Morphology of Nylon 6/Acrylonitrile–Butadiene–Styrene Blends Compatibilized by a Methyl Methacrylate/Maleic Anhydride Copolymer

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ABSTRACT: The morphologies of nylon 6/acrylonitrile–butadiene–styrene blends compatibilized with a methyl methacrylate/maleic anhydride copolymer, with 3–20 wt % maleic anhydride, were examined by transmission electron microscopy. Some staining techniques were employed for identifying the various phases. The binary blends were immiscible and exhibited poor mechanical properties that stemmed from the unfavorable interactions among their molecular segments. This produced an unstable and coarse phase morphology and weak interfaces among the phases in the solid state. The presence of the copolymer in the blends clearly led to a more efficient dispersion of the acrylonitrile–butadiene–styrene phase and consequently optimized Izod impact properties. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3512–3518, 2003

Key words: nylon; blends; compatibilization; morphology

INTRODUCTION

Multiphase polymer systems offer several advantages because of the combination of the attractive properties of their components and the improvement of the deficiencies of their components. New polymers can be obtained by copolymerization or polymer mixtures. Polymer mixtures or polymer blends are more economically attractive than the copolymerization process and offer a diversity of possible routes for obtaining materials with desirable properties. The use of polymer blending to improve the impact strength of semicrystalline thermoplastics is especially interesting and is known as a toughening process. The toughening process increases a material's capacity to absorb and dissipate plastic energy before fracture.[1] Nylon 6 (PA6) is an important engineering thermoplastic with many useful properties; however, PA6 materials have a strong notch sensitivity that impairs their impact properties. Many studies of the compatibilization of nylon blends by reactive processing have been documented.[2–40] Reactive compatibilization forms block or graft copolymers at the interface domain during processing by an *in situ* reaction of functional groups.[3,4,23,41] Blends of nylons with acrylonitrile–butadiene–styrene (ABS) materials have significant commercial interest.[6,7,9–14,16,17,23,24,29,31,42,43] This system is useful for exploring the concept because of the inherent reactivity of nylon and the abundant options for designing functional polymers that would be miscible with the styrene–acrylonitrile (SAN) copolymer matrix of ABS.[1] This article examines PA6/ABS blends compatibilized with a methyl methacrylate/maleic anhydride (MMA–MA) copolymer. This copolymer can be miscible with SAN and has functionalities that promptly react with the amine end groups in PA6 during melt processing.

EXPERIMENTAL

Table I summarizes the sources of and some pertinent information about the materials used in this study. The PA6 (number-average molecular weight = 21,000 g mol^{-1}) was a commercially available material with approximately equal concentrations of acid and amine end groups. The ABS material consisted of an SAN copolymer grafted to a butadiene-based latex (50 wt %) in the form of polydispersed particles (typically 0.18–0.20 μm in diameter) and an SAN matrix con-

TABLE I
Materials Used in This Study

Material	Description	Composition	Molecular weight (g/mol)	Haake torque (N m)[a]	Source
PA6	Ultramid B3	End-group content: NH_2, 43.2 μeqivn g^{-1}; COOH, 51.5 μeqivn g^{-1}	$M_n = 21{,}000^b$	1.07	BASF
ABS	SAN-grafted emulsion rubber	50% rubber 25% AN in SAN	$M_n = 40{,}000^c$ $M_w = 110{,}000^c$	10.4	Nitriflex SA (Bayer)
MMA–MA	Poly(methyl methacrylate-*co*-maleic anhydride)	3% MA	$M_n = 20{,}900^d$ $M_w = 40{,}400^d$	0.1	Synthesized in the laboratory
		5% MA	$M_n = 15{,}800^d$ $M_w = 37{,}900^d$	0.1	Synthesized in the laboratory
		10% MA	$M_n = 13{,}100^d$ $M_w = 26{,}200^d$	0.1	Synthesized in the laboratory

[a] Torque taken at 240°C and 60 rpm after 10 min.
[b] Measurements taken as a chemical analysis of the end groups.
[c] Molecular weight of the SAN matrix grafted free, determined by GPC.
[d] Determined by GPC.

taining 25 wt % acrylonitrile (AN). Before each processing step, all nylon-containing materials were vacuum-dried at least 24 h at 80°C to remove absorbed water. The MMA and MA monomers were supplied by Merck and Metacril and Reidel de Haen, respectively (São Paulo, Brazil) (see Table I).

