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Compatibilization of nylon 6/ABS blends using glycidyl methacrylate/methyl methacrylate copolymers

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Blends of nylon 6 with acrylonitrile/butadiene/styrene (ABS) materials and with its styrene/acrylonitrile copolymer (SAN) matrix were prepared using a series of glycidyl methacrylate/methyl methacrylate (GMA/MMA) copolymers as compatibilizing agents. These copolymers are miscible with SAN and the epoxide unit in GMA is capable of reacting with the polyamide end groups. This copolymer thus has the potential to form graft copolymers at the polyamide/SAN interface during melt processing. This study focuses on the effects of functionality and concentration of the compatibilizer on the rheological, morphological, and mechanical properties of these blends. In general, incorporation of this compatibilizer does not significantly improve the impact properties of nylon 6/ABS blends. In these blends, nylon 6 was always the continuous phase; TEM photomicrographs indicate that incorporation of the compatibilizer results in two distinct populations of ABS domains: large agglomerates, and small dispersed particles. The agglomerates become larger with increasing GMA content in the compatibilizer and result in a non-uniform distribution of rubber particles within the nylon 6 matrix. Torque rheometry was employed to identify the reaction mechanisms that may be responsible for the development of such morphologies. These experiments demonstrate that the cause of the poor ABS dispersion is the difunctionality of the nylon 6 end groups with respect to the epoxide group of GMA, which leads to cross-linking-type reactions. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: nylon 6/ABS blends; compatibilization; polymer morphology)

INTRODUCTION

Multiphase plastics offer a route to combinations of properties generally not available in any single polymeric material[1,2]. However, simple blends of immiscible polymers generally exhibit poor mechanical properties that stem from the unfavourable interactions between their molecular segments. This is manifested as a coarse, unstable phase morphology that develops during melt processing and weak interfaces between the phases in the solid state.

These problems of polymer–polymer incompatibility can often be mitigated by the incorporation of an appropriately formed block or graft copolymer, or compatibilizer, that resides preferentially at the polymer/polymer interfaces[3–7], which may be premade or formed *in situ* during melt processing through the use of appropriate reactive functionalities, i.e. reactive compatibilization. This latter approach has become the method of choice in the development of many commercial products. The judicious selection of a compatibilizer can often result in improved mechanical properties, often with synergistic effects, when the compatibilizer can effectively 'stitch' itself across the polymer/polymer interfaces. This process reduces the interfacial tension between the blend components[8–11] and retards dispersed phase coalescence via steric stabilization[12–16]. Both of these effects promote a stable, fine distribution of the dispersed phase within the matrix phase. In addition, this improves the interfacial adhesion between the blend components and, thus, reduces the possibility of interfacial failure[7,17,18].

Reactive compatibilization has been employed extensively in the development of blends based on polyamides, particularly toughened materials[11,15,19–34]. There are numerous ways in which anhydrides can be incorporated into polymers, and these anhydride units react readily with the amine end groups of polyamides to form block or graft copolymers. This process simultaneously improves the interfacial adhesion between the phases and allows for control of the size and distribution of the rubber particles, all of which are key factors in promoting toughness.

Blends of polyamide and acrylonitrile/butadiene/styrene (ABS) materials are of significant commercial interest. The latter, which consists of a butadiene rubber embedded within a matrix of styrene/acrylonitrile copolymer (SAN), are generally noted for their excellent toughness, aesthetics, and low cost. Thus, there is interest in developing compatible polyamide/ABS alloys with the goal being to retain the desirable properties of each of the blend constituents.

Various approaches to the reactive compatibilization of polyamide/ABS alloys have been reported[35–47]. For example, maleic anhydride can be grafted to the ABS[35,36]; however, the preferred route has been to add a material capable of reacting with the end groups of the polyamide and which is also miscible with the SAN phase of ABS. Patents and papers from Monsanto (now Bayer)[37–39] describe the use of terpolymers of styrene, acrylonitrile, and maleic anhydride (small amounts of methyl

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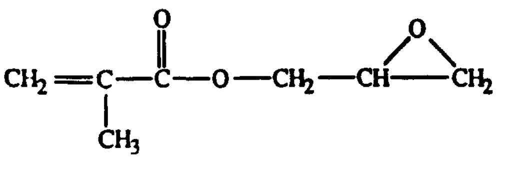
methacrylate have also been mentioned) as compatibilizers for polyamide/ABS blends. This strategy relies on the functional terpolymer dissolving in the SAN phase of ABS and reacting with the amine ends of the polyamide. Styrene/maleic anhydride (SMA) copolymers have also been employed as compatibilizers for polyamide/ABS blends, since they are miscible with SAN copolymers when the AN and MA contents are approximately equal[40,41,43,44]. The impact strength of these blends has been shown to be very sensitive to the amount and composition of the SMA copolymer[41], as well as the blending sequence. Angola *et al.* showed that the addition of SMA to polyamide/SAN blends can significantly enhance tensile and impact properties of these blends; this was attributed to the formation of a polyamide/SMA graft copolymer which improved the dispersion of SAN within the polyamide matrix[45]. More recent work by Majumdar *et al.* utilized a series of imidized acrylic (IA) polymers as compatibilizers for nylon 6/ABS blends[42,46,48]. These imidized acrylic materials, which can be miscible with SAN[48], also contain acid and anhydride functionalities capable of reacting with the amine end groups of polyamides. The effects that varying the reactive functionality and the miscibility characteristics have on the morphology and mechanical properties of these blends have been investigated in some detail. Examination of this prior work raises many fundamental issues regarding the optimal compatibilization scheme for these blends. Factors to be considered in the molecular architecture of the compatibilizer include the type and number of reactive functional groups, the method of incorporating the reactive functionalities (graft, comonomer or terminal group), the molecular weight of the compatibilizer, and the extent of miscibility with SAN.

This work explores another option for compatibilizing polyamide/ABS blends. In this study, a series of glycidyl methacrylate (GMA)/methyl methacrylate (MMA) copolymers is used as compatibilizing agents. Glycidyl methacrylate



contains an epoxide functionality capable of reacting with polyamide end groups, whereas poly(methyl methacrylate) has been shown to be miscible with the SAN phase of ABS over a range of AN contents[49,50]. Previous work by Gan *et al.* has demonstrated that GMA/MMA copolymers can be miscible with SAN over the range of AN contents typical of commercial ABS materials[49].

There has been much interest in the use of glycidyl methacrylate based copolymers as compatibilizing agents for polymer blends. Numerous epoxy-functional polymers have been prepared by the copolymerization of GMA with alkyl acrylates[51–59], styrene[60–64], and ethylene[65]. The literature describes the use of styrene/GMA copolymers to compatibilize several polymer pairs, including polystyrene/polyamide[66], polystyrene/poly(ethylene terephthalate)[67,68], polystyrene/poly(butylene terephthalate)[69], and poly(phenylene oxide)/polybutylene terephthalate)[70]. S/AN/GMA terpolymers have been suggested as compatibilizing agents for poly(butylene terephthalate)/ABS blends[71]. Attempts to compatibilize poly(butylene terephthalate)/polyolefin blends have been made using random or graft copolymers of GMA[72–77]. Reactive rubbers which contain GMA functionality have been synthesized, and these have been used us toughening agents for various polyesters[78–81].

The focus of this study will be to explore the use of various GMA/MMA copolymers to control the morphological, rheological, and mechanical characteristics of polyamide/ABS blends. Since ABS itself is a two-phase material, a portion of this work will focus on the simpler polyamide/SAN system. It will be demonstrated that these copolymers are not as effective as anhydride-based compatibilizers in generating an optimum phase morphology and toughening of nylon/ABS blends. We propose that this stems from the epoxide ring of GMA being difunctional with respect to nylon 6, i.e. both the acid and amine chain ends react with GMA, whereas anhydrides can only react with the amine ends of polyamide chains.

