

Effect of Compatibilizer in Acrylonitrile-Butadiene-Styrene Toughened Nylon 6 Blends: Ductile–Brittle Transition Temperature

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ABSTRACT: The ductile–brittle transition temperatures were determined for compatibilized nylon 6/acrylonitrile-butadiene-styrene (PA6/ABS) copolymer blends. The compatibilizers used for those blends were methyl methacrylate-*co*-maleic anhydride (MMA-MAH) and MMA-*co*-glycidyl methacrylate (MMA-GMA). The ductile–brittle transition temperatures were found to be lower for blends compatibilized through maleate modified acrylic polymers. At room temperature, the PA6/ABS binary blend was essentially brittle whereas the ternary blends with MMA-MAH com-

patibilizer were supertough and showed a ductile–brittle transition temperature at -10°C . The blends compatibilized with maleated copolymer exhibited impact strengths of up to 800 J/m. However, the blends compatibilized with MMA-GMA showed poor toughness at room temperature and failed in a brittle manner at subambient temperatures. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2643–2647, 2003

Key words: blends; compatibilization; toughness; nylon 6; acrylonitrile-butadiene-styrene

INTRODUCTION

Nylon 6 (PA6) is an attractive polymer for engineering applications; however, it has melt processing instabilities and a relatively low notched impact strength. Polymer blends constitute an alternative to achieve a combination of properties not available in a single polymeric material. Blends of PA6 with poly(phenylene oxide), acrylonitrile-butadiene-styrene (ABS), polyolefins, polycarbonate, ethylene-propylene-diene rubber (EPDM), and ethylene copolymers have been produced.^{1–4} Generally, these binary blends are immiscible and exhibit poor mechanical properties that stem from the unfavorable interactions between their molecular segments. Thus, there is great interest in developing compatible blends in order to retain the desirable properties from each of the blend constituents. For this reason, one of the preferred routes has been to use reactive compatibilization in which a copolymer is premade or formed *in situ* during melt processing through the use of appropriate reactive functionalities. In this case, a compatibilizer capable of reacting with a blend constituent and that is miscible

with another is added into the blend (i.e., it is necessary that it stays preferentially at the polymer–polymer interfaces).^{1,3,5–7} Nylons are attractive for this application because they have reactive functionality through amine and carboxyl end groups that are capable of reacting to form graft moieties.^{2,8–13}

This article examines the effects of two types of compatibilizers on the ductile–brittle transition temperature of PA6/ABS blends. A series of methyl methacrylate-*co*-glycidyl methacrylate (MMA-GMA) and MMA-*co*-maleic anhydride (MMA-MAH) copolymers are used as compatibilizing agents. GMA contains an epoxide functionality capable of reacting with both the acid and amine end groups of PA6, whereas PMMA is miscible with the styrene-acrylonitrile (SAN) phase in ABS over a broad range of AN contents.^{14–16} MAH reacts mainly with the amine ends of the PA6 chains.^{1,4,6,7,17–19}

EXPERIMENTAL

Table I summarizes the characteristics of the materials used in this study. The PA6 is a commercially available material with a number-average molecular weight (M_n) of 21,000 g/mol, and it has approximately equal concentrations of acid and amine end groups. Prior to each processing step, all nylon-containing materials were vacuum dried in an oven for at least 24 h at 80°C to remove absorbed water. An emulsion-pre-

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TABLE I
Materials Used in This Study

Material	Description	Composition	Molecular weight (g/mol)	Haake ^a torque (Nm)	Source
Nylon 6	Ultramid B3	End-group content: NH ₂ , 43.2 μ eq g ⁻¹ ; COOH, 51.5 μ eq 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-GMA	Methyl methacrylate- <i>co</i> -glycidyl methacrylate	10% GMA	M _n = 21,600 ^d M _w = 91,300 ^d		
MMA-MAH	Methyl methacrylate- <i>co</i> -maleic anhydride	3% MAH	M _n = 20,900 ^d	0.1	Lab synthesized
		5% MAH	M _w = 40,400 ^d M _n = 15,800 ^d	0.1	Lab synthesized
		10% MAH	M _w = 37,900 ^d M _n = 13,100 ^d M _w = 26,200 ^d	0.1	Lab synthesized

^a The torque was taken at 240°C and 60 rpm after 10 min.

