Reactive coupling of core–shell impact modifiers to polyamide matrices using styrene–maleic anhydride copolymers

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Core–shell impact modifiers have the advantage of a predetermined particle size; however, they must be appropriately dispersed in and coupled to the matrix polymer in order to be effective for toughening engineering plastics which are notch-sensitive. These functions can result from physical interaction of the shell material with the matrix or by chemical reaction. For the latter the most obvious route is to combine reactive moieties into the shell chains during fabrication by emulsion polymerization that subsequently react with the matrix during melt processing. An alternative is considered here for dispersing and coupling modifiers with shells based on poly(methyl methacrylate), PMMA, in a polyamide matrix. Certain styrene–maleic anhydride copolymers, SMA, are miscible with PMMA, yet through the maleic anhydride moiety these copolymers can react with polyamides during melt processing (via amine end groups). This concept leads to very tough blends based on nylon 6 but not to those based on nylon 6,6. Evidence for the proposed role of the SMA copolymer was demonstrated by transmission electron microscopy. Properties and morphology were examined for two different SMA copolymers, two core–shell impact modifiers (butadiene-based and acrylic-based rubber cores), various mixing protocols and component proportions. An attempt is made to explain the responses observed.

(Keywords: nylon 6; blends; core–shell impact modifiers; styrene–maleic anhydride copolymers; toughening)

INTRODUCTION

A number of approaches have been used for rubber toughening of polyamides[1–24]. Successful toughening of nylon requires coupling of the rubber phase to the matrix and control of the rubber particle morphology. The importance of rubber particle size or interparticle distance has been particularly emphasized by a number of authors[1–11]. A commercially important strategy is to blend maleic anhydride (MA)-grafted ethylene–propylene or similar elastomers with the polyamides[5–20]. The extent of reactive coupling of the functionalized rubber to the nylon matrix has a large effect on particle size[5–12,25–27]; in general, it is not possible independently to control the extent of coupling and the morphology.

Emulsion-made core–shell impact modifiers offer the advantage of independent control of particle size, but they require some means to achieve matrix–particle adhesion and to assure uniform dispersion of the particles. Typically, the core is based on butadiene or n-butyl acrylate rubber and is crosslinked, while the shell consists of grafted chains that physically interact with the matrix[28–32]. For example, poly(vinyl chloride) (PVC) is toughened by modifiers having grafted shells composed of poly(methyl methacrylate) (PMMA), or styrene–acrylonitrile copolymer (SAN) chains that are miscible with PVC[28]. *Figure 1* shows two chemical approaches to achieve coupling of the shell to the matrix. In the first, the grafted shell polymer contains sites capable of reacting with the matrix polymer that are chemically incorporated during the final stage of emulsion polymerization. Such materials are now commercially available[33]. The second approach involves addition of a polymer that is miscible with the shell chains and has chemical groups capable of reacting with the matrix. Accordingly, the interfacial interaction between such core–shell particles and a nylon matrix may be achieved by the incorporation of a polymer that is miscible with PMMA but that can react with nylon. Several styrene copolymers or terpolymers that incorporate acid- or anhydride-containing monomers may be useful for such purposes. For example, Brannock *et al.*[34] have shown that styrene–maleic anhydride or SMA copolymers containing from about 8 to more than 33% MA are thermodynamically miscible with PMMA. It is proposed that this physical miscibility will cause the SMA chains to tend to mix with the PMMA grafted chains that comprise the shell of the modifier particles. Subsequently, maleic anhydride units physically held in the brush[35–37] of the shell in this way can chemically react with the amine chain ends of the polyamide to form imide graft linkages. Thus, the nylon matrix and the rubber core are linked by the physical miscibility of SMA and PMMA chains and the chemical reaction of SMA with nylon. To achieve this sequencing of mixing and reaction events may require careful control of the protocol for combining the three ingredients of the blend:

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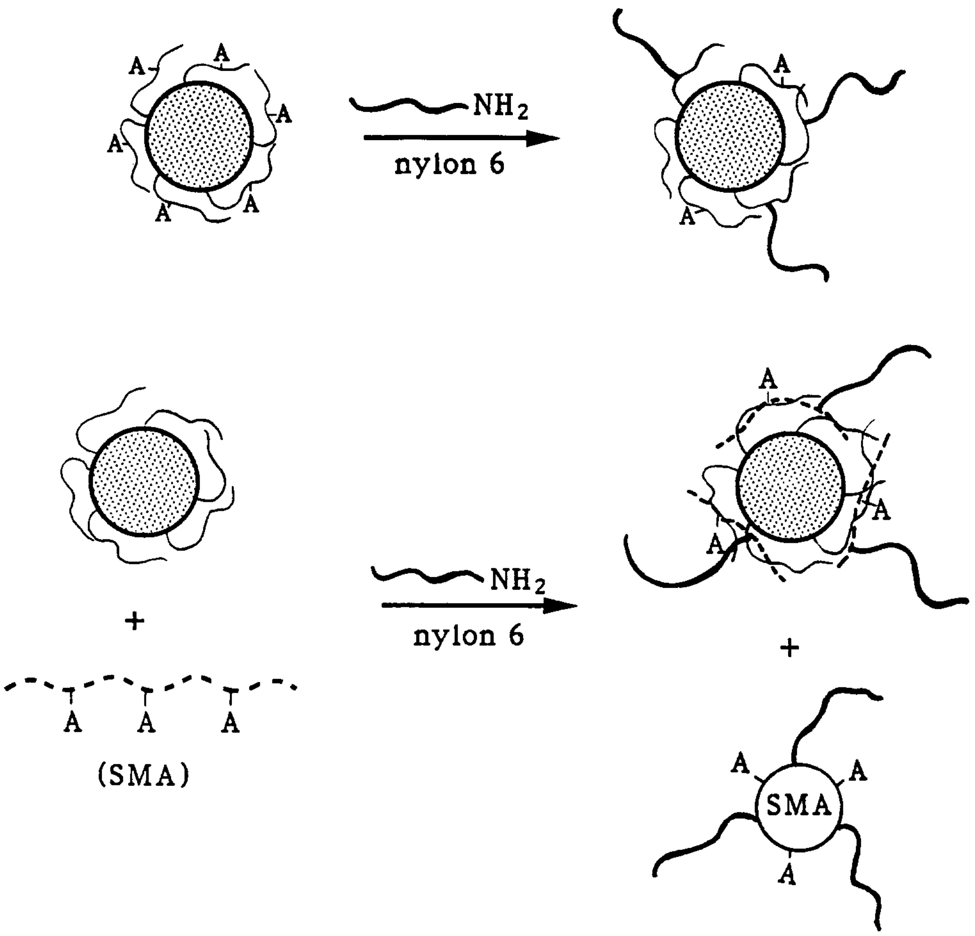

Figure 1 Schematic illustration of two mechanisms by which emulsion-made core–shell impact modifiers can be chemically coupled to and dispersed in a polyamide matrix. In the top scheme the functional groups are chemically bound to the PMMA-based chains in the shell while in the lower scheme these groups are part of an added polymer that is miscible with PMMA. The A groups can react with the polyamide, e.g. via its amine end groups

nylon, SMA and impact modifier. As will be discussed later, it is possible that the SMA chains can react with the nylon matrix but not be physically associated with the PMMA chains of the modifer shell, as suggested in *Figure 1*.