EXPERIMENTAL

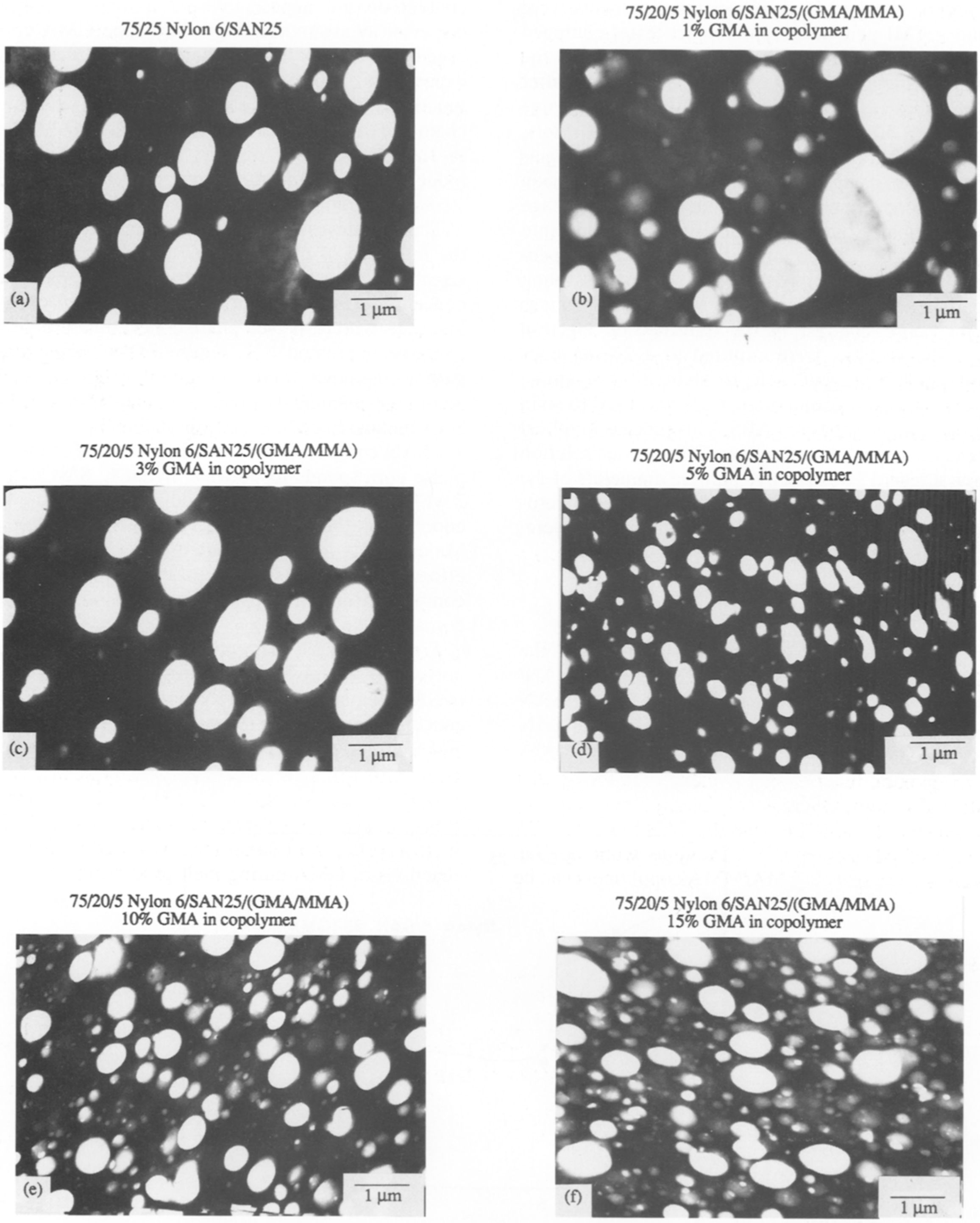
Table 1 summarizes the characteristics of the materials used in this study. The nylon 6 is a commercially available material with $\bar{M}_n = 22\,000$ and approximately equal concentrations of acid and amine end groups[82]. Prior to each processing step, all polyamide-containing materials were dried in a vacuum oven for at least 16 h at 80°C to remove sorbed water. An emulsion-prepared ABS material was used which contains 50 wt.% rubber in the form of polydisperse particles typically in the range 0.2 μm diameter and a SAN matrix containing 24% AN. Since ABS itself is a complex two-phase system, a SAN copolymer typical of commercial materials was used to explore blends in the absence of a rubber phase. A copolymer of ethylene and 6 wt.% glycidyl methacrylate, from Sumitomo, was used to model potential reactions of GMA during melt processing.

Table 1 Polymers used in this study

Polymer	Material/description	Composition	Molecular weight	Brabender torque[a] (N·m)	Source
Nylon 6	Capron 8207F	End-group content: NH_2, 47.9 μeq g^{-1}; COOH, 43.0 μeq g^{-1}	$\bar{M}_n = 22\,000$	7.3	Allied Signal
ABS	SAN-grafted emulsion rubber (BL-65)	50% rubber 24% AN in SAN	$\bar{M}_n = 44\,000^b$ $\bar{M}_w = 167\,000$	23.8	Sumitomo
SAN25	Styrene/acrylonitrile copolymer (Tyril 1000)	25% AN	$\bar{M}_n = 77\,000$ $\bar{M}_w = 152\,000$	6.8	Dow Chemical Co.
EGMA	Ethylene/glycidyl methacrylate copolymer	6% GMA	Not available	4.4	Sumitomo

[a] Measurements taken at 240°C and 60 rev min^{-1} after 10 min
[b] From g.p.c. using polystyrene standards; the information shown is for soluble SAN

Copolymers of glycidyl methacrylate and methyl methacrylate monomers, supplied by Aldrich Chemical Co., were synthesized in various proportions by bulk polymerization. Glycidyl methacrylate was first vacuum distilled to purify the monomer. Vacuum distillation of the GMA monomer is required to avoid cross-linking of the polymer during synthesis. The appropriate amounts of methyl methacrylate and glycidyl methacrylate was premixed in a flask, and 2 wt.% of ethyl acrylate were added to prevent unzipping of the polymer at melt processing temperatures. The solution of monomers was then placed in a reaction vessel and an azobisisobutyronitrile (AIBN) initiator (DuPont, Vazo 64) was added in the ratio 3.5 g AIBN to 100 g monomer. The reaction vessel was a Kapak heat-sealable pouch containing a polyester barrier film. The sealed pouch was immersed in a large water bath maintained at 60°C and allowed to react to essentially 100% conversion. Although the high yield obtained by this polymerization technique may tend to produce some composition drift, the reactivity ratios are close enough to unity ($r_{\mathrm{MMA}} = 0.76$, $r_{\mathrm{GMA}} = 0.88$)[53] that the compositions of the monomer feed and the resulting polymer should not be significantly different. The solid polymer mass was then crushed, cryogenically ground into a fine powder, and dried under vacuum for at least 12 h at



75/25 Nylon 6/SAN25

75/20/5 Nylon 6/SAN25/(GMA/MMA) 1% GMA in copolymer

75/20/5 Nylon 6/SAN25/(GMA/MMA) 3% GMA in copolymer

75/20/5 Nylon 6/SAN25/(GMA/MMA) 5% GMA in copolymer

75/20/5 Nylon 6/SAN25/(GMA/MMA) 10% GMA in copolymer

75/20/5 Nylon 6/SAN25/(GMA/MMA) 15% GMA in copolymer

Figure 1 TEM photomicrographs of (a) a 75/25 nylon 6/SAN25 blend and ternary 75/20/5 nylon 6/SAN25/(GMA/MMA) blends with varying amounts of GMA in the copolymer: (b) 1%; (c) 3%; (d) 5%; (e) 10% (f) 15%. The polyamide phase has been stained dark with phosphotungstic acid (PTA)

65°C. Copolymers containing 1, 3, 5, 10, and 15 wt.% GMA in the monomer feed were synthesized by W. Hale of this laboratory using this technique.

Blends in this study were prepared by the simultaneous extrusion of all components in a Killion single screw extruder ($L/D = 30$, 2.54 cm in diameter) at 240°C using a screw speed of 40 rev min^{-1}. In certain cases, blends were processed in a 15 mm Baker–Perkins fully intermeshing co-rotating twin screw extruder operated at 240°C and 170 rev min^{-1}. The extrudate was dried in a vacuum oven and injection molded into 0.318 cm thick Izod bars (ASTM D256) using an Arburg Allrounder injection molding machine. Test specimens were visually inspected for air bubbles and surface flaws; specimens with defects were discarded. Notched Izod impact measurements were made using a TMI pendulum-type impact tester equipped with an insulated chamber for heating and cooling the specimens. Rheological measurements were made after fluxing the various polymers in a Brabender torque rheometer with a 50 cm^3 mixing head and standard rotors, operated at 240°C and 60 rev min^{-1}. Blend morphologies were determined using a JEOL 200CX transmission electron microscope operating at an accelerating voltage of 120 kV. Samples were cryogenically microtomed into ultrathin sections (10–20 nm thick) from Izod bars perpendicular to the flow direction. Various selective staining techniques were used to induce electron density changes required for phase contrast in the transmission electron microsope. The sections were exposed to a 2% aqueous solution of phosphotungstic acid to stain the polyamide phase. In certain cases, osmium tetroxide was used to stain the unsaturated rubber phase in ABS. This process involved exposing the microtomed sections to a 2% aqueous solution of OsO_4 for at least 12 h. Effective particle diameters of the dispersed phase were determined from TEM photomicrographs by digital image analysis using NIH Image software.

EFFECT OF GMA/MMA COMPATIBILIZER ON NYLON 6/SAN MORPHOLOGY

The influence of the compatibilizer composition on the morphology and rheology of ternary nylon 6/SAN/compatibilizer blends are described here. The SAN material contained 25% AN which is typical of the SAN phases in many commercial ABS materials. The GMA content of the compatibilizer was varied to investigate the effects of compatibilizer functionality on morphology of the dispersed SAN phase and melt rheology of the blend.

Figure 1 shows TEM photomicrographs for a binary nylon 6/SAN25 blend and corresponding ternary blends containing the GMA/MMA compatibilizer. For the ternary blends, the copolymer contains different amounts of GMA, ranging from 1 to 15%. *Figure 2* shows the weight-average SAN particle diameter *versus* the GMA content in the compatibilizer. Addition of the compatibilizer appears to have little or no influence on the dispersed phase particle size up to 3 wt.% GMA in the copolymer; however, there is a significant reduction in the SAN domain size when the GMA content is increased to 5%. Further increases in GMA content do not appear to have a marked effect on the dispersed phase morphology. Since the GMA copolymers used here are fully miscible with the SAN phase[49], one may expect it to reside in the SAN phase while the epoxide functional groups form chemical linkages with the nylon 6 chain ends at the domain interfaces. This would be expected to reduce the SAN domain size to some degree by a reduction of interfacial tension and to a greater degree by steric stabilization of the SAN particles against coalescence.

