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Temperature dependence on free volume in cured natural rubber and styrene-butadiene rubber blends

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A systematic study on the evolution of free volume as a function of the temperature in vulcanized at 433 K natural rubber (NR) and styrene butadiene rubber (SBR) in 25-75, 50-50, 75-25 NR-SBR (percent content of pure NR and SBR, respectively) blends was studied by positron annihilation lifetime spectroscopy. All samples were prepared with sulfur and TBBS (n-t-butyl-2-benzothiazole sulfenamide) as accelerator. The glass transition temperatures of the samples studied were determined by differential scanning calorimetry (DSC) and from lifetime data. In general, a sigmoidal-like complex behavior of the long-lived lifetime component, linked to the nanohole free volume, as a function of the temperature was found. For SBR, the slope of the ortho-positronium lifetime against temperature curves could be well-fitted using a linear function. For blends and also for NR, two different linear functions were necessary. This last behavior is explained in terms of the supercooled process involving a reconfiguration of the elastomeric chains. In the case of blends, the state of cure of NR and SBR in each NR-SBR sample was also taken into account in the discussion of the results obtained. Besides, thermal expansion coefficients of the free volumes in the transition and glassy region of all compounds were estimated. The differences observed in the values of this parameter are discussed by taking into account the morphology and formulation of each blend, the crosslink densities, and the role of the interphases formed between both NR and SBR elastomers.

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I. INTRODUCTION

Polymers blends are of great industrial interest since blending is a relatively simple fabrication process for polymeric materials with significantly improved properties. Miscibility and phase-separation phenomena of polymer blends are the subject of considerable interest in polymer applications. In order to predict and enhance the mechanical properties for better commercial and industrial applications of blends, it is necessary to understand the atomic-scale microstructure and interaction between the phases.

The complete miscibility of polymers requires that the free energy of the mixing be negative, which implies an exothermic mixing or a large entropy of mixing [1]. Therefore, most blends of elastomers are immiscible because mixing is endothermic and the entropic contribution is small because of high molecular weights. Fortunately, miscibility is not a requirement for most rubber applications.

The physical properties of immiscible two-phase blends depend on the properties of each constituent phase; the morphology, dispersion, and stiffness of each phase play a significant role in the final properties of the blend.

Although immiscible blends show distinct glass transition temperatures T_g, which could shift with respect to the values of the component polymers [2], the situation is complicated by the presence of two T_g, also in miscible blends [3,4].

In the case of elastomers, the advantages for blending are numerous due to an alternative of synthesizing a new elastomer, older and better-characterized rubbers can be employed, hopefully yielding an ideal complement of properties from the blended materials. Natural rubber (NR) and styrene butadiene rubber (SBR) blends are of particular interest as a consequence of their use in tire applications.

The authors of the present work have recently used small angle x-ray scattering (SAXS) techniques to obtain valuable information about the interphase developed in the same NR-SBR blends studied in the present work [5]. On the other hand, Marzocca *et al.* [6] have used calorimetric tests and diffusivity measurements to discuss the thermal properties of the same blends on the basis of the structure formed during the vulcanization process. To this aim, the analysis was made by taking into account the crosslink density of each phase.

The free volume theory makes it possible to describe qualitatively and quantitatively the polymeric behavior under different processes such as physical aging, sorption and transport, and plasticization and miscibility of blends.

The concept of free volume, initially introduced to account for the dependence of the viscosity on the temperature in simple liquids [7] and subsequently extended to polymers [8], turns out to be useful to explain mechanical and viscoelastic properties of macromolecules.

Despite different experimental techniques being used to get information on the free volume, positron annihilation lifetime spectroscopy (PALS) [9] has become the most popular experimental technique due to the capability of ortho-positronium (o-Ps), the positron-electron bound system in the triplet spin state, to localize into the free volume holes. Indeed, o-Ps is repelled from the ionic cores of atoms and molecules

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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 $\tau_{\text{o-Ps}}$ and the size of the hole (in the spherical approximation of nanoholes of radius R), which in fact is cast in a quantitative form by using simple quantum mechanical models [10–12]:

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

The empirical parameter ΔR (0.166 nm [13]) takes into account the annihilation of o-Ps with the electrons belonging to the walls of the hole ("pickoff" process).

Therefore, changes of the average volume of holes v_{h} induced by variations of external parameters, such as temperature or mechanical stresses, can be directly monitored by studying the longest-lived o-Ps lifetime τ_3, in a positron annihilation spectrum. Specifically, $v_{\text{h}} = \frac{4}{3}\pi R^3$ in which R values are obtained from Eq. (1).

As is well known, free volume is related to the mechanical and chemical properties of polymers. Besides, PALS has already been used to study both miscible and immiscible polymer blends [9].

