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Electrical properties of mixed rubber composites

M. AMIN*, G. M. NASR*, M. S. SOBHY‡
*Physics Department, Faculty of Science, *Cairo University at Giza, and ‡Cairo University at Beni-Suef, Egypt*

Different rubbers (SBR, NR and IIR) were mixed together in different ratios and each mixture was loaded with 40 p.h.r. (parts of rubber per hundred parts by weight) of HAF (high abrasion furnace) carbon black in an attempt to obtain a composite of good mechanical as well as electrical properties. The rate of relative rate of change of swelling, Q, in Kerosene ($1/\tau = (1/Q)\mathrm{d}Q/\mathrm{d}t$) was found to decrease by increasing the ratio of both SBR and NR in the mixture, reflecting the difficulty of the solvent to penetrate the newly formed matrix. High electrical conductivity was detected in samples containing a high proportion of IIR. A slight decrease in the activation energies, associated with gradual decrease in the temperature coefficient of conductivity for all three mixed rubber composites, was noted. The $\sigma(T)$ curves were found to change appreciably with increasing pre-extension for different sensitivities of all samples.

1. Introduction

Many rubber composites are produced to meet specific requirements requiring good mechanical and electrical properties [1–4]. Composites containing several types of rubbers have been shown to have reliable properties. The addition of IIR to other types, together with other additives such as softeners, reinforcing fillers etc., yielded new research which still requires a deeper investigation of the electrical behaviour.

The present paper deals with a mixture of three types of rubber (SBR, NR and IIR) loaded with constant concentration of HAF carbon black. The direct relationship between both electrical and mechanical properties of these composites is discussed here, particularly to cover part of the problem of conduction and its dependence on the pre-extension.

2. Experimental procedure

Although some information is available regarding the effects of different types of rubber upon the resistivity of conductive rubber, it must be realised that modelled relationships are not precise since: (a) different rubbers, generally, will contain different ingredients and another assortment of base formulae might give different relative effects; (b) mixing techniques, even if nominally similar, will differ in fact, since at any stage in the process the mechanical response to the same operation depends on the type of rubber; and (c) one rubber may give a higher resistivity than another at a given concentration of a given type of carbon black, but a lower resistivity than the other at another concentration or with a different type of carbon black.

Bearing in mind the above conditions, styrene-butadiene rubber (SBR-1502), natural rubber (NR), and butyle rubber (IIR) are mixed together in different ratios and each mixture is loaded with a constant concentration of carbon black, *viz.* 40 parts per hundred parts (p.h.r.) of HAF.

Since sample properties depend largely on the method of preparation, i.e. the order of adding the materials and the time of mixing and processing, it is important that all samples should pass the same procedure under the same circumstances. All rubber mixtures were prepared on a two-roll mill with 170 mm diameter, working distance of 300 mm, speed of slow roll 24 r.p.m. and gear ratio 1–4 according to the compositions in Table I.

The compounded rubber was left for at least 24 h before vulcanization, which was conducted at 143 ± 2 °C, under a pressure of about 400 N cm^{-2} (4 MPa) for a period of 20 min, to ensure stable properties without affecting the electrical properties [5].

The rubber samples were left for 60 days at 70 °C in an electrical oven in order to produce accelerated ageing and hence to ensure reproducibility of results [6] which was manifested using the degree of swelling measurements.

The investigated rubber specimens were shaped during the vulcanization process into sheets of length 4.0 cm, breadth 0.35 cm and thickness 0.2 cm.

A device (Fig. 1) was used to carry out measurements of electrical conductivity of both un-extended and pre-extended samples. The sample was stretched in a certain ratio and the new position was sustained by means of a clamp.

A travelling microscope, with an accuracy of ± 0.001 cm (type J-Swift and Son, London), was used for detecting the pre-extension.

A regulated electrical oven was used to maintain a constant ambient temperature in the range from 20 to 140 °C.

