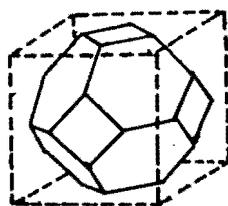


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INFLUENCE OF STATIC CYCLIC COMPRESSION ON THE ELECTRICAL CONDUCTIVITY OF CONDUCTIVE TERNARY RUBBER VULCANIZATES

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The effect of static cyclic compression on the electrical conductivity, σ , of a new conductive ternary rubber vulcanizates (based on NR, SBR and IIR) is discussed. There is a fluctuation of σ , upon loading and unloading due to breakdown and alignment of the filler chains in the direction of strain. Moreover, most samples show a slight hysteresis effect upon repeating cycles. The interspacing distance between carbon black aggregates is calculated on the basis of a previously suggested model.

Introduction

One of the major problems of polymer science is the complete analysis of the composition, structure and the correlation between these factors and the physical properties of a given polymer.

In tire industry, good dispersion of carbon black in the rubber matrix is very important to obtain optimum mechanical properties of the compound [1]. If it is desired to control the degree of dispersion of rubber compounds during the different processes in the factory, it would be necessary to have a simple and rapid test to do it. This may be achieved through the measurement of the electrical conductivity of the rubber compound with dc [2] or ac [3,4].

In recent years, different factors that affect the conductivity of the rubber compounds were studied in several research programs. The external factors include mixing level [2], pressure [5,6], temperature [7], ageing and contact resistance [4,8].

One of the goals of materials research is to create new materials with physical properties tailored to a particular application and to understand the physical mechanisms which determine their properties.

It is the purpose of this paper to study the influence of both step pressure and static cyclic compression on the electrical conductivity of a new tri-block rubber based on natural rubber (NR), styrene butadiene rubber (SBR) and butyl rubber (IIR). The results were analyzed by a model proposed by Fernandez et al [9].

Experimental Work

Material Used :

Natural rubber (NR) was mixed with different amounts of styrenebutadiene rubber (SBR-1502) and Butyl rubber (IIR) and each mixture was loaded with (40 phr) of high abrasion furnace (HAF) carbon black. All samples were prepared according to standard recipe and are presented in Table (1). The materials are arranged in the same order in which they were used during preparation. Two vulcanizing agents (sulphur and TMTD) were separately used to study their effects on the detected properties of the studied vulcanizates.

Sample Preparation Technique

The compounds were mixed in a laboratory size mixing mill at a friction - ratio of 1 : 1.19 according to ASTM D 3182, by careful control of temperature, nip gap, time of mixing and uniform cutting operation, the temperature range for mixing was 60-80 °C. The order and time period of mixing were as follows :

- 0 - 3 min. - Mastication of NR
- 3 - 6 min. - Addition and Mastication of the other two rubbers
- 6 - 9 min. - Addition of 1/3 filler plus 1/3 oil.
- 9 - 14 min. - Addition of 1/3 filler plus 1/3 oil.
- 14 - 20 min. - Addition of remaining filler and oil.
- 20 - 29 min. - Addition of other ingredients.
- 29 - 30 min. - Refining through tight nip gap and dump (the nip gap was 1.5 mm).

After mixing, the rubber compositions were molded in an electrically heated hydraulic press to the optimum cure (90% of maximum cure) using molding conditions

previously determined from torque data obtained by Monsanto rheometer (R - 100).

Measuring Systems

The rubber samples were left for 50 days at 70°C in an electrical oven to ensure accelerated ageing and consequently reproducibility of results. The vulcanized test specimens had the form of discs of radius 0.6cm and thickness of about 0.17 cm.

A simple device was used to carry out the measurements of d.c. conductivity, while the samples being under different amounts of precompression (hydrostatic pressure), described elsewhere [6]. It is to be noted that, there was no pressure release at all, because all samples have been subjected to pre-compression and then clamped using a screw bolt, until a new value of pre-compression was established.

The volume changes during pre-compression did not exceed about 0.24% (which are taken into account during the calculation of electrical conductivity (σ)).

A regulated electric oven was used to control the sample temperature ranging from (20-149 °C) with an accuracy ± 1 °C. A digital electrometer was employed in the case of lower voltage conductivity measurements. In a high - resistance circuit electric noise must be eliminated. This is accomplished by using coaxial cables, metal shielding, and common ground loops.

