Acrylonitrile–Butadiene–Styrene Toughened Nylon 6: The Influences of Compatibilizer on Morphology and Impact Properties

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ABSTRACT: Polymer alloys have been used as an alternative to obtain polymeric materials with unique physical properties. Generally, the polymer mixture is incompatible, which makes it necessary to use a compatibilizer to improve the interfacial adhesion. Nylon 6 (PA6) is an attractive polymer to use in engineering applications, but it has processing instability and relatively low notched impact strength. In this study, the acrylonitrile–butadiene–styrene (ABS) triblock copolymer was used as an impact modifier for PA6. Poly(methyl methacrylate-co-maleic anyhydride) (MMA-MA) and poly(methyl methacrylate-co-glycidyl methacrylate) (MMA-GMA) were used as compatibilizers for this blend. The morphology and impact strength of the blends were evaluated as a function of blend composition and the presence of compatibilizers. The blends compatibilized with maleated copolymer exhibited an impact strength up to 800 J/m and a morphology with ABS domains more efi8ciently dispersed. Moderate amounts of MA functionality in the compatibilizer (~5%) and small amounts of compatibilizer in the blend (~5%) appear sufficient to improve the impact properties and ABS dispersion. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 842–847, 2003

Key words: blends; compatibilization; toughness; nylon

INTRODUCTION

Nylon 6 (PA6) is an important engineering thermoplastic that generally requires the addition of impact modifiers to enhance its performance under impact. Blends of PA6 with different types of polymers have been produced to improve its toughness. The blend components include poly(phenylene oxide), acrylonitrile–butadiene–styrene (ABS), polyolefins, polycarbonate, ethylene-propylene-diene (EPDM) rubber, and ethylene copolymers.[1] The blend of PA6/ABS has an excellent balance of properties, as evidenced by the combination of toughness, chemical resistance, good dimensional stability, and good moldability.[2,3] Moreover, a number of coupling agents were developed to improve miscibility between these polymers that are inherently immiscible. A particularly strategy is the addition of a polymer that is miscible with the styrene–acrylonitrile (SAN) phase and that can react with the amine end groups of the nylon phase. Several works have been conducted with the PA6/ABS blend.[2,4–17] There has been much interest in the use of glycidyl methacrylate (GMA)- and maleic anhydride (MA)-based copolymers as compatibilizing agents for polymer blends. The epoxide ring of GMA is difunctional with respect to nylon 6; that is, both the acid and amine chain ends can react with GMA. The anhydrides can react only with the amine ends of PA6 chains.[14,18,19–30] The focus of this study will be to explore the use of various poly(methyl methacrylate-co-maleic anyhydride) (MMA-MA) and poly(methyl methacrylate-co-glycidyl methacrylate) (MMA-GMA) copolymers as compatibilizers of PA6/ABS blends to control the morphological, rheological, and mechanical characteristics of nylon6/ABS blends. It will be demonstrated that anhydride-based copolymers are more effective that glycidyl methacrylate-based compatibilizers in generating an optimum morphology and toughening of PA6/ABS blends.

EXPERIMENTAL

The characteristics of the materials used in this study are summarized in Table I. The nylon 6 (PA6) is a commercially available material, with $\bar{M}_n = 21{,}000$ and approximately equal concentrations of acid and amine end groups. Prior to each processing step, all nylon-containing materials were dried in a vacuum oven for at least 24 h at 80°C to remove sorbed water.

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TABLE I
Materials Used in this Study

Material	Description	Composition	Molecular Weight (g/mol)	Haake[d] Torque (Nm)	Source
Nylon 6	Ultramid B3	End-group content: NH_2 43,2 μeq g^{-1} COOH, 51,5 μeq g^{-1}	$\bar{M}_n = 21{,}000$[a]	1.07	Basf
ABS	SAN-grafted emulsion rubber	50% rubber 25% AN in SAN	$\bar{M}_n = 40{,}000$[b] $\bar{M}_w = 110{,}000$[b]	10.4	Nitriflex SA (Bayer)
MMA-GMA	Poly(methyl methacrylate-co-glycidyl methacrylate	10% GMA	$\bar{M}_n = 21{,}600$[c] $\bar{M}_w = 91{,}300$[c]		
MMA-MA	Poly(methyl methacrylate-co-maleic anhydride)	3% MA	$\bar{M}_n = 20900$[c]	0.1	Synthesized in laboratory
		5% MA	$\bar{M}_w = 40400$[c]		
		10% MA	$\bar{M}_n = 15800$[c] $\bar{M}_w = 37900$[c]	0.1	"
			$\bar{M}_n = 13100$[c] $\bar{M}_w = 26200$[c]	0.1	"

[a] Measurements taken chemical analysis of the end groups.
[b] Molecular weight of the SAN matrix grafted free, determined by gel permeation chromatography (GPC).
[c] Determined by GPC.
[d] Torque taken at 240°C and 60 rev min^{-1} after 10 min.