On the basis of previous experience of the authors in the study of rubbers and blends by means of PALS [14,15], the present work analyzes the temperature dependence in the supercooled process in NR-SBR blends. Specifically, a systematic and detailed study is performed of the evolution of the hole free volume as a function of temperature in vulcanized rubber compounds NR and SBR and of 25-75, 50-50, 75-25 NR-SBR vulcanized blends (where the numbers indicate the percent content of NR and SBR, respectively). In fact, PALS is an adequate technique to comprehend the atomic-scale microstructure with reference to the process of reconfiguration of the chains forming the elastomers of the blend. Preliminary results, based on rheological and PALS measurements, were presented at the 14th International Conference on Positron Annihilation [16].

Furthermore, the values of the respective thermal expansion coefficients of the free volumes, in the rubbery states as well as in the glassy phases, were estimated.

II. EXPERIMENTAL METHOD

A. Sample preparation

The rubber compounds used in this work were prepared with natural rubber (NR-SMR20) and styrene butadiene rubber (SBR–1502). The molecular weights of the pure elastomers, measured by gel permeation chromatography (GPC), were $M_n = 91.350$ g/mol with a polydispersity index of 3.60 for SBR and $M_n = 146.910$ g/mol with a polydispersity index of 8.27 for NR. The distribution of molecular weight for both elastomers is given in Fig. 1. The densities of the elastomers measured at room temperature by the Archimedes method were $\rho(\text{NR}) = 0.9170$ g/cm^3 and $\rho(\text{SBR}) = 0.9350$ g/cm^3.

Blends and the pure elastomers with the compound formulation given in Table I were mixed in a laboratory mill. First, a master batch with the two elastomers was prepared and then the curatives were added to complete the mixing.

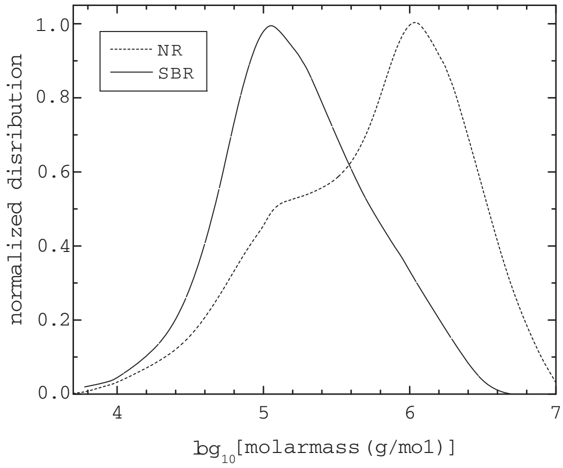

FIG. 1. Molecular weight distribution of the raw materials NR and SBR used in this work.

From Table I, in the formulation of the compounds, the ratio of accelerator TBBS to sulfur of the pure SBR compound (named sample E) is roughly 0.30. In a previous paper of the authors, SBR compounds were also prepared using TBBS and sulfur as a cure system [14]. In these compounds, the TBBS/sulfur ratio was in the range between 1.33 and 0.22, but the amount of TBBS in those formulations was 1.2 phr against 0.7 phr contained in the samples we are studying now. It is worth noting that, recently, Marzocca and Mansilla [17] analyzed the network structure of SBR samples cured at 433 K and containing different amounts of TBBS and sulfur in their formulations ranging from 0.5 to 2.5 phr.

The cure reaction of the compounds studied in the present work were characterized at 433 K by means of torque curves (Fig. 2), and the respective values of the time to achieve the maximum torque, t_{100}, are given in Table II.

Samples in form of sheets of $150 \times 150 \times 2$ mm^3 were cured in a mould at 433 K in a press up to the time t_{100}. At the end of the curing cycle the samples were cooled rapidly in an ice-water mixture. The density of each cured compound was measured as mentioned above and is given in Table II.

The density and T_g^{PALS} of the pure SBR compound, listed in Table II, are practically the same as those reported in Ref. [14]. In the case of t_{100}, the difference between the present value of this parameter and that previously reported is attributed to the fact that the samples belong to different batches of

TABLE I. Compound formulations (in part hundred rubber, phr).

