Dynamically Vulcanized Polypropylene/Nitrile Rubber Blends: The Effect of Peroxide/Bis-Maleimide Curing System and Different Compatibilizing Systems

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ABSTRACT: In this study, the efficiency of dicumyl peroxide (DCP) in combination with N,N'-m-phenylene-bis-maleimide (BMI) as a crosslinking system for the polypropylene (PP)/nitrile rubber (NBR) (30 : 70 wt %) thermoplastic elastomers was investigated in the presence of compatibilizing agents. The compatibilization was carried out by maleic anhydride-*grafted*-PP (PP-*g*-MA)/amino compound and glycidyl methacrylate-*grafted*-PP (PP-*g*-GMA) with or without amino compound. They were employed in a proportion of 5 wt % together with different amounts of carboxylated NBR (XNBR). Excellent mechanical properties were achieved without the addition of compatibilizer, suggesting that BMI should act as compatibilizing agent. The other functionalized systems exerted an additional improvement on tensile properties and reprocessing ability. The mechanical and dynamic mechanical properties, oil resistance, and morphology were investigated. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3566–3573, 2008

Key words: polypropylene; nitrile rubber; TPV; reactive compatibilization; dynamic vulcanization

INTRODUCTION

Thermoplastic elastomers prepared by blending thermoplastic with nitrile rubber (NBR) has been received a lot of interest because of the combination of the oil-resistant property, the excellent mechanical properties and processing behavior. Some of these blends include polyamide/NBR,[1–3] poly(vinyl chloride) (PVC)/NBR,[4–5] polyethylene/NBR,[6–8] styrene-acrylonitrile copolymers (SAN)/NBR,[9] poly(ethylene terephtalate) (PET)/NBR,[10] ethylene vinyl acetate copolymer (EVA)/NBR,[11–14] and polypropylene/NBR.[15–23] Most of these studies involve the dynamic vulcanization process, which consists of crosslinking the rubber particles during it melt mixing with molten thermoplastics. If the elastomer particles are small enough, several important properties are improved

with this procedure, such as permanent set, ultimate tensile properties, fatigue resistance, resistance to attack by fluids, stability of phase morphology in the melt, melt strength, and thermoplastic processability.[24] To achieve these characteristics, it is important to select an appropriate curing agent and a good interfacial agent. The addition of a suitable compatibilizer for binary immiscible blends should reduce the interfacial energy between the phases, permitting a finer dispersion during mixing and a better interfacial adhesion. The compatibilizing agent is usually a block or graft copolymer whose segments are miscible with each blend component. It can be previously prepared and introduced into the blend or be formed *in situ* through the reactive blend processing.[25] The last approach offers several technological advantages, such as the graft or block copolymers resulted from the reaction between the functionalized polymers are preferentially located at the interface, minimizing the formation of micelles inside the homopolymer phase; lower amount of these functionalized polymers are consequently required; functionalized polymers are easily prepared by copolymerization or by graft reactions during the extrusion process or batch mixing.[26]

Polypropylene/nitrile rubber blends prepared by dynamic vulcanization have been studied for more

than three decades ago, but still deserve attention nowadays because of its good properties that can be still improved by changing some processing parameters, introducing new additives or even combining different compatibilizing and curing systems. The first report regarding PP/NBR-based thermoplastic vulcanizates (TPV) was published by Coran and Patel in 1978,[15] but only a marginal success has been obtained because of the large surface energy difference between the two types of polymers. Lately, the same authors have published a good system to impart a technological compatibilization for this blend.[16] The blends were compatibilized by phenolic-modified polypropylene and cured with dimethylol phenolic compound in the presence of stannous chloride as the activator. The phenolic resin in the presence of a Lewis acid reacts with the double bond located at the end of the PP chain and also along the NBR chain, forming a good anchorage between the phases. This compatibilizing system was then employed by George et al.[17–19] in several studies involving PP/NBR blends dynamically vulcanized with accelerated sulfur, peroxide, or mixed systems. Polypropylene functionalized with maleic anhydride (PP-*g*-MA) was also employed in blends vulcanized with phenolic resin[16] and with accelerated sulfur system or peroxide.[18] The first system was used in combination with amine-terminated NBR to promote the coupling between the phases. The NBR containing amino groups was also substituted by a polyamine compound and carboxylated NBR.[20–22]