It is the purpose of this paper to determine the usefulness of this approach for toughening nylon. Two SMA copolymers containing 8 and 14% MA have been used in connection with two commercially available core–shell modifiers. The SMA copolymers are proposed to serve two related functions, i.e. to provide the required adhesion between the nylon matrix and the core–shell modifier particles and to assure uniform distribution of these particles in the matrix. The effects of mixing order, relative proportions of the ingredients, type of core rubber, MA content of SMA, and polyamide type (nylon 6 *versus* nylon 6,6) on toughness and especially the ductile–brittle transition temperature are explored.

MATERIALS AND METHODS

Table 1 summarizes information about the various commercially available materials used in this study. Owing to the hygroscopic nature of polyamides, all blends were dried at 100°C for at least 12 h in a vacuum oven prior to all melt processing steps.

Two types of core–shell impact modifiers were used. Paraloid EXL3300 is based on a n-butyl acrylate core with glass transition temperature (T_g) = -30°C measured by Rheovibron[38] and has a particle diameter of 0.3 μm[31,32]. Paraloid EXL3607 is based on a butadiene copolymer rubber core with $T_g = -60$°C measured by Rheovibron[38] and has a particle diameter of 0.18 μm[31,32]. Further details about these materials are given elsewhere[28–32]. The two random SMA8 copolymers, Dylark 232 and 332, contained 8 and 14% maleic anhydride by weight, respectively.

Rheological information was obtained using a Brabender Plasticorder with a 60 ml mixing head and standard rotors operated at 60 rev min^{-1} and 240°C. Typically, torque was recorded for 20 min.

Blends were prepared in a Killion single screw extruder ($L/D = 30$, 2.54 cm screw diameter) at 40 rev min^{-1}. The temperature of extrusion was 240°C for nylon 6 and 280°C for nylon 6,6 blends. The pelletized extrudates were dried before injection moulding in an Arburg Allrounder screw injection moulding machine. All moulded test specimens were placed in a sealed plastic bag and stored in a desiccator. They were tested dry as moulded. Tensile testing was carried out on an Instron machine in accordance with ASTM D638 using a crosshead speed of 5.08 cm min^{-1}. An extensometer strain gauge with a 5.08 cm gap was used to obtain the modulus and yield strain values. Notched Izod impact tests were conducted according to ASTM D256. All test specimens were 0.318 cm thick.

Table 1 Materials used

Designation used	Commercial designation	Composition	Molecular weight	T_g (°C)	Source
Nylon 6	Capron 8207F	Nylon 6	$\bar{M}_n = 25000$	50	Allied-Signal
Nylon 6,6	Zytel 101	Nylon 6,6	$\bar{M}_n = 17000$ $\bar{M}_w = 37500$	60	E.I. DuPont
EXL3300	Paraloid EXL3300 (impact modifier)	Core is n-butyl acrylate-based rubber, shell is based on PMMA		−30	Rohm & Haas
EXL3607	Paraloid EXL3607 (impact modifier)	Core is butadiene-based rubber, shell is based on PMMA		−60	Rohm & Haas
SMA8	Dylark 232	Styrene–maleic anhydride copolymer containing 8 wt% MA	$\bar{M}_n = 100000$ $\bar{M}_w = 200000$	117	Arco Chemical
SMA14	Dylark 332	Styrene–maleic anhydride copolymer containing 14 wt% MA	$\bar{M}_n = 90000$ $\bar{M}_w = 180000$	128	Arco Chemical

Table 2 Room temperature mechanical properties of polyamide materials and selected binary blends

Components	Composition	Yield stress (MPa)	Modulus (GPa)	Break strain (%)	Izod impact ($J m^{-1}$)
Nylon 6		72.0	2.61	145	50
Nylon 6/EXL3300	80/20	51.2	2.11	18	80
Nylon 6/EXL3607	80/20	50.1	1.94	10	50
Nylon 6/SMA8	79/1	77.5	2.88	27	50
	78/2	78.4	2.96	25	50
	75/5	80.0	3.05	260	60
	70/10	83.5	3.29	75	80
Nylon 6,6		76.7	2.78	40	50
Nylon 6,6/EXL3300	80/20	44.0	1.86	40	40

The morphology of selected blends was examined by transmission electron microscopy (TEM) using an Hitachi HU11-E. Ultrathin samples were obtained by microtoming moulded specimens using a Riechert–Jung ultramicrotome at −80°C. Staining was carried out by using OsO_4 (2% solution in water) for at least 24 h and/or RuO_4 (vapour) for a maximum of 15 min.

BINARY BLENDS

The properties of binary blends of the polyamide and the core–shell modifiers without any SMA present are of interest for comparison with the subsequent data on ternary blends. *Table 2* summarizes these results. Tensile properties of binary blends of either polyamide with the core–shell modifiers show typical trends in that strength and modulus are reduced due to the presence of a rubbery component. Elongation at failure is also lower than that of nylon, indicating poor interaction of the dispersed phase and the matrix. There is marginal improvement of notched Izod impact strength on addition of EXL3300 to nylon 6. A corresponding blend with nylon 6,6 also shows a reduction in toughness. *Figure 2* shows a series of TEM photomicrographs for blends containing nylon 6 and the impact modifier with the acrylic rubber core, EXL3300. The modifier particles appear as white spots since nylon 6 is more readily stained by the RuO_4 used than is the acrylic rubber core. In the absence of any dispersant, the modifier is agglomerated or poorly dispersed in the polyamide matrix as seen in *Figure 2a.* Similar results are seen in *Figure 3a* using the modifier with the butadiene-based rubber core, EXL3607. In the latter series of TEM photomicrographs, the modifier particles appear as dark spots since the unsaturated rubber is heavily stained by the OsO_4 used. As described below, addition of SMA8 greatly aids the dispersion of both modifiers in nylon 6.

Table 2 shows mechanical properties of binary blends of nylon 6/SMA8 which are useful for comparing with subsequent ternary blends. For this reactive pair, the stress–strain and impact properties are enhanced relative to those of nylon 6. The blend containing 12.5% SMA8 (70/10 nylon 6/SMA 8) shows especially interesting features including significantly higher modulus and somewhat improved impact strength as well. *Figure 4* shows that SMA8 is dispersed as extremely fine particles, generally below 0.1 μm in diameter, in the nylon 6 matrix. This demonstrates clearly that grafting of nylon 6 chains to SMA occurs during extrusion by reaction of the polyamide, most probably via the amine chain ends, with the maleic anhydride units.

MELT RHEOLOGY

Rheological measurements have been used frequently for demonstrating chemical reactivity in blends[8,9,24,39–41]. The reactivity of the SMA with nylon 6 is evident from Brabender torque rheometry (see *Figure 5*). The extent of this reaction will have an effect on the particle–matrix interface and on the mechanical behaviour of the composite. The effect of the relative rheological properties of the components may have some influence on the dispersion of the core–shell rubber particles.