These coalescence effects can be monitored by observing the influence of dispersed phase concentration on particle size. The probability of coalescence increases with the concentration of the particles; hence, particle size generally increases with dispersed phase concentration unless coalescence is suppressed[14–16]. *Figure 3* shows the average SAN particle diameter *versus* weight per cent of the dispersed phase for uncompatibilized and compatibilized nylon 6/SAN blends. Each of the compatibilized blends contained a 4:1 SAN/compatibilizer ratio, i.e. 10 wt.% of the dispersed phase corresponds to 90 wt.% nylon 6, 8 wt.% SAN, and 2 wt.% compatibilizer. In addition to the GMA/MMA copolymer, the imidized acrylic (IA) polymer used by Majumdar *et al.* was utilized in order to compare the effectiveness of anhydride-based *versus* epoxide-based compatibilizers in suppressing the coalescence of SAN domains.

Figure 3 clearly demonstrates that the imidized acrylic polymer is the most efficient in preventing the coalescence of SAN domains, as the SAN particle size is independent of concentration. Blends containing 10 wt.% GMA in the GMA/MMA copolymer also appear to be effective in

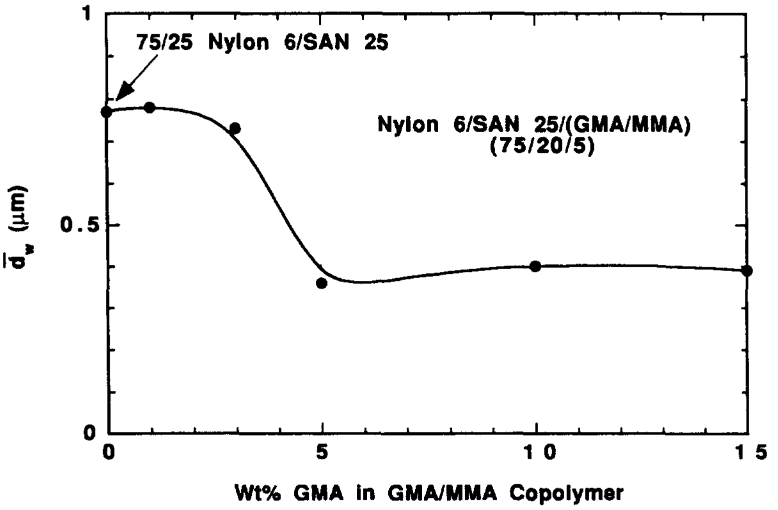


Figure 2 Dispersed phase domain size *versus* GMA content in the copolymer for 75/20/5 nylon 6/SAN25/(GMA/MMA) blends

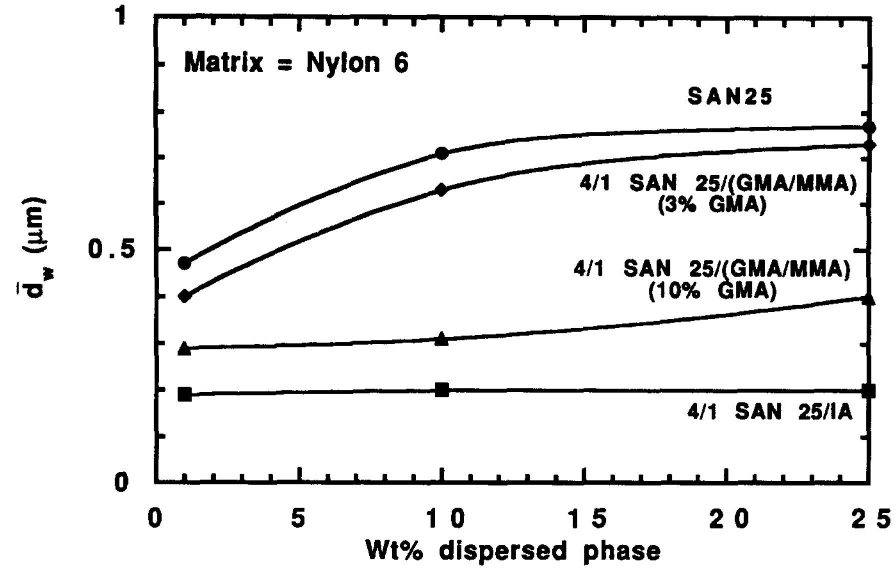


Figure 3 Dispersed phase domain size *versus* weight per cent of dispersed phase for an uncompatibilized nylon 6/SAN25 blend and nylon 6/SAN25 blends containing various compatibilizers. The compatibilized blends have a 4/1 ratio of SAN25/compatibilizer

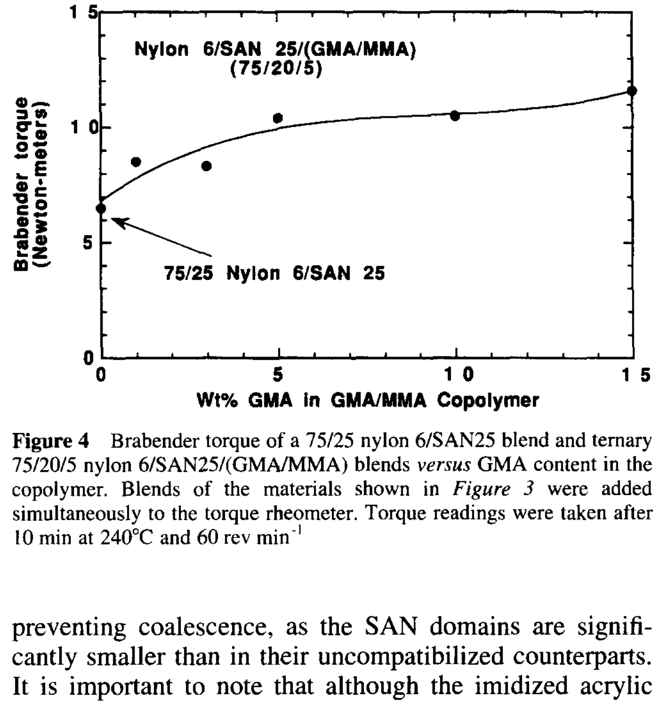


Figure 4 Brabender torque of a 75/25 nylon 6/SAN25 blend and ternary 75/20/5 nylon 6/SAN25/(GMA/MMA) blends *versus* GMA content in the copolymer. Blends of the materials shown in *Figure 3* were added simultaneously to the torque rheometer. Torque readings were taken after 10 min at 240°C and 60 rev $\min^{-1}$

preventing coalescence, as the SAN domains are significantly smaller than in their uncompatibilized counterparts. It is important to note that although the imidized acrylic contains approximately 2 mol% of an anhydride functionality, it suppresses coalescence more effectively than the GMA copolymers with a much higher degree (10 wt.%, or 7 mol%) of functionality, which suggests that anhydride-based compatibilizers are more effective in morphology stabilization than the epoxide-based compatibilizer used here. Blends containing 3 wt.% GMA in the GMA/MMA copolymer have a minimal influence on steric stabilization and contain larger domains than corresponding blends containing 10 wt.% GMA in the copolymer. It is evident that stabilization against coalescence does play a significant role in the reduction of SAN particle size with increasing GMA content.

Qualitatively, similar morphological changes could also stem from rheological effects even when the compatibilizer resides within the polyamide matrix rather than at the interface with SAN. The latter may occur if other forces remove the copolymer from the interface. It has been proposed that a high degree of reaction of a compatibilizer could result in a molecular structure that is no longer miscible with SAN[48]. In this case, the compatibilizer could form highly grafted micellar aggregates in the bulk polyamide phase, which will increase the viscosity of the polyamide matrix. This could in turn reduce the dispersed phase dimensions by transmitting a greater effective shear stress on the SAN particles during melt processing.

Brabender torque rheometry was used to assess the degree of grafting that occurs in this system during melt blending. *Figure 4* shows the torque after 10 min of mixing at 240°C as a function of GMA content in the copolymer for the series of blends shown in *Figure 3*. There is an increase in torque as the GMA content is increased, which is consistent with the formation of graft copolymers during melt mixing. As mentioned earlier, the reacting copolymer could reside at the polyamide/SAN interface or as micelles in the polyamide matrix away from this interface, or in both regions. The coalescence data shown in *Figure 3* indicate that a significant amount of grafting occurs at the polyamide/SAN interface when GMA copolymers having higher GMA contents are incorporated.

EFFECT OF GMA/MMA COMPATIBILIZER ON NYLON 6/ABS MORPHOLOGY AND MECHANICAL PROPERTIES

The influence of compatibilizer functionality and content on the impact properties of nylon 6/ABS blends was explored. *Figure 5* shows a plot of Izod impact strength *versus* temperature for nylon 6/ABS blends containing 5 wt.% compatibilizer with varying amounts of GMA; a binary, or uncompatibilized, nylon 6/ABS blend is shown for comparison. All blends contained a 1/1 ratio of nylon 6 to ABS by weight. The ductile–brittle transition of the uncompatibilized binary blend is approximately 50°C, near the T_g of nylon 6. Incorporation of the copolymer containing 3% GMA appears to make the impact properties somewhat worse. When the GMA content is increased to 5 or 10%, there is a modest improvement in the impact properties relative to the binary nylon 6/ABS blend. However, each of these blends has poor room-temperature impact toughness. Interestingly, the impact properties of the