Results and Discussion

It has already shown that the electrical conductivity of carbon black filled composites falls sharply above a certain range of black concentration [10,11]. The composite conductivity at this critical concentration is much more sensitive with respect to physical changes than in the case of high as well as low conductive compounds. This is the reason behind our choice of 40 phr from high abrasion furnace (HAF) black for this study.

I - Effect of Static Cyclic Compression on the Electrical Conductivity of Conductive Ternary Rubber Vulcanizates :

Conductive compounds filled with carbon black but based on different elastomers vary in their sensitivity to strain. A good dispersion of carbon black in the rubber matrix is very important to obtain optimum mechanical properties of the compound [1]. An appropriate method to detect the different degrees of dispersion is based on the measurements of the electrical conductivity of the rubber compounds [3,4,12].

Many works have been devoted to get an article which has reasonable reproducibility of properties under any working circumstances, e.g. loading and unloading. It was thus thought necessary to study the effect of cyclic compression on the electrical behaviour of the above mentioned ternary rubber composites.

In addition to the measurements quoted previously which all refer to the effect of physical ageing and swelling measurements [13] on the electrical properties of these vulcanizates, measurements have been made during and after subjecting the same previous test pieces to considerable number of static compression cycles. Strains were calculated using the original dimensions of the specimens.

The test pieces were first loaded discontinuously every 5-minutes and the conductivity being measured after one-minute and before further increase. After the ultimate load was reached, the test pieces were progressively unloaded and measurements were made in a similar manner. At zero load the test pieces were allowed to rest for 5 minutes and the cycle was repeated.

The results of such cycles for the different samples of the two vulcanizing agents are shown in Figure (1).

The general features of the above figures could be summarized as follows :-

There is fluctuation of σ upon loading and unloading due to breakdown and alignment of the filler chains in the direction of strain . In fact during the first compression of the rubber strip, the electrical conductivity slightly decreases, which is usually accepted as being due to the breakdown of the filler chains. Such breakdown would compensate for further alignment of the filler chains. During unloading, σ , also increases due to the alignment of the carbon chains. During further cycles of the same sample, the breakdown and reorientation in the filler structure takes place during both compression and retraction.

So, the effect of hydrostatic pressure on the conductivity is relatively small, as might be anticipated, since the pressure induced deformation is vary small. Moreover, most samples show a slight hysteresis effect upon repeating cycles.

With a lower IIR concentration for both groups (<10 phr for TMTD group and <20 phr sulphur group), the hysteresis is small owing to the fact that butyl rubber is less sensitive to oxidative ageing than SBR and NR, so it becomes soft rather than brittle on oxidative degradation owing to its low unsaturation [13]. However, in the case of pure hydrostatic pressure the strains are generally small, and there is no shear component. Thus, the effect is to force the carbon black particles into more intimate contact.

