

Accepted Manuscript

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PII: S0142-9418(17)30749-3

DOI: [10.1016/j.polymertesting.2017.07.025](https://doi.org/10.1016/j.polymertesting.2017.07.025)

Reference: POTE 5105

To appear in: *Polymer Testing*

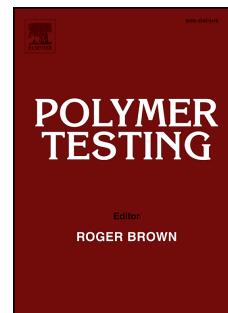
Received Date: 4 June 2017

Revised Date: 0142-9418 0142-9418

Accepted Date: 24 July 2017

Please cite this article as: M.A. Mansilla, A.J. Marzocca, C. Macchi, A. Somoza, Natural rubber/styrene-butadiene rubber blends prepared by solution mixing: Influence of vulcanization temperature using a Semi-EV sulfur curing system on the microstructural properties, *Polymer Testing* (2017), doi: 10.1016/j.polymertesting.2017.07.025.

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Material Properties

Natural Rubber/Styrene-Butadiene Rubber blends prepared by solution mixing: Influence of vulcanization temperature using a Semi-EV sulfur curing system on the microstructural properties.

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Abstract

Blends of natural rubber (NR) and styrene-butadiene rubber (SBR) were prepared by solution mixing and vulcanized with sulfur and accelerator in a Semi-EV system at 433 K and 443 K in order to study the vulcanization kinetic and the influence of vulcanization temperature on final structure of the blends. The vulcanization kinetic studied through the variation in rheometer curves was analyzed using the Ding and Leonov model, which takes into account the reversion effect during the cure process. The average free nanohole volume and the fractional free volume of samples with different NR/SBR ratio were estimated using positron annihilation lifetime spectroscopy (PALS). Also, the crosslink density was determined by means of solvent swelling tests. For all the compounds, a correlation between the free nanohole volume and the delta torque obtained from the respective rheometer curves was established.

Keywords: NR, SBR, rubber blends, vulcanization, PALS, swelling.

INTRODUCTION

Natural rubber (NR) and styrene-butadiene rubber (SBR) have numerous technological, environmental and commercial advantages when blended together to obtain a material that optimizes the mechanical properties. Vulcanized blends of NR/SBR constitute an important set of materials in industry; in particular, when combined with fillers as carbon black or silica, they are principally used as components in the manufacture of tires [1].

The final structure, mechanical performance and thermal stability of a vulcanized elastomer formulated with a system based on sulfur and an accelerator are strongly dependent on the type (mono-, di- and poly-sulfidic linkages) and extent of the crosslinks present in the compound. Vulcanization based

on accelerator and sulfur is classified as conventional (CV), semi-efficient (Semi-EV) and efficient (EV) systems, depending on the accelerator/sulfur ratio (A/S), usually ranging between 0.1 and 0.6 for a CV system, 0.7 to 2.25 for Semi-EV system and from 2.5 to 12 for an EV vulcanization system. Although, the vulcanization chemistry of the process is not completely understood, by varying the amount of sulfur and accelerator it is possible to adjust the concentration and type of crosslinks with important consequences on the physical properties of the cured compounds [2-5].

In recent years, we have studied the morphological and physical properties of NR/SBR blends mixed by the solution technique and melt mixing with a CV cure system with an A/S ratio of 0.75phr/2.25phr[6-11]. For this ratio, it is expected to have a high concentration of di- and poly-sulfidic crosslinks [3]. The aim of the present work is to study similar compounds, but for a Semi-EV system with an A/S ratio of 1.5phr/1.5phr, which normally generates a similar concentration of the different types of crosslinks. We have also varied the vulcanization temperature because its influence on the network structure is well documented [12-14]. It should be noted that it has the same total amount of sulfur and accelerator (3 phr) in both studies.

