

Dynamically Vulcanized Polypropylene/Styrene–Butadiene Rubber Blends: The Effect of a Peroxide/Bismaleimide Curing System and Composition

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ABSTRACT: Polypropylene (PP)/styrene–butadiene rubber blends were studied with special attention given to the effects of the blend ratio and dynamic vulcanization. Dicumyl peroxide (DCP) was used as the curing agent in combination with *N,N'*-*m*-phenylene bismaleimide (BMI) as the coagent for the curing process. Outstanding mechanical performance, especially with regard to the elongation at break, and better resistance to compression set were achieved with the dynamic vulcanization; this indicated that the DCP/BMI system also acted as a compatibilizing agent. This phenomenon was also confirmed by

Fourier transform infrared spectroscopy of the insoluble material, the crystallinity degree of the PP phase (as investigated by X-ray diffractometry), and scanning electron microscopy. The dynamic mechanical properties of the nonvulcanized and vulcanized blends were also investigated. The aging resistance of the blends was also evaluated. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 981–990, 2011

Key words: mechanical properties; polymer blends; rubber; vulcanization

INTRODUCTION

Polypropylene (PP) is one of the most popular thermoplastic commodities because of its good physical properties and processability. However, it has poor impact resistance at low temperatures. The use of a small amount of rubber is very common to improve the impact resistance of PP.¹ However, in several other applications, the material must present elastic characteristics, and this can be achieved through the use of a large amount of rubber. A combination of the rubber elasticity and the processability of PP and other thermoplastics is possible when a relatively high amount of rubber phase (>50 vol %) is finely dispersed inside the thermoplastic matrix. This occurs when the elastomer component is vulcanized *in situ* during melt blending with the thermoplastic at high shear and high temperature. This process, known as *dynamic vulcanization*, has an important technical advantage because the thermoplastic component remains the continuous phase; this preserves the processability and

recyclability of the materials, whereas the large amount of dispersed and vulcanized rubber particles impart elastic characteristic at room temperature.^{2,3} Because of the versatility of the technology involved in these preparations, their interesting mechanical properties and processability (by injection, extrusion, thermoforming, etc.), and the possibility of recycling, such thermoplastic elastomer materials are continuously replacing conventional vulcanized rubbers in several fields, mainly in automobile sectors. One of the most studied thermoplastic elastomeric vulcanizates (TPVs) is based on PP and ethylene–propylene–diene terpolymer (EPDM) because of the structural compatibility between these two polymers.^{2,4–7} Nevertheless, other rubbers have been selected depending on their end-use applications. For instance, PP–nitrile rubber^{8–15} and PP–acrylic rubber¹⁶ have been studied to prepare oil-resistant materials. PP–natural rubber,^{17–20} and PP–epoxidized natural rubber^{21,22} are also important because of their better elastic properties.

In this sense, styrene–butadiene rubber (SBR) should also be an interesting rubber partner for PP-based TPV because of its good elastic properties and low cost.

In addition to the type of rubber component, the nature of the crosslinking agent is another important parameter to be taken into account. Sulfur-based systems are very popular in elastomer industries, but they are not indicated for TPV technology because of the high

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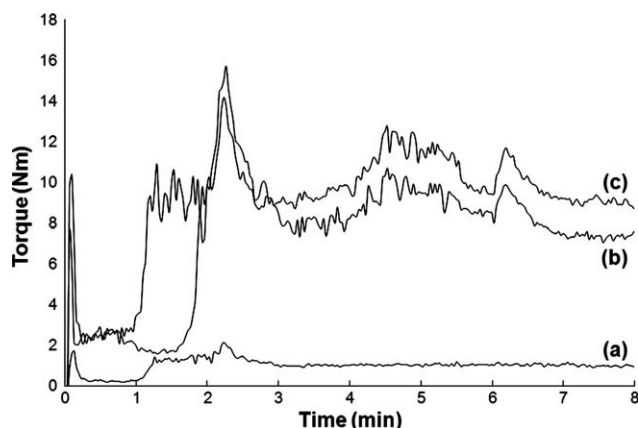


Figure 1 Dependence of the actual torque on the time for the PP/SBR (30 : 70 wt %) blends as a function of the dynamic vulcanization: (a) nonvulcanized blend (mix 1) and vulcanized blends with BMI/DCP = (b) 0.7/0.35 phr (mix 2) and (c) 0.7/0.7 phr (mix 5).

temperature involved in this process, which could result in the liberation of some toxic products derived from the accelerator decomposition.^{23,24} Peroxide-based systems are gaining special interest in this field because of the good high-temperature resistance of the corresponding vulcanizates; good elastic behavior, in particular, the compression set (CS); their ability to vulcanize both saturated and unsaturated rubbers; and their reversion resistance.^{17,25} In addition, they can be used to compatibilize blends containing one crosslinkable component through dynamic vulcanization.^{26,27} The main drawback of the use of peroxide in PP-based TPVs is the possibility of PP degradation, particularly by the β -scission mechanism, which decreases its melt viscosity and some mechanical performance.²⁸ This degradation process may be minimized by the introduction of a compound that improves the peroxide efficiency and decreases the extent of PP degradation. These compounds, namely, coagents, are multifunctional vinyl monomers that are highly reactive toward free-radical reactions.²⁹ Therefore, the PP macroradicals generated by the action of peroxide may rapidly react with the double bond of the coagents by an addition reaction; this will retard the PP chain degradation.^{30,31} In this