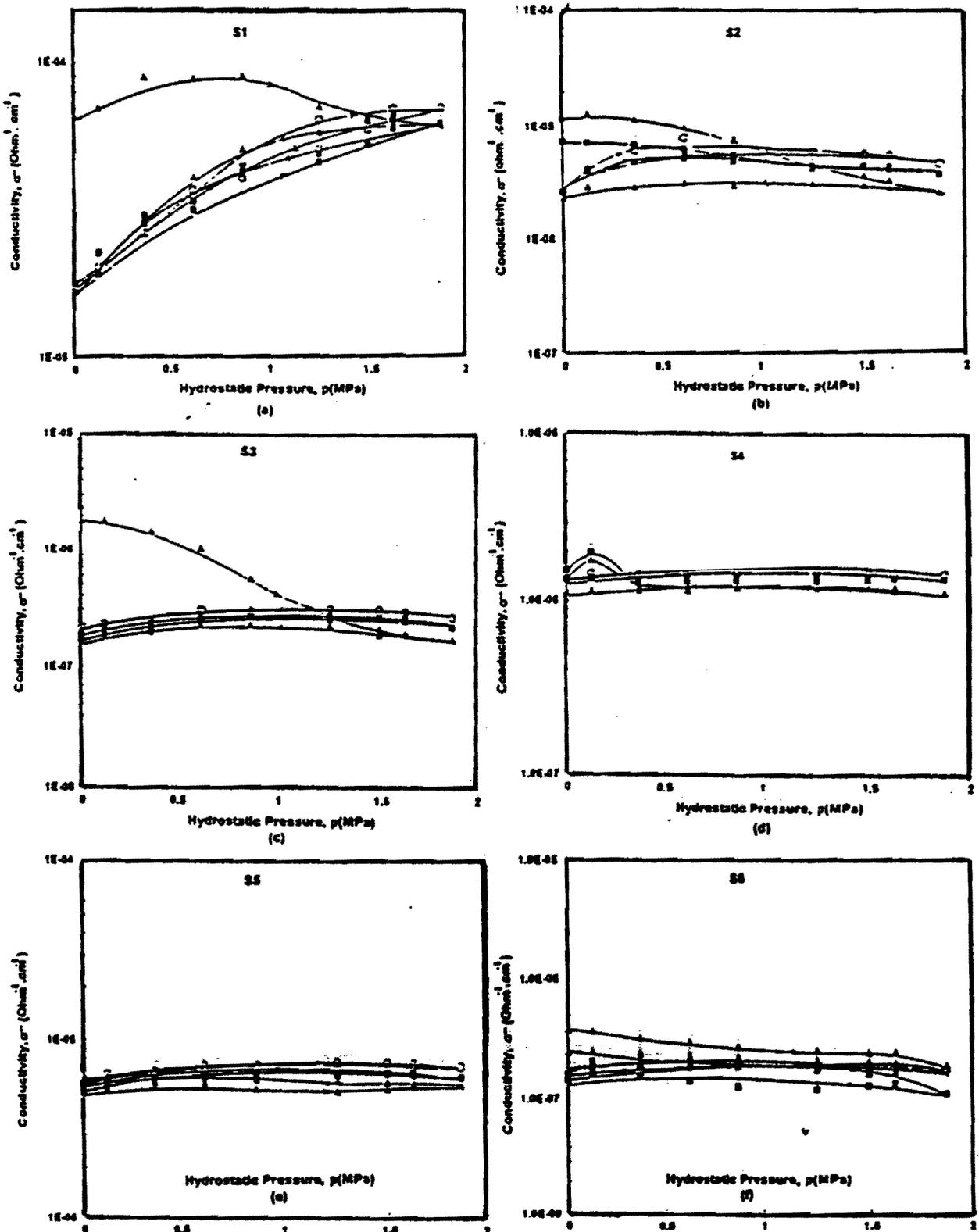


Figure (1) : Dependence of σ on the static cyclic compression (at 30 °C) for samples in group A :

- (a) S₁ (b) S₂ (c) S₃
 (d) S₄ (e) S₅ (f) S₆

- Δ 1st cycle \blacksquare 2nd cycle
 \circ 3rd cycle $*$ 4th cycle

It is clearly noticed that the hysteresis for all samples attains equilibrium after a definite number of cycles. (3 - cycles for 0,20 and 30 phr and 4 - cycles for 10 phr of IIR for samples in group A and 4 - cycles for 0 phr, 3-cycles for 10,30,40 phr and 2 - cycles for 20 phr of IIR content for samples in group B).

The above samples were exposed to repeated measurements to elucidate the effect of cyclic strain on the behaviour of σ versus T curves, Figures (2,3).

The molecular orientation develops vigorously on static cycles, along side softening and the fact that the polymer can not attain equilibrium after the release of the strain are responsible for the less sensitivity observed in the dependence of σ for all samples (except samples S_1 , S_4 , S_6 , S_8 , S_{10}).

The conduction mechanism does not change appreciably for all samples with static cyclic strain except for samples (S_6 0 phr of IIR group A and S_{10} 0 phr of IIR for group B). The mechanism of conduction change from the activated one to a descending behaviour for S_{10} and vice versa for sample S_6 , which reflect the important role of IIR for maintaining the conduction mechanism.