A Tesla picoammeter (type BM-483) was employed for measuring the current in the case of low voltage measurements. Coaxial cables, metal shielding, and

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TABLE I Composition of rubber samples with different ratios of three types of rubber

Mix components (p.h.r.)	Stock designation								
	S1	S2	S3	S4	S5	S6	S7	S8	S9
SBR	10	30	60	10	60	30	100	–	–
NR	30	10	30	60	10	60	–	100	–
IIR	60	60	10	30	30	10	–	–	100
Stearic acid	2	2	2	2	2	2	2	2	2
HAF (N-330)	40	40	40	40	40	40	40	40	40
Processing oil	10	10	10	10	10	10	10	10	10
MBTS[a]	2	2	2	2	2	2	2	2	2
PβN[b]	1	1	1	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5	5	5	5
Sulphur	2	2	2	2	2	2	2	2	2

[a] Diebenthiazyl disulphide.

[b] Phenyl-β-naphthylamine.

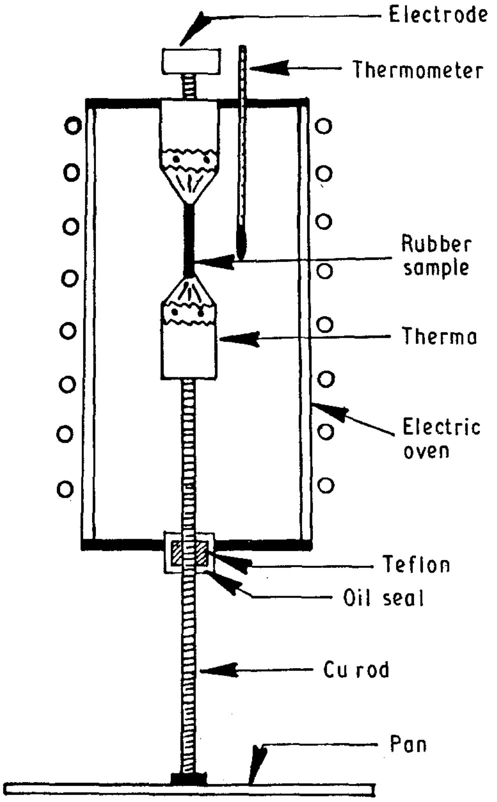

Figure 1 Cell used for the electrical measurements of conductivity for unextended and pre-extended samples.

common ground loops were used to avoid electronic noise.

3. Results and discussion

The electrical properties of the rubber-carbon black system are largely affected by the processing methods [7] and treatments, e.g. heat treatment, vulcanization, ageing, etc. [8].

Although a good reinforcing filler, such as carbon black (HAF), increases the tear and abrasion resistance of all the current major elastomers, it has no effect in enhancing the tensile strength of butyl rubber (IIR), in contrast to the marked tensile reinforcement it causes in natural rubber (NR) and Styrene-butadiene rubber (SBR) [9]. These differences are ascribed to a conflict between two effects: (a) a reinforcing filler stiffens and strengthens the structure by introducing a network of many relatively weak fix points, and (b) simultaneously, it may interfere with the ability of the polymer to crystallize at high elongations. So, it is expected that most of the rubber–carbon bonds will be formed between each of the other two rubbers (NR and SBR) loaded with (HAF) carbon black.

According to the results of the Monsanto Reheometer (see Table II), the scorch time, t_s, and optimum curing time, t_{90}, is found to increase slightly with increasing the concentration of IIR in the composite samples until it reaches a value when S1 is nearly equal to S4.

Moreover, the thermally accelerated ageing (60 days) at 70 °C of the prepared rubber samples may cause: (a) flocculation of the filler, and (b) formation of further chemical rubber–carbon bonds [7]. the latter may result from increased mobility of the long-lived free radicals which are produced during mixing by the dissociation of organic peroxides either naturally occurring in, or added to, the initial mixing process.

It has been found [10] that the presence of a double bond in the skeletel structure of a rubber is very important in enhancing the rate of absorption of oxygen and the presence of methyl side groups is also significant but less. Butyl rubber is, therefore, less sensitive to oxidative ageing than NR and SBR, i.e. IIR becomes soft rather than brittle on oxidative degradation.