Polypropylene functionalized with glycidyl methacrylate (PP-*g*-GMA) was employed together with polyamine compound as compatibilizing system for PP/NBR cured with sulfur, peroxide, or phenolic resin.[23] According to the authors, the highest tensile properties were achieved by using *tert*-butyl phenolic resin as the curing agent. On the other hand, George et al.[19] have achieved smaller rubber particle size and higher storage modulus in peroxide-cured PP/NBR blends when compared with the accelerated sulfur system.

As summarized in this section, several different combinations of compatibilizer/curing systems have been employed in PP/NBR blends, but it is difficult to compare the results because of the different polymer samples employed, different processing and molding conditions, and different characterization techniques.

The use of peroxide as the curing system on the development of thermoplastic vulcanizates is advantageous because of its known ability to impart good high-temperature resistance and good elastic behavior in particular compression set.[27] However, it can degrade the PP matrix during melt mixing 185°C. Bis-maleimide was found to be an effective cross-

linking agent in the presence of a radical activator, like an organic peroxide.[28–32] It has been successfully employed as curing agent in several elastomers,[29] and some thermoplastic elastomers based on PP and natural rubber, EPDM or SBR.[27,31–32] The success of this compound as a crosslinking agent for TPVs is based on its ability to crosslink the unsaturated elastomer particles in the polyolefin matrices without promoting degradation or crosslinking of the matrices, probably because the radical generated on the bis-maleimide molecule is not reactive enough to abstract hydrogen radical at the secondary or tertiary carbons of polypropylene.

To the best of our knowledge, there is no systematic study involving the use of bismaleimide as the cocuring agent for PP/NBR vulcanized blends.

The aim of this work is to investigate the efficiency of *N,N'-m*-phenylene-bis-maleimide (BMI) as the cocuring agent for the PP/NBR vulcanized blends compatibilized with PP-*g*-MA and PP-*g*-GMA. To promote an effective interaction between the phases, a small amount of XNBR was also employed. The compatibilization with PP-*g*-MA and XNBR as the coreactive functional groups was performed in the presence of a small amount of triethylene-tetramine (TETA) to impart the adhesion. The compatibilization with PP-*g*-GMA was performed in the presence or absence of TETA. In this case, TETA may not be necessary because the epoxide groups can react directly with the carboxyl groups. Figure 1 illustrates the possible reactions occurring during the reactive compatibilization with these different systems. The effect of the compatibilization on mechanical, dynamic mechanical, and morphological properties of PP/NBR dynamically vulcanized blends is discussed in detail.