regard, *N,N'*-*m*-phenylene bismaleimide (BMI) is a well known coagent system because it undergoes addition reaction rather than hydrogen abstraction. This characteristic is very important in preventing PP degradation during melt mixing. BMI can also act as a compatibilizer agent because it can react with free radicals of dissimilar polymer chains to give rise to copolymers; this increases the interfacial adhesion between immiscible polymers.³² This compatibilizing effect of BMI has been observed in several blend systems, including PP binary blends with waste tire dust,^{33,34} nitrile rubber,¹¹ natural rubber,^{35–37} ethylene octane copolymer,³⁸ and EPDM;³⁹ ternary blends containing PP and natural rubber/linear low-density polyethylene,³² and EPDM/natural rubber;⁴⁰ ethylene–vinyl acetate copolymer blended with epoxidized natural rubber;²⁹ and poly(vinyl chloride)/epoxydized natural rubber (ENR) blends.⁴¹ In addition, the crosslinks formed by BMI are very stable with heating; this is a very interesting characteristic for the development of dynamic vulcanized systems.^{32,42}

In this article, we report the effects of a dicumyl peroxide (DCP)/BMI system on the dynamic vulcanization of PP/SBR blends. For this purpose, the tensile, dynamic mechanical, and morphological properties were investigated as functions of the blend composition and curing agent concentration.

EXPERIMENTAL

Materials

SBR {SBR-1502; butadiene content = 76.5 ± 1.0 ; Mooney viscosity [ML (1+4)] at 100°C = 52 ± 6) was kindly supplied by Petroflex Industria e Comercio (Rio de Janeiro, Brazil). PP (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). BMI (HVA-2) was purchased by DuPont Dow Elastomers (Freeport, TX). DCP was supplied by Retilox (São Paulo, Brazil). Naugard 76 was purchased from Chemtura (São Paulo, Brazil). Irganox 565 was supplied by CIBA (São Paulo, Brazil). Zinc oxide (ZnO) and stearic acid were purchased from Vetec Industria Químicas (Rio de Janeiro, Brazil).

TABLE I
Mechanical Properties of the PP/SBR (30 : 70 wt %) Blends as a Function of the Curing System Concentration

Code ^a	BMI (phr)	DCP (phr)	σ_B (MPa)	ε_B (%)	CS (%)
Mix 1 (nonvulcanized)	0	0	11.5 ± 0.5	137 ± 9	79.3 ± 6.4
Mix 2	0.7	0.35	10.7 ± 0.1	480 ± 23	46.4 ± 1.9
Mix 3	1.0	0.50	12.6 ± 0.1	436 ± 14	50.0 ± 1.7
Mix 4	1.5	0.75	13.4 ± 0.3	403 ± 20	55.7 ± 2.0
Mix 5	0.7	0.7	12.1 ± 0.5	432 ± 28	47.9 ± 0.9
Mix 6	1.0	1.0	12.5 ± 0.3	393 ± 21	45.8 ± 1.9
Mix 7	1.5	1.5	12.6 ± 0.5	308 ± 20	53.3 ± 1.2

^a ZnO = 3.5 phr; stearic acid = 0.7 phr; Irganox = 1.4 phr; Naugard = 0.3.

Blend preparation

SBR, ZnO, stearic acid, and Irganox were first introduced into the chamber of a Brabender plastograph (Duisburg, Germany) equipped with a W50 EHT mixer and Banbury rotors at 80 rpm and 185°C for 2 min. Then, PP was added; this was followed by the addition of the other antioxidant, Naugard. After 2 min, BMI was added. Finally, 2 min later, DCP was added, and the dynamic vulcanization was performed for 2 min.

The mixes were injection-molded at 240°C with a pressure of 300 bar, in a Haake mini-injector (miniJet model, Duisburg, Germany).

Physical testing

Tensile experiments were performed on an Instron 5569 tensile testing machine (Boston, MA) at room temperature with dumbbell-shaped specimens (at least five specimens for each sample) as per ASTM D 638-5. It was used a crosshead speed of 100 mm/min. The experiments were performed before and after the specimens were aged in an air-circulating oven at 100°C for 22 h.

For the CS test, cylindrical test specimens (12.5 mm in diameter and 6.0 mm in thickness) were injected at 240°C. The tests were done by pressing the specimens to 45% of their original thickness as per ASTM D 2395-85 and aged in an air oven at 100°C for 22 h before we determined their thickness recovery upon release of the compressive force.

Characterization

The dynamic mechanical analysis (DMA) of the blends were obtained with the help of a DMA analyzer (Q800; TA Instruments, New Castle, DE). The specimens were analyzed in single-cantilever mode at a constant frequency of 1 Hz, a strain of 0.1%, and at temperatures ranging from -100 to +40°C, with a heating rate of 2°C/min. The temperature corresponding to the peak in the $\tan \delta$ versus temperature plot was taken as the glass-transition temperature (T_g).

Fourier transform infrared (FTIR) spectroscopy analyses were performed in an FTIR Excalibur 3100 from Varian (Mulgrave, Australia) equipped with an attenuated total reflection accessory with ZnSe. FTIR spectroscopy was performed with 100 scans at a 4-cm⁻¹ resolution.

