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Morphological, mechanical and rheological properties of nylon 6/acrylonitrile-butadiene-styrene blends compatibilized with MMA/MA copolymers

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The morphological, mechanical and rheological properties of nylon 6/acrylonitrile-butadiene-styrene blends compatibilized with MMA-MA [poly(methyl methacrylate-co-maleic anhydride)] copolymers were studied. A twin screw extruder was used for melt-blended the polymers and the injection moulding process was used to mold the samples. The main focus was on nylon 6/ABS blends compatibilized with one MMA-MA copolymer. This copolymer has PMMA segments that appear to be miscible with the styrene-acrylonitrile (SAN) phase of ABS and the anhydride groups can react with amine end groups of the nylon 6 (Ny6) to form graft copolymers at the interface between Ny6 and ABS rich phases. Tensile and impact and morphological properties were enhanced by the incorporation of this copolymer. Transmission electron microscopy (TEM) observations revealed that the ABS domains are finely dispersed in nylon 6 matrix and led to the lowest ductile-brittle transition temperatures and highest impact properties. It can be concluded that the MMA-MA copolymer is an efficient alternative for the reactive compatibilization and can be used as a compatibilizer for nylon 6/ABS blends. © *2003 Kluwer Academic Publishers*

1. Introduction

In recent years, there has been considerable interest in the development of multiphase polymer blends, motivated by the potential opportunities for combining the attractive features of each material while reducing their deficient characteristics. Nylon 6 is an attractive polymer for engineering applications; however, it presents melt processing instabilities and relatively low-notched impact strength. Blends of nylon 6 with polyphenylene oxide, 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 aiming to retain the desirable properties from each blend constituents. For this reason, block or graft copolymers have been used successfully as interfacial agents to control the morphology and to strengthen the interfaces in blends of immiscible polymers. An attractive alternative is the formation of block or graft copolymer *in situ* during blend preparation through interfacial reaction of added functionalized polymeric components. In this case, a compatibilizer capable of reacting with a blend constituent and which is miscible with another is added in 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 capable of reacting to form graft moieties [2, 8–13].

This article examines the effects of compatibilizer on morphological, mechanical and rheological properties

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of nylon 6/ABS blends. Maleic anhydride (MA) reacts mainly with the amine ends of the nylon 6 chains [1, 4, 6, 7, 17–19], whereas poly(methyl methacrylate) has been shown to be miscible with the SAN phase in ABS over a broad range of AN contents [14–16]. In this case, the MMA-MA copolymer should reside primarily in the SAN phase with its functional group forming chemical linkages with the nylon chains at the nylon 6/SAN interface.

2. Experimental

Table I summarizes the characteristics of the materials used in this study. The nylon 6 is a commercially available material with $M_n = 21000$ g/mol and 43.2 μeq $g^{-1}$of amine and 51.5 μeq $g^{-1}$of carboxyl 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-prepared ABS material was used as impact modifier, 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. Methyl methacrylate (MMA) and maleic anhydride (MA) co-monomers were supplied by Merck, Metacril, and Reidel-deHaen, respectively. The MMA-MA copolymer was synthesized with 3, 5, 10 and 20 wt% of MA by solution polymerization using dimethyl sulfoxide (DMSO) as solvent. The appropriate amounts of each co-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, supplied by Alfa Aesar. The procedures for synthesizing these copolymers are described in detail elsewhere [1].

The Ny6/ABS (50/50 wt%) binary blends and Ny6/ABS/MMA-MA (47, 5/47, 5/5 wt%) ternary 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 vacuum dried in an oven for 24 h at 80°C. Samples for tensile and Izod impact tests were prepared by injection molding in an Arburg Allrounder machine at 230°C, and mold temperature set at 50°C. Tensile properties were measured using a universal tensile machine (Instron model 5569) with a crosshead velocity of 50 mm/min according to ASTM D638. Izod impact tests were carried out on notched specimens at room, low and high temperatures using a CEAST, Resil 25, equipment with a thermal chamber, according to ASTM D256. 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. The ductile-to-brittle transition temperature was defined as the mid-point in the step-like change in plots of Izod impact strength versus temperature. Rheological measurements were made in a Haake torque rheometer with a 50×10^{-6} m^3 mixing head and standard rotors, operated at 240°C and 60 rev min^{-1}. The phase morphologies of the blends were observed by transmission electron microscope (TEM), 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 with a diamond knife using a Riechert-Jung Ultracut E 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 operations. 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 wt% aqueous solution of phosphotungstic acid (PTA) to stain the nylon phase. In certain cases, osmium tetroxide vapour (OsO_4) was used to stain the unsaturated rubber phase in ABS.

