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Anisotropic swelling of thin EPDM rubber discs by absorption of toluene

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Abstract

Anisotropic swelling of thin EPDM discs is observed when they are in contact with toluene resulting from the liquid absorption. The process is controlled by transient diffusion, with a concentration-dependent diffusivity and a finite coefficient of convective transfer at the liquid–rubber interface. Moreover a rather high swelling takes place during the stage of absorption, leading to an increase in dimensions of the flat discs. The increase in the thickness of the discs is around 1.17–1.18 times larger than that in the radius, exhibiting an anisotropic behaviour. The flat discs have been cured by pressing them in the heated slabs of a press, leading to a kind of orientation of the molecules. The state of cure of around 96% has been determined either by calorimetry in scanning mode or by a moving die rheometer under isothermal conditions at three temperatures within the 170–190 °C range. Various percent peroxide as a vulcanising agent have been used, e.g. 2, 10, and 20%. While the diffusivity is about similar for the three samples, the extent of liquid absorbed decreases with the percent peroxide. A numerical model based on finite differences taking into account all these facts has been built in order to describe the process. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ethylene–propylene diene monomer rubbers; Anisotropic swelling; Discs samples

1. Introduction

It is well known that when a rubber comes in contact with a liquid hydrocarbon, generally a mass transfer takes place. The liquid enters the rubbery state material by following a process controlled by Fickian diffusion [1,2]. Depending on the nature of the polymer, the extent of the liquid absorbed could be so large that a change in dimensions of the sample is observed. This fact especially appears in the case of rubbers and other elastomeric materials for which the amount of liquid absorbed might represent up to 100% of the initial volume of the polymer [3,4]. Generally, the stage of absorption is determined from the uptake of liquid measured by a gravimetric method when only one liquid is absorbed. Various examples are shown for ethylene–propylene diene monomer (EPDM) rubber [5], styrene–butadiene rubber (SBR) [6] or natural rubber (NR) [7]. Sometimes the process of absorption has been studied when the material was under constraint condition of elongation [8]. A more complex technique such as NMR was used to investigate the distribution of each liquid absorbed by polymers from mixtures of miscible liquids [9].

The process of absorption has been deeply studied through ethylene–vinyl acetate (EVA) beads spherical in shape by considering not only the diffusion through the polymer and a finite coefficient of convective transfer at the liquid–polymer interface, but also the subsequent swelling and a concentration-dependent diffusivity [10]. Moreover, a special method has been investigated in order to determine the various parameters of diffusion in this rather complex case, with four unknowns: the coefficient of mass transfer at the interface, the extent of swelling and two parameters necessary for the concentration-dependent diffusivity [11].

In the case of rubbers, an important factor is the state of cure. The uncured material is heated in the mould up to a temperature at which the cure reaction starts. The process of cure should be considered by taking into account not only the heat transfer by conduction through the material but also the heat generated by the cure reaction [12]. A literature survey shows that various techniques have been developed and tested for studying the cure of rubbers [13,14]. Some of these methods take into account the heat transferred through the rubber. One investigation was able to determine the degree of cure by swelling in toluene [15]. Other methods were developed in this way, by introducing a reference

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Nomenclature

α	coefficient in Eq. (14) expressing the concentration-dependency of the diffusivity
C	heat capacity of the rubber in Eqs. (1) and (5)
$C_{s,t}$	liquid concentration on the rubber surface at time t
C_{eq}	liquid concentration at equilibrium
D	diffusivity of the liquid through the rubber
D_0	value of the diffusivity when the concentration of the liquid is zero
Δt	increment of time for calculation
Δr, Δx	increments of space for calculation, radial, longitudinal
E	activation energy of the cure reaction
h	coefficient of convective transfer at the rubber surface
λ	thermal conductivity of the rubber
k_0	pre-exponential factor for the rate of the cure reaction in Eq. (2)
M	dimensionless number expressed by Eq. (5)
Q	heat generated by the cure reaction
r	radial abscissa
ρ	density of the rubber
S	function defined by Eq. (8) used for calculating the state of cure of the rubber
T	temperature (K)
x	longitudinal abscissa
Y_t	heat evolved from the cure reaction at time t as a fraction of the total heat evolved