Scanning electron microscopy (SEM) was performed on a JEOL 5610 LV instrument (Tokyo, Japan). The samples were cryofractured, and the surface was treated with osmium tetroxide (OsO₄) for 5 min to selectively stain the unsaturated rubber phase. The samples were then coated with a thin

TABLE II
Effect of Dynamic Vulcanization on the Mechanical Properties of the PP/SBR Blends

PP (%)	SBR (%)	ZnO (phr)	Stearic acid (phr)	Blend composition				Tensile properties										
				Irganox (phr)	BMI (phr)	DCP (phr)	Naugard (phr)	Yield stress (MPa)		σ_B (MPa)		ϵ_B (%)		CS (%)				
								A	B	A	B	A	B	A	B			
100	0	0	0	0	0	0	1.0	—	—	—	—	—	—	—	—	—	—	—
80	20	1.0	0.2	0.4	0.2	0.1	0.8	27.8 ± 0.4	38.0 ± 0.5	18.0 ± 0.3	24 ± 0.3	285 ± 25	120 ± 19	—	—	—	—	—
70	30	1.5	0.3	0.6	0.3	0.15	0.7	22.0 ± 0.3	32.7 ± 0.6	21.6 ± 0.5	12.0 ± 0.4	760 ± 56	648 ± 56	54.4 ± 2.4	77.9 ± 1.9	—	—	—
50	50	2.5	0.5	1.0	0.5	0.25	0.5	—	27.9 ± 0.4	10.0 ± 0.5	10.0 ± 0.5	480 ± 23	657 ± 56	64.6 ± 1.6	85.8 ± 2.8	—	—	—
30	70	3.5	0.7	1.4	0.7	0.35	0.3	—	20.0 ± 0.3	18.6 ± 0.5	19.0 ± 0.2	11.5 ± 0.5	136 ± 9	46.4 ± 1.9	79.3 ± 6.4	—	—	—
20	80	4.0	0.8	1.6	0.8	0.4	0.2	—	—	10.7 ± 0.2	11.5 ± 0.5	8.3 ± 0.2	164 ± 17	42.3 ± 0.9	73.9 ± 8.8	—	—	—
0	100	5.0	1.0	2.0	1.0	0.5	0	—	—	2.0 ± 0.1	—	100 ± 18	—	3.4 ± 0.1	—	—	—	—

A = dynamically vulcanized blends; B = nonvulcanized blends (for nonvulcanized blends, there was no BMI or DCP).

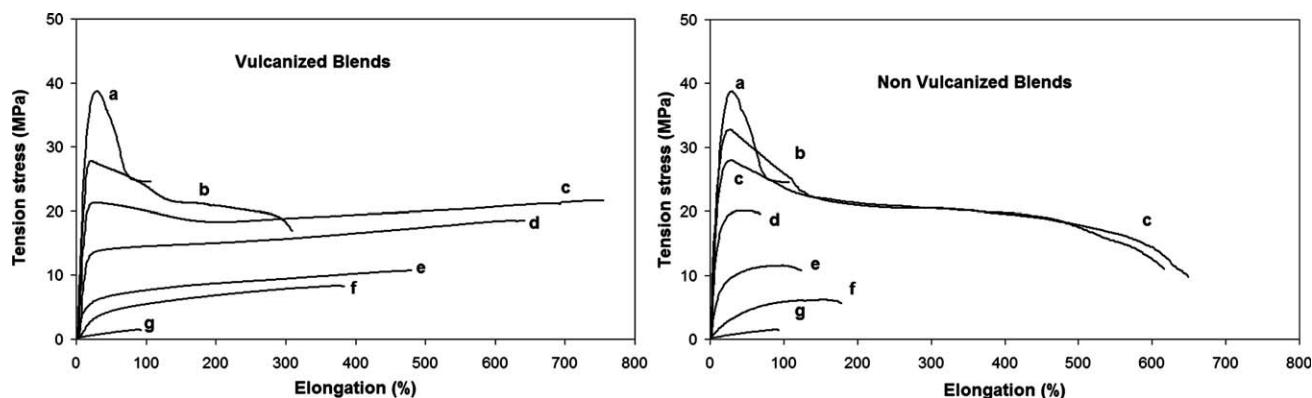


Figure 2 Stress–strain curves of the dynamically vulcanized and nonvulcanized PP/SBR blends with PP contents of (a) 100, (b) 80, (c) 70, (d) 50, (e) 30, (f) 20, and (g) 0 wt %.

layer of carbon and observed by SEM with a back-scattered electron detector and at a voltage of 15 kV.

We recorded the X-ray diffraction (XRD) patterns by monitoring the diffraction angle (2θ) from 2 to 40° on a DMAX-RC (Miniflex) X-ray diffractometer (Rigaku Co., Tokyo, Japan). The unit was equipped with a Cu $K\alpha$ radiation source operating at 30 kV and 15 mA. The scanning rate was $0.05^\circ/\text{min}$.

RESULTS AND DISCUSSION

Brabender data and mechanical properties

The effect of the dynamic vulcanization on the main properties of the PP/SBR blends was first studied with a blend composition corresponding to 70% rubber with the aim of developing an elastomeric processable TPV material. Figure 1 compares the evolution of the torque during blend preparation as a function of the dynamic vulcanization in the internal mixer. Curve a is related to the nonvulcanized PP/SBR (30:70 wt %) blend, and curves b and c represent the torque versus time during the preparation of the dynamically vulcanized blends containing BMI/DCP weight ratios of 2.0 and 1.0, respectively. All of these blends were prepared with 3.5 parts per hundred rubber (phr) ZnO, 0.7 phr stearic acid, 1.4 phr Irganox 565, and 0.3 phr Naugard 76.

