A Study About the Structure of Vulcanized Natural Rubber/Styrene Butadiene Rubber Blends and the Glass Transition Behavior

M. A. Mansilla,[1,2] L. Silva,[2,3] W. Salgueiro,[3,4] A. J. Marzocca,[1] A. Somoza[3,4]

[1]LPyMC, Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón I, C1428EGA, Buenos Aires, Argentina
[2]Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina
[3]IFIMAT, Facultad de Ciencias Exactas, UNCentro, Pinto 399, 7000 Tandil, Argentina
[4]Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Calle 526 entre 10 y 11, 1900, La Plata, Argentina

ABSTRACT: A study of the thermal behavior of cured elastomeric blends of natural rubber (NR) and styrene butadiene rubber (SBR) prepared by solution blending in toluene is presented. Binary blends with different compositions of NR/SBR were produced using a conventional cure system based on sulfur and TBBS (n-t-butyl-2-benzothiazole sulfonamide as accelerator. The compounds were vulcanized at 433 K up to an optimum time of cure determined by rheometric tests. From swelling tests, the crosslink densities of the compounds were obtained and compared with those obtained in similar blends prepared by mechanical mixing. The results were analyzed in terms of the disentangling of the chain structures of the SBR and NR phases and the achieved cure state of the blend. Using differential scanning calorimetry, the glass transition temperature T_g of each blend was measured. In most compounds, the value of T_g corresponding to each phase of the blend was determined, but in some blends a single value of T_g was obtained. The variation of T_g with the composition and cure level in each phase was analyzed. On the other hand, a physical mixture of two equal parts of NR and SBR vulcanized was measured and the results were compared to those of the NR50/SBR50 cured blend. Besides, to analyze the influence of the network structure, pure NR and SBR unvulcanized samples were measured. On the basis of all the obtained results, the influence of the interphase formed in the blend between SBR and NR phases is discussed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 992–999, 2012

Key words: blends; crosslinking; glass transition; differential scanning calorimetry (DSC)

INTRODUCTION

The main advantage of preparing elastomeric compounds from a mixture of two or more pure elastomers is the possibility of producing a new material, sometimes with a lower cost and combining the properties of the main polymers without resort to a new synthesis process.

One of the most important characteristics of the elastomeric materials is the transition, below a characteristic temperature, from an elastic phase to a glassy one. When considering possible applications of this kind of materials, this behavior should be taken into account. Such a change is characterized by the glass transition temperature, T_g. For temperatures below T_g, molecules are frozen on place and there is no relative movement among the polymer chains. At the glass transition, the material undergoes drastic changes in the values of some physical parameters like the thermal expansion coefficients, specific heat, and hardness.[1] There are many different experimental techniques that use these changes to detect the glass transition. One of the most used is the differential scanning calorimetry (DSC), in which the heat flow as a function of the temperature is measured. The presence of an inflection point in this DSC curve indicates a change in the heat capacity caused by structural changes in the material and it is associated with the T_g.[2]

In binary elastomeric blends, the phase behavior is very complicated since a macro and micro phase separation can take place.[3] Among the binary

TABLE I
Compound Formulations in (phr)

	A	B	C	D	E	F	G	H	I	J	K
						Compound					
NR	–	10	20	30	40	50	60	70	80	90	100
SBR	100	90	80	70	60	50	40	30	20	10	–
Stearic Acid						2					
ZnO						5					
Sulfur						2.25					
TBBS						0.7					

elastomer blends, there are cases in which both phases are perfectly miscible and, as a result, only one glass transition temperature is observed. On the other hand, the classical case of immiscibility is marked by the appearance of two unbroadened glass transition temperatures which remain unchanged when comparing to those corresponding to the component (non-blended) polymers. It is well-known that any shift in T_g indicates a partial solubility.[4] In a binary blend, the existence of two glass transitions temperatures may be observed at different temperatures from those of each elastomeric component of the blend. In such cases, the T_g for the elastomer with the lowest glass transition temperature increases and, conversely this characteristic temperature of the polymer with the highest glass transition temperature decreases. As a consequence, the temperature distance between the two glass transitions is shortened. The extent of this shortening is a measure of the miscibility; thus, in the ideal case of a miscible blend there exists a single T_g.