EXPERIMENTAL

Materials

NBR [28 wt % acrylonitrile; Mooney viscosity (ML 1 + 4 at 100°C) = 60] and carboxylated nitrile rubber (XNBR) (NX43G) [28 wt % of acrylonitrile; carboxyl content = 4%] were kindly supplied by Petroflex Ind. Com. S.A. Rio de Janeiro, Brazil. Polypropylene (melt flow index = 3.5 g/10 min at 230°C/2.16 kg) was supplied by Braskem S.A., Rio Grande do Sul, Brazil. Maleic anhydride-modified polypropylene (PP-*g*-MA) (Polybond 3200) (melt flow index = 115 g/10 min at 190°C/2.16 kg; 1 wt % of maleic anhydride) was purchased from Crompton, Middlebury, CT. Glycidyl methacrylate-modified PP (PP-*g*-GMA) (MFI = 3.25 g/10 min at 190°C/2.16 kg; 1 wt % of epoxide groups) was prepared according to the standard procedure.[33] BMI (HVA-2) was purchased by DuPont Dow Elastomers (São Paolo, Brazil).
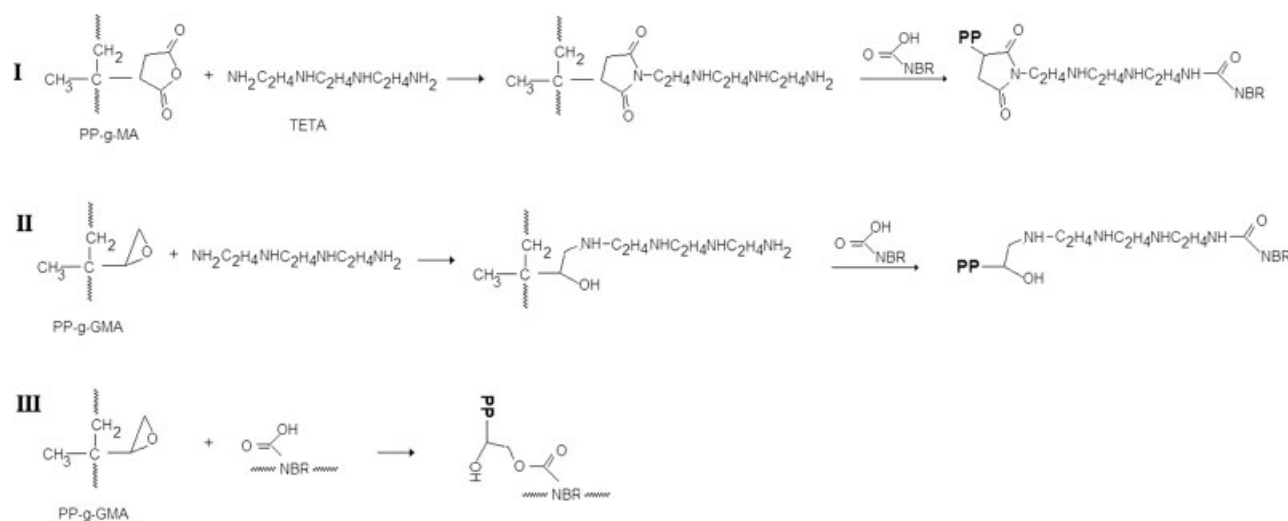
Figure 1 Schemes of the possible reactions that occur during the reactive compatibilization of NBR/PP blends by PP-*g*-MA or PP-*g*-GMA and XNBR, assisted by TETA.

Dicumyl peroxide was supplied by Retilox, São Paulo, Brazil; TETA was purchased from Dow Química do Brasil, São Paulo, Brazil; Naugard76 was purchased from Crompton; and dioctyl phthalate (DOP) was supplied by Petroflex Ind. Com.

Blend preparation

Masterbatch containing NBR and DOP (10 phr of DOP related to the NBR) was preblended in a Plastograph Brabender (Duisburg, Germany) equipped with a W50 EHT mixer and banbury rotors at 60 rpm and 50°C for 7 min. The preparation of NBR/PP thermoplastic elastomer was performed at 185°C and 80 rpm in the same Plastograph Brabender. PP was added together with the compatibilizer. Two minutes later, TETA was added and left to react for 1 min. Then, the masterbatch containing NBR and DOP was added followed by XNBR. Mixing was continued for 2 min, and then BMI (2.1 phr) with DCP (0.21 phr) were added. Three minutes after the addition of the curative, the antioxidant, Naugard (1 phr), was added and the mixing was stopped after 1 min.

The mixes were injection-molded at 240°C with a pressure of 300 Bar, in a Haake mini-injector, model.miniJet.

Physical testing

Tensile tests were carried out as per ASTM D 638-5 method using dumb bell-shaped samples at a crosshead speed of 200 mm/min with an Universal testing machine (Instron 5569).

For the compression set test, cylindrical test specimens (12.5-mm diameter and 6.0-mm thickness) were injected at 240°C. The tests were done by pressing the specimens to 45% of their original thickness, as per ASTM D 395-85 and aged in an air oven of controlled ventilation at 100°C for 70 h before determining their thickness recovery upon release of the compressive force.

Oil resistance

The test was conducted as per ASTM D 471-98. The test specimens were immersed in ASTM #3 oil at 100°C for 22 h. The test specimens were then removed from the oil, wiped with tissue paper to remove the excess oil from the surface, and then the weight was recorded.

