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Influence of static and cyclic compression on the electrical conductivity of FEF black-loaded rubbers

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Summary

The influence of static and cyclic compression on the temperature dependence of the electrical conductivity σ(T) of 100 phr FEF black-loaded rubber vulcanizates (SBR, NR, IIR, BR and NBR) has been studied. It was found that σ increases with static pressure for all rubber vulcanizates. The temperature coefficient of conductivity proved to be negative; its maximum value α ranges between -0.1 and -0.01 deg^{-1} depending upon the applied stress and type of rubber vulcanizate. The pressure coefficient of conductivity γ at room temperature varies with the static pressure from 0.78 to 0.04 $(kg/cm^2)^{-1}$. Menwhile, σ was found to decrease with the number and stress amplitude of the cyclic compressions, while α increases with the number of compression cycles.

1. Introduction

The correlation between electrical and mechanical properties is one of the major problems of carbon black-loaded rubber composites, since it has great impact on modern technological applications. It has been shown that pre-extension should certainly modify the distribution and arrangement of carbon black particles or aggregates in the rubber matrix[1]. This behaviour was interpreted in terms of the structure of the polymer and dispersed filler on the basis of an idealized model[2].

On the other hand, there is a strong evidence that static pressure largely affects electrical conductivity of SBR vulcanizate filled with different concentration of Fast Extrusion Furnace (FEF) black[3]. In a previous work[4] the effect of the strain amplitude and the number of strain cycles on the electrical conductivity of FEF black-loaded SBR vulcanizate has been studied.

The present work describes the influence of the static and cyclic compression on the electrical conductivity of several types of rubber: SBR, BR, IIR, NBR and NR loaded with FEF carbon black.

2. Experimental

Fast Extrusion Furnace (FEF) black was introduced into the investigated types of rubber namely: natural rubber (NR), butadiene rubber (BR), styrene butadiene rubber (SBR), butadiene acrylonitrile rubber (NBR), and butyle rubber (IIR) according to the recipe illustrated in Table (1). The test samples were prepared on a two roll mill 170 mm diameter, working distance 300 mm, speed of slow roll 18 rpm and gear ratio 1.4. The rubber composites were left for 24 hours before being vulcanized at 143 ± 2 °C under a pressure of about 40 kg/cm^2 for 30 minutes.

Test samples had the form of discs of radius 5 mm and thickness about 3.5 mm. The effect of static pressure P on the temperature dependence of electrical conductivity σ(T) was studied following a previously described method[3].

Table (1): Composition of the FEF black-loaded rubber composites.

Sample / Ingredients (phr)[a]	SBR	NR	IIR	BR	NBR
SBR-1502	100	-	-	-	-
NR	-	100	-	-	-
IIR	-	-	100	-	-
BR	-	-	-	100	-
NBR	-	-	-	-	100
Stearic acid	2	2	2	2	2
ZnO	5	5	5	5	5
Processing oil	10	10	10	10	10
FEF black	100	100	100	100	100
MBTS[b]	2	2	2	2	2
PBN[c]	1	1	1	1	1
S	2	2	2	2	2

a) Parts per hundred parts of rubber by weight
b) Dibenzthiazyl Disulphide c) Phenyl -β-naphthylamine

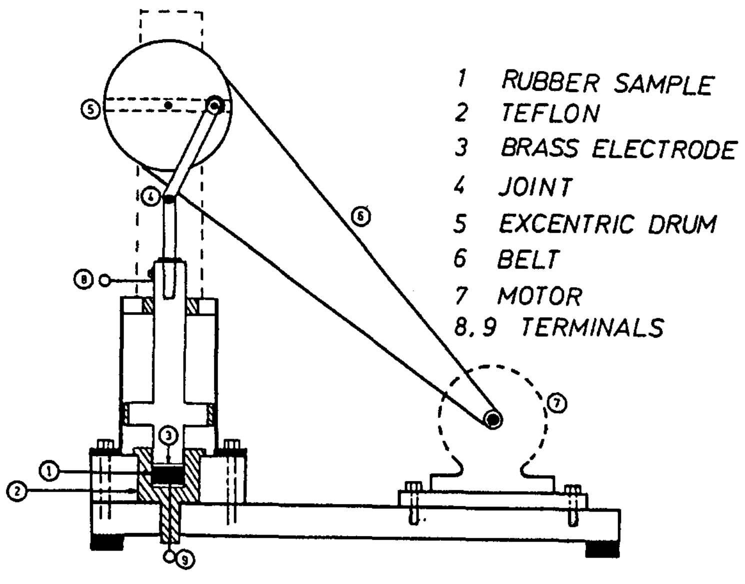

Fig. (1): Schematic diagram of the system used for cyclic compression of rubber samples.

