

Effect of Temperature on the Stress

Strain Characteristics of Styrene

Butadiene Rubber loaded with HAF and GPF Carbon Black

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SUMMARY

The true stress-true strain curves of HAF/SBR (styrene butadiene rubber SBR loaded with high abrasion furnace (HAF)) carbon black and GPF/SBR (Styrene butadiene rubber loaded with general purpose furnace) carbon black composites of different concentrations of carbon black have been determined.

The yield stress σ_y and the coefficient of stiffness or (young's modulus) E have been found to increase gradually with increasing the carbon black concentrations of both types. The fracture stress σ_f and the fracture strain ϵ_f exhibited peak values at certain concentrations (50 phr for HAF and 75 phr for GPF). The reduction in σ_f and ϵ_f at large concentrations of carbon black was considered as a result of dilution of effect due to the diminishing of the volume fraction of the polymer in the composite, where there is no enough polymer matrix to hold the filler particles together.

Meanwhile, all the stress- strain parameters mentioned above have been found to decrease with increasing the working temperature. The activation energy of fracture have been found to decrease with increasing the concentration of carbon black. This observation was explained on the basis of the fact that the fracture in the interfaces between polymer and carbon aggregates need less energy than fracture in the polymer.

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INTRODUCTION

Polymeric materials at elevated temperature above (T_g) generally exhibit two distinct regions in their stress-strain behavior⁽¹⁾. The origins of these regions can be traced to the molecular response of the individual polymer chains to the applied stress or strain. At low applied stress the material behaves as a linear elastic medium with an instantaneous modulus equal to the slope of the stress-strain curve. The modulus gives us a measure of the instantaneous material stiffness. On a molecular level we interpret this region as one where the individual backbone bond and rotational angles, and to a lesser degree bond length, open, rotate and stretch respectively, without any significant translational chain motion in the form of local conformational rearrangements. In a microscopic sense the deformation is affine, since the deformation is distributed uniformly through the sample. In the yield region that is a result of the non linearity of the sample under the experimental condition and the localization of the deformation in necking. On a molecular level we interpret this yielding in terms of a chain motion in the form of local conformational changes and associated chain slippage. In this respect we might term deformation microscopically non affine, since on the scale of the individual chains some sections are moving relative to others. Chain failure is unlikely to significantly contribute at these stress levels since the activation energy for bond breaking is much greater than that for conformational or translational motion. However, because these motions are relatively slow, this region of the stress-strain curve is particularly sensitive to temperature and to the rate of

application of the stress. The curve ends abruptly with material failure. Microscopically this increase in modulus occurs when most of the conformational softness has been 'stretched out' and we are once again in a mode of opening back bone bond angles and stretching bond lengths.

Since in case of polymers, the variation of the cross-sectional area of the specimen during the extension is very high with respect to that of metals, we have to calculate the true stress (σ_{true}) and the true strain (ϵ_{true}) rather than a nominal stress and nominal strain. The true stress and true strain can be obtained from the values of the nominal stress (σ) and the nominal strain (ϵ) as follows⁽²⁾.

$$\sigma_{\text{true}} = \sigma (1 + \epsilon) = \sigma \lambda \quad (1)$$

$$\epsilon_{\text{true}} = \int_{l_0}^l \frac{dl}{l} = \ln(1 + \epsilon) = \ln \lambda \quad (2)$$

From the stress-strain curves we can deduce the following parameters:

1. The maximum stress at the end of the linear region σ_y
2. The ultimate strength or fracture stress, σ_f
3. The percent ductility or the fracture strain ϵ_f
4. Activation energy for fracture stress-strain, $Q^{(3,4)}$

$$t_f = A \exp(-Q/KT) \quad (3)$$

5. Coefficient of stiffness or young's modulus, E

$$E = \partial \sigma_{\text{true}} / \partial \epsilon_{\text{true}} \quad (4)$$

EXPERIMENTAL

Styrene-Butadiene rubber with 50, 75 and 100 (phr) of (HAF) and (GPF) carbon black was prepared according to the recipe mentioned in (Table.1). The test samples were

shaped during vulcanization process into sheets of 2.5cm long, 0.3cm wide and 0.16cm thick. The rubber vulcanization was conducted at 143°C, under a pressure of 40Kg.f/cm² for 30 minutes. The stress-strain tests were performed on samples in the temperature range from 303 K to 383 K. A conventional type tensile testing machine was used⁽⁵⁾.