Dynamic mechanical analysis

The dynamic mechanical analyses of the blends were obtained by using the DMA analyzer (Q800; TA Instrument). The specimens were analyzed in single cantilever mode at a constant frequency of 1 Hz, strain amplitude of 30 μm, and temperature ranging from -60 to $+60$°C, with a heating rate of 2°C/min. The temperature corresponding to the peak in tan δ versus temperature plot was taken as the glass-to-rubber transition temperature (T_g).

Scanning electron microscopy

Scanning electron microscopy (SEM) was performed on a JEOL 5610 LV equipment using backscattered electron detector and a voltage of 15 kV. The samples were cryomicrotomed and the surface was treated with osmium tetroxide (OsO_4) for 5 min to selectively stain the unsaturated rubber phase. The samples were then coated with a thin layer of carbon and observed by SEM.

RESULTS AND DISCUSSION

Brabender data

Since the aim of this work was to develop materials with elastomeric characteristics at room temperature and thermoplastic processability at high temperature, it was decided to use a NBR/PP composition of 70 : 30 wt %. Figure 2 shows the dependence of the actual temperature and torque with the time for the blends as a function of the compatibilizing system. The amount of XNBR in these blends corresponded to 3.5 wt %. All blends exhibited an increase of the internal temperature in the mixer, which were higher than the setting temperature, because of the heat development during polymer processing. Before the addition of the peroxide, the actual temperature in the mixer reached around 195°C. After the peroxide addition (Point a), the actual temperature increased again and reached a value corresponding to around 200°C. This behavior was attributed to the frictional heat development resulted from the resistance to rotation imparted by the crosslinked rubber particles. In addition, the chemical reactions that occur during the curing process are exothermic and contribute for the heating of the mixer. There was no significant difference on the actual temperature of the mixer for compatibilized blends, probably because of the low concentration of the reactive groups which participate in the compatibilization process. Therefore, the heat development related to these reactions is not enough to influence the mixer temperature. The other systems containing 2 and 7 wt % of XNBR followed the same pattern.

The variation of torque during blend processing gives a better idea regarding the extent of reactions during the reactive compatibilization and dynamic vulcanization. At first, the torque increased because of the introduction of cold material (PP and NBR) into the hot chamber. Once the materials got melted, the torque came down. The stable torque before the addition of the curing system was slightly higher for compatibilized blends because of the occurrence of interactions between the functionalized polymers. After the addition of the curing system (Point a), the torque increased substantially due to the crosslinking of the rubber phase, which exerts greater resistance to rotation. After reaching the stable torque, there was no substantial decrease of the corresponding value, indicating that the degradation process of the PP matrix was not significant. The torque values after the curing process was higher for compatibilized blends. However, the concentration of XNBR in the blend did not affect the torque values before and after the introduction of the compatibilizing agent. After the introduction of the curing system, the increase of the torque value was of similar mag-
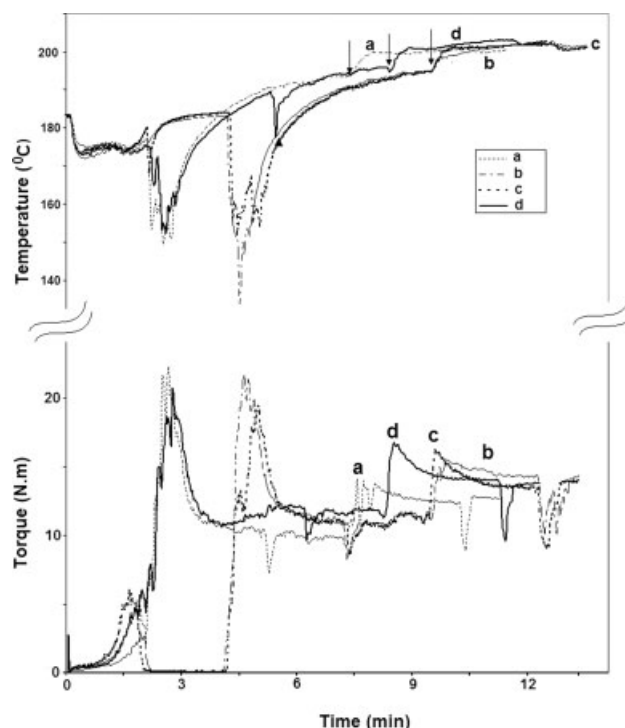