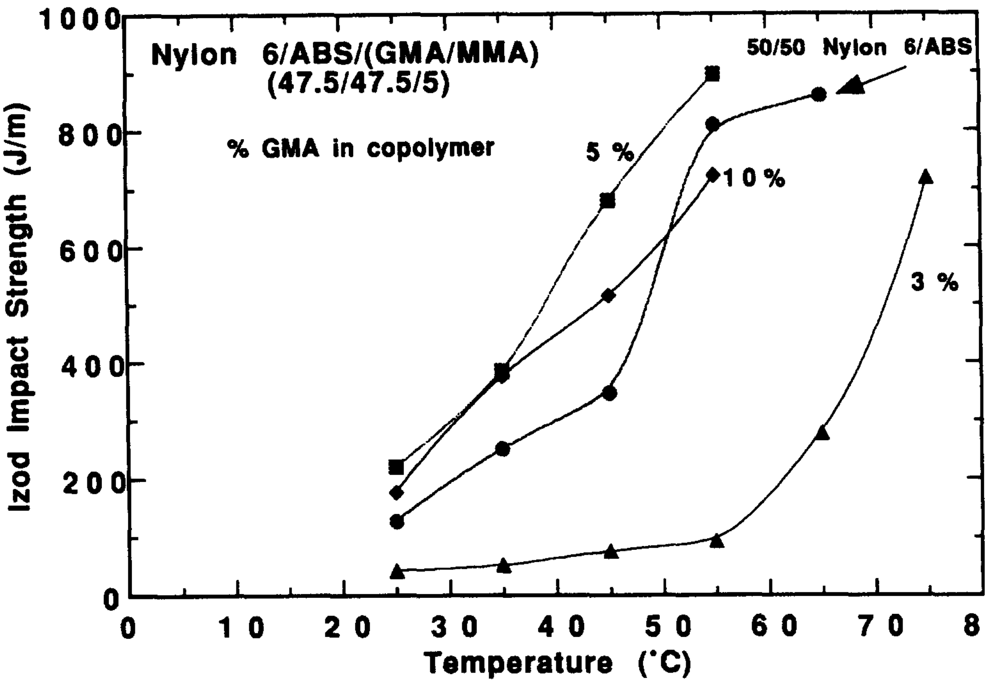


Figure 5 Effect of temperature on the Izod impact strength of a 50/50 nylon 6/ABS blend and ternary 47.5/47.5/5 nylon 6/ABS/(GMA/MMA) blends containing varying amounts of GMA in the copolymer

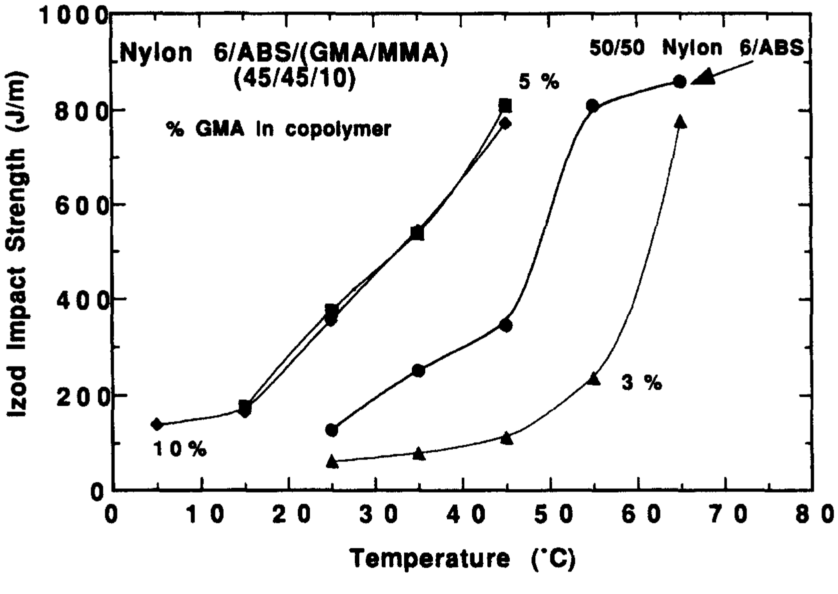


Figure 6 Effect of temperature on the Izod impact strength of a 50/50 nylon 6/ABS blend and ternary 45/45/10 nylon 6/ABS/(GMA/MMA) blends containing varying amounts of GMA in the copolymer

compatibilized nylon 6/ABS blends improve markedly at the same critical composition at which the SAN domain size is reduced (see *Figure 3*). Previous work in our laboratories has demonstrated a similar correlation between the ductile–brittle transition of compatibilized nylon 6/ABS blends and the dispersed phase domain size of their nylon 6/SAN analogues[42].

Figure 6 shows a similar plot of Izod impact strength *versus* temperature for nylon 6/ABS blends containing 10 wt.% of the GMA/MMA copolymer. Similar to *Figure 5*, incorporation of 3% GMA in the copolymer reduces the impact strength at a given temperature, whereas an improvement in impact properties is observed when the GMA content is increased to 5 or 10%. A comparison of *Figures 5 and 6* indicates that higher levels of the compatibilizer do improve the impact properties of these blends; however, all blends have poor low-temperature toughness and fail in a brittle manner at subambient temperatures.

Figures 7 and 8 show TEM photomicrographs of the blends described in *Figures 5 and 6*, respectively. In each of these photomicrographs, phosphotungstic acid was used to stain the polyamide phase. The binary nylon 6/ABS blend (*Figure 7a*) contains elongated ABS domains which have some degree of co-continuity. When the GMA/MMA compatibilizer is incorporated, the co-continuity of the ABS domains appears to become disrupted. The presence of the compatibilizer appears to restructure the ABS domains into two populations: large agglomerates and small domains. The ABS clusters appear to become larger as the

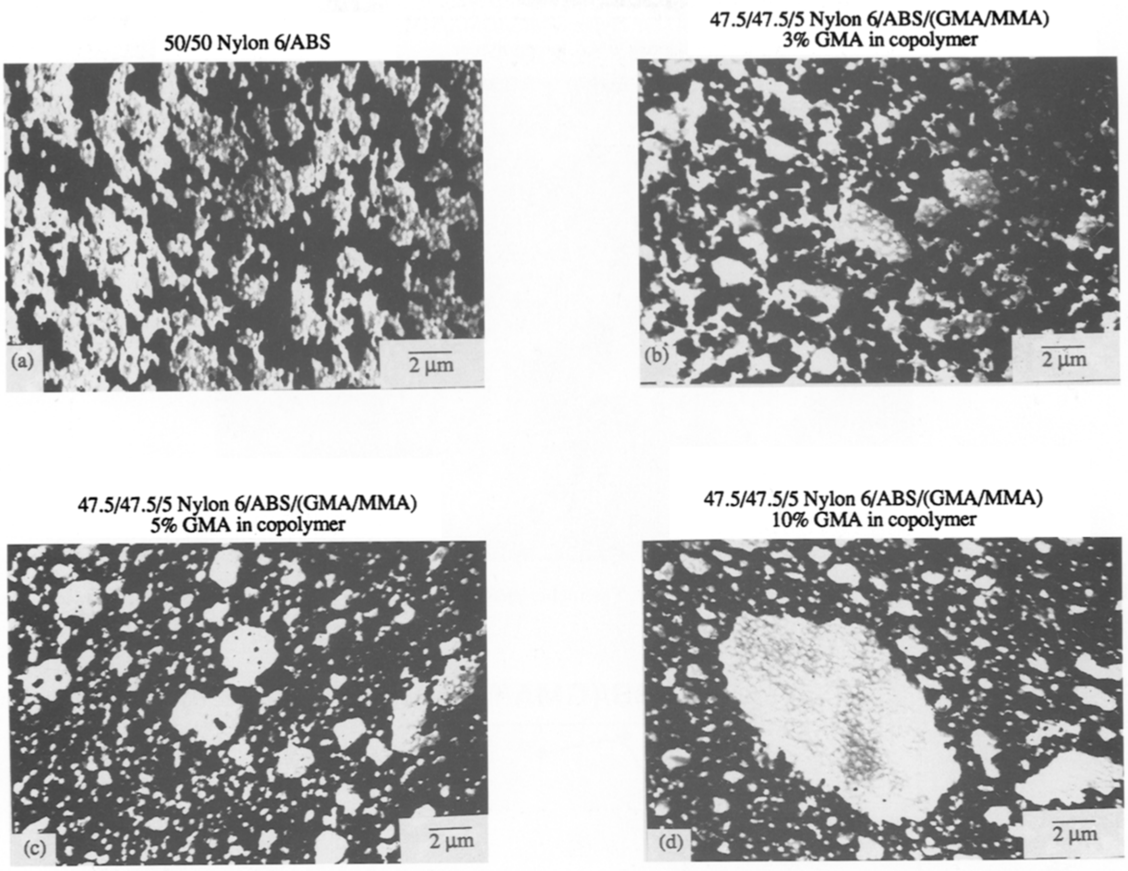


Figure 7 TEM photomicrographs of (a) a 50/50 nylon 6/ABS blend and 47.5/47.5/5 nylon 6/ABS/(GMA/MMA) blends containing (b) 3%, (c) 5% and (d) 10% GMA in the copolymer. The polyamide phase has been stained with PTA