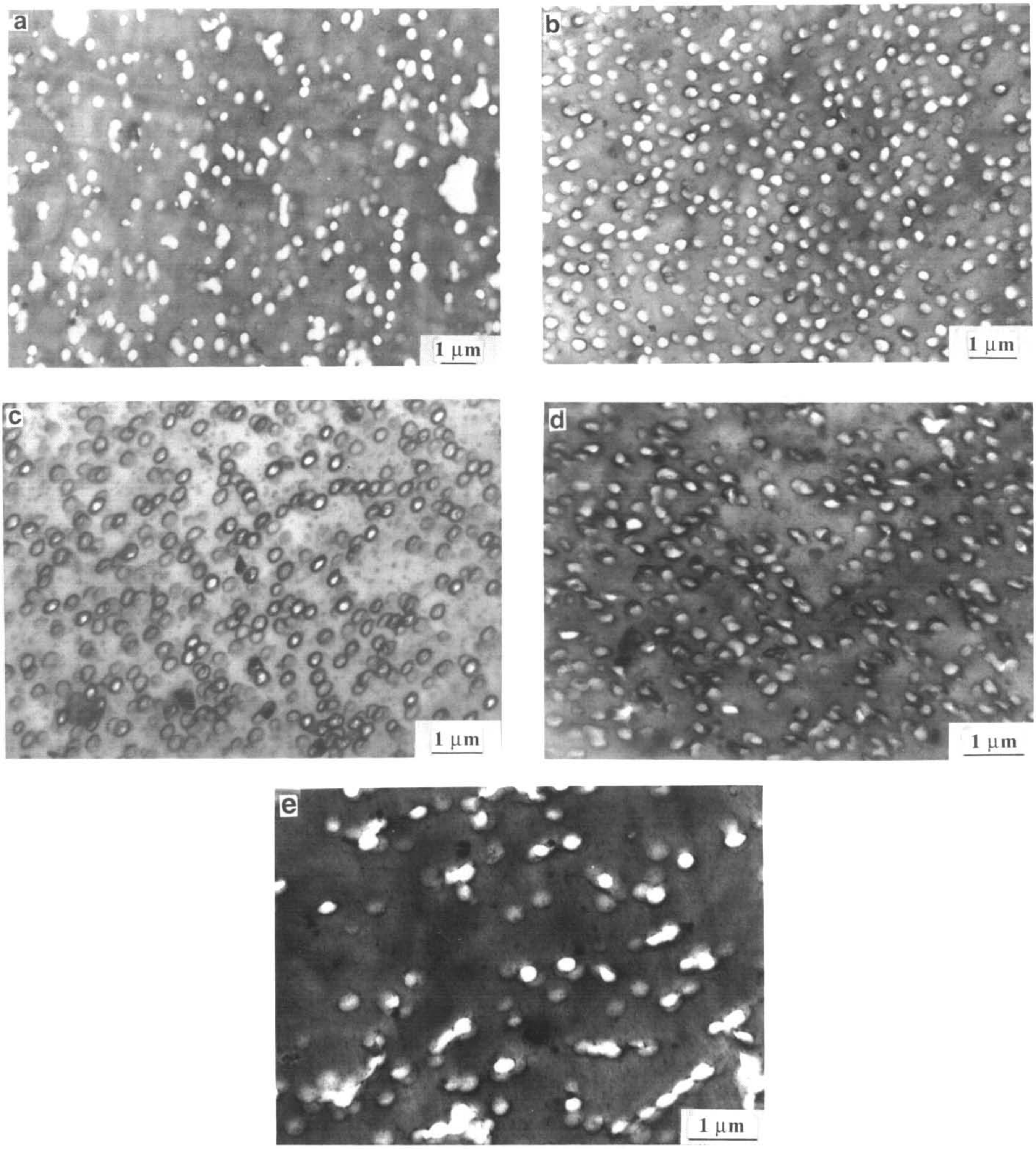

Figure 2 TEM photomicrographs of blends containing 20% EXL3300 with varying amounts of compatibilizer, SMA8, made using different blending protocols (+ sign indicates a second extrusion step): (a) 80% nylon 6/20% EXL3300; (b) 78% nylon 6+2% SMA/20% EXL3300; (c) 75% nylon 6+5% SMA8/20% EXL3300; (d) 75% nylon 6/5% SMA8/20% EXL3300; (e) 70% nylon 6+10% SMA8/20% EXL3300. In sample (c) SMA8 and EXL3300 were premixed and then blended with nylon 6, while in (d) the same mixture was made by simultaneously extruding all three ingredients. All the samples were cryogenically microtomed from injection-moulded bars and stained with RuO$_4$

Figure 5a shows Brabender torque plots as a function of mixing time for the major component polymers used in this study. Typically, after about 10 min, the torque values stabilize and no further changes occur. This is the case with nylon 6, SMA8 and SMA14. The three polymers have substantially similar viscosities, but nylon 6 is the least viscous. EXL3300 exhibits a steady decrease of torque over the 20 min period. Owing to its colloidal character it is difficult to give simple interpretations of the absolute torque or its time dependence. The latter, however, may reflect some degradation at 240°C in the Brabender.

Figure 5b demonstrates substantially higher torque for 75/5 nylon 6/SMA blends than would be expected from the behaviour of the individual components (*Figure 5a*). In the case of SMA8, the blend torque is more than twice as large as that of pure SMA8. The results using SMA14 are even more dramatic. A maximum torque of about