The MMA–MA copolymer was synthesized with 3, 5, 10 and 20 wt % MA by solution polymerization with dimethyl sulfoxide as a solvent. The appropriate amounts of each monomer were premixed in a flask, and 2 wt % ethyl acrylate was added to prevent the unzipping of the polymer at melt processing temperatures. 2,2′-Azobis-2-methylpropanonitrile was used as an initiator (Alfa Aesar, São Paulo, Brazil). The procedures for the synthesis of the copolymer have been well described elsewhere.[1]

PA6/ABS blends were prepared in a corotating 19-mm twin-screw extruder (B&P Process Equipment and Systems) at 230°C and 170 rpm. The blends were quenched in water, pelletized, and vacuum-dried for 24 h at 80°C. Samples for Izod tests (ASTM D 256) and transmission electron microscopy (TEM) were prepared by injection molding in an Arburg Allrounder machine at 230°C and a mold temperature of 50°C. Izod impact testing was carried out in notched specimens with a Ceast Resil 25 instrument.

The phase morphologies of the blends were observed by TEM with a Philips CM 120 operated at 120 kV. Samples were cryogenically microtomed from Izod bars perpendicular to the flow direction into ultrathin sections (~20 nm thick). The slicing process was carried out with a diamond knife with a Riechert-Jung Ultracut E device under cryogenic conditions (−50°C) inside the microtoming chamber. A cutting speed of 0.1 mm s^{-1} was maintained throughout the microtoming operation. The ultrathin sections were then collected on a copper grid for subsequent staining. Two selective staining techniques were used to induce electron density changes required for phase contrast in the transmission electron microscope. The sections were exposed to a 2% aqueous solution of phosphotungstic acid (PTA) to stain the nylon phase. In certain cases, osmium tetroxide (OsO_4) was used to stain the unsaturated rubber phase in ABS. This process involved exposing the microtomed sections to a 2% aqueous solution for at least 15 h.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 shows the variations in the room-temperature Izod impact strength with the MA content in the copolymer added to the ABS phase for blends containing 50% PA6. The incorporation of 5% of the copolymer is sufficient to toughen the blend. Actually, only 3% MA in the copolymer improves the impact strength to high levels (>800 J/m); that is, the blend is supertough. Apparently, it is not necessary to add large quantities of MA because there are not enough amine end groups in PA6 to react. Kudva et al.[36] reported that very small amounts of MA were sufficient to produce blends of supertough polyamide/polyethylene (PA/PE) and at the same time reduce the size of the disperse phase.
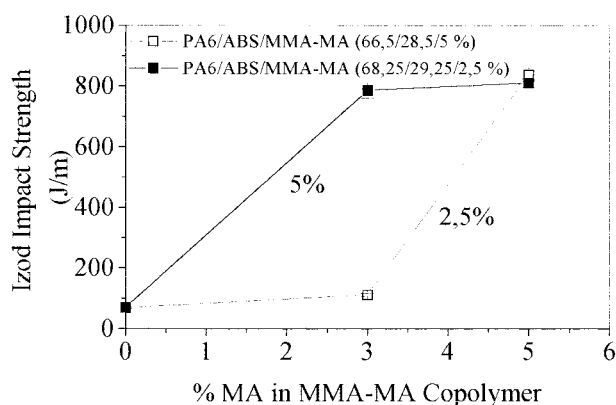
The effect of the incorporation of the MMA–MA compatibilizer was also studied in a 70/30 blend. Figure 2 shows the impact strength of this blend with 5
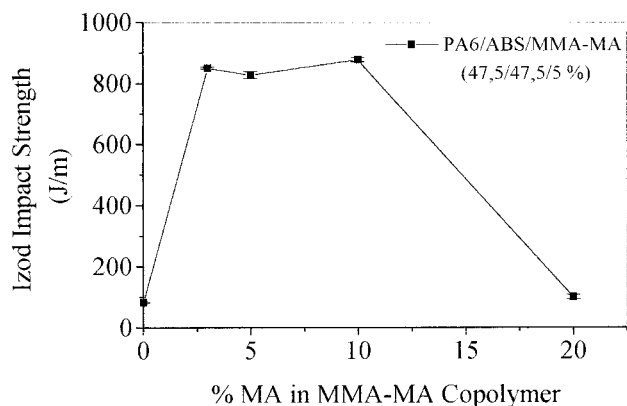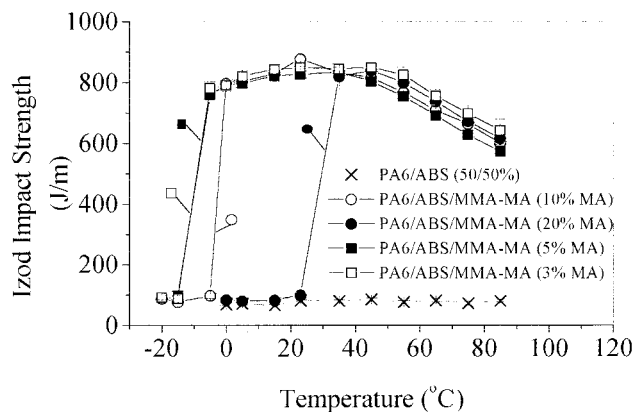
Figure 1 Notched Izod impact strength of a binary 50/50 PA6/ABS blend and ternary 47.5/47.5/5 PA6/ABS/MMA–MA blends at room temperature.

