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Material properties

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

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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.

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 crosslink 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 $\tau_{o\text{-}Ps}$ (in ns) and the size of the nanohole (in approximation to spherical nanoholes of radius R) by means of the following equation [22–25]:

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

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 $\tau_{o\text{-}Ps}$.

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 × 20 × 5) cm^3. The solvent was evaporated at room temperature (RT) until constant weight, achieving approximately (30 × 20 × 0.05) cm^3 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 τ_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 × 10 × 0.1) cm^3. 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 ν_{2m} was evaluated using the following equation:

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

where W_d is the weight of the sample after swelling and drying, W_s is the weight of the swollen sample, ρ_s the density of the solvent (0.8669 g/cm^3 for toluene) and ρ the compound density which was determined via the hydrostatic weighing method. All measurements were performed on an analytical balance with a resolution of ±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^3.

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

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

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,

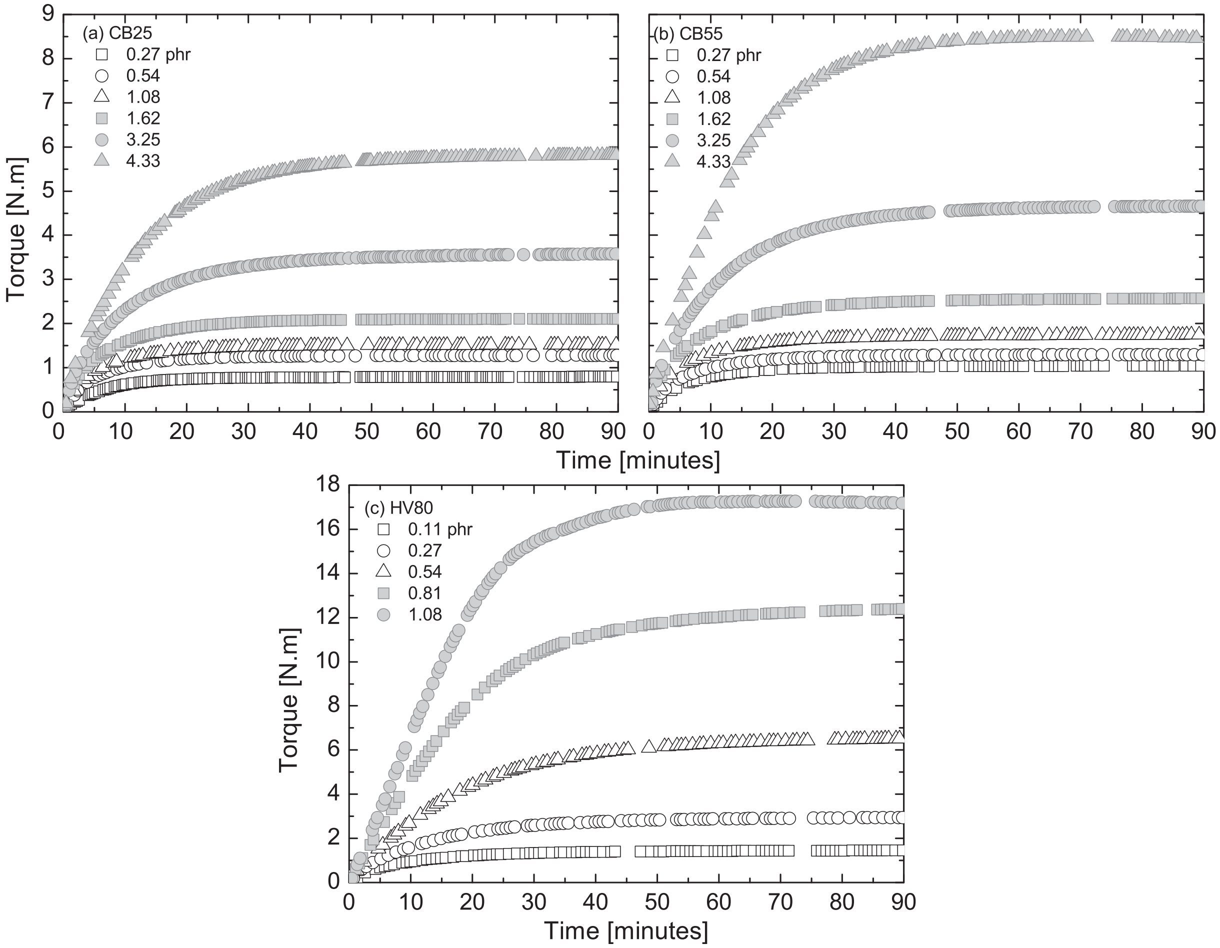

Fig. 1. Torque curves at 433 K for the compounds analyzed for different values of DCP per hundred of rubber: (a) CB25, (b) CB55, (c) HV80.