^b The measurements were taken by end-group chemical analysis.

^c Molecular weight of the SAN matrix grafted free, as determined by GPC.

^d Determined by GPC.

pared ABS material was used as an impact modifier, which contains 50 wt % rubber in the form of poly-disperse particles typically 0.18–0.20 μm in diameter and a SAN matrix containing 25 wt % AN. The GMA, MMA, and MAH comonomers were supplied by Merck, Metacril, and Reidel–deHaen, respectively. The MMA-GMA copolymer was synthesized with 10 wt % GMA by bulk polymerization. On the other hand, the MMA-MAH copolymer was synthesized with 3, 5, 10, and 20 wt % MAH by solution polymerization using dimethyl sulfoxide (DMSO) as a solvent. The appropriate amounts of each comonomer and 2 wt % 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 an initiator (Alfa Aesar). The procedures for synthesizing these copolymers are described in detail elsewhere.^{1,20}

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 subsequently quenched in water, pelletized, and vacuum dried in an oven for 24 h at 80°C. Samples for Izod impact tests were prepared by injection molding in an Arburg Allrounder machine at 230°C, and the mold temperature was set at 50°C. Izod impact testing was carried out with notched specimens at room and low temperatures using CEAST Resil 25 equipment with a thermal chamber. Typically, five or more sets of samples of a given blend were placed in the chamber at once, allowing the specimens to be conditioned at the desired temperature for up to 1 h before testing. After the impact strength for a set at a given temperature

was determined, the temperature was reduced and the entire process was repeated until –20°C. Approximately 10 specimens for each blend and temperature were tested. The temperature was reduced until the whole sample set failed in a brittle manner at two subsequent temperatures. The ductile–brittle transition temperature was defined as the midpoint in the steplike change in plots of the Izod impact strength versus temperature.

RESULTS AND DISCUSSION

Influence of compatibilizer type

The influence of the MMA-GMA compatibilizer on the impact strength of the PA6/ABS blend was studied. Table II shows the results obtained for the impact strength of the 70/30 and 50/50 blends. However, despite the fact that ABS presents a high impact strength because of the presence of a rubber phase in its microstructure, the impact strength of the binary blends was not increased sufficiently by simply adding ABS to PA6. The fracture aspect can be considered as brittle as a function of the values obtained. Incorporation of the MMA-GMA copolymer produces a significant increase in the impact strength of the blends compared to the uncompatibilized one. Kim et al.²¹ reported that the sequence of the mixture and the large viscosity difference between the two components alters the morphological, rheological, and dynamic mechanical properties of the blend. For this reason, blends were prepared in different sequences of mixture to improve these properties. However, PA6/

TABLE II
Notched Izod Impact Strength of PA6/ABS and PA6/ABS/MMA-GMA Systems (10 wt% GMA)

Materials	Izod impact strength (J/m)
PA6	32 ± 3
ABS	396 ± 8
PA6/ABS (70/30 wt %)	70 ± 3
PA6/ABS/MMA-GMA	191 ± 14
Sequence 1	123 ± 12
Sequence 2	135 ± 14
Sequence 3	109 ± 1
Sequence 4	99 ± 6
PA6/ABS (50/50 wt %)	82 ± 2
Sequence 5	229 ± 22
Sequence 6	145 ± 11

Measurements were taken at $23 \pm 2^\circ\text{C}$ and 65 wt % humidity. PA6/ABS/MMA-GMA = 66.5/28.5/5 wt %. Sequence 1 = PA6/MMA-GMA + ABS (66.5/5 + 28.5 wt %), sequence 2 = ABS/MMA-GMA + PA6 (28.5/5 + 66.5 wt %), sequence 3 = PA6/ABS + MMA-GMA (66.5/28.5 + 5 wt %), sequence 4 = PA6/MMA-GMA + ABS/MMA-GMA (66.5/2.5 + 28.5/2.5 wt %), sequence 5 = PA6/ABS/MMA-GMA (47.5/47.5/5 wt %), sequence 6 = ABS/MMA-GMA + PA6 (47.5/5 + 47.5 wt %).