3. Results and discussion

3.1. Rheological properties

Fig. 1 shows the torque after 10 min of mixing as for various MA contents in the copolymer. With 10 wt% copolymer in the mixture there is an increase in torque within relatively short times, ~1 min. It

TABLE I Materials used in this study

Material	Description	Composition	Molecular weight (g/mol)	Haake[d] torque (N · m)	Source
Nylon 6	Ultramid B3	End-group content: NH_2, 43.2 μeq g^{-1}; COOH, 51.5 μeq g^{-1}	$M_n = 21000^a$	1.07	Basf
ABS	SAN-grafted emulsion rubber	50% rubber 25% AN in SAN	$M_n = 40000^b$ $M_w = 110000^b$	10.4	Nitriflex SA (bayer)
MMA-MA	Poly(methyl methacrylate-co-maleic anhydride)	3 wt% MA	$M_n = 20900^c$ $M_w = 40400^c$	0.1	Synthesized in laboratory
		5 wt% MA	$M_n = 15800^c$ $M_w = 37900^c$	0.1	
		10 wt% MA	$M_n = 13100^c$ $M_w = 26200^c$	0.1	

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

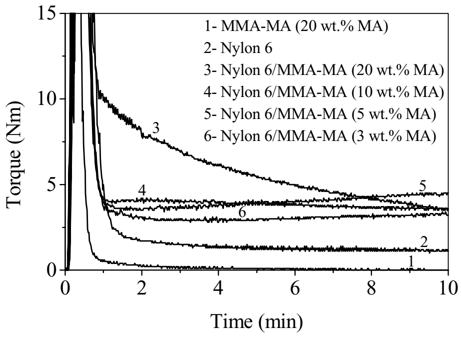

Figure 1 Haake torque for PA6/MMA-MA mixtures (90/10 wt%) versus time (fluxing temperature was 240°C).

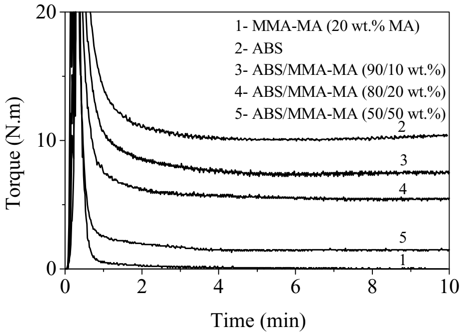

Figure 2 Haake torque for ABS/MMA-MA mixtures versus time (fluxing temperature was 240°C).

increases with increasing MA content in the copolymer. This is evidence of graft reactions of the end groups of Ny6 with MA. Fig. 2 suggests that there is no reaction with ABS, because the final torque is intermediate between that for the two pure polymers and it decreases when the copolymer quantity increases. This is evidence that just a mixing process is taking place and that the anhydride can react only with the amine ends of nylon chains. This type of copolymer seems to be ideal for compatibilization since it can react only with one phase and be miscible with the other phase, being located in the interface among the two phases. This process reduces the interfacial tension between the blend components and delays the coalescence of the dispersed phase via steric stabilization.

3.2. Mechanical properties

Figs 3–5 show the yield strength, tensile modulus and elongation at break of binary and ternary blends of Ny6, respectively. The effect of the compatibilizer was greater for 3 wt% MA in the copolymer where the yield strength and tensile modulus show the highest value in relation to the other concentrations. This can be attributed the large rigidity of this copolymer. In principle, when the molecular weight is increased it causes an increase in the yield strength and tensile modulus for any polymeric system [20]. The influence of MA concentration in the copolymer is hardly significant for all the compositions studied. The compositions used led to similar increases for all properties.

Fig. 6 shows the influence of the MMA-MA compatibilizer on the impact strength of the Ny6/ABS blend.

