 22 000 and then appears

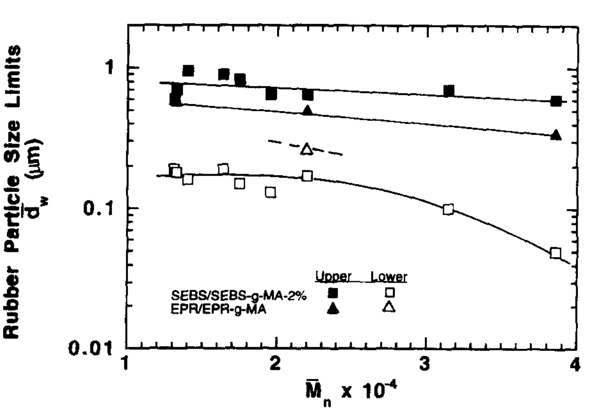

Figure 6 Effect of nylon 6 molecular weight on the upper and lower rubber particle size limits for effective toughening of 20% SEBS/SEBS-g-MA-20%/80% nylon 6 and 20% EPR/EPR-g-MA/80% nylon 6 blends

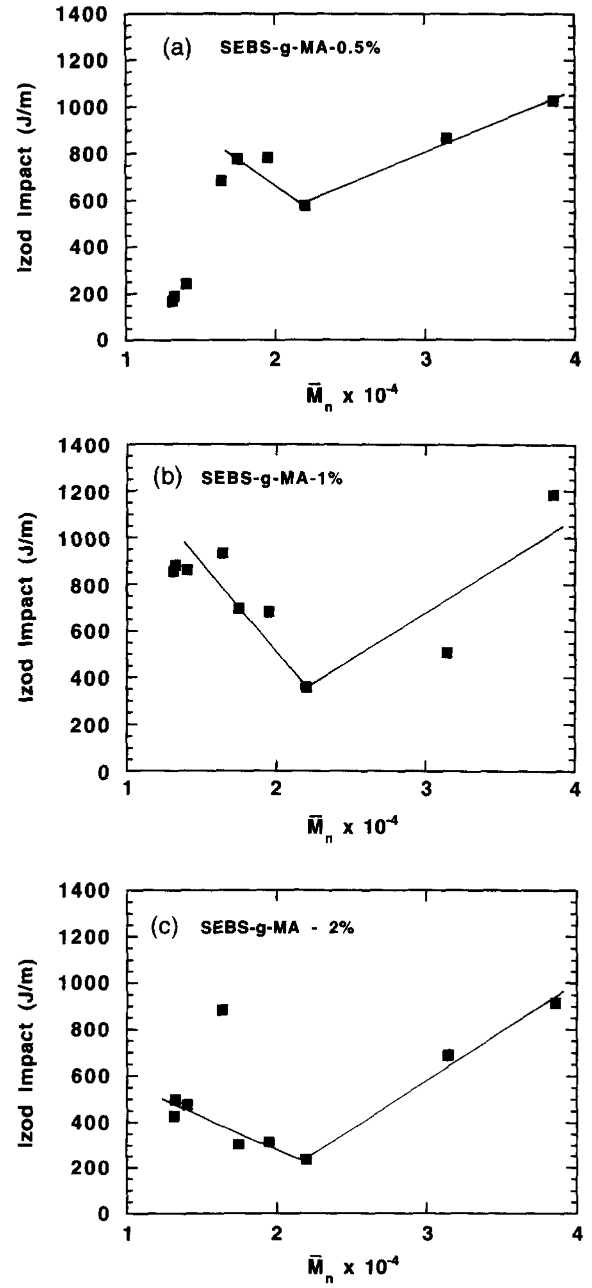

Figure 7 Effect of nylon 6 molecular weight on Izod impact strength of 20% SEBS-g-MA-X%/80% nylon 6 blends as a function of X: (a) X = 0.5%, (b) X = 1%, and (c) X = 2%