In technological applications, mainly in the tire industry, the most used elastomeric blends are based on natural rubber (NR), polybutadiene rubber (BR), and styrene butadiene rubber (SBR).[5–10] BR and SBR have the kindness of good resistance to crack propagation and NR has an excellent ultimate strength and low mechanical hysteresis. These properties make the rubbers mentioned highly attractive to develop blends in order to improve the performance of tires.[9,10]

Šebenik et al.[11] studied rheological and thermal properties of three binary uncured elastomeric blends BR/SBR, BR/NR, and NR/SBR. In the case of the BR/SBR and NR/SBR blends, they reported that the weight ratio between the elastomers used for the blend preparation determined the relation between the dispersed and the continuous phase in these systems.

In a previous article, on the basis of the structure formed during the vulcanization process, one author of the present work[12] used calorimetric tests and diffusivity measurements to discuss the thermal properties of similar blends to these studied in the present work. Recently, authors of the present work

used small-angle X-ray scattering (SAXS) and positron annihilation lifetime (PALS) techniques to get valuable information on the NR/SBR interphase developed in the same blends studied in the present work.[1,13,14]

In this work, we continue such research topics studying the thermal behavior of NR/SBR vulcanized blends considering, in particular, the influence of each elastomer content on the formulation of the binary blend. The experimental results obtained using DSC, swelling tests, and rheometry are analyzed in terms of the crosslink density and the composition of the blends. Besides, the role of the NR/SBR interphases is also analyzed and discussed.

EXPERIMENTAL

The binary blends studied are composed of NR (Standard Malaysian rubber SMR-20) with a molecular weight $M_n = 178,830$ g/mol and a polydispersity of 6.3, and an emulsion SBR-1502, Arpol(E-SBR) 1502 provided by Petrobras, with a molecular weight $M_n = 128,260$ g/mol and a polydispersity of 3.8, measured by the gel permeation chromatography (GPC) technique. The densities were ρ (NR) = 0.917 g/cm^3 and ρ (SBR) = 0.935 g/cm^3.

Eleven different blends of NR and SBR were prepared following the formulations given in Table I. All the compounds had a cure system based on sulfur and TBBS (*n-t*-butyl-2-benzothiazole sulfonamide).

The preparation method of the blends consisted of dissolving in toluene each elastomer with a relation of 18 g/dm^3 and 20 g/dm^3 for NR and SBR, respectively. The viscosities of these solutions, measured at room temperature with a Brookfield viscosimeter, were 55 cP and 9.8 cP for the NR/toluene and SBR/toluene solutions, respectively.

To prepare each blend, both solutions were mixed with the chosen proportions of each elastomer and chemicals were also incorporated. The mixture was further homogenized with mechanical agitation and in an ultrasonic bath. Finally, the solvent was evaporated at room temperature for 3 days until obtaining a constant weight.
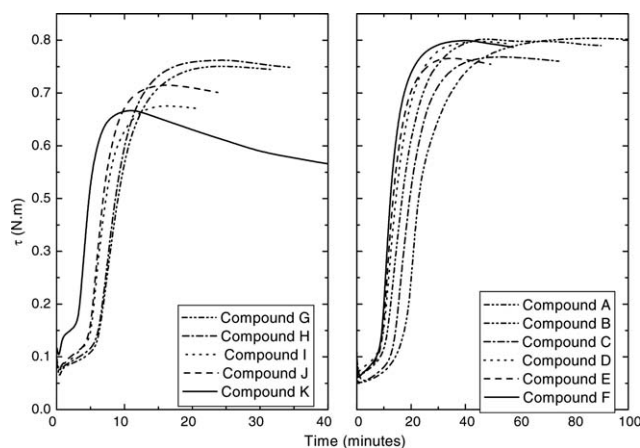
Figure 1 Rheometer torque curves of NR/SBR samples as a function of time. All samples were cured at 433 K.

In order to study the influence of the preparation method on the viscosity of NR and SBR, the Mooney viscosity (ML 1+3 100°C) was measured in an Alpha MV2000 Mooney viscosimeter, following ASTM D1646-04. In the case of NR, the obtained values were: 87.8 MU for the raw material and 33.5 MU for the elastomer dissolved in toluene and later on evaporated. For the SBR, the viscosities were: 56.5 MU and 43.7 MU for the raw material and the elastomer after the dissolving treatment, respectively.

A final mix of each compound was made in a laboratory mill and later characterized at 433 K by means of torque curves [see Fig. 1(a,b)] in an Alpha MDR2000 rheometer. From these curves the time taken to achieve the maximum degree of cure, t_{100}, for each compound was obtained. These values are given in Table II.

Due to the experimental techniques used, two kinds of samples were simultaneously cured in a mold with two cavities: strip samples of $50 \times 4 \times 2$ mm^3 and disc samples (17 mm diameter and 2 mm thickness). All the samples were vulcanized in a press at 433 K up to the time t_{100} with an applied pressure of 5 MPa. Then, at the end of the curing cycle, samples were rapidly cooled in an ice and water mixture.