In a recent work [11,], we reported that the preparation method of the NR/SBR compounds has a strong influence on their phase morphology and the molecular network structure of each rubber phase, with an important variation of the entanglements contribution. This last effect is more pronounced when the prepared blends are richer in NR. In both manufacturing methods, immiscible NR/SBR blends are obtained; however, in the case of the samples prepared by solution mixing the TEM images obtained show a smooth contrast at the interfaces. This implies better compatibility between the two phases. These results are a consequence of the dilution process that produces disentanglement effects in the polymeric chains, generating the different behavior observed in the two kinds of blends.

An indirect approach to evaluate the vulcanization level in elastomers is through the analysis of rheometer curves from which the formation of the elastically active crosslinks can be monitored as an increment in the torque value. This parameter is a direct consequence of the shear modulus. When the vulcanization proceeds, there is an initial stage (induction period) in which there is no crosslink formation; at the end of this period the reaction starts and goes on with a rate varying in time [15]. Another important parameter in the vulcanization process is the time during which the reaction occurs. All these parameters depend on the cure temperature. Hence, it is important to characterize the vulcanization reaction and different models have been proposed in the literature. One of them is the Kamal-Sourour model [16], which makes it possible to obtain the rate and order of reaction and the

induction time. Different authors, including some of the present work, have used this model to study the reaction processes in other rubber compounds [5,7,15,17,18]. It is worth mentioning that the Kamal-Sourour model is a very simple one because a unique energy of the reaction is supposed. However, this model is applicable until the maximum of the cure process, since it does not take into account the reversion phenomenon, which is an important effect for natural rubber.

Another approach to analyze the rheometer curves can be made using the Han model [19] which was recently used in references [6,20,21]. In this model, three first order reactions are considered, one of them being the degradation of unstable crosslinks; that is, reversion process. Therefore, this model is more appropriate when the cure process of NR is analyzed. The set of kinetic equations defining the Han model are summarized as follows:

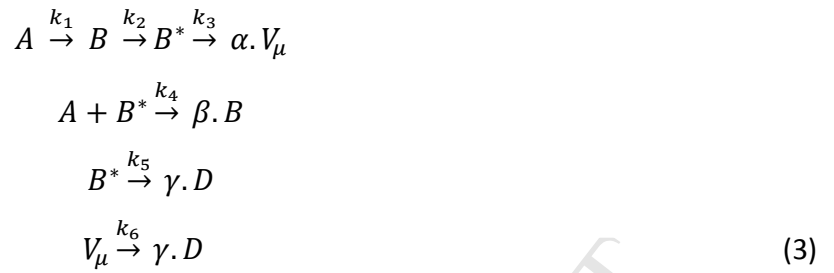


where S is the sulfur available for the crosslinks formation; C_1 represents the stable sulfur crosslinks formed during the vulcanization with a constant rate k_1 ; C_2 denotes the unstable sulfur crosslinks formed with a constant rate k_2 ; and P is the product of the reversion reaction corresponding to the degradation of unstable crosslinks with a constant rate k_3 . It is assumed that the reversion reaction is irreversible and the resultant sulfur is unavailable for the formation of new crosslinks. For the case of an isothermal cure, the analytical solution of the set of the equations (1) is given in terms of the degree of cure $\theta(t)$ as a function of the time and the different constant rates:

$$\theta(t) = \frac{k_1}{k_1+k_2} \{1 - \exp[-(k_1 + k_2)(t - t_i)]\} + \frac{k_2}{k_1+k_2-k_3} \{\exp[-k_3(t - t_i)] - \exp[-(k_1 + k_2)(t - t_i)]\} \quad (2)$$

where t_i is defined as the intersection of the time axis with the tangent of the $\theta(t)$ curve at the inflexion point. It must be taken into account that Eq. (2) is valid when $t > t_i$ and for $t < t_i$, it is assumed that $\theta(t) = 0$.

