

Development of Acrylonitrile-Butadiene (NBR)/Polyamide Thermoplastic Elastomeric Compositions: Effect of Carboxylation in the NBR Phase

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ABSTRACT: The current investigation was aimed at assessing the effect of carboxylation of NBR phase in dynamically vulcanized NBR/low-melting polyamide thermoplastic elastomeric compositions. Improved strength and set properties were achieved because of better compatibilization with carboxylated NBRs. The dispersion of the rubber became homogeneous and finer with increase in the degree of carboxylation. Glass transition studies by DMA and DSC suggested the presence of a compatibilizing block copoly-

mer generated *in situ* by the reaction between the —COOH groups in the rubber and the —NH₂ groups in the polyamide during melt-mixing. The reaction was studied for a representative 60 : 40 rubber/plastic blend by DSC. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1008–1012, 2006

Key words: polyamides; blends; compatibilization; glass transition

INTRODUCTION

In the past, much research has focused on the development of thermoplastic elastomeric compositions based on nylon polymers and nitrile rubber.^{1–5} Such blend combinations, when properly designed, are expected to have excellent hot oil resistance and good strength properties particularly at elevated temperatures. Coran¹ reported on NBR–nylon thermoplastic elastomeric compositions prepared by dynamic vulcanization. Similar studies were conducted on a NBR–nylon 6 system; dynamically vulcanized by various types of curing systems.² Meherazaden³ has studied the impact modification of polyamide 11 with NBR.

However, earlier studies have shown that, unless compatibilized, NBR/polyamide combinations have poor physical properties. Bhowmick^{4,5} has studied the role of various chemical compatibilizers in the reactive processing of a dynamically vulcanized 50 : 50 HNBR/nylon blend. In the past, mostly maleated rubbers were used for achieving better compatibility with polyamides. However, most of the maleated rubbers were prepared by melt mixing, wherein the volatility of maleic anhydride monomer reduced the grafting efficiency in such modifications. Carboxylated rubbers can provide a viable alternative. Peng⁶ has reported on

a polyamide 6-based thermoplastic vulcanizate using carboxylated SBR. Similarly in carboxylated NBRs, the carboxyl groups can react with the amino groups present in polyamides during melt mixing. However, the melting points of common nylons like nylon 6 and nylon 66 are overly high for safe processing with unsaturated elastomers like NBR. Lower melting polyamides provide an ideal opportunity in this respect. In this study, we report on the development of thermoplastic elastomeric compositions based on NBR and a low-melting polyamide resin. Its melting point (150°C) allowed safe processing of the elastomers. Compositions were prepared by melt-mixing and dynamic vulcanization techniques. Better properties were achieved with the carboxylated variants of the rubber used in this study.

EXPERIMENTAL

Materials

The low-melting polyamide, 6/66/610 terpolymer, used in this study was Elvamide 8061 ($T_m = 150^\circ\text{C}$, density = 1.08 g/mL) from DuPont (India). This polyamide resin, like nylons, is suitable for molding and extrusion. It is tough and abrasion resistant but is softer and more flexible than conventional nylons.

The acrylonitrile-butadiene (NBR) elastomers employed were Krynac 34.50 [33% ACN, ML (1 + 4) 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%

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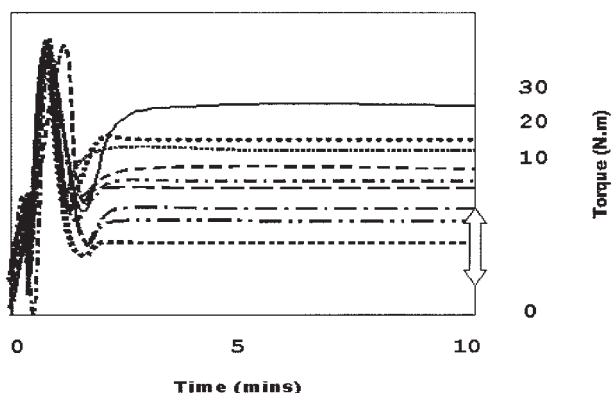


