Effect of Preextension on Electrical Conductivity and Physicomechanical Properties of Butyl Rubber (IIR) Loaded with Different Types of Carbon Black

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SYNOPSIS

The effect of preextension on the variation of the electrical conductivity (σ) of butyl rubber (IIR) loaded with high abrasion furance (HAF) and fast extrusion furance (FEF) carbon black with carbon concentration have been investigated. The change in σ has been explained as a result of the interaction between carbon and rubber and the effect of the occluded rubber.

The effect of preextension on the electrical resistivity (ρ) variation with strain has also been studied. The changes have been interpreted as being due to either breakdown or reagglomeration, depending on the concentration of carbon black.

INTRODUCTION

The reinforcement of rubber with particulate filler is a process of practical and technological importance. Carbon has been used as reinforcing agent in rubber-like materials for many years. In recent years, special grades of carbon black have been developed that serve the purpose of not only reinforcing these materials but also importing to them some electrical conductivity. However, understand exact mechanisms that are responsible for this reinforcing action and greatly increase electrical conductivity is still far from complete. Both reinforcing and electrical conductivity processes are closely related and increased knowledge of one will aid understanding of the other. The reinforcing action of fillers has been discussed in a series of theoretical papers. Past studies of electrical conductivity produced in rubber by carbon black have shown that the specific resistance of rubber compound is mainly due to the length of rubber chain. Stretching of loaded particles depends on the length of rubber molecules. Accordingly, the electrical and mechanical properties are greatly affected by such stretching.

In this work, we study the effect of preextension on the electrical resistivity and the physicomechanical properties. We have tried to correlate the change in resistivity with the change in the separation distance between carbon aggregates.

EXPERIMENTAL

Samples of butyl rubber (IIR) loaded with two types of carbon blacks (HAF and FEF) were prepared according to Table I. The method of preparation has been described before.[1] The samples used for testing were in dumbbell shape with width of 6 mm, thickness of 2 mm, and length of 60 mm. All samples studied in this work were vulcanized at $150 \pm 2°C$ under pressure of 40 kg/cm^2 for 30 min. Table II gives some specifications of the used carbon black. Figure 1 illustrates the set-up used for measuring the variation of the electrical resistivity with strain. All samples were thermally aged at 90°C for 35 d to attain reasonable stability and reproducibility.

RESULTS AND DISCUSSION

Effect of Preextension on the Variation of σ with Concentration of Carbon Black

Figure 2 shows the variation of σ with carbon black concentration (c) in phr for HAF and FEF com-

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Table I Composition of IIR Sample Containing HAF and FEF

Ingredients	phr[a]
IIR	100
Stearic acid	2
Zinc oxide	5
Processing oil	10
HAF	Variable 30–100
FEF	Variable 40–100
MBTS[b]	2
PBN[c]	1
Sulphur	2

[a] Parts per hundred parts of rubber.
[b] Dibenz thiozyle disulphides.
[c] Phenyl β-naphthylamine.

posites after preextension (100% elongation for five times) at room temperature. It has been found that the conductivity for FEF composites follows an exponential increase with c. Concerning HAF composites, σ has N shape. The first part extends from 30–60 phr, which represents a moderate range of concentration. The middle parts covers the range between 60 and 80 phr. The last region extends to 100 phr.

Figure 3 presents the variation of the elastic modulus (E) with c for both HAF and FEF composites. This behaviour has been explained before.[3] Both Figures 2 and 3 have the same features. This leads us to believe that the factors affecting both σ and E are the same: the interaction between rubber and carbon black and the occluded rubber. These factors affect the separation distance between the carbon aggregates and hence σ in the following manner. The physical interaction leads to an increase in the crosslink density.[4] As the crosslink density increases, more entanglements of rubber are trapped inside the network. This leads to the decrease in the separation distance between carbon aggregates. The chemical interaction improves the interficial adhesion and wetting.[4] The wetting and the adhesion between carbon and rubber may play an indirect role in the reduction of the separation
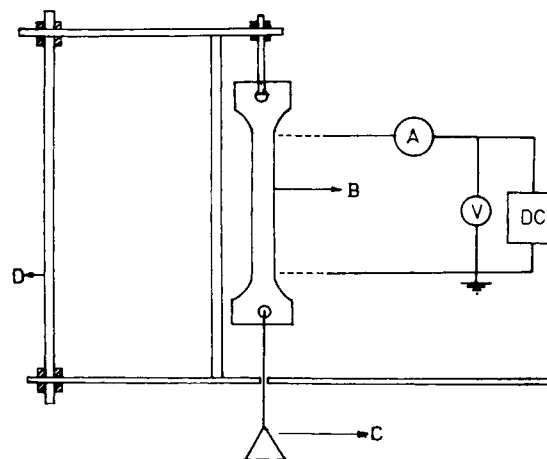