II - Effects of Pressure Steps On The Electrical Conductivity :-

Figure (4) represents an example for the changes of σ for sample (S_4) with time at different accumulative pressure steps (0.62 , 0.87 and 1.25 MPa) at room temperature (300 K). When pressure over the sample was increased, there was an increase in conductivity. This fact was also found in vulcanized rubber by Thompson, Besuden and Beumel [5], they suggested that the mechanism of this effect is the formation of

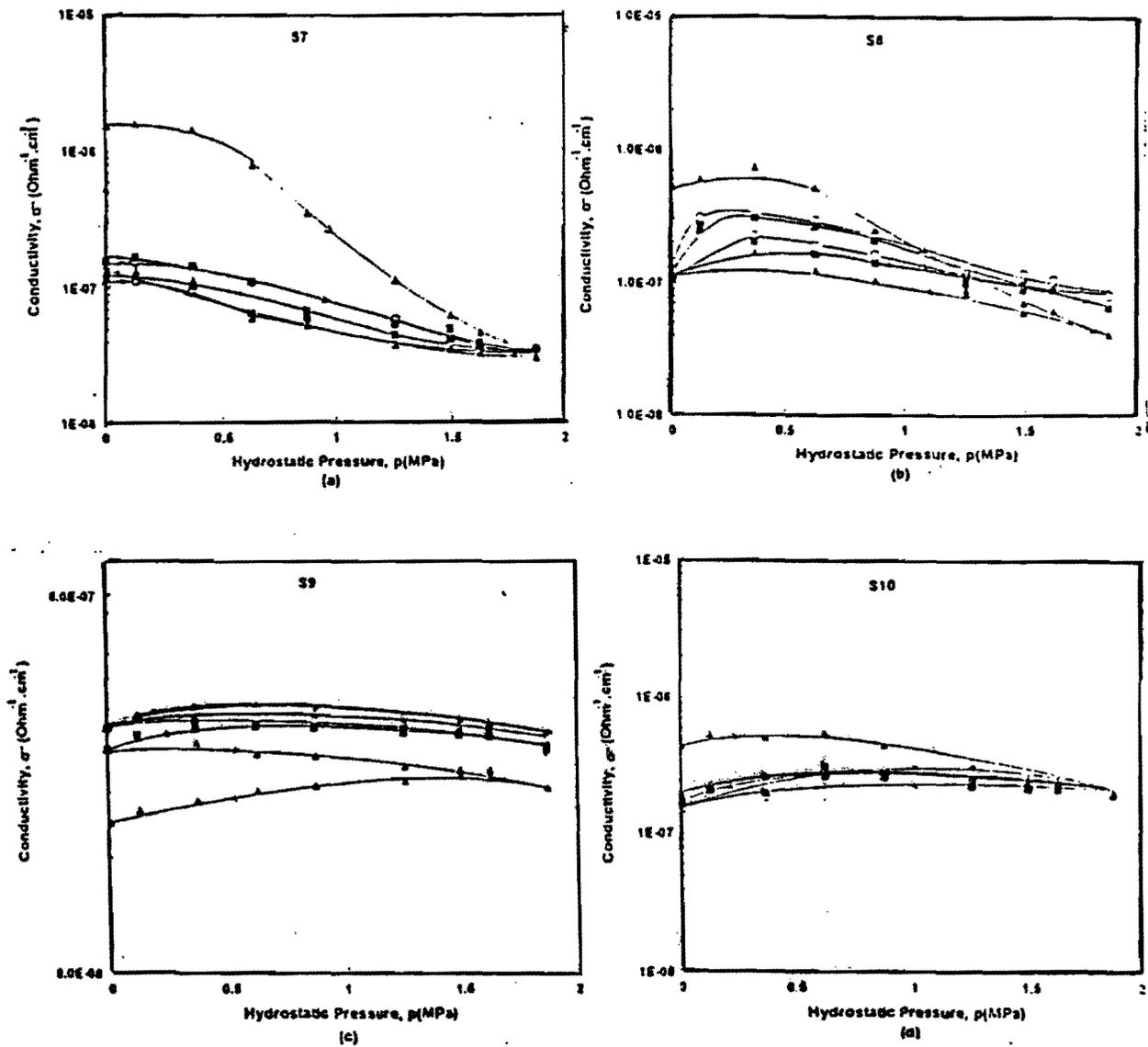


Figure (2) : Dependence of σ on the static cyclic compression (at 30 °C) for samples in group B :