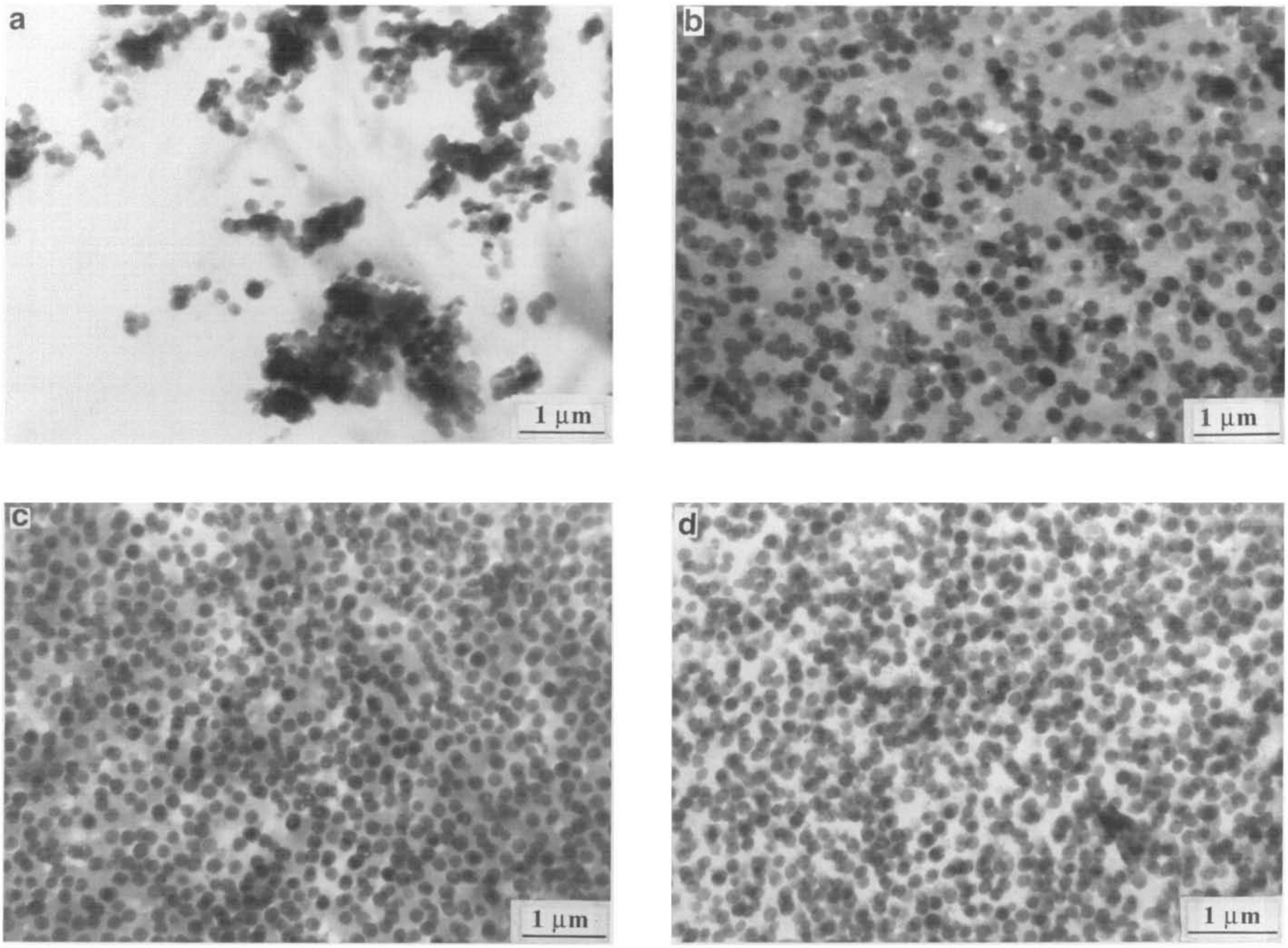

Figure 3 TEM photomicrographs of blends containing $(80-x)$% nylon 6 and x% SMA8/20% EXL3607 all prepared by the indicated two-step extrusion process: (a) 80% nylon 6/20% EXL3607; (b) 78% nylon 6+2% SMA8/20% EXL3607; (c) 75% nylon 6+5% SMA8/20% EXL3607; (d) 70% nylon 6+10% SMA8/20% EXL3607. Samples were cryogenically microtomed from injection-moulded bars and stained with OsO_4 and RuO_4

Table 3 Effect of mixing order and SMA8 concentration on room temperature mechanical properties of ternary blends

Composition (%)			Yield stress (MPa)	Modulus (GPa)	Elongation at break (%)	Izod impact ($J\,m^{-1}$)
Nylon 6	SMA8	EXL3300				
Nylon 6/SMA8/EXL3300[a]						
79	1	20	51.6	2.00	55	160
78	2	20	53.7	2.09	140	840
75	5	20	56.8	2.28	140	1400
70	10	20	56.1	2.36	90	1100
Nylon 6/SMA8+EXL3300[b]						
79	1	20	58.2	2.28	40	140
78	2	20	56.4	2.14	180	1200
75	5	20	58.0	2.20	160	1260
70	10	20	64.3	2.61	100	1240
Nylon 6+SMA8/EXL3300[c]						
79	1	20	56.0	2.11	24	150
78	2	20	57.3	2.19	92	600
76	4	20	59.7	2.27	160	1150
75	5	20	60.0	2.33	160	1230
72.5	7.5	20	60.6	2.36	160	1340
70	10	20	61.3	2.37	120	1280

[a] The three components were mixed simultaneously using a single extrusion step

[b] Nylon 6 and SMA8 were extrusion blended followed by addition of EXL3300 in a second extrusion step

[c] SMA8 and EXL3300 were extrusion blended followed by addition of nylon 6 in a second extrusion step

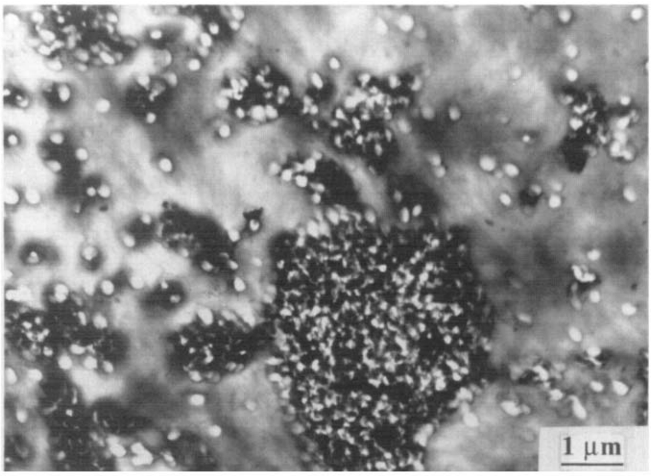

Figure 4 TEM photomicrograph of nylon 6/SMA8 (75/5) binary blend. Sample was cryogenically microtomed from injection-moulded bars and stained with RuO_4

5000 m g was reached, followed by a steady decrease to 1700 m g. The higher torque no doubt reflects the higher functionality of SMA14 than of SMA8 while the decrease with time probably results from mastication of the highly grafted structure with continued shearing[24].

Figure 5c demonstrates that ternary blends have dramatically higher torque values than the matrix or the matrix plus impact modifier. Ternary blends were prepared by two different mixing protocols but each yielded substantially similar results. Moreover, the blend made by mixing the three polymers in one extrusion step showed a higher torque early in the experiment, presumably because of more immediate exposure of MA groups to nylon.

TERNARY BLENDS

From the data summarized in *Table 3*, it is clear that ternary combinations of SMA8, EXL3300 and nylon 6 can lead to extremely tough materials, and this provides support for the proposal that SMA copolymers which are miscible with PMMA can serve to effectively compatibilize core–shell rubber particles with nylon 6 by chemical reaction.

Mixing protocol

To determine the most effective method of melt blending for achieving uniformly tough products, three mixing protocols were examined: (1) simultaneous blending of all three components using a single extrusion, (2) a first extrusion to blend nylon 6 and SMA followed by addition of EXL3300 in a second extrusion, and (3) a first extrusion to blend SMA and EXL3300 followed by addition of nylon 6 in a second extrusion.

The stress–strain and impact data in *Table 3* show that when the level of EXL3300 is held at 20% all three mixing protocols lead to high-strength, tough blends provided the SMA8 content is at least 5%. Indeed, *Figures 2* and *3* confirm that the dispersal of either modifier, EXL3300 or EXL3607, in nylon 6 is greatly facilitated by the addition of SMA8 to the blend. According to Trent *et al.*[42], SMA8 should be more readily stained by RuO_4 than the polyamides or EXL3300; thus, it was used as the staining agent on the premise that it would facilitate determination of the ultimate location of