ABS/MMA-GMA systems do not seem to be sensitive to the mixture sequence (i.e., no improvement was observed in the properties with changes in the mixture sequence), compared to the ternary blend mixed at once. Even so, the compatibilized blend can be considered as tough at room temperature if compared to other toughened plastics such as high impact polystyrene, which has an Izod impact strength of ~ 100 J/m. Although significant improvements in the impact strength were observed for PA6/ABS/MMA-GMA blends, no supertough composition was found as observed by Kudva et al.³

Table III shows the results for 70/30 and 50/50 blends compatibilized by MMA-MAH copolymer. When the MMA-MAH copolymer is added to the blend, the impact strength improves significantly. The values of the impact strength reach above 800 J/m, thereby leading to supertough blends. We observed that there is a narrow composition window for better efficiency of the MMA-MAH compatibilization. The introduction of 5 wt % copolymer in the blend having 3 wt % MA is sufficient to induce toughening (i.e., a low concentration of anhydride does toughen the blend). This is comparable to results obtained by Kudva et al.,¹³ who reported very small quantities of MAH are sufficient to produce supertough PA6/polyethylene blends with a reduced size dispersed phase.

Influence of temperature on impact properties

Figures 1 and 2 show the behavior of the notched Izod impact strength as a function of the testing temperature. The binary blend (i.e., the uncompatibilized

TABLE III
Notched Izod Impact Strength of PA6/ABS and PA6/ABS/MMA-MAH Systems with 3, 5, 10, and 20 wt % MAH

Materials	Izod impact strength (J/m)
PA6/ABS (70/30%)	70 ± 3
PA6/ABS/MMA-MAH (3.0% MAH) ^a	786 ± 24
PA6/ABS/MMA-MAH (5.0% MAH) ^a	811 ± 14
PA6/ABS/MMA-MAH (3.0% MAH) ^b	112 ± 5
PA6/ABS/MMA-MAH (5.0% MAH) ^b	839 ± 23
PA6/ABS (50/50%)	82 ± 2
PA6/ABS/MMA-MAH (3.0% MAH) ^c	850 ± 3
PA6/ABS/MMA-MAH (5.0% MAH) ^c	827 ± 11
PA6/ABS/MMA-MAH (10% MAH) ^c	878 ± 7
PA6/ABS/MMA-MAH (20% MAH) ^c	100 ± 7

Measurements were taken at $23 \pm 2^\circ\text{C}$ and 65 wt % humidity.

^a PA6/ABS/MMA-MA = 66.5/28.5/5 wt%.

^b PA6/ABS/MMA-MA = 68.25/29.25/2.5 wt%.

^c PA6/ABS/MMA-MA = 47.5/47.5/5 wt%.

blend) is essentially brittle over the entire range of test temperatures. When the MMA-GMA compatibilizer is incorporated into the blend, a modest improvement in the impact strength of the blend at room temperature is observed compared to the binary PA6/ABS blend. The ductile–brittle transition temperature (T_{D-F}) for the whole sequence remains in the range of 50–55°C, which is close to the glass-transition temperature (T_g) of PA6 as observed in Table IV. Incorporation of ABS and the MMA-GMA compatibilizer and sequence of the mixture did not improve the impact strength of the blend significantly at room temperature or below. Only above T_{D-F} did the blend show supertough behavior. It is evident that this copolymer promotes a compatibilizing effect in the PA6/ABS blend at room

