

Polymer Blends of Carboxylated Butadiene-Acrylonitrile Copolymer (Nitrile Rubber) and Polyamide 6 Developed in Twin Screw Extrusion

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Received 14 December 2004; accepted 27 February 2006

DOI 10.1002/app.24858

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polymer blends of carboxylated butadiene-acrylonitrile copolymer (nitrile rubber) and polyamide 6 (PA6) were developed in twin screw extrusion. The rubber was cured with SP 1045 methylol phenolic resin during melt mixing in twin screw. Effect of degree of carboxylation in the rubber phase on blend properties has been assessed. Phase morphologies have been characterized using transmission electron microscopy. A compatibilizing NBR-g-Nylon 6 graft copolymer generated *in situ* during melt mixing

via interfacial reaction between the —COOH groups in NBR and the —NH₂ end groups in nylon 6 has been effective in generating a fine and stable dispersion of the rubber within the polyamide matrix. The graft copolymer has been characterized by DMTA. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 372–377, 2007

Key words: nylon; blends; compatibilization; graft copolymers; miscibility

INTRODUCTION

Polyamide blends have attracted interest in the past. These engineering thermoplastics by virtue of their excellent strength properties, chemical and wear resistances, and high melting points are ideally suited for use in various critical applications. Thermoplastic vulcanizates based on polyamides, prepared by melt-mixing with suitable rubbers like butadiene-acrylonitrile copolymer (nitrile rubber) can also exhibit oil resistances. In the past, research has been conducted on the development of nitrile rubber/polyamide blends.^{1–7} Such combinations when properly designed are expected to exhibit good oil resistances and strength properties particularly at elevated temperatures. Coran¹ had reported on nitrile rubber/nylon thermoplastic elastomeric compositions prepared by dynamic vulcanization. Similar studies were conducted on nitrile rubber/nylon 6 systems; dynamically vulcanized by various types of curing agents.² Meherazaden³ has studied the impact modification of nylon 11 with nitrile rubber. However, earlier studies have shown that in absence of compatibilization, nitrile rubber/nylon combinations have poor physical properties. Unless interfacial tension between the two components is relatively low, fine dispersion of rubber within the plastic matrix is not achieved. In

such cases, compatibilization required to reduce interfacial tension is usually achieved by using a rubber with functional groups that can react with the terminal amino groups in case of nylon 6 during melt-mixing to form a block copolymer at the interface. Polyamides are attractive materials for studies of such reactive compatibilization by virtue of their inherent chemical functionality through the amine or carboxyl end groups and probably the amide linkages.

In the past, maleated rubbers⁸ were used to achieve such compatibilization with nylon 6. However, most of the maleated rubbers were prepared by melt grafting wherein the volatility of the maleic anhydride monomer reduced the efficiency in such melt modifications. Carboxylated rubbers can provide a viable alternative. Peng⁹ has reported on carboxylated SBR/nylon 6 based thermoplastic vulcanizates. Similarly in carboxylated nitrile rubbers (XNBR), the carboxylic functionalities present can react with amine end groups on nylon 6 during melt-mixing. In this study, we report the effect of carboxylation in NBR phase on compatibility with nylon 6 assessed through dispersion studies using transmission electron microscopy (TEM). A similar study on the effect of carboxylation in NBR phase on the development of NBR/nylon 6/66/610 terpolymer based thermoplastic elastomeric compositions has been reported.¹⁰

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EXPERIMENTAL

Materials

The butadiene-acrylonitrile copolymers (NBR) used in this study were Krynac 34.50 {33% ACN, ML(1 + 4)

TABLE I
Melt Blending Conditions

Stage	Barrel temperature (°C)
<i>Extrusion condition</i>	
1	200
2	210
3	215
4	215
5	220
6	225
Die	230
<i>Injection condition</i>	
1	230
2	240
3	240
Die	250

Screw speed: 100 rpm; Feeding rate: 1.5 kg/h; Composition: PA6 (50, 40, 30), NBR (50, 60, 70); Mold temperature: 70°C.

