

# Influence of Hydrostatic Pressure on the Electrical Properties of Unvulcanized FEF-Loaded SBR

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## Synopsis

Styrene butadiene rubber (SBR-1502) loaded with different concentrations of FEF carbon black was tested to find out the effect of pressure on its electrical properties during vulcanization. Using the thermodynamically calculated values of the pressure coefficient ( $K$ ), the thermoelastic coefficient ( $L = \partial T / \partial P$ ) was also estimated and compared with that obtained by other workers. The thermoelastic coefficient was found to be strongly dependent on the carbon black concentration.

## INTRODUCTION

During processing, and also during service, articles made from polymers, as a rule, are subjected to mechanical and thermal strains, radiation, and other types of influences simultaneously. The mechanochemical processes occurring during manufacturing of polymers into articles has been taken into account by some workers.<sup>1-3</sup> An extensive research has also been done to elucidate the considerable effect of processing on the electrical properties of polymers which incorporate conductive fillers. Meanwhile, the methods of vulcanization (i.e., press, open steam, etc.) may have considerable effect on the resistivity. Moreover, the effects of time and temperature of vulcanization on the resistivity have been studied by a number of authors.<sup>4-6</sup>

Recently, many workers studied the temperature changes as a result of a rapid extension and hydrostatic deformation for unvulcanized SBR.<sup>7-9</sup>

This work reports the findings of an experimental investigation on the changes of electrical conductivity ( $\sigma$ ) occurring during the application of hydrostatic pressure ( $P$ ) on styrene butadiene rubber (SBR) loaded with different concentrations of FEF carbon black. However, it seems interesting then to follow the changes in electrical resistivity of these composites during the creation of cross links, i.e., during vulcanization.

## EXPERIMENTAL

Different concentrations of FEF carbon black (30, 50, 70, 80, 90 and 100 phr\*) were introduced into SBR according to the standard recipe and are presented in Table I.

\*Parts per hundred parts by weight of rubber.

TABLE I  
Composition of SBR Samples with Different Concentration of FEF Carbon Black

Ingredients (phr)	Samples					
	$F_3$	$F_5$	$F_7$	$F_8$	$F_9$	$F_{10}$
SBR (1502)	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2
FEF/black	30	50	70	80	90	100
Processing oil	10	10	10	10	10	10
MBTS <sup>a</sup>	2	2	2	2	2	2
PBN <sup>b</sup>	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5
Sulfur	2	2	2	2	2	2

<sup>a</sup>Dibenzthiazyl disulfide.

<sup>b</sup>Phenyl- $\beta$ -naphthylamine.

TABLE II  
Change in Volume Percent with the Concentration of FEF Carbon Black for All Samples at Different Pressures

Concentration of FEF (phr)	Pressure ( $P$ ) (kg/cm <sup>2</sup> )					
	0	5	10	20	30	40
30	2.10	13.00	14.20	15.70	18.53	20.10
50	1.61	9.76	11.13	15.10	16.50	18.70
70	0.28	3.53	4.70	5.27	9.90	9.90
80	0.33	2.23	3.20	4.50	8.40	7.82
90	0.17	1.12	1.42	2.37	6.64	2.07
100	0.15	0.99	1.30	2.18	2.60	3.80

The materials are arranged in the same order in which they were used during preparation. All samples should pass the same procedure under the same circumstances during preparation, since sample properties depend largely on the order of adding the materials and time of mixing and processing.<sup>10,11</sup>

All rubber mixtures were prepared on a two-roll mill, 170 mm diameter, working distance 300 mm, speed of slow roll 24 rev/min, and gear ratio 1.4. The batch weights according to Table I are 152, 172, 192, 202, 212 and 222 g, respectively. The test samples had the form of discs of radius 0.4 cm and thickness of about 0.35 cm. The apparatus used for measuring the electrical conductivity during the application of pressure (precompression) was previously described.<sup>12</sup> All samples had the same weight (160 mg) in order to avoid any possible influences of mass during vulcanization.<sup>13</sup>

The changes in volume during precompression for all samples were tabulated in Table II. It is clear that the volume changes generally decrease with the concentration of FEF carbon black and increased with the amount of hydrostatic pressure.