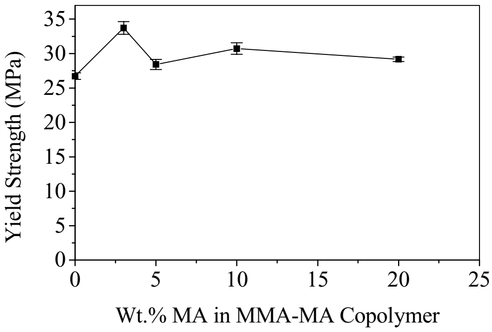

Figure 3 Yield strength of binary 50/50 wt% Ny6/ABS blend and ternary 47, 5/47, 5/5 wt% Ny6/ABS/MMA-MA blend.

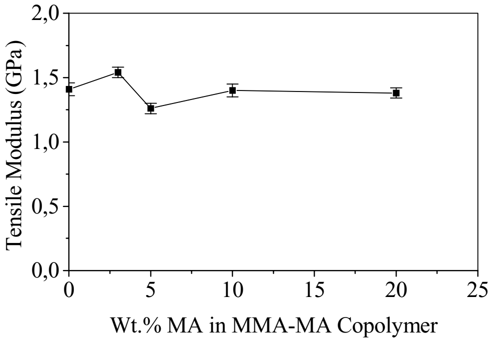

Figure 4 Tensile modulus of binary 50/50 wt% Ny6/ABS blend and ternary 47, 5/47, 5/5 wt% Ny6/ABS/MMA-MA blend.

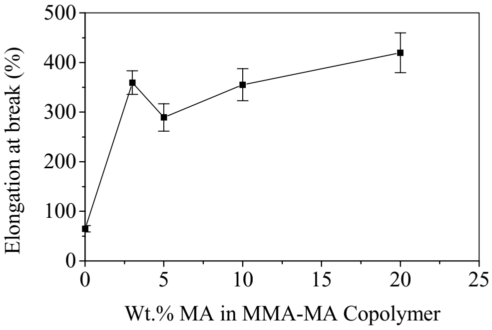

Figure 5 Elongation at break of binary 50/50 wt% Ny6/ABS blend and ternary 47, 5/47, 5/5 wt% Ny6/ABS/MMA-MA blend.

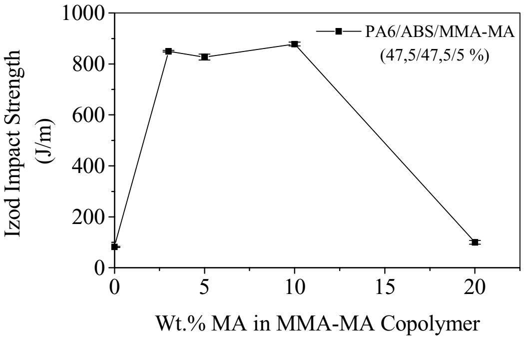

Figure 6 Notched Izod impact strength of binary 50/50 wt% Ny6/ABS blend and ternary 47, 5/47, 5/5 wt% Ny6/ABS/MMA-MA blend.

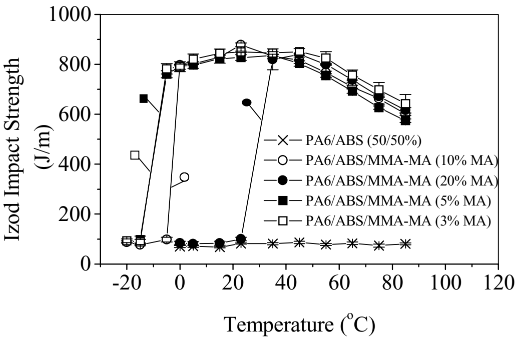

Figure 7 Effect of temperature on the Izod impact strength of a PA6/ABS binary (50/50 wt%) blend and PA6/ABS/MMA-MA ternary (47,5/47,5/5 wt%) blends containing different amounts of MA in the MMA-MA copolymer.