	Sample				
	A	B	C	D	E
SBR1502	0	25	50	75	100
NR (SMR20)	100	75	50	25	0
Stearic Acid	2	2	2	2	2
ZnO	5	5	5	5	5
Antioxidant	1.2	1.2	1.2	1.2	1.2
Sulfur	2.3	2.3	2.3	2.3	2.3
TBBS	0.7	0.7	0.7	0.7	0.7

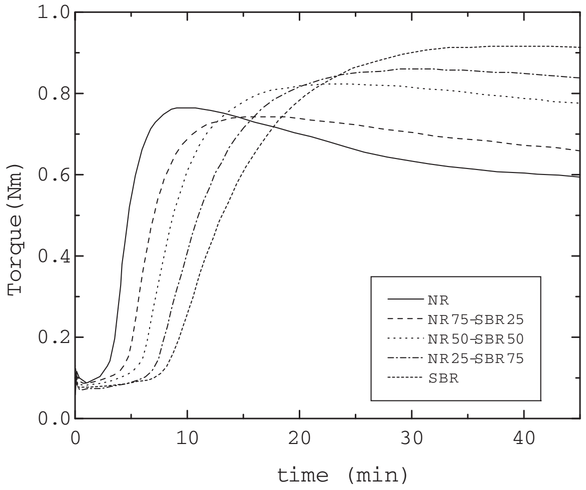

FIG. 2. Rheometer torque curves at 433 K as a function of the cure time for all the compounds analyzed.

compounds containing different amounts of accelerator in their formulations.

B. Morphology

Samples of the blends B, C, and D were cryogenically fractured under liquid nitrogen to be analyzed by scanning electron microscopy (SEM).

The cured samples were swollen in petroleum ether for 72 hours at room temperature and the swollen gel was placed in liquid nitrogen for several minutes, removed and fractured. The fractured samples were dried, sputter-coated with gold, and the fractured surfaces were observed by SEM using a microscope Zeiss Supra$^{\mathrm{TM}}$40.

C. Positron spectroscopy

A fast-fast timing coincidence system with two BaF_2 scintillator detectors was used as a lifetime spectrometer with a resolution of about 300 ps evaluated by means of the RESOLUTION code [18]. The positron lifetime spectra were recorded in the temperature range from 160 to 330 K with a liquid nitrogen cryostat (DN1714, Oxford Instruments) with a stability temperature within 0.3 K. The ^{22}Na positron source (deposited between two Kapton foils 7.5 μm thick which were afterwards sealed to each other, activity 2×10^5 Bq) was placed between two identical samples 2 mm thick and 15 mm in diameter and introduced into a Cu sample holder inserted in the cryostat. Each spectrum contained about 3 Mc. The spectra were deconvoluted by using the LT code [19]. Positron annihilation lifetime spectra were deconvoluted into three discrete components by taking into account a suitable correction for the positrons annihilated in the source support. According to the common interpretation for PALS measurements in polymers, we ascribed the longest component to o-Ps decay in the cavities forming the free volume. 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 para-Ps annihilations.

III. RESULTS AND DISCUSSION

The behavior of the longest-lived lifetime τ_3 with temperature for the various cured samples is shown in Fig. 3. These curves show a sigmoidal shape with well-known features in PALS studies in some polymers; that is, a slow increase of τ_3 in the glassy state followed by a sudden increase of this parameter when the glass transition temperature obtained by PALS T_g^{PALS} is overcome. In dynamic mechanical tests, this region is often called the rubber-to-glass transition zone.

At higher temperatures, with respect to T_g^{PALS}, there is a tendency to a quasisaturation of τ_3, and taking into account all the studied compounds in the present work, an average value of the saturation temperature $T_S = 297.2 \pm 1.2$ K can be considered.

This reduced increase of τ_3 has been attributed to the formation of a Ps bubble in the liquid phase, digging of holes by Ps itself [20], or to the fact that the relaxation time of the molecular chains [21] is comparable to τ_3, in which case Ps is no longer able to correctly probe the sizes of the voids trapping it. Independent of the adopted explanation, there is a general agreement on the contention that, in this temperature region, o-Ps does not give reliable information on the hole free volume.

It is interesting to analyze first the τ_3 curves of the pure cured compounds. In the case of SBR, the τ_3 curve is similar to that reported in previous works by our research group for SBR with different crosslink densities [14]. The glass transition temperature T_g^{PALS} was evaluated with the procedure described in Ref. [14], and a value of 220 K was obtained. For

TABLE II. Optimum time cure t_{100} (MDR2000, 433 K), density, and T_g of the compounds obtained by DSC [6] and PALS. In the case of NR75-SBR25 and NR50-SBR50 blends, in the DSC scans two values of T_g were detected [6]. The bending temperatures T_b obtained from Fig. 3 in the glass transition region are also given.

