



# Influence of vulcanization temperature on the cure kinetics and on the microstructural properties in natural rubber/styrene-butadiene rubber blends prepared by solution mixing

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## ARTICLE INFO

### Article history:

Received 10 December 2014

Received in revised form 22 May 2015

Accepted 23 May 2015

Available online 25 May 2015

### Keywords:

NR

SBR

Rubber blends

Vulcanization

PALS

Swelling

## ABSTRACT

Blends of natural rubber and styrene-butadiene rubber were prepared by solution mixing and vulcanized with a system sulfur–accelerator at 433 K and 443 K in order to study the vulcanization kinetic and the influence of the vulcanization temperature on the final structure of the blends. The kinetic of vulcanization was analyzed under the frame of the Han's model, which takes into account the reversion effect once the time to achieve the maximum torque in the rheometer curves is surpassed. The crosslink density was also determined in all samples by means of swelling in solvent. The average free nanohole volume was estimated using positron annihilation lifetime spectroscopy. When changing the vulcanization temperature of the blends, remarkable changes in the crosslink densities and the free nanohole volumes were detected. Furthermore, a correlation between the average fractional free nanohole volume and the fraction of polymer in the swollen state was established.

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## 1. Introduction

Natural rubber (NR) and styrene-butadiene rubber (SBR) have numerous technological, environmental and commercial advantages when blended together because they generate a new material with the combination of the components properties without resort to a new synthesis process. Vulcanized blends of NR/SBR constitute an important set of materials in the world wide industry; in particular, they are principally used as components of manufactured tires.

When considering separately each vulcanized elastomers of the NR/SBR blends, the main features are, in the case of NR: enhancement of the tear strength, lower tire temperatures under dynamic service conditions and lower tire rolling resistance, which improve vehicle fuel efficiency; whereas, SBR offers wet skid and good abrasion resistance and traction properties [1]. The NR/SBR compounds belong to the category of immiscible or partially miscible blends because the presence of two phases is detected in these materials [2–4]. However, blending process has a strong influence on the final rheological

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properties according to the phase morphology and the dispersion and distribution of the fillers achieved. In previous works we studied the morphological and physical properties of NR/SBR blends mixed by the solution technique [4–6].

On the other hand, in a vulcanized elastomer formulated with a system based on sulfur and accelerator, the final structure, mechanical performance and thermal stability are strongly dependent on the type and extent of crosslinks produced in the compound. Usually, networks are formed by a mixture of mono-, di- and polysulfidic linkages, and the type of crosslink network restricts the degree of swelling when the material is immersed in an adequate solvent. 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 material [7]. While short crosslinks tend to provide better thermal and aging characteristics, polysulfide links can improve dynamic fatigue resistance due to higher molecular flexibility.

During the vulcanization process of the immiscible elastomeric blends, the curing process of the constituent elastomers does not necessarily occur at the same rate. In fact, diffusion of curatives between the phases and the difference in the reactivity of each elastomer may lead to important differences in the crosslinking densities of the phases [8–10]. It is well-known that variations in the crosslinking distribution influence the properties of the elastomeric blend [11].

Another important parameter of the cure process of elastomers is the vulcanization temperature ( $T_{\text{vulc}}$ ) because it has a significant influence on the structure and mechanical properties of the blends, e.g., the chemical crosslink density and the types of crosslinks [12]. This effect was studied in several works on materials as BR, EPDM, NBR, NR and SBR [9,13–15], and some of these works were addressed to obtain the activation energy associated with the vulcanization process.

An indirect approach to evaluate the vulcanization level of blends is through the rheometer curves. In this case, the formation of the elastically active crosslinks can be inferred once they are being produced, because a change is taking place in the torque *versus* time curves.

In this work we have analyzed the state of cure of NR/SBR blends prepared by solution mixing by a kinetic model proposed by Han et al. [16]. This model is based on the assumption that, during the induction period, no crosslinks reaction takes place. Then, during the vulcanization both stable and unstable sulfur crosslinks can be formed where the unstable crosslinks can suffer a subsequent degradation. All the reactions are supposed to be of first order. The model was successfully used in recent works on rubber gum filled with carbon black vulcanized at different temperatures [17,18].

A direct consequence of the vulcanization process of rubber blends is the modification of the free volume as a function of the degree of cure. Recently we have used Positron Annihilation Lifetime Spectroscopy (PALS), swelling tests and differential scanning calorimetry to follow the above-mentioned process on polybutadiene rubbers [19].

It is well-recognized that PALS is the adequate technique to directly determine the average size of the free nanoholes volumes  $v_h$  in polymers. PALS technique was successfully used in several uncured and cured elastomers and/or miscible and immiscible elastomer blends (see for example Refs. [4,19–28]). Specifically, changes in the  $v_h$  of these elastomers were externally induced through different parameters, such as preparation and vulcanization conditions as well as mechanical stresses.

PALS lies in the capability of ortho-Positronium ( $o\text{-Ps}$ ), the positron–electron bound system in triplet spin state, to localize into the free nanohole volumes. Indeed,  $o\text{-Ps}$  is repelled from the ionic cores of atoms and molecules due to exchange interactions and it tends to be pushed into low electron density sites of the host matrix, such as cavities forming the free volume. A correlation can be expected between its lifetime  $\tau_{o\text{-Ps}}$  and the size of the nanohole (in spherical approximation of nanoholes of radius  $R$ ), as expressed using simple quantum mechanical model [29–31]:

$$\tau_{o\text{-Ps}} = 0.5 \cdot \left[ \frac{\Delta R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1} \quad (1)$$

where  $\Delta R = 0.166$  nm [32] is an empirical parameter that takes into account the annihilation of  $o\text{-Ps}$  with the electrons belonging to the walls of the hole ('pickoff' process).