Figure 2 Dependence of the actual temperature and torque with the time for the NBR/PP (70 : 30 wt %) blends as a function of the compatibilizing system containing 3.5 wt % of XNBR: (a) noncompatibilized blend and the compatibilized blends with (b) PP-*g*-MA/TETA/XNBR; (c) PP-*g*-GMA/TETA/XNBR; (d) PP-*g*-GMA/XNBR.

nitude regardless the XNBR concentration. These curves are not shown here.

Tensile properties

The compatibilization effect of the different systems is better indicated by the stress–strain behavior of the corresponding blends. Table I summarizes the physical and mechanical properties of these blends as a function of the compatibilizing system. It is interesting to point out the high ultimate tensile properties found in the noncompatibilized blend. These values, especially elongation at break, is very high considering the incompatibility of the blend components and it has not been reported before in other PP/NBR studies. This behavior may be attributed to a compatibilizing effect of BMI used as the coagent for the crosslinking system. It can act as a multifunctional radical acceptor to promote the combination of dissimilar polymer radicals to give a copolymer and reduce the interfacial tension. A probable mechanism suggested for this kind of compatibilization is illustrated in Figure 3.

The addition of functionalized PP in combination with XNBR resulted in a significant improvement of ultimate tensile strength and elongation at break, but there is no significant difference among the

TABLE I
Physical and Mechanical Properties of NBR/PP (70 : 30%) Dynamically Vulcanized Blends as a Function
of the Compatibilization

Sample	Compatibilization system				Properties				
	PP-g-MA (wt %)	PP-g-GMA (wt %)	XNBR (wt %)	TETA (wt %)	σ (MPa)	ε (%)	Young's modulus (MPa)	Compression set (%)	Oil swelling (%)
1	0	0	0	0	8.5 ± 0.3	380 ± 35	24	66 ± 2	9.6
2	5	0	2.0	0.2	11.7 ± 0.5	465 ± 40	36	68 ± 1	10.6
3	5	0	3.5	0.2	10.4 ± 0.1	480 ± 20	30	67 ± 1	9.9
4	5	0	7.0	0.2	10.9 ± 0.4	450 ± 30	34	66 ± 2	9.5
5	0	5	2.0	0.2	10.5 ± 0.7	450 ± 35	30	64 ± 1	10.7
6	0	5	3.5	0.2	9.9 ± 0.5	450 ± 32	28	64 ± 1	9.8
7	0	5	7.0	0.2	10.8 ± 0.6	460 ± 30	31	64 ± 0.5	10.6
8	0	5	2.0	0	11.1 ± 0.7	440 ± 40	32	62 ± 1	10.5
9	0	5	3.5	0	11.5 ± 0.4	450 ± 25	32	62 ±1	10.2
10	0	5	7.0	0	11.8 ± 0.5	450 ± 30	33	62 ± 1	10.1

compatibilizing systems used in this work and the XNBR concentration. All blends also presented similar oil resistance. A little improvement of compression set (lower values) was observed for compatibilized blend with PP-g-GMA without the presence of TETA.

The Young modulus values of the compatibilized blends are higher than noncompatibilized one. Since all systems are vulcanized, the increase on modulus may be better attributed to the presence of entanglements between the components, as a consequence of the reaction between the functional groups.

For the mechanical performance point of view, there is no significant difference among the compatibilizing systems and the choice of a system can be made based on the cost and availability of the material.

Morphology

The morphology of noncompatibilized NBR/PP blend is compared to that compatibilized with PP-g-MA and 3.5 wt % of XNBR in Figure 4. The white region corresponds to the rubber phase, which was selectively stained by OsO$_4$. Because of the high proportion of the rubber phase in the blends, the morphology in all blends is constituted by large rubber

particle domains surrounded by a thin PP phase (dark region). The compatibilized blend presents a slightly higher homogeneous morphology, with thinner PP phase. This behavior may be responsible for the considerable improvement of the ultimate tensile properties, specially the elongation at break. The morphology of the other compatibilized blends presented similar characteristics and are not shown here.

