

# Influence of a Crosslinked System on the Morphology and Properties of TPVs Based on PA/NBR

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Received 2 April 2010; accepted 13 May 2011

DOI 10.1002/app.34885

Published online 2 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The mechanical properties of thermoplastic vulcanizates (TPVs), depend strongly on their morphologies, which themselves depend on the properties of the primary polymers, the composition of the TPV, and the crosslink system and crosslink process. The morphology is defined during the dynamic vulcanization. This work deals with the study of the influence of crosslink systems on TPVs based on PA/NBR (copolyamide PA6/6-6 and nitrile rubber) in a 40/60 composition. Dicumyl peroxide, bismaleimide, phenolic resin, a sulfur-accelerated system, and dicumyl peroxide with two coagents were used as crosslinkers. TPVs were characterized by taking into

account their mechanical strength, solvent resistance, compression set, and morphology. The curing system constituted by dicumyl peroxide and sulfur/bismaleimide as coagents resulted in a more defined morphology, and therefore the TPV exhibited the best properties. For these TPVs, a morphology consisting of spherical domains of rubber distributed homogeneously on the polyamide matrix could be observed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3072–3080, 2012

**Key words:** thermoplastic vulcanizate; crosslinking; mechanical properties; nitrile rubber; polyamide

## INTRODUCTION

Thermoplastic elastomers exhibit some of the elastic behavior of thermoset rubbers with the advantages of the processability and recyclability of thermoplastic polymers.<sup>1</sup> The disadvantages of thermoplastic elastomers are related to an inadequate temperature resistance, which is limited by the softening temperature of the thermoplastic phase and by its high compression set values, especially above room temperature.

Thermoplastic vulcanizates (TPVs) are a special class within the broader family of thermoplastic elastomers. TPVs consist of a thermoplastic polymer matrix and a crosslinking rubber that are cured during melt-blending, resulting in a fine dispersion of micron-size rubber particles in the continuous thermoplastic matrix.<sup>1–3</sup> Dynamic vulcanization is a way to obtain new thermoplastic elastomers that have properties as good as or, in some cases, better than those of block copolymers. The improved properties resulting from dynamic vulcanization are the following: a reduced compression set, improved ultimate

mechanical properties, a greater resistance to attack by fluids, an improved high temperature utility, a greater stability of phase morphology in the melt, a greater melt strength, and more reliable thermoplastic processability.<sup>4</sup> Extensive studies on dynamically vulcanized TPVs were carried out by Coran and Patel in the early 1980s.<sup>2</sup> Compositions were prepared from several combinations of selected types of rubber and thermoplastics. The rubbers that were used included butyl rubber (IIR), ethylene-propylene-diene rubber (EPDM), natural rubber (NR), butadiene rubber (BR), styrene-butadiene-rubber (SBR), ethylene vinyl acetate (EVA), acrylate rubber (ACM), chlorinated polyethylene (CM), polychloroprene (CR), and nitrile rubber (NBR). The thermoplastics included the following: polypropylene (PP), polyethylene (PE), polystyrene (PS), acrylonitrile butadiene styrene (ABS), styrene acrylonitrile (SAN), polymethyl methacrylate (PMMA), polybutylene terephthalate (PBT), polycarbonate (PC) and polyamide (PA). Only a few thermoplastic/rubber combinations were commercialized because most of these blends were not technologically compatible and required one or more steps to make them compatible, making them economically unfeasible.

The TPVs are the second largest group of soft thermoplastic elastomers, after styrenic-based block copolymers. Commercialized dynamic vulcanizates are commonly based on blends of unsaturated EPDM rubber and polypropylene. This material resulted in

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Contract grant sponsors: CNPq, FAPERGS.

the commercialization by Uniroyal of TPR<sup>TM</sup> thermoplastic rubber in 1972. The curing agent plays an important role in the processing of TPVs. It influences the technological processing and the final performance of the material. Over time, several vulcanization agents, such as peroxides, coagent assisted peroxides, activated phenol-formaldehyde resins, silanes, sulfur and bismaleimides,<sup>3,5,6</sup> have been employed to crosslink the EPDM phase in PP/EPDM blends.

Systems based on PA/NBR were also investigated by Coran and Patel<sup>2</sup> in the 1980s. Polyamides like nylon 6, nylon 6-6, nylon 6-9, and nylon 10 were used, while NBR with 33 and 39% by weight of acrylonitrile was the most employed. These NBR TPVs have been crosslinked with sulfur, bismaleimide, peroxide, and phenolic resin SP1045. The study established that, besides the action of crosslinkers, a self curing of NBR can occur for TPVs based on polyamide with high melting point. This self crosslinking mechanism contributes to the final properties of the TPV. The authors<sup>2</sup> reported that, for TPVs with a nonself curing mechanism good mechanical properties, like ultimate tensile strengths of 10.9 to 17.3 MPa and hardnesses between 33 and 44 Shore D were obtained depending on the amount of the curing agent. Coran, Patel and Headd<sup>7</sup> described different TPVs included a TPV PA/NBR 35/65 (by mass) cured with phenolic resin SP1045 obtained in a mixing with different compatibilizers including a mixture 50/50 (by mass) of the PA/NBR TPV with another PP/EPDM TPV. They concluded that compositions possessing excellent mechanical properties can be prepared by melt-mixing TPVs because an adequate compatibilizer is used.

