

# Influence of Solvent Penetration on the Electrical Conductance of Pre-Extended FEF Carbon Black-Loaded Rubbers

M. AMIN, G. M. NASR, S. A. KHAIRY, and E. ATEIA, *Physics Department, Faculty of Science, Cairo University, Giza, Egypt*

## Synopsis

The penetration of organic solvent and its influence on the electrical conductance of pre-extended styrene butadiene (SBR), butadiene (BR), acrylonitrile butadiene (NBR), butyl (IIR), and natural (NR) rubbers are investigated. A model is proposed for a process by which it is possible to estimate the separation distance between carbon black particles (or aggregates) and its dependence on the extent of penetration of the liquid. An empirical formula is suggested to describe the variation of the conductance of rubber composites with swelling time in terms of the interspacing distance.

## INTRODUCTION

The property of swelling in low molecular weight liquids<sup>1</sup> is common to many polymers, both natural and synthetic. This property is markedly dependent on the nature of the liquids used.

Many attempts have been made<sup>2,3</sup> to apply the concept of cohesive energy density to elucidate the role of intermolecular interactions in the determination of swelling properties.

Swelling decreases the strength of rubber in different ways depending on the type of rubber,<sup>4</sup> the type of swelling liquid and the nature of interaction between the rubber and the liquid.<sup>5</sup>

A more complicated problem is to determine the equilibrium value of the degree of swelling,  $Q$ , in the presence of mechanical stress. This problem was first treated by Flory<sup>2</sup> and Rehner and also by Gee<sup>3</sup> for the case of a simple tensile stress.

Experiments on simple extension were carried out originally by Flory and Rehner, using butyl rubber swollen in xylene, and by Gee using natural rubber in a variety of swelling agents. The relationship between the extension ratio and the degree of swelling which was predicted theoretically was satisfactorily confirmed, except in the case of poor swelling agents.

In a previous work, the electrical conduction was investigated in different pre-extended rubber composites.<sup>6</sup> The aim of this work is to find some correlation between electrical conduction and the penetration of a typical solvent (kerosene) through some pre-extended rubber vulcanizates, on the basis of a model which we introduce.

TABLE I  
Composition of Different Rubber Composites Made Up of 100 phr of Rubber  
(SBR or BR or NBR or IIR or NR) and the Other Ingredients in the Following Proportions:

Ingredients	phr
Stearic acid	2
FEF black	100
Processing oil	10
MBTS <sup>a</sup>	2
PBN <sup>b</sup>	1
Zinc oxide	5
Sulfur	2

<sup>a</sup>2,2-Bisbenzothiozoyl disulfide.

<sup>b</sup>Phenyl-B-naphthylamine.

## EXPERIMENTAL

A suitable concentration, 100 phr\*, of fast extrusion furnace black (FEF) was introduced into styrene butadiene rubber (SBR), butadiene rubber (BR), acrylonitrile butadiene rubber (NBR), butyl rubber (IIR), and natural rubber (NR), according to the recipe illustrated<sup>7-9</sup> in Table I.

All samples passed through the same procedure, under the same conditions during preparation. The compounded rubber was left for at least 24 h before vulcanization. The rubber vulcanization was conducted at  $143 \pm 2^\circ\text{C}$  under a pressure of about  $40 \text{ kg/cm}^2$  for 20 min to ensure stable properties without affecting the electrical properties.<sup>10,11</sup>

A suitable device was used to carry out measurements of electrical conductance,  $Y$ , of the pre-extended samples as was described, in a previous work.<sup>12</sup> Electrical measurements were conducted using the same procedure as in Ref. 6.

## RESULTS AND DISCUSSION

From a practical point of view,<sup>7</sup> it is very important to know the capacity of crosslinked polymer for swelling in various liquids. This capacity is assessed by the degree or amount of swelling which is expressed as the amount of liquid sorbed by unit mass or volume of a given polymer. The degree of swelling may be taken as a measure for the degree of crosslinking. The smaller the degree of crosslinking in a polymer the higher the ability of a material to swell up.