The applied stress was increased successively and the strain was recorded immediately after applying the stress.

Table (1)

	(phr) ^a
Styrene-Butadiene rubber (SBR)	100.0
Zinc oxide	5.0
Stearic acid	2.0
Processing oil	5.0
HAF or GPF	0,25,50,75 and 100
(MBTS) ^b	1.5
(Anox H.B) ^c	1.0
(6ppD) ^d	1.0
Sulpher	2.0

- Part per hundred parts of rubber by weight.
- Debenzthiazole disulphide
- Poly 2, 4,6 trimethy 1-1, 2 dihydroquinoline
- N-(1,3 Dimethyl butyl)-N- phenyl-p- phenelenediamine.

RESULTS

The true stress σ_{true} , true strain ϵ_{true} of HAF/SBR and GPF/SBR samples of different carbon black concentrations and different working temperatures are shown in Fig (1). Each curve

consists of two distinct regions, the linear region and the plastic region. It is noticed that these curves are sensitive to the working temperature and the concentration of carbon black. For both groups of HAF/SBR and GPF/SBR samples, the stiffness of the samples increases with increasing the concentration of the carbon black and decreasing the working temperature.

Effect of Carbon Black Concentration and Temperature on σ_y , E, σ_f and ϵ_f :

For both groups of HAF/SBR and GPF/SBR samples the yield stress (the maximum stress of the linear region) σ_y and the coefficient of stiffness or (young's modulus) E have been found to increase by increasing carbon black concentration and decreasing the working temperature, (Figs 2,3). While the fracture stress σ_f (the maximum stress that the sample endures) and the fracture strain ϵ_f (the total strain of the stress-strain curve) have been found to decrease with increasing the working temperature. Moreover, σ_f and ϵ_f for both groups of HAF/SBR and GPF/SBR samples have been found to increase with increasing carbon black concentration reaching to a maximum at (50phr) for HAF and at (75phr) for GPF carbon black, and have been found to decrease with further increasing the carbon black concentration (Figs. 4.5).

Variations of Rubbery Modulus of the kinetic theory G and young's Modulus E :

Our result of true stress-strain relation have been found to verify the following modified equation of the classical theory of rubbery elasticity.⁽⁶⁾

$$\delta = \delta_0 + G (\lambda^2 - \lambda^{-1}) \quad (5)$$

Where: $\lambda = l/l_0$ is the extension ratio

δ_0 is a material constant.

G is the rubbery modulus of Kinetic theory.

The rubbery modulus F has been found to increase with carbon black concentrations of both groups of HAF/SBR samples and to decrease with increasing the working temperature (see Fig.6). Besides Young's Modulus (E) has been determined from the relation.

$$E = 3 G \quad (7)$$

To investigate the dependence of young's modulus (E) on the volume fraction of carbon black (c). We have applied Guth's relation ⁽⁷⁾

$$E_f = E_0 (1 + 0.67 fc + 1.62 F^2 c^2) \quad (7)$$

Where E_0 and E_f are young's modulus for unfilled and filled rubber, respectively, c is the volume fraction of carbon black and f is the shape factor. Our data have been found to fit a modified type of Guth's equation by adding another term ($xc^3 f^3$) and the modified Guth's equation becomes:

$$E_f = E_0 (1 + 0.67 fc + 1.62 F^2 c^2 + XF^3 c^3) \quad (8)$$

Where $x = 0.18$ (see Fig. 7), the solid line represents guth's equation, and dashed line represents the modified Guth's equation. It is clear that our data are in good agreement with the modified Guth's equation.