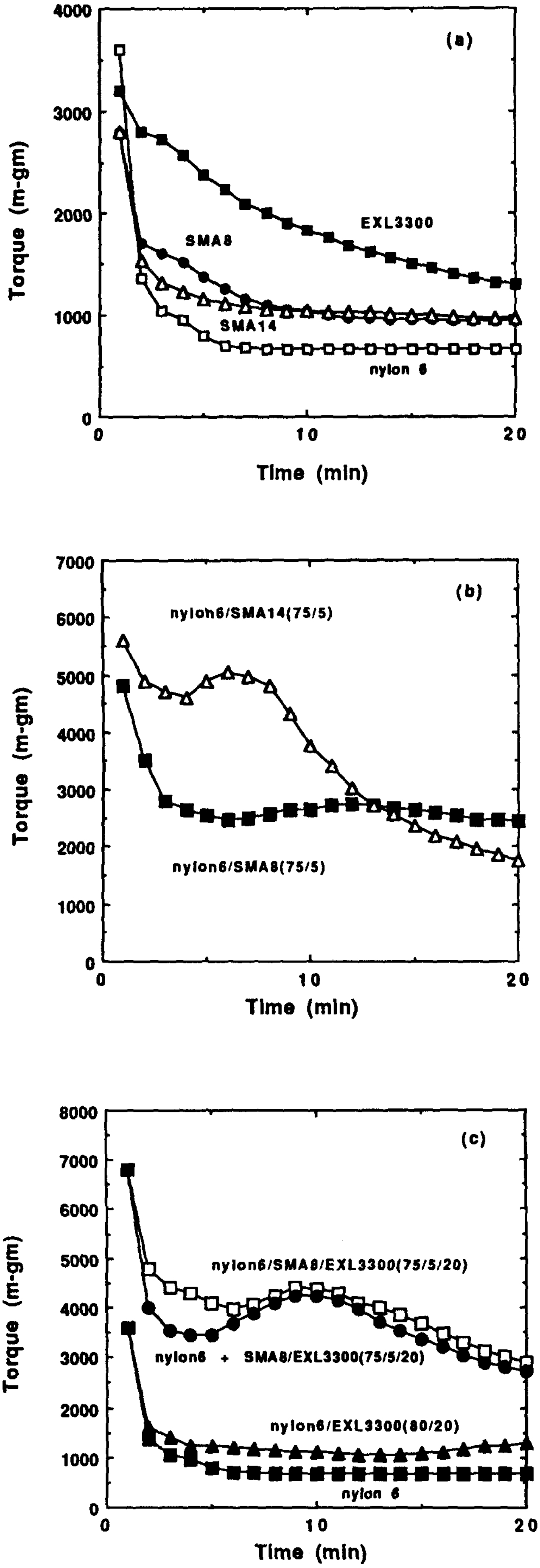

Figure 5 Brabender torque response for (a) individual blend components; (b) nylon 6/SMA (75/5) binary blends and (c) ternary blends. All the samples were measured at 60 rev min^{-1} and 240°C

the SMA8 in the ternary blend. At low levels of SMA8, the TEM photomicrographs in *Figure 2* clearly indicate the presence of SMA8 at the modifier–matrix interface. Since SMA8 is miscible with PMMA, which forms the shell of the modifier, this is where it is expected to locate. At higher SMA8 levels, it appears that some of the SMA8 is separately dispersed in the polyamide matrix as small RuO_4-stained domains (see *Figure 2c* and *d*). This is reflected as a very dark background in the matrix phase in *Figure 2c* where the SMA8 content is 10% of the total blend mass. This is an expected result for two reasons. First, there is some upper limit to how much SMA8 can be solubilized into the restricted domains of the grafted PMMA chains that form the particle shells[43–45]. The shell comprises about 20% of the mass of each modifier particle and at 20% modifier in the blend, 4% SMA8 would lead to a mass equal to that of the PMMA chains in the blend. Thus, an SMA8 level of this order is probably approaching the upper limit for solubilization in the shell region. Second, the SMA8 chains that react with nylon 6 probably experience strong stresses during processing, relative to the thermodynamic forces tending to hold them in the vicinity of the PMMA chains in the shell, that could drag them into the matrix. This balance of forces becomes more favourable for location in the matrix as the SMA8 content is increased. There is some evidence in the TEM photomicrographs and the property trends to suggest that addition of SMA8 beyond about 5% leads to poorer modifier dispersion in the matrix. In addition to the arguments mentioned above, increased viscosity of the matrix at the higher SMA8 level might also be a factor.

Each of the three mixing protocols used seems to lead to useful properties and to relatively good dispersion (compare *Figure 2c* and *d*) for the ternary blends. However, to reduce the scope of the work, further experiments were limited to protocol 3 where the SMA is first premixed with the modifier and then nylon 6 is added in a second extrusion step. It is reasonable that this would give the greatest opportunity for the SMA8 to play its proposed function and that use of two extrusion steps would provide greater opportunity for mixing. To some extent the data in *Table 3* suggest this as the best option.

Effect of modifier and compatibilizer types

A limited series of blends were examined using the modifier containing the butadiene-based rubber core, EXL3607, and the results are summarized in *Table 4*. For SMA8 as the compatibilizer, rather similar mechanical properties are achieved at room temperature to those using the modifier with the acrylic rubber core, EXL3300, as may be seen by comparing with the results in *Table 3*. Staining the microtomed sections with OsO_4 causes these particles to appear as dark spots in the TEM photomicrographs. The results in *Figure 3* indicate that, with the aid of SMA8 as a dispersant, these particles are well dispersed in the nylon 6 matrix. These photomicrographs do not reveal any information about the location of the SMA8 in the ternary blend since SMA8 is not preferentially stained in this case. *Table 4* briefly compares the ability of SMA14 to serve the role of compatibilizer. Very low levels of the order of 2% lead to very high room temperature impact strength; however, higher levels cause a reduction in toughness. Physically, SMA14 interacts more favourably with PMMA than does SMA8[34], and its larger number of maleic anhydride units per chain increases opportunities for reaction with nylon 6. The latter may be something of a disadvantage, as seen by the high viscosity in *Figure 5b* and its decline with processing time. Comb-like grafts are more likely to result from reaction of such high functionality molecules with nylon 6. This type of structure may not be optimum for an interfacial compatibilizer and clearly has potentially detrimental effects on rheological behaviour[24]. No further experiments with SMA14 were done.

The nylon 6 used here is estimated to have 40 μmol of amine end groups per gram. For blends containing 20% of modifier, it requires approximately 4% by weight of SMA8 and 2% of SMA14 to provide a stoichiometrically equivalent number of anhydride units as amine ends in these blends. These concentrations turn out to be very near the optimum levels for mechanical properties as seen by the data in *Tables 3* and *4*. However, it would be naive to believe that these reactions proceed far enough to completion to be limited by stoichiometry[24].

Effect of modifier and compatibilizer concentrations

It is well known that higher concentrations of impact modifier typically increase impact strength and lower the ductile–brittle transition temperature, while tensile strength and modulus are sacrificed[8,11,24]. Obviously, it is important to balance these opposing trends for best overall performance. Because of the potential contributions of both the high modulus SMA

Table 4 Effect of compatibilizer type and amount on mechanical properties of blends with EXL3607

Composition (%)			Yield stress[a] (MPa)	Modulus[a] (GPa)	Elongation at break[a] (%)	Izod impact[a] ($J m^{-1}$)	Ductile–brittle transition temperature (°C)
Nylon 6	SMA	EXL3607					
Nylon 6+SMA8/EXL3607							
79	1	20	55.6	2.16	27	120	55
78	2	20	56.7	2.19	190	130	45
75	5	20	58.0	2.21	96	990	−5
70	10	20	57.3	2.25	82	1230	−10
Nylon 6+SMA14/EXL3607							
79	1	20	53.7	2.02	120	430	50
78	2	20	59.1	2.34	130	1410	−10
75	5	20	64.0	2.56	80	620	30
70	10	20	62.7	2.38	36	420	35

[a] Values determined at room temperature, 22°C

compatibilizer and the soft core–shell modifier on the mechanical properties, it was difficult to address this optimization with limited experiments. What follows is intended to illustrate some important points rather than to deal with this optimization.

Having selected the mixing protocol in which SMA and EXL3300 are melt blended first, a series of four masterbatch blends of impact modifier (EXL3300) and SMA8 (5–33%) were prepared. Nylon 6 was blended with these masterbatches in different proportions of masterbatch from 5 to 40%, as seen in *Table 5*. The data indicate that tough compositions are possible even with the masterbatch where the SMA8/EXL3300 ratio is 1/20. Because of the small amount of SMA in the final blend, its physical contribution to the tensile properties is small so the modulus is low. As the SMA8 compatibilizer concentration is increased, blends with improved strength and ductility are obtained. The masterbatch containing SMA8/EXL3300 in the 5/20 ratio gives particularly attractive blends. For instance, a blend containing 75% nylon 6 and 25% of this masterbatch has excellent strength and the highest notched Izod impact, 1590 J m^{-1}. Furthermore, it has the lowest ductile–brittle transition temperature (−10°C) of all blends investigated. The effect of some variables that influence the ductile–brittle transition will be discussed below.