Since variation of electrical properties of rubber with time in the presence of mechanical deformation represents an actual problem[5], it was necessary to leave the test samples for a sufficiently long time (about 24 hours) under the applied static pressure before carrying out the experimental measurements.

Cyclic compressions of the rubber samples were carried out at a constant number of cycles, frequency and stress amplitude using a locally made set up (see Fig. 1).

3. Results and Discussion

The effect of static pressure on the $\sigma(T)$ dependence for 100 phr FEF black-loaded rubber composites is represented in Fig. (2). One may observe that the electrical conductivity σ increases with static pressure P for all rubber samples. The increase of P leads to a decrease of the length of

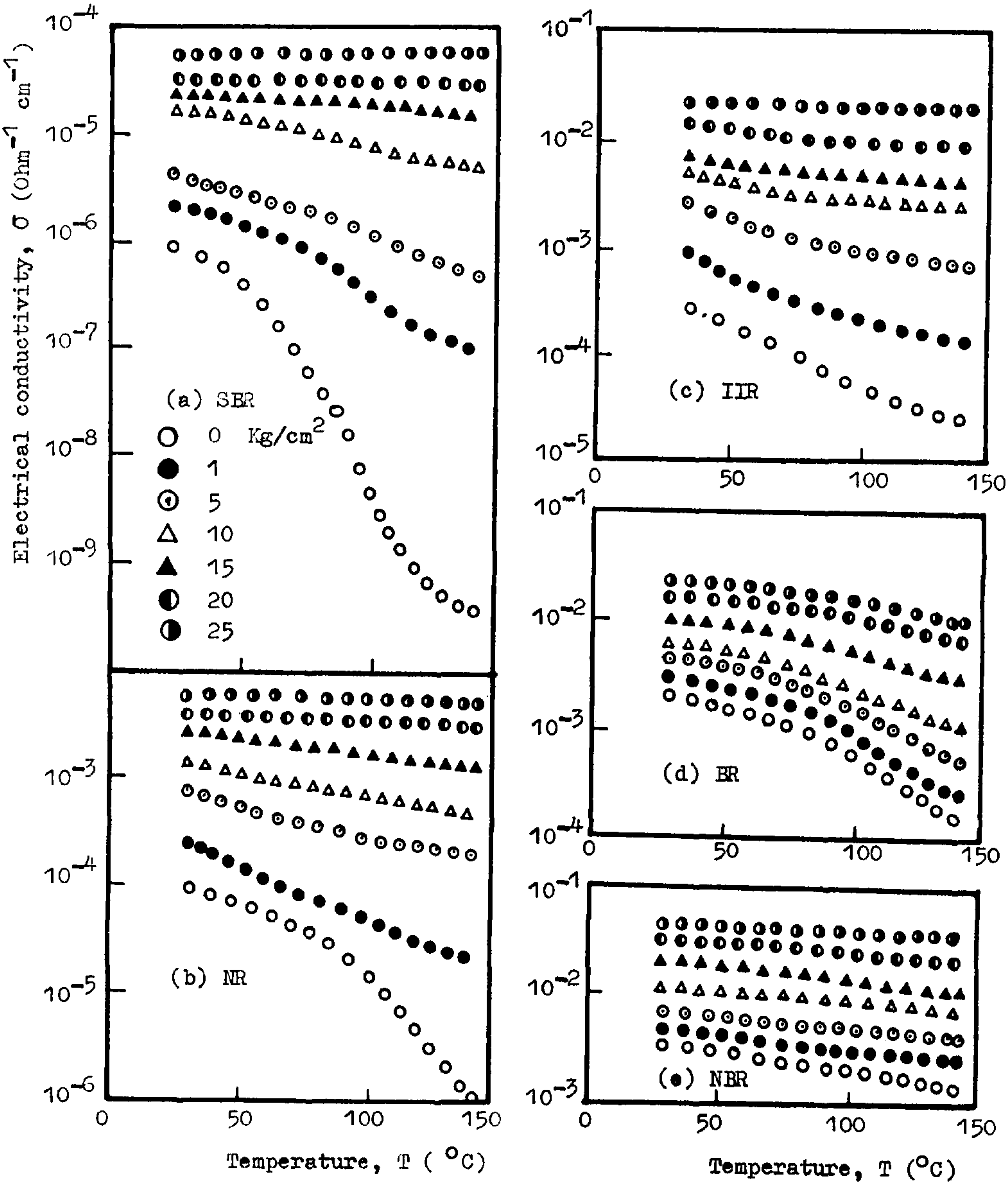

Fig. (2): Effect of static pressure on the $\sigma(T)$ dependence for 100 phr FEF black-loaded rubber composites. (a) SBR, (b) NR, (c) IIR, (d) BR, and (e) NBR.