The Activation Energy of Fracture Mechanism:

The activation energy of fracture has been calculated from the slopes of the straight lines relation $\ln t_f$ versus $1000/T$ (K^{-1}). The activation energy of fracture of HAF/SBR and GPF/SBR samples have been found to decrease with increasing carbon black concentrations (see Fig.8).

DISCUSSION

The developed kinetic theory of rubber elasticity attributed the high elasticity of rubber to the increase of the flexibility of the chain segments.

The present results are in a good agreement with the kinetic theory of rubber elasticity through the following relation.

$$\sigma_{\text{true}} = \sigma_0 + G (\lambda^2 - \lambda^{-1})$$

Where σ_{true} and λ are the true stress and the extension ratio respectively and G is the rubbery modulus ($\delta\sigma_{\text{true}} / \delta(\lambda^2 - \lambda^{-1})$). The value of σ_0 is found to be constant for the tested samples ($\sigma_0 = 0.2$ Mpa) and depends on the chemical nature of the rubber used and not on the cross-linking density.

True stress-true strains curves for SBR loaded with HAF and GPF carbon black with concentrations ranging from 25 to 100 phr have been studied under working temperatures ranging from 303K to 383K (see Fig.1). These curves have been found to be sensitive to the types and concentrations of carbon black as well as the working temperature. Each curve consists of two distinct deformation region, the linear region and the plastic region. In general as the stress increases the resulting true strain ($\epsilon = \ln(\lambda)$) increases. This character may be attributed to the increase in the flexibility of rubber chain segments by the addition of an external force.

The work hardening parameters, the yield stress σ_y , the fracture stress σ_f , the fracture strain and the coefficient of stiffness or Young's modulus (E) have been determined.

Figs (2-5) show that the parameters ϵ_f and σ_f are increased by increasing the concentrations of HAF and GPF carbon black in the tested samples attaining maximum values at 50 phr for HAF and 75 phr for GPF composites (see Fig.5).

These observations might be due to the formation of carbon black aggregates between the polymeric chain segments leading to diminishing their mobility. The arrangement of carbon black structure causes a reduction in the values of ϵ_f and σ_f resulting in brittle weak SBR products. This brittle weakness may be due to the flow of flexible elastomer chain segments around the carbon black aggregates or agglomerates with low product tensile strain and stress. We may distinguish between the first stage, strong primary breakdown of carbon structure until the perfect dispersion and the second stage of weak bonds of carbon black structure (aggregates or overlapping at higher concentrations). Besides, the place of the maximum depends on the particle size of carbon black. It moves towards higher concentrations of the filler of larger partical size. The maximum strength of the elastomer appears at small filler concentrations of smaller particle size because it has greater surface area, which in turn, gives rise to more probability of adhesive interaction between the polymer and the filler.

However, the decrease in σ_f and ϵ_f of the tested samples by further increasing of the carbon black concentration (above 50 phr for HAF and above 75 phr for GPF) might be discussed as follows. It is thought that the concentrations of maximum

strength of the tested samples corresponds to the optimum dispersion of carbon black. Besides, for higher concentrations of the filler there is a dilution effect due to the diminishing of the volume fraction of the polymer in the composite. Where in this case there is not enough polymer matrix to hold the filler particles together or due to the overlapping process at higher carbon content, in addition to reorientation of the carbon black structure in the direction of applied tensile stress. The values of σ_y , E , σ_f of the HAF/SBR composites have been found to be higher than those of the GPF/SBR ones of the same concentrations. The relative increase in stiffness of the HAF/SBR samples indicates that there are more dispersion of HAF black of smaller particle size than the GBF black in the SBR matrix leading to more adhesion to the polymer which results in more resistant to the slippage of the mobile chain segments.