An emulsion-prepared ABS material was used, which contains 50 wt % rubber in the form of polydisperse particles, typically in the range 0.18–0.20 μm diameter, and a SAN matrix containing 25 wt % AN. The GMA, MMA, and MA monomers were supplied by Merck, Merck and Metacril, and Reidel-deHaen, respectively. The MMA-GMA copolymer was synthesized with 10 wt % GMA by bulk polymerization. The MMA-MA copolymer was synthesized with 3, 5, 10, and 20 wt % by solution polymerization using dimethyl sulfoxide (DMSO) as solvent. The appropriate amounts of each monomer and 2 wt % of ethyl acrylate (added to prevent unzipping of the polymer at melt processing temperatures) were premixed in a flask. 2,2′-Azobis(2-methylpropanonitrile)-AIBN was used as initiator (Alfa Aesar, A Johnson Matthey Company). The procedures for synthesizing these copolymers are described in detail elsewhere.[3,31]

The PA6/ABS blends were prepared in a corotating twin-screw extruder (B&P Process Equipment and Systems) at 230°C and 170 rpm. The blends were quenched subsequently in water, pelletized, and dried in a vacuum oven for 24 h at 80°C. Samples for Izod tests and the transmission electron microscopy (TEM) were prepared by Arburg Allrounder injection molding machine at 230°C, with a mold temperature of 50°C. Notched Izod specimens measurements were made using Ceast Resil 25 equipment. Rheological measurements were made in a Haake torque rheometer with a 50-cm^3 mixing head and standard rotors,

operated at 240°C and 60 rev min^{-1}. The phase morphologies of the blends were observed by TEM using a Philips CM 120 operating at an accelerating voltage of 120 kV. Samples were cryogenically microtomed into ultrathin sections (~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 microscope. The sections were exposed to 2% aqueous solution of phosphotungstic acid (PTA) to stain the nylon phase. In certain cases, a 2% aqueous solution of osmium tetroxide (OsO_4) was used to stain the unsaturated rubber phase in ABS.

RESULTS AND DISCUSSION

Rheological properties

The variation in torque during the mixing of PA6/MMA-GMA with 10 wt % GMA content in the copolymer is shown in Figure 1. Haake torque rheometry was used to assess the degree of grafting that occurs in these systems during melt blending. There is an increase in torque with the PA6 and GMA mixture, which is an evidence of a viscosity increase. This increase is consistent with the formation of graft copolymers during melt mixing. However, as shown in Figure 2, an increase in torque was also observed with the ABS and MMA-GMA mixture. It is possible that metal ions and other contaminants from the polymerization and recovery processes of emulsion-made ABS
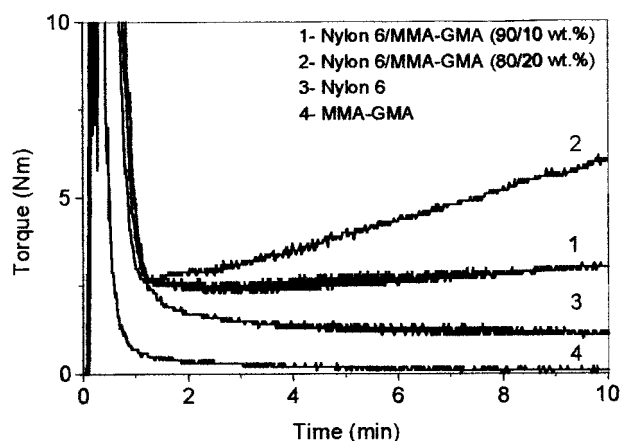
Figure 1 Haake torque of PA6/MMA-GMA mixtures versus time (fluxing temperature was 240°C).
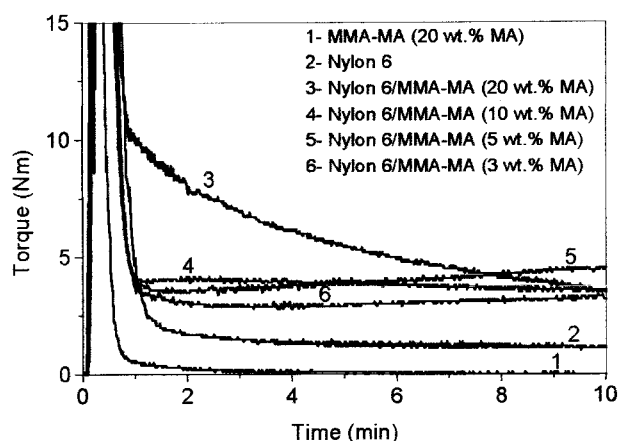