In some cases, coagents are the alternatives applied to improve the crosslinking<sup>3</sup> in thermoset rubbers manufacturing, for which sulfur is an adequate choice because of its low cost. With respect to physical mechanical properties, it was observed that the use of sulfur or the sulfur donor agent MBT (2-mercaptobenzothiazole) as a coagent for dicumyl peroxide (DCP) contributes to the curing process, resulting in TPVs with high modulus and tensile strength but with less resistance to aging.<sup>8</sup> A more recent work<sup>8</sup> described the use of bismaleimide and sulfur or a sulfur donor as coagents of dicumyl peroxide in the crosslinking of EPM rubber. With this crosslink system, a thermoset rubber with a high tensile strength, elongation and modulus could be obtained.

The general advantages of the use of peroxides as crosslinking agents are the following: (1) the ability to crosslink unsaturated and saturated elastomers; (2) the ability of formation networks with high temperature resistance; low compression set, particularly at an elevated temperature; (4) no moisture uptake; and (5) no staining or discoloration of the finished

products.<sup>8-11</sup> However, they also exhibit some disadvantages. Depending on the applied peroxide, the decomposition products are volatile. The peroxides often have a typical smell, show a blooming effect and can be extracted from the crosslinked material by solvents. For instance, the typical sweet smell of acetophenone, one of the decomposition products of dicumyl peroxide (DCP), is well known. Also, blooming phenomena can occur as a result of the formation of dihydroxy isopropyl benzene from the decomposition of di(*tert*-butylperoxyisopropyl) benzene because of its limited solubility in rubber.<sup>9</sup> To obtain a TPV with specific properties, besides needing the definition of the thermoplastic/elastomer couple, an adequate crosslink system must be applied.

The purpose of this work was to develop TPVs with good mechanical properties, good thermal stability and resistance to nonpolar solvents. To achieve this, the system PA/NBR (copolyamide PA6/6-6 and nitrile rubber) was chosen and blended in a proportion of 40/60 (m/m). Different crosslinking systems, such as dicumyl peroxide, bismaleimide, phenolic resin 1045, a sulfur-accelerated system, and dicumyl peroxide combined with two coagents (bismaleimide and sulfur), were investigated to determine which of them would be capable of producing a morphology with small rubber domains that are well-dispersed in the plastic phase. The literature<sup>2,12</sup> attributes good mechanical performance to TPVs with such morphology. The tensile properties, swelling behavior, hardness, compression set, and morphology were evaluated to determine the influence of the crosslinking system on the properties of the TPV (PA/NBR) under investigation.

## EXPERIMENTAL

### Materials and sample preparation

The following commercially available polymers and curing agents were used: copolyamide PA6/6-6; type Radilon CS LX 02066/C NAT, (purchased by Radici Group, Brazil); nitrile rubber with 45% acrylonitrile content, type Thoran 4560 (product of Petroflex, now Lanxess, Brazil); dicumyl peroxide, DCP, type DCP 40 (produced by Retilox, Brazil); the antioxidant ionol CP (Degussa, now Evonik, Brazil). Sulfur (Flexsys, Brazil), commercial grade bismaleimide, BMI, type CHEMAC HVA-2 (Chemicon, Brazil), the accelerator, *N*-cyclohexyl-2 benzothiazole-sulfenamide, Banac CBS (produced by Bann, Brazil), and the phenolic resin SP 1045 (Schenectady, Brazil) were used as received. The samples are designated as functions of the applied curing systems as follows: **D** for dicumyl peroxide, **SA** for sulfur accelerated with CBS, **B** for bismaleimide, **SP** for phenolic

resin and DBS for dicumyl peroxide and the coagents sulfur and bismaleimide. The mixture and the dynamic vulcanization were carried out in a mixing chamber (Haake Rheomix 600) and were based on the well-known procedures described in the literature<sup>9,13,14</sup> and on personal laboratory experience.<sup>15,16</sup> Preliminary experiments showed that a good homogeneity of the TPV was only reached if a two-step procedure was applied. In the first step, a master batch of the rubber with the powder ingredients (excluding the curing system) was prepared by mixing the components at 70°C with a rotor speed of 65 rpm for 4 min. In the second step, the polyamide was melted in the chamber at 195°C with a rotor speed of 65 rpm, and the rubber master batch was added after about 2 min. Approximately 4 min later, the curing system was introduced and 2 min later, the material was removed from the chamber. The mixture times were defined by the control of the evolution (decreasing and stabilization) of the torque as a function of mixing time. A typical curve for the composition DBS 2.4 is shown in Figure 1.