Various approaches were used to get the fractional free nanohole volume from positron data [33–36]. In the present work, we have used the simplest one in which the number of the nanoholes forming the free volume in polymers is related to the intensity associated with the  $o\text{-Ps}$  lifetime [37,38]. Under this frame, the fractional free volume  $f_V$  can be assumed to be proportional to the number of nanoholes and to the average volume of each nanohole. Then, the following semi-empirical equation can be used

$$f_V = A v_h I_{o\text{-Ps}} \quad (2)$$

where  $I_{o\text{-Ps}}$  is given in percentage and  $A = 0.0018$  is an empirical scaling constant [33].

The goal of the present work is to study the kinetic of vulcanization of several formulations of NR/SBR blends from the analysis of rheometric curves. To this aim, two different temperatures of cure were chosen (433 K and 443 K) since these temperatures are those normally used in technology applications. In order to get a better comprehension of the structure developed during vulcanization of the blends, PALS measurements were used to study the behavior of the free nanohole volumes; besides, swelling tests gave information on the network achieved. A correlation between PALS results and the diffusion process of the solvent in the vulcanized structure of the blends is also presented.

## 2. Experimental

### 2.1. Sample preparation

The blends studied in this work are composed of NR (SMR-20) with molecular weight  $M_n = 178,830$  g/mol and polydispersity of 6.3 (measured by the Gel Permeation Chromatography) and SBR-1502, Arpol (E-SBR) provided by *Petrobras* with  $M_n = 128,260$  g/mol and polydispersity of 3.8. The densities were  $\rho$  (NR) = 0.917 g/cm<sup>3</sup> and  $\rho$  (SBR) = 0.935 g/cm<sup>3</sup>.

The samples were prepared at room temperature by solution blending with the formulations given in Table 1. Details of the preparation method were described in a previous work [4]. In total, eleven compounds were prepared with NR/SBR compositions ranging from 0/100 to 100/0 varying every 10 phr (per hundred of rubber) in the content of each rubber (10/90, 20/80, 30/70, etc.).

The vulcanization systems consist in sulfur and the accelerator TBBS (n-t-butyl-2-benzothiazole sulfenamide). According to the relation accelerator/sulfur this is a conventional vulcanization system (CV) in which it is expected that most of the crosslinks be di- and polysulfidic types.

### 2.2. Rheometric tests

The set of blends cured at 433 K are the same as those used by some of the authors of the present paper in a previous work [4]. Additionally, we have prepared a set of blends using a cure temperature of 443 K. The samples were characterized in an *Alpha RPA2000* rheometer at a strain of 0.5° and a frequency of 100 cpm. For the sake of clarity, in Fig. 1 the most representative curves of real torque against time at vulcanization temperatures of 433 K and 443 K are shown. In each case, some characteristic parameters of the samples as the time  $t_{100}$  necessary to achieve the maximum torque  $\tau_h$  were obtained. Considering that  $\tau_l$  is the minimum torque, it is possible to estimate the parameter  $\Delta\tau = \tau_h - \tau_l$  which is related to the elasticity of the material coming from crosslinking produced during the vulcanization process. Values of  $t_{100}$  and  $\Delta\tau$  are also given in Table 1.

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

### 2.3. Swelling tests

When a vulcanized elastomer is immersed in an adequate solvent, the solvent molecules penetrate into the network and swell the sample. After a certain time, an equilibrium state is established due to the network forces and the osmotic pressure balances each other. The swelling degree depends on the solvent affinity with the material and on the crosslinks density. The applied technique to determine the polymer fraction at the maximum degree of swelling  $v_{2m}$  was already used [4] and new measurements were performed for both blends cured at 433 K and 443 K. This parameter was obtained using the following equation:

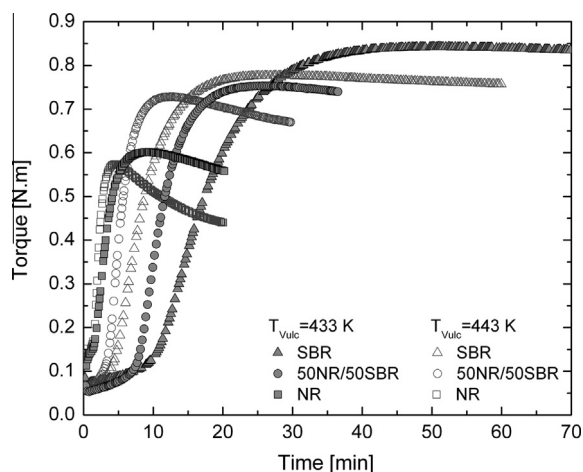
$$v_{2m} = \frac{[(W_d - W_f)/\rho]}{[(W_d - W_f)/\rho] + [(W_s - W_d)/\rho_s]} \quad (3)$$

where  $W_d$  is the weight of the sample after swelling and a further dried;  $W_f$  is the weight of the non-extractable filler in the sample;  $W_s$  is the weight of the swollen sample,  $\rho$  is the density of the compound and  $\rho_s$  the density of the solvent (0.8669 g/cm<sup>3</sup> for toluene [39]). In the specific case of the samples studied in the present work, they do not contain filler as carbon black or silica. However, in the compounds there are inorganic fillers (zinc oxide); therefore, to evaluate  $W_f$  we