For all rubber samples, the time dependence of the degree of swelling in Kerosene was investigated before and after ageing (where Q was established for all samples after 60 days indicating a stable structure) as is observed in Figs 2 and 3. These illustrate the relation between Q and t for both unaged and aged samples, respectively. This behaviour is represented by the growth relationship, $Q = Q_{\max}(1 - e^{-t/\tau})$, where $Q_{\max}$ is the maximum degree of swelling and τ is a characteristic time after which the change in Q with time is very small. From Table III the coefficient of change of the degree of swelling Q with time, given by $1/\tau = (1/Q)\mathrm{d}Q/\mathrm{d}t$, was found to decrease with the increasing ratio of both SBR and NR in the mixture,

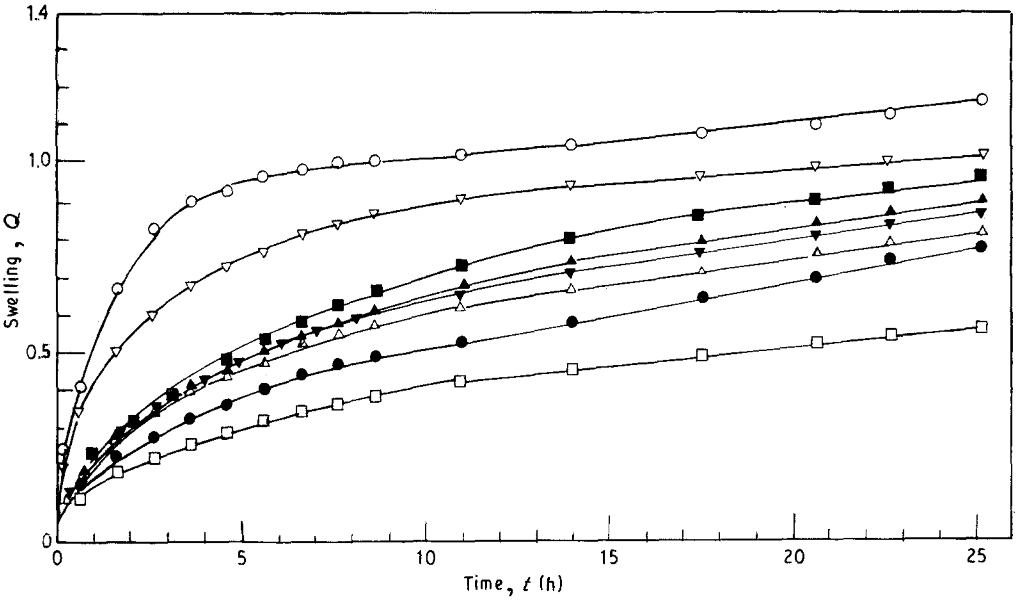

Figure 2 The time-dependence of the degree of swelling, Q, for unaged samples, except (S9): (○) S1, (●) S2, (△) S3, (▲) S4, (▽) S5, (▼) S6, (□) S7 and (■) S8.

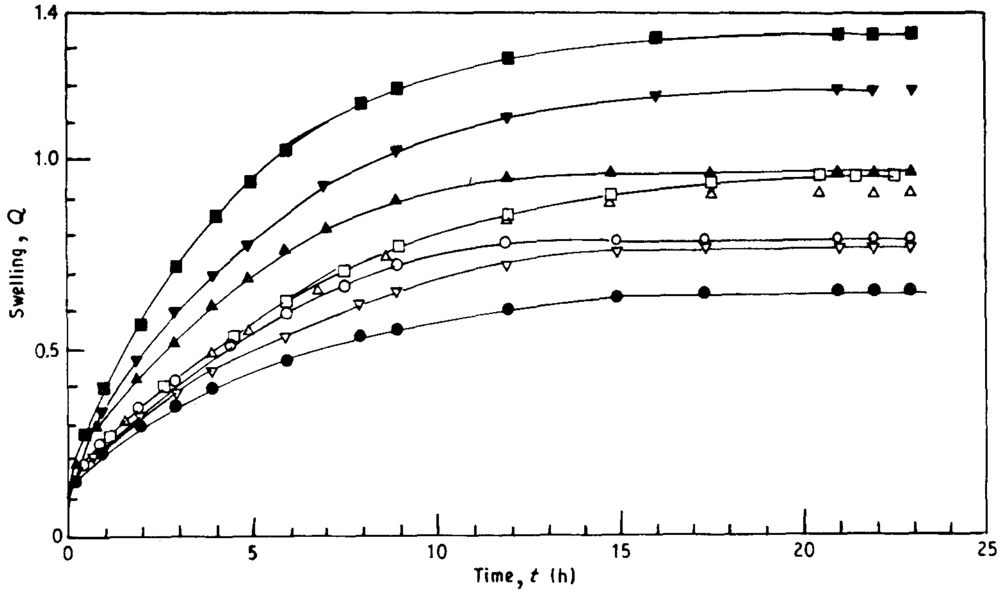

Figure 3 The time dependence of the degree of swelling, Q, for aged samples, except (S9). Key: as in Fig. 2.