A quantitative description of the conduction mechanisms through SBR during swelling can be done using a simple modification of the model suggested by Polley and Boonstra<sup>13</sup> and a specimen of SBR, containing 100 phr FEF carbon black (100 FEF/SBR), as an example. According to this model, the rubber matrix is visualized as composed of rubber globules (radius  $R$ , density  $\rho = 0.94 \text{ g cm}^{-3}$ )<sup>14</sup> enclosing no conducting filler, but each globule is inlaid with uniformly dispersed FEF carbon black particles (radius  $r = 210 \text{ \AA}$  density  $\rho_c = 1.86 \text{ g cm}^{-3}$ )<sup>8</sup> separated from one another by a narrow distance  $D$ .

\*phr: part per hundred part by weight of rubber.

The penetration of solvent molecules through composites is resisted by the crosslinks which restrict this movement. However, the elastomer does swell when the solvent molecules diffuse into the network and cause the chains to expand. The solvent molecules diffuse into the polymer matrix but not into the carbon black aggregations because the carbon black does not dissolve in kerosene as was found by a separate experiment.<sup>15</sup> Accordingly, the radius of the rubber globule will increase to a new value  $R'$ , calculated as follows. Consider an ideal rubber globule, the number  $N_S$  of carbon black particles on the surface is given by

$$N_S = 4\pi(R + r)^2 / (2r + D)^2 \tag{1}$$

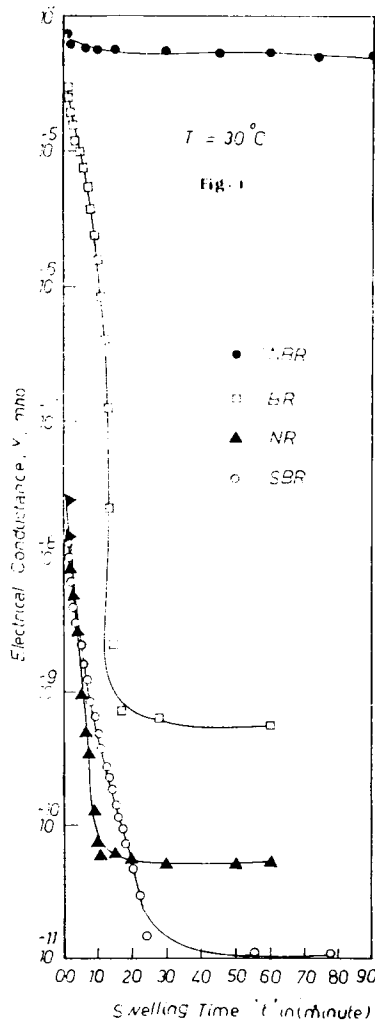


Fig. 1. The dependence of the electrical conductance, Y, on swelling time in kerosene for all rubber composites [SBR (○), BR (□), NBR (●), and NR (▲)] for the unextended samples.

TABLE II  
Illustrates the Fitting Parameters Used in Eq. (6)

Types of rubber	Q max		(min)t*(min)
IIR	—	—	—
NBR	0.05	59.6	Swelling resistant
BR	0.17	114.7	8
SBR	0.18	185.0	4
NR	0.25	265.6	2