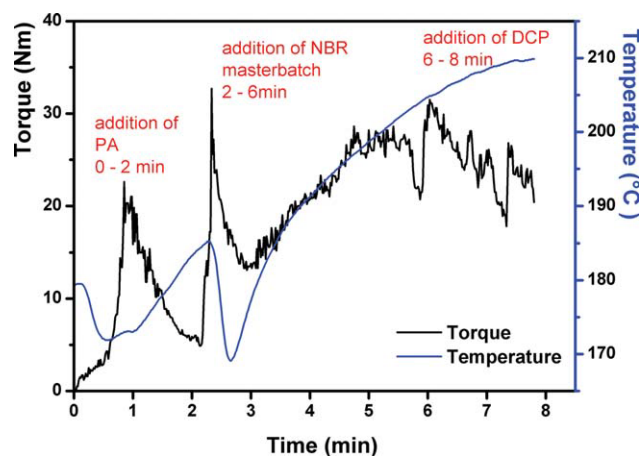
The composition was molded at 195°C into sheets of about 2 mm thickness in a Carver press. All of the TPVs have a proportion of PA/NBR 40/60 by mass and were designated as a function of the curing system as shown in Table I. The capital letter indicates the curing agent, and the number indicates the amount, in php, (weight parts per 100 parts of polymer) added. Thus D1.0 represents 1.0 php of dicumyl peroxide, while DSB2.4 represents 2.4 php of DCP having bismaleimide and sulfur as coagents. The amount of each component is listed in Table I.

### Stress-strain measurements

Tensile tests on the specimens were carried out by a tensile tester (EMIC DL 5000/10000) according to ASTM D 412<sup>17</sup> using dumbbell specimens with a crosshead speed of 500 mm min<sup>-1</sup>. At least five samples were measured, and the mean values were calculated. The stress at 100 and 200% of elongation, the ultimate tensile strength and the elongation-at-break were determined.

### Swelling measurements

Swelling experiments were done to evaluate the behavior of the TPVs in nonpolar and polar solvents. In this way, the degree of swelling was determined based on equilibrium solvent-swelling measurements in polar (Brazilian personal car fuel, gasoline with 25% ethanol) and nonpolar (isooctane and a typical 20W50 motor oil) solvents. Three samples of the same composition were immersed into the solvent, and, after the swelling equilibrium was reached, the mass of the solvent or oil was deter-



**Figure 1** Evolution of the torque as function of time for the composition DBS 2.4. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

mined according to the ASTM D 471.<sup>18</sup> The results were expressed in terms of the mass of solvent absorbed per gram of dried TPV.

### Hardness

The Shore D hardness was determined according to the ASTM D 2240<sup>19</sup> by using a Bareiss durometer. One sample was taken from each TPV, and five measurements were made for each sample. The hardness value was taken as the median value of the measurements.

### Compression set

The compression set values were determined according to the ASTM D 395 standard (70 h, 70°C).<sup>20</sup> The specimen consisted of two 6.0 mm  $\pm$  0.2 mm thick cylindrical disks. The specimen was compressed to 25% of its original height using spacers to accurately measure the compression. After removing the sample from the oven, the specimen was allowed to cool for 30 min before measuring the final thickness.

### Morphological investigation

The morphology investigation was carried out by scanning electron microscopy (SEM). The sample surface was etched with glacial acetic acid for 2 h at 100°C and then sputter-coated with gold. Micrographs were obtained using Jeol JSM-6060 microscopes at the Center of Microscopy at the Federal University of Rio Grande do Sul, UFRGS. The images were obtained by secondary electrons (SEI).

### Differential scanning calorimetry (DSC)

The DSC scans of the same representative PA/NBR 40/60 compositions were carried out by a DSC Q20

TABLE I  
Designation of the TPVs and the Cure System Used

Components	Blend	curedNBR	D 1.0	D 2.4	SA	B 1.0	B 2.0	SP4.0	DBS1.4	DBS2.4
NBR	60.00	100.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00
PA (6/6-6)	40.00		40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Ionol CP			1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
DCP 40		2.40	1.00	2.40		0.10	0.20		1.44	2.40
Sulfur		0.70	0.30	0.30	1.50				0.42	0.70
CBS					1.00					
ZnO					3.00					
Stearic acid					1.00					
BMI		0.40				1.00	2.00		0.24	0.40
SP1045								4.00		
SnCl <sub>2</sub>								0.50		

The amounts are expressed in php (weight parts per 100 parts of polymer, PA and NBR). DCP 40 has 40% of active DCP, BMI = bismaleimide, DCP = dicumyl peroxide, SA = sulfur accelerated system, SP = phenolic resin 1045.

TA differential scanning calorimeter. The melting temperature ( $T_m$ ) and glass transitions ( $T_g$ ) of the samples were determined. The temperature scans were conducted from  $-50$  to  $240^\circ\text{C}$  at a heating rate of  $20^\circ\text{C min}^{-1}$ . Liquid nitrogen was used as the coolant.