Scanning electron microscopy (SEM) micrographs of some of the NR/SBR blends studid in the present work were recently reported by the authors of this article.[1] Specifically, in that work an analysis of the morphology of the NR25/SBR75, NR50/SBR50, and NR75/SBR25 samples was given.

Swelling tests

The molecular weight of the network chain between chemical crosslinks M_{cs} was determined from swelling tests using the relationship[15,16]

$$M_{cs} = -\frac{\rho\,(1 - 2/\phi)\,V_1\,v_{2m}^{1/3}}{\ln(1 - v_{2m}) + \chi\,v_{2m}^2 + v_{2m}} \qquad (1)$$

TABLE II
Values of t_{90} and t_{100} Obtained by Rheometric Measurements at 433 K (Fig. 1), v_{2m}, and the Molecular Weight Between M_{cs}

| | Compound | | | | | | | | | | |
	A	B	C	D	E	F	G	H	I	J	K
t_{90} (min)	39.72	27.7	28.6	23.2	19.9	19.1	13.3	12.8	9.6	9.5	6.6
t_{100} (min)	87.6	57.2	53.8	47.2	36.8	41.6	28.1	25.1	16.7	15.8	10.6
v_{2m}	0.159 ± 0.009	0.155 ± 0.010	0.138 ± 0.009	0.136 ± 0.009	0.126 ± 0.011	0.137 ± 0.004	0.144 ± 0.010	0.136 ± 0.008	0.074 ± 0.006	0.062 ± 0.012	0.096 ± 0.010
M_{cs} ($\times 10^4$) [g/mol]	1.147 ± 0.173	1.160 ± 0.186	1.450 ± 0.244	1.421 ± 0.232	1.629 ± 0.326	1.280 ± 0.090	1.090 ± 0.175	1.183 ± 0.165	4.206 ± 0.684	5.658 ± 2.346	2.222 ± 0.482

where ρ is the density of the rubber network, ϕ the functionality of the crosslinks, v_{2m} the polymer volume fraction at equilibrium (maximum) degree of swelling, and V_1 the molar volume of solvent. χ is an interaction parameter between the polymer and the swelling agent. Sulfur cured elastomers are usually considered as a 4-functional network[17] and for the present work this functionality, $\phi = 4$, was used in eq. (1).

To estimate v_{2m} a method proposed by Cunnen and Russell was used.[18] For these tests, the cured disc samples were used and they remained in pyridine for 16 h at room temperature. Then, they were continuously extracted in acetone for 24 h (ASTM D297-93 (2006)) and dried. One probe of each sample was completely immersed in pure toluene ($V_1 = 106.29$ mL/mol[19]), in a sealed glass bottle, at room temperature until the equilibrium swelling occurred. As usual, this process took more than 48 h. When this step was completed, the samples were removed from the bottles, the excess toluene from the surface of the samples was wiped off and the swollen weight immediately measured using a Sartorius balance with an accuracy of 0.0001 g. Finally, the samples were dried at 323 K and weighed again when all the solvent was evaporated.

The volume fraction v_{2m} was calculated by means of the following relationship

$$v_{2m} = \frac{\left[(W_d - W_f)/\rho\right]}{\left[((W_d - W_f)/\rho) + ((W_s - W_d)/\rho_s)\right]} \quad (2)$$

being W_d the weight of the sample after swelling and drying, W_s the weight of the swollen sample, and ρ_s the density of the solvent (0.8669 g/cm^3 for toluene[19]). W_f is the weight of the non-extractable filler in the sample and was evaluated using the ASTM D297-93 (2006) method. The volume fractions v_{2m} for each blend composition are also given in Table II.

The interaction parameter polymer-solvent χ was evaluated using a mixture law, starting from χ for the systems NR/toluene and SBR/toluene. These values were $\chi(\text{SBR}) = 0.524 - 0.285v_{2m}$[20] and $\chi(\text{NR}) = 0.43 + 0.05v_{2m}$.[21]

Values of M_{cs} obtained for each vulcanized pure compounds and the binary blends are reported in Table II.

Thermal tests

The analysis of the thermal behavior of the blends was made with a differential scanning calorimeter Q20-TA Instruments. The instrument was calibrated in temperature and heat flow using indium and mercury as reference materials. The mass of the DSC samples, cut from the cured strip samples, was about 4 mg. The calorimeter was programmed for a heating/cooling/heating cycle between 183 K and 273 K with a rate of 10 K/min and measurements were performed under an argon atmosphere with a constant flux of 50 mL/min.