Figure 3 Haake torque of PA6/MMA-MA mixtures (90/10 wt %) versus time (fluxing temperature was 240°C).

materials have an influence on the reactions with epoxides.[26] On the other hand, various cross-linking-type effects may occur with difunctional molecules as PA6. The torque after 10 min of mixing for various MA contents in the copolymer is shown in Figure 3. With 10 % copolymer in the mixture, there is an increase in torque in relatively short times (~1 min) that continue to increase with increasing MA content in the copolymer. This result is evidence of graft reactions of the end groups of PA6 with MA. The results shown in Figure 4 suggest that there is no reaction with ABS because the final torque is intermediate among the two pure polymers and it decreases when the copolymer quantity increases. This result is evidence that only a mixing process is taking place and that the anhydride can react only with the amine ends of nylon chains. This type of copolymer seem to be ideal for reactions of compatibilization because it can react only with one phase and be miscible with the other phase that is located at the interface among the two phases.
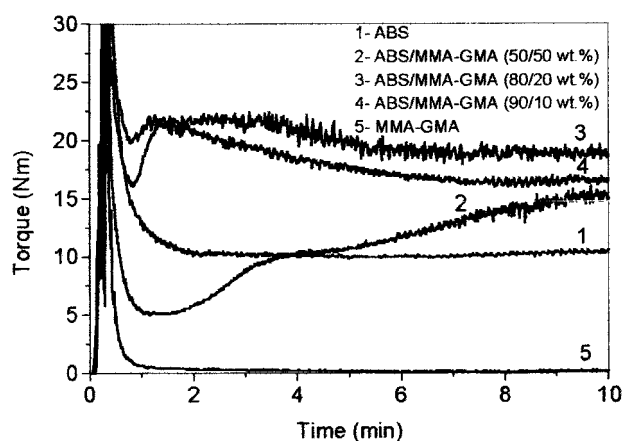
Mechanical properties

The influence of the compatibilizer functionality and content on the impact properties of nylon 6/ABS blends was investigated. The notched Izod impact strengths of pure materials and of the blends are shown in Figure 5. Impact strength increased slightly in the presence of ABS. When the MMA-GMA compatibilizer is incorporated, there is a modest improvement in the impact strength of the blend relative to the binary PA6/ABS blend. Interestingly, the impact properties of the compatibilized nylon 6/ABS blends with MMA-MA copolymer improved markedly. A plot of Izod impact strength of the nylon 6/ABS blend versus weight fraction of MA in the MMA-MA copolymer is given in Figure 6. Incorporation of 5% copolymer is sufficient to toughen the blend, and with only 3% MA in the copolymer, there is a significant improvement in impact strength (>800 J/m). As shown by the rheological studies, it is not necessary to add large quantities of anhydride because there is not
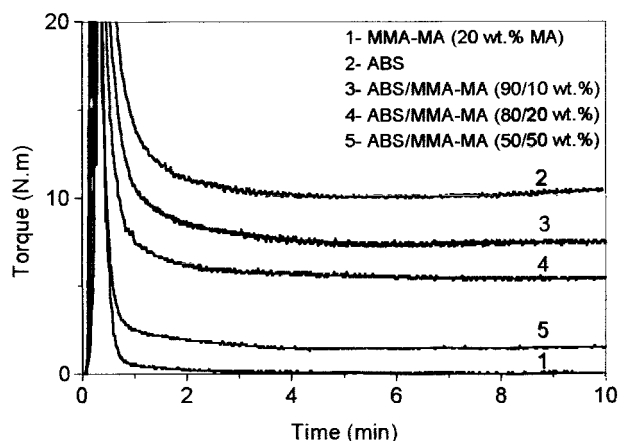

Figure 2 Haake torque of ABS/MMA-GMA mixtures versus time (fluxing temperature was 240°C).