On the other hand, to analyze the rheometer curves Ding and Leonov [22] proposed a more sophisticated kinetic model in which the competitive between the main and the side reactions is described below:



and the mass balance is given by:

$$A_0 = A + B + B^* + V_\mu/\alpha + D/\gamma \tag{4}$$

where A represents the active curing agents obtained from the reaction of sulfur, accelerator and activator ($A = A_0$ at $t = 0$). B is a crosslink precursor originated from the reaction of a sulfurating agent with the rubber chain. The constant k_1 is the conversion rate of the curing agents to crosslink precursor and seems only to influence the length of induction time [22]. B^* is an active form of B which could be free radicals or ions; D represents the inactive side products such as pendant sulfur branches and/or cyclic sulfur in rubber backbones; according to Coran [23], V_μ corresponds to the formation of a crosslink. The constant k_2 controls the rate of cure and is a function of temperature. Higher values of k_2 indicate a faster rate of cure. The constants k_3 and k_4 are the reaction rates to form crosslinks from B^* and to obtain precursors from $A + B^*$, respectively. Coran affirms [23] that, if the reaction through k_4 is much faster than through k_3 , there is less crosslink formation until A is substantially depleted because the crosslink precursors B^* are rapidly quenched.

On the other hand, k_5 y k_6 are rate constants of kinetic process that form inactive side products (D) from active precursor (B^*) or crosslinks (V_μ). In fact, k_6 symbolizes the reversion reaction in the over-cure process and represents the degradation of the crosslinks which transform into inactive side products (such as pendant and/or cyclic sulfurs). Finally, α , β and γ are stoichiometric parameters.

The evolution of the crosslinks as function of the curing time can be written as [20]:

$$V_\mu(t') = \frac{A_0 \cdot k_2 \cdot [\exp(-k_2 \cdot t') - \exp(-k_6 \cdot t')]}{(1 + \psi) \cdot (k_6 - k_2)}, \quad \psi = \frac{k_5}{k_3} \tag{5}$$

where t' is the cure time after the induction period, e.g. the difference between the cure time t and the induction time t_i ($t' = t - t_i$). The parameter $\psi = k_5/k_3$ represents the ratio between the formation rate of

inactive side groups (given by k_5) and the elastic crosslinks (given by k_3); both parameters come from active crosslinks precursors.

The evolution of crosslinks is obtained from the rheometric data based on the fact that crosslink density is proportional to the stiffness of the compound, characterized by the torque τ [24]. The Dingleonov model was successfully used in a recent work in which a study of a rubber gum filled with carbon black and vulcanized at different temperatures was carried out [24].

It is well-recognized that PALS is a suitable technique to directly determine the average size of the free nanoholes volume v_h in polymers.

PALS lies in the fact that ortho-Positronium (o -Ps), the positron-electron bound system in triplet spin state, is repelled from the ionic cores and molecules, therefore it tends to be localized in low electron density sites of the host matrix, such as cavities forming the v_h . Using a simple quantum mechanical model, a correlation between the o -Ps lifetime (τ_{o-Ps}) and the size of the nanohole (in spherical approximation of nanoholes of radius R) can be established [25-27]:

$$\tau_{o-Ps} = 0,5 \left[\frac{\Delta R}{R + \Delta R} + \frac{1}{2\pi} \operatorname{sen} \left(\frac{2\pi R}{R + \Delta R} \right) \right]^{-1} \quad (6)$$

where $\Delta R = 0.166$ nm [26] is an empirical parameter that takes into account the annihilation of o -Ps with the electrons belonging to the walls of the hole ('pickoff' process). Specifically, $v_h = 4/3 \pi R^3$ in which R values are obtained from Eq. (6).

In the case of elastomers, it was found that changes in v_h are externally induced through different parameters such as preparation method, vulcanization conditions and/or mechanical stresses [29, 30].

Various approaches were used to get the fractional free nanohole volume f_V from positron data [31-33]. As in previous works, we have used the simplest approach to get f_V values in which the number of the nanoholes forming the free volume is related to the intensity I_{o-Ps} associated with the o -Ps lifetime [34, 35]. Under this frame, f_V is assumed to be proportional to the number of nanoholes and to the average nanohole volume, that is,

$$f_V = A v_h I_{o-Ps} \quad (7)$$

where I_{o-Ps} is given in percentage and $A=0.0018$ is an empirical scaling constant [31].