RESULTS AND DISCUSSION

In Figure 1, the higher reactivity during the vulcanization reaction of NR with respect to SBR can be seen. For pure NR, the maximum of the torque curve, τ_{max}, is reached at times significantly lower than those of the pure SBR compound and of all the blends. As known, the torque curves obtained using the rheometer responds to the presence of elastically active crosslinks and also to the entanglements present in the chain structure. As it can be inferred from the curve corresponding to NR, a considerable degradation is produced in this pure compound when it is overcured. This result indicates that in the blends the NR phase is overcured because, according to Table II, in all the cases the time t_{100} of the blends is higher than the same characteristic time obtained for the pure NR compound (sample labeled K). The evident reversion observed in the pure NR compound when is overcured is a consequence of the vulcanization system used in the compound formulation. From Table I, the ratio accelerator/sulfur is 0.31 which indicates that we are dealing with a conventional system (CV).[22] An analogous behavior in vulcanized NR compounds was reported by different authors.[23–27]

A similar analysis can be made for the SBR phase in the cured blends. All blends have a lower t_{100} than that obtained for the pure SBR compound (sample labeled A). Then it could be inferred that the SBR in the blends is undercured.

Besides, from the results presented in Figure 1, it can be concluded that τ_{max} is higher in the cured SBR compound than that in the cured pure NR compound. It is interesting to notice that the rheometer curves of these pure compounds are quite different from those obtained for the same formulations but using a different preparation technique. In a previous study of some authors of the present research,[12,28,29] NR/SBR blends were prepared using a two-roll mill. In the mentioned works, rheometer tests were also performed at 433 K. In the reported results, it was found that the τ_{max} values obtained for all the compounds are higher than those obtained in this work, which are presented in Figure 1.

In Figure 2, the relative value of the torque $\Delta\tau = \tau_{\text{max}} - \tau_{\text{min}}$ (where τ_{min} is the minimum of the torque curve) is plotted as a function of the proportion of NR in the binary blend samples. $\Delta\tau$ is proportional to the elastic modulus of the material, which
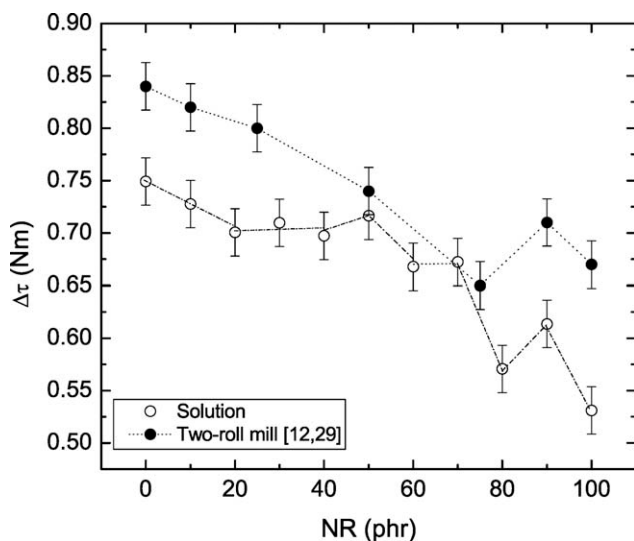
Figure 2 Relation between $\Delta\tau$ and NR proportion in the blend. Results of blends prepared in different ways are also shown (see text). Dash–dot lines are only an eye guide.

is changing during the vulcanization process due to the formation of sulfur crosslinks. In this figure, it can be observed that $\Delta\tau$ increases in the samples richer in SBR. This behavior can be analyzed considering the cure time t_{100} of each sample. According to the rheometer data reported in Table II, t_{100}(SBR) = 87.6 min and at this cure time $\Delta\tau$ reaches the maximum value for this sample, which is related with the maximum crosslink density developed in the compound.[26,30] As can be seen in Table II, in the cured blends t_{100}(NR/SBR blends) < t_{100}(SBR); then, the crosslink density in the SBR phase of each blend must be lower than that in the sample of pure SBR. In such a way, the cured compound NR90/SBR10 (sample J) has the lower crosslink density in the SBR phase. When analyzing the NR compound (sample K), the time to achieve the highest value of $\Delta\tau$ is t_{100}(NR) = 10.6 min; so, in the cured blends t_{100}(NR/ SBR blends) > t_{100}(NR). It is known that there is reversion in NR when the material is overcured due to the degradation of the crosslink structure.[24,27] Besides, there are evidences that during the vulcanization process curatives migrate from the SBR to the NR phase. In such a way, the degradation effect of the NR phase is compensated.[1,31]