temperature of 149 °C and a temperature coefficient assuming that the rate of reaction increases by a factor of 1.85 per 10 K [16] and in another by a factor of 2 for each 10 K increase in temperature [17]. More recent methods for determining the state of cure of the rubber are using two various techniques: the one with the moving die rheometer MDR introduced in 1985 [18] by following the viscosity of the rubber under isothermal conditions [19] or in scanning mode [20]. With the MDR technique, the state of cure is evaluated at time t at the measurement temperature as the change in torque at this time as a fraction of the total torque change, by assuming that the change in torque with time follows a first-order kinetics [21]. The effect of temperature on the rate of cure, expressed in terms of the activation energy, is evaluated by making three measurements at various temperatures within a narrow window for the temperature range over which data can be obtained [22]. With the calorimetry technique run in scanning mode, not only the kinetics parameters of the cure reaction are obtained but also the enthalpy of the overall reaction [23,24].

The first purpose in this paper in the case of EPDM rubbers with a given value of the state of cure obtained with various values of epoxide as vulcanising agent, is to evaluate the parameters of diffusion of toluene, e.g. the extent of swelling, the coefficient of convective transfer at the surface, the diffusivity and its dependence with the liquid concentration. A numerical treatment is undertaken in order to build a model able to calculate the kinetics of absorption in the case of a flat cylinder by considering the radial and longitudinal diffusion.

The other objective of this study is to show that the thin discs behave in an anisotropic way in the case of liquid absorption. Comparison is thus made between the kinetics of the change in dimensions, e.g. the radius and the thickness during the process of absorption and the kinetics of swelling in volume determined from the values of the weight uptake of liquid measured at intervals. A change in the numerical model is made by considering the anisotropic behaviour of the EPDM discs with respect to the swelling. Thus it can enable one to calculate the kinetics of the change in dimension for the thickness and the diameter of the discs.

2. Theoretical

The following two parts are considered:

(i) The calculation of the state of cure developed through the thickness of the rubber discs heated in the mould.
(ii) The kinetics of absorption of liquid controlled by diffusion and the kinetics of swelling in various directions: radial and longitudinal.

2.1. Process of heating and cure of the rubber discs in the mould

Some assumptions are made in order to make the process clear:

(i) The disc and mould are heated by unidirectional conduction through the thickness.
(ii) Good contact is obtained at the rubber–mould interface.
(iii) The internal heat generated by the overall cure reaction is described by a first-order reaction with respect to the vulcanising agent; the rate is expressed in terms of temperature by an Arrhenius equation.
(iv) The thermal properties do not vary with the temperature and the state of cure.

2.2. Mathematical treatment

The equation of unidirectional heat conduction is

$$\rho C \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \rho \frac{\partial Q}{\partial t} \qquad (1)$$

where the contribution of the exothermic cure reaction is on the right-hand side.

The rate at which heat is evolved from the cure reaction can be expressed by [12]

$$\frac{dY}{dt} = k_0(1 - Y)\exp\left(-\frac{E}{RT}\right) \tag{2}$$

with

$$Y = \frac{Q_t}{Q_\infty} \tag{3}$$

2.3. Numerical treatment

No analytical solution exists for the problem, and it is resolved by a numerical treatment [13]. The rubber disc is divided into slices of constant thickness Δx, each slice being defined by an integer n, while the time is divided into increments of time Δt.