The objective of the present work is to study the kinetic of vulcanization and the structure developed during the cure process of several formulations of NR/SBR blends, using a Semi-EV system to formulate the compounds. Toward this aim, two different cure temperatures were chosen (433 K and 443 K) since they are the temperatures normally used in technology applications. Information on the kinetic of the vulcanization process was obtained from the rheometric curves. Additional information regarding the network structure achieved in the compounds was obtained by means of PALS and swelling tests.

EXPERIMENTAL

Sample preparation

The blends studied in this work were composed of NR (SMR-20) with molecular weight $M_n = 178830$ g/mol and polydispersity of 6.3 (measured by the Gel Permeation Chromatography), and SBR-1502, Arpol (E-SBR) provided by *Petrobras* with $M_n = 128260$ g/mol and polydispersity of 3.8. The densities were $\rho(\text{NR}) = 0.917$ g/cm³ and $\rho(\text{SBR}) = 0.935$ g/cm³.

The compounds were prepared at room temperature by solution blending with the formulation given in Table 1. TBBS (n-t-butyl-2-benzothiazole sulfenamide) was used as accelerator. Details of the preparation method were described in a previous work [6]. Considering the relation accelerator/sulfur, this is a Semi-EV system in which a balanced proportion of polysulfide, di-sulfide and mono sulfide bridges is expected [2].

Sample	A	B	C	D	E	F	G
NR (SMR20) [phr]	0	10	30	50	70	90	100
SBR-1502 [phr]	100	90	70	50	30	10	0
Stearic Acid [phr]	2						
Zinc Oxide [phr]	5						
Sulfur [phr]	1.5						
TBBS [phr]	1.5						

$T_{\text{vulc}} = 433$ K	t_{100} [min]	88.3	48.6	46.7	33.5	21.6	14.7	13.7
	$\Delta\tau$ [N.m]	0.76	0.70	0.65	0.61	0.56	0.46	0.58
$T_{\text{vulc}} = 443$ K	t_{100} [min]	34.4	25.8	22.1	17.4	11.4	7.0	7.7
	$\Delta\tau$ [N.m]	0.74	0.71	0.64	0.63	0.58	0.49	0.45

Table 1: Blend formulations, optimum cure time t_{100} and $\Delta\tau$ values obtained from the rheometer torque curves at 433 K and 443K. The uncertainty in $\Delta\tau$ is 0.01N m and in t_{100} is lower than 5% of its absolute value.

Rheometric tests

The samples were characterized at 433 K and 443 K in an *Alpha RPA2000* rheometer at a strain of 0.5° and a frequency of 100 cpm. For the sake of clarity, the most representative curves of real torque against time at the vulcanization temperatures 433 K and 443 K are shown in Fig. 1. For each compound, some characteristic parameters as the time t_{100} necessary to achieve the maximum torque τ_{max} were obtained. Considering that τ_{min} is the minimum torque, it is possible to estimate the parameter $\Delta\tau = \tau_{max} - \tau_{min}$ which is related to the elasticity of the material coming from the crosslinks formed during the vulcanization process. In Table 1, values of t_{100} and $\Delta\tau$ are also given. It is well-accepted that the degree of cure estimated from the rheometric tests can be obtained using the following relationship

$$\theta(t) = (\tau(t) - \tau_{min}) / \Delta\tau \quad (8)$$

where $\tau(t)$ is the torque at the time t .

Figure 1: Rheometer torque curves as a function of the time for samples cured at 433 K and 443 K. Only the curves obtained for the more representative compounds are shown.

For each compound, two disk shaped samples (17mm diameter and 2mm thickness) were simultaneously cured in a mold at the chosen vulcanization temperature. The samples were placed between two heated plates under a pressure of 5MPa for time t_{100} . At the end of the curing time, the samples were rapidly cooled in an ice-water mixture.