## RESULTS AND DISCUSSION

### Mechanical properties

The stress-strain behavior of the TPVs that were processed with different curing systems is shown in Figure 2. The ultimate tensile strength, the stress at 100 and 200% of elongation and the elongation-at-break were determined, and the values are listed in Table II. It can be observed that the blend has very poor mechanical properties compared to the cross-linked compositions (TPVs). Compositions D1.0 and D2.4 exhibited similar performances, with a value of ultimate tensile strength close to 10 MPa and a very high elongation-at-break, reaching up to 300%. Based

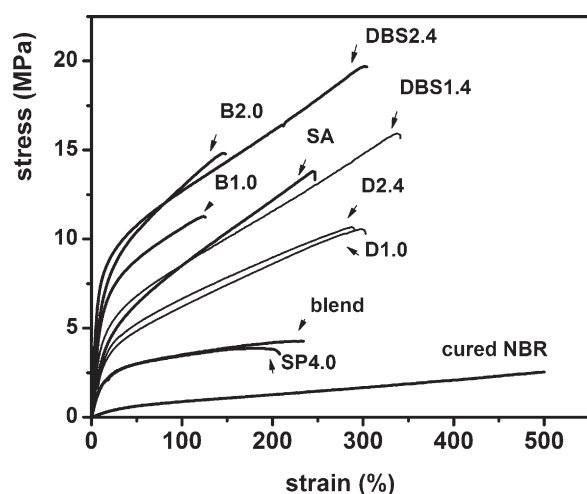


Figure 2 Stress-strain behavior of the different TPVs.

on these results, it can be concluded that 1 php of DCP is already enough to reach an appropriate crosslink density. Compositions B1.0 and B2.0 showed better performance than system D in terms of the ultimate tensile strength ( $\sim 15$  MPa for B2.0), but a reduction was observed in the elongation-at-break, reaching up to only 150%. For the DBS system, a rise in BMI increases both the ultimate tensile strength and the elongation-at-break. The SA system exhibited an ultimate tensile strength higher than the D system but lower than the B system, while the elongation was about 250% less than system D but was greater than system B. The DBS system exhibited a high value for the ultimate tensile strength and a very high elongation compared to the other systems, and this value increases as the crosslinker content increases. The curves of the DBS system with 1.4 and 2.4 php of DCP present very similar behaviors but differ in the value of the ultimate tensile strength, reaching 16 and 19.6 MPa, respectively. The elongation-at-break for the DBS system was close to 300%. To check the influence of the crosslinking on the final properties of the rubber, a sample of NBR crosslinked with the DBS system was prepared. It is observed that, despite the low ultimate tensile strength value (2.5 MPa), the elongation is very high, reaching values of 500%; this shows the influence of the crosslink system on tensile strength. Analyzing the stress at 100% of elongation, it is easy to see that samples B2.0 and DBS2.4 reached about 13 MPa, while the stress at 200% of elongation was 16.5 MPa for sample DBS2.4 and 12 MPa for samples DBS 1.4 and SA. We can clearly see that the ultimate tensile strength and the elongation-at-break depend on the curing system that is applied. As reported in the literature,<sup>3</sup> the stress-strain properties of the TPVs are strongly dependent on morphology, as will be discussed later. The tensile values achieved with the DBS 2.4 system are similar to those described in the literature.<sup>1</sup>

TABLE II  
Mechanical Properties of the TPVs

Sample	Ultimate strength (MPa)	Stress at 100% elongation (MPa)	Stress at 200% elongation (MPa)	Elongation at break (%)
Blend	4.8 ± 1.2	4.1 ± 1.0	4.8 ± 1.2	238 ± 40
Cured NBR	2.5 ± 0.4	0.9 ± 0.0	1.2 ± 0.0	558 ± 104
D 1.0	10.0 ± 1.4	6.6 ± 0.9	8.6 ± 0.6	271 ± 76
D 2.4	10.9 ± 0.8	6.7 ± 0.5	9.3 ± 0.6	287 ± 25
B 1.0	10.9 ± 2.0	10.4 ± 0.3	–	131 ± 51
B 2.0	15.1 ± 1.3	13.8 ± 1.1	–	135 ± 24
SA	14.2 ± 2.7	8.9 ± 0.6	12.8 ± 1.0	243 ± 63
SP 4.0	4.0 ± 0.3	3.5 ± 0.4	3.8 ± 0.3	254 ± 68
DBS 1.4	16.2 ± 1.3	9.2 ± 0.5	12.2 ± 0.5	341 ± 27
DBS 2.4	19.6 ± 1.3	13.0 ± 0.6	16.5 ± 0.9	285 ± 56

### Hardness and compression set

Given the advantages of processing and recycling, TPVs can replace thermoset rubber in many applications. However, they have limitations in regards to hardness and compression set. The hardness of a thermoplastic is higher than a thermoset rubber. Thus, the hardness of TPVs is determined mainly by the thermoplastic phase; only a small contribution is provided by the rubber domains and the crosslink density of the rubber phase. For thermoset rubbers, the hardness usually increases only slightly with the degree of crosslinking.<sup>21,22</sup> The hardness values of the TPVs and the blend are shown in Figure 3. The determined values are between 40 and 50 Shore D for the TPVs and ~ 30 Shore D for the blend. The overall hardness of the TPV is a consequence of its morphology, which consists of the rigid polyamide matrix and the crosslinking rubber domains of NBR. In the blend, because of the composition, PA/NBR 40/60, and the higher amount of rubber, a cocontinuous phase morphology or a morphology with large rubber domains must be formed and is responsible for the lower hardness of this material. Given the low hardness of NBR, this property was measured in the Shore A scale, and a mean value of 55 was obtained.

