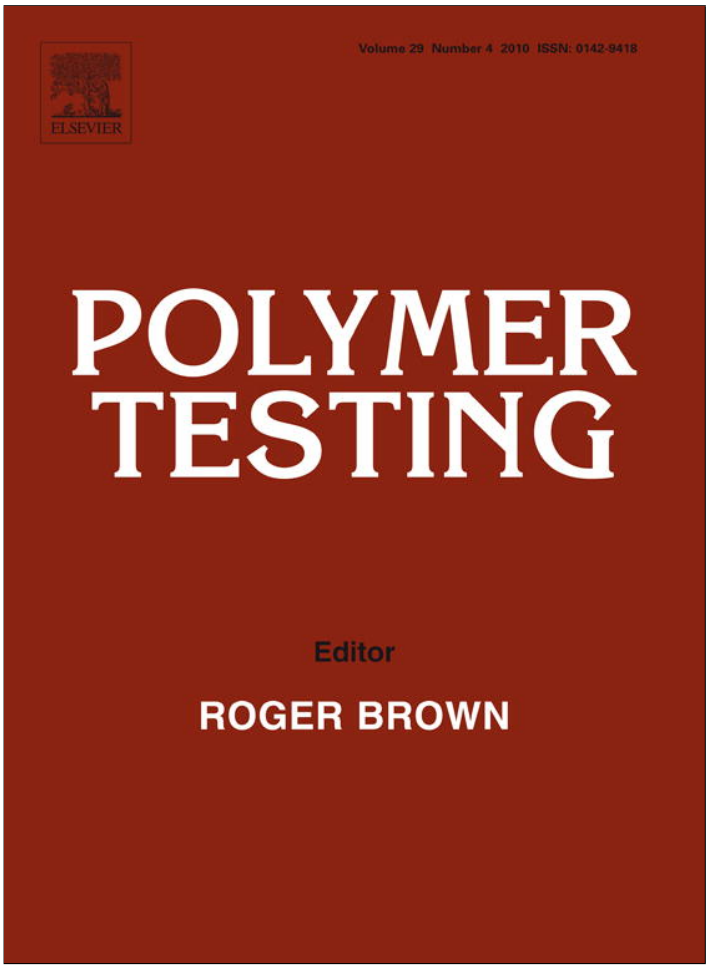
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Material Behaviour

Cure kinetics and swelling behaviour in polybutadiene rubber

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ABSTRACT

Two polybutadiene rubbers (BR) with different 1,4-*cis* content were used to prepare compounds with a cure system based on sulfur and TBBS (N-t-butyl-2-benzothiazole sulfenamide). Torque curves, measured with a moving die rheometer at a temperature of 433 K, were used to characterize the vulcanization process. Vulcanization kinetics of the two BR compounds was studied using the formalism proposed by Kamal and Sourour.
To vary the cure level, samples of each compound were vulcanized at 433 K at different times, according to the information obtained from the rheometer data.
From swelling data, the diffusion coefficient of toluene in BR was evaluated, taking into account the influence of polymer structure and crosslink density.

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1. Introduction

Due to its excellent mechanical properties, polybutadiene rubber, BR, is one of the most popular synthetic rubbers when combined to form blends. One of the most extended uses of BR is in the tread and sidewalls of tyres where it is blended with other rubbers such as natural rubber NR and styrene butadiene rubber SBR. Another important use of BR is as an impact modifier for polystyrene and acronitrile butadiene styrene resin (ABS).

Cured BR imparts excellent abrasion resistance and low rolling resistance in tyres due to its low glass transition temperature T_g. This low value of T_g is a consequence of the low vinyl content in the molecule. The vinyl content increases the T_g of the BR by creating a stiffer chain structure. Vinyl also tends to crosslink under high temperature conditions and, in consequence, polymers with high vinyl contents are less thermally stable than low-vinyl polymers. In the vinyl units, the double bonds are pendent to the main chain, producing special properties of high vinyl polymers.