Swelling tests

When a vulcanized elastomer is immersed in an suitable solvent, the solvent molecules penetrate into the network and swell the sample. After a certain time, an equilibrium state is established since the network forces and the osmotic pressures balance each other. The swelling degree depends on the solvent affinity with the material and the crosslink density. The elastomer fraction at the maximum degree of swelling v_{2m} was evaluated using the following equation:

$$V_{2m} = \frac{(W_d - W_f)/\rho}{[(W_d - W_f)/\rho + (W_s - W_d)/\rho_s]} \quad (9)$$

where W_s and W_d are the weights of the swollen and de-swollen samples, respectively. ρ is the density of the compound and ρ_s is the density of the solvent (toluene in our case, $\rho_s = 0.8669 \text{ g/cm}^3$). W_f is the weight of the non-extractable filler in the blends which was evaluated using the ASTM D297-93 (2006) method. More details are given in Ref. [6].

Positron Annihilation Lifetime Spectroscopy

Lifetime measurements were performed using a fast-fast timing coincidence spectrometer with a time resolution of 340 ps. PALS spectra were recorded at room temperature with a counting rate of 80 counts per second, and a total area of at least 2×10^6 counts in each spectrum was collected. A $20 \mu\text{Ci}$ source of ^{22}Na deposited on a thin Kapton foil ($7.5 \mu\text{m}$ thick) was used as positron emitter. The source was placed between two identical samples.

The spectra were deconvoluted using the *LT10* program [36] into three discrete components by taking into account a suitable correction for the positrons annihilated in the source support. The longest lifetime component corresponds to o-*Ps* annihilation with a lifetime τ_{o-Ps} . The intermediate component (0.35–0.50 ns) is attributed to positrons annihilated in low-electron-density regions of the structure. The shortest component (0.1–0.2 ns) is due to positrons annihilated in the bulk and to p-*Ps* annihilations.

RESULTS AND DISCUSSION

As observed in Fig. 1, the NR samples present more reactivity than the SBR ones and significant degradation of NR is reflected in a diminution in the torque value once its maximum level is achieved.

Due to the immiscible nature of the NR/SBR blends [6,10,11,37-40], these compounds have two phases: NR and SBR. Considering the t_{100} values given in Table 1, all NR/SBR blends could have an overcured NR phase since their t_{100} values are higher than that of the NR pure compound.

A similar analysis can be made for the SBR phase in the NR/SBR blends. In this case, for all blends, the t_{100} values are lower than that obtained for the SBR compound; hence it could be inferred that the SBR phase should be undercured in the blends studied.

Data of the measured torque from the rheometer tests are reported in Table 1. As can be seen, $\Delta\tau$ (SBR) > $\Delta\tau$ (NR) and the NR/SBR blends have intermediate $\Delta\tau$ values. As a consequence of the

undercured SBR phase in the blends, there is a minor contribution of this phase to the elastic crosslinks, therefore, a decrease in the $\Delta\tau$ values is expected. The same behavior is also expected for the overcured NR phase. However, it should be considered that, during the vulcanization process, there is a migration of curatives from the SBR to the NR phase [10, 40], compensating the degradation effect of the network in the NR phase. A similar effect was observed in NR/BR cured blends [41].

When the vulcanization temperature increases from 433 K to 443 K, an important and systematic decrease in the t_{100} values (by about 40% to 60%) can be observed; this behavior reflects the strong dependence of the reactivity of the vulcanization process on the curing temperature.

In a recent work, we prepared and analyzed NR/SBR compounds vulcanized with a CV system at the same temperatures as those used in the present work; that is, 433 K and 443K [6]. The rheometer curves of those compounds were satisfactorily fitted using the Han model (see Eqs. (1) and (2)). From the analysis of results above reported, the dependence of k_1 and k_2 with the NR content was evaluated. It was found that, for both cure temperatures, these parameters increase with the NR content being k_1 higher than k_2 . The increase of k_2 with the NR content was attributed to a higher thermal degradation in NR than in SBR, which implies the conversion of poly-sulfidic crosslinks into mono- and di-sulfidic ones as well as into cycles groups and pendant structures.