**Table 1**

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

Sample		A	B	C	D	E	F	G	H	I	J	K
NR (SMR20) (phr)		0	10	20	30	40	50	60	70	80	90	100
SBR-1502 (phr)		100	90	80	70	60	50	40	30	20	10	0
Stearic acid (phr)							2					
Zinc oxide (phr)							5					
Sulfur (phr)							2.25					
TBBS(phr)							0.7					
T (K)												
433	$t_{100}$ (min)	55.0	57.2	53.8	47.2	36.8	27.1	28.1	25.1	16.7	15.8	9.3
	$\Delta\tau$ (N m)	0.77	0.73	0.70	0.71	0.70	0.70	0.67	0.67	0.57	0.61	0.49
443	$t_{100}$ (min)	27.4	24.2	22.9	18.0	15.8	12.2	10.9	9.9	6.9	6.8	4.7
	$\Delta\tau$ (N m)	0.72	0.75	0.65	0.71	0.63	0.67	0.61	0.61	0.54	0.61	0.46



**Fig. 1.** Rheometer torque curves as a function of the time for samples cured at 433 K and 443 K. In the figure, only the curves obtained for the more representative blends are shown.

have used the ASTM D296-90 method. Then, assuming that in the swelling test the free volume is totally occupied by the solvent, the fraction volume of the absorbed solvent in the sample can be obtained through  $v_{\text{sol}} = 1 - v_{2m}$ .

#### 2.4. Positron Annihilation Lifetime Spectroscopy (PALS)

Lifetime measurements were performed using a fast-fast timing coincidence system spectrometer with a time resolution about 340 ps. PALS spectra were recorded at room temperature with a counting rate of 80 counts per second circa and a total area of at least  $2 \times 10^6$  counts in each spectrum was collected. As positron emitter a 20  $\mu\text{Ci}$  source of  $^{22}\text{Na}$  deposited on a thin Kapton foil (7.5  $\mu\text{m}$  thick) was used. The source was placed between two identical samples. PALS spectra were decomposed into three discrete lifetime components using the *LT10* program [40].

### 3. Results and discussion

In most of the cases, elastomer blends are prepared using the two-roll mill method [41–44]; previous studies on NR/SBR blends prepared using this method have shown that NR and SBR are immiscible [25]. On the other hand, it was recently reported that NR/SBR samples prepared by solution method maintain the immiscible character [4].

From the rheometer tests shown in Fig. 1 it can be seen a higher reactivity of NR with respect to SBR, that is, the pure NR samples reach the maximum torque for times lower than those for pure SBR. Furthermore, it can be observed that in the NR pure compound the effect of degradation for times  $t > t_{100}$ , that is when the sample is overcured, is the strongest one.

Due to the immiscible nature of the NR/SBR blends, in these compounds there exist two phases: NR and SBR, respectively. According to the  $t_{100}$  values given in Table 1, in all NR/SBR blends the NR phase appears overcured because their  $t_{100}$  values are higher than those of the NR pure compound ( $t_{100}$  (NR) = 9.3 and 4.7 min for vulcanization temperatures of 433 K and 443 K, respectively).

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 the one obtained for the SBR compound; then it could be inferred that in the blends that we are studying the SBR phase is undercured.

From the rheometer data it was also obtained that  $\Delta\tau$  (SBR)  $>$   $\Delta\tau$  (NR) and that the NR/SBR blends have intermediate  $\Delta\tau$  values (see Table 1). 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 must be considered that during the vulcanization process there is a migration of curatives from the SBR to the NR phase [8,10], and this process compensates the degradation effect of the network in the NR phase.

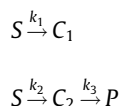
When the vulcanization temperature increases from 433 K to 443 K, an important and systematic decrease in the  $t_{100}$  values (about 40–50%) can be observed; this behavior reflects the strong dependence of the reactivity of the vulcanization process on the temperature.

To analyze the rheometer curves of each sample, it is convenient to calculate the change in time of the degree of vulcanization  $\theta(t)$ . To this aim, we have used a relationship proposed by Sun and Isayev [45]:

$$\theta(t) = \frac{\tau(t) - \tau_{\text{minT}}}{\tau_{\text{maxT0}} - \tau_{\text{minT0}}} \quad (4)$$

where  $\tau_{\min T}$  is the minimum value of the torque curve at a temperature  $T$ . The parameters  $\tau_{\min T_0}$  and  $\tau_{\max T_0}$  are the minimum and maximum torque values obtained for a cure experiment at the lower temperature  $T_0$  (433 K in our case), respectively; this means that we are taking as a reference a temperature  $T_0$  corresponding to the lower reversion in the compounds. In such a case, the samples vulcanized at 443 K will have a final degree of vulcanization lower than 100%.