Dynamic mechanical analysis

The dynamic mechanical properties such as storage modulus (E') and damping (tan δ) of the dynamically vulcanized NBR/PP blends were evaluated from −60 to +60°C. Figure 5 illustrates the variation of tan δ with the temperature as a function of the compatibilizing system for blends containing 3.5 wt % of XNBR. All bends show two tan δ peaks around −25°C and 10°C, which correspond to the glass–rubber transition of the NBR and PP phases, respectively. The transition of the PP phase is not well resolved because of the low damping of this component and its low concentration in the blend.

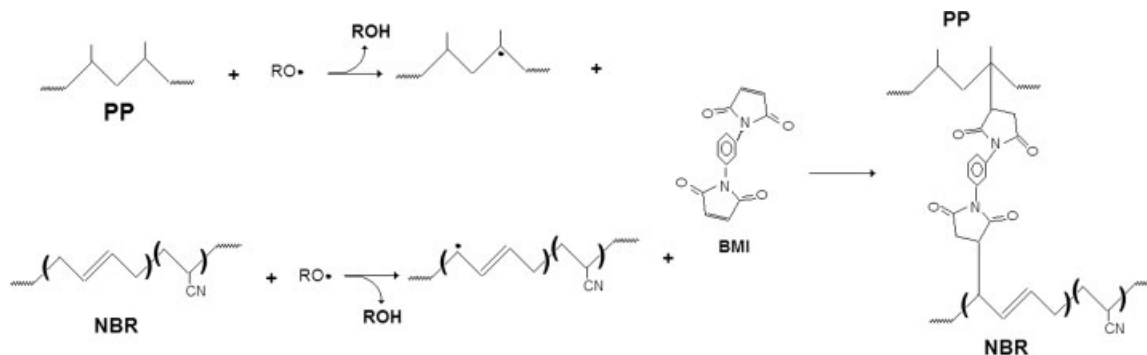The addition of the compatibilizing systems resulted in a slight decrease of damping, which is

Figure 3 Probable mechanism for the reaction between BMI and the blend components.
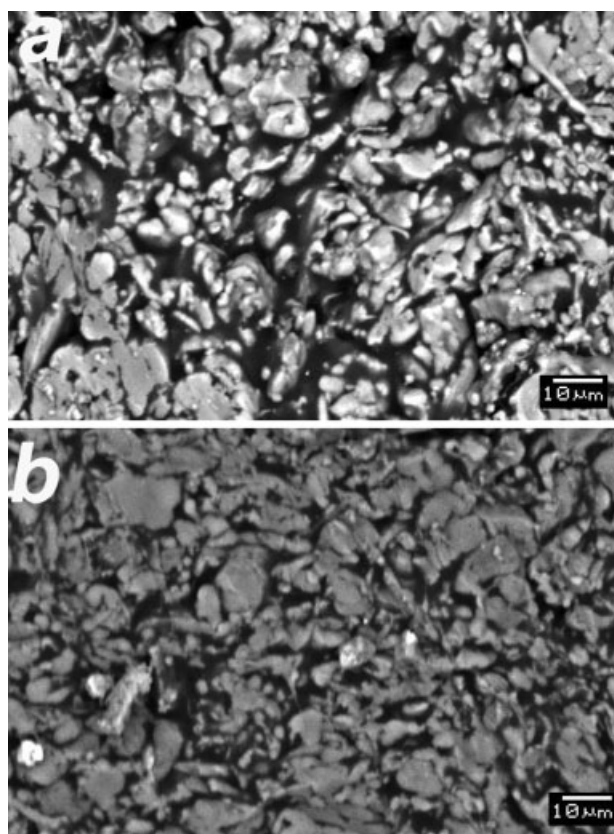
Figure 4 SEM micrographs of NBR/PP (70 : 30 wt %) blends: (a) noncompatibilized and (b) compatibilized with PP-*g*-MA/TETA/XNBR system containing 3.5 wt % of XNBR.

