POLYMER TESTING
ROGER BROWN

Material properties

Evolution of the free volume and glass transition temperature with the degree of cure of polybutadiene rubbers

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A R T I C L E   I N F O

A B S T R A C T

An investigation of the influence of the cure time on the glass transition temperature and nanostructure for two isomers of polybutadiene rubbers, CB25 (97% *cis*) and CB55 (38% *cis*), vulcanized at 433 K is presented. The samples were prepared with sulphur and TBBS (N-t-butyl-2-benzothiazole sulfenamide), and several crosslink densities were achieved at the different selected cure times. The studies on the samples were carried out using differential scanning calorimetry and positron annihilation lifetime spectroscopy. The variation of the glass transition temperature with the degree of cure and its relation with the crosslink density is analyzed for each type of isomer. A correlation between the free nanohole volume and the crosslink density is also analyzed. From swelling tests, the absorbed solvent at room temperature is discussed in terms of the obtained free nanohole volumes, showing a correspondence between these parameters. In the frame of the obtained results, the *cis* to *trans* isomerisation of the elastomer with high *cis* content during the vulcanization is discussed.

1. Introduction

In recent years, we focused our research activities in the study of the influence of the network microstructure formed during vulcanization of polybutadiene rubber, BR, on several physical properties.

It is known that polybutadiene rubber is one of the most popular synthetic rubbers due to its excellent mechanical properties when combined to form blends. This elastomer when vulcanized is used in several technological goods such as treads and sidewalls in tires. BR also has a major application as an impact modifier for polystyrene and acrylonitrile-butadiene-styrene resin (ABS), with about 25% of the total volume going into these applications. Another important application, in the case of the high *cis* polybutadiene, is in golf ball cores due to its outstanding resiliency.

The network structure formed during the vulcanization of elastomers with the addition of sulphur and accelerator is strongly influenced by the compound formulation and the process conditions: pressure, cure temperature and cure time.

The isomeric composition of polybutadiene has a strong influence on its mechanical properties [1]. In particular, the glass transition temperature, T_g, increases with the vinyl content by creating a stiffer chain structure. In these vinyl units, the double bonds are pendent to the main chain; on the contrary, 1,4-*cis* and 1,4-*trans* units have their double bonds in the main chain [2,3]. The vinyl units tend to crosslink when submitted to high temperature conditions,

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and elastomers with high vinyl content have a lower thermal stability than the low-vinyl ones.

The present work is the fourth, and the last, part of a systematic study on the structural properties of two types of BR vulcanized using sulphur and TBBS (n-t-butyl-2-benzothiazole sulfenamide) as accelerator. In our previous works, we analyzed the rheometric properties, the swelling in solvent and dielectric properties of these materials submitted to different degrees of cure by vulcanization at a particular temperature, specifically 433 K [4–6]. On the basis of previous experience of the authors in the study of rubbers and blends by means of Positron Annihilation Lifetime Spectroscopy (PALS) [7–10] and Differential Scanning Calorimetry (DSC) [11], the present work was addressed to study the evolution of the free nanohole volume, v_h, and the glass transition temperature with the vulcanization process of the BR samples mentioned.

The free volume theory makes it possible to describe qualitatively and quantitatively the polymer behavior under different processes such as physical aging, sorption and transport, plasticization and miscibility of blends. The free volume was initially introduced to account for the dependence of the viscosity on the temperature in simple liquids [12] and, subsequently, extended to polymers [13]. It turns out to be useful to explain mechanical and visco-elastic properties of macromolecules.

PALS is an suitable technique to comprehend the atomic-scale microstructure referred to the process of reconfiguration of the chains forming the elastomer. Among the different experimental techniques used to get information on the free volume, PALS [14] has become the most popular due to the capability of ortho-Positronium (o-Ps), the positron-electron bound system in triplet spin state, to localize into the free nanohole volumes. It is well-known that there is a correlation between the o-Ps lifetime, $\tau_{o\text{-}Ps}$, and the size of the hole (in spherical approximation of nanoholes of radii R). Using simple quantum mechanical models [15–17], this relationship is expressed as follows:

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

The empirical parameter ΔR (0.166 nm [18]) takes into account the annihilation of o-Ps with the electrons belonging to the wall of the hole ('pickoff' process). Thus, the average free nanohole volume can be calculated according to $v_h = 4\pi R^3/3$.