In the case of the NR/SBR compounds prepared for the present work using the Semi-EV system, they cannot be adequately fitted using the Han model. As an example, the torque curve obtained for the NR compound vulcanized at 443 K is shown in Fig. 2 (dots line). The dashed line was obtained using the Han model to fit the experimental data. The theoretical curve of the torque τ is obtained combining eq. (2) and eq.(8). As can be observed, for this model the best fit is not good enough ($R^2 = 0.777$). Therefore, to analyze the rheometer data obtained from the measurements of the NR/SBR blends vulcanized with the Semi-EV system, we have used the Ding-Leonov model expressed by eq.(5) which, as mentioned above, is related to the torque measured in the rheometric test. Using the Ding-Leonov model, a better fit was obtained ($R^2 = 0.983$), see solid line.

The data obtained in the present work were analyzed following ASTM D 2084-95 [42]. Under this frame, the experimental data corresponding to the point ($t_i, \tau_i + 1$ dN m) was taken as the origin of the torque curves, where $\tau_i + 1$ dN m is a torque value 1 dN m higher than τ_i . The corresponding time t_i is considered as the induction time. As a consequence, it can be concluded that the Ding-Leonov model does not take into account the induction process.

Fig. 3 shows the rheometer curves for all the compounds studied in the present work. As a result, excellent fitting to all the experimental data was obtained using the Ding-Leonov model. During the fitting procedure, the mass balance value A_0 (see Eq. (4)) was forced to be the same value for all the compounds; under this assumption the value $A_0 = 1.051$ was obtained.

Figure 2: Rheometer curve obtained for the NR compound vulcanized at 443 K. The experimental data were fitted using Han's and the Ding-Leonov model, respectively.

Figure 3: Torque curves as a function of the time for all the compounds studied in this work. Solid lines represent the fit to the experimental data using the Ding-Leonov model.

In Fig. 4, the values of the kinetic parameters k_2 , k_6 and ψ as a function of the blend composition and the vulcanization temperature are shown. As can be seen, both constant rates k_2 and k_6 increase with the vulcanization temperature and with the amount of NR in the blend.

Figure 4: Evolution of the parameters k_2 , k_6 and ψ as a function of the NR content and vulcanization temperature. Lines are only eye guides.

According to the Ding-Leonov model, higher values of k_2 indicate a faster rate of cure. As can be seen in Fig. 4(a), this parameter increases with the amount of NR in the compound. This behavior can be attributed to the fact that the vulcanization rate depends on the number of allylic hydrogens. It is worth mentioning that each NR and SBR unit has 7 and 3.3 allylic hydrogens, respectively; consequently, NR has higher reactivity than SBR [14]. Also, k_2 values for samples vulcanized at 443K are systematically higher than those cured at 433K, which implies considerable temperature dependence.

In Fig. 4(b), it can be seen that k_6 is strongly dependent on the NR content in the blend and on the vulcanization temperature. In the literature, changes have been reported in the type of crosslinks of the NR phase in NR/SBR blends for increasing time and temperature of vulcanization. This behavior was observed in cases in which NR is overcured [6, 9, 43, 44], and is responsible for the evolution of k_6 versus the blend composition and cure temperature.

In Fig. 4(c), the evolution of the ψ parameter as a function of the NR content in the NR/SBR blend is shown. As can be seen, this parameter increases for increasing NR content in the NR/SBR blends. For

the two vulcanization temperatures chosen in this work, there are not significant differences in the respective evolutions of ψ versus the NR content.

A value of $\psi > 1$ indicates that the formation rate of inactive side groups is higher than that of elastic crosslinks; in our case, this behavior is observed for samples with NR content in the blends higher about 50%. These data would confirm that more inactive side groups are produced in the cured samples when NR is added to the blend. The particular case of the NR compound vulcanized at 433K deserves to be highlighted, in which a strong decrease of ψ is observed when compared with the trend of systematically ψ increase with the NR content in the blends. This behavior would indicate that a structure with a lesser formation of inactive side groups is obtained for the lower vulcanization temperature.