Therefore

$$D = 2R\sqrt{\pi/N_S} + 2r(\sqrt{\pi/N_S} - 1) \quad (2)$$

After swelling Eq. (2) becomes

$$D' = 2R'\sqrt{\pi/N_S} + 2r(\sqrt{\pi/N_S} - 1)$$

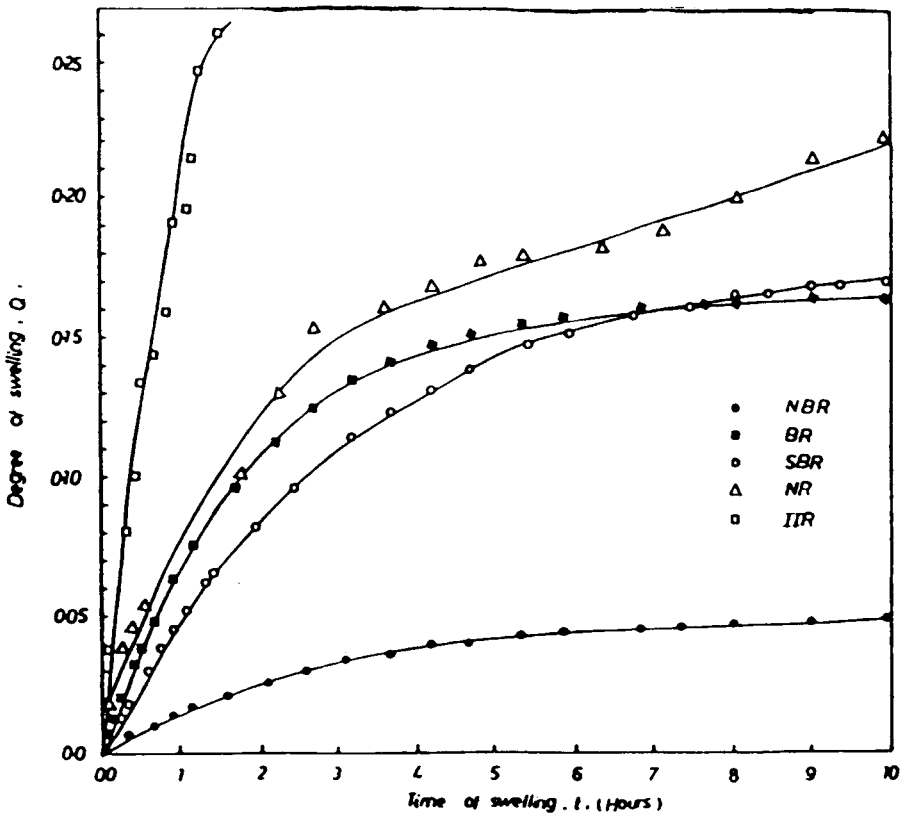


Fig. 2. The dependence of the degree of swelling,  $Q$ , for the rubber composites [SBR (○), BR (■), NBR (●), IIR (□), and NR (△)] on time,  $t$ , of swelling in kerosene.

TABLE III  
The Variation of the Carbon-Carbon Interspacing Distance,  $D'$ , with Swelling Time for Extended and Unextended 100 FEF/SBR

0%		50%	
$t$ (min)	$D'$	$t$ (min)	$D'$
0	42.00	0	22.60
5	43.23	10	25.03
10	44.43	30	29.46
20	46.72	60	35.13
30	48.86	90	39.84
40	50.43	120	43.77
50	52.76	150	47.05
60	54.53	200	51.39
75	57.00	230	53.46
90	59.24	270	55.71
110	61.98	310	57.52
130	64.33	360	59.27
145	65.94	400	60.73
180	69.20	430	61.04
210	71.52	500	62.25
240	73.47	560	62.97
270	75.11	610	64.41
310	76.92	670	63.81
360	78.67	740	64.13
24 h	84.22	24 h	64.82