	Sample				
	A	B	C	D	E
t_{100} [min] [6]	10.7	17.0	24.7	34.4	42.3
ρ [g/cm^3]	0.9536	0.9566	0.9648	0.9722	0.9786
T_g [K] [6]	213.1	214.3–226.7	214.5–226.4	228.2	229.6
T_g^{PALS} [K]	191	202	196	203	220
T_b [K]	239	246	250	254	

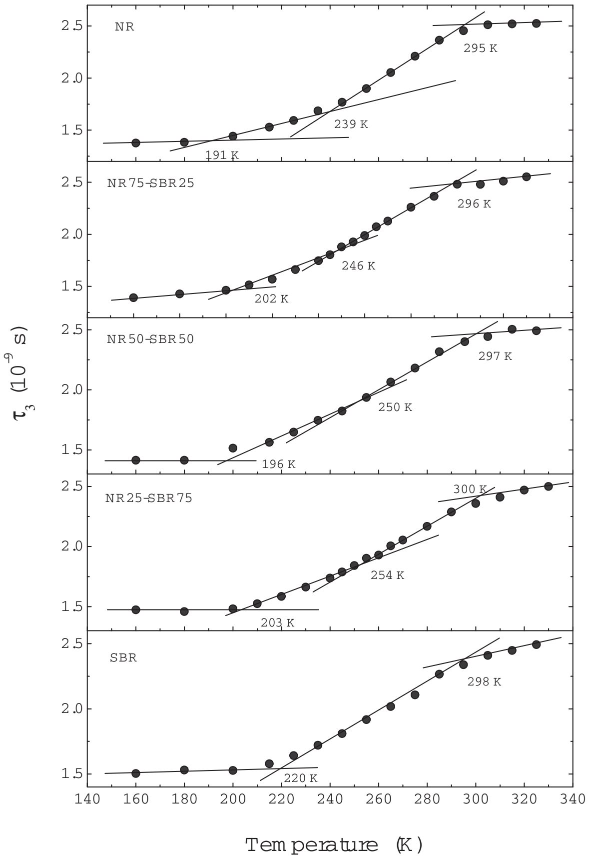

FIG. 3. Longest lifetime component τ_3 as a function of the temperature for all studied compounds. The different cross points indicate the T_g^{PALS}, T_b, and T_S temperatures (see text).

the temperature range between T_g^{PALS} and T_S the lifetime data could be satisfactorily fit by a straight line.

In the case of the NR compound, a value of $T_g^{\mathrm{PALS}} \approx 191$ K was obtained. On the other hand, a special feature is observed for the curve ($T > T_g^{\mathrm{PALS}}$) in the glass transition zone. We note a change of the slope at a bending temperature $T_b \approx 239$ K. This leveling off has been observed in other polymers [22–24] and, in some cases, it was not discussed in detail or simply omitted. The origin of this change is still under debate (see Ref. [25]).

In the three NR-SBR blends studied in this work, a bending temperature was also observed and these values are given in Table II together with the corresponding T_g^{PALS} values. As can be seen, T_b increases when the blend is richer in SBR. In these blends, T_b is higher than T_g^{PALS} (SBR) and this fact implies that, at T_b, the blends have both phases (SBR and NR) in the rubbery state or at least in the glass transition region.

Bartoš *et al.* [24] analyzed the behavior of the positronium (o-Ps) annihilation lifetime parameters with temperature for a series of molecular and structurally simple polymer glass formers, including *cis*-polyisoprene. In this frame, these authors also presented experimental data for *cis-trans*-1,4 polybutadiene, polyisobutylene, and *trans*-1,4-polychloroprene. Although the paper mentioned mainly focused on the study of *cis-trans*-1,4 polybutadiene, the authors observed a clear connection between the characteristic bend temperatures in the liquid state and the glass transition temperature and, as a consequence, they proposed the following relationship: $T_b \cong 1.15 - 1.4 T_g^{\mathrm{PALS}}$. From the data reported in Fig. 3, the glass transition temperature of the NR compound T_g^{PALS} (NR) was estimated to be approximately 191 K and $T_b \approx 239$ K, then the ratio $T_b/T_g^{\mathrm{PALS}} \cong 1.25$. This value is very close to that reported for *cis*-polyisoprene, which is 1.28 [26].

Following Bartoš *et al.* [24], the change in the slope of τ_3 curves at T_b, may indicate a subtle transition in the liquid phase from liquid-like to quasi-solid-like character on cooling the supercooled liquid due to the onset of certain constraints on an expansion of the free volume.

In glass-forming polymers, at least two relaxation processes take place: the main, or α relaxation, is related to the segmental relaxations of the main chain; and the β relaxation is the second, which has been assigned to the local relaxation of the flexible parts of the chain, for example side groups and twisting or crankshaft motion in the main chain [26]. Apparently, the β relaxation, also called the Johari-Goldstein (J-G) relaxation, is a universal feature and an important characteristic of the dynamics of supercooled glass-forming liquids [27].

In SBR, the β relaxation is well detected by means of mechanical dynamic spectroscopy and the position of the peak in the tanδ as a function of the temperature plot does not depend on the crosslink density [28]. In the case of NR, the β relaxation was not detected by mechanical dynamic spectroscopy.