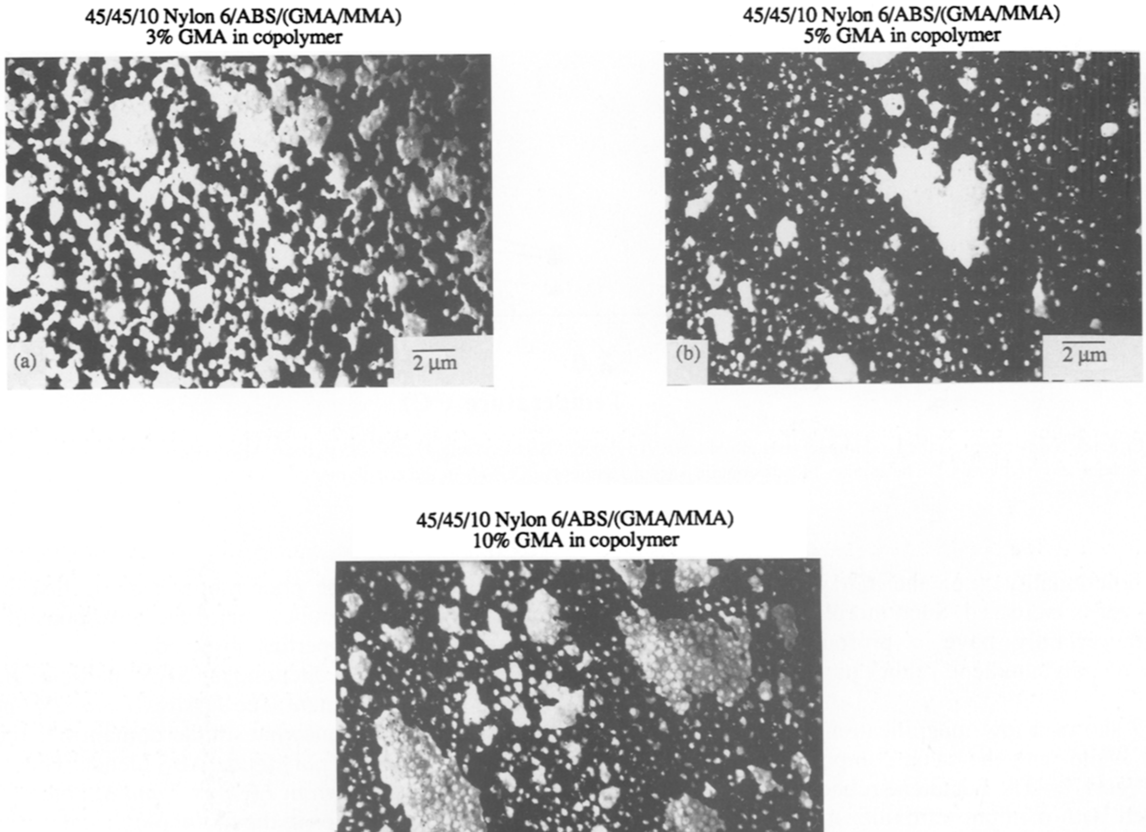


Figure 8 TEM photomicrographs of 45/45/10 nylon 6/ABS/(GMA/MMA) blends containing (a) 3%, (b) 5% and (c) 10% GMA in the copolymer. The polyamide phase has been stained with PTA

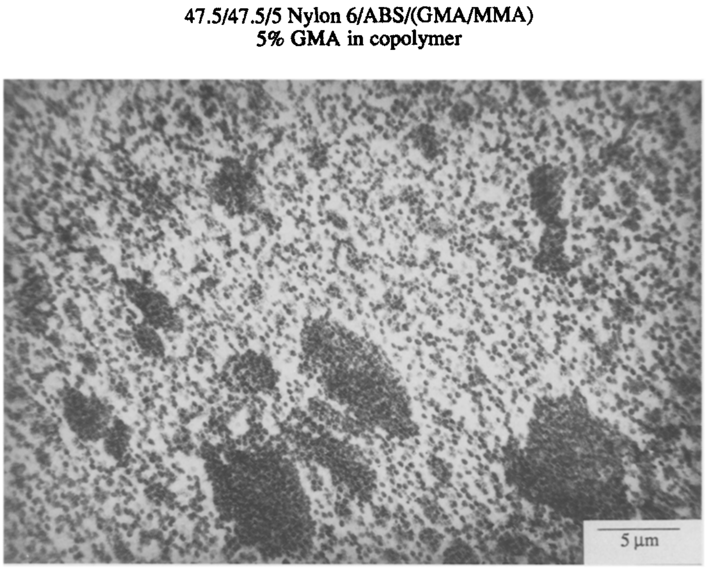


Figure 9 GMA/MMA blend containing 5% GMA in the copolymer. The rubber phase of ABS has been stained with osmium tetroxide (OsO_4)

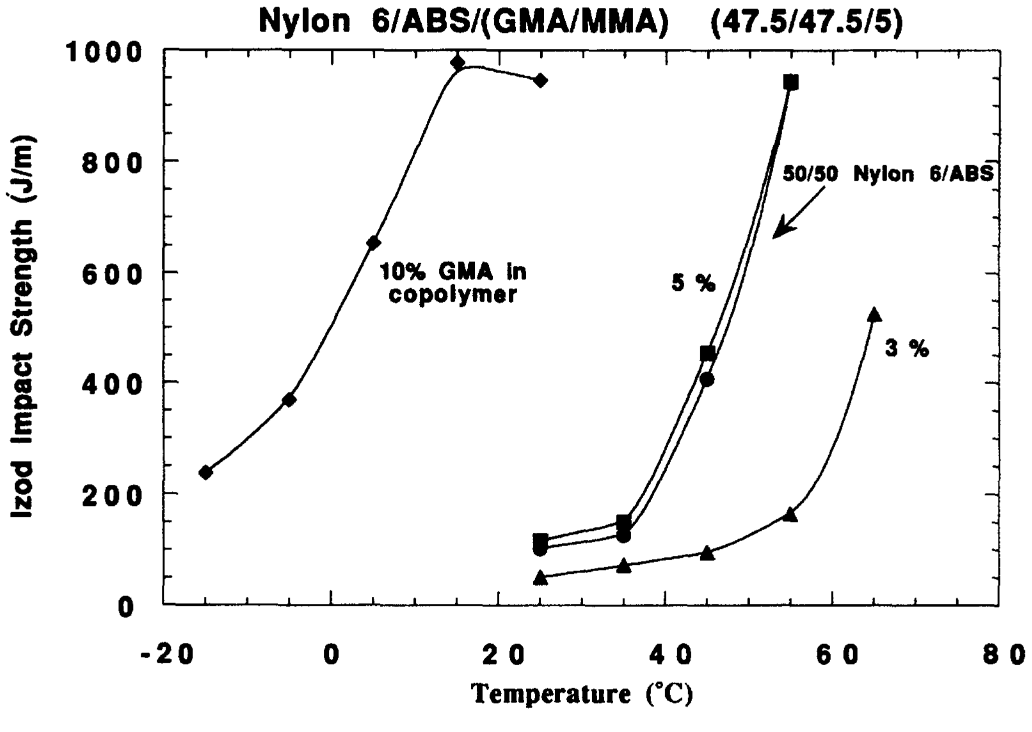
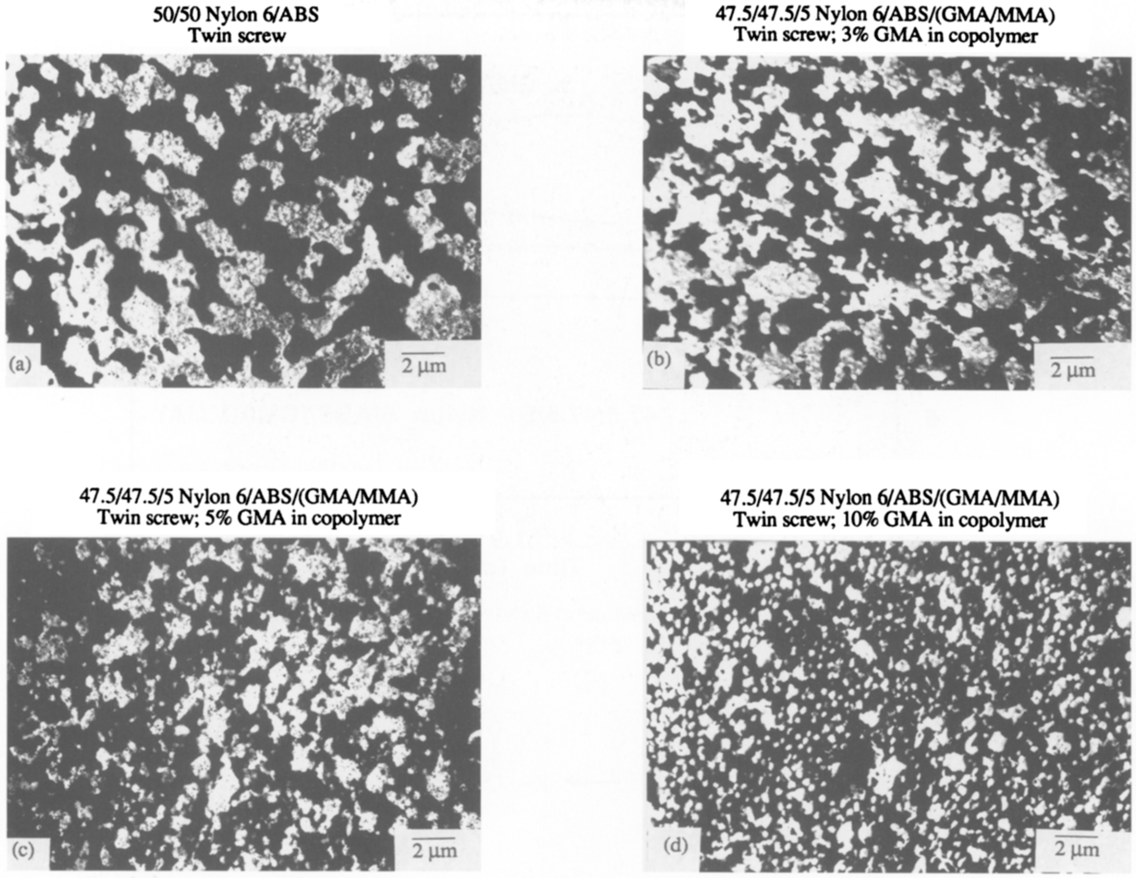


Figure 10 Effect of temperature on the Izod impact strength of a 50/50 nylon 6/ABS blend and 47.5/47.5/5 nylon 6/ABS/(GMA/MMA) blends processed in a twin screw extruder at 170 rev min^{-1}. The ternary blends contain varying amounts of GMA in the copolymer

level of functionality (i.e. the GMA content) of the compatibilizer is increased. Such morphological rearrangements will certainly have a profound effect on the uniformity of polybutadiene rubber particle distribution in the blend.