TABLE II Scorch time, t_s, optimum curing time, t_{90}, and cure rate index of all samples, except S9

Samples code	t_s (min)	t_{90} (min)	Cure rate index
S8	1.22	1.60	1.57
S6	1.52	2.00	1.78
S4	1.68	2.27	2.06
S7	2.10	3.04	1.94
S3	1.88	2.65	2.14
S1	1.30	2.08	2.38
S5	1.87	2.53	3.09
S2	1.77	2.35	4.02

TABLE III Maximum degree of swelling, Q_{max}, and the characteristic time, τ, of all samples, except S9; aged and unaged

Samples code	Unaged		Aged	
	Q_{max}	τ(h)	Q_{max}	τ(h)
S8	0.97	6.62	1.34	3.90
S6	0.86	6.58	1.19	4.00
S4	0.91	7.13	0.97	3.11
S7	0.56	6.50	0.96	5.26
S3	0.81	6.39	0.91	4.41
S1	1.13	2.50	0.79	2.18
S5	1.01	3.68	0.77	3.79
S2	0.75	7.55	0.65	2.45

reflecting the difficulty of the solvent to penetrate the newly formed matrix obtained at higher concentrations of NR and/or SBR in the mixtures, e.g. S3.

The above samples were subjected to a repeated measurement for the σ against T curves. The conduction mechanism is expected to be a thermally activated in nature owing to the small ratio of carbon–rubber bonds with respect to carbon–carbon bonds in 40 HAF/IIR (S9). Also, it could be interpreted on the

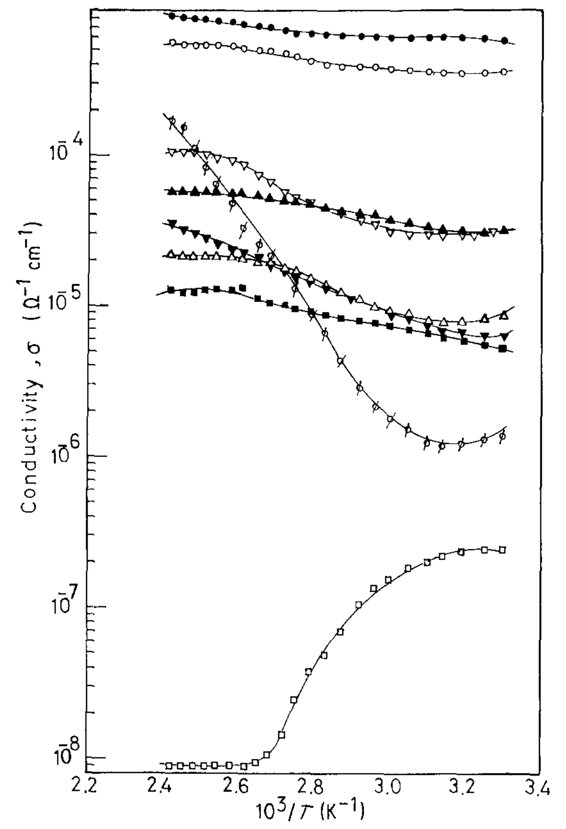

Figure 4 The temperature dependence of the electrical conductivity for all samples at zero pre-extension. Key: as in Fig. 2 with (∅) S9.

basis of the decrease of the IIR viscosity with temperature which, in turn, increases the mobility of charge carriers through the rubber matrix as shown in Fig. 4.

The conduction mechanism through 40 HAF/SBR (S7) vulcanizates may be discussed on the basis of quantum mechanical tunnelling or hopping mechanisms of the charge carriers in carbon-black particles or aggregates [11] as shown in Fig. 4. Meanwhile, the conduction mechanism through 40 HAF/NR (S8) is thermally activated in nature.

The temperature-dependence of the electrical conductivity of all mixed rubber composites is represented in Fig. 4. It is clearly observed that samples S1 and S2 show high values of the electrical conductivity in the range (30–140 °C) with respect to the other samples. This behaviour confirms the suggestion of the important rôle of IIR in order to get composites with good mechanical as well as electrical properties. The rest of specimens have almost the same $\sigma(T)$ behaviour as that of 40 HAF/NR (S8) reflect the equally probable role of both IIR and SBR within the new matrix.