Although vulcanization takes place by heat and pressure in the presence of sulfur, the process is relatively slow. A faster process is normally achieved by the addition of small amounts of chemicals known as accelerators. The quantity and kinds of crosslinks formed during vulcanization are determined by the relative amounts of accelerator and sulfur used in the compound formulation, and also by the time, temperature and pressure conditions in the cure process.

Smith and Koenig [1] studied, using solid-state C-13 NMR, the vulcanization chemistry at 423 K of high *cis*-1,4 BR formulated with the cure system TMTD (tetramethylthiuram disulfide) and sulfur. In that case, *cis* to *trans* isomerization was observed when the cure process advances. The research showed evidences of the formation of di and possible higher-rank sulfur linkages with a slower network accumulation of monosulfidic crosslink structure. It was also concluded that the network possesses a significant portion of mechanically ineffective crosslinks as vicinal and cyclic structures. An early work of Bishop also showed the sulfur-induced *cis–trans* isomerization of polybutadiene [2].

Crosslinking generally restricts the degree of swelling in polymers. The influence of crosslink type and crosslink density on swelling in styrene butadiene rubber was analyzed in

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Table 1
Microstructure and density (ρ_p) of the polybutadiene 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]
BR (Buna CB-25)	97	2	1	130,000	2.6	15	0.91
BR (Buna CB-55)	38	51	11	125,000	1.3	<5	0.91

several research works [3–5]. George et al. [6,7] studied the molecular transport of aromatic hydrocarbons through crosslinked SBR using swelling techniques. The density and types of crosslinks formed during vulcanization have a strong effect on the diffusion coefficient of the solvent in the cured rubber.

The present work is a continuation of a previous one where the uniaxial stress strain behaviour and the swelling of BR in toluene were studied [8]. In this paper, by means of rheometric analysis, the cure reaction of two compounds of high and medium *cis* BR prepared with the systems TBBS (n-t-butyl-2-benzothiazole sulfenamide)/sulfur was evaluated using the model proposed by Kamal and Sourour [9] and the kinetic parameters were obtained when cured at 433 K. The swelling behaviour in toluene of the cured compounds was also studied. The diffusion kinetics of the solvent in the compounds was obtained and the influence of the structure on the diffusion coefficient of the solvent was evaluated at room temperature.

2. Experimental

The rubber compounds used in this work were prepared with two types of commercial polybutadienes provided by Lanxess: Buna CB-55 NF and Buna CB-25. The differences in the microstructure of these isomers are summarized in Table 1 and the molecular weights, polydispersity, degree of branching and density of the polymers, provided by the supplier, are also included. Buna CB 25 is produced by neodymium catalysis and Buna CB-55 is lithium grade BR.

The samples were prepared with the compound formulations indicated in Table 2. More details are given in Ref. [8]. These blends were characterized at 433 K by means of torque curves obtained with an Alpha MDR 2000 rheometer that are plotted in Fig. 1a and b.

Samples in the form of square sheets with sides of 150 mm and a thickness of 2 mm were press cured in a mould at 433 K. Several cure times were selected to prepare the samples and the values are given in Table 3. The samples were cooled rapidly in ice and water at the end of the curing cycle. A cure level of $\theta = 1$ implies that all the elastically active crosslinks were formed in the compound.

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

	Sample 1	Sample 2
BR (97% *cis*)	100	–
BR (38% *cis*)	–	100
Zinc oxide	5	
Stearic acid	2	
Antioxidant	1.2	
Accelerator (TBBS)	1.0	
Sulfur (S)	1.5	

For both compounds, two samples in an overcured situation were prepared (Table 3).

The density, ρ, of each cured compound was measured by the Archimidean method and the values are included in Table 3.