The principle is as follows: the new temperature T_{N_n} at position n after elapse of time Δt is expressed in terms of the previous temperatures at the same and adjacent places

$$T_{N_n} = \frac{1}{M}[T_{n-1} + (M - 2)T_n + T_{n+1}] + \frac{\Delta Q}{C} \tag{4}$$

with the dimensionless number M

$$M = \frac{(\Delta x)^2}{\Delta t}\frac{\rho C}{\lambda} \tag{5}$$

The state of cure is expressed by:

$$\mathrm{SOC} = 100Y \tag{6}$$

while Y is obtained by integrating Eq. (2)

$$Y_t = 1 - \exp(-S_t) \tag{7}$$

where the function S is defined by

$$S_t = k_0\int_0^t \exp\left(-\frac{E}{RT_t}\right)dt \tag{8}$$

with the recurrent relationship

$$S_{t+\Delta t} = S_t + k_0\Delta t\exp\left(-\frac{E}{RT_t}\right) \tag{9}$$

and

$$S_0 = 0 \tag{10}$$

2.4. Process of absorption of toluene by the rubber discs

The following assumptions are made:

(i) The process of absorption of liquid is controlled by transient diffusion through the rubber and convection at the liquid–rubber interface.
(ii) The volume of the disc at any time is equal to the sum of the volumes of the rubber and of the liquid.
(iii) The transfer of liquid is both radial and longitudinal.

2.5. Mathematical treatment

The basic equation of radial and longitudinal diffusion is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial C}{\partial r}\right) \tag{11}$$

with at each radial and longitudinal interface the boundary conditions:

$$-D\frac{\partial C}{\partial x} = h(C_{\mathrm{eq}} - C_{\mathrm{s},t}) \tag{12}$$

$$-D\frac{\partial C}{\partial r} = h(C_{\mathrm{eq}} - C_{\mathrm{s},t}) \tag{13}$$

The diffusivity is expressed in terms of the concentration of liquid by

$$D = D_0\exp\left(\alpha\frac{C}{C_{\mathrm{eq}}}\right) \tag{14}$$

where C is the local concentration of liquid at time t and C_{eq} is the liquid concentration at equilibrium.

2.6. Numerical treatment

There is no analytical solution for the problem because of the concentration-dependent diffusivity and the change in dimensions. A numerical model should be built by taking into account the additivity of the volumes of the rubber and the liquid, and all the other facts, e.g. the radial and longitudinal diffusion through the rubber disc with a concentration-dependent diffusivity, a finite coefficient of convective transfer at the surface, and the change in dimensions. An implicit Crank–Nicolson method is used with the increment of time Δt and increment of volume ΔV resulting from the absorption of liquid as well as the increments of thickness and radius Δx and Δr.

The volume of the annulus used for calculation, when free from liquid is:

$$2\pi n(\Delta r_0)^2\Delta x_0 \tag{15}$$

and at time t the increments are Δr_t and Δx_t, expanding with the volume of liquid absorbed.

The ratio of these volumes gives:

$$\left(\frac{\Delta r_t}{\Delta r_0}\right)^2\frac{\Delta x_t}{\Delta x_0} \tag{16}$$

Two ways are followed for the change in dimensions of the rubber discs:

(i) A classical one, assuming that the change in the dimensions of the radius and thickness are similar, meaning that the rubber disc behaves in an isotropic way.
(ii) A new one, taking into account the anisotropy of the rubber disc with respect to the swelling. Thus the change in dimensions of the radius and thickness is different at any time.

In both cases, there is no fixed frame of reference, e.g. the

Table 1
Main components of the three EPDM samples (wt%)

EPDM	Carbon black	Plasticizer	Chemicals	Peroxide
33	49	13	3	2
30	46	11	3	10
27	42	9	2	20

disc free from liquid [1]. The dimensions of the disc expand with time resulting from the absorption of liquid. This is a moving boundary problem arising from the absorption of liquid, with a moving grid and increments expanding with the local concentration of the liquid absorbed.

3. Experimental

3.1. Materials used for the cure and liquid absorption

EPDM compounds containing various percentages of peroxide are used (Hutchinson). Their main composition is shown in Table 1. The peroxide is the Perkadox 14-40 or bis(*tert*-butyl-peroxy-isopropopyl)benzene.