The temperature coefficient of conductivity (T.C.C.) and the activation energy which was calculated from the well-known expression $\sigma = \sigma_0 e^{-E/kT}$ (from a linear curve not presented here), of all samples except 40 HAF/SBR (S7) are tabulated in Table IV. Samples S1, . . . , S6 have different variable values of activation energy which increases with both SBR and NR content. There is a slight decrease in T.C.C. for all mixed rubber composites (S1, . . . , S6) as compared to 40 HAF/IIR (S9).

TABLE IV The temperature coefficient of conductivity (T.C.C.) and the activation energy of all samples, except S7

Samples code	Activation energy (10^{-3} eV)	(T.C.C.) × 10^{-3} (°C⁻¹)	
		at 50 °C	at 100 °C
S9	3.00	8.3	5.5
S5	0.93	0.9	15.9
S6	0.86	43.5	17.7
S3	0.67	25.5	11.2
S8	0.42	12.0	7.6
S4	0.39	10.6	6.9
S2	0.27	5.9	5.0
S1	0.25	5.5	4.8

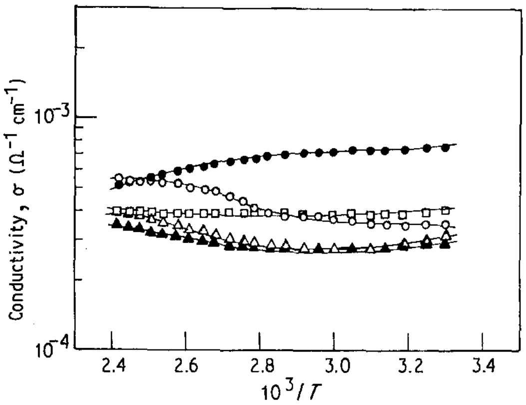

Figure 5 The temperature dependence of the electrical conductivity for sample S1 at different values of pre-extension: (○) 0.0%, (●) 10%, (△) 30%, (▲) 50% and (□) 100%.

Thus, all rubber ratios of mixed composites lead to the arrangements of the carbon structure. Also, the increase of temperature leads to the intensification of the micro-Brownian motion of molecules.

In addition to the above measurements, a repeated measurement of the temperature dependence of the d.c. electrical conductivity σ of the prepared rubber sample composites has been studied under different amounts of pre-extension. The results of such measurements are shown in Figs 5–13. The general features of the above figures could be summarized as follows:

For all mixed rubber composites, the initial pre-extension values on σ against $1/T$ curves lead to an increase in the conductivity, σ, due to the alignment of carbon particles. Further pre-extension values above approximately 30% decreases, σ, due to the created internal stresses, which destroy the contacts between carbon particles. It is interesting to indicate that the role of HAF carbon black upon pre-extension contradicts that FEF (fast extraction furnace) carbon black as was mentioned in previous works [12, 13].

The successive extension leads to the arrangement of the carbon structure. As one changes the values of pre-extension, the conduction mechanism qualitatively changes, i.e. from a thermally activated one to a tunnelling or hopping one passing by the conduction due to direct contact between carbon particles (depending on both the rubber ratios in the composite and the pre-extension values).

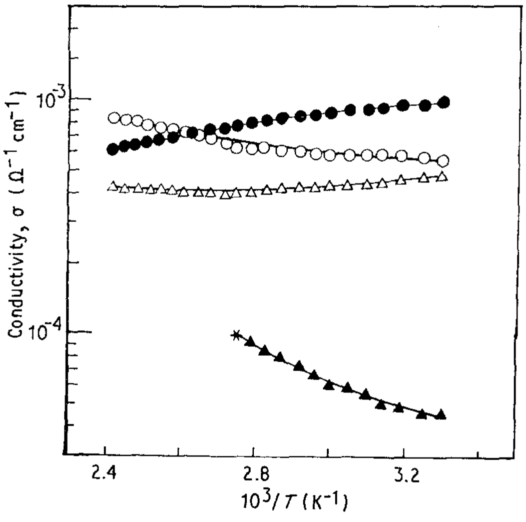

Figure 6 The temperature dependence of the electrical conductivity for sample S2 at different values of pre-extension. Key: as in Fig. 5. Note: * = fracture point.