Fig. 1

DC : 0-400 volt regulated DC voltage supply.
V : DC voltmeter.
A : Picoameter.
B : Specimen.
C : pan for using different loades.
D : Holder

Figure 1 Set-up used for measuring the variation of the electrical resistivity with strain.

distance between carbon aggregates. As the chemical interaction decreases above 60 phr for HAF composites,[5] a sudden drop in σ is observed at 70 phr. On the other side, the occluded rubber, which is partly shielded from deformation and acts as a part of filler rather than a part of matrix,[6] may also be shielded from conduction processes. So, the occluded rubber plays an indirect role in the decrease of the separation distance between carbon aggregates by increasing the effective filler concentration and decreasing the contribution of the soft phase (rubber) to the conduction processes. Therefore, the effect of the occluded rubber on σ and E is known as the shift factor (a). According to Medalia,[7] the shift factor is a linear function on the structure (A) of the carbon black and is given by

$$a = 1 + 0.02139 \, A/1.46, \qquad (1)$$

where A is in cc/100 g.

Table II Specifications of the Used Carbon Black[2]

Carbon Black	ASTM Designation	Particle Diameter (Å)	Surface Area (m²/g)	DBP[a] (cc/g)
HAF	N330	290	80	1.05
FEF	N550	360	55	1.34

[a] Dibutyl phthalate absorption.
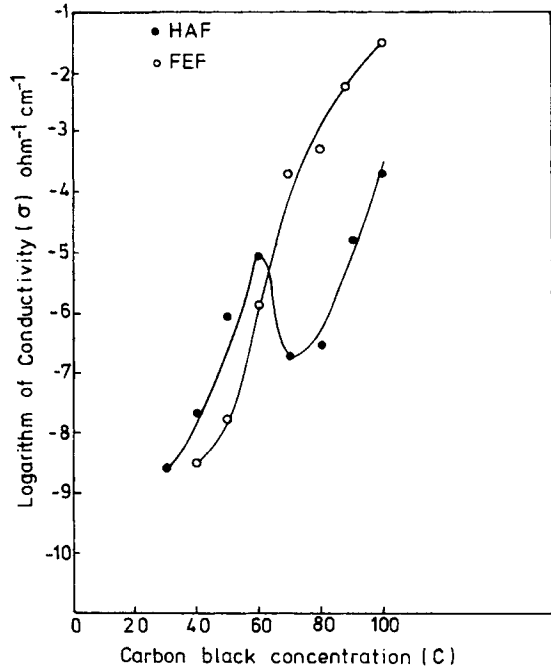
Figure 2 Variation of logarithm of conductivity (σ) with carbon black concentration c (phr) for HAF and FEF composites.
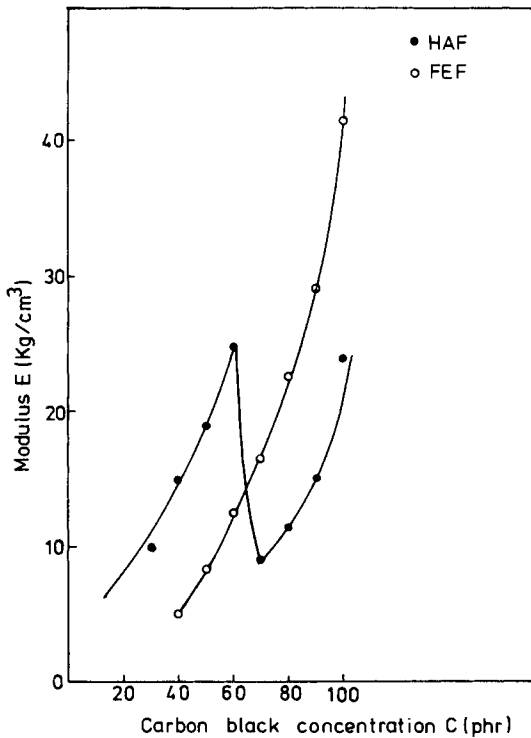
Therefore, the effective filler concentration (C_{eff}) is ac instead of c.

Consider the equation used for calculating the separation distance (D)[8] which is:

$$D = r[4/3\pi)^{1/3}(1 + 200/c)^{1/3} - 2], \quad (2)$$

where r is the radius of carbon particle or aggregate. One can use $C_{eff} = ac + K$ instead of c in eq. (2). So we have

$$D = r[(4/3\pi)^{1/3}(1 + 200/ac + K)^{1/3} - 2], \quad (3)$$

where K is a constant dependent upon the type of the used carbon black. Equation (3) is used to calculate D.