Figure 1 The torque *versus* time for the following combinations: (—) 70 : 30 NBR/polyamide; (···) 70 : 30 XNBR (1% —COOH)/polyamide; (- - -) 70 : 30 XNBR (7% —COOH)/polyamide; (---) 60 : 40 NBR/polyamide; (-·-·) 60 : 40 XNBR (1% —COOH)/polyamide; (— — —) 60 : 40 XNBR (7% —COOH)/polyamide; (— · — ·) 50 : 30 NBR/polyamide; (— · · —) 50 : 30 XNBR (1% —COOH)/polyamide; (← ← ←) 50 : 30 XNBR (7% —COOH)/polyamide.

ACN, ML (1 + 4) 100°C = 47, carboxylic acid = 7%] from Bayer were used in this study.

Blend preparation

The NBR/Elvamide blends were prepared by melt-mixing in a Brabender Plasticorder PL 2200 mixer, using cam type rotors at 160°C and 80 rpm. For dynamic vulcanization, the curing agents (0.2 parts of sulfur, 2 parts of tetramethylthiuram disulfide, 1 part of morpholinobenzothiazole, 5 parts of zinc oxide, and 1 part of stearic acid per 100 parts of rubber used in the blend) were added after the initial homogenization of the polymers manifested by constant torques and all the mixing cycles were continued up to 10 min.

Measurement of properties

Mechanical characterization

The melt-mixed samples were compression molded into sheets used for dumbbells suitable for tensile

testing. Five replicate samples were tested for tensile data. Dumbbells were strained using a crosshead at a speed of 500 mm/min in a Zwick 1445 model universal testing machine. Dumbbells used for determination of tension set were stretched to 50% strain for 10 min and then relaxed for another 10 min.

Swelling studies

Swelling behavior of the samples was investigated using the standard procedure in ASTM oil 3 for 20 h at 70°C.

Thermal analysis

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

DSC. The DSC scans of the representative 60 : 40 rubber/plastic blend composition were made by analyzing them in a PerkinElmer DSC 7 model differential scanning calorimeter. The temperature scans were taken from -100°C to +100°C at a heating rate of 10°C/min. Liquid nitrogen was used as the coolant.

For analysis of the possible reaction between the carboxylic groups in the rubber and the amino functionalities in the polyamide, 60 : 40 rubber/plastic compositions were selected. The polyamide was first dissolved in formic acid and the resulting viscous solution was subsequently added to the rubber in a Brabender PL2200 internal mixer and mixed at 80 rpm at room temperature. The resulting blends were made into sheets and dried overnight for complete evaporation of the acid. The blends were subsequently analyzed by DSC. The samples were ramped to 160°C in 2 min and were isothermally held at that temperature for a period of 6 min.

TABLE I
Physical and Mechanical Properties of Polyamide/NBR Blends

| Composition | Tensile strength (MPa) | 100% modulus | Elongation at break (%) | Hardness shore D | Volume swell in oil (%) | Tension set (%) |
|--|------------------------|--------------|-------------------------|------------------|-------------------------|-----------------|
| NBR/Elvamide (50 : 50) | 5.6 | 5.3 | 150 | 36 | 2 | 29 |
| NBR/Elvamide (1% carboxylic acid; 50 : 50) | 8.5 | 7.5 | 170 | 40 | 1.7 | 17 |
| NSR/Elvamide (7% carboxylic acid; 50 : 50) | 20.5 | 9.6 | 370 | 42 | 1.5 | 13.5 |
| NBR/Elvamide (60 : 40) | 4.2 | 3.2 | 180 | 32 | 4.8 | 25 |
| NBR/Elvamide (1% carboxylic acid; 60 : 40) | 7.5 | 6.3 | 240 | 37 | 3.6 | 14 |
| NBR/Elvamide (7% carboxylic acid; 60 : 40) | 15.0 | 6.6 | 380 | 39 | 3 | 11 |
| NBR/Elvamide (70 : 30) | 2.6 | 2.0 | 200 | 20 | 6.7 | 20 |
| NBR/Elvamide (1% carboxylic acid; 70 : 30) | 5.0 | 3.8 | 260 | 23 | 6 | 11 |
| NBR/Elvamide (7% carboxylic acid; 70 : 30) | 9.4 | 4.1 | 400 | 25 | 5.3 | 8.75 |