The vulcanization (curves b and c) resulted in a significant increase of final torque because of the increase in the viscosity imparted by the formation

of the rubber network during processing. With regard to the vulcanized blends, the increase in the DCP amount in the system (curve c) gave rise to an additional increase in the final torque; this indicated an increase in the crosslink density.

The effects of the concentration of the curing system on the mechanical properties of PP/SBR (30 : 70 wt %) blends is summarized in Table I. The first trend to be taken into account was the great difference in the tensile properties of the nonvulcanized blend compared to those of the vulcanized blends. The former (mix 1) presented lower ultimate tensile properties and a higher CS. The dynamic vulcanization resulted in a substantial improvement in the tensile properties and a significant decrease in CS. Among the vulcanized blends, the ultimate tensile strength (σ_B) was not greatly influenced by the BMI/DCP content. The elongation at break (ϵ_B) decreased with increasing DCP content. For similar BMI contents, the highest ϵ_B was achieved with a BMI/DCP weight ratio of 2.0, whereas a lower CS was observed in the blends prepared with a BMI/DCP ratio equal to 1.0. The lower ϵ_B in blends with a higher amount of DCP may have been due to an increase in the crosslink density and agreed with the value of the final torque during the mixing process.

The mechanical properties of the PP/SBR blends prepared at different compositions are summarized in Table II. The tensile stress–strain curves of the blends are shown in Figure 2 for the nonvulcanized and dynamically vulcanized blends. Blends with

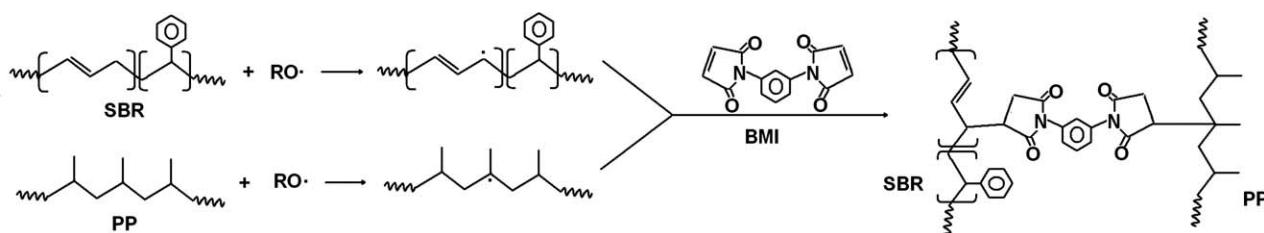


Figure 3 Probable reactions involved in the reactive compatibilization process of BMI.

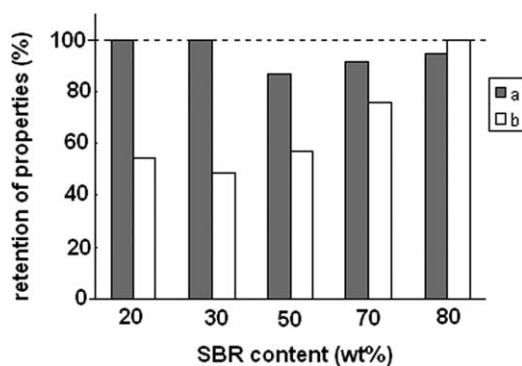


Figure 4 Retention of the tensile properties of PP/SBR TPVs as a function of the blend composition: (a) σ_B and (b) ϵ_B .

higher PP contents presented yield points. The maximum stress at the yield point was higher for pure PP and decreased as the amount of SBR in the blend increased. The nonvulcanized blends (series B) presented higher yield stress values than the vulcanized blends. This phenomenon was attributed to a decrease in the crystallinity of the PP phase with the vulcanization. This feature is discussed later.

The σ_B values decreased as the amount of SBR in the blend increased. However, for similar blend compositions, the vulcanized blends, mainly those with higher PP contents, generally presented higher σ_B values.

The blend composition and vulcanization exerted significant influence on ϵ_B . These values increased as the rubber content in the blend increased up to 30% rubber. Beyond this rubber concentration, the value decreased, and this phenomenon was more accentuated in the nonvulcanized blends. For blends with similar compositions, ϵ_B of the vulcanized blends was significantly higher than that of nonvulcanized blends, except for the 80:20 wt % PP/SBR blend. The difference in the ϵ_B values of the nonvulcanized

and vulcanized PP/SBR blends found in our study was higher than those obtained by Chatterjee and Naskar⁴ for PP/EPDM blends cured with DCP. The outstanding mechanical performance of the dynamically vulcanized PP/SBR blends obtained in this study may have been due to the compatibilization effect exerted by BMI, according to the scheme illustrated in Figure 3. In addition, BMI prevented the PP degradation during melt mixing because underwent an addition reaction with the PP macroradicals before chain scission.

The dynamic vulcanization also resulted in lower CS values, mainly in blends containing high amounts of rubber. These results confirmed the thermoplastic elastomeric nature of these blends.

The tensile properties were also determined from aged specimens. Figure 4 presents the retention of the tensile properties of the blends after treatment in an air-circulating oven at 100°C for 22 h. The tensile strength remained constant after the heat treatment for PP-richer blends. With increasing amounts of rubber, there was a slight decrease in this property. ϵ_B was significantly influenced by the aging process, and this phenomenon was more important in blends containing higher amounts of PP. These results suggest that the presence of PP in high amounts negatively affected the aging resistance of the PP-SBR TPVs, probably because of the presence of some amount of active peroxide, which contributed to the degradation of the PP phase. Nevertheless, the values found for the mechanical properties of the aged TPV samples were still acceptable for several applications.