Figure 9 shows a low magnification TEM photomicrograph of a blend with the same composition as the blend shown in *Figure 7c*. The butadiene rubber phase of ABS has been stained with osmium tetroxide. It is evident that the rubber particles are not evenly distributed throughout the material due to the large ABS domains. In certain regions the rubber particles exist as large clusters, whereas other areas contain a sparse number of particles. Well-dispersed rubber particles are essential for the successful toughening of polyamides[83]. The poor rubber particle distribution in these blends is no doubt a major factor responsible for the poor mechanical properties observed.

Based on the reduction in SAN particle size with increasing GMA content (see *Figures 1 and 2*), one would expect to observe somewhat similar domain size reductions in the corresponding polyamide/ABS blends. This is clearly not the case, as shown in *Figures 7 and 8*. Potential causes for these discrepancies in the morphological behaviour may stem from differences in the rheological and viscoelastic nature of the ABS *versus* SAN materials. As shown in *Table 1*, the ABS has a Brabender torque that is more than three times that of the SAN25 material. In addition, the incorporation of a rubber phase into SAN imparts some


50/50 Nylon 6/ABS
Twin screw

47.5/47.5/5 Nylon 6/ABS/(GMA/MMA)
Twin screw; 3% GMA in copolymer

47.5/47.5/5 Nylon 6/ABS/(GMA/MMA)
Twin screw; 5% GMA in copolymer

47.5/47.5/5 Nylon 6/ABS/(GMA/MMA)
Twin screw; 10% GMA in copolymer

Figure 11 TEM photomicrographs of blends processed in a twin screw extruder: (a) a 50/50 nylon 6/ABS blend and 47.5/47.5/5 nylon 6/ABS/(GMA/MMA) blends containing (b) 3%, (c) 5% or (d) 10% GMA in the copolymer. The polyamide phase has been stained with PTA

additional degree of melt elasticity to the polymer[84]. One can envisage both of these factors causing the ABS domains to be more difficult to disperse than their SAN counterparts.

The more intensive mixing provided by a co-rotating twin screw extruder compared with the single screw used to prepare the above blends should promote a greater reduction in the dispersed phase domain size and improved mechanical properties. *Figure 10* shows how the Izod impact strength varies with temperature for blends prepared in such a co-rotating twin screw extruder operated at 170 rev min^{-1}. Surprisingly, the incorporation of a low degree of functionality appears to have a harmful effect on the impact properties even in this case. As the GMA content in the copolymer is increased, the impact strength improves at a given temperature. The blend containing 10% GMA in the copolymer is in the supertough range (above 800 J m^{-1}) at room temperature, and remains tough as the temperature drops into the subzero range. This is comparable to results obtained by Majumdar *et al.* using the same ABS and nylon 6 materials, plus 10 wt.% of an imidized acrylic compatibilizer[42]. This blend was also supertough at room temperature but had a ductile/brittle transition temperature about 15°C lower than that found here.

Figure 11 shows how the morphology changes within this series of blends processed in the twin screw extruder. Phosphotungstic acid was used to stain the polyamide phase. The uncompatibilized blend (*Figure 11a*) contains clusters of somewhat continuous ABS domains. When 3 or 5% GMA is incorporated in the compatibilizer, there is still some degree of clustering; these blends do not seem to have significantly different impact properties than corresponding blends made in the single screw extruder. When the GMA content is increased to 10%, the ABS domains appear to become more efficiently dispersed. *Figure 10* demonstrates that this improvement in dispersion is accompanied by a dramatic increase in the room temperature (25°C) impact strength. Based on these results, it appears that the mechanical properties can be improved only in limited cases by the more intensive shearing conditions imposed by the twin screw extruder.

The inability to produce well-dispersed ABS domains in nylon 6 to give a high level of toughness using the GMA/MMA copolymer is reminiscent of earlier attempts to compatibilize nylon 6,6/ABS blends using a compatibilizer containing anhydride functionality. It is well documented that the difunctionality of nylon 6,6 (some chains have two amine end groups) *versus* the monofunctionality of the current nylon 6 (one amine and one acid end group per chain) leads to cross-linking-type effects that make it very difficult to achieve good dispersion in such cases[46]. We propose that the current response is due to the fact that both the amine and the acid end groups of the nylon 6 can react with the epoxide rings, *i.e.* this nylon 6 is difunctional with respect to reaction with the GMA/MMA compatibilizer. This is explored in the next section.

TORQUE RHEOMETRY AND REACTION MECHANISMS

Figure 12 shows the Brabender torque *versus* time for the uncompatibilized binary nylon 6/ABS blend and various ternary blends containing varying amounts of GMA in the compatibilizer. After an initial fluxing period, each of the blends reached a relatively constant torque value. It is

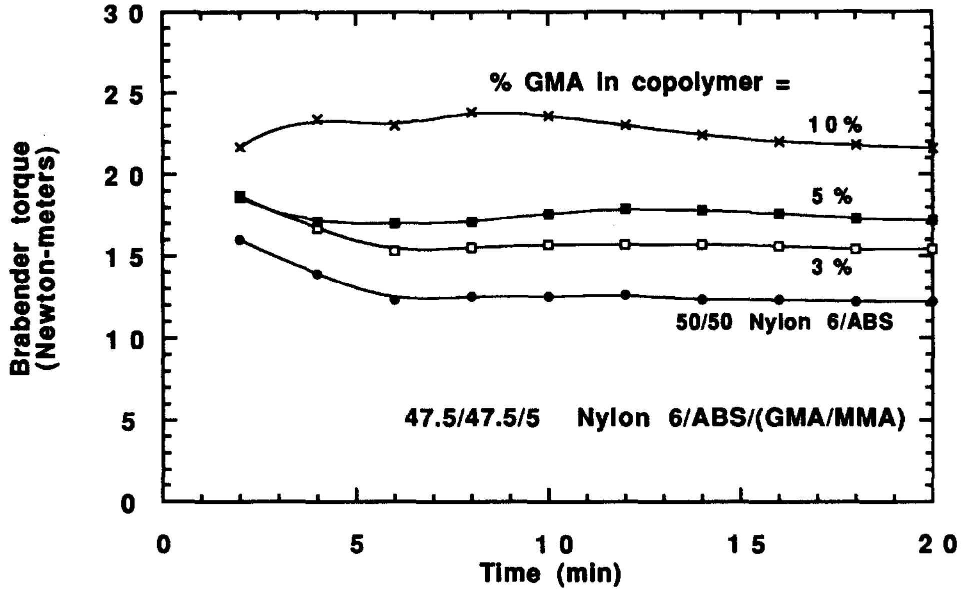


Figure 12 Brabender torque *versus* time for a 50/50 nylon 6/ABS blend and 47.5/47.5/5 nylon 6/ABS/(GMA/MMA) blends containing varying amounts of GMA in the copolymer. Torque readings were taken at 240°C and 60 rev min^{-1}

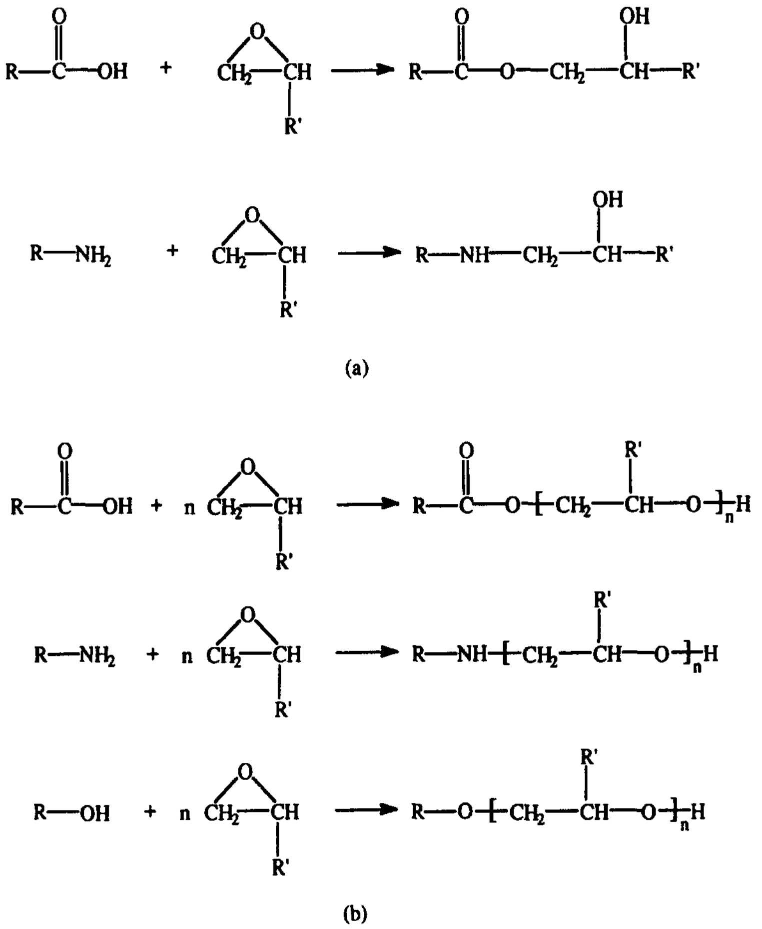


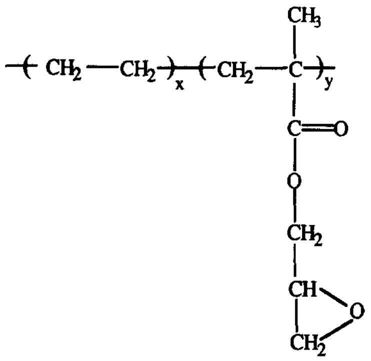
Figure 13 (a) Reactions of the epoxide ring with acid and amine end groups. (b) Polymerization of epoxide initiated by acid, amine, and hydroxyl groups

evident that the melt viscosity increases due to the incorporation of the compatibilizer, which indicates that some degree of grafting occurs during melt blending. The torque values consistently increase with increasing GMA content in the copolymer.