In a previous work, we measured and analyzed the crosslink density, μ_{cs}, present in each sample by means of swelling in toluene [8]. The values obtained are also given in Table 3. For this paper, the crosslink density of the overcured samples was also evaluated using the swelling technique mentioned in Ref. [8]. The crosslink density in a 4-functional network is defined by [10]

$$\mu_{cs} = \frac{\rho}{2}\left(\frac{1}{M_{cs}} - \frac{1}{M_n}\right) \quad (1)$$

where M_n is the number molecular weight. M_{cs} is the molecular weight of the network chain between crosslinks,

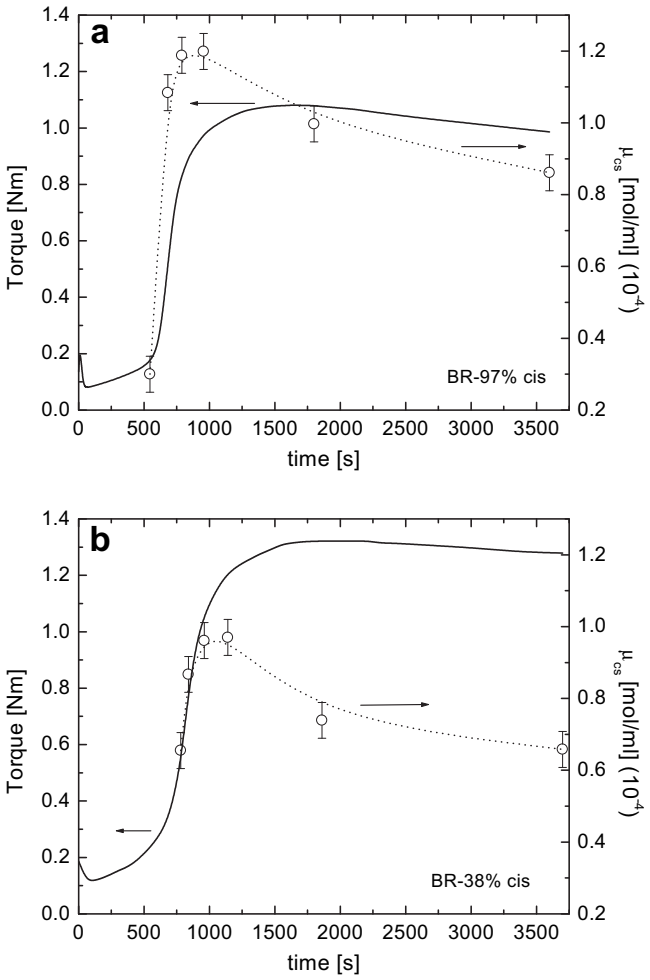


Fig. 1. Curves of torque at 433 K and crosslink density as a function of the cure time for the BR compounds with a) 97% 1,4-*cis* content in the molecular structure. b) 38% 1,4-*cis* content in the molecular structure.

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Table 3
Cure times, cure levels θ, densities of the cure samples ρ, volume fraction of polymer at the equilibrium (maximum) degree of swelling v_r and crosslink densities μ_{cs}, for the both BR compounds.

Sample	Cure time [s]	θ	ρ [g/cm^3]	v_r [8]	μ_{cs} (10^{-4}) [mol/ml] [8]
1 (97% *cis*)	555	0.10	0.941	0.0749	0.300
	690	0.50	0.941	0.1443	1.084
	780	0.75	0.943	0.1776	1.188
	960	0.90	0.942	0.1843	1.199
	1800	1.00	0.944	0.1791	0.977
	3600	Overcured	0.944	0.1705[a]	0.861[a]
2 (38% *cis*)	775	0.30	0.932	0.1473	0.655
	825	0.50	0.933	0.1667	0.867
	950	0.75	0.938	0.2060	0.961
	1130	0.90	0.939	0.2004	0.970
	1850	1.00	0.939	0.1918	0.739
	3700	Overcured	0.939	0.1778[a]	0.658[a]

[a] Measured in this research.

which is given by the Flory–Rehner relationship for a 4-functional network [11,12]

$$M_{cs} = -\frac{0.5\rho V_1\left(v_r^{1/3} - 0.5v_r\right)}{\ln(1-v_r) + \chi v_r^2 + v_r} \quad (2)$$

where v_r is the volume fraction of polymer at the equilibrium (maximum) degree of swelling and V_1 is the molar volume of solvent; χ is an interaction parameter between the polymer and the swelling agent known as the Flory–Huggins interaction parameter.