As a first approach, to explain the behavior of τ_3 versus temperature for the blends we have used a mixture law. Therefore, a function of the form

$$\tau_3^{\mathrm{blend}} = \omega_{\mathrm{NR}} \tau_3^{\mathrm{NR}} + \omega_{\mathrm{SBR}} \tau_3^{\mathrm{SBR}} \tag{2}$$

was used, where ω_{NR} and ω_{SBR} represent the volume fractions of the NR and SBR phase in the blend, respectively; and τ_3^{NR} and τ_3^{SBR} are the o-Ps lifetimes for the pure NR and SBR. The τ_3 curves for both compounds were taken from those plotted in Fig. 3. Finally, using Eq. (2) the different evolutions of τ_3^{blend} with the temperature for the three blends measured in this work were obtained. The results are presented in Fig. 4. As can be seen, in all cases the fits to the experimental data show a rather good agreement. The slight differences observed in Fig. 4 can be associated with the influence of the interphase present in each blend, which has not been taken into account in Eq. (2). Indeed, the analysis of the role of the interphase in the physical properties of vulcanized NR-SBR blends is an open issue that has been explored in recent works by our research group [5,6].

Figure 5 shows SEM micrographs of the cryofracture surface for the three NR-SBR blends studied in this work. In the case of NR75-SBR25 [see Fig. 5(a)], it can be concluded that the remaining structure is largely that of the NR phase of the blend. It must be remembered that, in this sample, the cure time t_{100} was 17 min. If we take into account the rheometer curves (see Fig. 2) obtained for pure NR and SBR, it could be concluded that, in the NR75-SBR25 sample, the SBR and NR phases are undercured and overcured, respectively. However, this assumption would be adequate if an even distribution of curatives into the phases existed.

Mallon and McGill [29] studied IR (polyisoprene rubber)/SBR blends and they reported that a diffusion of curatives from the SBR phase to the IR phase could be taking place, therefore enriching in curatives the interphase between both

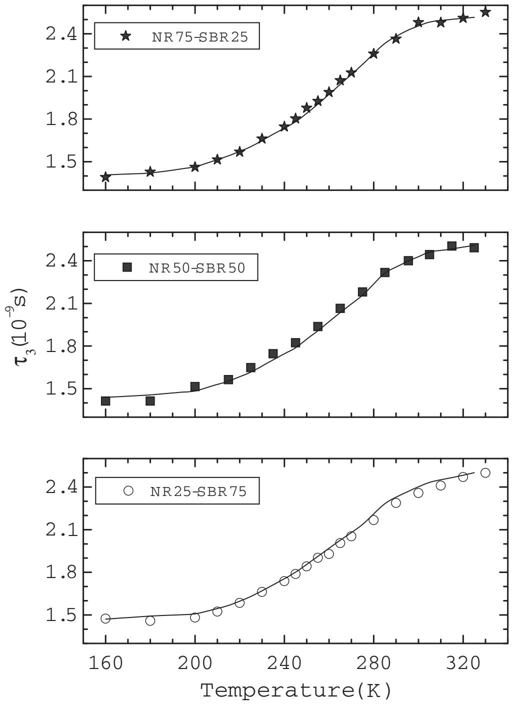

FIG. 4. Comparison for the studied blends between the experimental data of long-lived lifetime component τ_3 as a function of the temperature with the mixture law curves calculated following Eq. (2) (represented by the solid lines).

elastomers, and consequently reducing the amount of curatives in the SBR phase. Applying the same analysis to our NR-SBR blends, it could be considered that a diffusion process produces a reduction in curatives into the core of the SBR phase. Therefore, in the case of the NR75-SBR25 blend, the process described above implies that, at the time t_{100}, some portion of the SBR phase has not yet begun to crosslink.

It is worth mentioning that, during the preparation of the samples to obtain SEM images, the solvent would solve this uncrosslinked region, producing the structure shown in Fig. 5(a). Furthermore, the voids observed in this figure can be attributed to the uncrosslinked portion of the SBR phase. Such a presence of uncrosslinked regions in the SBR phase in the NR75-SBR25 blend explains the decrease in the value of the maximum torque already shown in Fig. 2.

In Fig. 5(b), an image that corresponds to the NR50-SBR50 sample cured for a time $t_{100} = 24.7$ min is shown. As can be seen, in comparison with the image presented in Fig. 5(a), the fraction of the voids is significantly reduced. According to the rheometer curve, at this cure time the SBR phase is more crosslinked than was the case for the NR75-SBR25 blend.

Once the blend is richer in SBR, when it is vulcanized at t_{100} the uncrosslinked region of the SBR phase disappears. This effect can be seen in Fig. 5(c) in which the image corresponds to the NR25-SBR75 blend.