As postulated earlier, reaction of the epoxide ring of GMA with both the acid and amine end groups of nylon 6 may be a significant factor in the morphology development in these ternary blends. Previous studies have demonstrated that both amines[53,85-89] and carboxylic acids[89,90] are capable of reacting with epoxide groups. The kinetics of the reaction of epoxide rings with amine and with acid

$H_2N(CH_2)_{13}CH_3$	$HOOC(CH_2)_{15}CH_3$
1-tetradecylamine **("monoamine")**	**heptadecanoic acid** **("monoacid")**
$H_2N(CH_2)_{12}NH_2$	$HOOC(CH_2)_{10}COOH$
dodecamethylene diamine **("diamine")**	**1,10 decanedicarboxylic acid** **("diacid")**

(a)



(b)

Figure 14 (a) Low molecular weight compounds used to model the end groups of nylon 6. (b) 94/6 Ethylene/glycidyl methacrylate (EGMA) copolymer

groups under the melt processing conditions used here can be judged through Brabender torque rheometry using compounds which model the nylon 6 end groups. *Figure 13a* shows potential reactions between acid and amine end groups and the epoxide ring of GMA. The epoxide group itself can also undergo a ring-opening polymerization in the presence of an acid, amine, or alcohol end group, as shown in *Figure 13b*[86,90].

The compounds shown in *Figure 14a*, obtained from Aldrich Chemical Co., were used to model the end groups of nylon 6. These materials were chosen based on their aliphatic character and their thermal stability at the processing temperatures. A 94/6 ethylene/glycidyl methacrylate copolymer (EGMA), shown in *Figure 14b*, was used as the matrix. The EGMA material was used instead of the GMA/MMA copolymer to avoid synthesizing the large amounts of the copolymer that would be required for these experiments. Each of the compounds in *Figure 14a* was melt mixed with EGMA in the Brabender and the torque response was monitored. Cross-linking effects induced by reaction of these model compounds with EGMA should be observable by a rapid increase in viscosity, or Brabender torque.

Based on the reaction paths shown in *Figure 15*, melt blending EGMA with the monofunctional amine compound would result in a ring-opening reaction, forming a structure containing a secondary amine. The reaction with the monoacid compound would be expected to generate an ester. If the amine end group reacts readily with the epoxide, one can expect the reaction between the diamine and EGMA

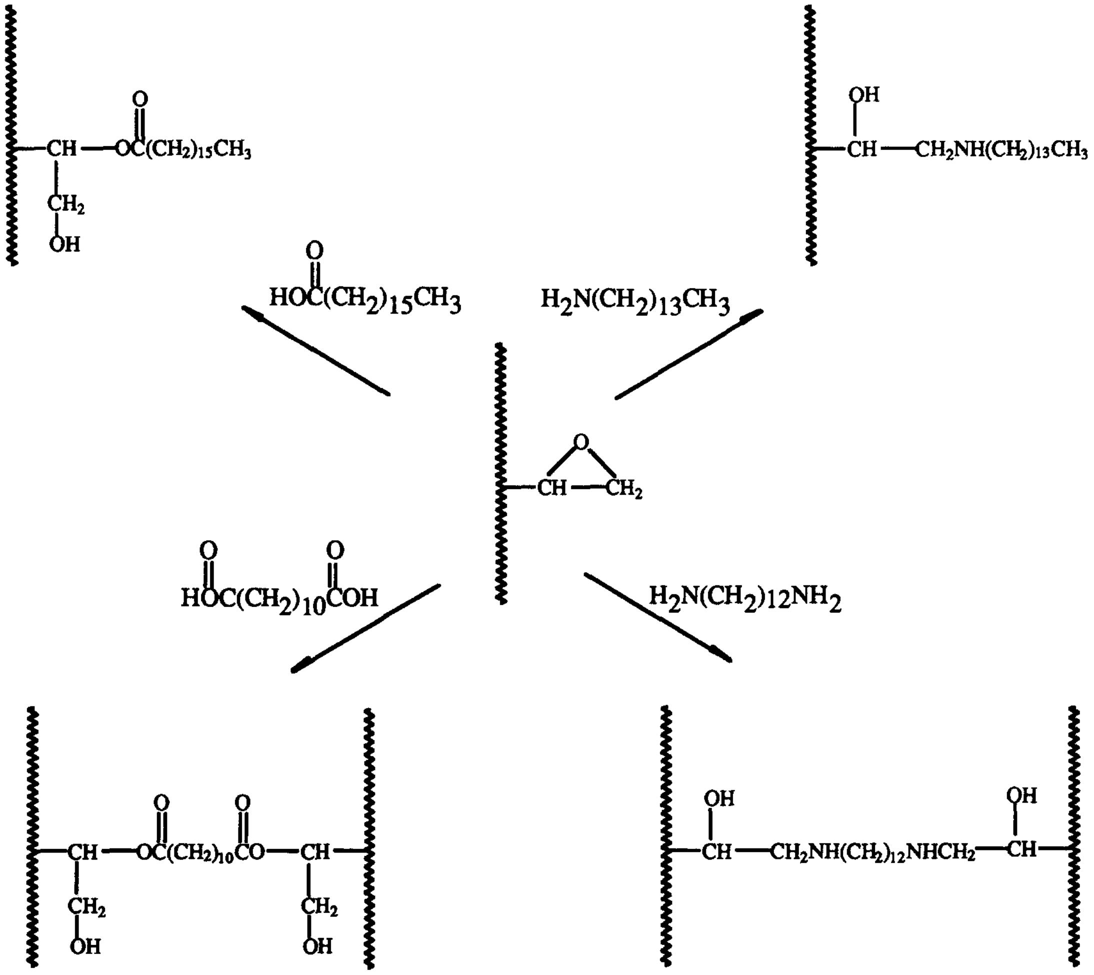


Figure 15 Potential reactions between EGMA and low molecular weight model compounds

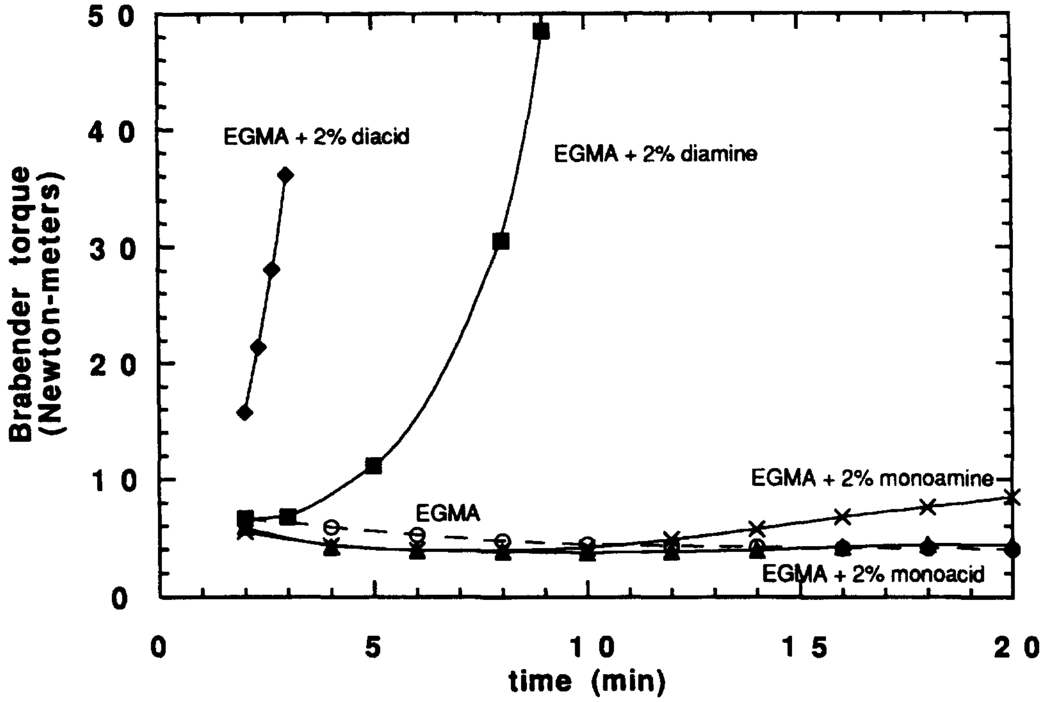


Figure 16 Brabender torque *versus* time for EGMA and EGMA melt blended with 2% of the model compounds. Torque readings were taken at 240°C and 60 rev min^{-1}

to result in cross-linked structures; the same situation applies for the reaction between the diacid and EGMA. In all of these cases, cross-linking or epoxide polymerization could also occur via the hydroxyl functionalities generated by amine/epoxide and acid/epoxide ring-opening reactions. The key difference between these model compounds is that the difunctional species can promote cross-linking through two-point amine or acid end group attachments, whereas the monofunctional compounds cannot. Secondary amines generated by the reaction between EGMA and the monofunctional amine could potentially induce further polymerization and/or cross-linking through reactions with another epoxide ring. However, it will be demonstrated that this effect is not significant.