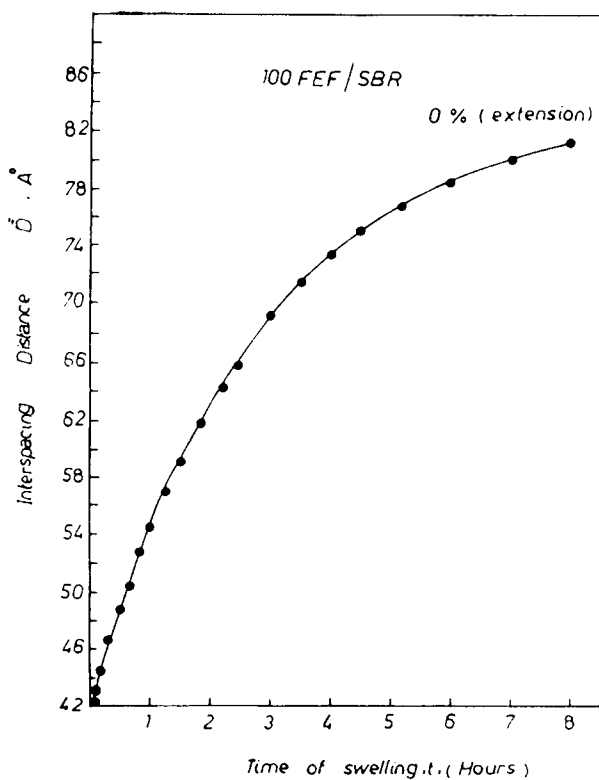


Fig. 3. The calculated interspacing distance,  $D'$ , and its variation with the swelling time,  $t$ , for FEF/SBR sample.

Therefore,

$$D' - D = 2(R' - R)\sqrt{\pi/N_S} \quad (3)$$

using the conventional definition of the degree of swelling  $Q$ , namely the ratio between the mass of penetrated solvent to the mass of the unswelled rubber we have

$$\left(\frac{4}{3}\pi R'^3 - \frac{4}{3}\pi R^3\right)\rho_k = \frac{4}{3}\pi R^3\rho Q(t)$$

therefore

$$R' = \left(1 + \frac{\rho}{\rho_k}Q(t)\right)^{1/3} R$$

which can be approximated as

$$R' \approx \left(1 + \frac{1}{3} \frac{\rho}{\rho_k} Q(t)\right) R \quad (4)$$

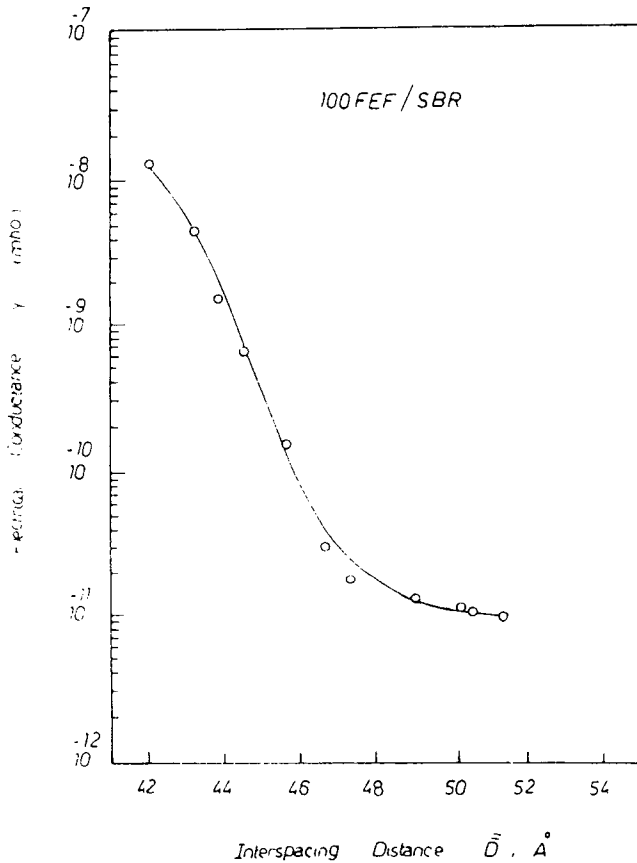


Fig. 4. The dependence of electrical conductance,  $Y$ , on the calculated interspacing distance,  $\bar{D}$ , for FEF/SBR.

where  $\rho_k$  is the density of solvent used ( $\rho_k = 0.81 \text{ g cm}^{-3}$ ).<sup>16</sup> Substituting Eq. (4) into Eq. (3), we get the separation distance  $D'$