On the other hand, it is worth mentioning that, when SBR is added to blend, the migration of curatives from the phase SBR to NR modifies the cure rate correlated with an important decrease of ψ . Particularly, for the 90NR/10SBR blend, the presence of a non-vulcanized SBR phase dispersed in the overcure NR matrix alters the kinetic properties of the compound. This behavior can be attributed to the fact that there is no crosslinking in the SBR phase, leading to a k_3 decrease reflected in an increase of the ψ value. More research work is necessary to go into deeper discussion of this issue.

From PALS measurements, values of the free nanohole volume and fractional free volume were obtained for each sample at the two vulcanization temperatures used. In Figs. 5(a) and 5(b), the evolutions of both parameters as a function of the NR content in the samples are shown. From Fig. 5(a), it can be observed that the free nanohole volume linearly increases with the increment of NR content. Also, for all the compounds, the increase of v_h for increasing NR content in the compounds is independent, within the error bars, of the vulcanization temperature.

In the case of the fractional free volume (see Fig. 5(b)), the analysis of the evolution of this parameter with the increase of NR in the blends should be split. For the vulcanization temperature of 433 K, f_v maintains, within experimental scatter, the value obtained for the SBR pure compound until a composition of the blend equal to 70SBR/30NR. In the range of 30 and 90 phr NR content, the fractional free volume linearly decreases for increasing NR content. Finally, f_v shows a strong decrease in its value for the pure NR compound. For the higher vulcanization temperature, within the error bars, f_v remains approximately constant at the same value obtained for the pure SBR compound. When the NR content in the blend increases above 70 phr (*i.e.*, 30SBR/70NR) a linear decrement of the fractional free volume is

observed. Finally, the f_v value for the pure NR compounds is considerably higher than that for the NR sample vulcanized at 433 K.

There are several researches made on NR that indicate an evident change in the type and concentration of sulfur linkages when the vulcanization temperature increases; the total crosslink density decreases and the fraction of mono- and di-sulfides linkages increases at expense of polysulfide linkages [43-45]. Therefore, the changes produced in the NR network structure of the SBR/NR blends studied in this work could explain the differences in the f_v values at high NR content and for both vulcanization temperatures

Figure 5: (a) Free nanohole volumes and (b) fractional free volume as a function of the NR content in the compounds vulcanized at two different temperatures. Lines are only eye guides.

On the basis of the data obtained, the influence of the vulcanization system on the free nanohole volume was also analyzed. Specifically, in Fig. 6, the different values of v_h for compounds vulcanized are reported, using both Semi EV and CV systems. The data for the -EV system were reported above in Fig. 5(a), while those for the conventional vulcanization system were taken from a recently published paper (see Ref. [6]).

From a general discussion, for those compounds vulcanized using the Semi EV system at 433 K and 443 K a linear increase in the evolution of v_h versus NR is observed. Similar behavior, but with systematically lower v_h values, was observed for the samples formulated with the CV system and vulcanized at 443 K. Different behavior is observed for the data obtained measuring samples vulcanized with the CV system but at 433 K. The differences in the evolutions of v_h against NR content for the blends vulcanized at 433 K and 443 K using this last system were already discussed in a previous work [6]; briefly, such differences were attributed to the different nature of the achieved vulcanized networks. Conversely, for the samples prepared using the Semi-EV formulation at the same vulcanization temperatures mentioned above, no differences are observed in the v_h versus NR content.

Figure 6: Evolution of the free nanohole volume as a function of the NR content for the SBR/NR blends prepared using two vulcanization systems (i.e., Semi-EV and CV). v_h values for the samples prepared by means of the Semi-EV system are those reported in Fig. 5(a). Lines are only eye guides.

It has been reported that the amount and types of crosslinks produce changes in the values of the free nanohole volume [6,46-48].