related to the decrease of the chain mobility as a result of the interfacial adhesion. The temperature corresponding to the maximum peak corresponding to the NBR transition did not change but the temperature related to the PP transition was slightly shifted toward lower values, which is also an indication of the interactions between the phases. This phenomenon also occurred in noncompatibilized blend, confirming the compatibilizing action of the
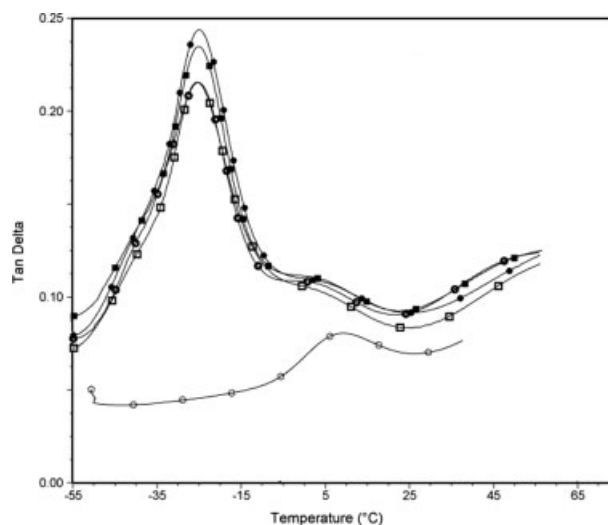

Figure 5 Dependence of tan δ with the temperature as a function of the compatibilizing system for blends containing 3.5 wt % of XNBR: (○) pure PP; (●) noncompatibilized blend and the compatibilized blends with (□) PP-*g*-MA/TETA/XNBR; (■) PP-*g*-GMA/TETA/XNBR; (¤) PP-*g*-GMA/XNBR.

BMI/DCP system. The main dynamic mechanical parameters of all blends studied in this work are summarized in Table II.

The storage modulus versus temperature plots are shown in Figure 6 as a function of the compatibilization system. The modulus in the rubbery region of the curves (at 20°C) is higher for compatibilized blends, probably because of the interactions between the functional groups of the compatibilizing systems.

Effect or reprocessing

An important advantage of TPVs over conventional thermosetting rubbers is the possibility of reprocessing. To illustrate the reprocessing ability of NBR/PP vulcanized blends, those compatibilized blends containing 3.5 wt % of XNBR were reprocessed twice by

TABLE II
Dynamic Mechanical Properties of NBR/PP (70 : 30%) Dynamically Vulcanized Blends as a Function of the Compatibilization

| Sample	Compatibilization system				Dynamic mechanical properties			
	PP-*g*-MA (wt %)	PP-*g*-GMA (wt %)	XNBR (wt %)	TETA (wt %)	tan δ	T_g (°C)	Storage modulus (−55°C) (MPa)	Storage modulus (20°C) (MPa)
1	0	0	0	0	0.24	−25	2,100	114
2	5	0	2.0	0.2	0.21	−25	1,970	150
3	5	0	3.5	0.2	0.21	−25	2,000	140
4	5	0	7.0	0.2	0.21	−23.5	2,080	150
5	0	5	2.0	0.2	0.22	−24.5	1,950	140
6	0	5	3.5	0.2	0.23	−25	2,070	125
7	0	5	7.0	0.2	0.22	−24	1,980	135
8	0	5	2.0	0	0.22	−25	1,900	130
9	0	5	3.5	0	0.22	−25.5	1,860	140
10	0	5	7.0	0	0.22	−24	2,000	135
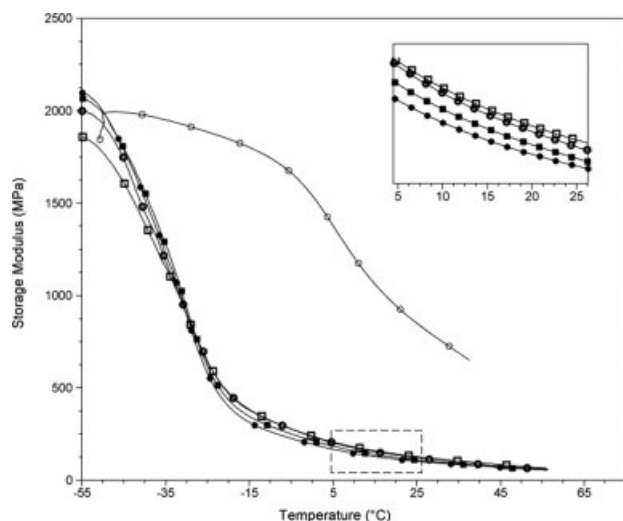
Figure 6 Dependence of storage modulus with the temperature as a function of the compatibilizing system for blends containing 3.5 wt % of XNBR: (○) pure PP; (●) noncompatibilized blend and the compatibilized blends with (□) PP-*g*-MA/TETA/XNBR; (■) PP-*g*-GMA/TETA/XNBR; (¤) PP-*g*-GMA/XNBR.