As mentioned, to analyze the reaction processes during vulcanization, the kinetic model proposed by Han et al. [16] was used. Under this frame, the different first order reactions can be described as follows:



where  $S$  is the sulfur available for the formation of crosslinks;  $C_1$  represents the stable sulfur crosslinks formed during vulcanization with a constant rate  $k_1$ ;  $C_2$  denotes the unstable sulfur crosslinks formed during vulcanization, 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, Han et al. gave an analytical solution that makes it possible to represent the degree of cure  $\theta(t)$  as a function of the time and the different constant rates  $k_i$ . For  $t > t_i$ :

$$\theta(t) = \frac{k_1}{k_1 + k_2} \{1 - \exp[-(k_1 + k_2)(t - t_i)]\} + \frac{k_2}{k_1 + k_2 - k_3} \{\exp[-k_3(t - t_i)] - \exp[-(k_1 + k_2)(t - t_i)]\} \quad (5)$$

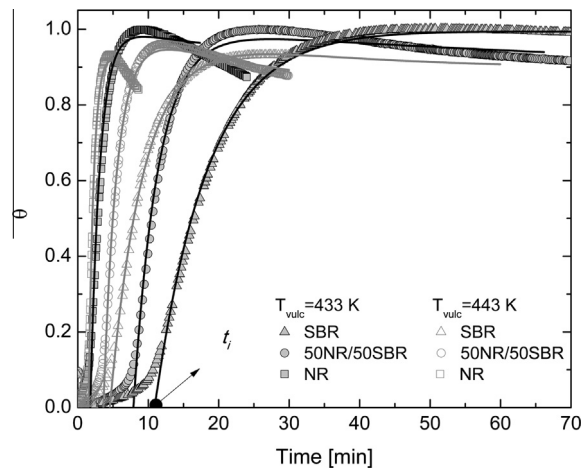
where  $t_i$  is defined as the intersection of the time axis with the tangent of the  $\theta(t)$  curve at the inflexion point (see an example in Fig. 2). In the model it is assumed that for  $t < t_i$ ,  $\theta(t)$  is equal to zero. From the experimental data shown in Fig. 1, the rheometer normalized curves were obtained using Eq. (4). Then, for each NR/SBR blend we have fitted these curves using Eq. (5). In Fig. 2, the experimental data and their respective fits are shown for some selected curves  $\theta(t)$  versus time.

From the fitting procedures, the values of the kinetic parameters were obtained as a function of the blend composition and the vulcanization temperatures. In Fig. 3,  $k_1$  and  $k_2$  values are shown as a function of the NR content in each blend. As can be seen, both constant rates increase with the amount of NR in the compound and with the vulcanization temperature.

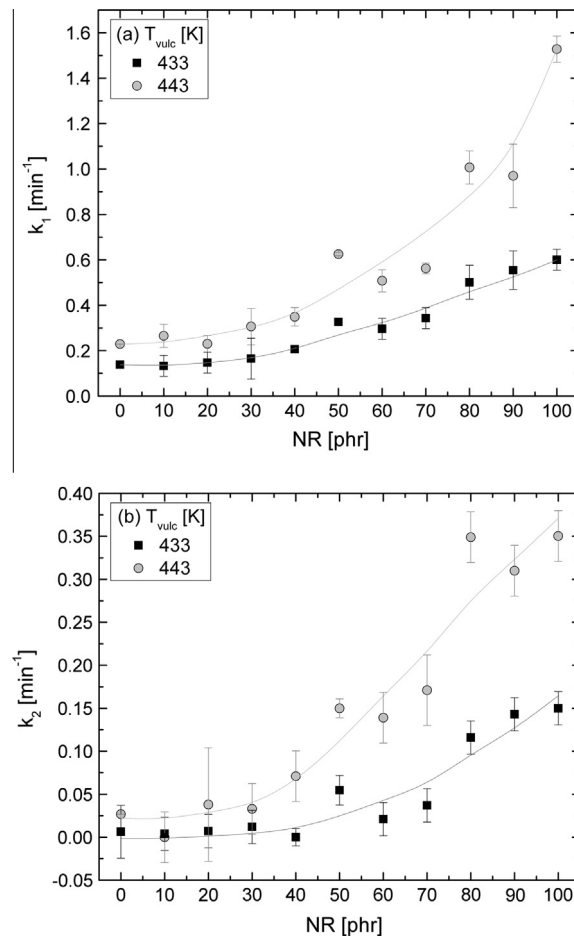
According to the model proposed by Han et al., parameters  $k_1$  and  $k_2$  are related to the formation of stable and unstable crosslinks, respectively. As can be seen from Fig. 3,  $k_1$  is higher than  $k_2$ , meaning that more stable crosslinks than unstable ones are formed at a given time. The kinds of the stable and unstable crosslinks were not investigated in this work; however, it is known that depending on the type of elastomers, curatives, curing temperature and times, different kinds of crosslinks are formed in the compounds. In the case of natural rubber, a certain amount of polysulfidic crosslinks becomes to other network structures (di-sulfidic, mono-sulfidic and cycle crosslinks) when the cure reaction advances [15,46]. This process of change in the network structure with the curing time is more pronounced in NR than in SBR. From the  $k_i$  values the percentage of formation of stable and unstable crosslinks with respect to the total crosslinks were calculated as a function of the NR content. Results are presented in Fig. 4. As can be seen, for all blends the percentages of stable crosslinks formed at 433 K are higher than those formed at 443 K; instead, the unstable crosslinks present an opposite behavior. Specifically, the percentage of unstable crosslinks increases with the amount of the NR phase in the compound, having maxima values for the 90NR/10SBR and 80NR/20SBR blends for the vulcanization temperatures 433 K and 443 K, respectively. The crosslink structure of cured NR has a more pronounced thermal degradation than the cured SBR [7,15,25] at the same vulcanization temperature, then the amount of unstable crosslinks is expected to grow in the blends richer in NR. To discriminate the type of the unstable crosslinks more experiments must be done, but it is fairly safe to say that labile polysulfidic crosslinks are formed during curing.