Figure 16 shows the Brabender torque response *versus* time for EGMA and its mixtures with 2 wt.% of the model compounds. It is evident that incorporating the monoacid has an insignificant effect on the melt viscosity of the blend. This suggests that cross-linking or epoxide polymerization through the hydroxyl group itself does not play a significant role in these reactions. After some time, there is an increase in the torque of the blend of EGMA with the monoamine, which implies that there may be some degree of reaction between the epoxide ring and the secondary amine that is generated. However, these torque increases are not of a great magnitude and do not occur until a significant amount of time has elapsed. Thus, it appears that the kinetics of the secondary amine/epoxide reaction are quite slow relative to the time scale of reactive processing.

It is obvious that incorporation of both the diamine and diacid result in rapid increases in torque well above the level of EGMA itself. These viscosity increases are no doubt due to the formation of the cross-linked structures suggested in *Figure 15*. Since these reactions do not occur to a significant extent through the hydroxyl moieties, it appears that these increases in torque are caused by cross-linking through the acid and amine groups, respectively. This cross-linking behaviour would suggest that both acid and amine end groups are both quite reactive with the epoxide ring of GMA. Since this plot indicates that the increase in torque of the EGMA/diacid reaction is more rapid than that of the EGMA/diamine reaction, one could construe that the epoxide/acid reaction is faster. However, it is important to note that in both of these reactions, there appeared to be a slight degree of volatilization of the model compounds upon addition to the melt mixer. In addition, these experiments were halted at an early time, since the torques were approaching the limits of the mixer. In light of this, one must interpret the relative kinetics of the amine/epoxide *versus* the acid/epoxide reaction with caution. However, it is evident that both the acid and the amine end groups are capable of reacting extensively with the epoxide ring of GMA during melt processing.

Figure 17 shows a simplified schematic of the reactions that can occur between nylon 6 and the GMA/MMA copolymer during melt processing. We have shown evidence that both the amine and the acid end groups of nylon 6 react with the epoxide; the difunctional nature of the polyamide creates complex loop and bridge structures between the ABS domains. Higher degrees of epoxide functionality in the compatibilizer, i.e. higher GMA contents, result in a greater degree of these cross-linking-type effects, which are manifested in larger ABS domains. The difunctional character of nylon 6 with respect to the GMA/MMA copolymer makes it difficult to disperse the ABS domains and to toughen the blend.

CONCLUSIONS

The effect of a series of glycidyl methacrylate/methyl methacrylate (GMA/MMA) copolymers on the behaviour of nylon 6/SAN and nylon 6/ABS blends has been investigated. Incorporation of these copolymers can reduce the dispersed phase domain size of nylon 6/SAN blends if the

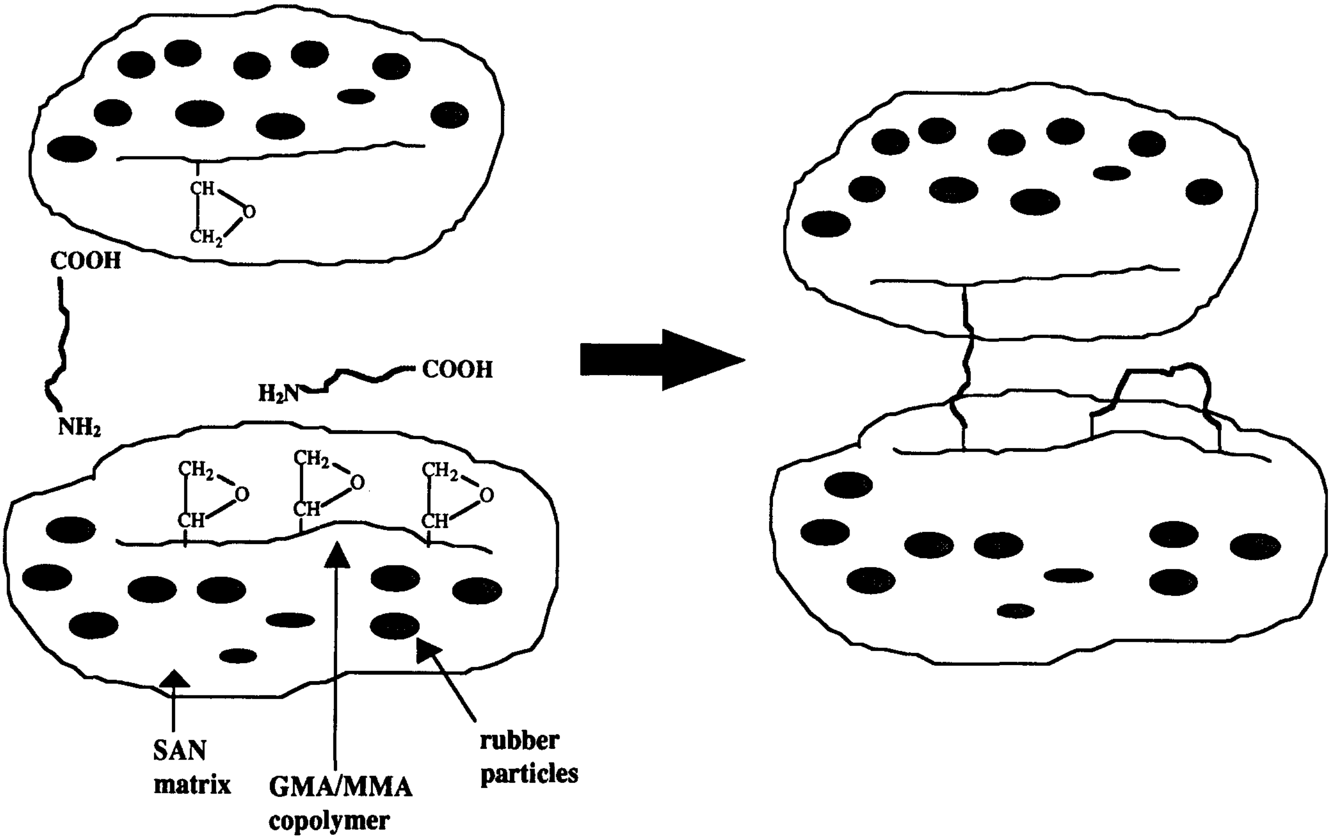


Figure 17 Schematic representation of potential reactions between nylon 6 and the GMA/MMA copolymer during the melt processing of nylon 6/ABS/(GMA/MMA) blends. Both the acid and the amine end groups of nylon may be able to react with the epoxide ring of GMA. This can result in the formation of complex loops and bridge structures which make it difficult to form well-dispersed ABS domains or can lead to their agglomeration

GMA content is above a certain level. These changes in the dispersed phase morphology stem from reactions between the nylon 6 end groups and the copolymer; this occurs to some degree by steric stabilization of the SAN domains against coalescence.

Incorporation of the copolymer generally does not promote effective toughening of nylon 6/ABS blends in a single screw extruder. At low GMA contents in the copolymer, the Izod impact strength actually becomes somewhat worse than that of a binary nylon 6/ABS blend. While there are marginal improvements in impact strength when the GMA content is increased, all blends had poor low-temperature toughness. These trends appear to be independent of the copolymer content in the blend.

The addition of GMA/MMA copolymers to nylon 6/ABS blends appears to break up the co-continuity of the ABS phase and promote the formation of two populations of ABS domains. One group of ABS domains consists of large clusters which become larger with increasing GMA content in the copolymer, while the other group consists of small ABS domains. It is clear that there are profound differences between the dispersed phase morphologies of compatibilized nylon 6/SAN and nylon 6/ABS blends. It is proposed that this stems from differences in the rheological and viscoelastic nature of the SAN and ABS material used in this study.

The morphological rearrangements in nylon 6/ABS blends caused by the incorporation of the GMA/MMA copolymer lead to a non-uniform distribution of rubber particles within the blend. The cause of the observed morphologies is the difunctional nature of nylon 6 with respect to the copolymer. Reaction of both the acid and the amine end groups of nylon 6 with the epoxide ring of GMA induces cross-linking-type effects through a two-point grafting mechanism. Experiments using torque rheometry demonstrate that these amine/epoxide and acid/epoxide reactions both occur to a significant degree.

This work emphasizes the importance of the reactive nature of the compatibilizing species on blend morphology development and toughening capacity. Two criteria established for the effective compatibilization of nylon 6/ABS blends have been the ability of the compatibilizer to react with the polyamide matrix and the ability to remain miscible with the SAN phase of ABS. In the classical view of compatibilization, one would expect these characteristics to lead to improved mechanical properties due to a decrease in the interfacial tension, stabilization against coalescence, improved interfacial adhesion, *etc.* While in some cases these characteristics of the compatibilizer may be sufficient for developing toughened nylon 6/ABS alloys, they clearly do not ensure toughness, as demonstrated in this work. In this case, the difunctional nature of the nylon 6 matrix with respect to the compatibilizer leads to a poor dispersion of rubber particles. Clearly, it is of paramount importance to understand the grafting reactions which can occur between the compatibilizing species and the blend components. These reactions can have a profound effect on the dispersed phase morphology and mechanical properties of the blend. Future papers will address other fundamental issues which affect the toughness of nylon 6/ABS blends.

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