## RESULTS AND DISCUSSION

All samples have been exposed for the same period (24 h) to a specified hydrostatic pressure, since electrical properties depend largely on such period.<sup>14</sup>

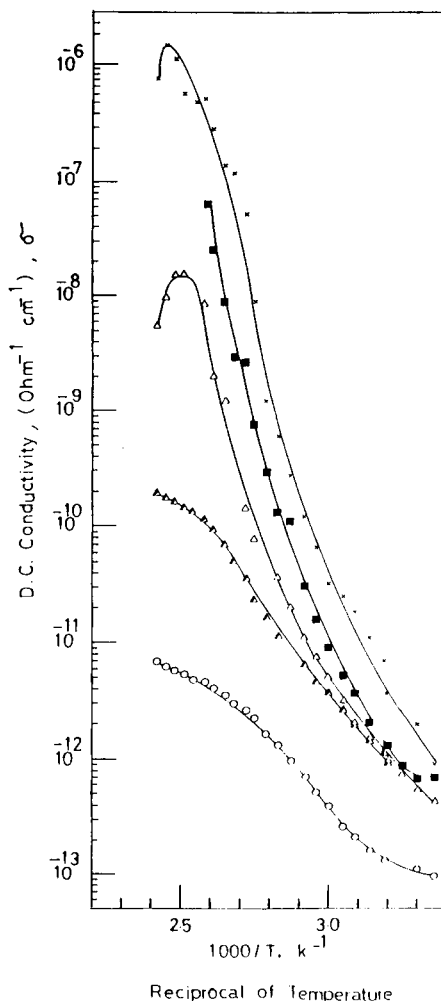


Fig. 1. Temperature dependence of  $\sigma$  for 30 FEF/SBR at different hydrostatic pressures ( $\text{kg}/\text{cm}^2$ ): (○) 0; (▲) 10; (■) 20; (△) 30; (×) 40.

Figures 1–6 represent the temperature ( $T$ ) dependence of the electrical conductivity ( $\sigma$ ) (calculated using the original dimensions) for different concentrations (30, 50, 70, 80, 90, and 100 phr) of FEF carbon black-loaded SBR at various hydrostatic pressures (0, 5, 10, 20, 30, and 40  $\text{kg}/\text{cm}^2$ ).

During mixing, rubber—carbon bonds are formed and there is a net reduction of carbon—carbon bonds. Heating of test pieces especially to temperature of  $\sim 140^\circ\text{C}$  may cause: (a) flocculation of the carbon particles and (b) formation of further chemical rubber—carbon bonds. The latter may result from increased mobility of the long-lived free radicals, which are produced during mixing.

The obvious increase in the electrical conductivity ( $\sigma$ ) for all FEF concentrations may reflect the reformation of the structure of FEF carbon black. There may also be some further reaction of the carbon black with the free