Table 1
Density of the studied compounds (±0.005 g/cm^3).

	ρ [g/cm^3]							
DCP [phr]	0.11	0.27	0.54	0.81	1.08	1.62	3.25	4.33
BR-CB25	–	0.906	0.908	–	0.912	0.916	0.931	0.943
BR-CB55	–	0.897	0.902	–	0.911	0.912	0.931	0.954
BR-HV80	0.912	0.925	0.935	0.957	0.962	–	–	–

20 μCi of ^{22}Na deposited on a thin Kapton foil (7.5 μm thick) was used. The positron source was placed between two identical samples. The spectra were recorded at RT with a counting rate of circa 80 counts per second; in each spectrum at least 2×10^6 counts were collected. PALS spectra were decomposed into three discrete lifetime components using the LT10 program [30].

4. Results and discussion

From the rheometric curves, the minimum τ_l and the maximum torque value τ_h were obtained and $\Delta\tau = \tau_h - \tau_l$ was calculated for each compound. This parameter is related to the elasticity of the material due to the network structure produced during the vulcanization process.

Delta torque values, the glass transition temperatures and the polymer fractions at the maximum degree of swelling were plotted as a function of the DCP content in Fig. 2(a), (*b*), and 2(c), respectively.

Two different effects can be observed when the results of Fig. 2 are analyzed. First, the increase of the DCP content in the compounds has the logical consequence of the higher crosslink density, reflected in an increase of both ν_{2m} and $\Delta\tau$ parameters. Also, the mobility of the chains is reduced with the consequent increase of T_g. The other subject to be considered is the role of the polymer structure. The increase of the *vinyl* content, following the sequence CB25 → CB55 → HV80, shows the most important difference at the glass transition temperature (see Fig. 2(b)). In the case of the compounds with the highest *vinyl* content (HV80), for a small variation in the DCP content, a notorious increase of the three parameters reported in Fig. 2 is observed. This behavior can be related to the high reactivity of the HV80 BR isomer [8].

As can be seen in Fig. 2(a) and (c), for high DCP amounts,ν_{2m} values for the medium *cis* content sample (CB55) are slightly higher than those measured for the high *cis* sample (CB25). The same behavior is observed when comparing the respective $\Delta\tau$. In fact, the higher torque of the CB55 compounds can also be related to the linear structure and the low degree of branching of the lithium grade BR, which improves some mechanical properties such as the maximum torque and the modulus [27,28] compared with those of the neodymium grade BR (CB25).

From Fig. 3, it can be concluded that, for each isomeric compound, a good linear correlation exists between T_g and $\Delta\tau$. The following relationship for the glass transition temperature of the cured samples is proposed:

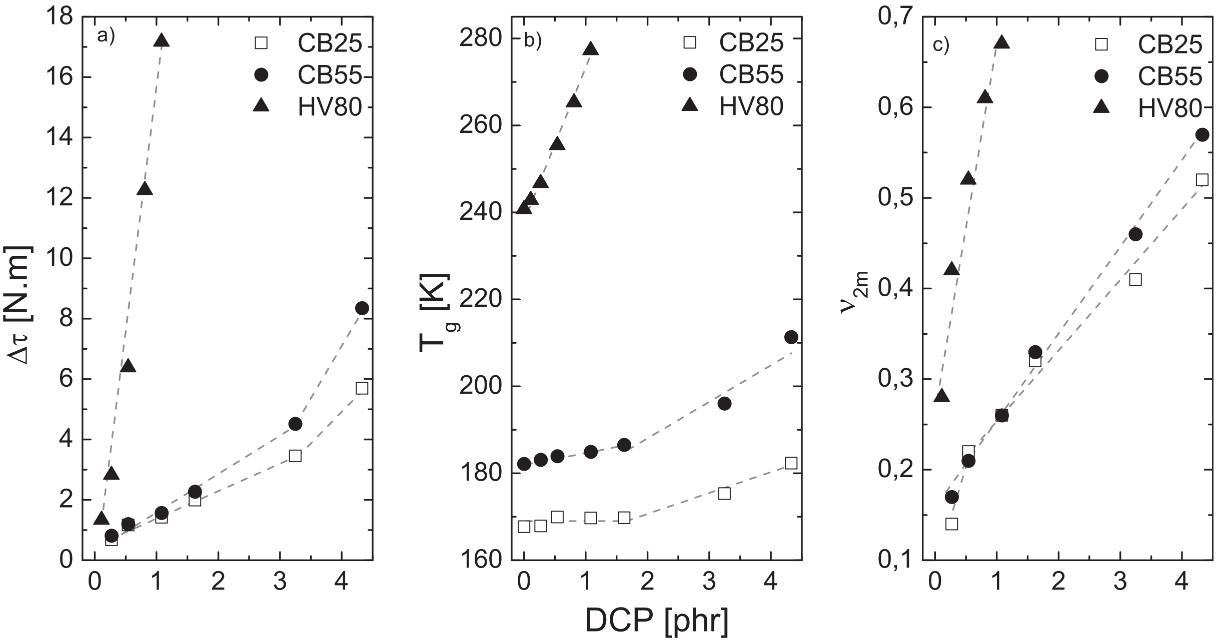

Fig. 2. (a) Delta torque, (b) glass transition temperature and (c) fraction of polymer at the maximum degree of swelling as a function of the dicumyl peroxide content (in parts per hundred of rubber). Lines are only eye guides.

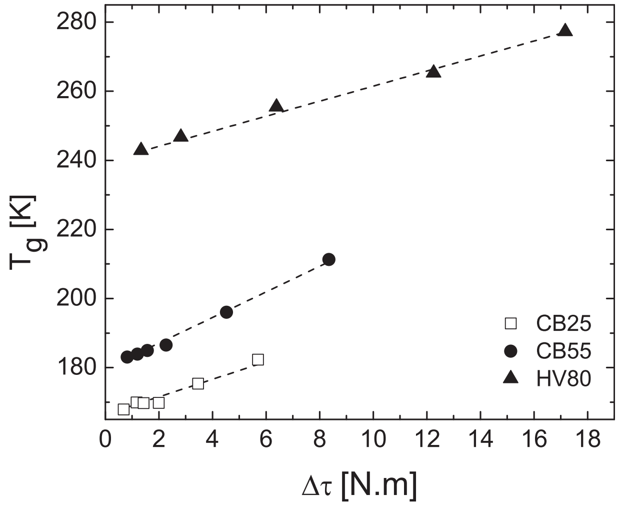

Fig. 3. Glass transition temperature as a function of the torque variation. A linear fit was made, see text.

$$T_g(K) = \alpha.\Delta\tau + T_g^o \tag{4}$$

where T_g^o corresponds to the value of T_g at $\Delta\tau = 0$ and α is a constant. In Table 2, the different values of T_g^o and α, obtained using Eq. (4) to fit the experimental data of Fig. 3 are reported. The different T_g values obtained from the DSC scans for uncured pure elastomers are also reported in the table. It is well-known that there are no crosslinks in uncured elastomers; therefore, the small differences observed when comparing the measured T_g with the parameter T_g^o obtained from the fitting procedure can be ascribed to the presence of entanglements in the studied elastomers.

Table 2
Values of the parameters α and T_g^o obtained using Eq. (4) to fit the experimental data reported in Fig. 3 for each BR isomer. T_g values are the experimental ones obtained from the DSC scans.