In order to calculate M_{cs} for the overcured samples, v_r was evaluated using

$$v_r = \frac{(W_d - W_f)/\rho}{((W_d - W_f)/\rho) + ((W_s - W_d)/\rho_s)} \quad (3)$$

where W_d is the weight of the sample after swelling and drying, W_f, the weight of the non extractable filler in the sample, W_s, the weight of the swollen sample and ρ_s the density of the solvent (0.8669 g/cm^3 for toluene). The ISO 247:2006 method was used to evaluate W_f. Then $v_r = 0.1700$ and 0.1778 were obtained for the overcured samples of high *cis* and medium *cis* BR respectively.

The parameter χ for the system BR/toluene is evaluated considering the relationships $\chi = 0.19 + 1.13v_r$ for high *cis* BR, and $\chi = 0.22 + 1.16v_r$ for medium *cis* BR [8]. Using this information and Eqs. (1) and (2), the crosslink densities for the two overcured samples were calculated and are included in Table 3.

Swelling tests can also be used to determine the amount of moles of solvent uptake by 100 g of crosslinked BR samples, at a given time t of the test, Q_t, by means of [6]

$$Q_t = \frac{(m_{ss}/M_{solv})}{m_{pol}} \times 100 \quad (4)$$

where m_{ss} is the mass of solvent absorbed at time t, m_{pol} is the mass of the polymer and M_{solv} is the molar mass of the solvent.

Each sample was completely immersed in pure toluene ($M_{solv} = 92.1$ g/mol), in a sealed glass bottle at room temperature. The equilibrium swelling normally takes more than 48 h. The samples were removing from the glass bottles at several times, their surfaces wiped, and weighed with a precision of $\pm 10^{-4}$ g. Then, using Eq. (4) Q_t was obtained at each analyzed time for each sample of both compounds.

3. Results and discussion

An indirect approach for the evaluation of the cure level of rubber compounds is based on rheometer torque curves. The value of maximum torque of the rheometer curves is a parameter sensitive to the crosslink density. The retractive force to resist a deformation is proportional to the number of network-supporting polymer chains per unit of elastomer and the higher number of junctures increases the number of supporting chains. Fig. 1a and b show the rheometer torque curves together with the crosslink density measured in samples cured at 433 K at several cure times. Comparing both compounds at the same cure time, the crosslink density is lower in the case of the polybutadiene with medium *cis* content. However, this compound has the highest values of torque and this fact is related not only to the crosslink density but also to the

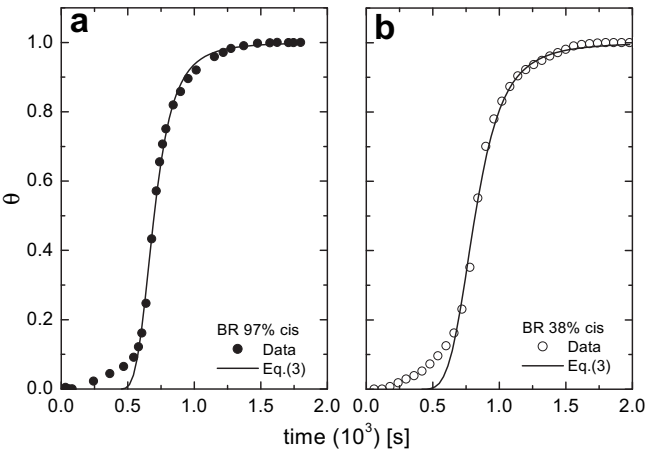


Fig. 2. Comparison between the normalized curves of torque (experimental data) and Eq. (6) for BR 97% 1,4-*cis* (a) and BR 38% 1,4-*cis* (b).

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Table 4
Kinetic parameters of the rheometer curves for Sample 1 and Sample 2, according to Eq. (6). The regression coefficient R^2 is included.