to reach a plateau[27]. The dashed upper and lower limits shown are those established for SEBS/SEBS-g-MA-2% mixtures (see *Figure 6*) which should approximate but not exactly represent those for the SEBS-g-MA-X% materials. When the maleic anhydride content is 1% or greater, the curves representing the size of the rubber particles crosses the lower limit at a nylon 6 molecular weight below about 16 000; a maximum deviation between the two curves occurs at approximately 22 000 before the solid curve crosses above the lower limit at higher molecular weights. It is the fortuitous crossing of these curves that leads to the minimum Izod values near a nylon 6 molecular weight of approximately 22 000. For SEBS-g-MA-0.5%, the two curves do not cross but approach each other near 22 000 and the poor Izod impact strength associated with the nylon 6 molecular weights of 13 100 to 16 400 is due to their rubber particle sizes being too large for super-toughening; however, as seen in *Figure 8* these blends do not cross the upper size limit line. It is important to recall that the size limits shown in *Figure 8* were determined for SEBS/SEBS-g-MA-2% mixtures; there were insufficient data available to define precise curves of this type for the SEBS-g-MA-X% elastomers. As discussed above, the SEBS-g-MA-X% elastomers appear to have toughening characteristics that are different from the SEBS/SEBS-g-MA-2% mixtures in the region of the upper size limit, i.e. the SEBS-g-MA-X% elastomers seem to require significantly smaller rubber particles ($<0.5\,\mu$m) before super-toughening occurs. Thus, the size of the SEBS-g-MA-0.5% rubber particles for the three lowest molecular weight nylon 6 materials in *Figure 7a* may be larger than the upper size limit for SEBS-g-MA-X% elastomers and, hence, result in brittle blends. In the following section, the effect of nylon 6 molecular weight on toughness will be examined at fixed rubber particle size with the intention of eliminating such effects which are important from a formulation point of view but are not informative from a mechanistic perspective.

Fixed rubber particle size

As described above, both rubber particle size and polyamide molecular weight influence the room temperature toughness of these blends. To single out the effect of nylon 6 molecular weight alone, it is useful to examine blends of rubber toughened nylon 6 with the same rubber particle size. This is feasible when a wide range of rubber particle sizes can be generated by varying the proportions of the maleated and non-maleated rubbers blended with each of the nylon 6 materials shown in *Table 1*. For the blends based on SEBS/SEBS-g-MA-2% mixtures, it turns out that rubber particles with $\bar{d}_w \sim 0.2 \pm 0.05$ and $\sim 0.35 \pm 0.05\,\mu$m were generated for each of the various nylon 6 materials. For the EPR/EPR-g-MA mixtures, no rubber particle sizes, within the effective toughening range, were found to be in common for each of the three nylon 6 materials blended with this rubber system. Thus, the following analysis must be limited to blends based on the SEBS/SEBS-g-MA-2% system. The Izod impact strength of these blends with roughly the same rubber particle size is plotted *versus* the nylon 6 molecular weight in *Figure 9*. These results show that the impact strength can increase (*Figure 9a*) or remain essentially constant (*Figure 9b*) as the molecular weight of the nylon 6 matrix increases. To interpret these trends it is necessary to understand where the fixed rubber particle sizes are in relationship to the upper and lower limits for toughening for each matrix molecular weight. *Figure 10* shows this relationship for the two rubber particle sizes common for the blends of SEBS/SEBS-g-MA-2% with the nine nylon 6 materials. Blends having a rubber particle size of $\sim 0.2 \pm 0.05\,\mu$m are at the lower limit for effective toughening with nylon 6 molecular weights less than 17 000 and consequently will have lower Izod impact strengths, see *Figure 9a*. On the

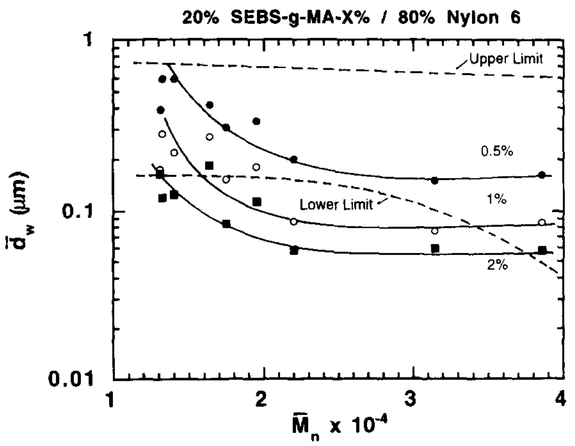

Figure 8 The weight average rubber particle diameter of 20% SEBS-g-MA-X%/80% nylon 6 blends relative to the upper and lower size limits for effective toughening as a function of nylon 6 molecular weight and maleic anhydride content (X)