Nylon 6 blends with the masterbatch containing the highest ratio of SMA8 to EXL3300 (10/20) showed some rather unexpected trends as the amount of masterbatch increased. While the impact strength at room temperature remained high over the range of 20–35% masterbatch content, the best low-temperature toughness was achieved at only 20% of the masterbatch. It is apparent that there is an optimum concentration of the SMA8 compatibilizer that gives rise to high impact strength over a wide temperature range.

It is clear from comparing the TEM photomicrographs in *Figures 2* and *3* that SMA8 aids uniform dispersion of these impact modifiers in the nylon 6 matrix. *Figure 2b* shows that only 2% SMA8 is enough to give a nearly uniform dispersion of 20% EXL3300 in nylon 6. Comparison of *Figures 2b* and *c* suggests that 2 and 5% of SMA8 lead to essentially equivalent dispersion; however, both the tensile and impact properties are substantially higher at 5% SMA than at 2%, as seen in *Figures 6* and *7*. Evidently, the mechanical properties are influenced by factors other than how well the impact modifier is dispersed in the matrix. According to our original hypothesis we may expect that to some degree use of 5% SMA will further strengthen the interface between the modifier shell and the matrix relative to that at 2% SMA. However, it should be noted that all of the SMA8 may not reside in this interfacial region but may be dispersed in the matrix (see *Figure 4*). Addition of SMA8 alone to nylon 6 tends to cause increases in the tensile and impact properties (see *Table 2*), although not to the same extent as shown in *Figures 6* and *7*. Comparison of *Figure 2b* and *c* hints that the shell region is thicker for the blend containing 5% SMA8 than for that containing 2% SMA8.

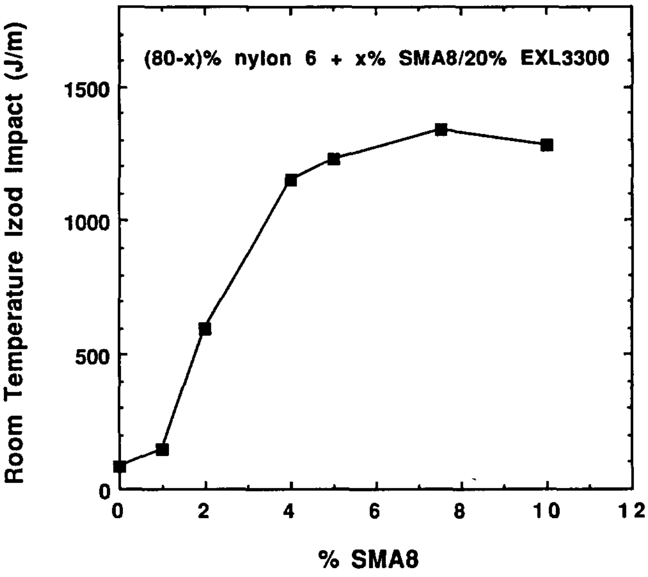

Figure 6 Effect of SMA8 content on room temperature notched Izod impact strength for nylon 6 blends containing 20% EXL3300

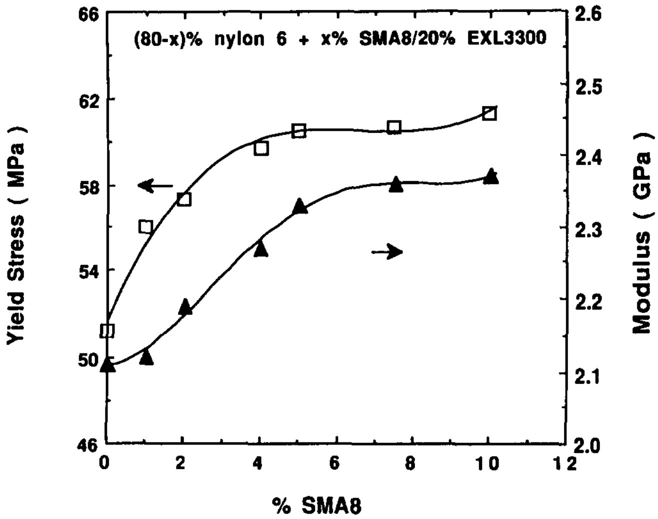

Figure 7 Effect of SMA8 content on yield stress (□) and tensile modulus (▲) for nylon 6 blends containing 20% EXL3300

Ductile–brittle transition temperature

Changes in a number of factors such as rubber content, blend morphology, testing rate, notch radius, temperature etc, can cause an abrupt transition from ductile to brittle behaviour. Many of these factors have been studied in some detail for blends of polyamides with maleic anhydride-modified elastomers[5–20]. After considering the effects of the MA graft concentration, rubber phase volume fraction and particle size in nylon 6,6-based blends, Wu[5] proposed that the surface-to-surface interparticle distance is an important factor influencing the ductile–brittle transition. He concluded that the critical interparticle distance is a material property of the matrix, independent of rubber volume fraction and particle size. Borggreve *et al.*[6,12–16] studied variables affecting ductile–brittle transitions in modified rubber blends with nylon 6 and concluded that the interparticle distance model of Wu is generally useful, although aspects of the physical basis for this have been questioned[6]. Furthermore, they showed that toughening efficiency varies with the type of rubber modifier[14]. Two separate studies using different elastomer systems and approaches to morphology control have demonstrated that there is a minimum particle size below which the toughening effectiveness is reduced[8,46]. This phenomenon obviously invokes mechanisms not anticipated by the critical interparticle distance hypothesis. In principle, core–shell modifiers appropriately coupled to the polyamide matrix permit independent control of modifier concentration without varying particle size.

Even though ductile–brittle transition temperatures have been widely discussed recently in the literature[5–7,11], there appears to be no comment on how this quantity is actually extracted from experimental results. Therefore, it seems appropriate to describe the convention adopted here since the transition region does have a finite width. Well below the transition region, we plot the average Izod impact strength values for all the samples that failed in a brittle manner, while well beyond the transition region we plot the average for all that failed in a ductile manner. In each region, the averaging included the vast majority of the samples. In the transition region, the mix of ductile and brittle failures became more nearly equal, so the average of all samples was computed. The ductile–brittle transition is defined as the midpoint of the jump in the notched Izod impact strength.

Figure 6 shows the effect of SMA8 concentration on the impact strength of nylon 6 blends at a constant modifier (EXL3300) content of 20%. Room temperature Izod impact strength increases dramatically upon adding small amounts of SMA8, and by about 4% SMA8 the major increase in toughness is achieved. The impact strength of these same blends was evaluated as a function of test temperature with the results shown in *Figures 8* and *9*. These transition temperatures, shown in *Figure 9*, decrease as a function of the % SMA8 in the ternary blend up to about 7.5% but then appear to increase. As a practical matter, little gain results from using more than 4% SMA8. Increasing SMA8 concentration above 7.5% is detrimental to low-temperature toughness. Factors that might contribute to this trend include: an excess of SMA8 in the modifier–matrix interfacial region; separate dispersion of SMA8 in the nylon 6 matrix; subtle changes in dispersion; or the relatively high glass transition temperature of the acrylic rubber core of EXL3300.