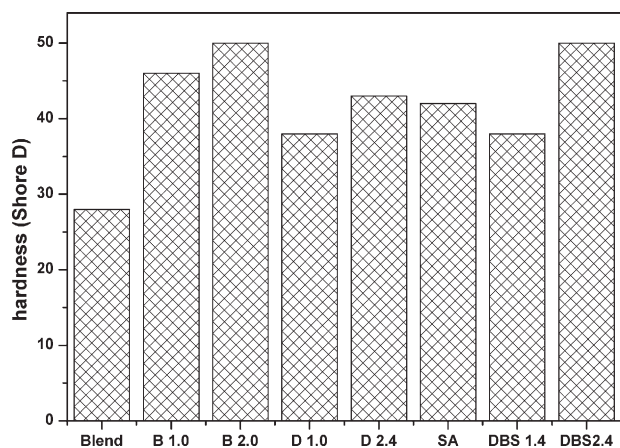


Figure 3 Hardness (Shore D) of the TPVs.

The compression set, i.e., the amount of deformation (expressed as a percentage of the original dimensions) retained by a material at a given temperature after compressive stress is released, is a very important property for many applications. However, the fact that the plastic phase begins to suffer irreversible deformation at a specific temperature limits the application of TPVs even at relatively low temperatures compared with the applicable temperatures of thermoset rubbers. Given this limitation, knowing the compression set values of TPVs is very important for defining the range of temperature for its application. The compression set values of the TPVs under investigation are shown in Figure 4. Values between 60 and 70% were obtained for the TPVs, while for the blend, a value of 100% was found; these results indicate that the blend exhibits a total plastic deformation. For the cured NBR, a compression set of 30% was determined, which confirmed that thermoset rubber exhibits better compression set values than TPVs. Moreover, the TPVs have a better performance than the respective blend. The dynamic vulcanization of the rubber phase is essential for the ultimate properties of the TPVs.

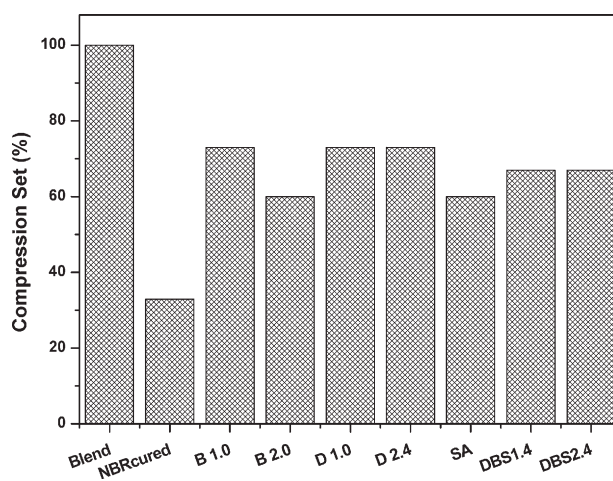
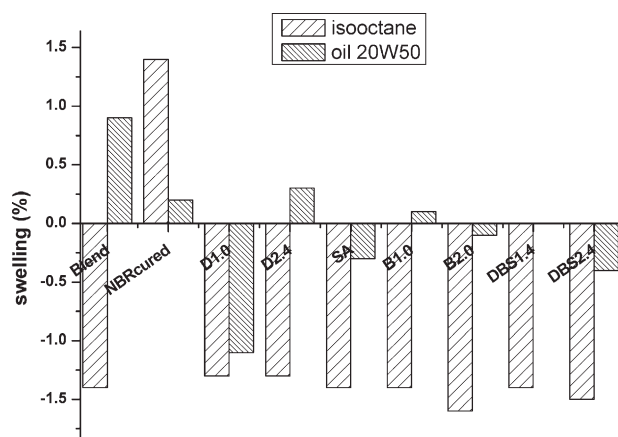


Figure 4 Compression set of the TPVs.



**Figure 5** Swelling behavior of the TPVs in nonpolar solvents: isooctane and motor oil (20W50).

### Swelling behavior

It should be recalled that this work aimed to manufacture TPVs with resistance in nonpolar solvents. TPVs are widely applied in automotive parts and could easily come into contact with oils, grease and fuel. Thus, in our analysis, the degree of swelling was determined in representative solvents for technological applications, i.e., oil and Brazilian fuel, and in a normal nonpolar organic solvent, isooctane. The solubility and the degree of swelling of a polymer network depend on the solubility parameters of the solvent and polymer and in the case of a thermoset rubber, also depend on its crosslink density.<sup>23,24</sup> For TPVs, they depend largely on the chemical nature of the partially crystalline thermoplastic matrix and only weakly on the crosslink density of the rubber phase. Thus, the effect of the plastic matrix is determinant, and it is difficult to detect the differences in the crosslink density of the rubber phases by this procedure.