- (a) S₇ (b) S₈
 (c) S₉ (d) S₁₀

Δ 1 st cycle

○ 3rd cycle

■ 2 nd cycle

* 4th cycle

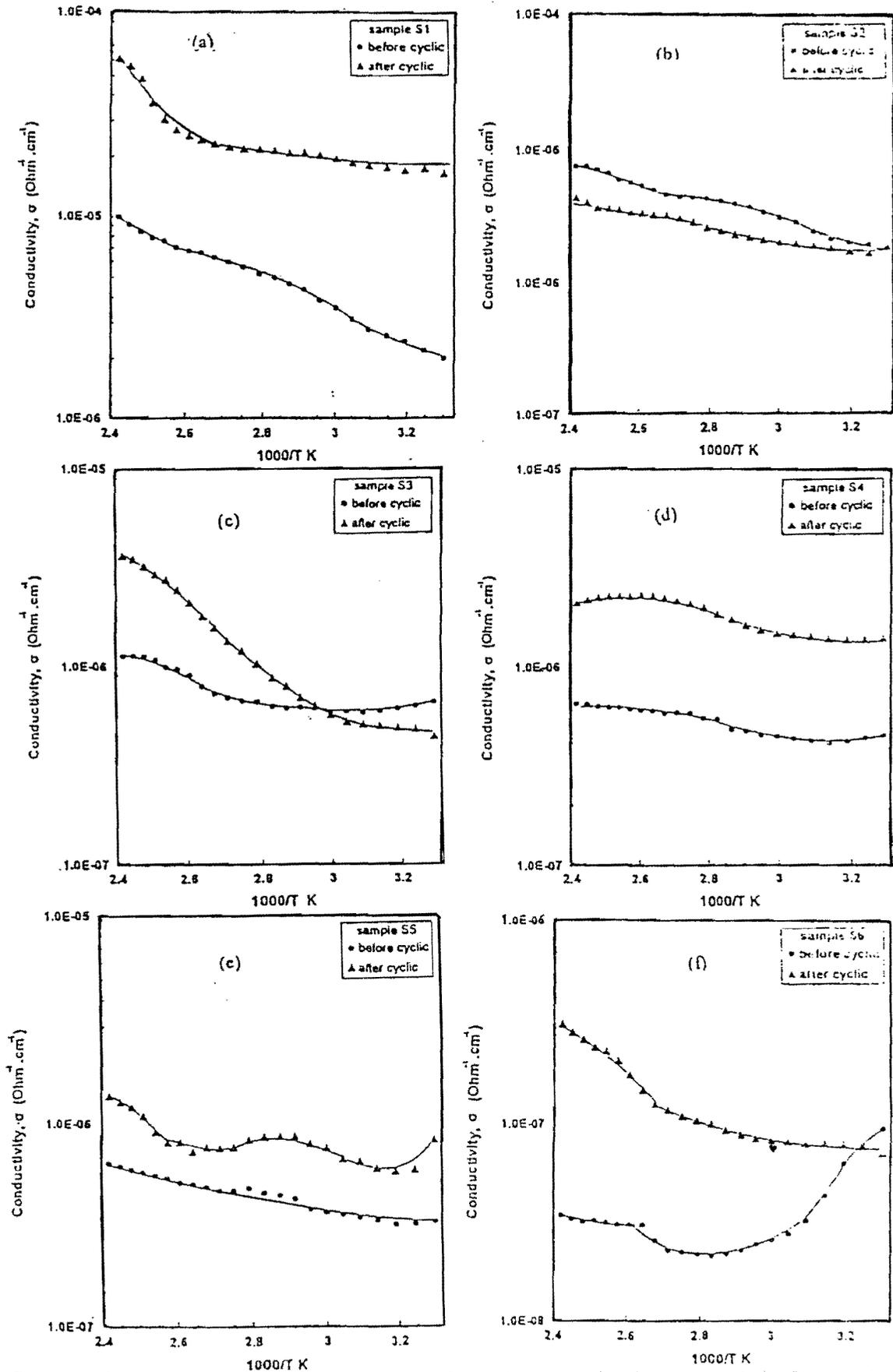


Figure (3) : Temperature Dependence of σ for samples in group A before and after static cyclic compression :
 (a) S_1 (b) S_2 (c) S_3 (d) S_4 (e) S_5 (f) S_6

change in σ when a pressure step is made over the sample at constant temperature and compoision [9]. Using equation (1), it is easy to obtain.

