Influence of the Crosslinking Content on the Structural Properties of Polybutadiene Rubbers with Different Isomeric Composition

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Abstract. In the present work first results on structural properties of three commercial isomers of polybutadiene rubber are presented. To this aim, rheometry, PALS, DSC and swelling techniques were used. Different samples were prepared containing diverse amounts of dycumil peroxide as crosslinking agent and vulcanized at 433 K.A correlation among the experimental results obtained using different techniques is also discussed.

Introduction

Polybutadiene rubber (BR) is the second largest volume synthetic rubber produced at global scale, next to styrene-butadiene rubber. The huge interest in this kind of synthetic polymer is due to its excellent mechanical properties, especially when is used as cured rubber blend. The molecule of butadiene can polymerize in three different ways: *cis*, *trans* and *vinyl* (see Fig. 1). Physical and mechanical properties on these materials depend on the differences of the molecular structures [1].
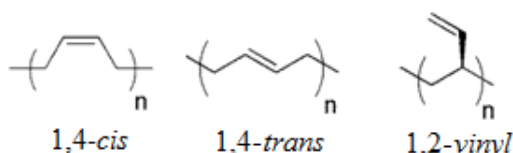

Figure 1: Isomeric structures of polybutadiene.

When a rubber is vulcanized, polymer chains crosslink with each other improving the mechanical properties of the material. The network structure generated is strongly dependent on the compound formulation and the processing conditionsof the vulcanization (i.e., cure) process [2].

Unsaturated rubbers can be vulcanized by the action of organic peroxides. BR has readily abstractable allylic hydrogen atoms as well as many double bonds and, therefore peroxide can crosslink by abstraction or addition pathways mechanisms [3]. Addition reactions are more favored with increasing vinyl content. [4-5].

PALS is a suitable technique to get information on the atomic-scale structure in solids. In the case of polymers, it is possible to study the process of reconfiguration of the macromolecules. PALS was successfully used in several uncured and cured elastomers and/or elastomer blends [6-8]. In this work, the structural evolution of three commercial isomers of polybutadiene rubber as a function of the dycumil peroxide (DCP) content is presented. To this aim, typical parameters as free nanohole volumes, volume fractions and fraction of absorbed solvent at the maximum degree of swelling were obtained. The present work is part of a general study aimed to get structural information of BR compounds [7,11].

Experimental

The isomeric compositions of the commercial BRstudied were: Buna CB25 with high *cis* content (96 % *cis*, 3 % *trans* and 1 % *vynil*), Buna CB55 with half *cis* content (38 % *cis*, 52 % *trans* and 10 % *vynil*) and HV80 with high *vynil* content (10 % *cis*, 20 % *trans* and 70 % *vynil*). The respective molecular weights were 130 000, 125 000 and 140 000 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 with an ultrasonic bath. Finally, the solvent was evaporated at room temperature until obtaining constant weight. In the case of the CB25 and CB55 samples, the DCP amount added to prepared the compounds was 0.27, 0.54, 1.08, 1.62, 3.25 and 4.33phr (parts per hundred of rubber). In the case of HV80DCP contents were 0.11, 0.27, 0.54, 0.81 and 1.08.

The compounds were characterized at 433 K by means of torque curves obtained with an *Alpha RPA 2000* rheometer. These curves for each compound are showed in Fig. 2 and the time t_{100} to reach the maximum torque τ_{100} was estimated. As there was not reversion, all the compounds were vulcanized up to 90 min, in order to guarantee that the maximum degree of cure was reached. Samples were press cured in a mould of dimensions (12x12x0.1) cm^3 at 433 K.

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

$$v_{2m} = \frac{W_d/\rho}{\left[W_d/\rho + (W_s - W_d)/\rho_s\right]} \ .$$ (1)

where W_d is the weight of the sample after swelling and a further dried; W_s is the weight of the swollen sample, $\rho$is the density of the cured compound determined by the Archimedean method and ρ_s the density of the solvent (toluene, 0.8669 g/cm^3). The weight was determined using an analytical balance with a precision of 0.0001 g.Then, the fraction volume of the absorbed solvent in the sample was obtained through $v_{sol} = 1 - v_{2m}$.

The glass transition temperature T_g was determined by using a calorimeter *Q2000-TA Instruments* under a nitrogen atmosphere with a constant flux of 25 ml/min at a rate of 10 K/min.