On the other hand, in Fig. 6 the evolution of the fractional free volume f as a function of the temperature for the different compounds studied is presented. Although the procedure followed to obtain the f values was detailed in a previous work (Ref. [14] and references therein), in this work we are

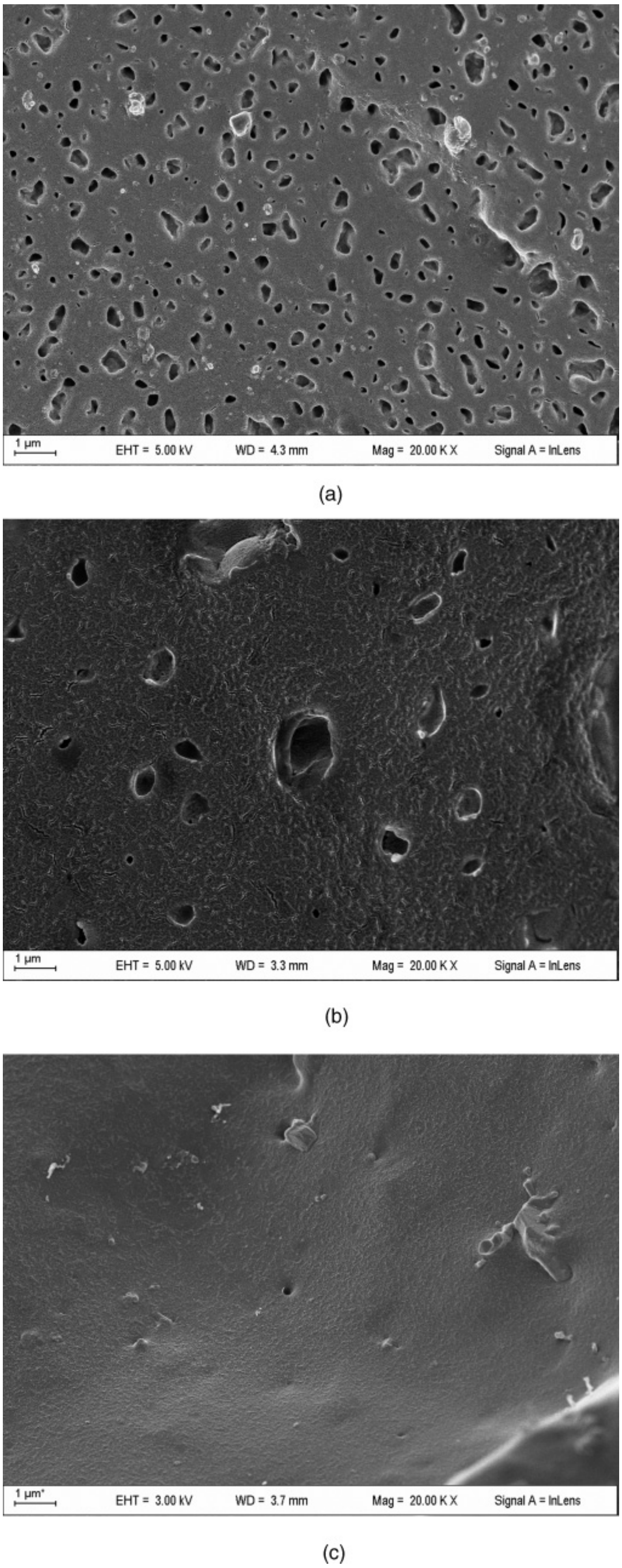

FIG. 5. SEM micrograph of cryofracture surface of NR-SBR blends vulcanized at 433 K and t_{100}. (a) NR75-SBR25 (sample B), (b) NR50-SBR50 (sample C), (c) NR25-SBR75 (sample D).

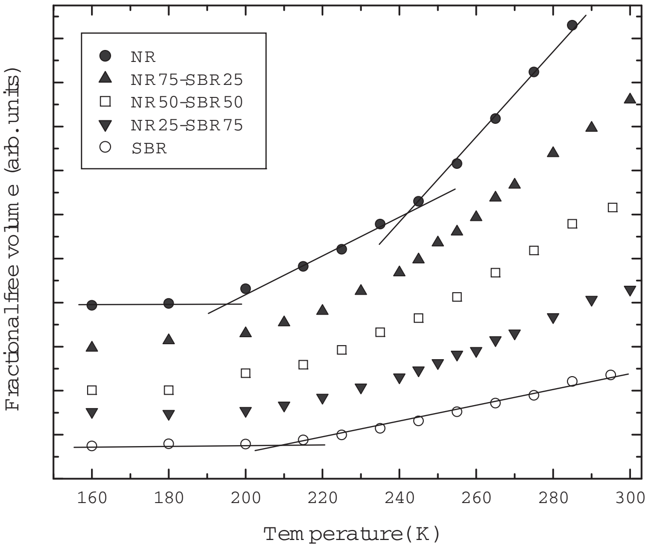

FIG. 6. Fractional hole free volume f as a function of the temperature for all studied compounds (see text). The vertical scale is shifted in order to show changes in the slope of the f versus T curves.

presenting a brief summary that allows the reader to understand how we obtained the data presented in Fig. 6.