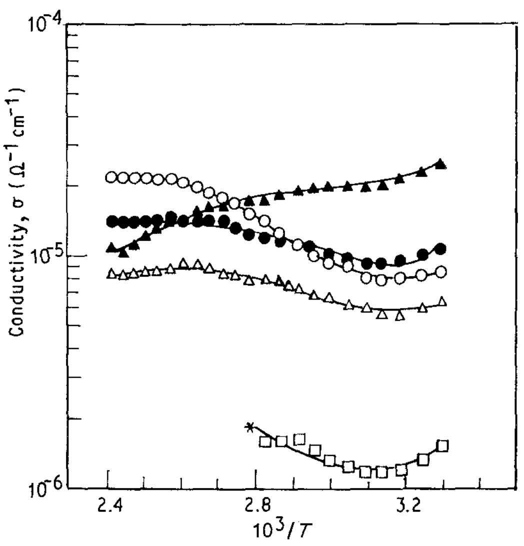

Figure 7 The temperature dependence of the electrical conductivity for sample S3 at different values of pre-extension. Key as in Fig. 5. Note: * = fracture point.

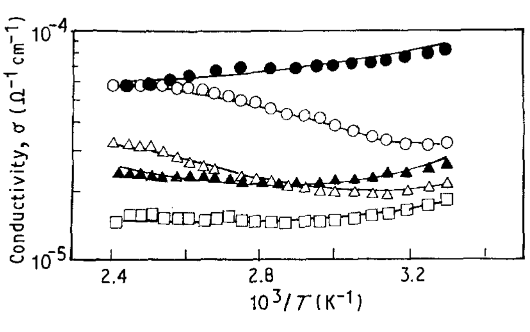

Figure 8 The temperature dependence of the electrical conductivity for sample S4 at different values of pre-extension. Key: as in Fig. 5.

Samples 40 HAF/SBR (S7), and 40 HAF/IIR (S9), show a detectable response upon pre-extension (*c.f.* Figs 11 and 13), respectively. The destruction of carbon structure predominates above 10% extension (for 40 HAF/SBR (S7)). Meanwhile, the probability of

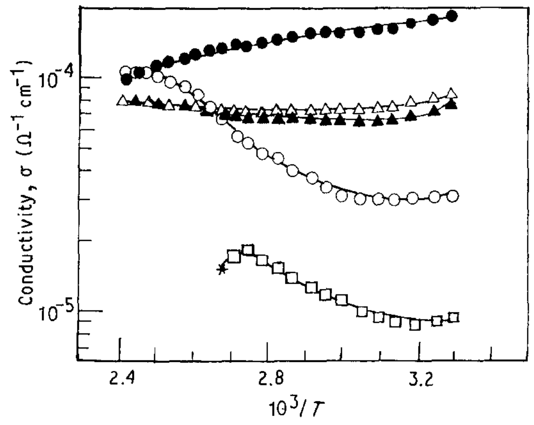

Figure 9 The temperature dependence of the electrical conductivity for sample S5 at different values of pre-extension. Key: as in Fig. 5. Note: * = fracture point.

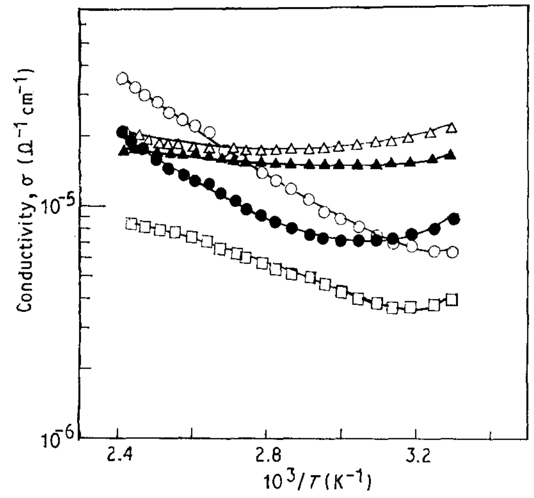

Figure 10 The temperature dependence of the electrical conductivity for sample S6 at different values of pre-extension. Key: as in Fig. 5.