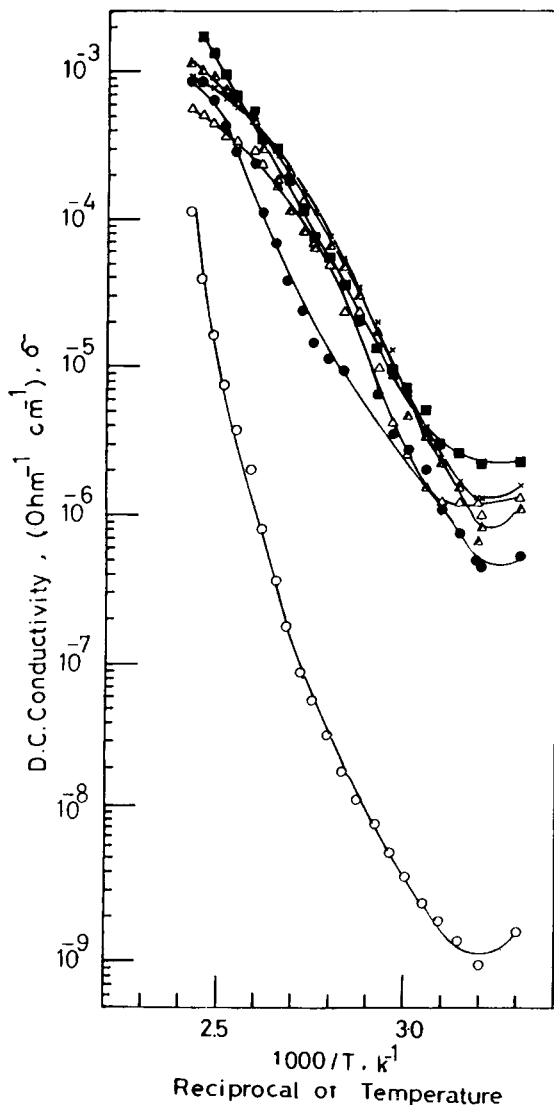


Fig. 2. Temperature dependence of  $\sigma$  for 50 FEF/SBR at different hydrostatic pressures ( $\text{kg}/\text{cm}^2$ ): ( $\circ$ ) 0; ( $\bullet$ ) 5; ( $\blacktriangle$ ) 10; ( $\blacksquare$ ) 20; ( $\triangle$ ) 30; ( $\times$ ) 40.

radicals produced by (a) the milling process due to their increased mobility with temperature or (b) thermal decomposition of the reactive groups.

The noticeable increase of conductivity for all samples which results from increasing the hydrostatic pressure may be interpreted on the basis of the viscosity effects. The electrical conductance of liquids as well as amorphous viscous materials (resins, compound, etc.) is appreciably affected by the viscosity of matter.<sup>15</sup> In other words, the conductivity is inversely proportional to the viscosity of the amorphous material. Therefore, at high temperatures, the viscosity of all test pieces was diminished, and, at the same time, the pressure gave rise to the flocculation of carbon black, which in turn increases the conductivity.

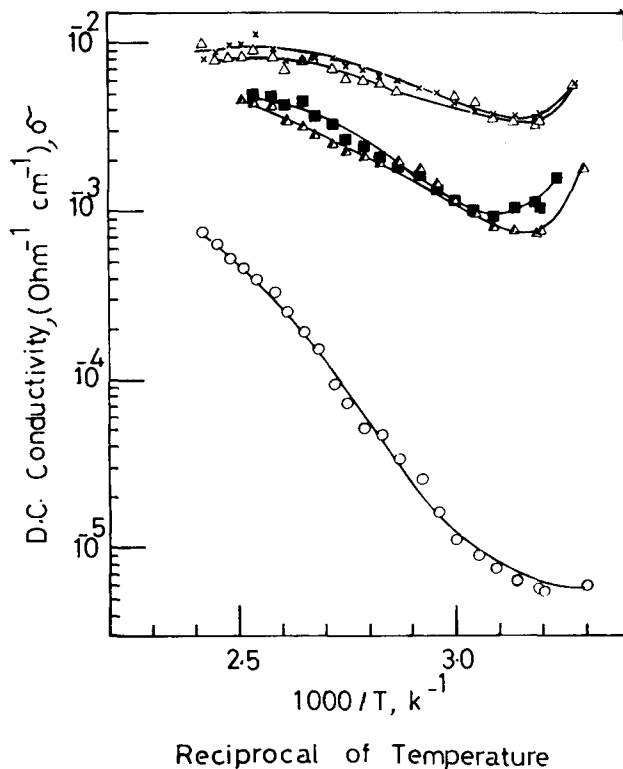


Fig. 3. Temperature dependence of  $\sigma$  for 70 FEF/SBR at different hydrostatic pressures ( $\text{kg}/\text{cm}^2$ ): (○) 0; (▲) 10; (■) 20; (Δ) 30; (×) 40.

It is clear that the breakdown of carbon black structure resulting from the flow produced by molding rubbers tends to lower  $\sigma$ , whereas the pressure acts in the opposite way due to the reformation of carbon-carbon bonds during heating. The hindrance of flocculation of carbon black caused by viscosity is clearly diminished with carbon black concentration. The sharp increase of  $\sigma$  with temperature ( $T$ ) for samples 30 and 50 FEF/SBR is basically due to both the large decrease of the viscosity and at the same time the detectable decrease of the thickness of the sample (cf. Table II). There is a general tendency for larger changes in  $\sigma$  with applied pressures and temperature to occur in the less conductive samples owing to their relative instability, as it is clear in Figures 3-6.