This property improved markedly. Incorporation of 5 wt% compatibilizer is sufficient to toughen the blend, and with only 3 wt% MA in the copolymer, there is a significant improvement in impact strength (>800 J/m). Probably, there is an optimum copolymer content capable of toughening the blend. As shown by the rheological studies, it is not necessary to add large quantities of anhydride because there is not enough amine end groups in the Ny6 to react. According to Kudva *et al.* [13], very small quantities of MA are enough to produce super-tough blends of Ny6/PE and to reduce the disperse phase domain size. These results can be observed too in Fig. 7 that shows the behavior of notched Izod impact strength as a function of the temperature. Izod impact strength was measured at various temperatures for blends of nylon as a function of maleic anhydride content in the copolymer. Table II shows the ductile-brittle transition temperatures ($T_{\text{D-F}}$) for the Ny6/ABS/MMA-MA blends. The binary blend, i.e., the uncompatibilized blend, is essentially brittle over the entire range of the testing temperatures. Interestingly, the impact properties of the compatibilized Ny6/ABS blends with MMA-MA copolymer improved markedly near room temperature and below this. When the MA content in the copolymer is reduced (from 20 to 3 wt%), the $T_{\text{D-F}}$ is lowered from 28 to -10°C. The blends with 3, 5 and 10 wt% MA in the copolymer are supertough (above 800 J/m) at room temperature and at low temperatures too. These results can be compared with results from Majumdar *et al.* [10]. Similar results were observed for a PBT/ABS system [21]. It was reported that moderated quantities of glycidyl methacrylate (GMA) functionality in the compatibilizer and a small amount of compatibilizer in the blend are sufficient to reduce significantly the $T_{\text{D-F}}$ and to improve the ABS dispersion. Moreover, a higher functionality increases the blend viscosity and this is undesirable for some processing techniques. The efficiency of MMA-MA as compatibilizer for Ny6/ABS blends can be considered significant.

TABLE II Ductile-brittle transition temperature of the PA6/ABS/MMA-MA blends

PA6/ABS/MMA-MA	$T_{\text{D-F}}$ (°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

The ductile-brittle transition temperature ($T_{\text{D-F}}$) has been defined as the mid-point of the sharp drop in notched Izod impact strength as the testing temperature was reduced.

3.3. Morphology

Fig. 8 shows the TEM photographs of binary Ny6/ABS and ternary Ny6/ABS blends with MMA-MA copolymer. Dark regions in Fig. 8a represent the unsaturated rubber phase in ABS that has been stained with OsO_4. Dark regions in Fig. 8b, c and d represent the Ny6 phase that has been stained with PTA. The photographs correlate with the compatibilizer effect on the mechanical properties described before. In Fig. 8a, nylon6 clearly forms a continuous phase while the ABS forms large domains with some tendency for interconnectivity. The poor rubber particle distribution in these blends is without doubt a major factor responsible for the poor mechanical properties observed. Moreover, these blends are brittle over the entire range of temperature studied, in agreement with the observed morphology. In Fig. 8b, the ABS dispersed phase forms uniformly diminished particles in the Ny6 matrix. When the MA content is increased to 5 and 10%, the ABS domains become clearly more efficiently dispersed. Fig. 8c and d show the morphology of other compatibilized blends with MA. 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. Well-dispersed rubber particles are essential for the successful toughening of nylons. The Ny6/ABS/MMA-MA blend (Fig. 8b and d) is supertough (above 800 Jm^{-1}) at room temperature, and remains tough as the temperature drops into the subzero range. This is corroborated by the results obtained by Majumdar *et al.* [10] using similar ABS and Ny6 grades. The presence of the compatibilizer in the blends (Fig. 8) clearly demonstrates that an improved dispersion is generally accompanied by a dramatic decrease in the $T_{\text{D-F}}$. The blends with 3 and 5 wt% MA in the copolymer displayed very similar mechanical behavior. The blend with 10 wt% MA possessed small domains. Probably, there is a lowest size within a critical limit for toughening, according to the literature [4, 18]. Further, 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 at the particle equator but also in crack arrest and delaying. Therefore, the size and distribution of the particles are of fundamental importance for development and control of these mechanisms [22]. Not only the particle size but the distance between them influences the properties, especially the ductile-brittle transition temperature [23].