Figure (4) shows the variation of ρ after previous elongation and the calculated D with c for both HAF and FEF composites at room temperature. The value of K that can fit D with ρ is found to be numerically equal to the surface area of the specified carbon black. For HAF composites with concentration above 60 phr, the constant $K = 0$. This may be due to the fact that over 60 phr the interaction between HAF and rubber shows a pronounced decrease.[5] This means that the surface area has no contribution in the calculated D above 60 phr, while the occluded
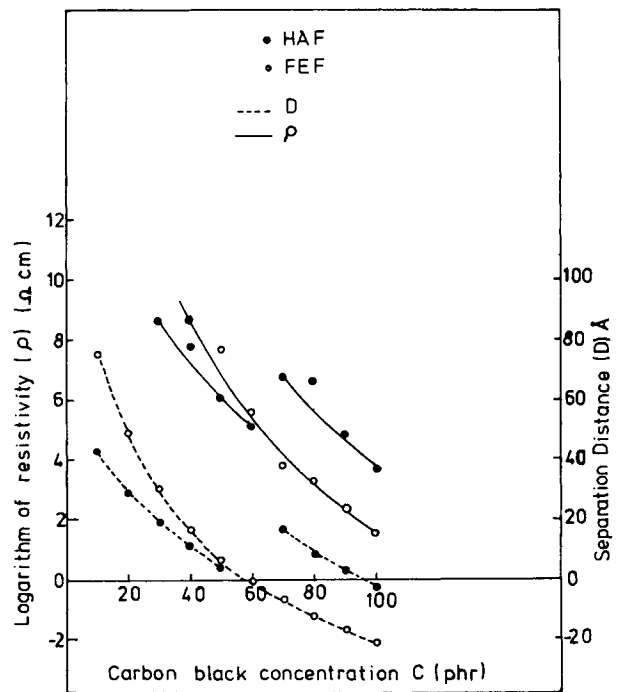

Figure 3 Modulus dependence on carbon black concentration c (phr) for HAF and FEF composites.

Figure 4 Change of logarithm of resistivity (ρ) and separation of distance (D) with carbon black concentrtion c for HAF and FEF composites.

rubber continues. So ρ shows an increase at 70 phr for HAF composites. The solid curves tend to intersect at 60 phr, as do the broken curves. This intersection corresponds to $D = 0$, which means that the carbon aggregates are in touch for both HAF and FEF composites at 60 phr. The contribution of the surface area and occluded rubber in the reduction of D will continue to higher concentration for FEF composites. For composites with FEF concentration higher than 60 phr, D has negative values. This may be due to the overlapping of FEF aggregates to form large agglomerates. These agglomerates suffer from intensive breakdown at relatively high temperature.[9] The highly loaded composites of HAF carbon black from 70 to 100 phr, which show a poor reinforcement, also show a relatively high resistivity values. This may be due to the fact that the secondary agglomerates of HAF carbon black that are prominent in highly loaded compounds suffer from breakdown with previous extension.

Accordingly, we can conclude that there is a good agreement between the estimated value of D and the experimental value of ρ. This leads us to believe that there is a correlation between E and σ. This means that the structure and surface area of carbon black that combines to give best reinforcement also combines to give good electrical conductivity. It is
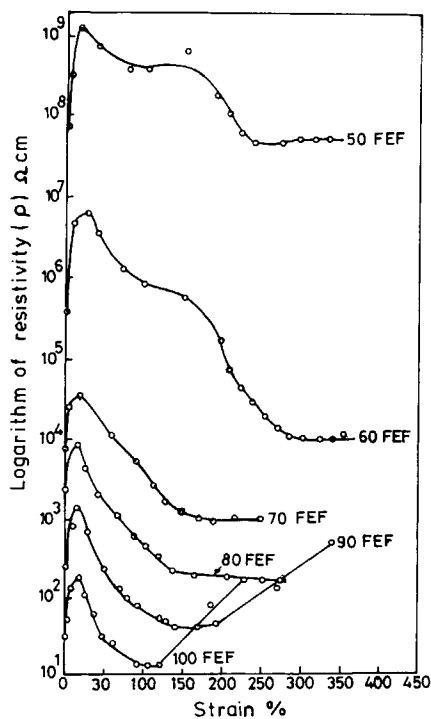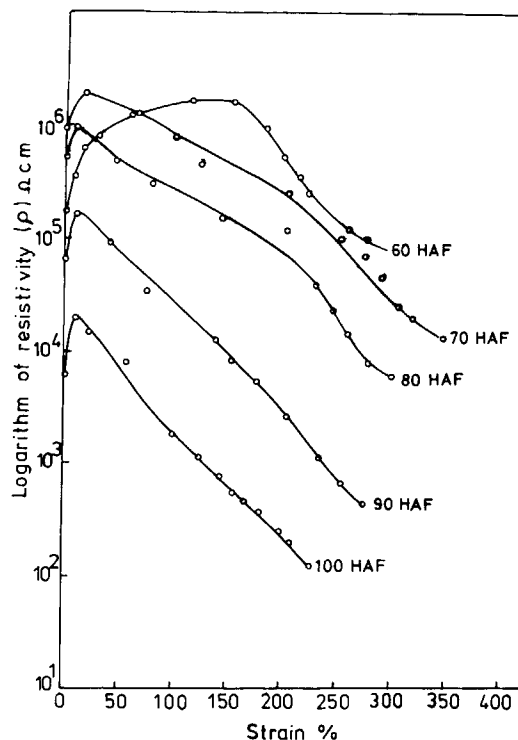

