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Electrical Conductance of Fast Extrusion Furnace Carbon Black-Loaded Styrene-Butadiene Rubber during Swelling in Kerosene

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ABSTRACT

The effect of swelling in kerosene on the electrical conductance of 60, 80, and 100 part per hundred parts of rubber by weight of Fast Extrusion Furnace (FEF) carbon black-loaded styrene-butadiene rubber (SBR, 1502) was studied. It was found that there is a characteristic time of swelling after which a sudden decrease in conductivity appears. An ideal and simple model is suggested to calculate the carbon-carbon interspacing distance, D, in the carbon/rubber matrix. The dependence of D on the swelling time is also discussed.

INTRODUCTION

The interaction of polymeric materials with different solvents is a problem from both the academic and technological points of view [1-7]. Cross-linked polymers brought in contact with different solvents during service applications usually exhibit the phenomenon known as swelling. The capacity of cross-linked polymers for swelling is assessed by the degree or the amount of swelling

TABLE 1. The Composition of SBR Samples Containing Different Concentrations of FEF Carbon Black[a]

Ingredients (phr)	Sample 60 FEF/SBR	Sample 80 FEF/SBR	Sample 100 FEF/SBR
SBR (1502)	100	100	100
Stearic acid	2	2	2
FEF black	60	80	100
Processing oil	10	10	10
MBTS[b]	2	2	2
PBN[c]	1	1	1
Zinc oxide	5	5	5
Sulfur	2	2	2

[a] The ingredients are arranged in the same order used during preparation.
[b] Dibenthiazyl disulfide.
[c] Phenyl-β-nepthylamine.

expressed as the amount of liquid (or its vapor) absorbed by the polymer. The degree of swelling is a function of time, and after a certain time the amount of swelling becomes constant. This is known as the maximum degree of swelling.

In previous work some factors affecting the electrical conductivity of carbon black-loaded rubber have been discussed by our group [8-11]. The present work deals with the effect of swelling in kerosene on the carbon-carbon interspacing distance, D, and how this affects the electrical conductance of the carbon/rubber composites.

EXPERIMENTAL

Styrene butadiene rubber (SBR 1502) loaded with 60, 80 and 100 parts per hundred parts of rubber by weight (phr) of Fast Extrusion Furnace (FEF) black has been prepared according to the recipe mentioned in Table 1. The investigated rubber specimens were shaped during the vulcanization process into the form of sheets 2 cm long, 0.5 cm wide, and 0.3 cm thick. The rubber vulcanization was conducted at 143° C under a pressure of 40 kg/cm^2 for 20 min. The sample holder consists of two parallel rods held by screw bolts which enter two holes in the specimen 1.6 cm apart and coated with silver paste. The screws are closed by a nut to govern the

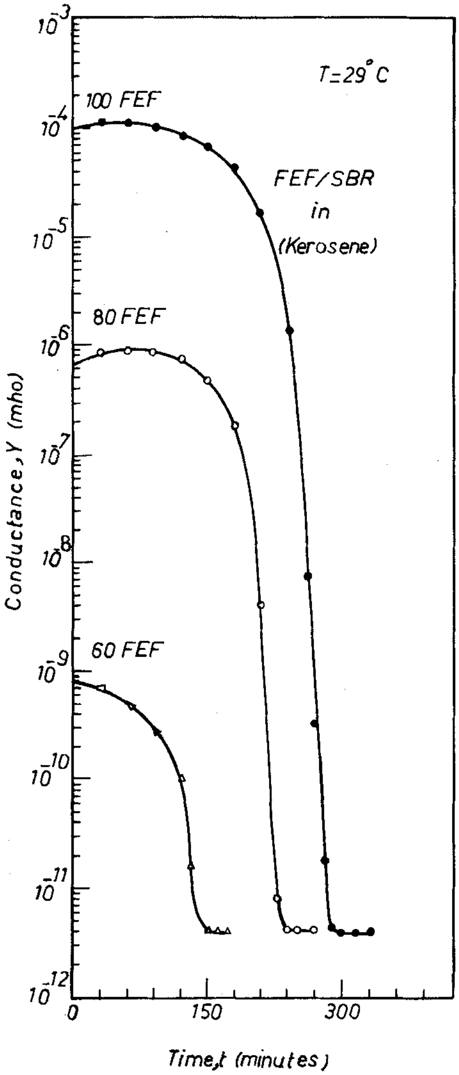

FIG. 1. Time dependence of the electrical conductance of different concentrations of FEF carbon black-loaded SBR vulcanizates during swelling in kerosene at 29°C.

