



## Material properties

## Comparative study of thermal, mechanical and structural properties of polybutadiene rubber isomers vulcanized using peroxide



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## ARTICLE INFO

## Article history:

Received 8 March 2016

Accepted 13 April 2016

Available online 14 April 2016

## Keywords:

Polybutadiene rubber

Vulcanization

Rheometry

Positron annihilation lifetime spectroscopy

Swelling

Differential scanning calorimetry

## ABSTRACT

Three commercial polybutadiene rubber (BR) compounds (high *cis*, medium *cis* and high *vinyl* content) were vulcanized at 433 K, using different amounts of dicumyl peroxide (DCP) as curing agent. To analyze the structural changes produced by the vulcanization process of the three BR isomers, different experimental techniques (rheometry, swelling tests, differential scanning calorimetry and positron annihilation lifetime spectroscopy) were used. The evolution of the free nanohole volumes, the glass transition temperatures and the polymer fractions at the maximum degree of swelling as a function of the DCP content in the formulation of the different BR compounds are discussed. A correlation between the glass transition temperature and torque variation and a relationship between the fraction of absorbed solvent and free nanohole volume as a function of the DCP content are also considered.

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## 1. Introduction

Polybutadiene rubber (BR) is the second largest volume synthetic rubber produced on a global scale, next to styrene-butadiene rubber. The main interest in this synthetic polymer is the excellent mechanical properties when blended with other polymers. BR is obtained through the polymerization of 1,3-butadiene, which can polymerize in three different ways: *cis*, *trans* and *vinyl*. The catalyst used in the BR polymerization determines the amount of *cis*, *trans* and *vinyl* units and, therefore, different types of polybutadiene are obtained. Physical and mechanical properties of BR depend on the proportion of each isomer. It should be noted that, in the *vinyl* units, the double bonds are pendent to the main chain, whereas *cis* and *trans* units have their double bonds in the main chain.

During the vulcanization of elastomers, polymer chains cross-link with each other, improving the mechanical properties of the material. These crosslinks build a network structure which is strongly dependent on both the compound formulation and the processing conditions [1–6].

Unsaturated rubbers such as BR have many easily-abstractable allylic hydrogen atoms as well as many double bonds [7]. These sites could serve for radical addition and, when the rubber recipe includes peroxides as vulcanization agent, the high concentration of these reactive sites makes it possible that the cure mechanism is by abstraction or addition. Addition reactions are more favored with increasing *vinyl* content [8].

A polymer in a good solvent will absorb a portion of the solvent and subsequently swell. In the case of cured elastomers, the polymer network begins to elongate under the swelling action and also generates an elastic restoring force in opposition to this deformation. The volumetric swelling reaches a steady state when these two forces balance each other. The elastic restoring force is proportional to the crosslinks generated in the cure process. Therefore, the swelling test is a useful technique to characterize the network structure generated during the vulcanization process.

Positron annihilation lifetime spectroscopy (PALS) is a suitable technique to get information on the atomic-scale structure in solids; it is made possible to directly determine the average size of the free nanohole volume  $v_h$  in a non-destructive way. In the case of polymers, with PALS it is possible to study the process of reconfiguration of the macromolecules. This technique was successfully

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used for the analysis of several uncured and cured elastomers and/or elastomer blends [9–21]. 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 on the fact that ortho-Positronium (*o*-Ps), the positron-electron bound system in triplet spin state, 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 nanohole volume  $v_h$ . Using a simple quantum mechanical model that takes into account the annihilation of *o*-Ps with the electrons belonging to the walls of the hole ('pickoff' process), it is possible to establish a correlation between its lifetime  $\tau_{o-Ps}$  (in ns) and the size of the nanohole (in approximation to spherical nanoholes of radius  $R$ ) by means of the following equation [22–25]:

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

where  $\Delta R = 0.166$  nm [26] is an empirical parameter. Thus,  $v_h$  can be calculated as  $v_h = 4\pi R^3/3$ .

Usually in polymers, the lifetime spectrum is decomposed into three components, where the longest one is ascribed to  $\tau_{o-Ps}$ .

In previous works, we have studied polybutadiene of high and medium *cis* content, prepared in a laboratory mill and using sulfur as crosslink agent, and vulcanized at 433 K at different degrees of cure [9,27–29].

The aim of the present work is to go into deeper analysis of the role of both the amount of the crosslinking agent, specifically dicumyl peroxide instead of sulfur, and the isomeric composition (high *cis*, medium *cis* and high *vinyl* content) in the final structure of the cured compounds. To get information on thermal, mechanical and structural properties, values of the parameters glass transition temperature, free nanohole volume and fraction of polymer and absorbed solvent at the maximum degree of swelling were obtained and analyzed.