Figure 4 Haake torque of ABS/MMA-MA mixtures versus time (fluxing temperature was 240°C).
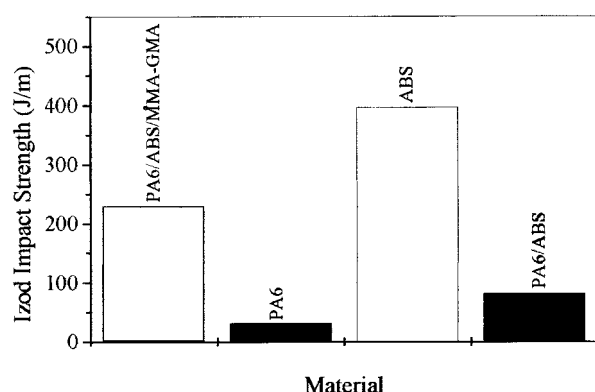
Figure 5 Notched Izod impact strength of PA6, ABS, binary 50/50 PA6/ABS blend, and ternary 47, 5/47, 5/5 PA6/MMA-GMA blend.

enough amine end groups in the PA6 to react. According to Kudva et al.,[21] very small quantities of MA are enough to produce super-tough blends de PA6/PE and to reduce the disperse phase domain size.

Morphology

The TEM photographs of binary PA6/ABS and ternary PA6/ABS blends with MMA-GMA and MMA-MA copolymers are shown in Figure 7. Dark regions in Figure 7b–e represent the PA6 phase that has been stained with PTA. Dark regions in Figure 7a represent the unsaturated rubber phase in ABS that has been stained with OsO_4. The photographs in Figure 7 give an important information about the compatibilizer effect on the mechanical properties described before. The binary blend and compatibilized blend with GMA contain elongated ABS domains with some degree of co-continuity (Figures 7a and b). Apparently, the large agglomerates of ABS in the blend become disrupted. However, there is a tendency toward co-continuity with large clusters and small ABS domains . The poor rubber particle distribution in these blends is without doubt a major factor responsible for the poor mechanical properties observed. In Figure 7c, the ABS dispersed phase forms uniformly diminished particles in the PA6 matrix. When the MA content is increased to 5 and 10%, the ABS domains become clearly more efficiently dispersed. The morphology of other compatibilized blends with MA are shown in Figures 7d and 7e. The presence of the MMA-MA compatibilizer appears to restructure the ABS domains. The compatibilized blend with MA presents a significant increase in the mechanical properties under impact compared with the GMA blend. The inability to produce well-dispersed ABS domains in PA6 and hence to improve the toughness using MMA-GMA copolymer can be compared with the attempts to compatibilize nylon

6,6/ABS blends. The difunctionality of nylon 6,6 relative to the monofunctionality of the PA6 can lead to cross-linking-type effects, making it very difficult to achieve good dispersion. Both the amine and the acid end groups of the PA6 can react with the epoxide rings of the MMA-GMA copolymer, whereas only the amine end groups of the PA6 can react with the anhydride. The PA6 in this case is difunctional with respect to reaction with the MMA-GMA compatibilizer. Well-dispersed rubber particles are essential for the successful toughening of nylons. The PA6/ABS/MMA-MA blend (Figures 7c and 7e) is supertough (>800 Jm^{-1}) at room temperature, and remains tough as the temperature drops into the subzero range.

CONCLUSIONS

The effect of the MMA-GMA and MMA-MA copolymers on the behavior of PA6/ABS blends has been investigated. Incorporation of the MMA-GMA copolymer as a compatibilizing agent did not promote effective toughening of PA6/ABS. Probably, the cross-linking-type reactions of this copolymer with both the acid and the amine groups of PA6 and ABS hindered the domains dispersion of ABS in PA6. The addition of MMA-MA copolymer to PA6/ABS blends significantly improved the impact properties. Mechanical properties were improved by the better interaction between two phases, made possible by the presence of MMA-MA compatibilizer. These results are evidence that the MMA-MA copolymer is an efficient alternative for reactive compatibilizing to the PA6/ABS system.
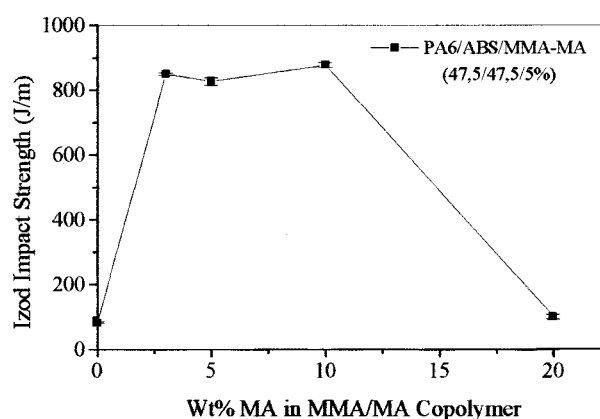
Figure 6 Notched Izod impact strength of binary 50/50 PA6/ABS blend and ternary 47, 5/47, 5/5 PA6/MMA-MA blend.