3.2. Cure conditions

A Monsanto 2000 E Moving Die Rheometer (MDR Alpha Technologie) is used under isothermal conditions within the 170–190 °C range.

A calorimeter C80 (SETARAM) is run in scanning mode with a heating rate of 0.2 K min^{-1}.

The heat flux is recorded as a function of temperature (or time). Samples around 6 g are placed into a cylindrical holder with an internal diameter of 1.7 cm.

Discs with a thickness of 0.2 cm and a diameter of 6 cm are cured in the slabs of a heated press kept at 187 °C.

3.3. Measurements of absorption

The previously cured rubber discs are immersed in toluene with a slight stirring. During the stage of absorption, the discs are weighed at intervals and the dimensions measured at given places in order to follow the kinetics of absorption and the kinetics of the change of dimensions as the thickness and diameter (Table 2).

Table 2
Parameters for the cure

k_0	$3 \times 10^9\ \text{s}^{-1}$
E	101 kJ mol^{-1}
ρ	1170 kg m^{-3}
C	2.34 kJ $\text{kg}^{-1}\ \text{K}^{-1}$
λ	0.48 W $\text{m}^{-1}\ \text{K}^{-1}$
SOC	96% at 187 K for 20 min

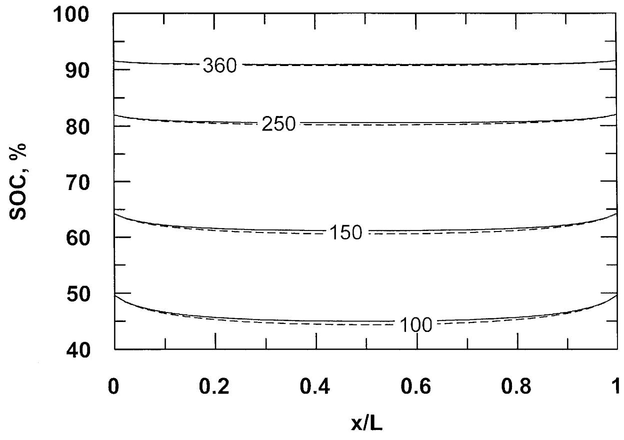

Fig. 1. Profiles of SOC developed through 0.2 cm thick EPDM rubber discs cured at 187 °C at various times (s). Dashed line: 2% peroxide. Full line: 10% peroxide.

4. Results and discussion

The following aspects are considered:

(i) The cure of rubber discs and evaluation of the state of cure, SOC.
(ii) The kinetics of absorption obtained either by experiments or calculation.
(iii) Evaluation of the characteristics of the swelling by experiments and calculation of the kinetics of the change in dimensions.

4.1. Cure of the EPDM rubber discs

The discs of thickness of 0.2 cm are cured at 187 °C, and the value of the state of cure is calculated at various times for the EPDM discs with different percent peroxide. The validity of the process of cure as well as the accuracy of the parameters has been tested by comparing the profiles of temperature obtained at the midplane of 0.8 cm thick sheets either by experiments or by calculation. As shown in earlier papers [12,24], rather good agreement has been obtained between these curves with the same rubber.

The profiles of state of cure are shown (Fig. 1) as they are calculated through the thickness of 0.2 cm thick discs at various times. The following facts are worth noting.:

(i) The cure reaction starts on the surface of the discs in contact with the mould. At 250 s, when the temperature reaches that of the mould, the state of cure is far from the maximum value. At 600 s, the profiles of state of cure are nearly similar for the two discs with 2 and 10% peroxide.
(ii) A slight difference in the profiles of state of cure can be observed for the discs with 2 (dot line) and 10% (full line) peroxide. Resulting from the larger cure enthalpy with the 10% peroxide sample, the state of cure is higher for this sample at the beginning of the process.
(iii) The time necessary to reach the value of 90% is 6 and