Sample	n	k_r [s^{-1}]	t_o [s]	R^2
1	3.5 ± 0.6	0.0038 ± 0.0007	436 ± 46	0.999
2	3.9 ± 0.9	0.0024 ± 0.0006	400 ± 98	0.995

linear structure and the low degree of branching of the lithium grade BR that improves some mechanical properties. The incidence of the content of *cis* structure in the network structure of the polybutadiene was also detected by Short et al. [13]. In that paper, in order to obtain the same crosslink density the sulfur content was increased in the polymer with medium *cis* structure,

The degree of cure is estimated using the relationship

$$\theta = \frac{\tau_t - \tau_l}{\tau_h - \tau_l} \tag{5}$$

where τ_l and τ_h are the minimum and maximum torque. τ_t is the torque value at time t.

The curves of θ as a function of the time of cure, calculated from the data of Fig. 1, are shown in Fig. 2 for the two compounds analyzed.

In previous works [14–16] rheometer data of *cis* BR and SBR compounds using the TBBS/sulfur cure system were analyzed, considering a kinetic relationship for the degree of cure for isothermal curing, as in [9]

$$\theta = \frac{\{k_r(t - t_o)\}^n}{1 + \{k_r(t - t_o)\}^n} \tag{6}$$

where k_r is the rate constant for the vulcanization, n is the order of the kinetic equation, t_o is the induction time and t is the reaction time. Fig. 2 shows the fitting of Eq. (6) to the curves of θ as a function of time, with the parameters given in Table 4. The adjustment of the model to the experimental data is quite good, especially for cure times higher than t_{10}.

As it can be observed in Table 4, the order of the kinetic equation n is higher in the compound with medium *cis* content in the structure. The constant rate k_r is higher in the

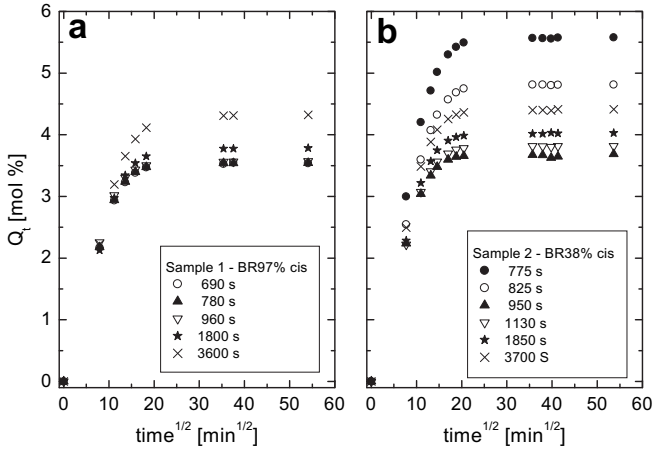


Fig. 3. a) Solvent uptake of sample 1 (BR 97% 1,4-*cis*, vulcanized at 433 K) at different times of cure. b) Solvent uptake of sample 2 (BR 38% 1,4-*cis*, vulcanized at 433 K) at different times of cure.