2. Experimental

The samples were prepared with two types of commercial polybutadiene provided by Lanxess: Buna CB-25 (produced by neodymium catalysis) and Buna CB-55 NF

Table 2
Compound formulations in parts per hundred rubber (phr).

	BR1	BR2
BR Buna CB25	100	–
BR Buna CB55 NF	–	100
Zinc Oxide	5	
Stearic acid	2	
Antioxidant	1.2	
Accelerator (TBBS)	1.0	
Sulfur	1.5	

(lithium grade BR). The main characteristics of these isomers are summarized in Table 1. The compound formulations are indicated in Table 2, and further details are given in Refs. [4,5]. The high-*cis* compound will be designated as BR1 and the medium-*cis* compound as BR2.

These compounds were characterized at 433 K by means of torque curves obtained with an Alpha MDR 2000 rheometer [4]. Samples in the form of square sheets of 150×150 mm^2 and a thickness of 2 mm were press cured in a mould at 433 K.

The degree of cure of the compounds was changed by curing samples at different times, as given in Table 3. At the end of the curing cycle, the samples were rapidly cooled in an ice and water mixture. The crosslink density μ_{cs}, evaluated by swelling in toluene was determined in a previous work [5]; values of this parameter are also given in Table 3.

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

A fast-fast timing coincidence system was used as lifetime spectrometer for the PALS measurements with a time resolution of about 330 ps. Positron lifetime spectra were recorded at room temperature with a counting rate circa 90 counts per second and a total of at least 2×10^6 counts had been recorded in each spectrum. A 20μCi source of ^{22}Na deposited on a thin Kapton foil (7.5 μm thick) was used as positron emitter. The source was placed between two identical rectangle-shaped samples of 2 mm thickness obtained from the same sheets used for the calorimetric tests. PALS spectra were decomposed into three discrete lifetime components using the LT10 program [19]. In the present work, we discuss the lifetime τ_3 of the most long-lived component which represents the so-called via pick-off annihilation with the electrons from the surrounding molecule (i.e., $\tau_3 \equiv \tau_{o\text{-}Ps}$).

Table 1
Structural characteristics and density of the polybutadiene rubbers studied in this work (as provided by the supplier).

Polymer	*cis* 1,4 content (%)	*trans* 1,4 content (%)	*vinyl* content (%)	M_n (g/mol)	Polydispersity	Degree of branching	ρ_p (g/cm^3)
Buna CB-25	97	2	1	130,000	2.6	15	0.91
Buna CB-55 NF	38	51	11	125,000	1.3	<5	0.91

Table 3
Degree of cure and crosslink density of the BR1 and BR2 compounds cured at 433 K during different times.

BR1			BR2		
Cure time [s]	θ	μ_{cs} ($\times 10^{-4}$) [mol/ml]	Cure time [s]	θ	μ_{cs} ($\times 10^{-4}$) [mol/ml]
650	0.30	0.750	775	0.30	0.655
690	0.50	1.084	825	0.50	0.867
780	0.75	1.188	950	0.75	0.961
960	0.90	1.199	1130	0.90	0.970
1800	1.00	0.977	1850	1.00	0.739
3600	Overcured	0.861	3700	Overcured	0.658

3. Results and discussion

The glass transition temperatures of each elastomer used in this research (Buna CB 25 and Buna CB55) are given in Table 4. As can be seen, in polybutadiene rubber an increment of the *vinyl* content produces an increase of the T_g value [20,21]. The corresponding T_g values of the uncured compounds of these elastomers are also given in the table. As expected, a shift of T_g to higher values when the chemicals are incorporated into the rubber is observed because, in the uncured condition, they act as fillers in the polymer matrix.