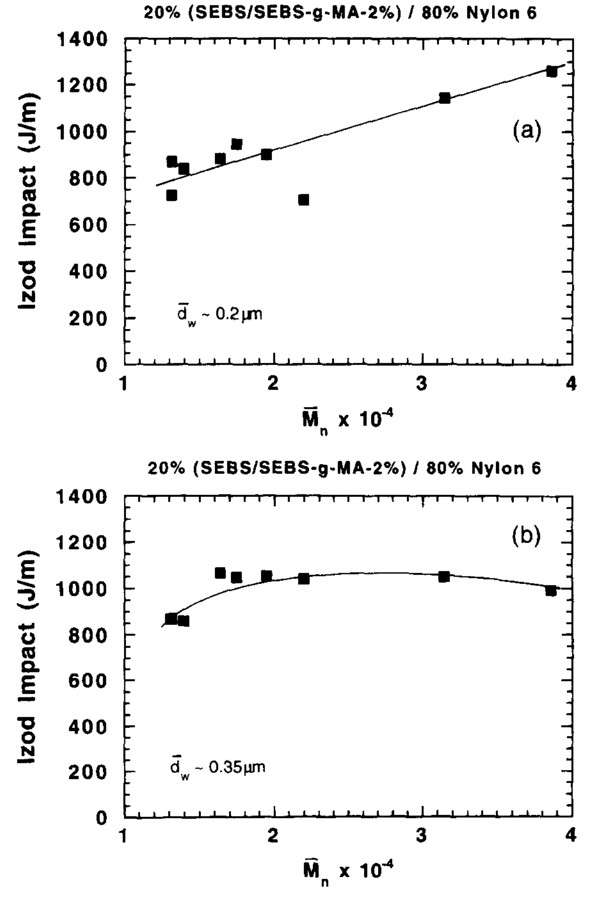

Figure 9 Effect of nylon 6 molecular weight on Izod impact strength at a fixed weight average rubber particle diameter for blends of 20% rubber/80% nylon 6: (a) SEBS/SEBS-g-MA-2% mixtures with $\bar{d}_w \sim 0.2\,\mu$m, (b) SEBS/SEBS-g-MA-2% mixtures with $\bar{d}_w \sim 0.35\,\mu$m

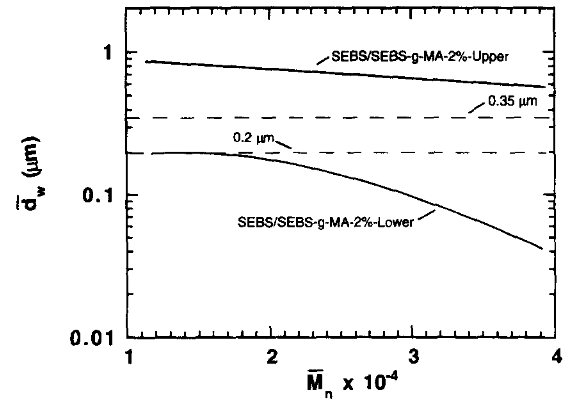

Figure 10 Comparison of the fixed weight average rubber particle diameters relative to the particle size limits for effective toughening for blends of 20% rubber/80% nylon 6 as a function of nylon 6 molecular weight for SEBS/SEBS-g-MA-2% mixtures (where $\bar{d}_w \sim 0.2$ and $\sim 0.35\,\mu$m)

other hand for $\bar{d}_w \sim 0.35 \pm 0.05\,\mu$m the rubber particles are within the range of super-toughening for all nylon 6 molecular weights. *Figure 9b* shows that in this case the Izod impact strength is effectively independent of nylon 6 molecular weight. The seemingly contradictory trends seen in *Figure 9* appear to be rationally explained in terms of the upper and lower limits of rubber particle size for toughening and how these limits depend on the molecular weight of the nylon 6. However, it must be remembered that the size limits are defined by when the Izod strength crosses a rather arbitrary value of 700 J m^{-1}.