FTIR analysis

To illustrate the compatibilizing effect of BMI, the 50 : 50 wt % PP/SBR vulcanized blend was submitted to extraction with hot xylene for 48 h, and the residue was analyzed by FTIR spectroscopy.

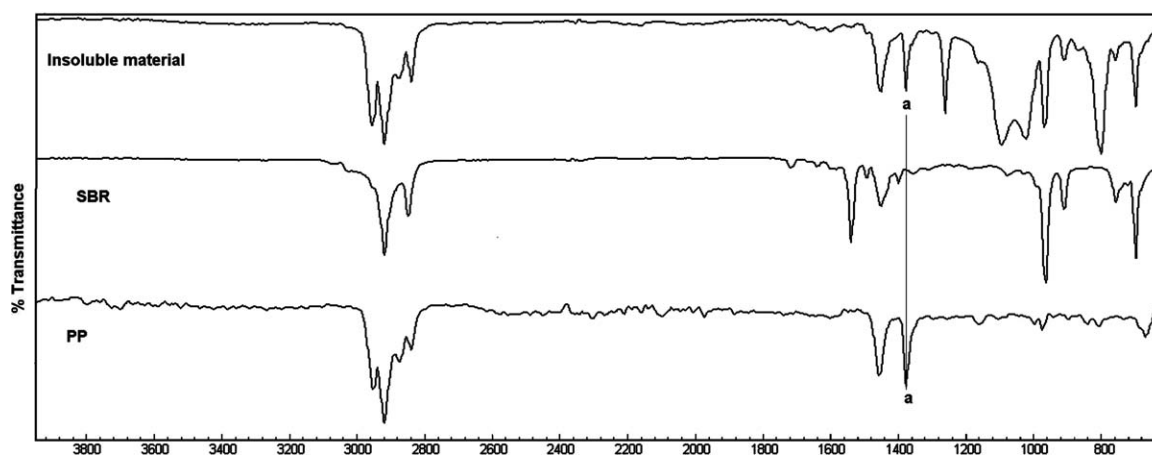


Figure 5 FTIR spectra of pure PP, vulcanized SBR, and the insoluble residue obtained from the dynamically vulcanized PP/SBR blend.

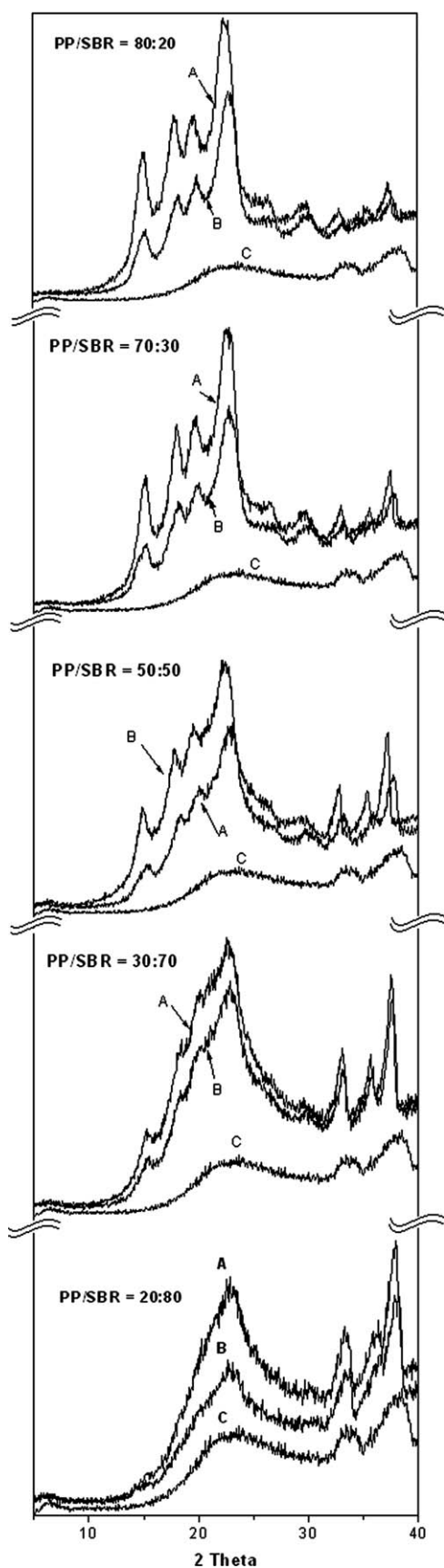


Figure 6 XRD patterns of the PP/SBR blends as a function of the composition and vulcanization: (A) nonvulcanized blends, (B) vulcanized blends, and (C) SBR.

Figure 5 compares the FTIR spectra of pure PP, vulcanized SBR, and the residue obtained from the vulcanized blend. The PP spectrum presented a characteristic absorption at 1380 cm^{-1} related to the methyl groups situated along the PP chain (peak a). This absorption was not detected in the SBR sample. The insoluble residue obtained from the blend extraction presented the main absorption peak related to the SBR phase but also some peak attributed to the PP phase, mainly the absorption at 1380 cm^{-1} . This result suggests that some PP chains were chemically linked to the SBR phase, which characterized the reactive compatibilization. As illustrated in the scheme of Figure 3, BMI acted as a bridge between the PP and SBR phases and just formed a graft copolymer during the melt mixing.