In Figure 2, data of $\Delta\tau$ obtained in previous research works are also plotted. As mentioned, these data belong to similar compounds but prepared in other experimental conditions[12,28,29]; i.e., blends were prepared by mixing NR and SBR in a roll mill without a previous dissolution of the elastomers in toluene. It is interesting to note that the $\Delta\tau$ values are systematically lower in the samples prepared with the technique used in the present work, mainly

when the blends are richer in NR. This behavior can be attributed to the lower viscosity of both solutions (NR/toluene and SBR/toluene) in the preparation of the blend by solution, comparing to the viscosity of both elastomers previously to the roll mill mixing. As can be seen, for both solution blending and mechanical mixing preparation $\Delta\tau$ values are similar in the NR50/SBR50 samples. To understand this result it should be assumed that the morphology of the phases plays an important role in the preparations of the blends. In fact, according to the literature,[32,33] the very different initial viscosities of both NR and SBR used in the solution blending and in the mechanical mixing samples preparation would have a significant influence on the co-continuity of the phases. Therefore, the sample preparation methods could modify the mechanical properties of the compounds. However, additional work must be done to elucidate this issue.

From the swelling tests, the molecular weight between crosslinks M_{cs} was obtained using eq. (1), values of this parameter for all samples are presented in Table II.

For 4-functional networks the total crosslink density is defined by[17]:

$$\mu_{cs} = \frac{\rho}{2}\left(\frac{1}{M_{cs}} - \frac{1}{M_n}\right) \qquad (3)$$

For blends, this equation can be used as a first approach, considering a mixture law for the compound density and the corresponding molecular weights. In Figure 3, the obtained crosslink density values are shown. In this figure, μ_{cs} values calculated using the M_{cs} that we have previously reported for samples prepared with a mill[13,29] are also shown. The main differences between both preparation methods are observed when the samples are richer in NR. These results are in agreement with the $\Delta\tau$ behavior for the same samples.

The more noticeable difference in the crosslink densities corresponds to the compounds of pure NR and those with high proportion of NR in the formulation. The explanation for this behavior can be found in the effect of the preparation of the compounds in its initial viscosity. After dilution with toluene, and the subsequent evaporation, the Mooney viscosity drops more than a half of its value. This behavior is consequence of a sharp decrease in the density of entanglements in rubbers prepared with the methodology we have used. It must be considered that, when analyzing the data of the swelling test, the Flory-Rehner's model used to estimate the molecular weight between crosslinks does not discriminate the contribution coming from crosslinks than that from the entanglements. Thus, when compounds are prepared by mixing in a mill the amount
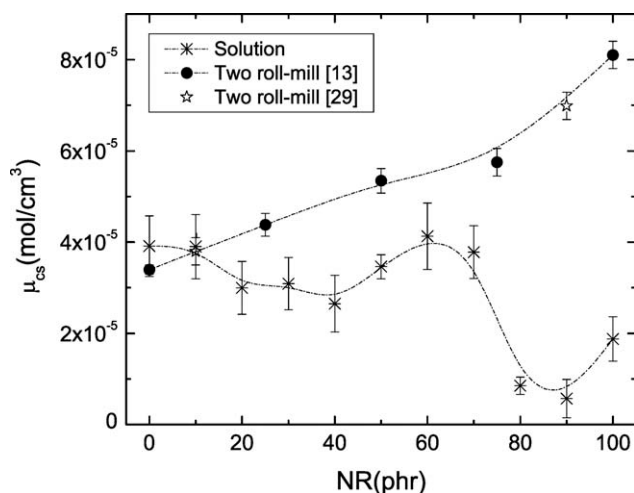
Figure 3 Total crosslink density μ_{cs} as a function of the NR content in the blend. Results of blends prepared in different ways are also shown. Dash–dot lines are only an eye guide.

of entanglements is higher than that obtained for compounds prepared using the solution preparation.

In the case of SBR, the disentanglements obtained by the preparation using a previous dissolution in toluene are not so remarkable, and the drop in the Mooney viscosity is lower. Consequently, as can be seen in Figure 3 the crosslink densities obtained by both methodologies are similar.

The entanglement contribution to the modulus can be discriminated from the crosslinks using the tube model for crosslink networks.[34] It was reported that in NR and SBR compounds prepared by mechanical mixing, and with similar formulations to that used in our work, the contribution of crosslinks and entanglements to the shear modulus is of the same order.[26,35]

DSC tests give the variation of the heat flow, Q, as a function of the temperature at a constant temperature rate. The glass transition temperature is usually evaluated as the inflection point of this curve.