100°C, 45} and two grades of its carboxylated variants Krynac X1.46 {32.5% ACN, ML(1 + 4) 100°C, 45, Carboxylic acid 1%} and Krynac X7.50 {27% ACN, ML(1 + 4) 100°C, 47, Carboxylic acid 7%} obtained from Bayer A.G., Germany. Rubbers with additional carboxylations of 0.5, 3, and 5% were made by blending the selected grades in required proportions in a two-roll mill. Polyamide 6, Gujlon M40RC (T_m 220°C, MFI 4) was provided by Gujarat State Fertilizers and Chemicals Limited, India.

Melt mixing

Methylol phenolic resin SP 1045 (3 phr) used as a crosslinking agent for the NBR phase was first mixed into the rubber in a brabender plasticorder under ambient conditions to prevent the crosslinking of the elastomer. The purpose was to ensure that crosslinking of NBR only occurred during melt blending with nylon 6 in the twin screw environment. The methylol phenolic resin premixed elastomer was then cold extruded into strands for subsequent pelletization using talc powder as the partitioning agent. Rubber pellets and the predried nylon 6 granules were separately fed into the twin screw extruder using loss-by weight feeding systems at different proportions as listed in Table I, melt mixed in a corotating 20 mm twin screw extruder (L/D 40, TM 20 Lab/40D model of Maris Corp., Italy). Using a recirculation channel, a mixing time of 5 min was kept for all the compositions. Das¹¹ has reported on a similar residence time at 225°C for the melt mixing of the same polyamide resin with hydrogenated nitrile rubber (HNBR).

Injection molding

Twin screw extruded blend pellets obtained from melt mixing were dried in oven at 100°C for 4 h and then injection molded using an Engel ES 200/45 injec-

tion molding machine as per the conditions listed in Table I.

DSC studies

Melting temperature T_m of the blend samples were measured using a Perkin-Elmer DSC 7 differential scanning calorimeter with the following procedure: the samples were heated up to 240°C and kept at this temperature for 10 min. Thereafter, the samples were cooled down to room temperature at 10°C/min and