	α[K/N.m]	T_g^o[K]	T_g [K]
BR-CB25	2.9	165.6	167.7
BR-CB55	3.8	179.1	182.2
BR-HV80	2.1	240.7	240.7

In Fig. 4, for all the compounds analyzed, values of the glass transition temperature against the polymer fraction at the maximum degree of swelling are plotted. As can be seen, T_g values for the BR samples with low *vinyl* content (CB25 and CB55) do not substantially change until v_{2m} reaches approximately 0.3. For higher v_{2m} values, an almost linear increase of T_g is observed; this behavior is more pronounced in the case of the CB55 compounds. For HV80 compounds, there is a linear correlation between T_g and

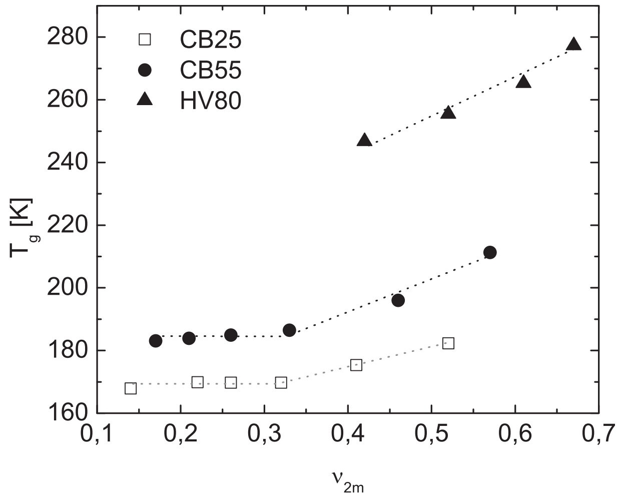

Fig. 4. Glass transition temperature as a function of polymer fraction at the maximum degree of swelling. Lines are only eye guides.

ν_{2m}. Changes in the slopes of the linear behavior described above can be interpreted considering that, once the structure of the polymer network is more closed, the mobility of the chains is restricted and more thermal energy is necessary to exceed the glass region of the polymer.

From DSC measurements, the variation in the specific heat Δc_p was calculated for the three BR isomers when the samples changed from the glassy to the rubbery state. The results are presented in Fig. 5(a). For cured BR compounds with medium *cis* content (CB55) and high *vinyl* content (HV80), Δc_p decreases as the DCP content increases. This behavior differs from that obtained for the CB25 samples; in this case it must be taken into account that, for CB25 compounds, a certain degree of crystallization for DCP contents below 1.6 phr was detected (see Fig. 5(b)). On the other hand, for DCP contents higher than 1.6 phr, the evolution of Δc_p *versus* DCP content is similar to the non-crystallized CB55 isomer. From the present results, it could be concluded that, for high cis BR compounds, the increment of crosslinking and the decrease of the degree of crystallization have a balanced effect on Δc_p.

In Fig. 6, the evolution of the free nanohole volume as a function of the amount of DCP in the studied compounds is shown. As can be seen, ν_h depends on the isomeric composition of the BR isomers. For the pure polybutadienes (i.e., without DCP), ν_h increases with the percent of vinyl units. When the compounds are vulcanized, the free nanohole volume is reduced as the curing agent produces a more closed polymer network. For the compounds CB25 and CB55, at low DCP content, ν_h values are almost constant, then a decrease of this parameter is observed for DCP contents higher than 1.5 phr. In the case of the HV80 compounds, ν_h values are systematically lower than those corresponding to CB25 and CB55 samples. Furthermore, an important decrease of this parameter is observed when the DCP content increases. This behavior indicates that the high amount of reactive *vinyl* units in the HV80 BR isomer increases the crosslink density, resulting in a tighter network structure.

In Fig. 7, a comparison of the respective evolutions of ν_h values and the volume fraction of the absorbed solvent as a function of the DCP content in the cured BR compounds is shown. During the swelling test, the network is subjected to a stretching force due to the penetration of the solvent until reaching an equilibrium state. As can be seen, both ν_{sol} and ν_h diminish with the increase of the DCP content. As can be observed in Figs. 6 and 7, a high DCP content diminishes the ν_h values; assuming that in the swelling test ν_h is totally occupied by the solvent, these nanoholes are the sites where the absorbed solvent is hosted. In particular, it can be observed that HV80 compounds absorb a lower amount of solvent; this result is consistent with the high T_g values measured in these compounds (see Fig. 2(b)).