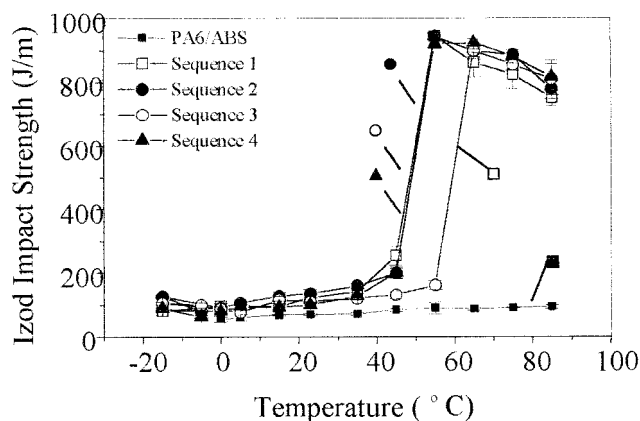


Figure 1 The effect of temperature on the Izod impact strength for a binary PA6/ABS (70/30) blend and ternary PA6/ABS/MMA-GMA (66.5/28.5/5) blends with different mixture sequences. Sequence 1: PA6/MMA-GMA + ABS; sequence 2: ABS/MMA-GMA + PA6; sequence 3: MMA-GMA + PA6/ABS; sequence 4: PA6/MMA-GMA + ABS/MMA-GMA.

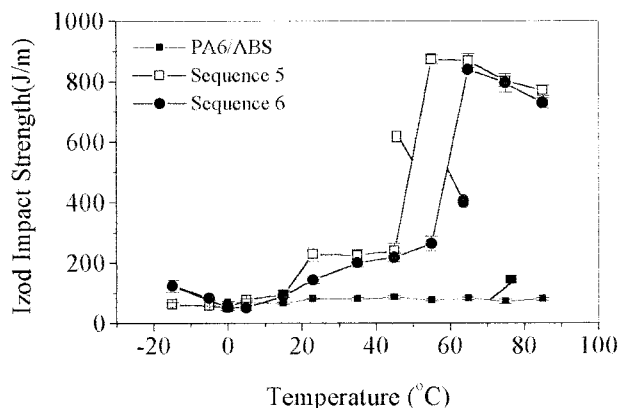


Figure 2 The effect of temperature on the Izod impact strength of a binary PA6/ABS (50/50) blend and ternary PA6/ABS/MMA-GMA (47.5/47.5/5) blends with different mixture sequences. Sequence 5: PA6/ABS/MMA-GMA; sequence 6: ABS/MMA-GMA + PA6.

temperature, but it cannot be compared to the values obtained by Kudva et al.³ However, the blend can be considered as tough at room temperature.

The Izod impact strength was measured at various temperatures for blends of nylon as a function of the MAH content in the copolymer. Table V shows the ductile–brittle transition temperature for the PA6/ABS/MMA-MAH blends. The impact properties of the compatibilized PA6/ABS blends with MMA-MAH copolymer improved markedly at room temperature and below. Figure 3 shows curves of the Izod impact strength of the PA6/ABS blend versus the temperature. The blend without compatibilizer is essentially brittle over the temperature range that was investigated. For most of the PA6/ABS/MMA-MAH ternary (47.5/47.5/5) blends, the T_{D-F} shifts to tem-

TABLE IV
Ductile–Brittle Transition Temperature of PA6/ABS/MMA-GMA Blends and Pure Components

Materials	T_{D-F} (°C)
ABS	-84.0
PA6	69.5
Sequence 1	54.7
Sequence 2	53.3
Sequence 3	65.5
Sequence 4	47.7
Sequence 5	46.7
Sequence 6	64.3

The ductile–brittle transition temperature (T_{D-F}) has been defined as the midpoint of the sharp drop in the notched Izod impact strength as the testing temperature is reduced. Sequence 1 = PA6/MMA-GMA + ABS (66.5/5 + 28.5 wt %), sequence 2 = ABS/MMA-GMA + PA6 (28.5/5 + 66.5 wt %), sequence 3 = PA6/ABS + MMA-GMA (5 + 66.5/28.5 wt %), sequence 4 = PA6/MMA-GMA + ABS/MMA-GMA (66.5/2.5 + 28.5/2.5 wt %), sequence 5 = PA6/ABS/MMA-GMA (47.5/47.5/5 wt %), sequence 6 = ABS/MMA-GMA + PA6 (47.5/5 + 47.5 wt %).