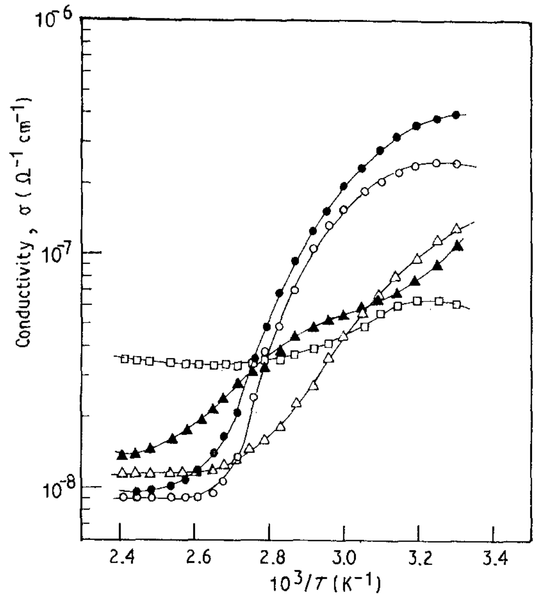

Figure 11 The temperature dependence of the electrical conductivity for sample S7 at different values of pre-extension. Key as in Fig. 5.

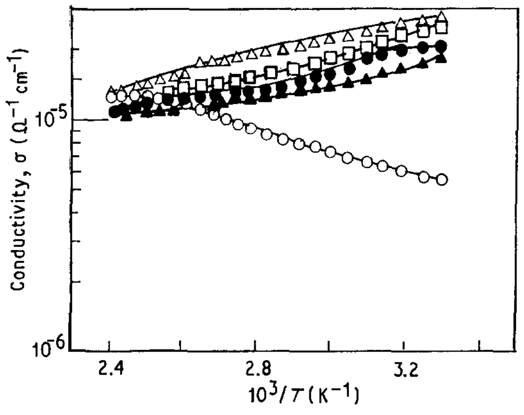

Figure 12 The temperature dependence of the electrical conductivity for sample S8 at different values of pre-extension. Key: as in Fig. 5.

carbon–carbon collision increases which makes the process of destruction and reconstruction equally probable and lead to the approximately stable behaviour of σ for 100% in the temperature range (60–140 °C). Fig. 13 shows the effect of pre-extension on the σ against $1/T$ curves for S9, the rapid extension leads to the stable behaviour for 10–30%, i.e. σ is stabilized.

4. Conclusion

The scorch time, the maximum curing time and electrical conductivity, σ, were found to increase slightly with increasing the concentration of IIR in the composite samples.

The conduction mechanisms for all samples were thermally activated in nature with different activation energies except sample S7 in which the conduction mechanism discussed on the basis of quantum mechanical tunnelling or hopping mechanism.

For all samples, the initial pre-extension values on σ against $1/T$ curves led to an increase in σ due to the alignment of carbon particles. Further pre-extension above approximately 30% decreases, σ, due to the created internal stresses, which destroy the carbon–carbon contacts.

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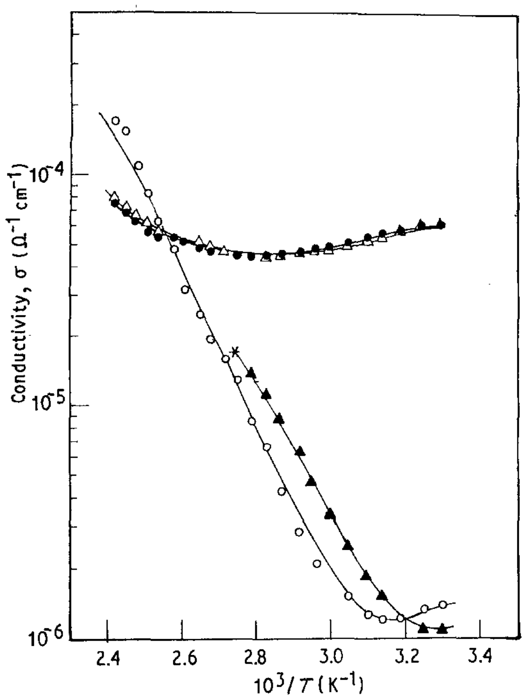

Figure 13 The temperature dependence of the electrical conductivity for sample S9 at different values of pre-extension. Key: as in Fig. 5.

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