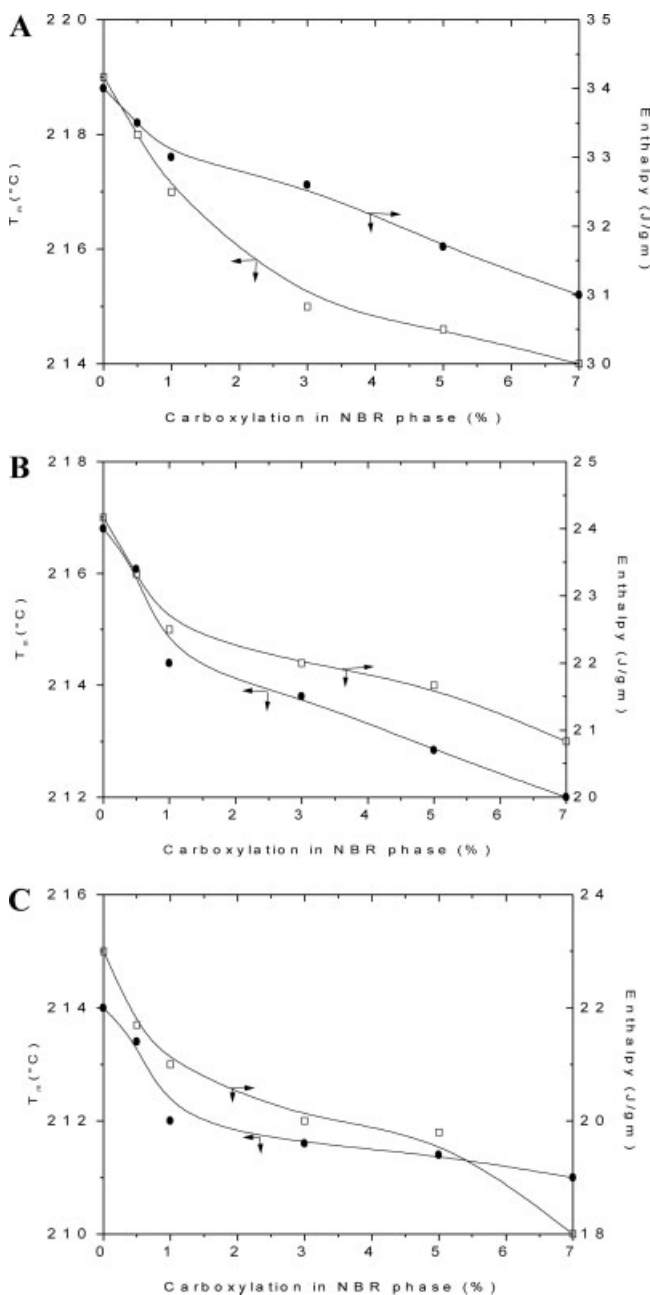


Figure 1 Variation of melting temperature T_m and enthalpy of melting, ΔH , with carboxylation in the NBR phase: (A) NBR/nylon 6 (50 : 50), (B) NBR/nylon 6 (60 : 40), (C) NBR/nylon 6 (70 : 30).

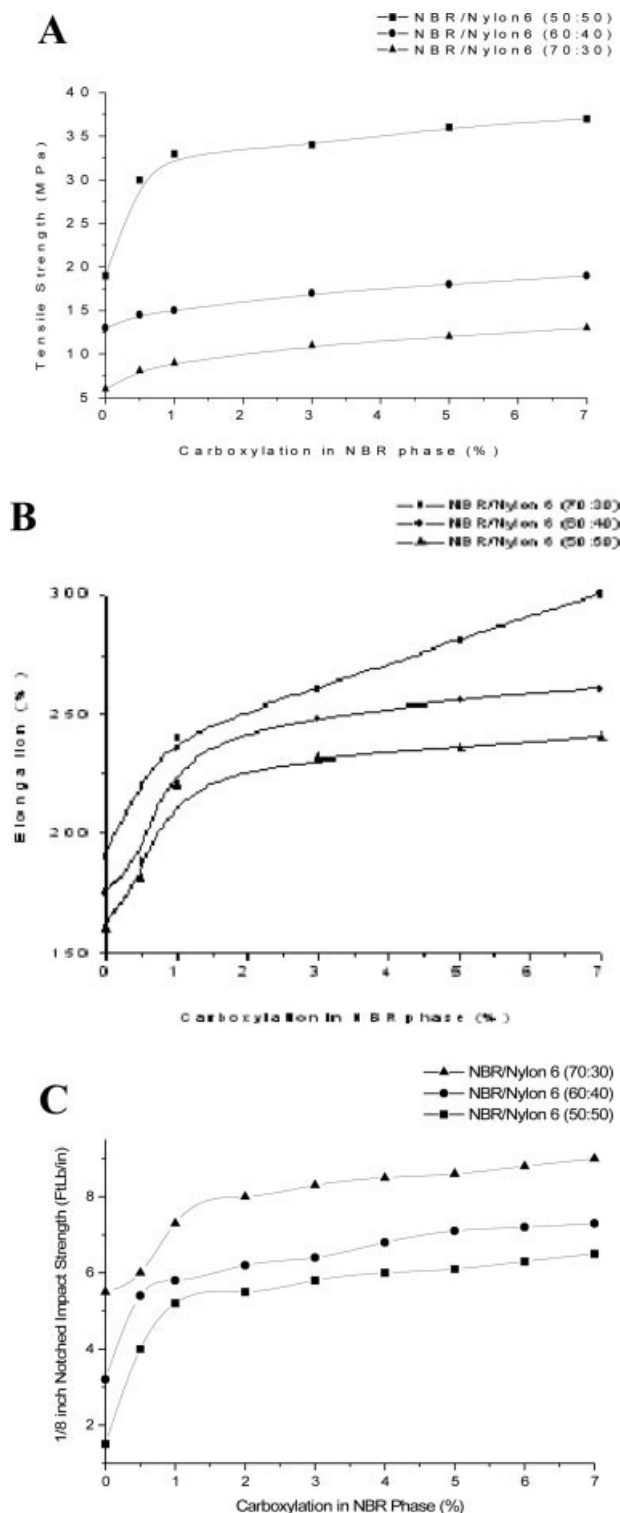


Figure 2 Variation of physical properties with the degree of carboxylation in the NBR phase: (A) tensile strength, (B) elongation at break, (C) notched Izod impact strength.

were again heated using the same ramp. T_m and enthalpies of melting ΔH obtained from the maximum and the area, respectively, of the melting peaks in the reheating scans are shown in Figure 2.