TABLE 2. Characteristic Constants of Y(t) Behavior for FEF Black-Loaded SBR during Swelling in Kerosene

Sample	Y (mho)	α (min^{-1})	β (min^{-1})	t* (min)
60 FEF/SBR	0.19	0.17	0.16	119
80 FEF/SBR	3.16×10^{12}	0.23	0.23	188
100 FEF/SBR	2.68×10^{28}	0.33	0.32	230

sample-holder contact during swelling. The sample container is a Teflon-stoppered glass tube filled with kerosene. A regulated electrical furnace was used in order to keep the ambient temperature constant.

RESULTS AND DISCUSSION

Figure 1 illustrates the dependence of the electrical conductance (Y) of FEF/SBR vulcanizates on the time of swelling in kerosene. It is noticed that there is a characteristic time of swelling, t*, after which a sharp decrease in Y with time appears. This descending behavior of Y(t) is similar to what happened in the thermal expansion of a rubber matrix [10]. We assume a similar empirical formula:

$$Y = Y_0 \exp(-\alpha t)/[1 + \exp \beta(t^* - t)] \qquad (1)$$

where Y_0, α, β, and t* are constants that depend on the carbon black concentration. Table 2 presents the calculated fitting parameters which are close to obeying the above experimental data.

It is obvious from the above data that the characteristic time t* increases with the carbon black concentration. This may be attributed to the high probability of the formation of a primary and/or secondary structure of carbon black by increasing its concentration in the rubber matrix. This stable structure probably resists the breakdown effects during the early stages of the swelling process and results in the bend obtained in the curve below t*.

It is suggested here that the swelling process affects the electrical conductance of the carbon black-laoded rubber composites in two steps. The first one is the diffusion of the solvent molecules into the rubber matrix and not the carbon black aggregations, because the carbon black does not dissolve in this solvent as shown in a separate confirming experiment. This results, below t*, in the swelling of the separation distance, D, between carbon black aggregates, and the swelling of the rubber matrix causes a breakdown in the carbon black

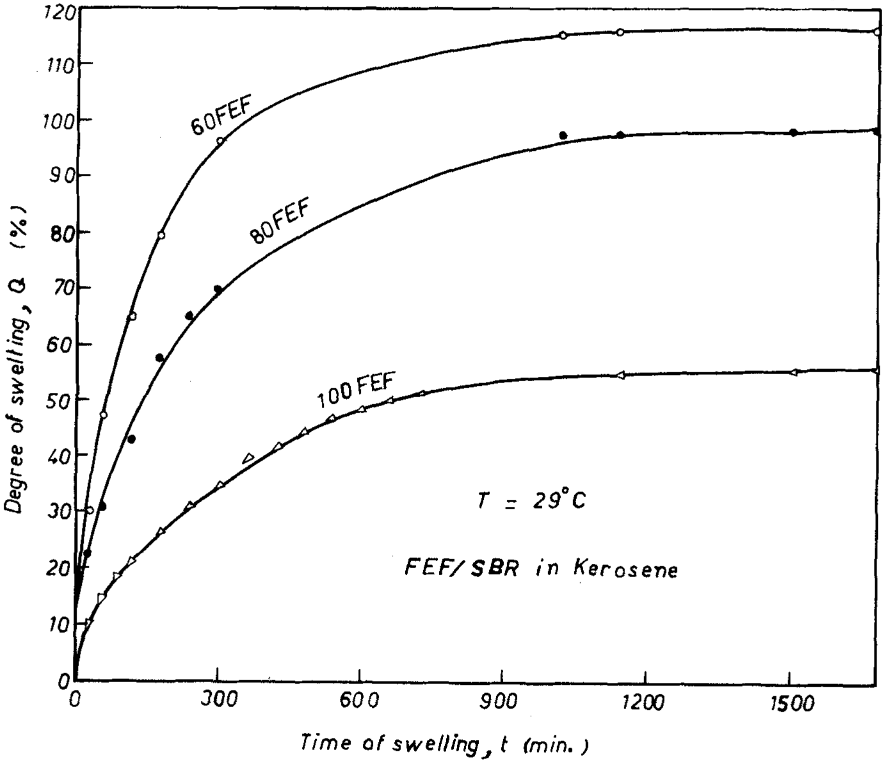

FIG. 2. Time dependence of the degree of swelling in kerosene for different concentrations of FEF carbon black-loaded SBR vulcanizates at 29° C.

structure. Second, the formation of an insulating cluster in the solvent around the carbon black particles and/or aggregates results in a sharp decrease in the electrical conductance above t*.