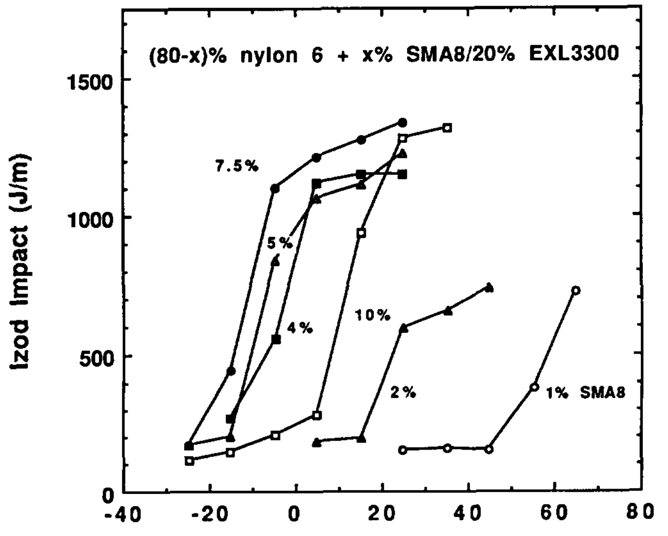

Figure 8 Effect of SMA8 content on notched Izod impact strength as a function of temperature for nylon 6 blends containing 20% EXL3300. SMA8 content (%): □, 10; ●, 7.5; △, 5; ■, 4; ▲, 2; ○, 1

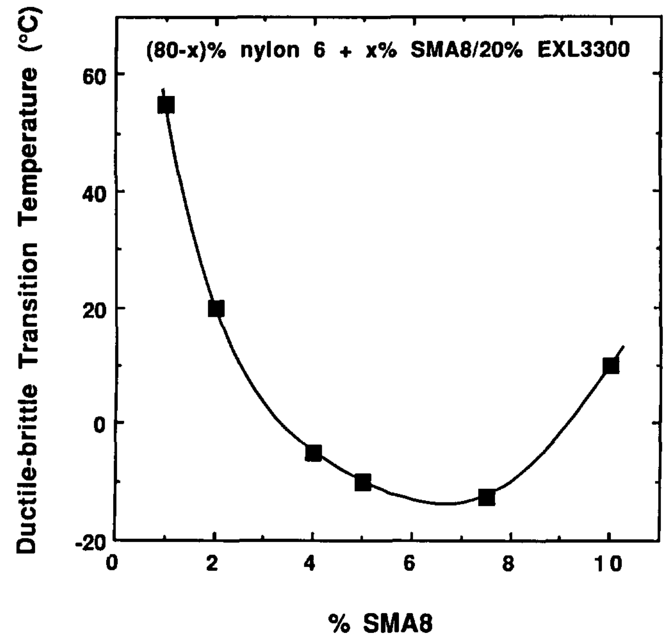

Figure 9 Effect of SMA8 content on the ductile–brittle transition temperature for nylon 6 blends containing 20% EXL3300

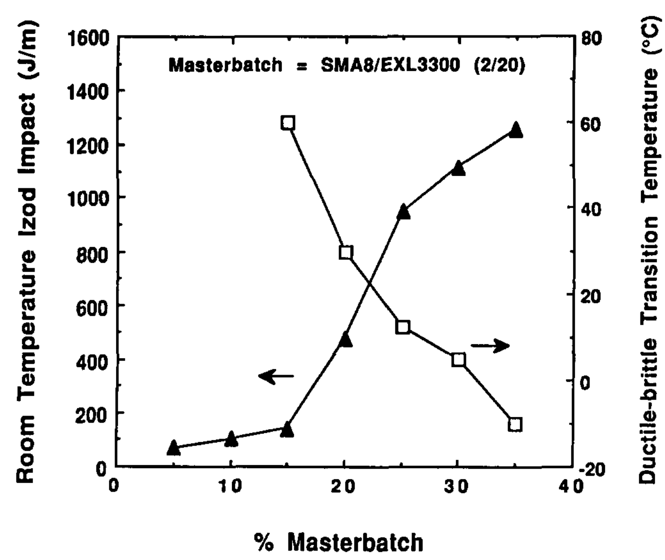

Figure 10 Room temperature notched Izod impact strength (▲) and the ductile–brittle transition temperature (□) of nylon 6 blends as a function of masterbatch SMA8/EXL3300 (2/20) content

Increasing the rubber content of toughened polymers typically elevates room temperature impact strength and lowers the ductile–brittle transition temperature. As illustrated in *Figure 10*, these trends are realized for a masterbatch of SMA8 and the modifier with the acrylic core (EXL3300) in a fixed weight ratio of 2/20. However, for a masterbatch with a higher SMA8/modifier ratio (5/20), the room temperature impact strength goes through a maximum while the ductile–brittle transition temperature exhibits a minimum as more masterbatch is added to nylon 6, as illustrated in *Figure 11*. As seen in *Table 5*, lower SMA8 contents give trends like those in *Figure 10* while higher levels give trends like those in *Figure 11*.

It becomes apparent that an excessive concentration of compatibilizer is detrimental to the ductility of the blends at low temperatures. The question remains, whether this is due to the excess SMA8 locating at the

Table 5 Mechanical properties of nylon 6 blends with various SMA8/EXL3300 masterbatches

Composition (%)				Yield stress[a] (MPa)	Modulus[a] (GPa)	Elongation at break[a] (%)	Izod impact[a] ($J m^{-1}$)	Ductile–brittle transition temperature (°C)
Nylon 6	Masterbatch	SMA8	EXL3300					
Nylon 6+masterbatch-1 (SMA8/EXL3300(1/20))								
95	5	0.2	4.8	71.6	2.72	12	75	
90	10	0.5	9.5	65.1	2.54	14	86	
85	15	0.7	14.3	58.6	2.33	15	130	60
80	20	1.0	19	54.5	2.20	21	140	45
75	25	1.2	23.8	50.3	1.96	44	770	20
70	30	1.4	28.6	46.7	1.79	130	1060	5
65	35	1.7	33.3	43.3	1.55	140	1300	−10
Nylon 6+masterbatch-2 (SMA8/EXL3300(2/20))								
95	5	0.5	4.5	74.7	2.81	9	70	
90	10	0.9	9.1	67.6	2.56	17	100	
85	15	1.4	13.6	62.2	2.40	19	140	60
80	20	1.8	18.2	59.1	2.24	26	480	30
75	25	2.3	22.7	53.3	2.07	45	950	12
70	30	2.7	27.3	51.3	1.91	110	1110	5
65	35	3.2	31.8	44.2	1.67	150	1250	−10
Nylon 6+masterbatch-3 (SMA8/EXL3300(5/20))								
95	5	1.0	4.0	76.7	2.92	14	70	
90	10	2.0	8.0	68.3	2.70	29	110	60
85	15	3.0	12.0	62.9	2.65	180	190	45
80	20	4.0	16.0	58.7		130	810	10
75	25	5.0	20.0	54.3	2.33	170	1590	−10
70	30	6.0	24.0	52.1	2.12	120	1300	5
65	35	7.0	28.0	45.9	2.02	110	460	25
Nylon 6+masterbatch-4 (SMA8/EXL3300(10/20))								
95	5	1.7	3.3	80.4	3.02	12	72	
90	10	3.3	6.7	73.8	2.72	40	110	50
85	15	5.0	10.0	68.1	2.65	140	440	30
80	20	6.7	13.3	66.5	2.62	130	1170	10
75	25	8.3	16.7	65.7	2.53	120	1190	12
70	30	10.0	20.0	61.5	2.44	125	1220	15
65	35	11.7	23.3	57.5	2.38	100	1280	20
60	40	13.3	26.7	54.2	2.27	40	770	25