Crystallinity degree

The effect of the dynamic vulcanization on the crystallinity degree of the PP phase was evaluated by XRD analysis. Figure 6 shows the XRD spectra of the blends as a function of the composition and vulcanization. The A curves represent the nonvulcanized blends, and the B curves are related to the vulcanized blends. The reflection of the pure SBR sample is also included in Figure 6 (curve C), only for comparison. Blends containing higher amounts of PP presented some diffraction peaks related to the crystalline phase of the PP component. As the amount of PP decreased, the intensity of these diffraction peaks became smaller, as expected. In almost all of the blends, the dynamic vulcanization resulted in a decrease in the crystallinity degree, as indicated by the smaller intensity of the reflection peaks. These results were attributed to the increase in the interaction between the two phases, as promoted by the presence of BMI. This behavior was in agreement with the values of the stress at the yield point observed for vulcanized blends containing higher amounts of PP. The only blend composition that presented a higher crystallinity degree for the vulcanized blends was that corresponding to PP/SBR = 50 : 50 wt %.

Morphology

The effect of the dynamic vulcanization on the morphology of the PP/SBR (50 : 50 wt %) blends was evaluated by SEM micrographs, shown in Figure 7. The white region corresponds to the rubber phase, which was selectively stained by OsO_4 . Nonvulcanized blends presented a gross phase-separate morphology, as expected for incompatible blends. The dynamic vulcanization decreased the size of both the rubber and PP phases because of the better interaction between the phases.

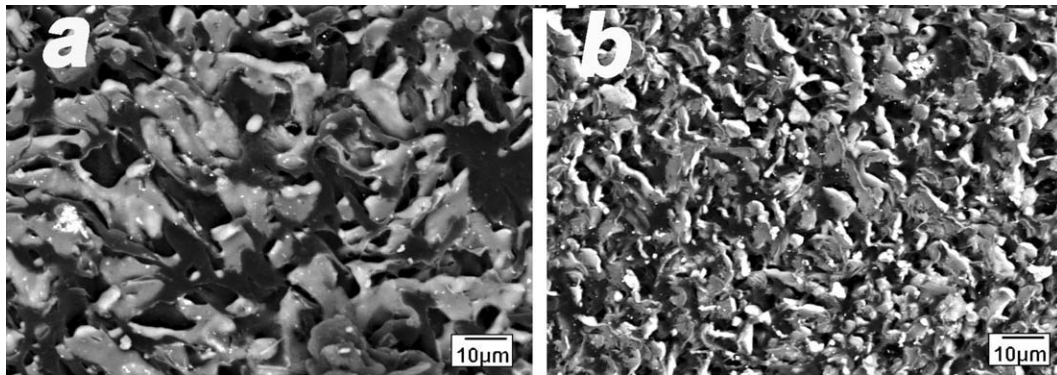


Figure 7 SEM micrographs of the PP/SBR (50:50 wt %) blends: (a) nonvulcanized and (b) vulcanized blends.

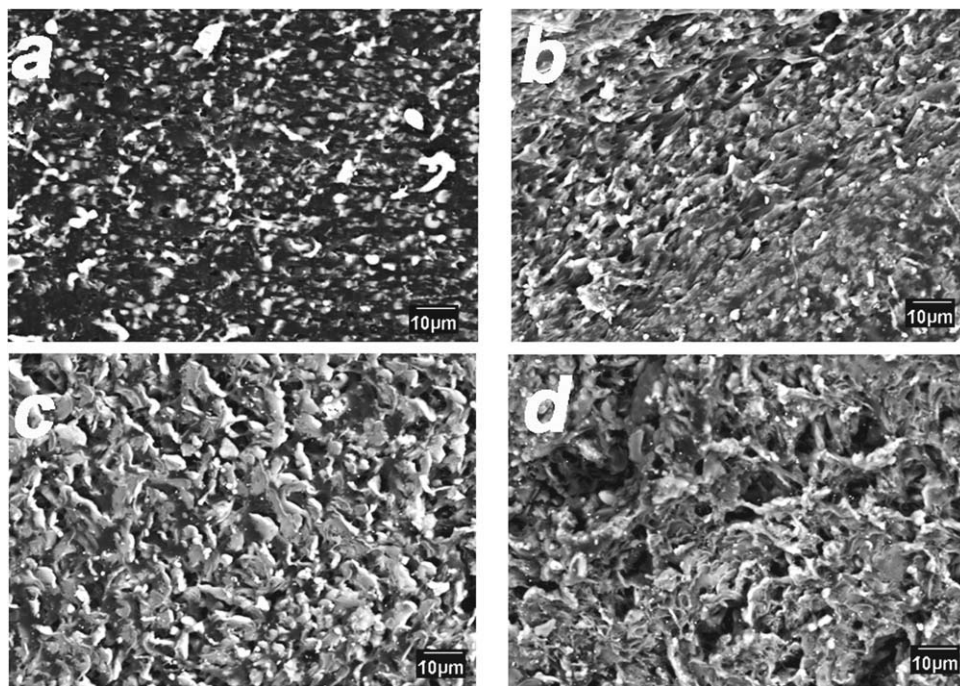


Figure 8 SEM micrographs of the PP/SBR vulcanized blends as a function of the composition: (a) 80, (b) 70, (c) 50, and (d) 30% of PP.