As seen in *Figure 3*, the toughness vs $\bar{d}_w$ curves reach a plateau region between the two size limits. Typically, the plateau region extends from approximately $0.05\,\mu$m from the upper size limit to about $0.1\,\mu$m above the lower limit as defined earlier; consequently the limits for effective toughening eliminate a considerable amount of information regarding the effect of nylon 6 molecular weight on toughness. The level of the Izod impact strength in the plateau region of the toughness curve and the rubber particle size range over which the plateau extends are plotted in *Figure 11* for the various nylon 6 materials. To determine the effect of nylon 6 molecular weight on Izod impact strength at a fixed rubber particle size, vertical lines can be drawn through the various plateau regions. Plateau regions for a given nylon 6 molecular weight that are not intersected by a vertical line of constant $\bar{d}_w$ will have an Izod impact strength less than the value corresponding to the plateau value. When rubber particle size is fixed at $0.3\,\mu$m and less, the Izod impact strength increases with nylon 6 molecular weight (as seen in *Figure 9a*) and when the rubber particle size is between 0.5 and $0.3\,\mu$m all but the two highest molecular weight nylon 6 materials are intersected which results in curves like that seen in *Figure 9b*. Clearly, Izod impact strength increases with nylon 6 molecular weight when the rubber particle size is within the plateau region or below about $0.3\,\mu$m.

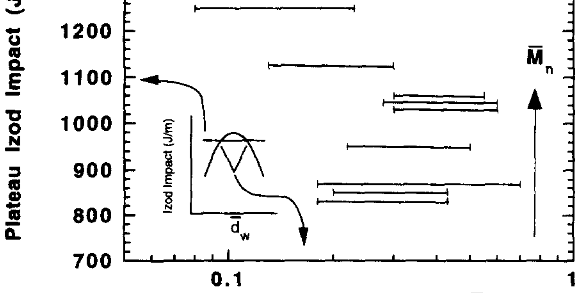

Figure 11 Effect of nylon 6 molecular weight on the plateau Izod impact strength of 20% SEBS/SEBS-g-MA-2%/80% nylon 6 blends as a function of the plateau weight average rubber particle size range

CONCLUSIONS

The effect of nylon 6 molecular weight on room temperature toughness of its blends with various rubber systems has been investigated. Izod impact strength is strongly influenced by rubber particle size in addition to any effect of the matrix molecular weight. The rubber particle size generated during processing is also significantly affected by the polyamide melt viscosity or molecular weight as shown in Part 1[27]. By varying the amount of maleic anhydride grafted to the rubber, rubber particle size can be reduced several orders of magnitude which allowed the determination of an upper and lower size limit for effective toughening for the SEBS/SEBS-g-MA-2% and EPR/EPR-g-MA mixtures. These limits vary with rubber type and are dependent on the nylon 6 molecular weight. The range of rubber particle sizes for effective toughening, i.e. the difference between the upper and lower size limit, increases with polyamide molecular weight. The SEBS type elastomers produce super-toughness over a broader range of particle sizes and lead to higher Izod impact strength when the particle size is within these limits than the EPR/EPR-g-MA mixtures.

The effect of nylon 6 molecular weight on the room temperature Izod impact strength of these blends depends critically on how the comparison is made, e.g. constant rubber particle size, constant maleic anhydride content of the rubber, etc. In general, however, higher levels of toughness can be achieved the higher the nylon 6 molecular weight. Intuitively, this conclusion seems reasonable, but additional work will be required to understand the mechanistic reasons for this trend. The next paper in this series shows that the high molecular weight nylon 6 materials also have better low temperature toughness, i.e. lower ductile–brittle transition temperatures.

ACKNOWLEDGEMENTS

This research was supported by the US Army Research Office. The authors would like to thank Allied-Signal Inc., Exxon Chemical Co., BASF Corp., and Shell Development Co. for the materials and technical communications.

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