Various approaches were used to get the fractional free volume from positron data. Among them, the most-used definition (over the last decade) of the fractional free volume is:

$$f = \frac{V_f}{V} = \frac{N^f v_h}{N^f v_h + V_{occ}}. \tag{3}$$

where N^f is the hole density, V is the specific volume, V_{occ} is the occupied volume, and the free volume V_f is given by

$$V_f = N^f v_h. \tag{4}$$

To get information on N^f we followed the method used in Ref. [23], and to obtain the specific volume V we used the Simha-Somcynsky equation of state for polymers [30] at atmospheric pressure, which can be approximated by the following universal scaling relationship [31] for $T > T_g$:

$$\ln \frac{V}{V^*} = a + b\left(\frac{T}{T^*}\right)^{3/2}, \tag{5}$$

where $a = -0.1033$ and $b = 23.835$ are universal constants; V^* and T^* are scaling parameters and are dependent on the specific structure of polymer. Concerning V^*, it is given, to a very good approximation, by $V^* = 1.45V_W$, where V_W is the Van der Waals volume [32].

In the case of uncured SBR, $V_W = 0.672$ cm^3/g [14]; then $V^* = 0.974$ cm^3/g. For NR $V_W = 0.700$ cm^3/g [32], we have $V^* = 1.015$ cm^3/g. For the NR-SBR blends we calculated V^* according to the weighted mean of the pure components, obtaining the values 1.005, 0.995, and 0.984 cm^3/g for samples B, C, and D, respectively. In addition, in Eq. (5) the different values of V^* were calculated using $T = 293$ K (i.e., room temperature).

In Table III values of the scaling temperature T^*, N^f and the occupied volume V_{occ} for all the compounds studied are reported.

TABLE III. Scaling temperature T^*, hole density N^f, occupied volume V_{occ}, and thermal expansion free volume coefficients in the rubbery (α_{r1}, α_{r2}) and in the glassy (α_g) phases.

	Sample				
	A	B	C	D	E
T^* [K]	9179	8887	8827	8688	8547
$N^f \times 10^{21}$ [g^{-1}]	0.51	0.61	0.66	0.74	0.75
V_{occ} [cm^3/g]	0.976	0.961	0.947	0.935	0.925
$\alpha_{r1} \times 10^{-4}$ [K^{-1}]	6.4	6.6	6.3	6.9	6.1
$\alpha_{r2} \times 10^{-4}$ [K^{-1}]	2.8	4.6	5.2	4.6	
$\alpha_g \times 10^{-4}$ [K^{-1}]	0.6	1.1	1.3	1.0	0.7

When comparing different parameters reported in Table III for sample E with those previously published for a similar pure SBR compound (see Ref. [14]), we find the following results: (i) in the present work the scaling temperature T^* is the lowest one, (ii) the hole density N^f of sample E is about 20% higher than that reported by Salgueiro *et al.* [14], and (iii) the occupied volumes V_{occ} show the same tendency; namely, they increase with the increment of the TBBS/sulfur ratio. The differences pointed out in the items (i) and (ii) can be attributed to the different network structures obtained after curing the pure SBR samples containing different TBBS and sulfur content in their formulations [17].

On the other hand, from the analysis of the different values of the three parameters for each compound (A to E) it can be concluded that, when SBR is added to the pure NR compound (sample A) to form a blend, T^* and V_{occ} show a systematic decrease; conversely, N^f presents a slight and monotonic increase.

In a recent study of these blends made by our research group [5], SAXS and swelling measurements were performed in order to elucidate some aspects of the network structure of the compounds. When analyzing the cured samples by swelling in toluene at room temperature, the polymer volume fraction at equilibrium (maximum) degree of swelling, v_2m, decreases when the blend is richer in SBR. This result is in good agreement with those obtained in the present work in which the parameter N^f increases and V_{occ} decreases with increasing SBR content in the compounds.

Values of the fractional free volume f as a function of the temperature were obtained using Eq. (3). In the same way as in a previous work [14], this equation was also used in the glassy state, assuming for N^f the same value found above T_g. In Fig. 6, the evolution of f versus T for each studied sample is shown.