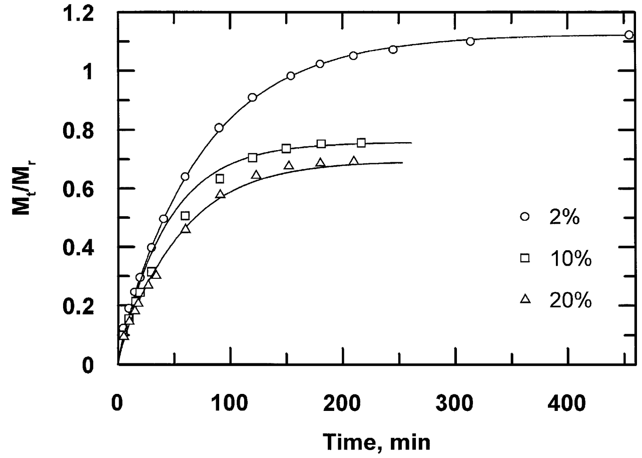

Fig. 2. Kinetics of toluene absorption by the three EPDM rubber discs with 2, 10, and 20% peroxide; amount (w/w) of toluene as a fraction of the initial weight of rubber free from liquid.

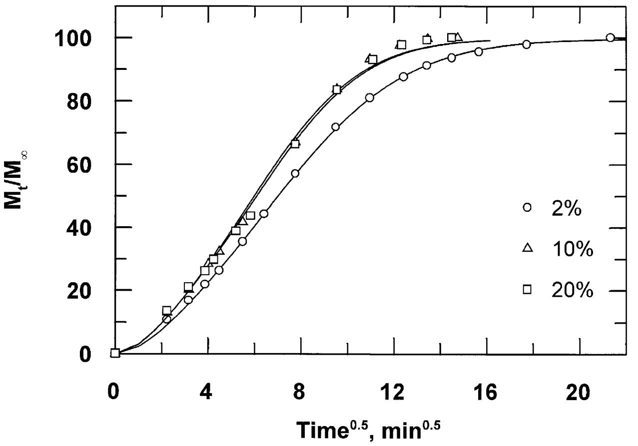

Fig. 3. Amount of toluene absorbed by the three EPDM rubber discs as a function of the square root of time (w/w % of initial rubber free from liquid). 2, 10 and 20% peroxide.

20 min for 96%, for 0.2 cm thick discs, when the amount of peroxide is either 2 or 10%.

(iv) For these times of 6 and 20 min, the profiles of state of cure are nearly flat through the rubber discs, meaning that these materials are homogeneous as far the state of cure is concerned.

4.2. Kinetics of absorption of toluene by the EPDM rubber discs

The kinetics of absorption of toluene by the EPDM rubber discs are drawn (Fig. 2) as they are obtained from experiments (dots) and by calculation (full line) when the percentage of peroxide is 2, 10 and 20. The dimensionless number is used by expressing the weight of toluene absorbed as a fraction of the initial weight of the discs free from liquid.

These results obtained either by calculation or by experiments are expressed in terms of the square root of time, and using as dimensionless number the weight of toluene absorbed at time t as a fraction of the corresponding value extrapolated for infinite time (Fig. 3).

These curves lead to the following conclusions:

(i) Calculation is made by assuming an isotropic behaviour of the rubber disc with respect to the swelling. The data used are shown in Table 3.

(ii) Good agreement is shown between the kinetics of absorption obtained from experiments and by calculation for the three EPDM samples, whatever the percent peroxide (Fig. 2).

(iii) The slope at the beginning of the stage of absorption is oblique in Fig. 2. This is due to the finite coefficient of convective transfer on the surface of the rubber discs [1,2]. It should be said that a vertical tangent is associated with an infinite value of the coefficient h in Eqs. (12) and (13), meaning that the liquid concentration on the rubber surface reaches its value at equilibrium as soon as the process starts. This fact is also proved by the shape of the curves in Fig. 3, since the straight lines do not pass through the origin.