The slope of the thermally activated part of the conductivity (i.e., the rise of  $\sigma$  with  $T$ ) for all samples has almost disappeared upon compression. This was accompanied by a decrease in the activation energy for all samples except the 30 FEF/SBR, one, which reflects the favorable breakdown of carbon black structure upon increasing pressure, as shown in Table III. Meanwhile,  $\sigma$  was found to rise owing to the change in contact resistance between adjacent carbon particles in the rubber. A higher concentration of carbon black ( $> 70$  FEF/SBR) would be expected (as shown in Figs. 4-6) to produce a greater orientation effect owing to the large numbers of possible contacting conductive elements.<sup>14</sup>

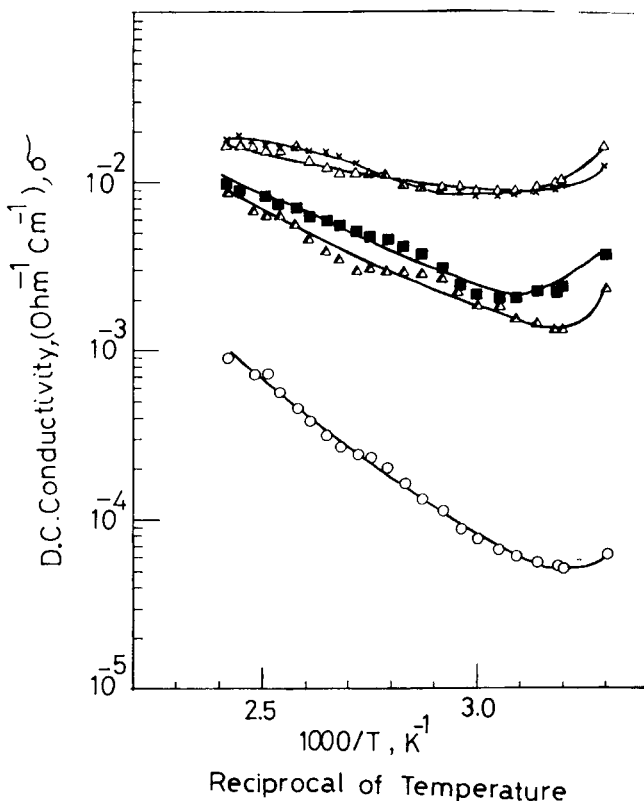


Fig. 4. Temperature dependence of  $\sigma$  for 80 FEF/SBR at different hydrostatic pressures ( $\text{kg/cm}^2$ ): (○) 0; (▲) 10; (■) 20; (△) 30; (×) 40.

At  $140^\circ\text{C}$  the dependence of conductivity (as calculated using the original dimensions) on the time of vulcanization was observed (not present here). It was shown that the major change in electrical conductivity occurs at the first 2 min of vulcanization process. This is followed by a slight decrease of  $\sigma$  which then becomes constant after 20 min. There are three possible reasons to explain the change in  $\sigma$  during the early stages: (1) an equilibrium state of carbon black structure may have been reached; (2) the increase of sulfur crosslinks restricts the free motion of carbon black particles; or (3) the shrinkage of the rubber may be substantially completed during the early stages. In the latter stages of hardening when the resin is very viscous, the conductivity remain substantially constant.

After a test piece was removed from the cell, it was exposed directly to a repeated measurement of the degree of swelling  $Q$  (in kerosene at room temperature  $30^\circ\text{C}$ ) using the expression  $Q = (M - M_0)/M_0$ , where  $M$  and  $M_0$  are the mass of the test pieces after and before swelling in kerosene, respectively. The dependence of the degree of swelling ( $Q$ ) on the hydrostatic pressure for FEF/SBR unvulcanizates is shown in Figure 7. It is obvious from this figure that the noticeable decrease in  $Q$  with pressure ( $P$ ) reflects the main part of crosslinking results during the vulcanization treatment. An