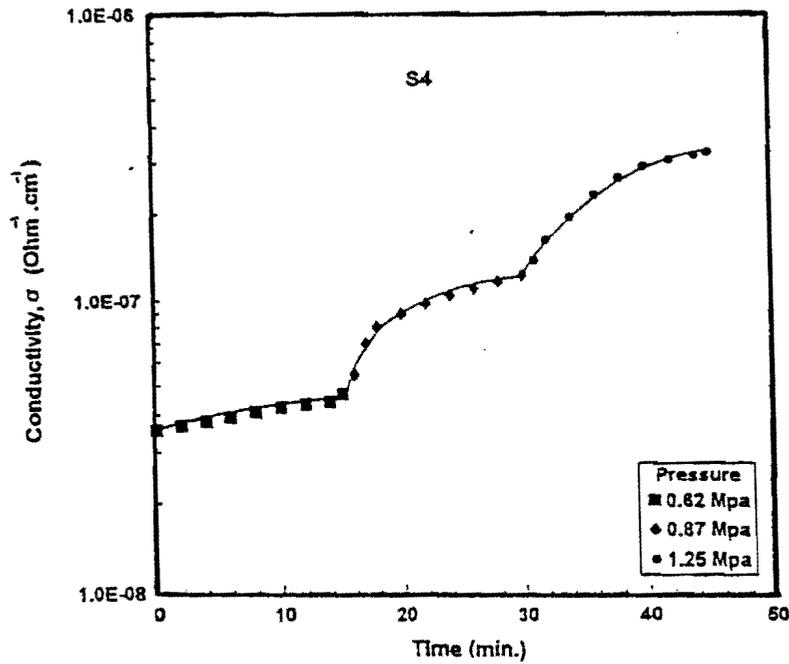


Figure (5) : The change of σ (for S4) with time at different accumulative pressure steps .

$$\frac{\delta \ln \sigma \cdot}{\ln p} = \frac{p \delta \ln \sigma \cdot}{\delta p} = \frac{pv}{kT} \tag{2}$$

If an incremental step pressure is made, a change in the derivative of the conductivity can be measured, then it has

$$\frac{\delta \ln \sigma \cdot}{\delta \ln p} \equiv \frac{\Delta \ln \sigma \cdot}{\Delta \ln p} = \frac{\ln \sigma \cdot_2 - \ln \sigma \cdot_1}{\ln p_2 - \ln p_1} = \frac{\ln (\sigma \cdot_2 / \sigma \cdot_1)}{\ln (p_2 / p_1)} \tag{3}$$

where $\sigma \cdot_1$ and $\sigma \cdot_2$ are the values of the conductivity derivatives before and after the change in pressure (p_1 and p_2 respectively) . Using equations (2) and (3), the activation volume can be written as :

$$v = \frac{kT}{p} \cdot \frac{\ln (\sigma \cdot_2 / \sigma \cdot_1)}{\ln (p_2 / p_1)} \tag{4}$$

Figure (4), the change in $\sigma \cdot$ was evaluated before and after the application of pressure step. The values of v obtained for all samples are summarized in Table (2). Hence, if a cubic unit is considered, the characteristic activation distance ω , will be calculated. It

is clearly observed that ω is highly dependent on the type of used vulcanizing agent and on the IIR content. S_1 and S_7 samples have smallest ω values, which reflect the detected higher relative conductivity values with respect to the other.

The calculated values of ω , for our samples is higher than that detected by Fernandes et al [9] (for SBR loaded with 70 HAF unvulcanizates $\omega = 0.9$ nm) owing to the relatively low HAF content in these blends.

The mechanism of conduction may be the overlap of wave function [5] if the gap distance is less than (1.5 nm). The value obtained for ω by the volume activation analysis in our case is approximately in accordance with the gap distance mentioned above for sample S_1 .