injection molding, with the product being reground after each molding cycle. The tensile properties and compression set were measured after each cycle, and the results are summarized in Table III. The ultimate tensile strength displayed a slight increase after the first cycle probably because of an additional crosslink process during this reprocessing step. This behavior also influenced the compression set, since a significant improvement was observed after the first processing cycle. The elongation at break values have not changed after the first cycle for blends compatibilized with PP-*g*-MA and PP-*g*-GMA containing TETA/XNBR. All these results suggested

that, in general, the thermoplastic elastomer developed in this work can be reprocessed at least twice without loosing their main properties.

CONCLUSION

From the results obtained in this work it is possible to conclude that

- Thermoplastic elastomer blends consisted of NBR/PP dynamically vulcanized by DCP/BMI system was successfully prepared in an internal mixer. The excellent ultimate tensile properties and compression set achieved in noncompatibilized blend suggest that BMI acts as a coagent for the curing process and also as compatibilizing agent.
- The PP-*g*-MA/TETA/XNBR, PP-*g*-GMA/TETA/XNBR, and PP-*g*-GMA/XNBR are efficient compatibilizing systems, since they promote an improved tensile properties and compression set when compared with noncompatibilized blend.
- The amount of XNBR as the coreactive functionalized polymer did not exert significant influence on the mechanical and dynamical mechanical properties.
- All these blends presented good reprocessing ability.
- Considering the good results obtained with different compatibilizing systems, one can suggest that the choice of the system would be based on the cost and availability of each functionalized polymer. For cost reduction reasons, commercial compatibilizer should be preferred. Therefore, the system that fulfills all technological and economical requirements is PP-*g*-MA. It is commercially available and its preparation involves easy process and low-cost materials.

TABLE III
Physical and Mechanical Properties of NBR/PP (70 : 30 wt %) Blends as Functions of Compatibilization and Processing Cycle

Compatibilizing system					Properties		
PP-*g*-MA (wt %)	PP-*g*-GMA (wt %)	XNBR (wt %)	TETA (wt %)	Cycle	σ (MPa)	ε (%)	Compression set (%)
0	0	0	0	1	8.5 ± 0.5	380 ± 15	66 ± 2
				2	9.0 ± 0.3	350 ± 23	65 ± 1
				3	8.0 ± 0.2	310 ± 15	69 ± 1
5	0	3.5	0.2	1	10.4 ± 0.1	483 ± 20	67 ± 2
				2	11.5 ± 0.3	475 ± 17	57 ± 2
				3	11.3 ± 0.2	433 ± 22	62 ± 2
0	5	3.5	0.2	1	9.9 ± 0.6	452 ± 32	64 ± 2
				2	10.9 ± 0.3	462 ± 18	59 ± 1
				3	10.5 ± 0.3	443 ± 10	66 ± 1
0	5	3.5	0	1	11.5 ± 0.5	450 ± 30	62 ± 1
				2	11.5 ± 0.4	430 ± 20	57 ± 2
				3	11.2 ± 0.2	425 ± 25	62 ± 1

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