For PALS measurements at room temperature, a fast-fast timing coincidence system was used as lifetime spectrometer with a resolution of 340 ps. Each spectrum at least 2x10^6 counts was collected. Lifetime spectra were decomposed into three components, using the *LT10* program [12]. The correlation between the o-Ps lifetime τ_{o-Ps} and the size of the free nanohole volume v_h (in spherical approximation) was obtained using the Tao – Eldrup model [12-16].
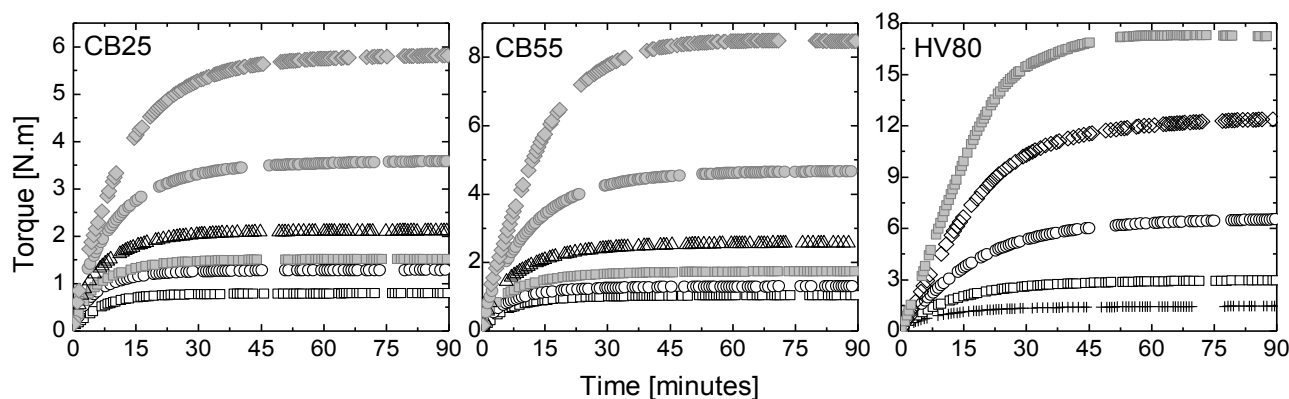

Figure 2: Torque curves at 433 K for the compounds analyzed. Parts of DCP per hundred of rubber: + 0.11, ☐0.27,◯0.54, ◇ 0.81,▨ 1.08,△ 1.62, ● 3.25 and ◆ 4.33.

Results and Discussion

The glass transition temperature value for each polybutadiene and their compounds were obtained from the calorimetric response as the onset point. In the case of pure CB25 a T_g value of 167.6 K was obtained, and for the cured compounds this parameter varies from 167.8 up to 170.2 K. The measured T_g in pure CB55 was 182.2 K and for their compounds varies from 183.1 up to 186.5 K. Finally, for pure HV80 $T_g = 239.3$ K and the values of the compounds fluctuate from 255.3 up to 271.1 K. Summarizing, T_g values depend on the type of BR: a higher content of *vinyl* units produce an increase of T_g. Moreover, a higher torque values are reached when the *vynil* units increase in BR (see fig. 2). This is due to a higher reactivity of the *vynil* units in comparison to *trans* and *cis* ones. When the compound is cured, the formed crosslinks restrict the chain movement which is reflected as an increase T_g, this increment is more pronounced in the HV80 isomer.

Fig. 3 shows the variation of the free nanohole volume as a function of the DCP content. As can be seen, v_h depends on the isomeric composition of the BR isomers. For pure polybutadienes (0 phr of DCP), v_h increases with the percentage of *vinyl* units. When the compounds are vulcanized, a decrease of v_h with the addition of DCP is observed. This behavior can be attributed to the reticulation between the polymer chains during vulcanization. Reticulation is higher when the DCP content increases, then a more closed polymer network is achieved and, therefore, v_h decreases. In the case of the compounds CB25 and CB55, for low amounts of DCP the free nanohole volume maintains almost constant; then, for DCP content higher than 2 phr a decrease in the v_h values is observed. For all HV80 compounds, the decrease of v_h for increasing amounts of DCP is more pronounced. Besides, in this BR isomer for the same range of high DCP content v_h values are systematically lower than those of the CB25 and CB55 samples.

To estimate the fractional free volume f_v we have used the simplest approach in which it is assumed that f_v is proportional to the density of nanoholes, which is related to the intensity $I_{o\text{-}Ps}$ associated with $\tau_{o\text{-}Ps}$, and the average free nanohole volume:

$$f_v \propto v_h \, I_{o\text{-}Ps}. \tag{2}$$

where $I_{o\text{-}Ps}$ is given in percentage.