$$D' = \alpha Q(t) + D \tag{5}$$

where

$$\alpha = \frac{1}{3} \frac{\rho}{\rho_k} R \sqrt{\pi / N_s}$$

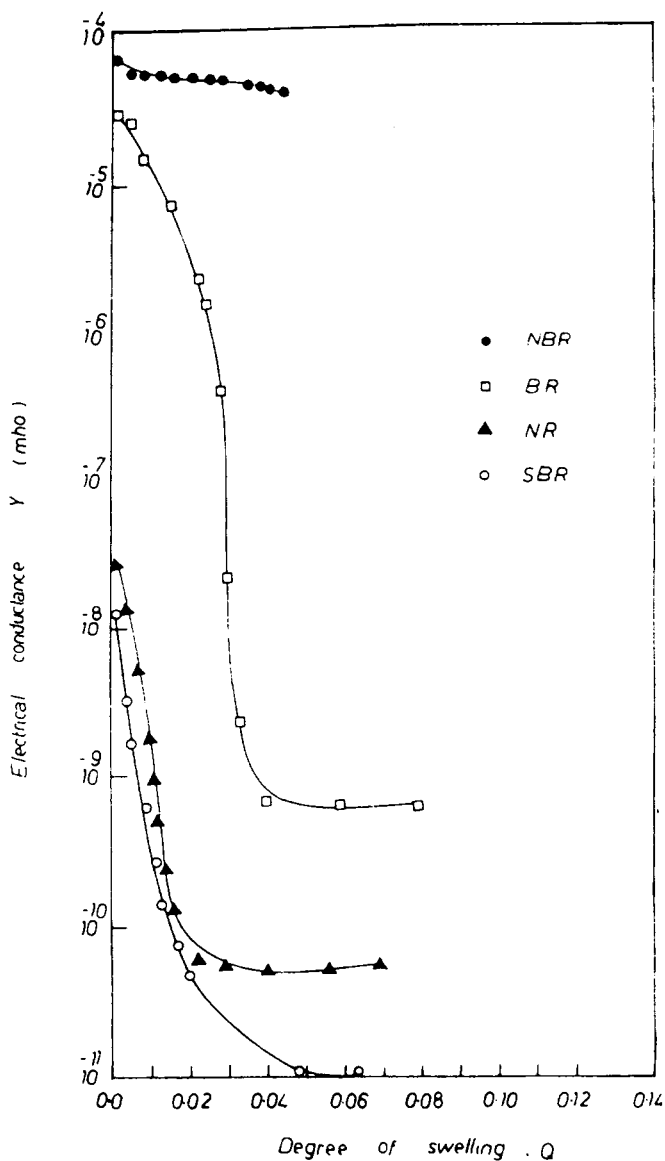


Fig. 5. The dependence of the electrical conductance,  $Y$ , on the degree of swelling,  $Q$ , for the rubber composites [SBR (○), BR (□), NBR (●), and NR (▲)].

Equation (5) illustrates clearly the dependence of interspacing distance  $D'$  on the degree of swelling  $Q$ . It is clear that as  $Q$  increases  $D'$  also increases which in turn directly affects the electrical conductance.

Figure 1 represents the dependence of the electrical conductance  $Y$  in (mho) on the swelling time in kerosene (in minutes) for all rubber composites at 0% pre-extension. It is obvious that any agent which may cause appreciable swelling of carbon black-filled rubber should certainly lead to a sharp reduction in conductivity as was the case with the samples used. The slight difference in the behavior of the samples is probably due to the relevant changes in the formation of network structure (or crosslinking density) in the different types of rubbers. The conductance of these samples is hardly affected by the presence of the solvent (kerosene). The different samples can be arranged in descending order of their resistance to solvent penetration as