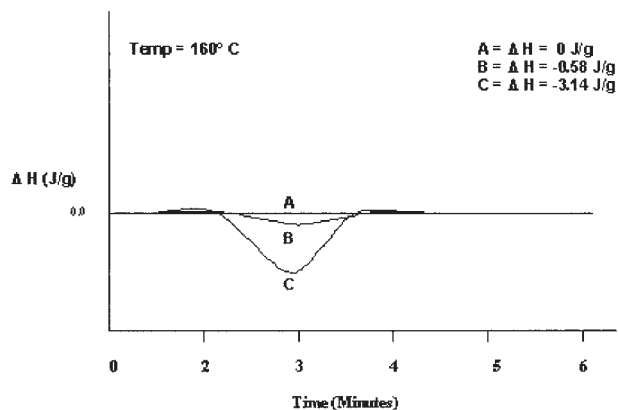


Figure 2 Isothermal DSC scans for a representative 60 : 40 NBR/polyamide composition: (A) 60 : 40 NBR/polyamide; (B) 60 : 40 XNBR (1% —COOH)/polyamide; (C) 60 : 40 XNBR (7% —COOH)/polyamide.

Structure analysis

The morphology of the representative 60 : 40 rubber/plastic composition was analyzed with a Philips 500 model scanning electron microscope (SEM). The molded specimens were fractured in liquid nitrogen. The rubber phase was subsequently stained with a 2% OsO₄ solution. Prior to analysis the samples were sputter coated with Au/Pd alloy.

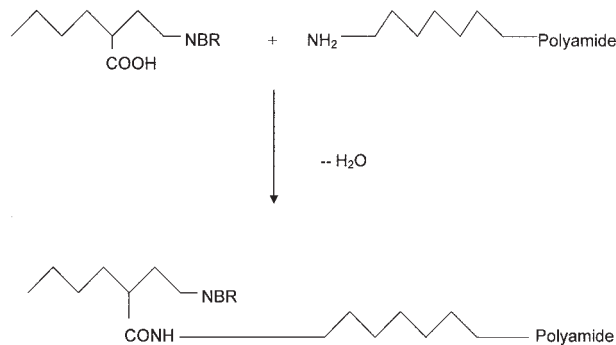
RESULTS AND DISCUSSION

Blending

Figure 1 shows the torque *versus* time plots for all the compositions mixed and cured by the dynamic vulcanization technique. Increase in the NBR proportion led to enhanced torques. During dynamic vulcanization, the torque increased for all the compositions because of crosslink generation. Compositions with higher rubber contents exhibited higher torque values during cure. In compositions where NBRs with 0% carboxylation were used, the increase in the torque values were less, probably on account of lower viscosities due to poor compatibility among the polymeric phases involved. This was also evident from the inferior physical and mechanical properties obtained in such blends.

Physical and mechanical properties

Table I lists the physical and mechanical properties of the blends. Carboxylation in the NBR phase resulted in significant improvement in strength properties observed at all blend proportions. As expected the strength properties deteriorated with increase in the rubber proportion in the blends, with concurrent improvements in the tension set properties. However, with increase in rubber content, the hardness de-



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

creased, compositions with carboxylated NBRs showed higher hardnesses. The swelling properties improved with reduction in rubber proportion and with a higher degree of carboxylation in the rubber phase. However, the higher elongation values, observed with the increase in the degree of carboxylation, were probably due to better compatibilization of the carboxylated elastomers with the polyamide resin. The Elvamide resins are known to have reactive —NH₂ groups,⁷ which could have undergone *in situ* amide formation with the —COOH groups in NBR. This had probably reduced the interfacial tension between the two phases enhancing the interfacial adhe-