The $\Delta\tau$ values obtained from the rheometric tests are correlated with the amount of crosslinks formed in the compound during vulcanization. In Fig.7, the evolution of the values of $\Delta\tau$ reported in Table 1 as a function of v_h for the two vulcanization temperatures is shown. It can be observed that, within the error bars, all the $\Delta\tau$ values decrease linearly when the increase of the free nanohole volume. As mentioned in the literature, a diminution of $\Delta\tau$ values is a consequence of a decrease of the crosslink density in the vulcanized compounds reflecting in bigger free nanohole volume [6,46]. A similar trend in the evolution of $\Delta\tau$ vs. v_h for both vulcanization temperatures implies that the nature of the network structure is the same.

Figure 7: Variation of $\Delta\tau$ as a function of the free nanohole volume in NR/SBR blends prepared using the Semi-EV vulcanization system. Dot line is only an eye guide.

In Fig. 8, values of the fraction of polymer in the swollen state as a function of the NR content in the compounds and for the vulcanization temperatures 433 and 443 K are shown. It can be seen the evolution of v_{2m} versus the NR content in the compounds present a similar trend. The maxima v_{2m} values are those corresponding to the pure compounds, that is, SBR and NR. On the other hand, in the blends, lower v_{2m} values are obtained. A value of the fraction of polymer in the swollen state depends on the vulcanization degree of each component in a blend; in particular, the lower v_{2m} values can be understood in terms of being the SBR phase in an undercured state while the NR phase is in an overcured one.

Figure 8: Polymer volume fraction at the maximum degree of swelling as a function of the NR content in the compounds vulcanized at two different temperatures. Lines are only for eye guide.

CONCLUSIONS

This paper addresses a study of NR/SBR blends prepared by solution mixing and vulcanized with a Semi-EV system at two different vulcanization temperatures typically used in the rubber industry.

From all the results obtained, the main conclusions can be summarized as follows:

- Analyzing the rheometric curves using the Ding and Leonov model, the kinetic parameters obtained from the fitting procedure indicate that the cure reactivity and the degradation of the crosslinks into inactive side products are strongly dependent on the NR content in the SBR/NR blends and on the cure temperature. Also, the degradation effect is more evident at the higher vulcanization temperature. On the other hand, blends with a NR content higher than 50 phr show that the formation rate of inactive side groups is higher than that of elastic crosslinks. This means that more inactive side groups are produced in the cured samples when NR is added to the blend.
- The free nanohole volume increases with the increment of the NR content in the compounds. This behavior is independent of the vulcanization temperature. Conversely, the evolution of the fractional free volume not only depends on the vulcanization temperature but mainly on the NR content. In particular, the differences in the f_v values at high NR contents and for both cure temperatures can be attributed to changes produced in the NR network structure of the SBR/NR blends; that is, a decrease of the total crosslink density and a change in the types of sulfur linkages.
- The variation of the polymer fraction at the maximum degree of swelling, as a function of the NR content in the compounds shows a similar trend.
- It was possible to establish a simple relation between $\Delta\tau$ and the free nanohole volume. In fact, the results obtained indicate that $\Delta\tau$ linearly decrease for increasing v_h values; this behavior is independent of the temperature. As a result, largerr v_h implies a lower crosslink density.

Finally, during this research, we have compared the experimental results of cured NR/SBR compounds prepared using a Semi-EV system with those obtained with a CV-system. It is interesting to note that the samples cured with the semi-EV system have fewer variations in their microstructure than those prepared with the CV system, when cured in the range of 433 K and 443 K. This fact can be an interesting point when deciding the formulation to be used in the fabrication of different products.

ACKNOWLEDGMENTS

We acknowledge funding from University of Buenos Aires (Argentina) (Project UBACYT 20020120100051, 2013-2016), Agencia Nacional de Promoción Científica y Tecnológica (Argentina) (PICT 2015-1832), Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) (PIP 112-201101-00793), Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (Argentina) and Universidad Nacional del Centro de la Provincia de Buenos Aires (Argentina).

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