In our study, the degree of swelling and the amount of absorbed solvent per gram of TPV was determined in isooctane, typical oil (20W50) and Brazilian car fuel to check the chemical resistance of the TPVs in these kinds of solvents. Figures 5 and 6 show the results of these measurements. The negative values indicate a loss of mass by extraction. It should be noted that only about 1.5% of the mass was extracted in the nonpolar solvent and that the swelling was almost negligible. However, in the polar solvent (fuel with ethanol), a high degree of swelling ( $\sim 40\%$ ) was found. This result is a consequence of the affinity of the polar matrix (PA 6/6-6 with the polar solvent). However, the fact that all of the other compositions, except the SA, show similar values indicates that the crosslink density of the rubber phase must be similar. The lowest degree of swelling combined with a lower value of compression of TPV SA can be an indication that its cross-

link density is higher. It is also observed that the blend exhibits a higher degree of swelling (about 50%), which is an indication that the crosslinking contributes to a better response to solvent resistance of the TPV.

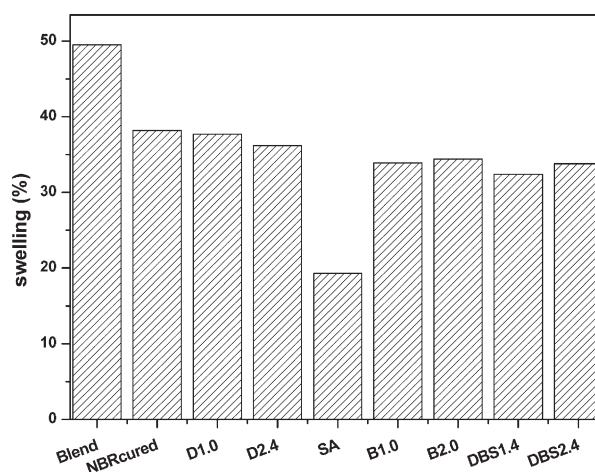
These results concerning the chemical nature of the polymers confirmed that TPVs based on PA/NBR exhibit a good resistance to nonpolar solvents but are not appropriate for use in polar solvents.

### Morphological investigation

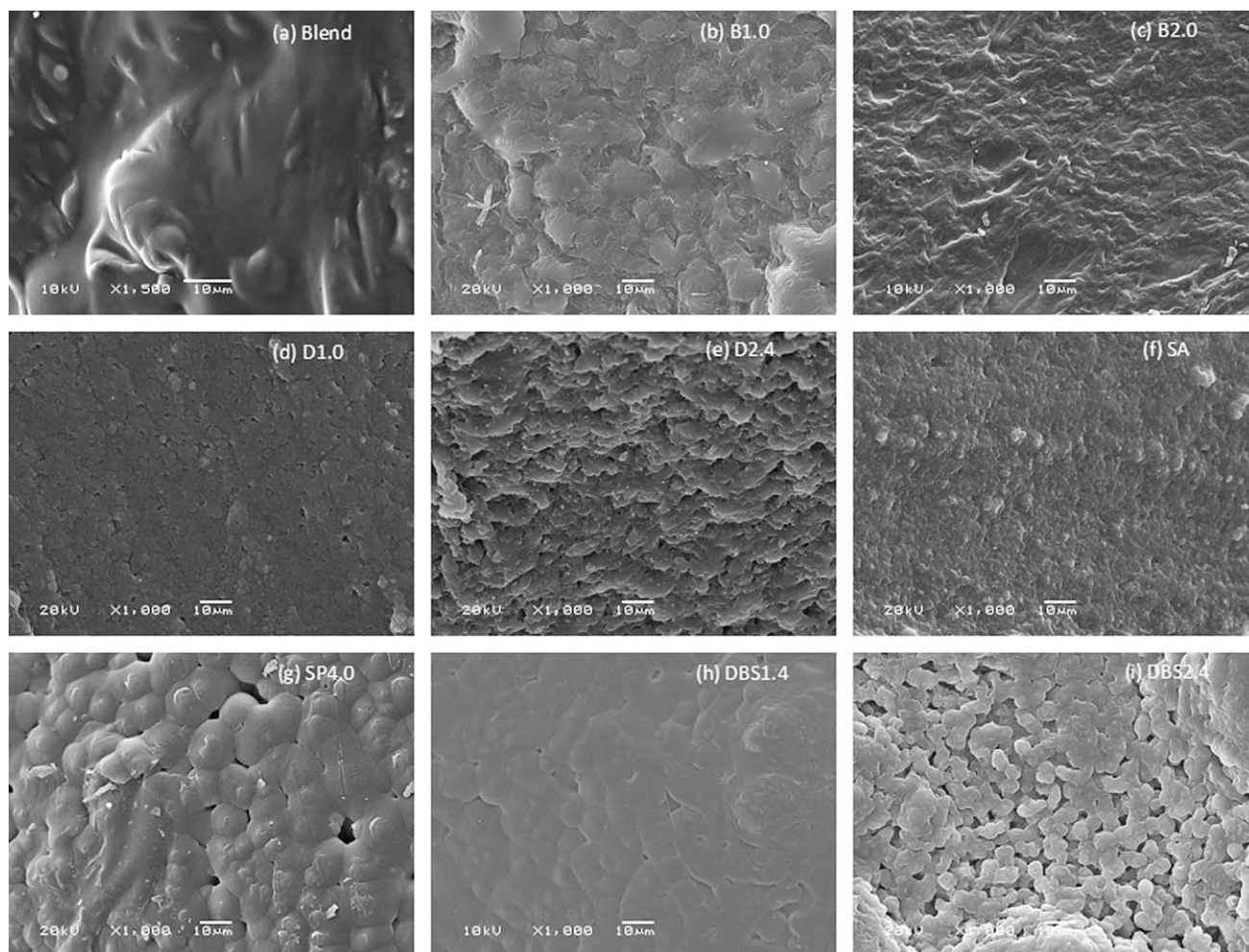
The morphologies of the TPV samples determined by SEM are shown in Figure 7. The morphological evaluations performed by SEM help us to understand and to relate the microstructure to the macroscopic properties of the material.