Through the analysis of the thermograms measured, it was possible to determine the T_g values for each vulcanized compounds: pure elastomeric samples and the binary blends. In Figure 4, T_g values as a function of the NR content were plotted. In this figure, full circles represent the values of the glass transition temperatures coming from the NR phase, T_g^{NR}, while full triangles represent the transition temperatures characteristic of the SBR phase T_g^{SBR}. It is worth noting that in most of the blends it was possible to distinguish two glass transition temperatures, i.e. the T_g for each phase. This behavior is reasonable due to the fact that two rubbers forming the blends are immiscible. Despite this property, from the DSC scans for the blends NR10/SBR90 (sample B) and NR20/SBR80 (sample C) only one T_g could be revealed.

As it is expected, in both pure compounds the vulcanization process increases the glass transition temperature due to the crosslink formation that limits the movement of the polymer chains. When comparing the T_g values for uncured (represented by open circles in Fig. 4) and cured pure compounds, the observed increase in this parameter is more pronounced in the case of the SBR.

Moreover, it is worth analyzing the behavior of the glass transition temperature for each phase in particular. It results that, as the blend becomes richer in NR the T_g^{SBR} value slightly decreases. This behavior can be attributed to the fact that such SBR phase is decreasingly vulcanized with the consequent diminution of the crosslink density in its structure. Besides, it can be observed that the T_g^{NR} decreases when the NR content in the blend increases and that the pure sample of NR, which has the optimum cure degree, has the lower T_g value. Meanwhile, the higher value of this characteristic temperature was observed for the blend NR30/SBR70. This result deserves to be discussed separately, because in this sample the NR phase is overvulcanized, and therefore its crosslink structure should be degraded; on the other hand, the SBR phase should have an almost optimal structure. The fact that the higher T_g^{NR} occurs for the sample NR30/SBR70 could be interpreted as a consequence of the migration of curatives from the SBR phase to the NR phase.[31] In the NR phase, this process could generate a higher crosslink density than that it would have as a result of the degradation of this elastomer.

In the present discussion, an additional issue that should be taken into account is the fact that there exists a high increase of the crosslink density in the NR zone within the NR/SBR interphase region. In
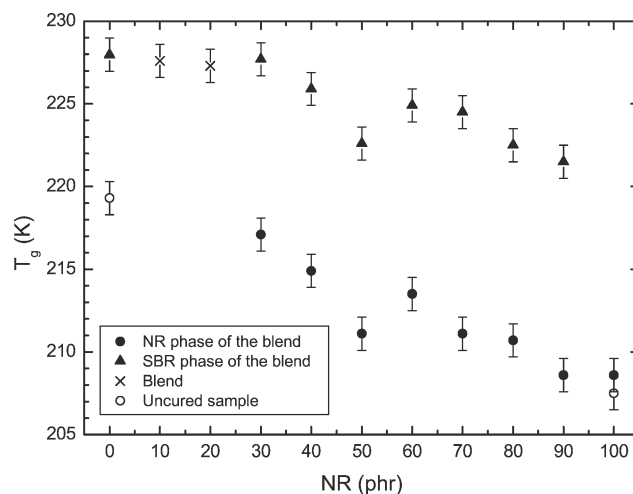
Figure 4 Glass transition temperature T_g as a function of the NR content. As can be seen, in most cases the two glass transition temperatures corresponding to each phase forming the binary blend were obtained.
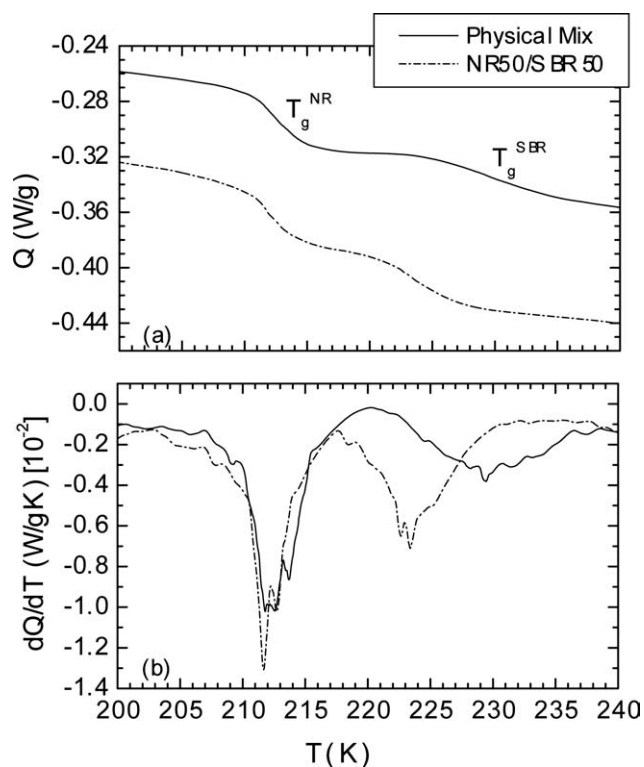
Figure 5 (a) Heat flow as a function of temperature. (b) Derivative of the heat flow as function of temperature. In this figure, the thermogram obtained for the compound blend NR50/SBR50 is compared to that one for samples prepared as a physical mix of 50% NR and 50% SBR (see text).