hopping paths between carbon black particles or aggregates[6], and consequently to the observed rise in σ. However, at any given pressure, the increase of temperature causes these hopping paths to expand appreciably, causing the descending behaviour of conductivity with temperature. This would imply that pressure and temperature have opposite effects on conductivity, and hence the observed value of σ is determined by competition of these two mechanisms.

The maximum temperature coefficient of conductivity α has been calculated from the data of Fig. (2) for the investigated rubber composites at different values of the static pressure (Cf. Table 2). Calculations of α was performed in the temperature interval of maximum variation of σ with T.

Table (2): Variation of the maximum temperature coefficient of conductivity with static pressure P for the investigated rubber composites.

P (kg/cm^2)	$\alpha \times 10^3$ (deg^{-1})				
	SBR	NR	IIR	BR	NBR
0	-99	-61	-26	-35	- 9
1	-46	-25	-15	-30	- 7
5	-20	-13	- 6	-23	- 6
10	- 9	- 8	- 5	-18	- 5
15	- 5	- 6	- 5	-11	- 6
20	- 1	- 2	- 4	-10	- 2
25	0	- 1	- 1	- 9	- 1

Figure (3) represents the σ(P) relations at room temperature for the investigated rubber composites. This σ-P dependence can be divided into two regions (I) and (II) each of which being characterized by certain value of the pressure coefficient of conductivity γ [= (1/σ) dσ/dP] (Cf. Table 3).

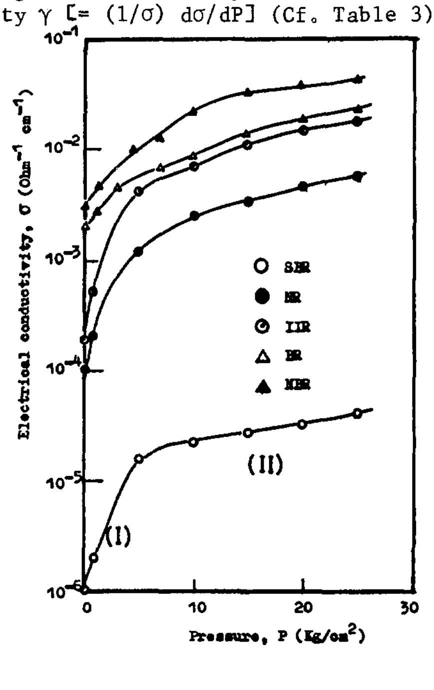

Fig. (3): Dependence of electrical conductivity σ upon static pressure P at room temperature.

Table (3): Calculated values of the pressure coefficient of conductivity (γ) for the investigated rubber composites at room temperature.

Sample	$\gamma \times 10^3$ $(kg/cm^2)^{-1}$	
	Region (I)	Region (II)
SBR	639	42
NR	767	51
IIR	776	63
BR	289	58
NBR	280	40

Figure (4) demonstrates the $\sigma(T)$ dependence at different values of static pressure for SBR and NR samples after being subjected to 100 compression cycles of stress amplitude (1 kg/cm^2) at a rate of about 3.4 cycles/second. A comparison of Fig. (2 a,b) with Fig. (4 a,b) indicates that cyclic compression of NR and SBR samples leads to a slight decrease of conductivity, probably due to an increase of the length of hopping paths between carbon particles or aggregates as they relax to more stable positions within the rubber matrix under the effect of the applied cyclic stress.

Table (4) summarizes the calculated values of TCC for SBR and NR composites after 100 cycles of compression. From this table one can notice that TCC decreases, in general, with cyclic compression.

Table (4): Variation of the temperature coefficient of conductivity α with the static pressure P after the samples have been subjected to 100 cycles of compression.

P (kg/cm^2)	$\alpha \times 10^3$ (deg^{-1})	
	SBR	NR
0	-130	-43
1	- 72	-53
5	- 30	-33
10	- 10	-17
15	- 7	-13
20	- 3	-11
25	- 2	-10

The fact that cyclic compression causes some decrease in the electrical conductivity of NR and SBR showed that it might be useful to study the effect of stress amplitude and number of compression cycles on the σ(T) relationship for the FEF/SBR sample; the results being illustrated in Fig. (5). As might be observed from this figure the temperature coefficient of conductivity increases as the number of compression cycles increases at a constant stress amplitude and decreases as the stress amplitude increases at a constant number of compression cycles (Cf. Table 5).