Figure 3 Effect of the temperature on the notched Izod impact strength of a binary 50/50 PA6/ABS blend and ternary 47.5/47.5/5 PA6/ABS/MMA–MA blends with various amounts of MA in the copolymer.

and 2.5 wt % of the copolymer. For the 5% content composition, 3% MA is sufficient to toughen the blend (~800 J.m^{-1}). However, for the composition with 2.5% of the compatibilizer, a 3% MA content does not appear to be sufficient to toughen the blend. This can only be achieved with 5% MA, which results in an impact strength value greater than approximately 800 J m^{-1}. Hence, there is probably an optimum copolymer content capable of toughening the blend. Indeed, as reported by Araújo,[1] it appears that poly(methyl methacrylate) segments are miscible with the SAN phase of ABS and that the anhydride groups can react with the amine end groups of PA6. In this case, the compatibilizer appears to stay at the interface between PA6- and ABS-rich phases. The process reduces the interfacial tension between the blend components and delays the coalescence of the dispersed phase via steric stabilization.

Figure 3 shows the impact strength for compatibilized PA6/ABS blends as a function of the temperature. In the 50/50 PA6/ABS blends with 5 wt %

of the copolymer, when the MA content in the copolymer is reduced (from 20 to 3 wt %), the ductile–brittle transition temperature (T_{D-F}) is lowered from 28 to −10°C. Without the compatibilizer, the blend is brittle over a broad range of temperatures. Only the blends with 3 and 5 wt % MA remain tough when the temperature becomes subzero. These results can be compared with the results of Majumdar et al.[13] They used ABS and PA6 grades similar to the ones used in this work. Similar results were obtained for a poly(butylene terephthalate (PBT)/ABS system.[27] It was reported that moderate quantities of the glycidyl methacrylate (GMA) functionality in the compatibilizer and a small amount of the compatibilizer in the blend were sufficient to reduce significantly T_{D-F} and to improve the ABS dispersion. However, larger quantities of the GMA functionality improved the impact strength at room temperature but not sufficiently at low temperatures.