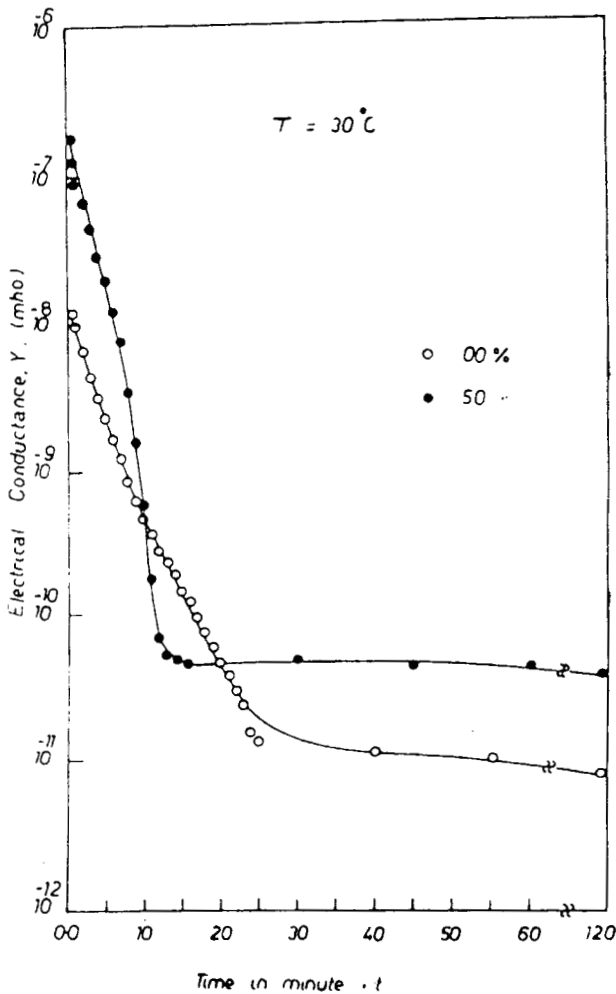


Fig. 6. The dependence of the electrical conductance,  $Y$ , on the swelling time in kerosene for 100 FEF/SBR [at (O) 0% and (●) 50% pre-extension].



follows: 100 FEF with NBR/BR/SBR and NR. It is noticed from Figure 1 that there is a characteristic time  $t^*$  during which there is a sharp decrease in  $Y$ . This time  $t^*$  is sensitive to the type of rubbers used (see Table II). A preliminary experiment has been done using the degree of swelling test as a criterion to confirm the above fact.

Figure 2 represents the dependence of the degree of swelling  $Q$  for the given rubber composites on time  $t$  of swelling in kerosene. The behavior can be approximated by an empirical function of the form

$$Q = Q_m [1 - \exp(-t/\tau)] \quad (6)$$

where  $Q_m$  is the maximum degree of swelling and  $\tau$  is a certain time to be determined as fitting parameter. It depends as was shown in Table II on the type of rubber used.

It is evident from Figure 2 that due to its low unsaturation the butyl rubber composites were not completely vulcanized by the sulfur vulcanizing agent, that is, the samples have a low degree of crosslinking.

A direct relationship between the interspacing distance  $D'$  and the time of swelling can be obtained by substituting for the value of  $Q$  from Eq. (5) into Eq. (6), we get,

$$D' = Q_m [1 - \exp(-t/\tau)] + D \quad (7)$$

Calculated values of  $D'$  at different exposure times are shown in Table III. The values are also plotted in Figure 3 for the unextended 100 FEF/SBR sample.

A direct dependence of the electrical conductance  $Y$  on the interspacing distance  $D'$  is depicted in Figure 4 for the 100 FEF/SBR.

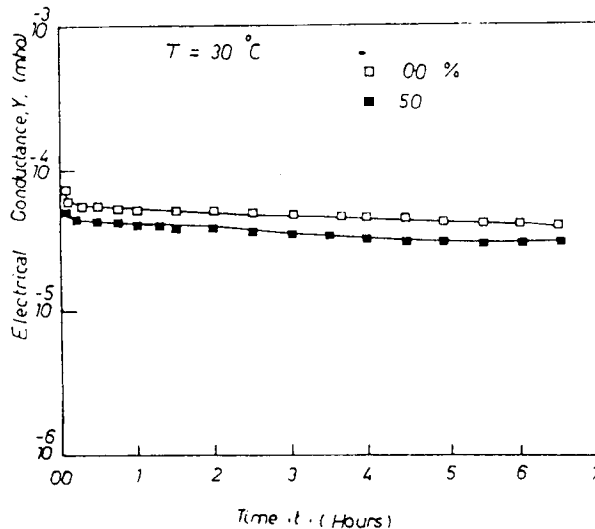


Fig. 7. The dependence of the electrical conductance,  $Y$ , on the swelling time in kerosene for 100 FEF/NBR [(□) 0% and (■) 50% pre-extension].