Mechanical properties

Tensile tests were carried out on the injection molded dumbbells using a crosshead speed of 500 mm/min in a Zwick 1445 model universal testing machine. Five replicate samples were tested for tensile data. Notched Izod impact tests were carried out on 1/8 in. molded bars as per ASTM 256 standard procedure on a Ceast impact testing machine. The impact values reported were averages of six measurements.

Dynamic properties

Dynamic mechanical properties were assessed for a representative (60 : 40) NBR/nylon 6 composition on a Metravib Viscoanalyseur VA 4000 model DMTA system for loss tangent ($\tan \delta$) measurement. The experiment was conducted under a tension-compression mode from -60°C to $+100^\circ\text{C}$ at a frequency of 5 Hz and 0.1% dynamic and 0.5% static strain at a programmed heating rate of $3^\circ\text{C}/\text{min}$.

Morphology studies

Morphological characterization of the melt-mixed strand cross sections were carried out on a Hitachi HT-300 model transmission electron microscope. Microtomed slices (80 nm) used for the study were stained with OsO_4 solution for 24 h to enhance contrast between the rubber and nylon phases.

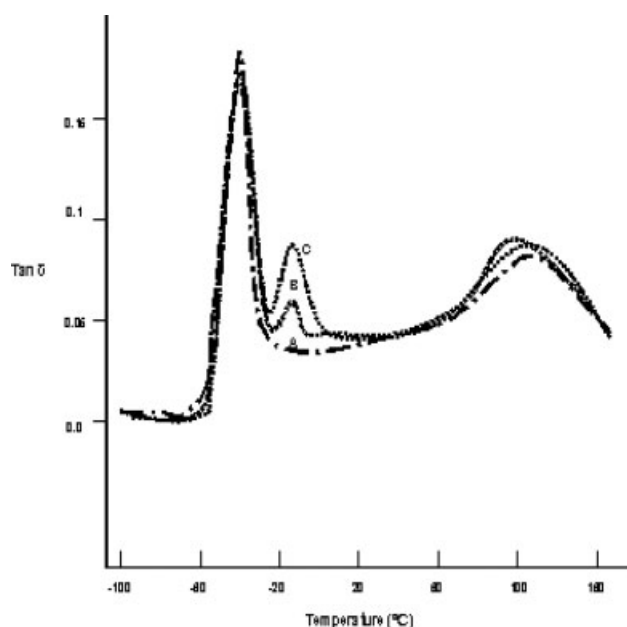


Figure 3 $\tan \delta$ traces for a representative NBR/nylon 6 (60 : 40) blend with (A) 0%, (B) 1%, and (C) 7% carboxylation in the NBR phase.