Figure 2 Notched Izod impact strength of a 70/30 PA6/ABS blend with the MMA–MA copolymer at room temperature.
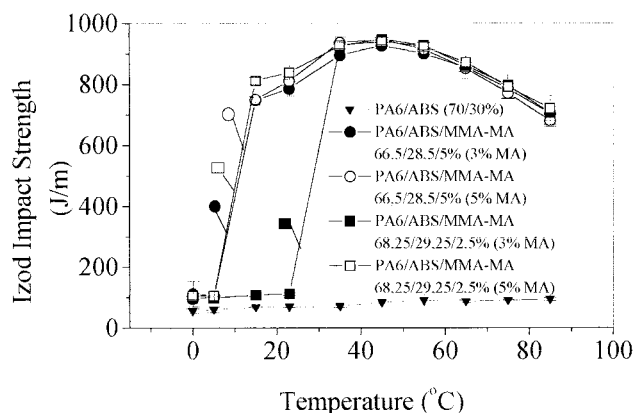
Figure 4 Effect of the temperature on the notched Izod impact strength of a 70/30 PA6/ABS blend and ternary 66.25/28.5/5 and 68.25/29.25/2.5 PA6/ABS/MMA–MA blends containing 3 and 5 wt % MA in the copolymer.

TABLE II.
T_{D-F} **of PA6/ABS/MMA–MA Blends**

PA6/ABS/MMA–MA (wt %)	T_{D-F} (°C)[a]
47.5/47.5/5	
3% MA	−10.0
5% MA	−10.0
10% MA	−2.5
20% MA	28.0
66.5/28.5/5	
3% MA	9.4
5% MA	9.4
68.25/29.25/2.5	
3% MA	28.2
5% MA	11.2

[a] Taken as the midpoint on the steplike change in the Izod impact strength/temperature curve.

Moreover, a higher functionality increased the blend viscosity, and this is undesirable for some processing techniques. Figure 4 shows the impact strength curves as a function of the temperature for 70/30 PA6/ABS blends. Without the compatibilizer, the blend is brittle over a broad range of temperatures. With 5 wt % of the compatibilizer, the blend is supertough (~800 J/m) at room temperature and remain so up to 15°C. With 2.5 wt % of the compatibilizer, it is tough at room temperature up to 5 wt % MA, For lower MA contents (3 wt %), the blend is brittle at room temperature. Moreover, T_{D-F} is higher than for the latter blends, according to Table II. These results are probably due to the large amount of PA6 in the blend. Therefore, the incorporation of a large PA6 content in the blend appears to shift the transition temperature toward higher values. It can also be concluded that the MA content influences T_{D-F} and that there is an optimum con-

tent of MA for toughening the blend. According to the aforementioned considerations, it is evident that the MMA–MA copolymer can be used as a PA6/ABS blend compatibilizer.

Morphology

Effect of the ABS content

Figure 5 shows TEM photomicrographs of binary PA6/ABS blends (70/30 and 50/50 w/w) for butadiene-based rubber particles in an ABS phase stained with OsO_4. PA6 clearly forms a continuous phase, whereas ABS forms large domains with some tendency for interconnectivity. The tendency toward a cocontinuous morphology is also evident in the photomicrograph. The mechanical properties of these blends reflect this type of morphology. The 70/30 PA6/ABS blend shows a lower impact strength at room temperature than the blends with higher rubber contents. Moreover, these blends are brittle over the entire temperature range studied, in agreement with the observed morphology.