Alternatively, one could get a direct dependence of the electrical conductance  $Y$  on the degree of swelling  $Q$  as shown in Figure 5, accordingly  $Q$  can be determined from electric conductance measurements.

The composites of 100 FEF with SBR, NBR, and BR were subjected to repeated measurements of the dependence of electrical conductance  $Y$  on swelling time in kerosene at two settings of pre-extension (0% and 50%) as shown in Figures 6, 7, and 8, respectively.

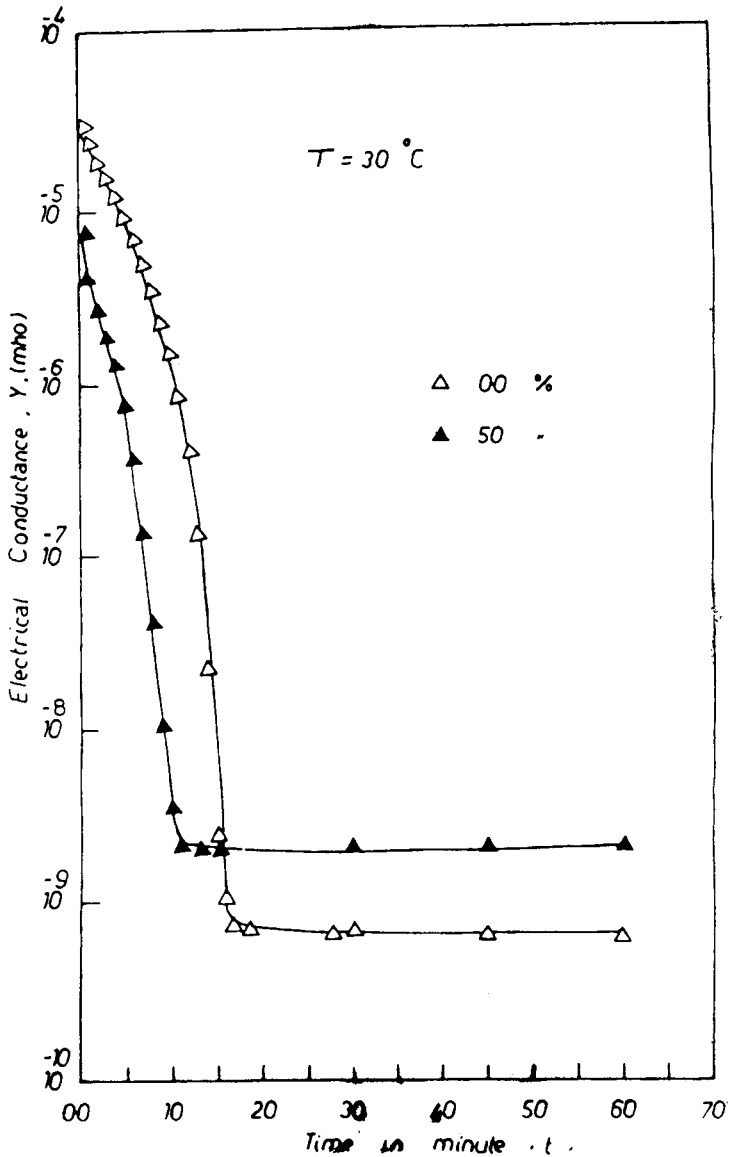


Fig. 8. The dependence of the electrical conductance,  $Y$ , on the swelling time in kerosene for 100 FEF/BR [at ( $\triangle$ ) 0% and ( $\blacktriangle$ ) 50% pre-extension].

The above data leads to the following conclusion: as a pre-extension increases, the swelling is rendered lower due to the relative increase in the stable ordered structure induced by pre-extension.

The swelling in kerosene of unextended rubber composites (except 100 FEF/NBR) shows a drastic drop in the electrical conductance,  $Y$ , with swelling time.

An empirical formula (5) is suggested to account for the effect of swelling on  $D'$ . It was found that as the swelling time increased,  $D'$  increased exponentially.

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Received September 22, 1987

Accepted February 25, 1988