this sense, the presence of three components of the binary blend, instead of the two phases, should be taken into account: the structures of each pure NR and SBR phases plus an NR/SBR interphase.[13,31] This topic is discussed in detail below.

On the other hand, following the ideas proposed by Hourston and Song,[36] a calorimetric study of a physical mix made by equal parts of the elastomers NR and SBR was also carried out. In this case, both elastomers were vulcanized following the same procedure applied to treat the NR50/SBR50 blend. Then, the thermogram obtained was compared to that of the NR50/SBR50 compound [see Fig. 5(a)]. From an analysis of the figure, it can be seen that the T_g^{SBR} value for the NR50/SBR50 compound has an important shift to lower temperature values when compared to the same parameter obtained measuring the physical blend. This behavior in the compound can be attributed to the vulcanization process that takes place with the NR and SBR mutually interacting, allowing the migration of the curatives from the SBR phase to the NR phase.[31] As it was already mentioned, it should be expected that in blends the crosslink density in the SBR phase be lower than that of pure vulcanized SBR. Under this frame, the differences in the T_g^{SBR} values can be associated with the variation of the crosslink density in

the SBR phase of the blend; therefore, a lower energy is necessary to produce the transition in the blend. Conversely, the T_g^{NR} values do not show significant changes. Although the NR phase in the compound NR50/SBR50 is degraded ($t_{100}^{NR50/SBR50} = 41.6$ min and $t_{100}^{NR} = 10.6$ min, respectively), the similarity in the T_g^{NR} values could be associated with the fact that the curative migration from the SBR to the NR phase would produce a recovery of the crosslink structure. In such a sense, it is interesting to compare each thermogram in the intermediate region between the two transition temperatures where the glass and elastic states coexist. As can be seen in the DSC scans of both kinds of samples, in the intermediate temperature zone there are differences in the respective slopes. In order to highlight this effect, in Figure 5(b), we have represented for each DSC curve dQ/dT as a function of temperature. As a result, for the sample prepared as a physical mix the derivative function is practically zero in the intermediate region between the two transition temperatures, while the same function for the NR50/SBR50 compound presents a different behavior. This difference could be assigned to the presence of an interphase region formed between the NR and SBR phases. In fact, it seems reasonable to assume that this interphase should have a different crosslink structure from those of the NR and SBR phases. Work in progress will allow us supporting this interpretation.

CONCLUSIONS

The present work was addressed to the study of the structure and the thermal behavior of NR/SBR binary blends prepared with different contents of both elastomers using the solution method and vulcanized at 433 K.

1. Rheometric and swelling studies show that the compounds richer in NR have lower crosslink densities and lower values of the corresponding relative torque. When comparing these results to those obtained on samples prepared in a mill, it could be concluded that the crosslink density shows pronounced differences in the compounds richer in NR. This behavior was explained in terms of degradation during the vulcanization treatment of sulfur crosslinks in the NR phase and, at the same time, to the increase of the crosslink density in the SBR phase.

2. The glass transition temperature of each phase depends on the blend composition and the crosslink level attained in each phase. The results obtained allowed to infer that, during the vulcanization process, there is a curative migration from the SBR to the NR phase. In

order to go deeper into this analysis, samples were prepared by a physical mix of the two rubbers (NR and SBR), specifically these samples contained equal amounts of each elastomer. Then, calorimetric results of these samples were compared to those obtained for the blend compound NR50/SBR50. As a result, it was possible to conclude that to analyze the discrepancies between the respective DSC curves of both blends it is necessary to consider the existence of a third component (i.e., interphase) between both elastomers with a different network structure from those of the pure phases.