(iv) The effect of the percent peroxide on the resistance of the EPDM discs to the liquid is shown in Fig. 2 and Table 3. The diffusivity slightly varies with the percent peroxide as well as the factor α characterising its concentration-dependence. The main parameter is the amount of liquid absorbed which decreases when the percent peroxide is increased.

(v) The process of adsorption is thus controlled by radial and longitudinal diffusion through the rubber disc and convective transfer on the surface with a concentration-dependent diffusivity [2,11].

4.3. Anisotropic swelling of the EPDM rubber discs

The kinetics of absorption of toluene have been determined by weighing the uptake of liquid as a function of

Table 3
Parameters of diffusion

Percent peroxide	D_0 ($\times 10^7$ cm^2 s^{-1})	α	h ($\times 10^4$ cm s^{-1})	M_l/M_r	V_l/V_r
2	7.9	2.5	1	1.11	1.50
10	9.7	2.5	1	0.76	1.03
20	8.6	2.5	1	0.7	0.945

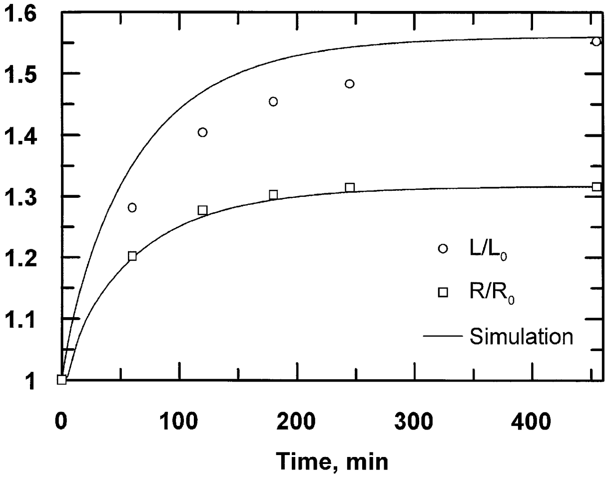

Fig. 4. Kinetics of the increase in dimensions of EPDM rubber discs with 2% peroxide. Full line: calculation made by considering the anisotropic conditions. (○) Increase in the thickness. (□) Increase in the radius.

time, which is the more accurate method [14]. Nevertheless at the same times, measurements are made in the same position for the thickness and the diameter. The results for these values are shown in Figs. 4–6 for the discs with 2, 10 and 20% peroxide. The kinetics of the change in dimension for the thickness and radius are also drawn as they are calculated by considering the anisotropic behaviour of the rubber discs to the swelling. Various conclusions can be drawn from these curves.

(i) There are two kinetics for the swelling from the experimental values, the one expressed in terms of the change in the thickness and the other in terms of the change in the radius.

(ii) The kinetics of these changes in dimensions can be calculated by using the same parameters of diffusion as shown in Table 3, except for the values of the increments of thickness and radius Δx and Δr, which are shown in Table 4 to account for the anisotropy of the rubber discs to swelling. A rather good agreement is thus obtained between the calculated and experimental kinetics, by considering that the accuracy is not so favourable for these measurements of dimensions as those made on the weight.

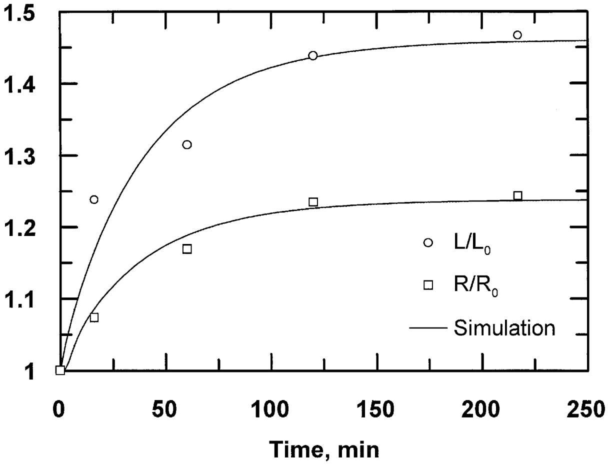

Fig. 5. Kinetics of the increase in dimensions of EPDM rubber discs with 10% peroxide. Full line: calculation made by considering the anisotropic conditions. (○) Increase in the thickness. (□) Increase in the radius.