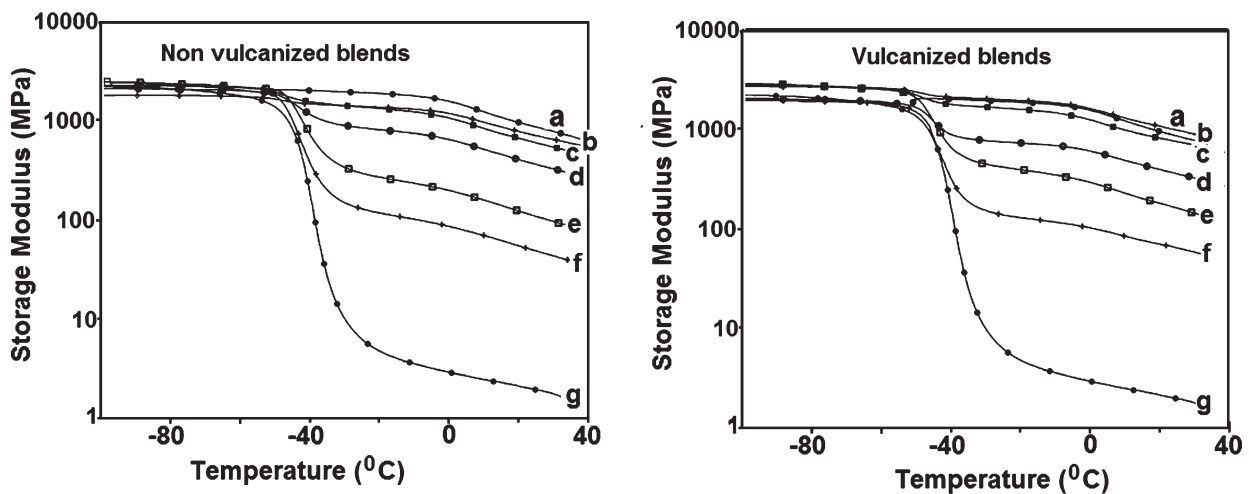


Figure 9 Dependence of E' with the temperature for the nonvulcanized and vulcanized PP/SBR blends with PP contents of (a) 100, (b) 80, (c) 70, (d) 50, (e) 30, (f) 20, and (g) 0 wt %.

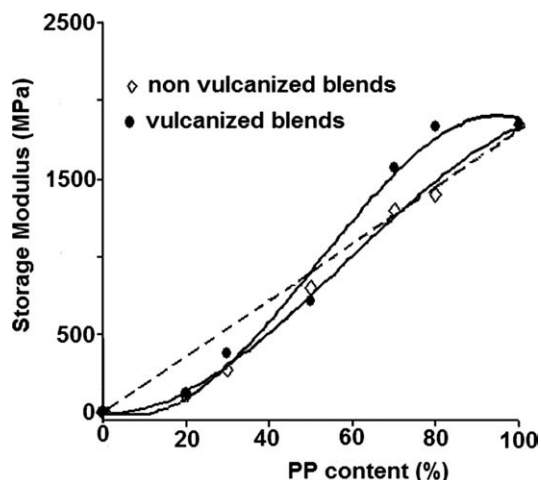


Figure 10 E' at -20°C versus the PP content for the vulcanized and nonvulcanized blends (the dot line corresponds to the calculated modulus on the basis of the mixture rule).

Figure 8 presents the micrographs of the vulcanized PP/SBR blends as a function of the composition. The blend containing 80% PP presented a clear rubber-dispersed phase morphology. As the rubber content in the blend increased, the morphology changed to a more elongated rubber-dispersed phase. In the blend containing 70% rubber, the PP phase appeared as domains and also as a continuous phase.

DMA

The dynamic mechanical properties, such as storage modulus (E') and damping ($\tan \delta$), of the PP/SBR blends with different compositions were studied over a wide temperature range (from -100 to $+40^{\circ}\text{C}$). Figure 9 compares the dependence of E' on the temperature for the vulcanized and nonvulcanized blends. Below T_g , the E' values were not significantly influenced by the blend composition.

However, above the glass–rubber transition, the modulus decreased as the amount of the rubber in the blend increased, and this effect was more pronounced for blends containing higher amounts of rubber. For PP-richer blends, the modulus did not change considerably because the SBR rubber phase was dispersed inside the PP phase, and the solid-state properties of the matrix dominated. As the amount of SBR in the blend increased, the contribution of this soft phase to the E' values became important because of the increase in the rubber particle size. Figure 10 illustrates the dependence of E' at -20°C on the blend composition. The nonvulcanized blends displayed E' values lower than those calculated from the mixture rule, as expected for incompatible blends. Dynamic vulcanization resulted in an increase in the modulus for PP-richer blends as a consequence of the network formation inside the rubber matrix and also due to the compatibilizing effect of the curing system.

The damping behavior of the nonvulcanized and vulcanized blends is illustrated in Figure 11, in terms of $\tan \delta$. The main dynamic mechanical parameters are also summarized in Table III. The temperature corresponding to the maximum $\tan \delta$ is usually related to T_g . The blends presented two T_g values: the first, around -40°C , corresponded to the transition of the SBR phase, and the other, around 10°C , was related to the glass–rubber transition of the PP phase. The transition of the PP phase was not well resolved in the blends with low amounts of PP because of the low damping of this component. T_g of the PP phase shifted slightly toward a higher temperature when compared to that of the pure PP. This behavior was more important in the nonvulcanized blends and indicated a decrease in the mobility of the PP phase.