A preliminary experiment has been made using the degree of swelling test in kerosene [12] to confirm the above suggestion. Figure 2 shows the variations in the degree of swelling, Q (%), for FEF/SBR vulcanizates with the time of swelling, t. This behavior can be explained by an exponential growth function of the form

$$Q(t) = Q_m[1 - \exp(-t/\tau)] \qquad (2)$$

where Q_m is the degree of maximum swelling and τ is a characteristic time which depends on the concentration of carbon black (Table 3).

TABLE 3.

Sample	Q_m (%)	τ (min)
60 FEF/SBR	120	234
80 FEF/SBR	108	300
100 FEF/SBR	57	325

It is noticed that τ increases with the concentration of carbon black. In other words, the rate of the relative change of swelling ($dQ/Qdt = 1/\tau$, Eq. 2) decreases with an increase in the concentration of carbon black.

In order to obtain a rough estimate of the separation distance between the carbon black particles (or aggregates), let us consider the following ideal and simple model. We assume that the carbon/rubber matrix is divided into cubic elements (cells), each of which contains one carbon black particle (or aggregate) of average volume ℓ^3. Furthermore, the carbon particles are homogeneously distributed in the rubber matrix with an average separation distance D. Therefore, the total number of cells is equal to the total number of aggregates, i.e.,

$$V_t/(\ell + D)^3 = V_c/\ell^3 \tag{3}$$

where V_t (= $V_c + V_r$) is the total volume of carbon black and rubber. Therefore,

$$D = \ell[(V_t/V_c)^{1/3} - 1] \tag{4}$$

Considering the volume density of carbon black as equal to 1.86 g/cm^3 [13], which is approximately twice that of rubber, 0.94 g/cm^3 [14], Eq. (4) becomes

$$D = \ell[\left(\frac{200}{F} + 1\right)^{1/3} - 1] \tag{5}$$

Where F is the weight fraction of carbon black, in phr, in the rubber matrix.

From Eq. (5) it is obvious that the insulating gap D depends on both F and ℓ, which are responsible for the concentration and the type of carbon black, respectively. Considering the low tendency of FEF carbon black to form aggregates, we confine ourselves here to being equal to the particle size (420 Å) [15] of this type of black.

TABLE 4. Calculated Values of D (Eq. 8) for FEF/SBR Composites at Different Swelling Rates

Swelling time (min)	Carbon-carbon interspacing distance, D (Å)		
	60 FEF/SBR	80 FEF/SBR	100 FEF/SBR
0	299	248	212
60	448	342	250
119	491[a]	376	267
188	523	401[a]	281
230	547	418	292[a]
300	562	431	301
360	569	441	310
420	577	451	317
480	584	458	323
540	589	465	328
600	592	470	331
660	594	476	335
1020	599	489	345
∞	607[b]	494[b]	349[b]

[a] D at t*.
[b] D_m.

TABLE 5.

Sample	D_m (Å)[a]	τ_D (min)[b]
60 FEF/SBR	607	240
80 FEF/SBR	494	313
100 FEF/SBR	349	432

[a] D_m is the maximum value of D (corresponding to Q_m).
[b] τ_D is a characteristic time which also depends on the carbon black concentration.

In the case of swelling, D becomes a function of time, using Eq. (4):

$$D(t) = \ell\left[\left(\frac{V_c + V_r + V_s(t)}{V_c}\right)^{1/3} - 1\right] \tag{6}$$

where V_s is the volume of the diffused solvent. Considering the definition of the degree of swelling, Eq. (6) becomes,

$$D(t) = \ell\left[\left(\frac{V_c + V_r(1 + \frac{\rho_r}{\rho_s} Q(t))}{V_c}\right)^{1/3} - 1\right] \tag{7}$$

where ρ_r and ρ_s are the volume densities of rubber and solvent, respectively. Substituting Eq. (2) into Eq. (7):

$$D(t) = \ell\left(\left[1 + \frac{V_r}{V_c}\left(1 + \frac{\rho_r}{\rho_s} Q_m(1 - \exp(-t/\tau))\right)\right]^{1/3} - 1\right) \tag{8}$$

This equation shows the direct relationship between the carbon-carbon interspacing distance D and the time of swelling t. Table 4 presents the calculated values of D at different degrees of swelling.

The plots (not presented here) obtained for D(t) from Table 4 show an exponentially growth function similar to that obtained in Eq. (2). This enables us to calculate two useful parameters, D_m and τ_D, which depend on the concentration of carbon black (Table 5).

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