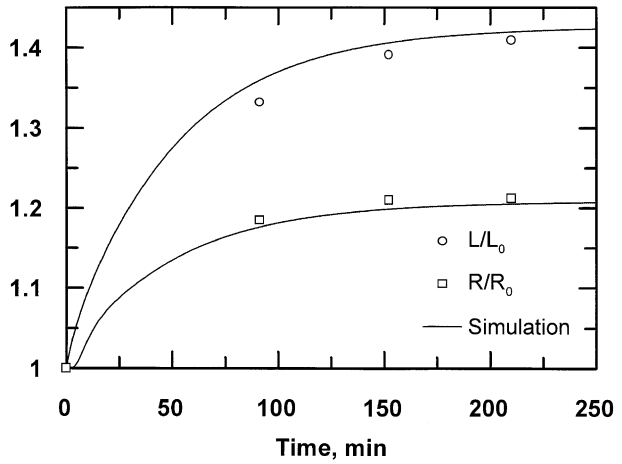

Fig. 6. Kinetics of the increase in dimensions of EPDM rubber discs with 20% peroxide. Full line: calculation made by considering the anisotropic conditions. (○) Increase in the thickness. (□) Increase in the radius.

(iii) A large and significant difference appears between the kinetics of swelling expressed in terms of the thickness or of the radius. The increase in the thickness is more important than that in the diameter. The ratio of these ultimate values, when equilibrium is attained, is around 1.17, this ration being about the same whatever the percent peroxide used for the cure of the rubber discs.

(iv) Of course, the kinetics of swelling expressed in terms of volume is located between the other kinetics describing the change in dimensions of the thickness and of the radius with the following ratio:

$$\left(\frac{R_t}{R_0}\right)^2\left(\frac{L_t}{L_0}\right)=\left(\frac{V_t}{V_0}\right)$$

(v) This fact is a proof for the anisotropy of the rubber discs, the swelling being larger in the thickness than in the radius whatever the percent peroxide used for the cure. It can be explained by an orientation of the macromolecules along the flat parallel faces of the discs which is obtained during the cure when the rubber is pressed into the slabs.

5. Conclusions

The main conclusions are of three types: the first with the

Table 4
Increments used for calculation

Increments	Isotropic	Anisotropic
Δr	1	0.853
Δx	1	1.353

process of absorption of toluene by the EPDM rubbers, the second with the effect of the percent peroxide, and the last with the anisotropic behaviour of the rubber discs to the swelling.

The process of absorption of toluene by EPDM rubber discs is controlled by transient radial and longitudinal diffusion with a concentration-dependent diffusivity and a finite coefficient of convective transfer at the surface, and a subsequent swelling. A numerical model taking all these facts into account is able to describe the process and thus to evaluate the value of the parameters and to calculate the kinetics of absorption with EPDM rubbers.

The percent peroxide used for the cure of the rubbers acts on the process of absorption, especially on the amount of liquid absorbed with the following statement: the higher the percent curing agent the lower the amount of liquid absorbed.

An important result is worth emphasising with the anisotropic behaviour of the EPDM rubber discs to swelling. Thus a much larger increase in the thickness than in the radius is observed for these discs. This fact occurs whatever the percent peroxide, with nearly the same ratio for the increase in thickness and in radius. It can be explained by an orientation of the macromolecules taking place during the cure resulting from the pressure of the slabs of the press. The kinetics for these changes in dimensions of the thickness and of radius are similar to that for the absorption of liquid.

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