References

1. Salgueiro, W.; Somoza, A.; Silva, L; Consolati, G.; Quasso, F.; Mansilla, M. A.; Marzocca, A. J. Phys Rev E 2011, 83, 051805.
2. Gallagher, P. K. In Thermal Characterization of Polymeric Materials; Turi, E. A., Ed.; Academic Press: New York, 1997; p 73.
3. Vilgis, T. A.; Heinrich, G. Kautsch Gummi Kunstst 1995, 48, 323.
4. Sircar, A. K. In Thermal Characterization of Polymeric Materials; Turi, E. A., Ed.; Academic Press: New York, 1997; p 887.
5. Atashi, H.; Shiva, M. Asian J Chem 2010, 22, 7519.
6. Bijarimi, M.; Zulkafli, H.; Beg, M. J Appl Sci 2010, 10, 1345.
7. Gunasekaran, S.; Natarajan, R. K.; Kala, A. Spectrochim Acta A 2007, 68, 323.
8. Fernández-Barridi, M. J.; González, N.; Mugica, A.; Bernicot, C. Thermochim Acta 2006, 444, 65.
9. Joseph, R.; George, K. E.; Francis, D. J. J Appl Polym Sci 1988, 35, 1003.
10. Datta, S. In The Science and Technology of Rubber; Mark J. E.; Erman, B.; Eirich, F. R., Eds.; Academic Press: California, 2005; p 529.
11. Šebenik, U.; Zupančič-Valant, A.; Kranjc, M. Polym Eng Sci 2006, 46, 1650.
12. Goyanes, S.; Lopez, C. C.; Rubiolo, G. H.; Quasso, F.; Marzocca, A. J. Eur Polym J 2008, 44, 1525.
13. Salgueiro, W.; Somoza, A.; Marzocca, A. J.; Torriani, I.; Mansilla, M. A. J Polym Sci Polym Phys 2009, 47, 2320.
14. Salgueiro, W.; Somoza, A.; Marzocca, A. J.; Consolati, G.; Quasso, F. Rad Phys Chem 2007, 76, 142.
15. Flory, P. J.; Rehner, J. J Chem Phys 1943, 11, 512.
16. Flory, P. J.; Rehner, J. J Chem Phys 1943, 11, 521.
17. Gronski, W.; Hoffman, U.; Simon, G.; Wutzler, A.; Straube, E. Rubber Chem Technol 1992, 65, 63.
18. Cunneen, J. I.; Russell, R. M. Rubber Chem Technol 1970, 43, 1215.
19. Lide, D. R., Ed. CRC Handbook of Chemistry and Physics, 78th ed.; CRC Press: New York, 1997; p 3.
20. Marzocca, A. J. Eur Polym J 2007, 43, 2682.
21. Kraus, K. Rubber Chem Technol 1957, 30, 928.
22. Aprem, A. S; Kuruvilla, K.; Thomas, S. Rubber Chem Technol 2005, 78, 458.
23. Skinner, T. D. Rubber Chem Technol 1972, 45, 182.
24. Loo, C. T. Polymer 1974, 15, 357.
25. Chen, C. H.; Collins, E. A.; Shelton, J. R.; Koenig, J. L. Rubber Chem Technol 1982, 55, 1221.
26. Cerveny, S.; Marzocca, A. J. J Appl Polym Sci 1999, 74, 2742.
27. Marzocca, A. J.; Steren, C. A.; Raimondo, R. B.; Cerveny, S. Polym Int 2004, 53, 646.
28. Mansilla, M. A. Master Thesis, Department of Physics, University of Buenos Aires, 2007.
29. Mansilla, M. A.; Quasso, F.; Marzocca, A. J. In Proceedings Jornadas SAM/CONAMET, San Nicolás, Argentina, 2007; p 1111, http://www.materiales-sam.org.ar/sitio/biblioteca/CONAMET-SAM2007/sam%20conamet%2007/pdf/T%C3%B3pico%2010%20-%20Materiales%20Polim%C3%A9ricos/10–14%20MansillaM%20(O).pdf
30. Ding, R.; Leonov, A. I.; Coran, A. Y. Rubber Chem Technol 1996, 69, 81.
31. Mallon, P. E.; Mcgill, W. J. J Appl Polym Sci 1999, 74, 1264.
32. Avgeropoulos, G. N.; Weissert, F. C.; Biddison, P. H.; Böhm, G. G. A. Rubber Chem Technol 1976, 49, 93.
33. Roland, C. M. Rubber Chem Technol 1989, 62, 456.
34. Heinrich, G.; Straube, E.; Helmis, G. Adv Polym Sci 1988, 85, 33.
35. Marzocca, A. J.; Goyanes, S. J Appl Polym Sci 2004, 91, 2601.
36. Hourston, D. J.; Song, M. J Appl Polym Sci 2000, 76, 1791.