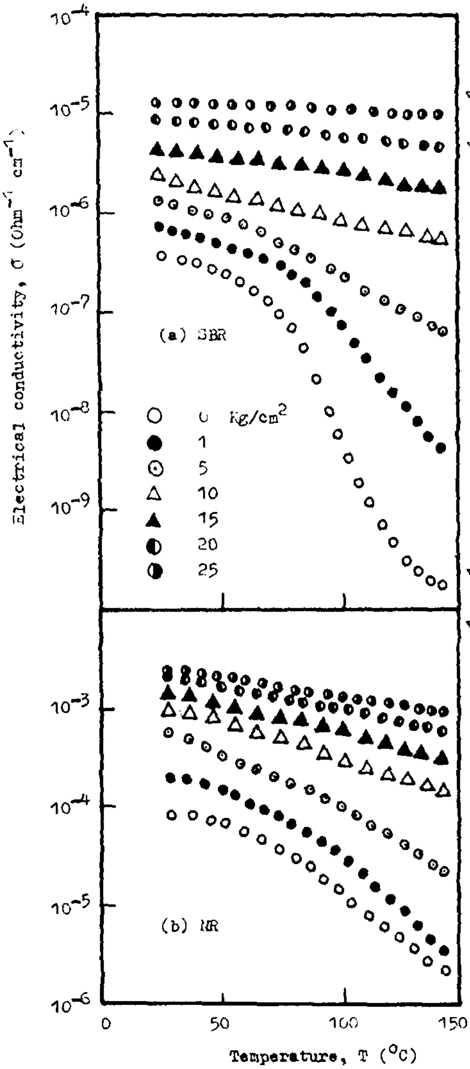

Fig. (4): The σ(T) dependence at different values of static pressure for rubber samples after being subjected to 100 compression cycles: a) 100 FEF/SBR and b) 100 FEF/NR.

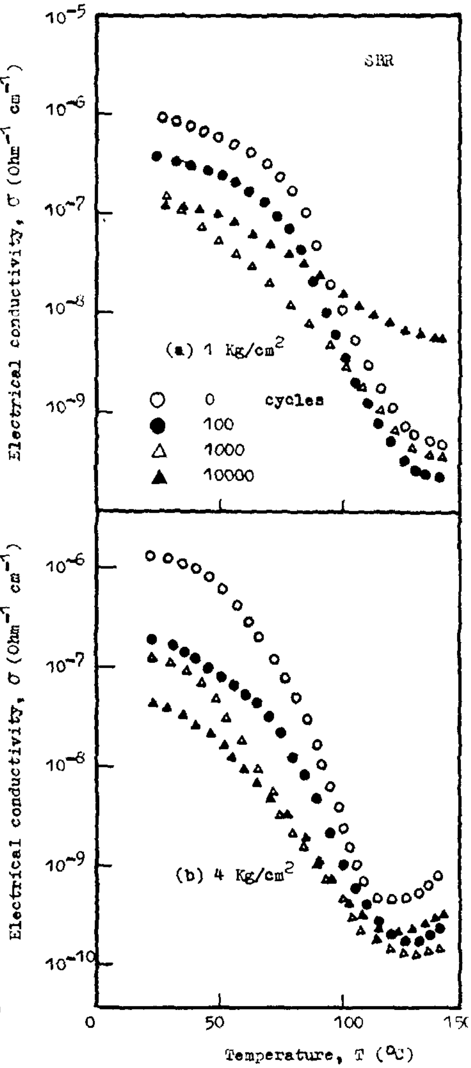

Fig. (5): Effect of stress amplitude and number of compression cycles on the σ(T) dependence for the 100 FEF/SBR composites: a) 1 kg/cm^2 and b) 4 kg/cm^2.

Table (5): Temperature coefficient of the conductivity (α) for 100 FEF/SBR sample at different numbers of compression cycles, N and stress amplitude A.

N	$\alpha \times 10^3$ (deg^{-1})	
	$A = 1\ kg/cm^2$	$A = 4\ kg/cm^2$
0	-150	-150
100	-130	-137
1000	- 66	- 91
10000	- 43	- 75

Such a behaviour of σ and TCC may be interpreted as a consequence of an increase of the percentage breakdown of carbon black structure under the effect of the applied cyclic compression.

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