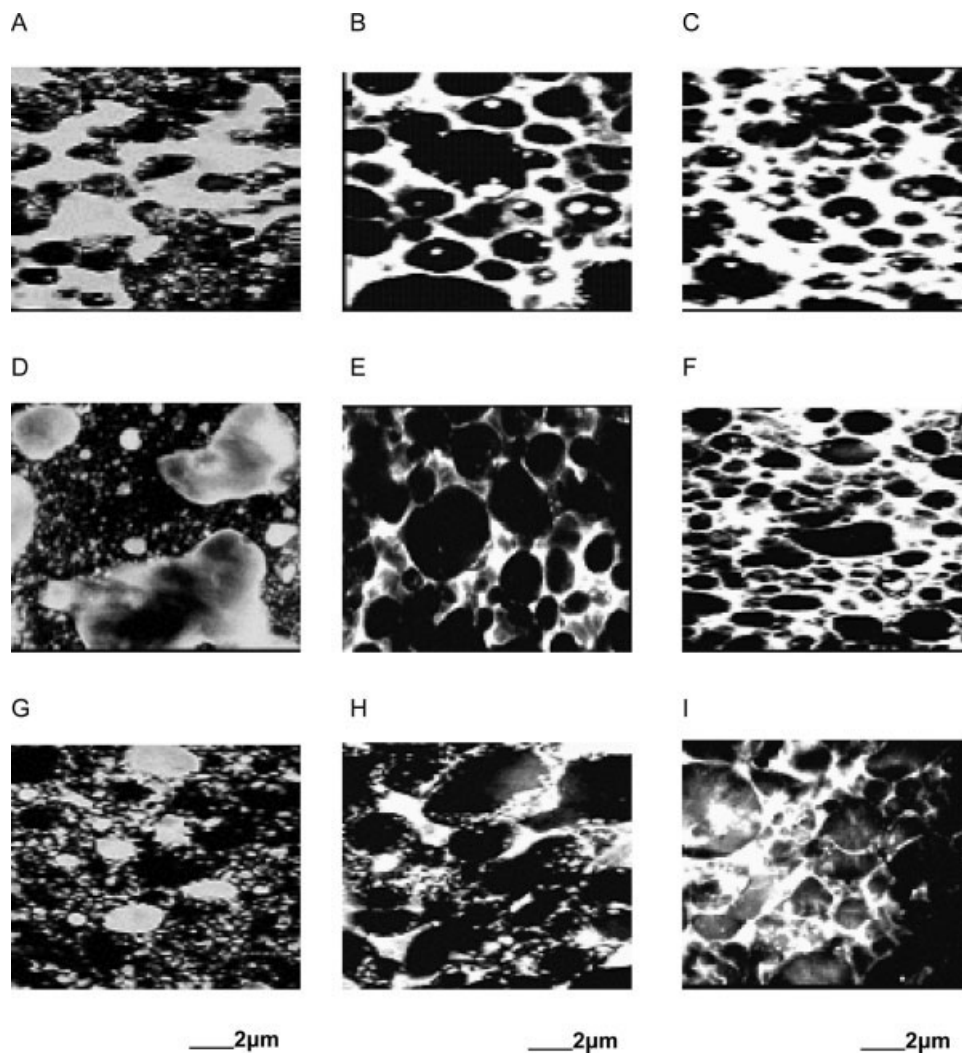


Figure 4 TEM micrographs of NBR/nylon 6 blends: (A) NBR (0% $-\text{COOH}$)/nylon 6 (50 : 50), (B) NBRNBR (1% $-\text{COOH}$)/nylon 6 (50 : 50), (C) (7% $-\text{COOH}$)/nylon 6 (50 : 50), (D) NBR (0% $-\text{COOH}$)/nylon 6 (60 : 40), (E) NBR (1% $-\text{COOH}$)/nylon 6 (60 : 40), (F) NBR (7% $-\text{COOH}$)/nylon 6 (60 : 40), (G) NBR (0% $-\text{COOH}$)/nylon 6 (70 : 30), (H) NBR (1% $-\text{COOH}$)/nylon 6 (70 : 30), (I) NBR (7% $-\text{COOH}$)/nylon 6 (70 : 30).

RESULTS AND DISCUSSION

Thermal behavior

Figure 1 shows melting temperatures T_m and the corresponding enthalpies for all blend compositions as a function of the degree of carboxylation in NBR phase. It is evident that with carboxylation in the rubber phase both T_m and ΔH values for nylon 6 decreased through all the blend proportions.