The quality of the micrographs depends on the contrast between the phases and the sample preparation. To obtain a better definition of the phases, the polyamide matrix was superficially extracted in acetic acid for 2 h at 100°C. The dry surface was sputter-coated with gold. All of the samples, including the PA/NBR blend, were submitted to the same treatment.

Coran and Patel<sup>25,26</sup> observed that the smaller the size of the elastomer phase dispersed in the plastic matrix, the better the mechanical behavior, higher tensile strength and higher elongation at break. The morphology is defined during the mixing process and depends on the compatibility of the mixture components, the mixing process itself, the chemical nature and the crosslink efficiency. Even though rubber has the largest mass fraction, it will be the crosslinked dispersed phase.<sup>12,27</sup> Figure 7(a–i) shows the photomicrographs of different compositions. In the SP4, D1.0 and D2.4 images, some hole-like dark regions can be detected. The authors attribute this to



**Figure 6** Swelling behavior of the TPVs in polar solvent: (gasoline with 25% of ethanol, by mass).



**Figure 7** SEM photomicrographs of the samples PA-6-66/NBR 40/60; (a) blend; the TPVs, (b) B1.0; (c) B2.0; (d) D1.0; (e) D2.4; (f) SA; (g) SP4.0; (h) DBS1.4; (i) DBS2.4.

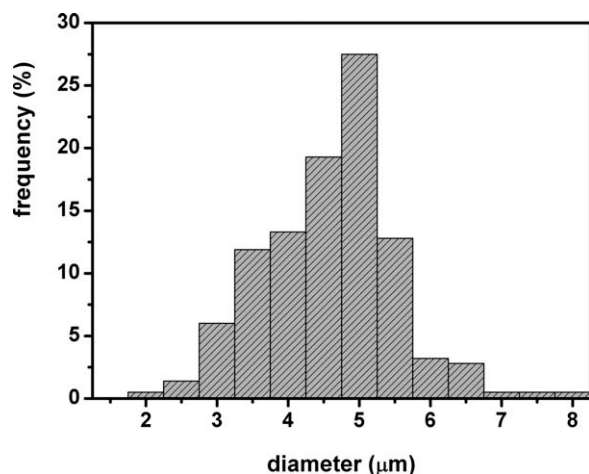
a deeper extraction of the polyamide matrix, because a rigorous control of the extraction is not easy. It depends on the contact surface as well as on time and on temperature of exposition. They cannot be holes because, qualitatively, the samples were totally homogeneous. The homogeneity of the samples was confirmed by the results of the stress–strain measurements, in which the tensile strength values of the different test specimens of a given sample were very similar.

The uncured blend and the cured samples B1.0, B2.0, D1.0, D2.0, SA, and DBS 1.4 exhibited a nearly cocontinuous phase morphology. Similar results were described in the literature by other authors<sup>13,14</sup> for TPVs based on PA/NBR. In the case of B1.0 and DBS 1.4, a coalescence of the rubber domains apparently occurred. It should be noted that sample SP4.0 and sample DBS2.4 exhibit a typical TPV morphology whose difference is in the size of the rubber domains. While for sample SP4.0 a rubber domain size of  $\sim 10 \mu\text{m}$  can be observed, sample DBS2.4 shows a rubber domain of  $\sim 5 \mu\text{m}$ .

It is easy to see that, for the DBS 2.4 sample, a homogeneous morphology of rubber domains well-dispersed in the PA matrix were obtained, while in the other samples, the size of the domains is bigger and not as well-defined. A size distribution determined from the image analysis of the DBS 2.4 TPV is shown in Figure 8 and a size average of  $4.3 \pm 0.9 \mu\text{m}$  could be determined. This small size average must be the reason for the excellent mechanical performance of this material, with an ultimate tensile strength of about 20 MPa and elongation close to 300%, which is similar to other studies,<sup>28,29</sup> where it is shown that stress–strain behavior in dynamic vulcanization is a direct function of the particle size of the rubber phase.<sup>1,30,31</sup> Coran<sup>25</sup> showed that rubber phase domains of about  $5 \mu\text{m}$  reached 20 MPa under stress and about 500% strain.