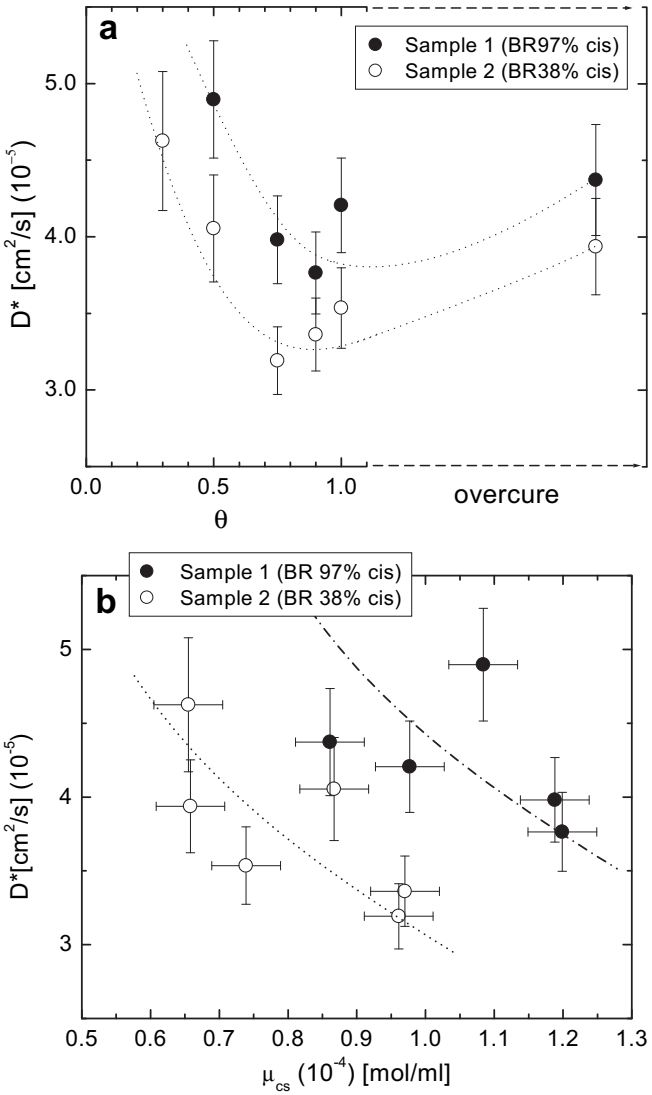


Fig. 4. Dependence of the intrinsic diffusion coefficient, D^*, of vulcanized BR for samples 97% 1,4-*cis* and 38% 1,4-*cis* contents a) with the level of cure θ. b) with the crosslink density μ_{cs}.

case of the polybutadiene with 97% *cis* in the microstructure. This fact implies a higher reactivity in this polymer structure, which is also confirmed by the higher crosslink density obtained. There is information in the literature that the rate of addition of sulfur to rubber increases with increasing the content of the 1,4-structure in the polybutadiene molecule [17].

The plots in Fig. 3 describe the sorption behaviour of both kinds of cured polybutadienes, where the influence of the cure times of the samples is shown. In all cases, the shape of the curves is close to those observed by George et al. [6,7] in similar tests of other cured elastomers. Kang also showed that sorption experiments of n-hexane in uncured *cis*-polybutadiene follow Fick's second law [18].

For Fickian transport, reduced sorption curves are generally independent of the sample thickness. If within the range of concentration values of interest the diffusivity may be considered as independent of concentration, then the diffusivity of the solvent in the polymer can be calculated from the following relationship [19,20]

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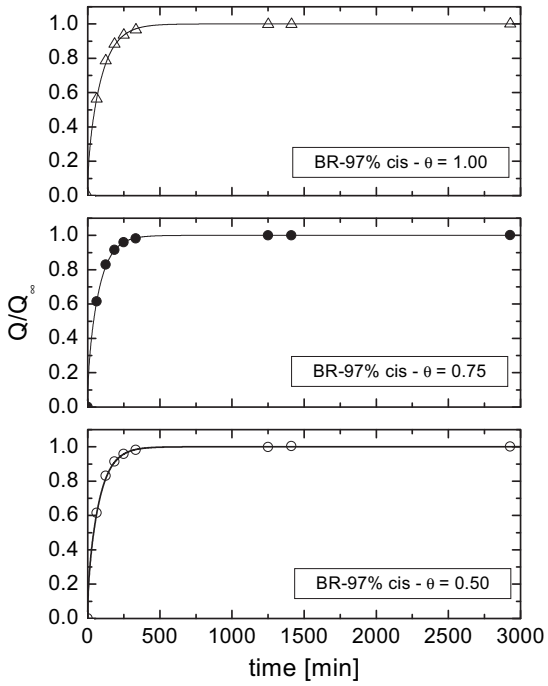


Fig. 5. Comparison between experimental and theoretical (Eq. (7)) sorption curves for sample 1 (BR 97% 1,4-*cis*, vulcanized at 433 K). Results are shown for samples with different cure levels.