Conclusion :

It may be pointed out that :

The static cyclic compression of the vulcanized ternary rubber leads to fluctuation of σ , upon loading and unloading due to both destruction and alignment of the filler chains. Most samples show slight hysteresis effects upon repeating cycles. This hysteresis disappears after a definite number of cycles (3 cycles for 0.20, and 30 phr and 4 cycles for 10 phr of IIR for samples in group B, and 4 cycles for 0 phr, 3 cycles for 10,30,40 phr and 2 cycles for 20 phr of IIR content for samples in group A).

Samples containing TMTD (vulcanizing agent) show less sensitivities to the applied cyclic pressure. The interspacing distance ω [calculated by using Fernandes model] is lower for TMTD group than sulphur one which reflect the existence of more intensive crosslinking density for this group.

Table (1)
 Composition of NR Samples with different ratios of SBR and IIR rubbers with 40 phr HAF Carbon black .

Samples Ingredients	Group A						Group B			
	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	S ₁₀
NR	50	50	50	50	50	50	50	50	50	50
SBR	0	10	20	30	40	50	20	30	40	50
IIR	50	40	30	20	10	0	30	20	10	0
Stearic acid	2	2	2	2	2	2	2	2	2	2
HAF / back	40	40	40	40	40	40	40	40	40	40
Processing Oil	10	10	10	10	10	10	10	10	10	10
NBTS (a)	2	2	2	2	2	2	2	2	2	2
PβN (b)	1	1	1	1	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5	5	5	5	5
Sulphur	0	0	0	0	0	0	2	2	2	2
TMTD(e)	3	3	3	3	3	3	0	0	0	0

a- Dibenzthiazyl disulfide.

b- Phenyl - β - naphthylamine

c- Tetramethyl thiuram disulphide.

Table (2)

The calculated interspacing distance between carbon particals using equation (4)

(2.a) TMTD group

Sample	P1 (Mpa)	P2 (Mpa)	σ_1 x(10 ⁻⁸)	σ_2 x(10 ⁻⁸)	v (nm)	w (nm)	w (nm)
S1	0.37	0.62	170	250	6.248	1.842	1.83
	0.62	0.87	190	237	3.626	1.536	
	0.87	1.25	90	230	9.529	2.12	
S2	0.37	0.62	52	150	17.16	2.58	2.38
	0.62	0.87	70	120	8.84	2.06	
	0.87	1.25	60	266	16.05	2.52	
S3	0.62	0.87	0.85	6.00	32.06	3.18	2.59
	0.87	1.25	3.25	6.80	7.96	2.00	
S4	0.37	0.62	7.40	19.50	15.70	2.50	2.75
	0.62	0.87	2.50	9.20	21.37	2.78	
	0.87	1.25	1.60	18.40	26.32	2.97	
S5	0.37	0.62	0.75	4.25	28.10	3.04	2.77
	0.62	0.87	0.83	2.25	16.36	2.54	
	0.87	1.25	0.68	4.50	20.37	2.73	
S6	0.37	0.62	0.16	0.65	22.41	2.82	2.96
	0.62	0.87	0.10	0.70	31.92	3.17	
	0.87	1.25	0.08	0.75	24.12	2.89	

(2.b) Sulphur group

Sample	P1 (Mpa)	P2 (Mpa)	σ_1 x(10 ⁻⁸)	σ_2 x(10 ⁻⁸)	v (nm)	w (nm)	w (nm)
S7	0.37	0.62	6.22	9.50	6.86	1.90	2.44
	0.62	0.87	3.38	14.70	24.11	2.89	
	0.87	1.25	3.71	17.00	16.41	2.54	
S8	0.37	0.62	7.20	24.40	19.77	2.70	2.74
	0.62	0.87	4.00	25.50	21.36	2.77	
	0.87	1.25	4.57	31.00	20.63	2.74	
S9	0.37	0.62	9.75	10.50	12.00	2.29	2.54
	0.62	0.87	3.38	13.40	22.59	2.83	
	0.87	1.25	5.00	17.00	15.59	2.50	
S10	0.37	0.62	0.20	1.20	29.03	3.07	3.13
	0.62	0.87	0.10	0.93	36.63	3.32	
	0.87	1.25	0.09	1.08	27.39	3.01	

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