## 2. Materials

Three types of commercial BR with different isomeric composition were studied: Buna CB25, Buna CB55 (both produced by Lanxess) and Europrene BR HV80 (produced by Eni-Versali).

Buna CB25 is a solution high *cis* polybutadiene polymer produced with neodymium catalyst (96% *cis*, 3% *trans* and 1% *vinyl*). The molecular weight of this BR is 130000 g/mol.

Buna CB55 is a solution medium *cis* polybutadiene polymer produced with an organolithium catalyst (38% *cis*, 52% *trans* and 10% *vinyl*); its molecular weight is 125000 g/mol.

Europrene BR HV80 is a solution polymerized high *vinyl* butadiene polymer produced by a continuous process using an alkyl lithium catalyst (10% *cis*, 20% *trans* and 70% *vinyl*). In this case, its molecular weight is 140000 g/mol.

Compound samples were prepared by dissolving the polymer in toluene, and then the DCP was incorporated. The mixture was further homogenized with mechanical agitation and in an ultrasonic bath. The solution was placed in a glass container ( $30 \times 20 \times 5$ ) cm<sup>3</sup>. The solvent was evaporated at room temperature (RT) until constant weight, achieving approximately ( $30 \times 20 \times 0.05$ ) cm<sup>3</sup> of uncured film. At the end of the process, approximately 30 g of each compound was obtained with different amounts of DCP in the recipe.

In the case of the CB25 and CB55 samples, the DCP amount added to prepare the compounds was 0.27, 0.54, 1.08, 1.62, 3.25 and

4.33 phr (parts per hundred of rubber). In the case of HV80, the DCP contents were 0.11, 0.27, 0.54, 0.81 and 1.08 phr.

## 3. Experimental

### 3.1. Rheometric tests

The compounds were characterized by means of torque curves obtained with an *Alpha RPA 2000* rheometer at 433 K with a frequency of 100 cpm and a deformation of 0.5°. From the rheometer curves of the compounds (see Fig. 1), reversion was not observed and the curves reach a maximum torque  $\tau_h$  for the plateau values, indicating that crosslinking were no longer produced.

From the torque curves, it is difficult to exactly determine the time at which the maximum torque  $t_{100}$  is reached. Consequently, all the compounds were vulcanized up to 90 min to guarantee that the maximum degree of cure was reached.

### 3.2. Swelling tests

The samples were vulcanized at 433 K in a press using a mold of dimensions ( $10 \times 10 \times 0.1$ ) cm<sup>3</sup>. At the end of the curing cycle, the samples were cooled in an ice and water mixture.

From the cured samples, disks of 17 mm diameter were cut to perform swelling tests in toluene at RT.

The polymer fraction at the maximum degree of swelling  $v_{2m}$  was evaluated using the following equation:

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

where  $W_d$  is the weight of the sample after swelling and drying,  $W_s$  is the weight of the swollen sample,  $\rho_s$  the density of the solvent (0.8669 g/cm<sup>3</sup> for toluene) and  $\rho$  the compound density which was determined via the hydrostatic weighing method. All measurements were performed on an analytical balance with a resolution of  $\pm 0.0001$  g. The average density of at least three samples per compound is summarized in Table 1; the deviation was less than 0.005 g/cm<sup>3</sup>.

The volume fraction of the absorbed solvent in the sample was obtained through

$$v_{sol} = 1 - v_{2m} \quad (3)$$

### 3.3. Differential scanning calorimetry (DSC)

The glass transition temperature  $T_g$  and the variation of the specific heat  $c_p$  through the glass transition were determined using a *Q2000-TA Instruments analyser*, which was previously calibrated using indium as a reference. Hermetic aluminum pans were used.

Measurements were performed under a nitrogen atmosphere with a constant flux of 25 ml/min. The calorimeter was programmed for a cooling/heating cycle between 123 K and 303 K with a rate of 10 K/min for the CB25 and CB55 compounds. In the case of the HV80, the temperature cycle was from 123 K up to 423 K.

From the inflection point of the endotherm curve, the glass transition temperature for each compound was determined with an uncertainty of 0.5 K.

### 3.4. Positron annihilation lifetime spectroscopy (PALS)

For PALS measurements, a fast-fast timing coincidence system was used with a resolution of about 340 ps As positron emitter,

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