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2}\sum_{j=0}^{j=\infty}\frac{1}{(2j+1)^2}\exp\left[-D(2j+1)^2\pi^2 t/h^2\right] \qquad (7)$$

where Q_t and Q_∞ are the values of solvent uptake (per 100 g of polymer) of crosslinked BR samples at time t and at equilibrium respectively, D is diffusion coefficient and h is the initial sample thickness. At short times, Eq. (7) can be approximated by

$$\frac{Q_t}{Q_\infty} = \frac{8}{\pi^{1/2}}\left(\frac{Dt}{h^2}\right)^{1/2} \qquad (8)$$

From Eq. (8), the value of the diffusion coefficient (at room temperature) was evaluated for each compound as a function of the cure level, using the slopes, at short test times, of the curves plotted in Fig. 3.

During the sorption experiments, significant swelling of the samples was observed, and then a correction to the diffusion coefficient under the swollen condition is necessary. This was done by calculating the intrinsic diffusion coefficient, D^*, from the volume fraction of the swollen rubber by using the following relation [7,21]

$$D^* = D/v_r^{7/3} \qquad (9)$$

Fig. 4a and b, show the dependence of D^* on the cure level and the crosslink density for the two compounds. From these results, it is evident that the D^* has a minimum value in both compounds close to the optimum level of cure and higher values in the under-cured and overcured samples.

When analyzing the results regarding the crosslink density, D^* decreases with higher crosslink densities in both polybutadiene rubbers studied in this research (Fig. 4b). This behaviour is in line with that postulated in literature [22].

Comparing both samples, the one that has higher *cis* content has a higher value of the intrinsic diffusion coefficient at the same crosslink density (Fig. 4b).

The normalized sorption curves for each polymer cured at different cure times are given in Figs. 5 and 6. These data were fitted to Eq. (7) considering the diffusion coefficient obtained previously. A fairly good agreement between experimental and theoretical diffusion profiles can be observed. This indicates that for both cured polybutadienes, solvent transport at room temperature is in accordance with the Fickian model.

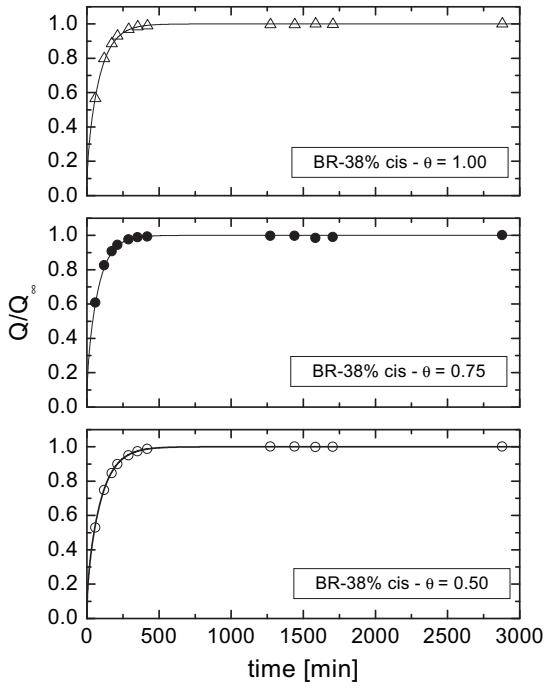


Fig. 6. Comparison between experimental and theoretical (Eq. (7)) sorption curves for sample 2 (BR 38% 1,4-*cis*, vulcanized at 433 K). Results are shown for samples with different cure levels.

4. Conclusions

The cure kinetics, at 433 K, of compounds of polybutadiene rubber with different 1,4-*cis* content, using a formulation based on sulfur and TBBS, was studied by means of rheometric tests. The curves of torque *vs* time can be fitted using the Kamal and Sourour relationship and it was established that the reaction order n is slightly higher for the compound with lower *cis* content. On the other hand, the rate of cure, k_r, is higher for the sample with higher *cis* content.

Although the measured crosslink density is slightly higher in cured samples with higher *cis* content in its molecular structure, the maximum torque achieved in this sample is lower than the sample with 38% *cis* content. This could be related to the lower degree of branching of this sample.

The transport process of toluene molecules in both cured polybutadienes rubbers studied in this work seems

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to follow the classical behaviour predicted by Fick's model with a constant diffusion coefficient. The intrinsic diffusion coefficient of toluene in cured BR decreases when the crosslink density increases.

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