Figure 6   Variation of logarithm of resistivity (ρ) with strain for HAF composites.

noticed that the values of D obtained in this work are more reasonable than those calculated by Verhelst and coworkers.[10]

Effect of Preextension on the Variation of the Electrical Resistivity with Strain

Figure 5 shows the effect of previous elongation (100% for five times) on the variation of the electrical resistivity with strain for FEF composites at room temperature. We notice that the maximum resistivity ρ_m occurs at strain value about 20% for all concentrations. This means that the strain required to begin orientation of the rubber molecules is independent of concentration of carbon black. The constant resistivity level reached at the end of the orientation of rubber molecules for concentrations from 50 to 80 phr may be due to the counterbalance between two processes: the breakdown and reagglomeration of carbom agglomerates during extension.[11,12] These two processes have opposite effects on the resistivity; while the breakdown tends to increase ρ, we find that reagglomeration leads to decrease ρ and the result is a constant resistivity with strain, as shown in Figure 5. As the carbon black concentration increases above 80 phr, the number of carbon agglomerates increases and the probability

Figure 5   Variation of logarithm of resistivity (ρ) with strain for FEF composites.

of breakdown of these agglomerates is greater than the probability of reagglomeration with extension. Therefore, the range of constant resistivity decreases with increasing concentration. The sudden increase in ρ for concentration 90 and 100 phr may be explained as follows. At high elongation, the particles of carbon black inside carbon aggregates are forced to move against each other. This frictional motion leads to production of heat. The result is that occluded rubber inside the aggregates will diffuse over some of the broken carbon—carbon aggregates. This prevents carbon—carbon aggregates from approaching each other sufficiently to form carbon agglomerates, and the resistivity will again increase. We may expect the same behaviour for lower concentration at higher values of extensions. The temperature dependence of the electrical conductivity for 90 and 100 phr of FEF composites shows a fast decrease in σ above certain temperatures. This was attributed to the intensive breakdown of carbon agglomerates at a relatively high temperature.[9]

Figure 6 shows the variation of the electrical resistivity (ρ) with strain for HAF composites for concentrations between 60 and 100 phr at room temperature. The general feature of these curves are an increase in ρ at low strain followed by a decrease at a certain value. The behaviour of 60 phr composite may be attributed to the fact that this composite is characterized by the best reinforcement.[3] So, its carbon agglomerates have a great tendency to resist the breakdown with extension, i.e., the reagglomeration with extension is more pronounced than the breakdown processes in highly loaded compounds, which are characterized by a poor reinforcement. The maximum resistivity is obtained at strain 12.5%. The decrease in ρ may be explained as follows. HAF carbon black has a small particle size (290 Å) and hence small agglomerate size compared with FEF aggregate size. Since the smaller the agglomerate size the higher is resistance to extension breakdown, the reagglomeration of HAF black with extension is higher than the breakdown. Therefore, the constant resistivity level observed at relatively high ex-

tension for FEF composites was not observed for HAF composites. The increase in the electrical resistivity followed the constant resistivity level observed for composites 90 and 100 phr of FEF black and not observed for the same concentration of HAF black. The temperature dependence of the electrical conductivity for HAF composites of concentration 90 and 100 phr show a slight decrease in the electrical conductivity with temperature.[9] This may be attributed to a slight breakdown of HAF agglomerates with temperature. Therefore, we concluded that HAF carbon black tends to form agglomerates that have a high resistance to breakdown either by extension or temperature.

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