As can be seen in Fig. 4, the fractional free volume of the CB25 and CB55 BR isomers is almost constant for DCP contents lower than 2 phr, for higher amounts of the curing agent in both kinds of isomers f_v diminished to halved approximately. In the case of the HV80, f_v shows a slight systematically decrease when the amount of DCP decreases from ~ 0.25 to ~ 1.10 phr. Furthermore, the range of variation of the fractional free volume is very similar for the three BR isomers studied.
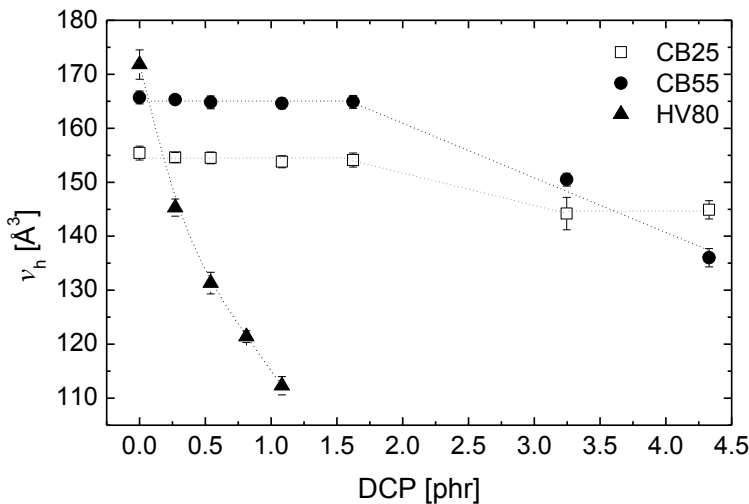

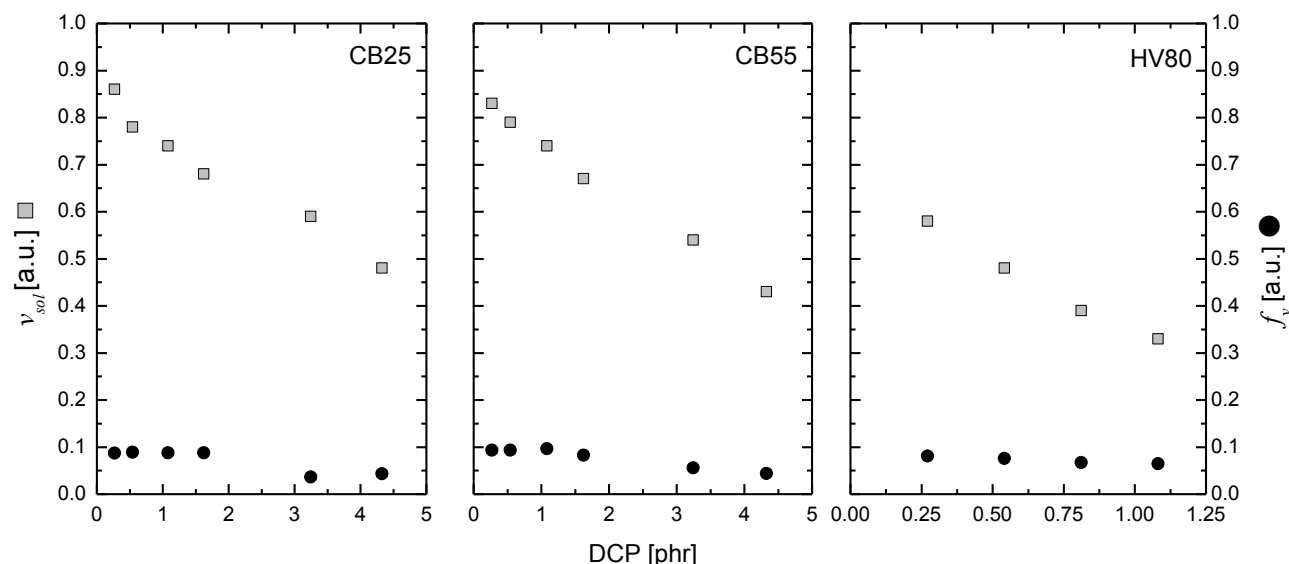Figure 3: Free nanohole volume as a function of the DCP content. Lines are only eye guides.

Figure 4: Fraction of the absorbed solvent and the free volume fraction as a function of the DCP content.

In Fig. 4 we have plotted together f_v (right axis) and v_{sol} (left axis) as function of the DCP content. It must be pointed out that during the swelling tests the network is subjected to a stretching force due to the penetration of the solvent up to an equilibrium state. Therefore, it is expected that the values of v_{sol} are higher than those of f_v, as can be observed in Fig. 4. In both cases v_{sol} and f_v diminish when the amount of DCP increases. As mentioned, a higher DCP content diminishes v_h (see Fig. 3) and therefore, it could be assumed that free nanohole volumes are the sites were the absorbed solvent is hosted (assuming that in the swelling test v_h is totally occupied by the solvent). In particular, the compounds of HV80 are the ones that absorb less solvent. This behavior is consistent with the lowest v_h values observed in Fig. 3 and with the high variation on the T_g in these compounds.

From the results reported in this work, we can conclude that DCP is a crosslinking agent with a higher reactivity for HV80 than for CB55 and CB25, which could be directly related to the amount of *vinyl* units in the BR chains.

Acknowledgements

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