TABLE V
Ductile–Brittle Transition Temperature of PA6/ABS/MMA-MA Blends

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

The ductile–brittle transition temperature (T_{D-F}) has been defined as the midpoint of the sharp drop in the notched Izod impact strength as the testing temperature is reduced.

peratures below the room temperature. Ternary blends with MMA-MAH copolymer with 3, 5, and 10 wt % MAH are supertough at room temperature and below. Similar results were observed with a poly(butylene terephthalate)/ABS system.²² The Izod impact strength for compatibilized 70/30 blends is shown in Figure 4 as a function of temperature. Similar to PA6/ABS (50/50) blends, this blend is essentially brittle without compatibilizer over our temperature range. For 5 wt % compatibilizer, the blends were found to be supertough at close to room temperature. For 2.5 wt % compatibilizer, the blend showed a T_{D-F} above room temperature for MMA-MAH containing 3 wt % MAH. When the MAH content was increased to 5 wt % in the compatibilizer, the blend became supertough at room temperature and had a T_{D-F} well below room temperature. Table V shows the T_{D-F} values for all PA6/ABS (70/30) blends. The efficiency of MMA-MAH as a compatibilizer for PA6/ABS blends can be considered to be significant. Even for lower amounts of ABS in the

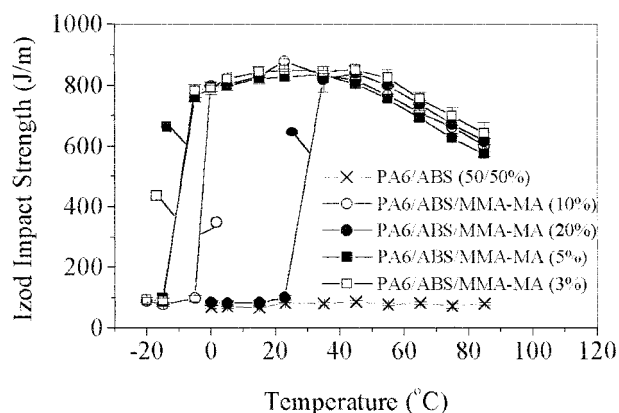


Figure 3 The effect of temperature on the Izod impact strength of a binary PA6/ABS (50/50) blend and ternary PA6/ABS/MMA-MAH (47.5/47.5/5) blends containing different amounts of MAH (%) in the MMA-MAH copolymer.

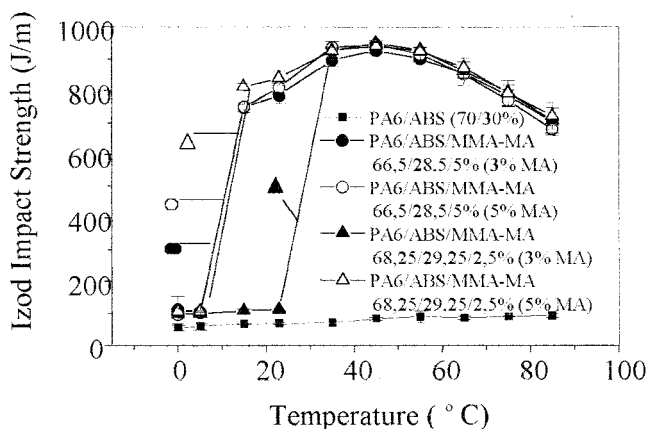


Figure 4 The effect of temperature on the Izod impact strength of a binary PA6/ABS (70/30) blend and ternary PA6/ABS/MMA-MAH (66.5/28.5/5 and 68.25/29.25/2.5) blends containing 3 and 5 wt % MAH in the copolymer.

blends, the T_{D-F} values were shifted to temperatures well below room temperature. Considering that ABS has approximately 50 wt % rubber phase, the MMA-MAH copolymer has toughened PA6/ABS blends for less than 15 wt % rubber phase in that system.

CONCLUSIONS

MMA-GMA and MMA-MAH compatibilizers showed an improvement in the T_{D-F} of PA6/ABS blends. Incorporation of MMA-GMA copolymer as a compatibilizing agent did not improve the T_{D-F} of the blends as well as MMA-MAH. The latter copolymer showed excellent toughening performance for PA6/ABS blends. This behavior was observed even for lower amounts of ABS in the blend. The notched Izod impact strength for PA6/ABS blends reached values above 800 J/m at room temperature, which was due to the

presence of MMA-MAH copolymers. Supertough blends were obtained by using this compatibilizer.

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