(a) PA6/ABS (50/50 %)

(b) PA6/ABS/MMA-GMA (10% GMA)

(c) PA6/ABS/MMA-MA (3% MA)

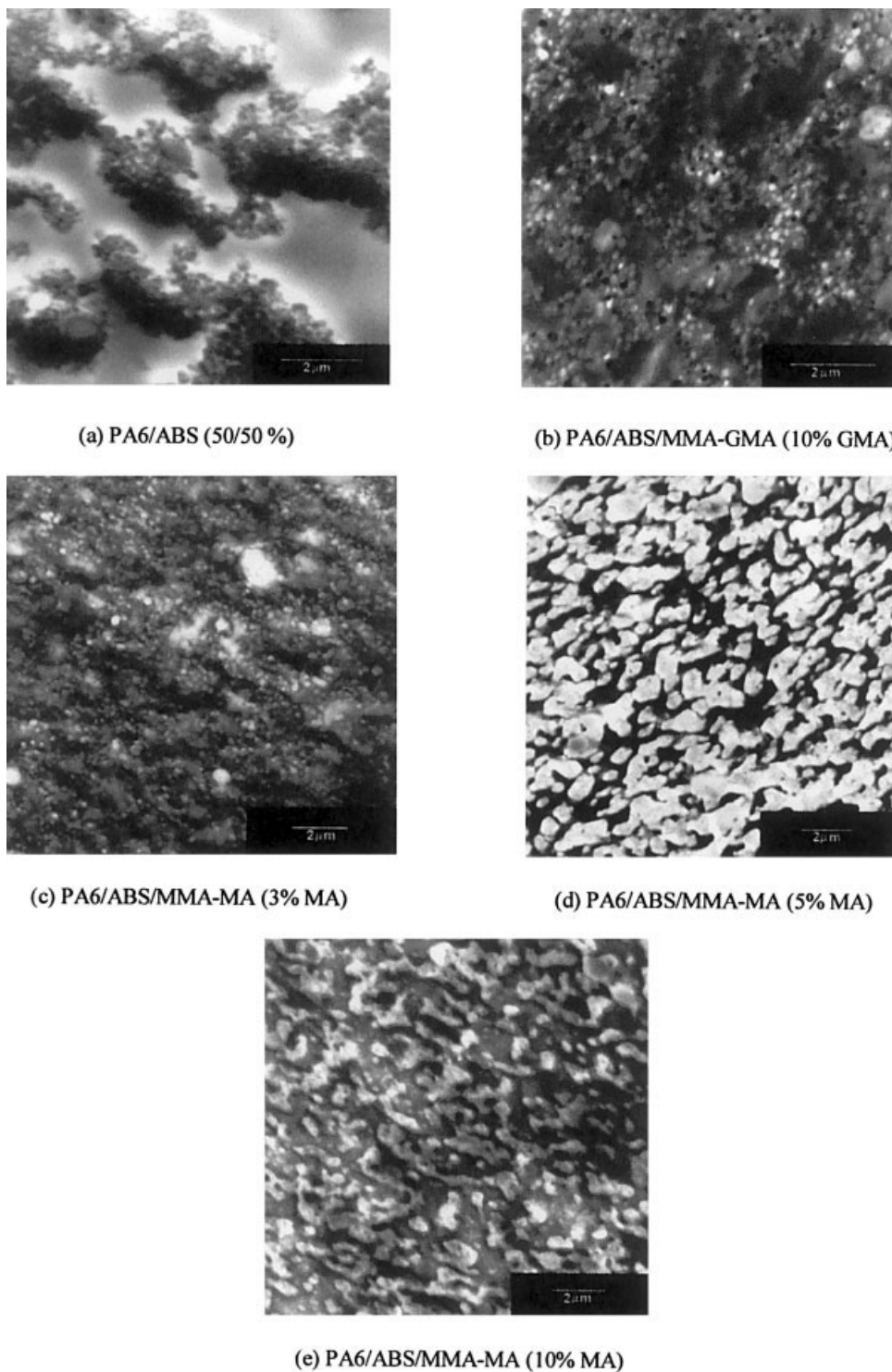(d) PA6/ABS/MMA-MA (5% MA)

(e) PA6/ABS/MMA-MA (10% MA)

Figure 7 TEM photomicrographs of blends: (a) 50/50 PA6/ABS blend; (b) 47, 5/47, 5/5% PA6/ABS/MMA-GMA blend with 10% GMA in the copolymer and 47, 5/47, 5/5% PA6/ABS/MMA-MA blends containing (c) 3% MA, (d) 5% MA and (e) 10% MA in the copolymer. The polyamide phase was stained with PTA in Figures 7b–e. The unsaturated rubber phase in ABS was stained with OsO_4 (Figure 7a).

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