



Material properties

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



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ABSTRACT

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.

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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 viscoelastic properties of macromolecules.

PALS is a 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, τ_{o-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 $150 \times 150 \text{ mm}^2$ 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 $20\mu\text{Ci}$ 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., $\tau_3 \equiv \tau_{o-Ps}$).

Table 1

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

Polymer	<i>cis</i> 1,4 content (%)	<i>trans</i> 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

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