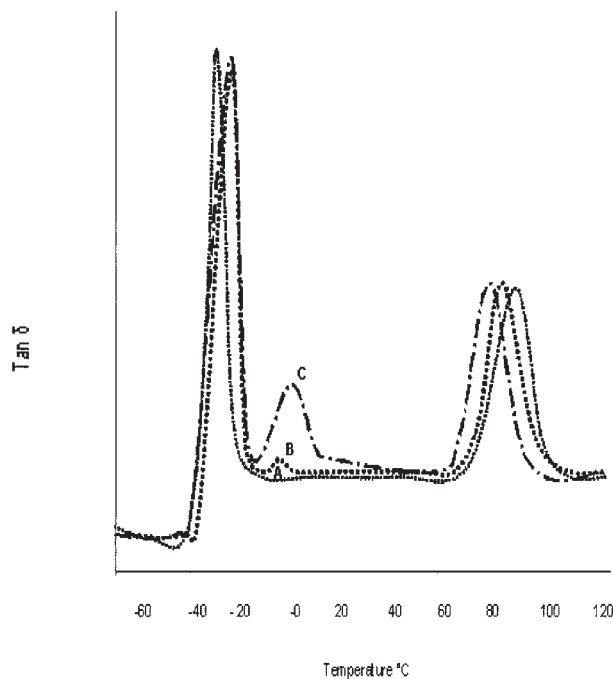


Figure 3 Tan δ traces for a representative 60 : 40 NBR/polyamide composition: (A) 60 : 40 NBR/polyamide; (B) 60 : 40 XNBR (1% —COOH)/polyamide; (C) 60 : 40 XNBR (7% —COOH)/polyamide.

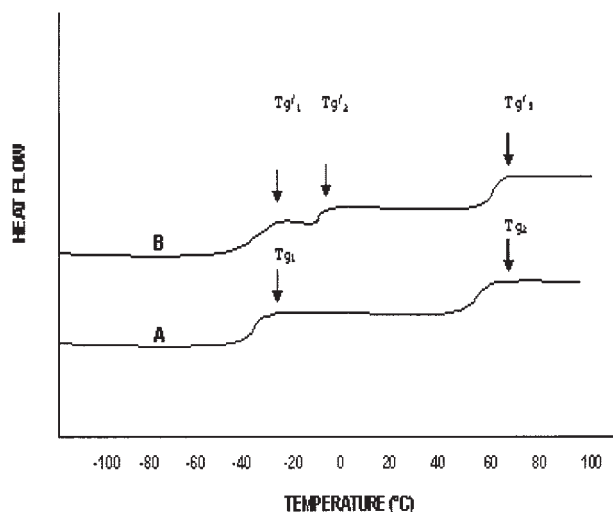


Figure 4 DSC scans traces for a representative 60 : 40 NBR/polyamide composition: (A) 60 : 40 NBR/polyamide; (B) 60 : 40 XNBR (7% —COOH)/polyamide.

sion. To study this reaction the samples with 60 : 40 rubber/plastic blend proportions were prepared at room temperature for DSC analysis, employing the method described earlier. Figure 2 shows the isothermal DSC scans at 160°C. For all the samples no endothermic transitions were observed. This suggested that the polyamide had already melted before the isothermal scans were initiated. The compositions with carboxylated NBRs exhibited exothermic transitions at around 3 min. This was not observed in the blend where the NBR phase was not carboxylated. An exothermic enthalpy of -0.58 J/g was observed for the combination with 1% —COOH in the NBR phase as compared to that of -3.14 J/g in the blend with 7% —COOH in the rubber phase. Such an exothermic event can be described in terms of the condensation reaction between the —COOH groups in the NBR phase and the —NH₂ groups in the polyamide. The higher heat of reaction observed for the blend with 7% —COOH in the NBR phase suggests the quantitative nature of the reaction being studied. A schematic representation of such a reaction is given in Scheme 1.