Finally, we estimated the values of the respective thermal expansion coefficients of the free volumes, $\alpha = df/dT$ in the rubbery states (α_{r1}, α_{r2}) as well as in the glassy phases (α_g). In Fig. 7, values of these coefficients for each rubber compound are plotted as a function of the SBR content. The same values are also reported in Table III.

Regarding the α parameters, a first analysis can be done comparing the respective values for the thermal expansion coefficients obtained for sample E and those reported for a similar pure SBR compound [14]. It is interesting to notice that α_r increases with TBBS/sulfur ratio.

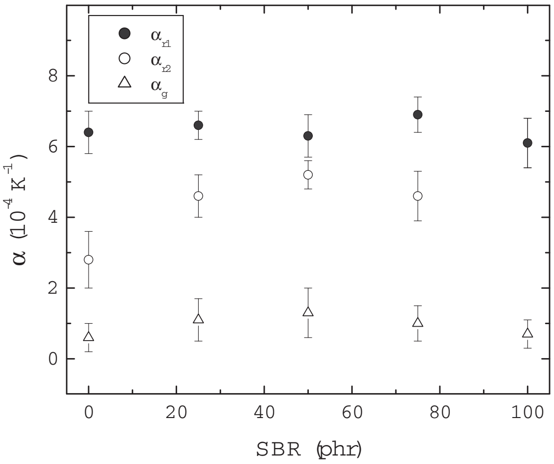

FIG. 7. Thermal expansion free volume of the cured samples as a function of the SBR content in the compound.

In the case of the glassy region, an analysis of the α_g value obtained for the pure SBR sample does not show a clear dependence of this parameter on the network structure.

On the other hand, looking at the α_{r1} and α_{r2} values obtained for the different compounds, it can be concluded that:

(a) The values of α_{r1}, which correspond to the first rubbery state, as a function of the SBR content presented in Fig. 7, are almost constant, within the experimental scatter.

(b) Conversely, as expected from the evolution of τ_3 versus NR content (see Fig. 3), a thermal expansion coefficient of the free volume in the second rubbery state α_{r2} does not exist for the pure SBR compound. Furthermore, for the three NR-SBR blends studied, values of the coefficient mentioned do not clearly change. However, an important decrease of α_{r2} was obtained for the pure NR compound. The presence of a slightly cured SBR phase in the sample NR75-SBR25 produces an increase of the α_{r2} value, which is stabilized for higher SBR content in the blend. This behavior could not be only linked to the different content of every elastomer in each phase, but also to the crosslink density of each phase and to the development of an interphase that should be considered as a third phase into the analysis. This is an open issue and further research should be carried out.

In Fig. 7 we can also see that the α_g values are very similar for the pure compounds (samples A and E). The highest value is obtained for the NR50-SBR50 blend, stressing our interpretation on the influence of the developed interphases into this temperature region.

IV. CONCLUSIONS

The behavior of the longest-lived lifetime τ_3 with temperature of vulcanized rubber compounds made of NR, SBR, and blends of 25-75, 50-50, and 75-25 NR-SBR were studied by means of the PALS technique. The measurements did not allow us to identify the two glass transition temperatures for all blends. However, it is important to point out that, in the temperature range between transition glass temperature T_g^{PALS} and the saturation temperature T_S, lifetime data for SBR can be well fit by a straight line, while in NR a change of the slope at a bending temperature T_b was revealed. For the blends, the same behavior as in NR was observed.

From an analysis of the experimental data it was established that the increase of T_b was correlated with an SBR enrichment of blends. Besides, it was found that, for all blends, T_b was higher than T_g^{PALS} (SBR), which means that, at T_b, the blends have both SBR and NR phases in the rubbery state or at least in the glass transition region.

For blends, the dependence of τ_3 with the temperature was satisfactorily fitted using a mixture law of the τ_3 of the pure components of the blend, and the small deviations among the fitting curves and the experimental data were attributed to the presence of an interphase developed in the blends between the two phases involved (NR and SBR).

From PALS data it was possible to estimate the nanohole density N^f and the occupied volume V_{occ} for each rubber compound. Thus, it was found that, while the first parameter monotonically increases with increasing SBR content in the compounds, V_{occ} diminishes in the same way. The described behavior of both parameters is attributed to the network structure formed during the vulcanization process of the different rubber compounds.

In addition, the following significant information on the rubber compounds was obtained:

The morphology of the studied blends, vulcanized at the time t_{100} obtained from rheometer curves, shows the presence of voids in the SBR phase of the blends due to an uncrosslinked zone that diminishes when the blend is richer in SBR.

The thermal expansion coefficients of the free volumes in the transition and glassy region were estimated for all the cured samples. The differences among the values of the respective parameters for each blend were ascribed not only to the two elastomer contents in each sample, but also to the crosslink density and to the interphase formed. More work must be done in future research in order to elucidate this issue.

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