The values of the volume fraction of polymer in the swollen state for the samples cured at 433 K and 443 K are shown in Table 2. It is interesting to notice that this behavior is different, depending on the vulcanization temperature when increasing the NR content in the blend. At 433 K there is a tendency to a lowering of  $v_{2m}$  at higher NR content in the blend, and at 443 K a clear change is not observed.

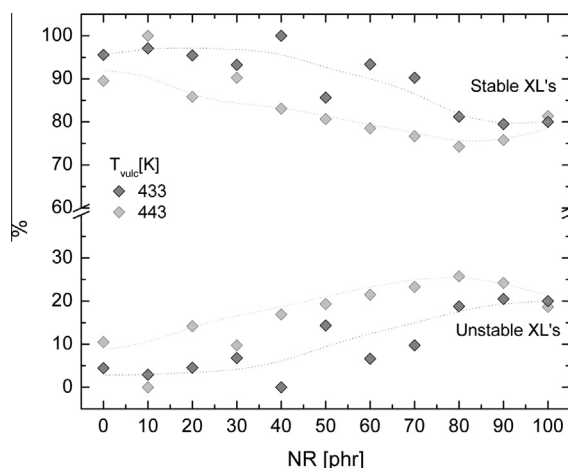
The variation of the torque in the rheometric curves is directly proportional to the number of crosslinks achieved in the network through vulcanization, and also this last parameter is directly related to the  $v_{2m}$ . Fig. 5 shows the relation obtained between the values of  $v_{2m}$  and those of  $\Delta\tau$  and a good correlation is obtained in the set of samples vulcanized at 433 K. However, this is not fulfilled in those cured at 443 K. The crosslink densities are lower for the samples cured at 433 K than in those cured at 443 K mainly in the samples richer in NR, but there is not a significant change in  $\Delta\tau$ . The cure temperature is a decisive factor in the network structure achieved by the vulcanization process because it has an influence on the type of crosslinks (ratio between mono-, di- and polysulfidic crosslinks) and their spatial distribution. For example, the reversion process, that is strongly dependent on the vulcanization temperature, involves rearrangement of the polysulfidic crosslinks to the more stable mono- and disulfidic crosslinks [15,46,47]. This process could be responsible for the almost constant behavior in the values of  $v_{2m}$  for the samples vulcanized at 443 K, particularly in the samples richer in NR content. In the blends, the NR phase is in an overcured state because their cure times to reach the maximum torque value exceed that obtained for the NR pure compound. Therefore, in the NR phase the reversion process takes place. This effect is stronger when the NR content in the blend increases. Furthermore, it should be noted that NR and SBR phases must have different



**Fig. 2.** Normalized torque curves as a function of the time. For the normalization procedure Eq. (4) was used (see text). Solid lines represent the fit to the data using the Han's model, Eq. (5).



**Fig. 3.** Constant rates as a function of the NR content and vulcanization temperature. Lines are only for eye guide. (a)  $k_1$  and (b)  $k_2$ .



**Fig. 4.** Percentage of stable and unstable crosslinks (XL's) formed during vulcanization, over the total crosslinks, as a function of the NR content and the vulcanization temperature. Lines are only for eye guide.

network structures as a consequence of the cure time of each blend and the migration of curatives between both phases [8,15,46,47]. This effect could be enhanced by increasing the cure temperature [10], in our case from 433 K to 443 K. Then, when analyzing NR/SBR blends not only the amount of crosslinks formed during the cure process must be taken into consideration for the analysis of the rheometer curves, but also how they are distributed in both phases and the interphase. To elucidate these points, other techniques as NMR or neutron scattering measurements must be employed [48–50].

The ortho-Positronium lifetime values and their associated intensities are reported in Table 3 for each blend and vulcanization temperature. It can be seen that in both cases  $\tau_{o-Ps}$  shows a slight increase when the NR content in the blends increases. In the case of  $I_{o-Ps}$ , this parameter increases for the sample cured at 433 K specially when blends are richer in NR and in the compounds cured at 443 K a different behavior is observed, that is, a significant decrease of  $I_{o-Ps}$  when the blend compounds contain 50 phr of NR or more. Besides, in both sets of samples,  $\tau_{o-Ps}$  and  $I_{o-Ps}$  for the samples vulcanized at 443 K are systematically above those values obtained for compounds cured at the lower temperature.

Using the data reported in Table 3 and Eq. (1) free nanohole volume values were obtained for each sample at both vulcanization temperatures 433 K and 443 K. In Fig. 6 we have plotted  $v_h$  for both vulcanization temperatures as a function of the NR content in the compounds. From this figure, it can be observed that the vulcanization temperature has an important influence on the microstructure of the samples. In the case of the higher cure temperature, for all samples  $v_h$  is considerably higher than the values of this parameter calculated for the compounds vulcanized at 433 K; the extreme case is observed for the pure compound SBR (*i.e.*, NR = 0) in which the free nanohole volume doubles when the vulcanization temperature increases. When analyzing general trends of  $v_h$  for increasing amounts of NR in the compounds, it can be observed that for the samples cured at 443 K the free nanohole volume presents a slight monotonous increase (from 145 Å<sup>3</sup> for pure SBR compound until ~160 Å<sup>3</sup> corresponding to the pure NR compound). Conversely, when samples are vulcanized at the lower temperature  $v_h$  shows a more complex behavior; in fact, from the pure SBR compound up to the 20NR/80SBR blend the  $v_h$  rapidly increases from 75 to 100 Å<sup>3</sup>. For increasing NR contents up to the 70NR/30SBR blend the mentioned parameter maintains almost constant; between 70 and 80 phr of NR a new increase of  $v_h$  is produced reaching an almost constant value of 110 Å for higher NR content and coincident with that obtained for the NR compound. From the present results and the previous ones, it can be inferred that variations in the free nanohole volumes are a consequence of the different nature of the achieved vulcanized network.