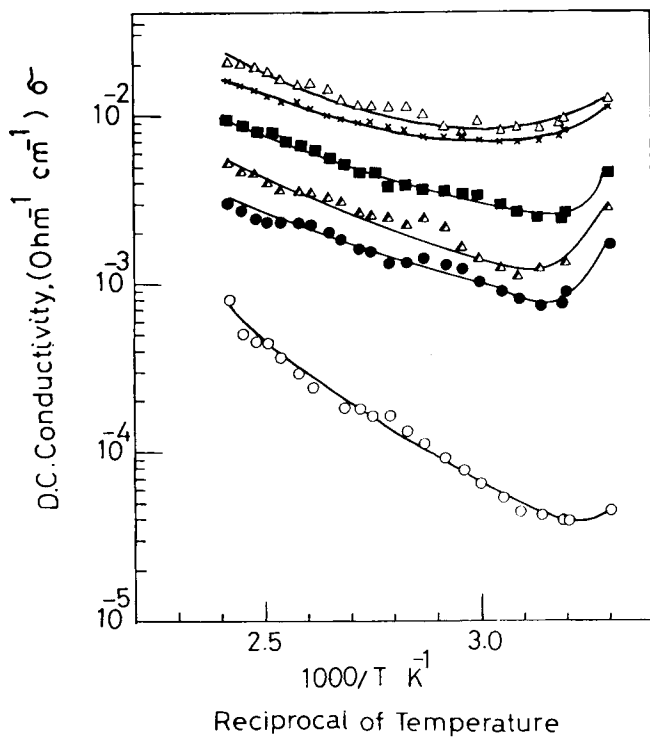


Fig. 5. Temperature dependence of  $\sigma$  for 90 FEF/SBR at different hydrostatic pressures ( $\text{kg}/\text{cm}^2$ ): (○) 0; (●) 5; (▲) 10; (■) 20; (△) 30; (×) 40.

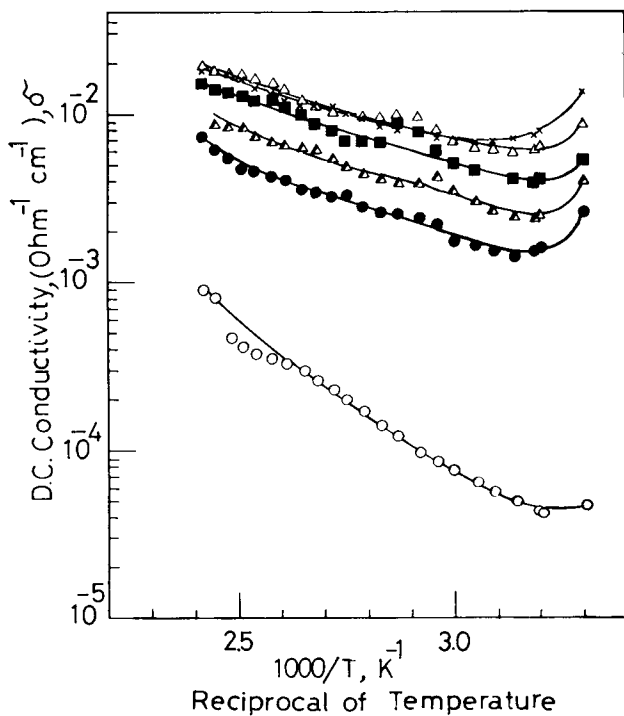


Fig. 6. Temperature dependence of  $\sigma$  for 100 FEF/SBR at different hydrostatic pressures ( $\text{kg}/\text{cm}^2$ ): (○) 0; (●) 5; (▲) 10; (■) 20; (△) 30; (×) 40.

TABLE III  
Change of the Activation Energy ( $E$ )<sup>a</sup> (eV) with the Applied Hydrostatic Pressure ( $P$ ) (kg/cm<sup>2</sup>) at Different Concentrations of FEF Carbon Black

$P$ (kg/cm <sup>2</sup> )	$E$ (eV)					
	30	50	70	80	90	100
0	0.17	0.64	0.29	0.16	0.11	0.14
5	—	0.48	—	0.12	0.07	0.06
10	0.78	0.36	0.24	0.12	0.06	0.08
20	0.79	0.39	0.13	0.09	0.07	0.08
30	0.91	0.34	0.05	0.074	0.07	0.069
40	0.97	0.33	0.06	0.08	0.06	0.05

<sup>a</sup>Calculated from the well-known formula  $\sigma = \sigma_0 e^{-E/kT}$ , where  $\sigma$  is the conductivity at a temperature  $T$ ,  $\sigma_0$  is a constant,  $k$  is the Boltzmann constant, and  $E$  is the activation energy in eV.

empirical formula could be suggested to correlate  $Q$  to  $P$  as follows:

$$C(Q - Q_\infty)(P - P_0) = 1$$

where  $C$ ,  $Q_\infty$ , and  $P_0$  are constants that depend on both the carbon black concentration and temperature,  $Q_\infty$  is the degree of swelling at infinite pressure, and  $P_0$  is a characteristic pressure after which no change of  $Q$  could be observed. The formula, of course, holds true only for values  $P$  greater than  $P_0$  which for this test piece are shown in Table IV.