T_g of the rubber phase in the blend decreased significantly when compared to that of the pure SBR, and this behavior was more important as the

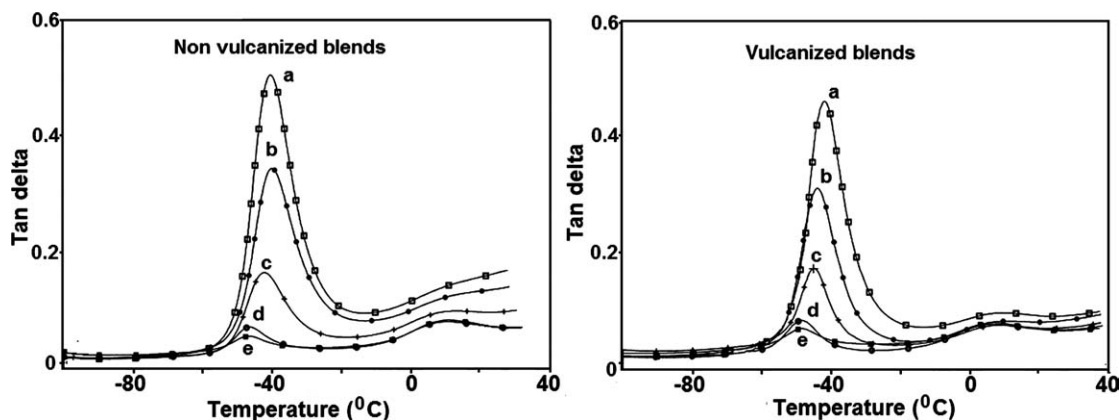


Figure 11 Dependence of the $\tan \delta$ on the temperature for the nonvulcanized and vulcanized PP/SBR blends with SBR contents of (a) 80, (b) 70, (c) 50, (d) 30, and (e) 20 wt %.

TABLE III
Dynamic Mechanical Properties of the PP/SBR Blends as a Function of the Composition and Dynamic Vulcanization

Blend composition (%) ^a		E' at -80°C (MPa)		E' at -20°C (MPa)		Tan δ of the SBR phase		T_g of the SBR phase ($^{\circ}\text{C}$)		Tan δ of the PP phase		T_g of the PP phase ($^{\circ}\text{C}$)	
PP	SBR	A ^b	B	A ^b	B	A ^b	B	A ^b	B	A ^b	B	A ^b	B
100	0	—	—	—	1850	—	—	—	—	—	0.080	—	8.9
80	20	2640	1760	1930	1340	0.07	0.05	-48	-47	0.079	0.084	7.5	10.6
70	30	2720	2200	1580	1300	0.08	0.07	-48	-46	0.076	0.080	7.0	10.1
50	50	1980	2050	720	800	0.17	0.16	-44	-42	0.075	0.098	7.8	9.3
30	70	2760	2360	400	270	0.30	0.34	-43	-40	0.080	0.123	8.3	10.0
20	80	1900	2230	130	116	0.46	0.50	-41	-40	0.096	0.142	8.8	10.0
0	100	2100	—	5	—	1.40	—	-36	—	—	—	—	—

^a Other ingredients related to the rubber content: ZnO = 5.0 phr; stearic acid = 1.0 phr; Irganox = 2.0 phr. Other ingredients related to the PP content: Naugard = 1.0 phr.

^b For vulcanized blends, we used a BMI/DCP weight ratio equal to 1.0:1.0 phr related to the rubber content.

amount of rubber in the blend decreased. This phenomenon was also observed in other systems, such as polystyrene/ethylene-vinyl acetate copolymer blends,⁴³ PP/polyolefin elastomer blends,⁴⁴ and TPVs constituted by PP/EPDM,⁴⁵ the behavior was attributed to an increase in the free volume as a consequence of the contraction of the rubber phase during the cooling process of the sample when it was submitted to DMA analysis. This behavior occurred because of the higher thermal expansion coefficient of the rubber, as compared to that of the PP component.

In almost all of the blend compositions, the vulcanized blends presented lower damping behavior; this indicated more elastic materials.

CONCLUSIONS

Thermoplastic vulcanizates consisting of PP/SBR blends were successfully prepared by dynamic vulcanization in an internal mixer in the presence of DCP and BMI as the curing system. The excellent ultimate tensile properties achieved in the vulcanized blends suggest that BMI acted as a coagent for the curing process and also as a compatibilizing agent.

The good interaction between the polymer phases, PP and SBR, may have been responsible for the decrease in the crystallinity degree of the PP phase in the vulcanized blends. The dynamic vulcanization also resulted in a more homogeneous morphology, with a smaller rubber particle size.

The PP/SBR thermoplastic vulcanizates, even with a higher amount of SBR (70 wt %), presented good processing ability because they could be processed by injection molding after the curing process. The aging resistance was not very high, as expected for a system containing a highly unsaturated rubber. However, the best results were observed for blends containing a higher amount of SBR.

With regard to the low cost and high elasticity of SBR, this system should be a very good candidate for the preparation of thermoplastic elastomer artifacts by injection molding and may be a substitute for PP/EPDM TPVs in several applications that do not require a high service temperature because of the outstanding CS of the samples imparted by the SBR rubber component.

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