Normally, it is expected that at higher crosslink density, the free nanohole volume decreases. This behavior it is expected in the case of samples prepared with a pure elastomer. In fact, it was observed when measuring samples vulcanized with sulfur with an increasing amount of curatives but with the same relative percentages between different types of formed crosslinks [24].

The total crosslink density changes may also be produced as a consequence of a change in the vulcanization temperature. However, in this case crosslinks might not be of the same type due to their degradation and reformation [51]. Therefore, it should be considered that the relative distribution of crosslinks can change too. In our case, as a general trend the crosslink density increases with the vulcanization temperature (Table 3); besides an increase of the free volume is observed. The

**Table 2**

Values of  $v_{2m}$  obtained in the vulcanized NR/SBR blends cured at 433 K and 443 K.

$T_{vulc}$ (K)	NR (phr)	0	10	20	30	40	50	60	70	80	90	100
433	$v_{2m}$	0.168	0.155	0.147	0.146	0.141	0.132	0.144	0.1480	0.066	0.079	0.070
443		0.155	0.174	0.167	0.172	0.161	0.167	0.163	0.171	0.169	0.181	0.177

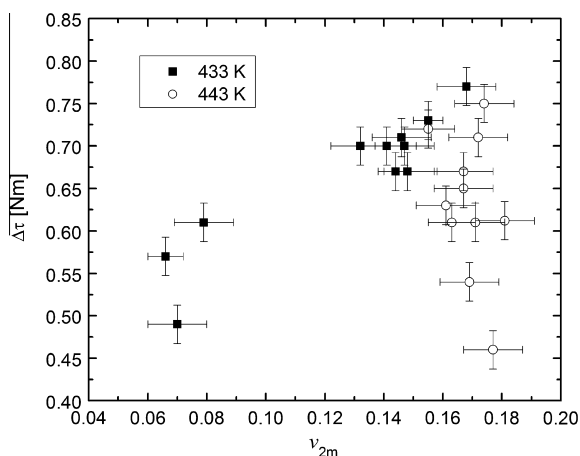


Fig. 5. Variation of  $\Delta\tau$  as a function of  $v_{2m}$  in NR/SBR blends for samples cured at 433 K and 443 K.

discrepancy in the behavior expected for the relation between crosslinks density and free nanohole volume with our results can be attributed to differences in the type of crosslinks formed.

As mentioned previously, the value of  $\Delta\tau$  estimated from the rheometric tests is related to the crosslinks elastically actives in the network formed by vulcanization. The amount and types of crosslinks produce changes in the values of the free nanohole volume as it was reported in several works [19,52,53]. In Fig. 7 the evolution of the parameter  $\Delta\tau$  against  $v_h$  for the two vulcanization temperatures is shown. As can be seen in both cases  $\Delta\tau$  almost linearly decreases when the free nanohole volume increases. As reported in the literature, it is expected that cured samples with low crosslink density have higher free volume [19] and therefore this behavior is directly related to a decrease in  $\Delta\tau$ .

Fig. 8(a) and (b) shows the fractional free volume  $f_v$ , calculated using Eq. (2), as a function of the NR content in the blend and for the two vulcanization temperatures, 433 K and 443 K respectively. It can be seen that this parameter behaves differently when the vulcanization temperature changes. Specifically,  $f_v$  decreases when the NR content increases in the case of blends vulcanized at the higher temperature, while an opposite behavior is observed when the samples were cured at 433 K. In both figures, in the left axis, the change in the volume fraction of the solvent at equilibrium (maximum) degree of swelling  $v_{sol}$  for each cured sample is also shown. From the view of each figure, the shapes of  $v_{sol}$  and  $f_v$  curves as a function of the NR content are very similar. This behavior should be expected as a consequence that the solvent diffuses to the nanoholes. In fact, during the swelling test the network is being deformed because more solvent enters in the compounds until equilibrium is reached; therefore, it is expected that  $v_{sol}$  be higher than  $f_v$ . The difference between the values of  $v_{sol}$  and  $f_v$  is due to the nanoholes expansion of the cured network that makes it possible the penetration of the solvent. Considering the expansion of the nanoholes in the swelling test, the following equation is proposed for  $v_{sol}$ :

$$v_{sol} = f_v + \varepsilon \quad (6)$$

where  $\varepsilon$  is related to the deformation of the free nanohole volumes as a consequence of the diffusion of the solvent inside them. In the case of a two phase blend as NR/SBR, this parameter depends on the deformation of each phase under this solvent diffusion, in these conditions we propose as a first approximation a mixture law of the type:

$$\varepsilon = \varepsilon_1 w_{NR} + \varepsilon_2 w_{SBR} \quad (7)$$

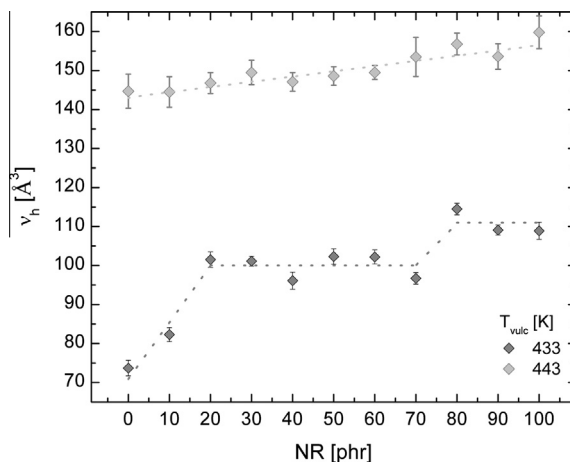
where  $w_{NR}$  and  $w_{SBR}$  are the weight fractions of NR and SBR in the blend.  $\varepsilon_1$  and  $\varepsilon_2$  are the expansion coefficient of the fractional free volume due to the swelling in each phase. Using Eq. (6) with the experimental values of  $f_v$  and  $v_{sol}$ , the  $\varepsilon$  values were obtained for each sample at the corresponding cure temperature. These values are shown in Fig. 8(c). In this plot, the  $\varepsilon$  values were fitted using Eq. (7). As a result, values of  $\varepsilon_1 = 0.59$  and  $\varepsilon_2 = 0.66$  for the samples cured at 433 K and  $\varepsilon_1 = 0.38$  and  $\varepsilon_2 = 0.24$  for the samples cured at 443 K were obtained respectively.

Table 3

*o*-Ps lifetime and its associated intensity as a function of the NR content in the compounds for each vulcanization temperature. The error associated with  $I_{o-Ps}$  and in  $\tau_{o-Ps}$  is less than 0.5% and 50 ps, respectively.

$T_{vulc}$ (K)	NR (phr)	0	10	20	30	40	50	60	70	80	90	100
433	$\tau_{o-Ps}$ (ps)	1743	1841	2050	2046	1992	2058	2057	1999	2185	2130	2127
	$I_{o-Ps}$ (%)	9.9	10.5	13.5	13.0	13.0	14.0	13.2	13.9	16.6	16.2	15.9
443	$\tau_{o-Ps}$ (ps)	2486	2484	2506	2532	2509	2523	2549	2573	2601	2571	2630
	$I_{o-Ps}$ (%)	21.5	22.3	21.4	21.9	22.0	17.9	21.0	17.3	16.2	16.8	15.2





**Fig. 6.** Free nanohole volumes as a function of the NR content in the compounds vulcanized at two different temperatures. Lines are only for eye guide.

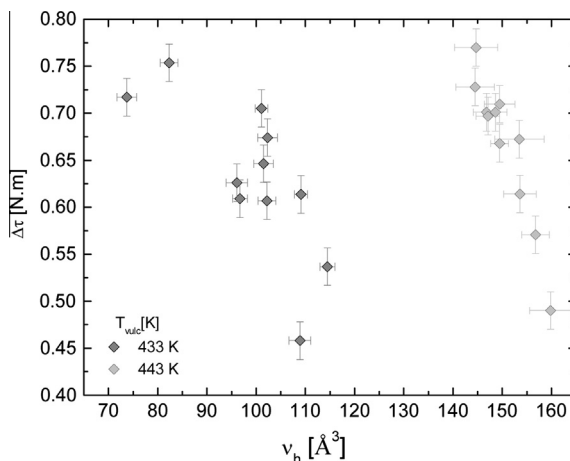
In Fig. 8(a) and (b)  $v_{\text{sol}}$  was calculated for each sample by means of Eqs. (6) and (7), as can be seen an acceptable fit to the experimental data was obtained. It must be pointed out that for our analysis values of  $\varepsilon_1$  and  $\varepsilon_2$  corresponding to the pure compound (NR and SBR) were used.

As previously mentioned, we consider that the phases in the samples studied in the present work do not have the same structure to that corresponding to the pure compounds mainly due to the migration of curatives and the state of cure of each blend. Therefore it could be assumed that  $\varepsilon_1$  and  $\varepsilon_2$  depend on the crosslink degree of both phases in each blend. It must be considered that our approach is only of first order; for a better understanding of the present issue it should be used a more complex model that allows to take into account the different aspects above mentioned.

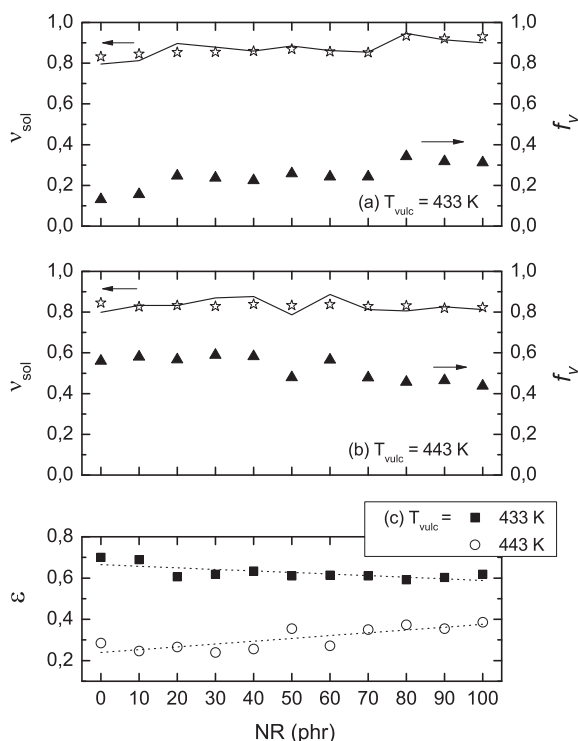
Fig. 8(c) shows the calculated variation of  $\varepsilon$  as a function of the NR content in each sample, and it is interesting to see the increase of this value mainly for the samples richer in NR and cured at 433 K. It is clear that the more open structure obtained in the NR phase at 433 K has a big influence on this result. At this cure temperature, our tests show that the samples richer in NR have a higher deformation at the maximum degree of swelling than for 443 K.