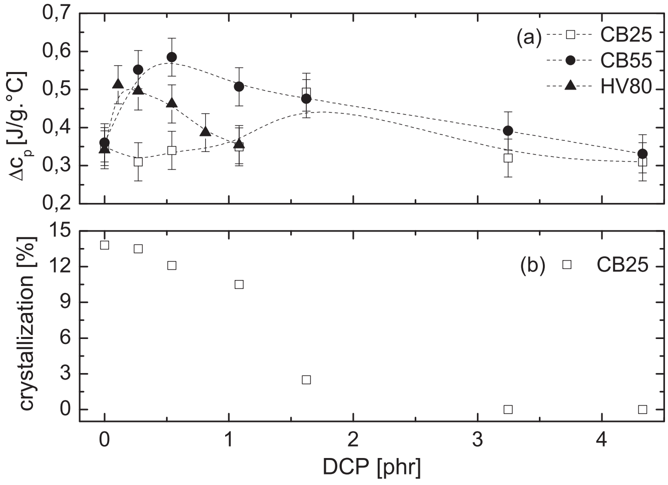

Fig. 5. (a) Variation in the specific heat through the glass transition as a function of the DCP content, (b) degree of crystallization as a function of the DCP content for the CB25 compound. Lines are only eye guides.

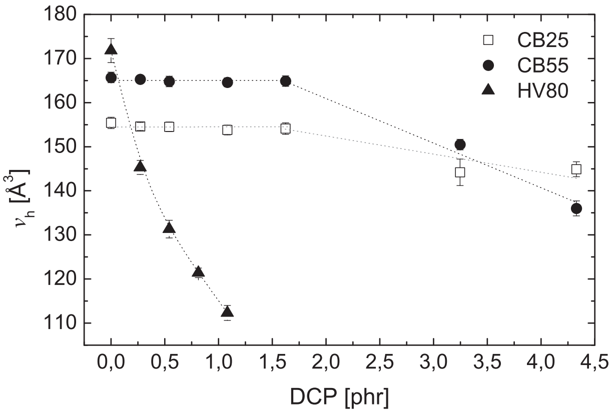

Fig. 6. Free nanohole volume as a function of the DCP content. Lines are only eye guides.

In a previous work, PALS measurements and swelling tests were performed to study properties of samples of CB25 and CB55 vulcanized at 433 K for different times and using a cure system based on sulfur and TBBS (n-t-butyl-2-benzothiazole sulfenamide) [9]. As a result, different crosslink levels were obtained depending on the curing time. To draw some conclusions, it may be illustrative to compare the reported results with those presented here. For this reason, in Fig. 8 the variation of the free nanohole volume as a function of the polymer fraction at the maximum degree of swelling for CB25, CB55 and HV80 BR isomers cured using the agent DCP are presented together with the values of the same parameters obtained for the samples CB25 and CB55 cured with sulfur/TBBS. Independently of the curing system used, the ν_h values obtained for the CB25 compounds are systematically lower than those corresponding to the CB55 compounds. This behavior makes it possible to conclude that, for ν_{2m}, with values between 0.1 and 0.25, the nanohole generated depends on the microstructure of the BR isomer and the cure system. Then, it can be concluded that linkages C—C formed in the peroxide vulcanization generate higher free nanohole volumes than those produced by the C-S$_x$-C linkages. Additional measurements on the CB25 and CB55 cured with the system sulfur/TBBS for ν_{2m} values higher than 0.25 would allow us to go deeper into this issue.

5. Conclusions

The present work addresses a study of the structural, physical and thermal properties of three polybutadiene isomers cured with dicumyl peroxide at 433 K. The results obtained can be summarized as follows:

1. The BR compound richer in *vinyl* configuration has the highest rheometric properties associated with the crosslink level.
2. The glass transition temperature increases with the *vinyl* concentration and the DCP content in the BR compounds. As a consequence, an empirical relationship between the torque variation and the glass transition temperature is proposed.
3. It was found that, in the case of the compounds with high *cis* content, the degree of crystallinity is reduced to zero when the amount of DCP is higher than approximately 2 phr. This