Moreover, in Table 4, values of the free nanohole volume for all the mentioned samples are reported. When comparing the values of both pure elastomers, it is found that the sample with medium-*cis* content (CB55) has a higher v_h value than that obtained for the sample with high-*cis* content (CB25). This difference can be attributed to the dissimilar microstructure of the respective polymers. With the addition of curatives to CB25 and CB55 to obtain the BR1 and BR2 compounds, respectively, a systematic decrease of the free nanohole volume with respect to the pure elastomers is observed. The presence of the vulcanization reagents generates a more significant v_h change in the compound with medium-*cis* content (BR2) than that in high-*cis* content (BR1). It is important to point out that in previous works we found that the inclusion of fillers generates an increase of the hydrostatic internal pressure in the polymer matrix, which is reflected in a decrease of the free nanohole volume [22,23]. This effect was also observed in some filled styrene butadiene rubber systems [24,25].

In Fig. 1, the glass transition temperature for the different cured samples of each compound is shown. These values are presented in terms of the degree of cure, θ, obtained from the rheometer curves reported in Ref. [4]. As expected, T_g values rise with the reticulation development.

Table 4
Glass transition temperature and free nanohole volume for the pure elastomers (Buna CB 25 and CB55) and the uncured compounds (BR1: 97% *1,4-cis* and BR2: 38% *1,4-cis*). The errors associated with T_g and v_h are 0.5 K and 1 Å^3, respectively.

|	T_g (K)	v_h (Å^3)
Buna CB25	166.8	149.4
BR1 (uncured)	167.5	139.5
Buna CB55	180.3	159.3
BR2 (uncured)	181.4	115.8
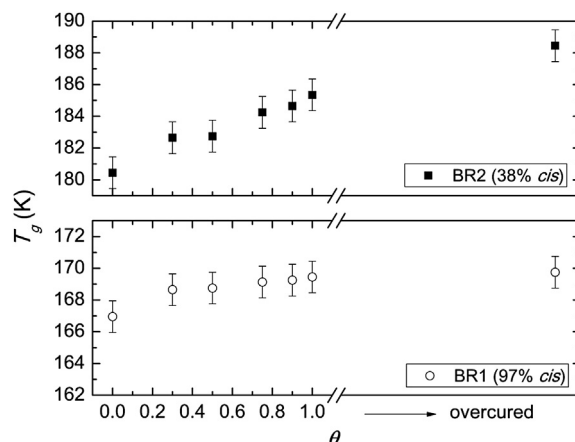
Fig. 1. Glass transition temperature with the degree of cure for BR compounds with different molecular microstructure.

In Fig. 2, T_g values as a function of the crosslink density are presented. As can be seen when comparing the cured state of both compounds with that uncured ($\mu_{cs} = 0$), there is an increase of the glass transition temperature. This behavior can be attributed to lower freedom of movement of the macromolecular segments in the cured state compared to the uncured one [26]. Moreover, changes in T_g are more significant in the case of the compound that contains in its structure a higher concentration of *vinyl* groups (see Fig. 1).