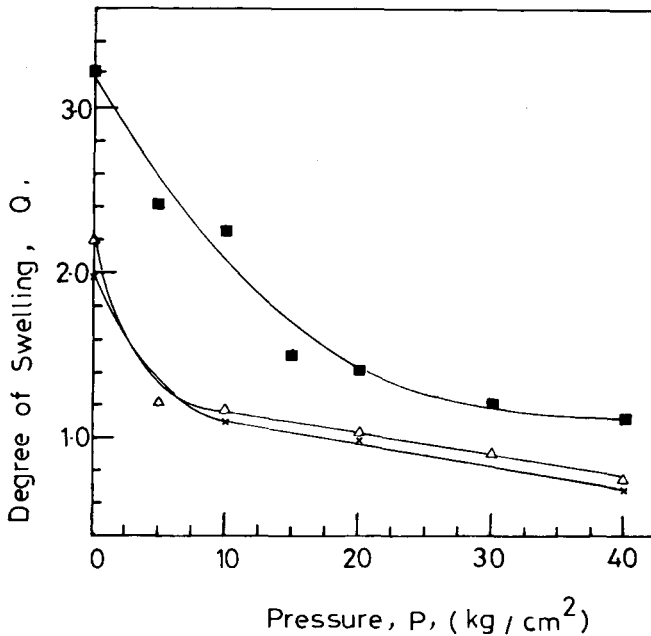


Fig. 7. Dependence of the degree of swelling ( $Q$ ) on the hydrostatic pressure ( $P$ ) for different concentrations (phr) of FEF/SBR unvulcanizates: (□) 50; (△) 70, (×) 90.



TABLE IV  
Value of the Constants  $Q_\infty$ ,  $P_0$ , and  $C$  in the Formula  $C(Q - Q_\infty)(P - P_0) = 1$ ,  
for Some Concentrations of FEF/SBR

Concentration of FEF (phr)	$P_0$	$Q_\infty$	$C$
50	15	1.10	0.59
70	12	0.60	0.23
90	10	0.55	0.19

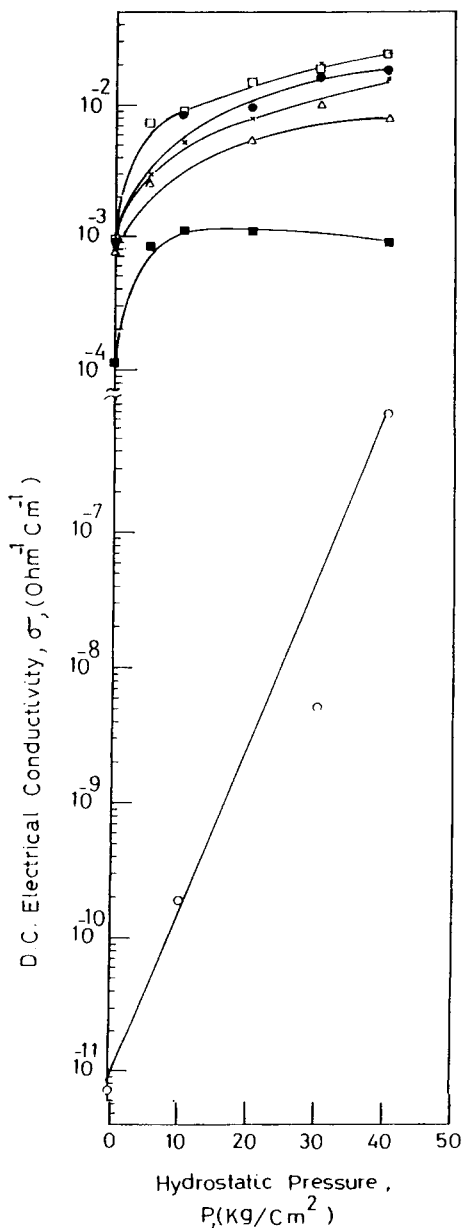


Fig. 8. Dependence of  $\sigma$  for all samples on the hydrostatic pressures: (○) 30 phr; (■) 50 phr; (△) 70 phr; (●) 80 phr; (×) 90 phr; (□) 100 phr.