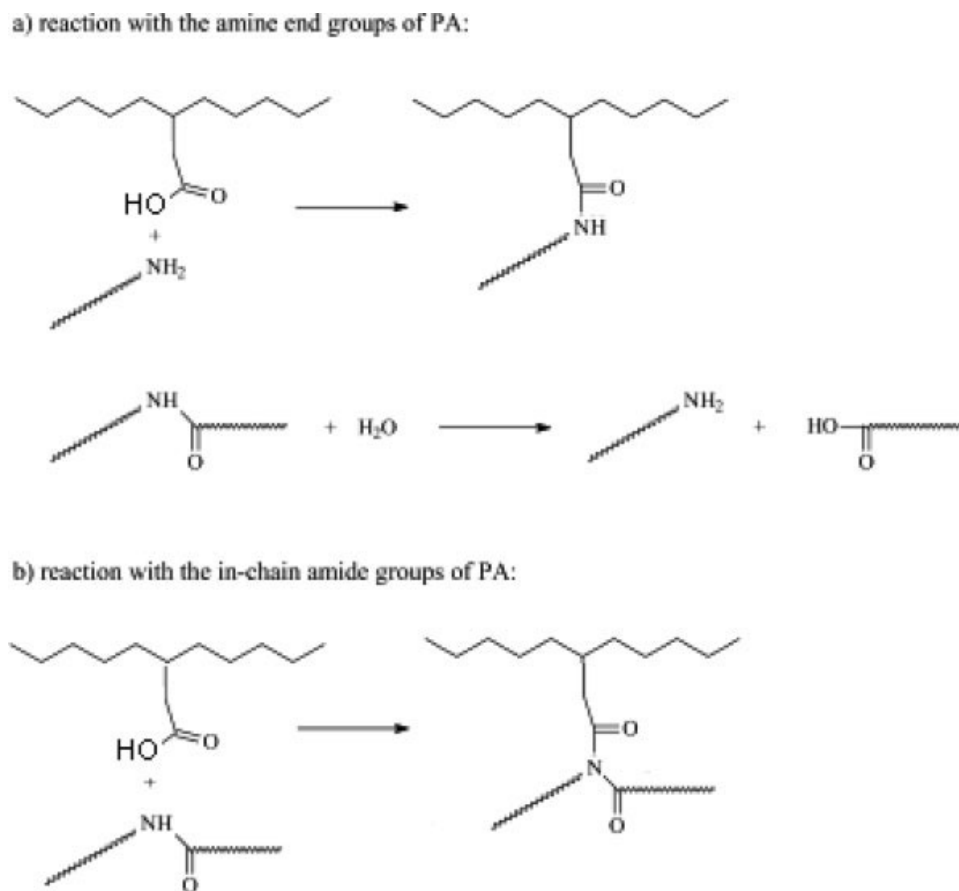
Mechanical properties

Figure 2(A) shows that the tensile strength of blends increased with carboxylation in the NBR phase. For example, tensile strength of the NBR/nylon 6 = 50/50 blends increased from 18.5 to 37 MPa as the degree of carboxylation was increased to 7%. Corresponding blends with lower degrees of carboxylation

resulted in relatively lower tensile strengths as shown in Figure 2(A). Similar trends were observed through the other blend proportions.

Tensile elongations from these blends also improved with degree of carboxylation in the NBR phase [Fig. 2(B)]. These carboxylated blends in general had finer phase domain size, greater interfacial contact, and higher interfacial adhesion when compared with the uncarboxylated blends. The *in situ* generated NBR-g-Nylon 6 graft copolymer is believed to be responsible for such a highly effective compatibilization for the NBR/Nylon 6 blends. Formation of this compatibilizer increased miscibility between NBR and nylon 6, which reflected in the improvement of mechanical properties.

The notched impact values [Fig. 2(C)] increased with the NBR content and also with increased degree of carboxylation in the rubber phase. Improved impact



Scheme 1 Plausible mechanism of reactive compatibilization of nylon-6 with carboxylated NBR through *in-situ* amide formation.

values were indicative of enhanced compatibility and better interfacial adhesion.

Dynamic properties

Figure 3 shows the $\tan \delta$ traces of (60 : 40) NBR/nylon 6 blends. Glass transition (T_g) of the blend components were well characterized by the two distinct $\tan \delta$ peaks. As the degree of carboxylation in NBR phase was increased, the respective glass transitions moved closure indicating better miscibility. With carboxylation, an additional $\tan \delta$ peak was observed when compared with the uncarboxylated blends. This was probably due to the graft copolymer generated by *in situ* amide formation between the $-\text{COOH}$ groups in carboxylated NBR and the $-\text{NH}_2$ end groups in nylon 6.

Morphology studies

TEM micrographs of the blend samples are shown in Figure 4. In the 50 : 50 NBR/nylon 6 blend, a co-continuous phase was obtained. This can be seen from micrograph in Figure 4(A) for the NBR/Nylon 6 blend in which the rubber used was without carboxylation.