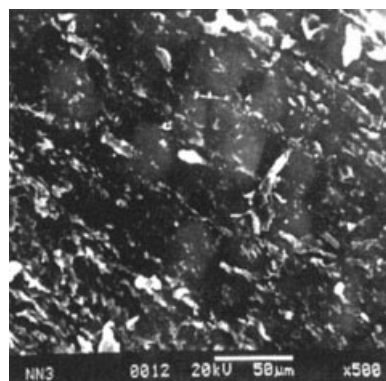
Performance in oil

Table I lists the percentage swelling for all the compositions. Harder compositions, with higher proportions of polyamide, had reduced swelling. Again, with increased percentage of carboxylation in the NBR phase, better swelling resistances were observed.

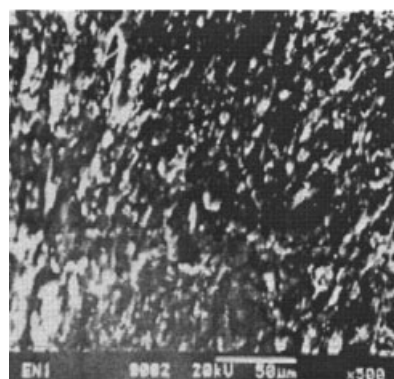
Thermal properties

Figure 3 shows the $\tan \delta$ traces of sulfur-cured 60 : 40 NBR/polyamide blends. As the degree of carboxyla-

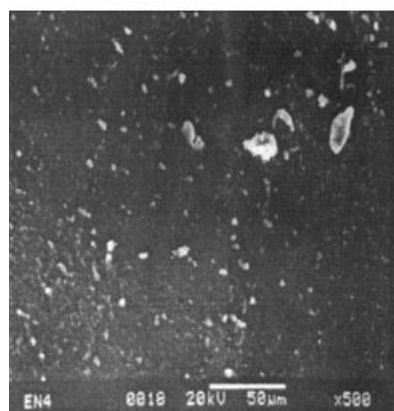
tion in the NBR phase was increased, the glass transition temperature (T_g) values of the NBR and the polyamide shifted towards each other indicating better compatibility. Additional $\tan \delta$ peaks were observed in the carboxylated samples, probably due to the block copolymer generation by *in situ* amide formation be-



A



B



C

Figure 5 SEM micrographs of a 60 : 40 NBR/polyamide composition: (A) 60 : 40 NBR/polyamide; (B) 60 : 40 XNBR (1% —COOH)/polyamide; (C) 60 : 40 XNBR (7% —COOH)/polyamide.

tween the —COOH groups in the carboxylated NBR and the —NH₂ groups in the polyamide resin.

Figure 4 shows the DSC scans of the sulfur-cured 60 : 40 NBR/polyamide blends. Both the NBR and polyamide phases showed distinct glass transitions. Sample B, with 7% carboxylation in the NBR phase, exhibited an additional glass transition at around 0°C. The observation was in accordance with DMA results.

Morphology

The fractured surface of a representative 60 : 40 NBR/polyamide composition was studied by using SEM. Figure 5 shows the SEM micrographs. Without carboxylation in the rubber phase, a cocontinuous phase morphology was obtained [Fig. 5(a)]. However, with carboxylation phase inversion occurred [Fig. 5(b)] and the rubber was dispersed within the polyamide matrix, the domain size of which decreased with increased carboxylation [Fig. 5(c)]. This is indicative of better compatibilization being achieved, as was also manifested in the superior physical properties obtained. With carboxylation, the XNBR-polyamide block copolymer generated during melt-mixing reduced the interfacial tension between the two phases by positioning itself between the phases, thereby en-

hancing interfacial adhesion assessed by SEM studies and improved physical properties in such blends.

CONCLUSIONS

Thermoplastic elastomeric compositions, based on a low-melting polyamide resin and NBR, were investigated. Better compatibility was achieved through the carboxylated variants of the NBR leading to improvement in tensile properties, hardness, swelling in oil and set properties. DMA and DSC suggested enhanced compatibility in the case of carboxylation in the rubber phase, because of a compatibilizing XNBR-polyamide block copolymer generated by *in situ* amide formation between the —COOH groups in the carboxylated NBR and the —NH₂ groups in the polyamide resin.

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