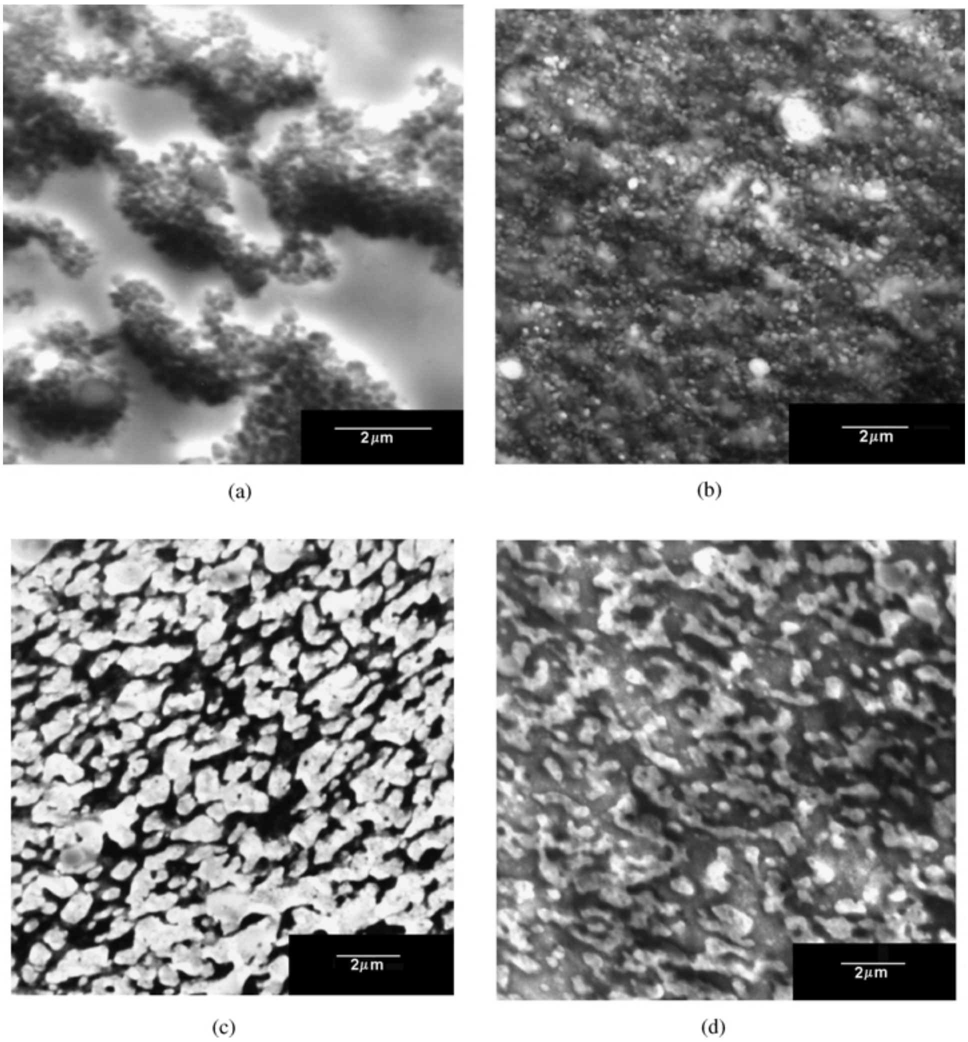

Figure 8 TEM photomicrographs of blends: (a) 50/50 Ny6/ABS blend; (b) 47, 5/47, 5/5% Ny6/ABS/MMA-MA blends containing (b) 3% MA, (c) 5% MA and (d) 10% MA in the copolymer. The polyamide phase has been stained with PTA of (b) to (d). The unsaturated rubber phase in ABS has been stained with OsO_4 (a).

4. Conclusions

The effect of MMA-MA compatibilizer on a variety of properties of Ny6/ABS blends was studied. Incorporation of MMA-MA in the Ny6/ABS blend enhanced considerably the mechanical properties such as yield strength, tensile modulus and elongation at break. The notched Izod impact strength for Ny6/ABS/MMA-MA blends reached values above 800 J/m at room temperature and remained tough as the temperature dropped into the subzero range. Incorporation of the compatibilizing agent can reduce the dispersed phase size of Ny6/ABS blends and promote effective toughening of the blends. Probably, this occurs due to reactions between the nylon 6 amine end groups and the copolymer during melt processing. Thus, the mechanical properties were improved by a higher interaction between the two phases with incorporation of the MMA-MA compatibilizer. These results are evidence that the MMA-MA copolymer is an efficient alternative for the reactive compatibilization of the Ny6/ABS system.

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