In the case of the compound with medium-*cis* structure, the overcured sample shows an unusual feature: an increase of T_g is correlated with a decrease of μ_{cs} (see Fig. 2). In a previous work on the same compound, we used Nuclear Magnetic Resonance (NMR) to study the vulcanization process; as a result, no remarkable changes in the relative content of *cis*, *trans* and *vinyl* structures were observed [6]. Some authors observed a drop of the crosslink density in sulfur/accelerator BR overcured compounds [27,28]. Additionally, in the overcured state, together with the crosslink
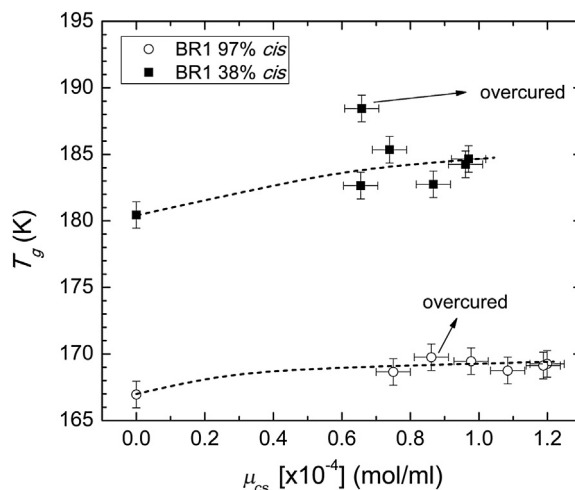
Fig. 2. Glass transition temperature as a function of the crosslinks density for BR compounds with different molecular microstructure.
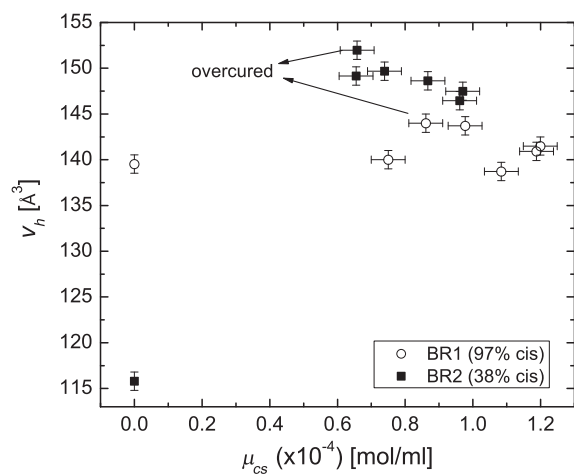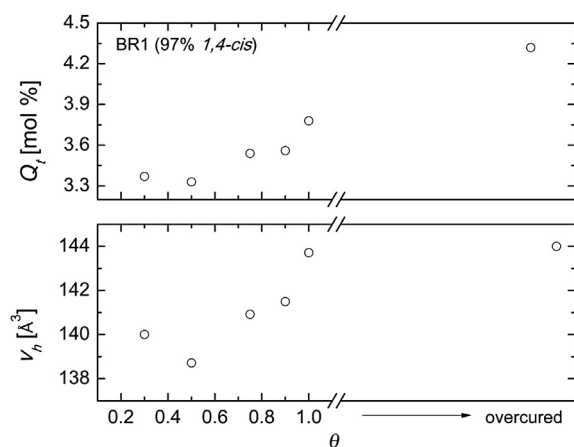
Fig. 3. Free nanohole volume average as a function of the crosslinks density for BR compounds with different molecular microstructure.

Fig. 5. Solvent uptake and free nanohole volume as a function of the degree of cure for the BR2 sample.
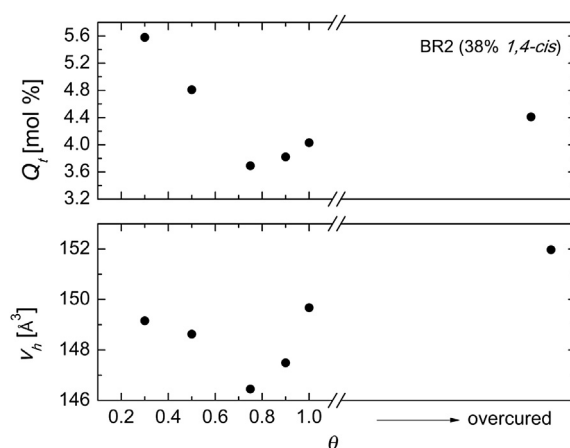
degradation, a change in the type of crosslinks was reported; specifically, an increase of the monosulfide crosslinks and a decrease of the polysulfide ones [27,28]. Under this scenario, the above-mentioned anomaly detected in T_g could be assigned to a process known as crosslink reversion [29].