Morphology in such a blend represents the final balance of rubber particle break down and coalescence rates at the end of the melt mixing in twin screw extruder.¹² However, using carboxylated NBR, it was possible to achieve a fine dispersion of the rubber within nylon matrix as shown in Figure 4(B,C). Blends with 7% carboxylation [Fig. 4(C)] resulted in even finer dispersion of the rubber when compared with that obtained with 1% carboxylation in the NBR phase. [Fig. 4(B)] The principle of reactive compatibilization is assumed to be due to the formation of NBR-g-Nylon 6 graft copolymer as illustrated in (Scheme 1). The copolymer may form by the reaction of the carboxylic acid groups in NBR either with the amine end groups of Nylon 6 or with the in-chain amide linkages. According to the first mechanism, the formation of the amide bond linking the nylon graft to the NBR chain involves the evolution of a water molecule. In the blending conditions, water may promote the hydrolysis of Nylon 6, so that the two reaction mechanisms do in-fact lead to the same products.¹³ According to the results of the model experiments carried out by Maréchal,¹⁴ the reactions involved in mechanism are (a) considerably faster than that of mechanism, (b) despite the much higher concentration of the amide

groups with respect to the amine end groups. This graft copolymer might have preferentially situated between the dispersing nylon and the dispersed NBR phase thereby reducing the interfacial tension between the two phases and enhancing steric hindrance between the rubber droplets resulting in a finer and stable dispersion of NBR in Nylon 6 matrix.

By increasing the proportion of rubber from 50 to 60 wt %, phase inversion took place. Morphologies of NBR/Nylon 6 blends with 60 wt % of rubber with 0%, 1 wt %, and 7 wt % carboxylation are presented in the Figure 4(D–F), respectively. In absence of reactive compatibilisation (0% carboxylation in NBR phase), a phase inversion took place as the amount of rubber was increased to 60 wt % [Fig. 4(D)] wherein nylon seemed to be dispersed within the continuous NBR matrix. However, through reactive compatibilization using carboxylated NBRs, phase inversion occurred with the rubber being dispersed in nylon 6 matrix¹⁰ [Fig. 4(E,F)].

NBR formed the continuous phase with nylon 6 remaining dispersed in blends with 70 wt % of rubber [Fig. 4(G)]. Even with reactive compatibilization (1% carboxylation in NBR phase), phase inversion did not occur during melt mixing, probably because of limited steric hindrance between NBR particles due to insufficient amount of NBR-g-Nylon 6 graft copolymers formed with 1% carboxylation. As the degree of carboxylation was increased to 7 wt %, sufficient quantity of the graft copolymer generated during melt mixing ensured phase inversion and subsequent steric stabilization of the dispersed rubber droplets [Fig. 4(I)].

CONCLUSIONS

Generally, immiscible NBR/Nylon 6 blends have inferior mechanical properties when compared with those of the individual blend components. The phase morphology in such blends depends strongly on their processing history. Such an immiscibility between blend components arise out of unfavorable interaction between their molecular segments which leads to (a) large interfacial tension in the melt, which makes it difficult to disperse one component finely into the other during mixing and encourages subsequent coalescence and (b) poor interfacial adhesion in the solid state, leading to mechanical failure through interfacial defects.

In our present study on polymer blends of nitrile rubber (NBR) and nylon 6, developed by twin screw blending, a stable and fine dispersion of the former into the latter was achieved through compatibilization using carboxylated nitrile rubber (XNBR). The resulting NBR-g-Nylon 6 graft copolymer generated *in situ* during melt mixing via the interfacial reaction between the —COOH groups in XNBR, and the —NH₂ end groups in nylon 6 have been effective in generating a fine and stable dispersion of the rubber within the polyamide matrix achieved by the use of the intense mixing capabilities of the fully intermeshing, corotating twin screw extruder. This has been established from the morphology studies using transmission electron microscopy.

The success in the compatibilization has also been reflected in the improvement of physical properties of the carboxylated blends. The fact that through compatibilization simultaneous improvements in tensile and elongation properties were achieved is indicative of the elastic nature of the compatibilized blends having finer dispersion of the nitrile rubber within the polyamide matrix.

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