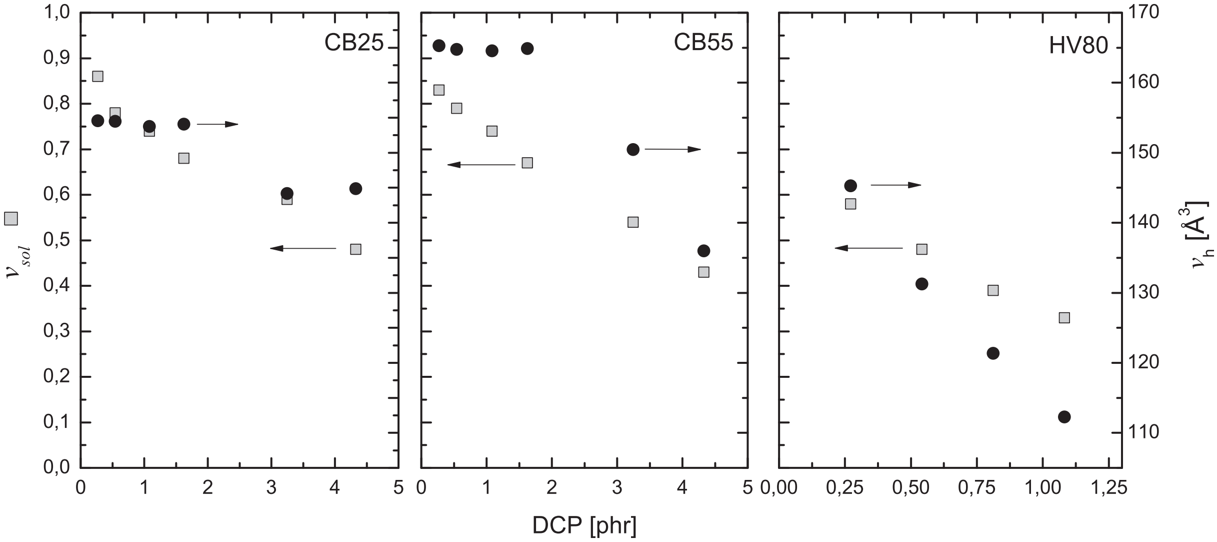

Fig. 7. Fraction of absorbed solvent and free nanohole volume as a function of the DCP content.

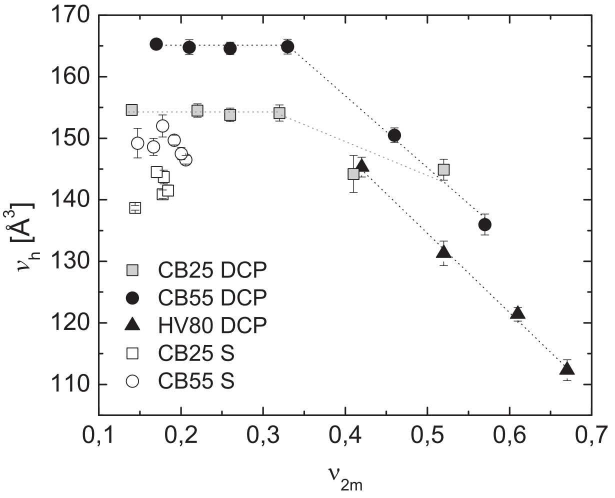

Fig. 8. Free nanohole volume versus polymer fraction at the maximum degree of swelling for two different vulcanization agents: fill symbol for dicumyl peroxide (DCP) and open symbol for sulfur (S). Lines are only eye guide.

behavior has a remarkable influence on the Δc_p value. The cured samples that present crystallization have lower Δc_p values.

4. In all the studied compounds, good correlation was observed between the free nanohole volume and the volume fraction of absorbed solvent in the samples. Independently of the BR isomer, ν_h decreases for high DCP contents (i.e., high crosslinking levels) in the formulation of the samples.
5. The effect of the cure system (i.e., DCP or sulfur/TBBS) on the free nanohole volume was analyzed for the samples with high and medium *cis* content. It was concluded that the presence of C—C bridges produced during the peroxide vulcanization generates a little more open network, which is reflected in higher ν_h values than those produced by the C-S$_x$-C bridges in the same BR isomers using S/TBBS as cure system.

Acknowledgments

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