As previously mentioned, experimental evidence shows that NR/SBR blends are immiscible. However, the curatives diffusion at the NR/SBR interphase changes the properties of each phase in the blends with respect to those of the pure compounds. Under this frame, it could be assumed that for each composition of the NR/SBR blend the microstructure of both phases presents slight differences when compared with the pure compounds. Besides, it must be taken into account that blends were vulcanized to the optimum time,  $t_{100}$ , which are very different from the respectively value for the NR and SBR pure compounds.

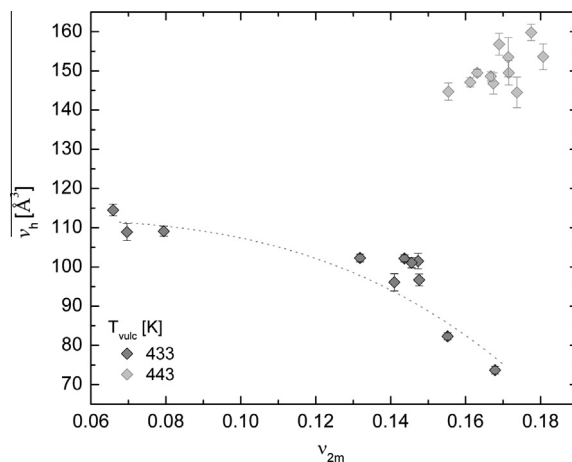
From the data reported in Fig. 9, it is worthy to point out that, for the samples vulcanized at 443 K, the values of the free nanohole volume and those of the fraction of polymer in the maximum degree of swelling have a correlation much more limited than in the case of the samples vulcanized at the lower temperature, in which the correlation between  $v_h$  and  $v_{2m}$  exists in a wider range of  $v_{2m}$  values.



**Fig. 7.** Variation of  $\Delta\tau$  as a function of the free nanohole volume in NR/SBR blends.



**Fig. 8.** Volume fraction of the solvent at equilibrium degree of swelling and fractional free volume for the different NR/SBR compounds vulcanized at 433 K (a) and 443 K (b). The line represents the fit to the data using Eqs. (6) and (7). The error associated with  $v_{sol}$  is less than 0.1%. (c) Dependence of  $\varepsilon$  with the blend composition at both vulcanization temperatures 433 K and 443 K according to Eq. (7).



**Fig. 9.** Free nanohole volume as a function of the polymer fraction at the maximum degree of swelling for all the compounds studied and the cure temperatures used.

We assume that a higher polymer fraction in the swollen state implies a minor free nanohole volume; as can be seen in Fig. 8 this behavior is observed for the set of samples vulcanized at 433 K. On the contrary, in the case of samples vulcanized at the higher temperature, a more homogeneous network structure is obtained independently from the composition of the sample. As mentioned previously, a deeper knowledge about these results could be obtained using other experimental techniques as proton multiple-quantum NRM and/or neutron scattering [48–50].

#### 4. Conclusions

The present work was addressed to the study of NR/SBR immiscible blends prepared by solution and vulcanized at two different vulcanization temperatures (433 K and 443 K). The kinetics studies were performed using rheometry at both cured temperatures. Data obtained from the rheometric curves were analyzed using a well-recognized model that takes into account the reversion effect once the time to achieve maximum torque in the rheometer curves is surpassed. Depending on the composition of the blend, the presence of unstable crosslinks can reach the value of 25% in the samples richer in NR. At the higher vulcanization temperature, there is an increase of the unstable crosslinks in the NR/SBR samples.

Swelling tests in toluene and Positron Annihilation Lifetime Spectroscopy (PALS) measurements were used to analyze the network structure formed during vulcanization.

PALS results show that the average free nanohole volume increases with the NR content in the blends. This effect increases when the vulcanization temperature varies from 433 K to 443 K. This behavior influences the torque variation in all the samples and at higher free nanohole volumes a decrease of  $\Delta\tau$  was measured.

On the other hand, the fractional free volume of the blends obtained by means of PALS correlates with the volume fraction of the solvent at equilibrium (maximum) degree of swelling obtained in the swelling test. Such correlation was assigned to the diffusion of solvent inside the nanoholes present in the elastomeric samples, which are deformed in this process with the consequent increase of their volumes.

#### Acknowledgments

We would like to acknowledge University of Buenos Aires (Argentina) for funding under Project UBACYT 20020120100051(2013–2016), Agencia Nacional de Promoción Científica y Tecnológica (Argentina) (PICT 2011–1088), and Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) (PIP 112–201101–00793).

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