In Fig. 3, evolution of the average free nanohole volume as a function of the crosslink density for each compound is shown. Results obtained for the two overcured samples are also included in this figure. It can be seen that, once the vulcanization reaction at 433 K takes place, the evolution of v_h versus μ_{cs} is strongly dependent on the BR isomer used to prepare each compound. In fact, the medium-cis compound BR2 shows a sharp v_h increase when the networking development starts. For higher μ_{cs} values, the free nanohole volume shows a slight decrease.

As reported in Ref. [6], from RMN results in the BR1 sample the content of vinyl structure was not detected. Conversely, this technique made it possible to clearly reveal the cis to trans isomerisation, which is one of the most

important features of the cure process of this compound. On the other hand, as can be seen in Fig. 3 in the BR1 compound, there is not a well-defined correlation between the free nanohole volume and the crosslink density. However, in this case it is important to note that during vulcanization different processes act simultaneously: a change in the molecular microstructure (cis to trans isomerization), the crosslinks formation and a reversion from the polysulfide to monosulfide crosslinks [28,29]. More research must be done to distinguish the contribution of each of these processes on v_h.

In the case of the medium-cis compound, during the vulcanization process a non-significant change involving isomerization was detected [6]. However, in Fig. 3 for the BR2 sample it can be observed that v_h decreases with the increment of μ_{cs}. This behaviour can be attributed to a closer structure formed at higher crosslink levels.

It is interesting to analyze the relation between the v_h values obtained in the present work and the solvent uptake Q_t at the equilibrium of the swelling tests. It is worth mentioning that in a previous work some authors of the present paper reported Q_t values obtained for the BR1 and BR2 compounds [4]. For the same compounds, in Figs. 4 and 5, respectively, v_h as well as Q_t are plotted as a function of the degree of cure. As can be seen, qualitatively the evolution of both parameters for each compound is similar. This behavior would indicate that the absorbed solvent is hosted in the free volume. Going further into the analysis of the data reported in the figures, it can be observed that at the beginning of the reticulation process the nanohole free volumes and the solvent uptake values decrease; specifically, both parameters reach their minimum values at $\theta = 0.5$ and 0.75 for the BR 1 and 2, respectively. For higher θ values, v_h and Q_t, increase even when the compounds arrive at the overcured state.

4. Conclusions

This is the last of four papers dealing with a study of structural and mechanical properties of two types of polybutadiene compounds when reticulation agents are

Fig. 4. Solvent uptake and free nanohole volume as a function of the degree of cure for the BR1 sample.

added. Specifically, the CB25 (97% *cis*) and CB55 (38% *cis*) designated as BR1 and BR2 compounds, respectively, were studied. The results obtained were:

- The glass transition temperature is higher in the compound BR2 than that of BR1; this result was attributed to the major quantity of vinyl in the first compound.
- In both compounds, the glass transition temperature increases when the degree of cure increases. This result is in correspondence with the development of the physical crosslinks between the polymer segments.
- In particular, in the overcured state of the BR2 compound, the increase of the glass transition temperature was correlated with a decrease of the crosslink density. This effect was attributed to a reversion phenomenon of the reticulation structure.
- In the two pure elastomers (CB25 and CB55), the addition of curatives induces a decrease of the free nanohole volume. In fact, curatives generate an increase of the internal pressure in the matrix. It was found that this effect is more marked for the BR2 compound.
- In the BR2 compound, it was found that cure treatment produces a sharp increase of the free volume. For higher crosslink densities, v_h slightly decreases generating a more closed structure of this compound. In the case of the BR1, compound, there is not a well-defined correlation between v_h and μ_{cs} due to during the cure process in this type of polybutadiene three concomitant processes occur: the evolution of the crosslink density, isomerization and reversion. For the two compounds studied, good correlation was found between the absorbed solvent and the corresponding free nanohole volume as the degree of cure increases. This made it possible to infer that the free volume hosts the uptake of solvent.

Acknowledgments

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