Effect of the compatibilizer content

Figure 6 shows changes in the morphology for various MA contents in the copolymer. The 50/50 PA6/ABS blend containing 5 wt % of the MMA–MA compatibilizer and the PA6 phase have been stained with PTA. These compositions correspond to the maximum attained Izod impact strength shown in Figure 1 (>800 J/m) and remain tough as the temperature drops into the subzero range. This is corroborated by the results obtained by Majumdar et al.[13] with similar ABS and PA6 grades. The presence of the compatibilizer in the blends (Fig. 6) clearly demonstrates that an improved
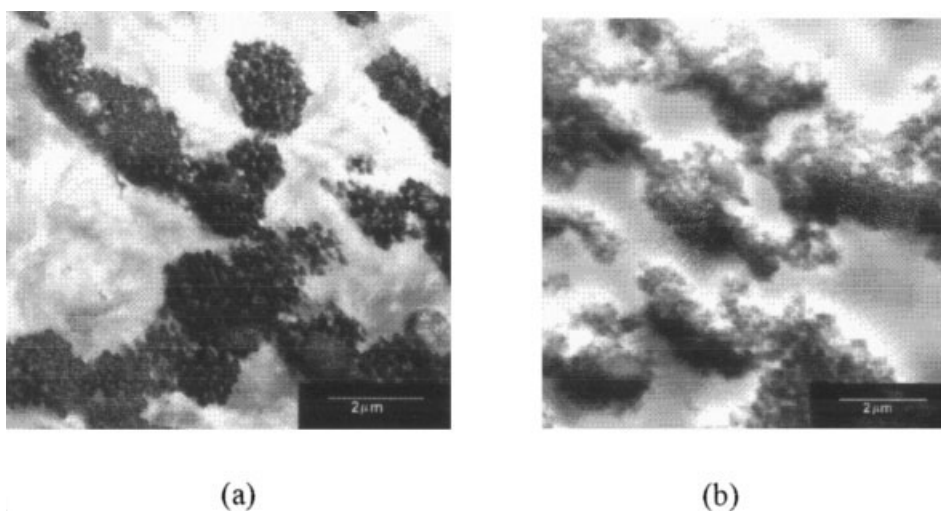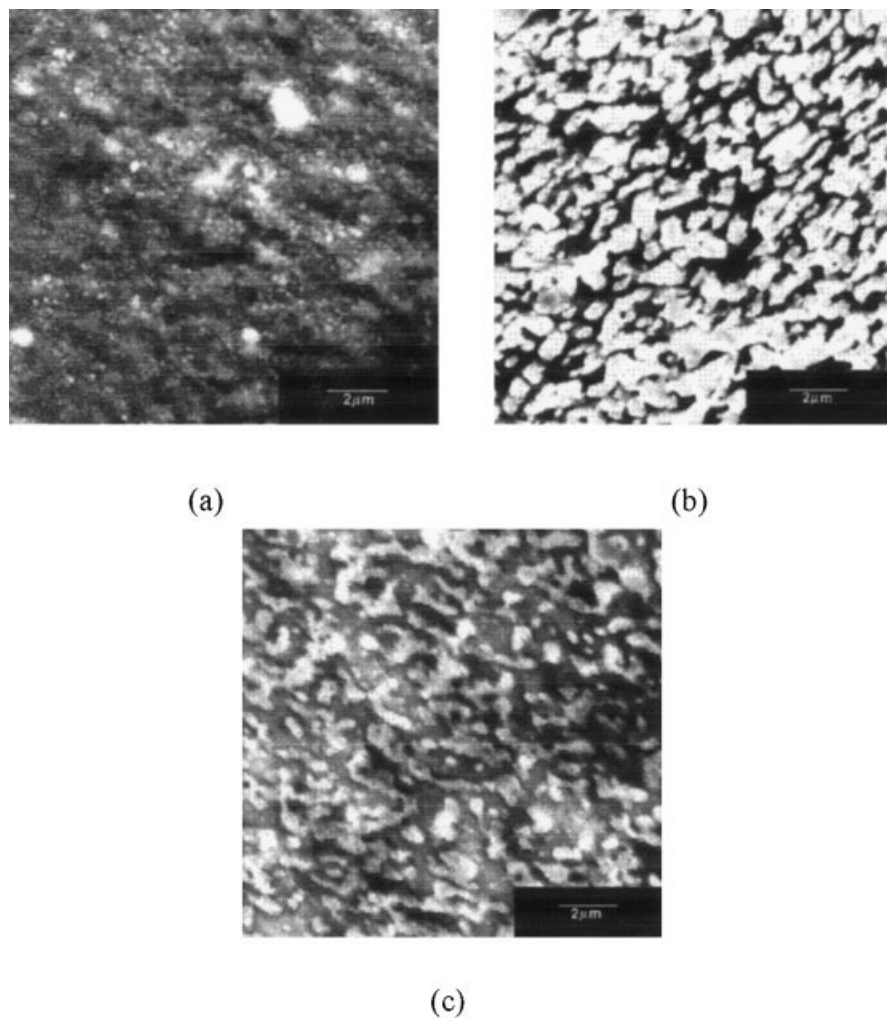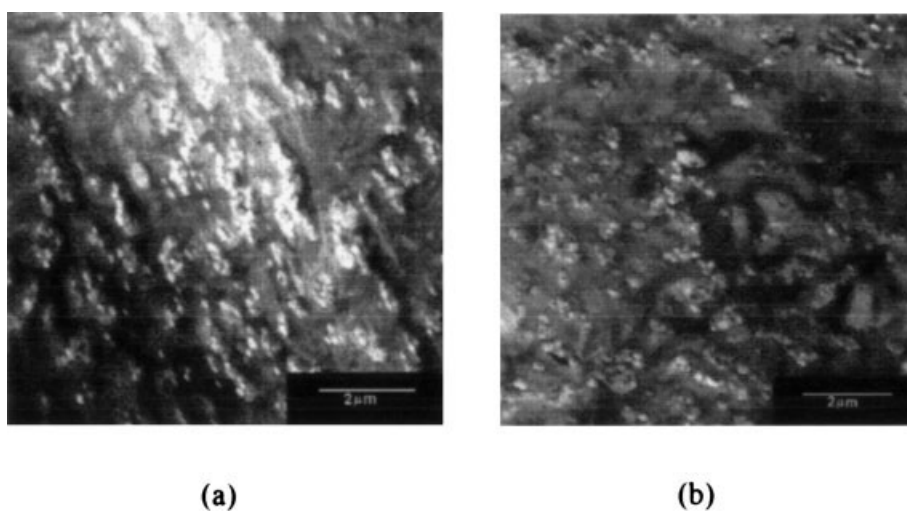