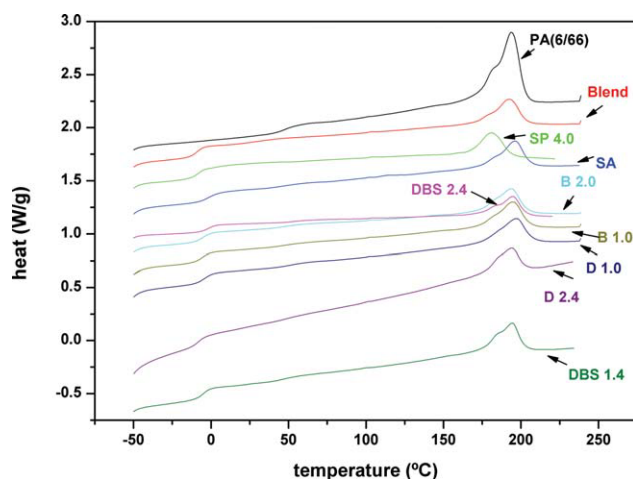
#### Thermal behavior of the TPVs

The thermal behavior of the polyamide and of some TPVs was investigated by DSC measurements.



**Figure 8** Size distribution of the domains of the TPV DBS2.4.

Figure 9 shows the DSC scans, and Table III presents the corresponding transitions determined through TA Instruments Universal Analysis 2000 version 4.1D software. The software allows for the expansion of the areas and a clear visualization of any transition. For the pure polyamide, two  $T_g$ s, at 48 and 139°C, and two  $T_m$ s points, at 188 and 194°C, could be detected. This polyamide is a copolymer that justified the double transitions. For the blend and for the TPVs, the  $T_g$  of the NBR at -9°C is also detected. The  $T_g$  of the NBR is likely shifted to higher values as a consequence of crosslinking, indicating that the flexibility of the rubber decreases as the crosslink density increases. Higher values were determined for the SA and DBS 2.4 samples, which can be attributed to a higher crosslinking density. In the blend and the TPVs composition, the second  $T_g$  of the polyamide phase is detected at a lower temperature, which may be an indication of a partial miscibility



**Figure 9** DSC curves of the primary polymers and of the TPVs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE III**  
 $T_g$  and  $T_m$  Values for the Samples

Sample	$T_{m1}$ (°C)	$T_{m2}$ (°C)	$T_{g1}$ (°C)	$T_{g2}$ (°C)	$T_{gNBR}$ (°C)
PA6/6-6	184	194	48	139	-
Blend	178	194	43	102	-9
B 1.0	183	195	48	-	-6
B 2.0	183	194	28	101	-5
D 1.0	185	197	51	101	-4
D 2.4	179	192	48	100	-8
S.A	186	196	47	110	-2
SP 4.0	160	181	49	102	-8
DBS 1.4	185	195	44	100	-5
DBS 2.4	185	195	52	-	-2

of the polyamide phase with the rubber phase, whereas the melting point does not change.

From the experimental values of  $\Delta H_f$ , which were determined by the area under the endothermic peak (melting peak) and by the use of a tabulated reference value<sup>32</sup> for a hypothetical 100% crystalline sample,  $\Delta H_{fo}$ , it is possible to calculate the degree of crystallinity,  $x$ , of any semicrystalline polymer. The following relationship was applied<sup>33-35</sup>:

$$x = \frac{\Delta H_f}{\Delta H_{fo}}$$

In our case, for the copolyamide (PA 6/6-6), an average value was calculated considering 100% crystallinity for both PA6 and PA6-6. Both polymers have very similar values<sup>32,35</sup> ( $\Delta H_{foPA6} = 204.8 \text{ J g}^{-1}$ ,  $\Delta H_{foPA6-6} = 196 \text{ J g}^{-1}$ , resulting in an average value of  $\Delta H_{fo}(\text{average}) = 200.4 \text{ J g}^{-1}$ , for a 50/50 composition). The calculated values are shown in Table IV. The compositions exhibit very similar crystallinity, indicating that the presence of the elastomeric crosslinking phase does not significantly affect the polyamide crystallization.

## CONCLUSIONS

Different crosslink systems can be used to obtain TPVs based on PA(6/6-6)/NBR in a composition of

**TABLE IV**  
Degree of Crystallinity of PA

Sample	Crystallinity of PA (%)
PA6/6-6	17
Blend	15
B 1.0	17
B 2.0	17
D 1.0	15
D 2.4	12
S.A	14
SP 4.0	15
DBS 1.4	15
DBS 2.4	13



40/60 by mass, by dynamic vulcanization in a mixing chamber. The mechanical performance of the TPVs depends on their morphologies, which, in turn, depend on the curing system used for the dynamic vulcanization. In our study, all the applied curing systems produced TPV, but the consisting of dicumyl peroxide combined with the coagents bis-maleimide and sulfur (DBS 2.4), in particular, showing an excellent mechanical performance. Up to now it is not known whether this system has been applied to obtaining TPVs. The morphological investigation of this system showed small rubber domains homogeneously distributed in the polyamide phase. The low degree of swelling in oil and isooctane is a good indication that the composition has a good resistance to nonpolar solvents. DSC measurements indicated that the crystallization of the polyamide phase is not significantly affected by the dynamic vulcanization. These results show that the system developed here has great potential for a technological application given the fact that both polymers and curing systems are well known in the technology of thermoset rubbers as well as easily available. It is believed that the processability of this material in a twin screw extruder will further improve their properties.

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