TABLE V  
Variation of the Pressure coefficient  $K$  ( $\text{cm}^2/\text{kg}$ ) with the Different Concentrations  
of FEF/SBR at All Different Pressures

Concentration of FEF (phr)	$K_1$	$K_2$
30	0.010	—
50	0.019	$-3.67 \times 10^{-4}$
70	0.012	$1.44 \times 10^{-3}$
80	0.021	$3.58 \times 10^{-3}$
90	0.018	$3.95 \times 10^{-3}$
100	0.028	$3.50 \times 10^{-3}$

Another point of interest is the calculation of the thermal effect produced through these composites by the application of hydrostatic pressure. This could be indirectly calculated with the aid of the dependence of  $\sigma$  on the hydrostatic pressure ( $P$ ) (Fig. 8) and simple thermodynamic relations.

The pressure coefficient ( $K$ ) is defined as  $K = (1/\sigma) d\sigma/dP$  and largely depends on the FEF carbon black concentration, as is shown in Table V. As is obvious from Table V,  $K$  decreases with FEF concentration due to the relative instability of structure in the less conductive composites.

A simple calculation of the thermal effect of the hydrostatic pressure (for 70 FEF/SBR, e.g.) could be done using the simple thermodynamic equation:

$$\left(\frac{\partial T}{\partial P}\right)_\sigma = \left(\frac{\partial T}{\partial \sigma}\right)_P \left(\frac{\partial \sigma}{\partial P}\right)_T,$$

where  $(\partial T/\partial P)$  is the thermoelastic coefficient ( $L$ ), while  $(\partial \sigma/\partial T)$  and  $(\partial \sigma/\partial P)$  may be calculated from the slopes of Figures 4 and 8, respectively. A slight disagreement of our calculated values of the thermoelastic coefficient ( $L$ ) with that obtained by both Rodriguez<sup>16</sup> and Thomson<sup>17</sup> was detected for SBR samples (cf. Table VI).

This conflict may be due to the presence of FEF carbon black in our composites. Table VII represents the dependence of the thermoelastic coefficient  $L_\sigma = (\partial T/\partial P)_\sigma$  on the carbon black concentrations. It is clear that  $L_\sigma$  increases with FEF concentration.

Finally, a correlation between  $\sigma$  and hydrostatic pressure of FEF/SBR unvulcanizates is done and could be summarized as follows: Hydrostatic pressure tends to rearrange the carbon black particles insider the rubber mixture which leads to a clear increase in  $\sigma$  for all composites. There is a

TABLE VI  
Calculated Values of Thermoelastic Coefficient [ $L_\sigma = (\partial T/\partial P)_\sigma$ ] for 70 FEF/SBR  
and That Obtained by Rodriguez and Thomson for Pure SBR (at 413 K).

Pressure ( $P$ ) ( $\text{MN m}^{-2}$ )	Thermoelastic coefficient $L_\sigma$ calculated by		
	Thomson	Rodriguez	Nasr
0.1	0.15	0.34	—
4.0	—	0.14	4.10

TABLE VII  
Dependence of the Thermoelastic Coefficient  $L_{\sigma}$  ( $\text{K}/\text{MN m}^{-2}$ ) on the Concentration of FEF/SBR

Concentration of FEF (phr)	30	50	70	80	90	100
$\partial T/\partial P$	—	-0.35	4.1	5.1	5.4	7.5

general tendency for the greater changes in  $\sigma$  with the applied pressure and temperature to occur in the less-conducting samples ( $< 70$  phr of FEF black). A major change in  $\sigma$  occurs (at  $140^{\circ}\text{C}$ ) at the first 2 min of the vulcanization process. This is followed by a slight decrease of  $\sigma$  which then becomes constant after 20 min. Moreover, a new attempt to calculate the thermoelastic coefficient and compare the result with Thomson's thermodynamic techniques was done, which gives a fair agreement.

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