[a] Values determined at room temperature, 22°C

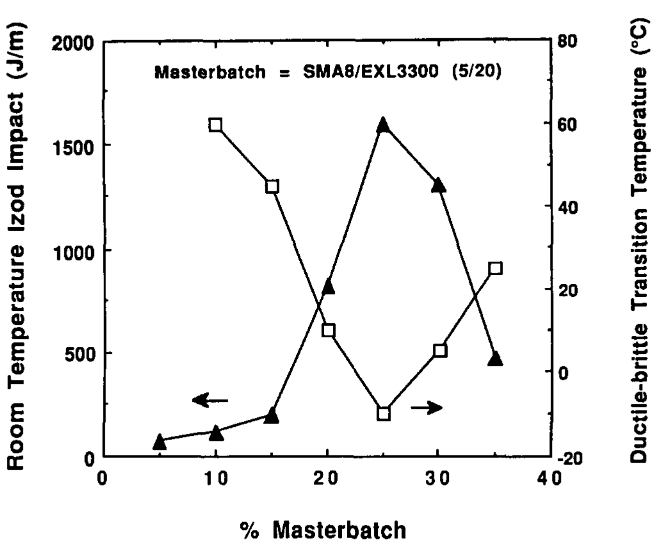

Figure 11 Room temperature notched Izod impact strength (▲) and the ductile–brittle transition temperature (☐) of nylon 6 blends as a function of masterbatch SMA8/EXL3300 (5/20) content

matrix–particle interface and somehow reducing the effectiveness of the rubber, or the distribution of excess SMA8 in the matrix and reducing its propensity for being toughened. It is apparent that the T_g of the rubber phase has little to do with the ductile–brittle transition temperatures found in these experiments.

To verify the latter statement, further EXL3607 was chosen as the core–shell modifier. Its core is a butadiene-based rubber, with a T_g of −60°C, which is 30°C lower than that of EXL3300. The data from a limited number of experiments are listed in *Table 4*. The effectiveness of SMA8 appears to be less with EXL3607 than it was with EXL3300, as 1 and 2% do not give tough compositions at room temperature. This may be due to the fact that the EXL3607 particles are smaller. These particles have a larger surface area per mass of modifier and may require more compatibilizer to achieve adequate dispersion and interfacial adhesion. SMA8 at 5 and 10% levels is very effective, but the ductile–brittle transition temperature is not improved relative to the best composite based on EXL3300. Use of SMA14 instead of SMA8 for dispersing EXL3607 into nylon 6 did not lead to a reduction in

Table 6 Room temperature mechanical properties of nylon 6,6 + SMA8/EXL3300 blends[a]

Composition (%)			Yield stress (MPa)	Modulus (GPa)	Break strain (%)	Izod impact ($J m^{-1}$)
Nylon 6,6	SMA8	EXL3300				
100	0	0	76.7	2.78	40	50
80	0	20	44.0	1.86	9	39
79	1	20	51.7	2.03	8	34
78	2	20	54.9	2.12	5	41
75	5	20	52.1	2.13	7	50
70	10	20	53.1	2.18	5	65

[a] All blends were prepared by first mixing SMA8 and EXL3300 followed by addition of nylon 6,6 in a second extrusion step

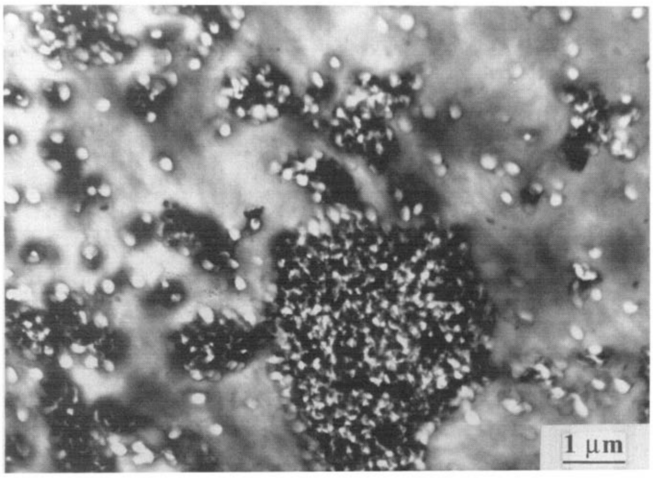

Figure 12 TEM photomicrograph of 75% nylon 6,6 + 5% SMA8/20% EXL3300 blend. Sample was cryogenically microtomed from injection-moulded bar and stained with RuO_4

low-temperature toughness as shown in *Table 4*. Thus, the T_g of the rubber phase is evidently not the limiting factor in achieving low ductile–brittle transition temperatures in these systems.

Table 4 compares the use of SMA8 and SMA14 as compatibilizers for EXL3607 and nylon 6. The most effective content of SMA14 is 2% as mentioned earlier. Even though SMA14 is a more efficient compatibilizer than SMA8, it does not give rise to any further reduction in the ductile–brittle transition temperature.

Nylon 6,6 blends

Ternary blends based on nylon 6,6 were made by first mixing SMA8 and EXL3300 and then adding the polyamide in a second extrusion step. All blends contained 20% EXL3300 and the amount of SMA8 varied up to 10%. All blends exhibited brittle failure (see *Table 6*). Recent work by Oshinski *et al.*[8,9] showed that nylon 6,6 generates quite different morphologies than nylon 6 when blended in a single screw extruder with a maleic anhydride-grafted elastomer. These differences were attributed to chemical differences between the two types of polyamides. Nylon 6 of the type used here has only one amine end group per chain, whereas some nylon 6,6 chains can have two amine end groups. This leads to different modes of coupling to an anhydride-containing phase in addition to simple end-grafting and affects blend morphology in dramatic ways. Primarily it is more difficult to achieve the same fine dispersion in a single screw extruder that is possible for nylon 6 type materials. Further work on a variety of systems confirms this hypothesis[47,48]. We believe similar issues are involved here. *Figure 12* shows severe agglomeration of particles of impact modifier in a nylon 6,6 matrix that added SMA8 fails to disperse adequately.

CONCLUSIONS

Polyamides cannot be toughened effectively by addition of simple core–shell impact modifiers since they fail to disperse uniformly as individual emulsion particles in the polyamide matrix. This no doubt reflects an inadequate physical interaction between the polyamide and the PMMA-based shell of the modifier particles. To some extent the same feature may provide inadequate adhesion between the matrix and the modifier particle even if the dispersion problem could be solved. It was proposed that addition of appropriate dispersants to these blends might provide solutions to the two problems mentioned. Specifically it was suggested that a polymer that is miscible with, or has a physical affinity for, the PMMA shell but which can also react with the polyamide could serve this purpose. Styrene–maleic anhydride copolymers meet both criteria[34]. Use of commercially available SMA copolymers and impact modifiers clearly demonstrated both improved dispersion of modifier and impact properties of the blends when the matrix is nylon 6. Neither were improved in the case of nylon 6,6 which we believe relates to chemical differences between the two polyamides as demonstrated in other reactive blends[8,9].

This approach fails to improve low-temperature toughness to the extent demonstrated for maleic anhydride-grafted ethylene–propylene[6] and styrene-based block copolymer elastomers[11] and for core–shell modifiers containing chemically bonded functionality in the shell[33]. This limitation might be mitigated to some degree by dispersants and modifiers of more optimal design and by more aggressive processing procedures. A subsequent paper will demonstrate that a styrene/acrylic acid copolymer can also serve as a dispersant for these impact modifiers in nylon 6, although its efficiency is less than that of SMA copolymers.

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