(a)   (b)

Figure 5 TEM photomicrographs of binary PA6/ABS blends: (a) 70/30 and (b) 50/50. The rubber phase in ABS has been stained dark with OsO_4 (8000×).

Figure 6   TEM photomicrographs of ternary 47.5/47.5/5 PA6/ABS/MMA–MA blends containing (a) 3, (b) 5, and (c) 10 wt % MA in the copolymer. The polyamide phase has been stained with PTA (5000×).

Figure 7   TEM photomicrographs of ternary 66.25/28.5/5 PA6/ABS/MMA–MA blends containing (a) 3 and (b) 5 wt % MA in the copolymer. The polyamide phase has been stained with PTA (8000×).
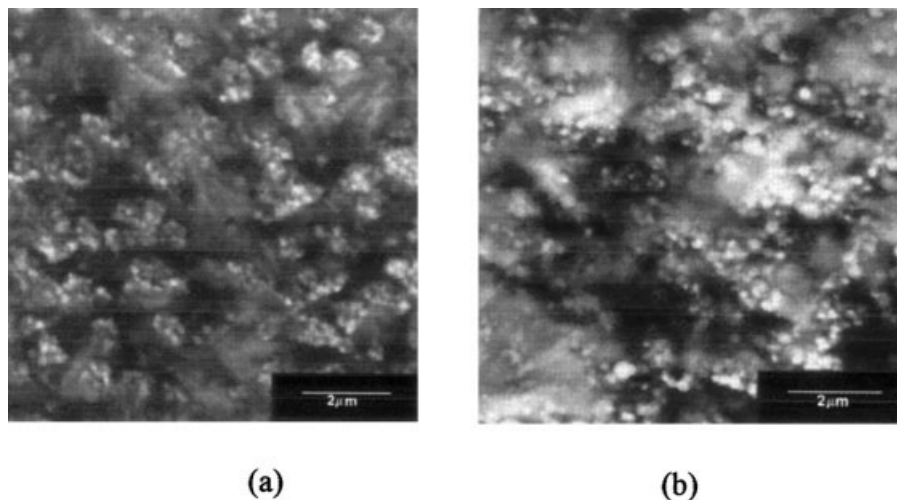
Figure 8 TEM photomicrographs of ternary 68.25/29.5/2.5 PA6/ABS/MMA–MA blends containing (a) 3 and (b) 5 wt % MA in the copolymer. The polyamide phase has been stained with PTA (8000×).

dispersion is generally accompanied by a dramatic decrease in T_{D-F} (Table II). The blends with 3 and 5 wt % MA in the copolymer present very similar mechanical behaviors. The blend with 10 wt % MA presents low size domains, probably the lowest size within a critical limit for toughening, according to the literature.[34,38] Furthermore, it can be argued that an increase in the functionality group content reduces the dispersed phase size domains and improves the impact properties when the particles are large enough for effective toughening. The rubber particles should work not only by triggering toughening mechanisms that start in the particle equator but also by arresting and delaying cracks. Therefore, the size and distribution of the particles are of fundamental importance for the development and control of these mechanisms.[44] Both the particle size and the distance between particles influence the properties, especially the ductile–brittle transition.[45]

Other compositions that have been studied include a 70/30 composition with 5 and 2.5 wt % of the compatibilizer in the blend. Figure 7 shows the photomicrographs of 66.5/28.5/5 PA6/ABS/MMA–MA blends with 3 and 5 wt % MA in the copolymer. The PA6 phase has been stained with PTA. As shown previously in Figure 5(a), the morphology in Figure 7 shows that the compatibilizer significantly reduces the ABS domain size. Actually, they appear to become more efficiently dispersed and distributed. This improvement in dispersion is accompanied by a significant increase in the room-temperature impact strength. These blends remain tough up to 15°C, but the T_{D-F} values are higher (~9,4°C) than those of 50/50 compositions. This fact can be attributed to a larger PA6 content in these blends.

Figure 8 shows the morphology of 68.25/29.25/2.5 PA6/ABS/MMA–MA blends with 3 and 5 wt % MA in the copolymer. The PA6 phase has been stained with PTA. The ABS domains of this blend appear to be slightly larger than those in Figure 7, with a tendency to coalesce. However, with a lower compatibilizer content, the structure appears more refined in relation to the blend without the compatibilizer [Fig. 5(a)]. The blend with 5 wt % MA in the copolymer is tough at room temperature and at 15°C. T_{D-F} of this blend is around 11°C, and the blend behaves similarly to that shown in Figure 7(b).

CONCLUSIONS

The effect of the MMA–MA copolymer on the behavior of PA6/ABS blends has been investigated. The incorporation of the MMA–MA copolymer can reduce the dispersed phase domain size of PA6/ABS blends and promote the effective toughening of the blends. These changes in the dispersed phase morphology in relation to the binary blends stem from reactions between the PA6 amine end groups and the copolymer during melting processing. This occurs to some extent through steric stabilization of the SAN domains against coalescence. Thus, the mechanical properties are improved by a higher interaction between the two phases with the incorporation of the MMA–MA compatibilizer. PA6/ABS/MMA–MA is supertough (>800 J/m) at room temperature and remains tough as the temperature drops into the subzero range. These results are evidence that the MMA–MA copolymer is an efficient alternative for the reactive compatibilization of the PA6/ABS system.

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