From Figs (6,7) it has been found that the rubbery modulus G and young's modulus (E) increase with increasing the carbon black content. This character may be due to the increase in the density of carbon black and cross-linking primarily of the rubber to filler attachment, i.e the increase of viscosity or elastic modulus of the SBR samples are caused by suspension of the solid carbon particles, aggregates or agglomerates. The calculated values of E have been found to verify a modified Guth's equation by addition of a fourth term ($0.18f^3c^3$) to Guth's equation⁽⁷⁾ as follows.

$$E_f = E_o (1 + 0.67fc + 1.62f^2c^2 + 0.18f^3c^3)$$

Where c is the volume fraction of carbon black, E_f and E_o are young's modulus for filled and unfilled rubber, respectively and f is the shape factor ($f=7$).

The increase in the elastic or rubbery modulus $G=E/3$, depends not only on the filler concentration but also on the particle size of carbon black filler. The small HAF particles have much greater effect than the GPF coarse filler. This effect of small particle size of HAF carbon black increases the modulus due to the more extent between the HAF carbon and SBR (surface area= $80\text{m}^2/\text{gm}$). The sharp drop in G with increasing the working temperature was attributed to the increase in the interatomic distance and hence the decrease in the cohesive and adhesive forces between the atoms constituting the carbon black filler-the SBR matrix. The decrease in G , E and σ_y results simply from the decreasing of the interaction friction forces and the increasing of the rotational motion in many parts of the molecular chain segments.

The activation energy of the fracture mechanism of the HAF/SBR and GPF/SBR composites as given in Fig.(8) has been found to decrease from about 0.2eV to 0.08eV with increasing the concentration of carbon black of both types. The fracture processes of the filled SBR vulcanizates under stress-strain test seems to be caused by the scission of the chemical bonds of the polymer molecules and the bond of the interfacial adhesion between the SBR and the carbon black particles, aggregates or agglomerates.

The initiated cracks may propagate through the regions of the polymer and also along the interfaces between the polymer and the filler. The fracture of the polymer region needs a relatively higher energy than the fracture of the interfaces. This fact may explain the decrease in the activation energy of fracture by increasing the concentration of carbon black of both types.

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FIGURES CAPTIONS

Fig. (1): Stress-strain curves at different working Temperature for
(a) HAF/SBR (b) GPF/SBR composites

Fig. (2): A) The variation of σ_y (MPa) at different working Temperature with the concentration of carbon black
For (a) HAF/SBR (b) GPF/SBR composites
B) The temperature dependence of σ_y (MPa) for
(C) HAF/SBR (d) GPF/SBR Composites

Fig. (3): A) The variation of E (MPa) at different temperature with the concentration of carbon black for (a) HAF/SBR
(b) GPF/SBR composites.
B) The temperature dependence of E (MPa) for
(a) HAF/SBR (b) GPF/SBR composites.

Fig. (4): The temperature dependence of σ_f (MPa) and ϵ_f (%) for (a-b) HAF/SBR (c-d) GPF/SBR composites.

Fig. (5): The variation of σ_f (MPa) and ϵ_f (%) at different working temperature with the concentration of carbon black for (a-b) HAF/SBR (c-d) GPF/SBR composites.

Fig. (6): A) The variation of rubbery modulus, G (MPa) with the concentration of carbon black for (a) HAF/SBR (b) GPF/SBR composites.
B) The temperature dependence of G (MPa) for (c) HAF/SBR(d) GPF/SBR composites

Fig. (7): The variation of young's modulus, E (MPa) with the concentration of carbon black, at working temperature, T= 303K for (a) HAF/SBR (b) GPF/SBR composites.

Fig. (8): A) The variation of $\ln t_f$ with $1000/T(K)$ for (a) HAF/SBR (b) GPF/SBR composites.
B) The variation of Q (eV) at different working temperature with the concentration of carbon black for (c) HAF/SBR (d) GPF/SBR composites.

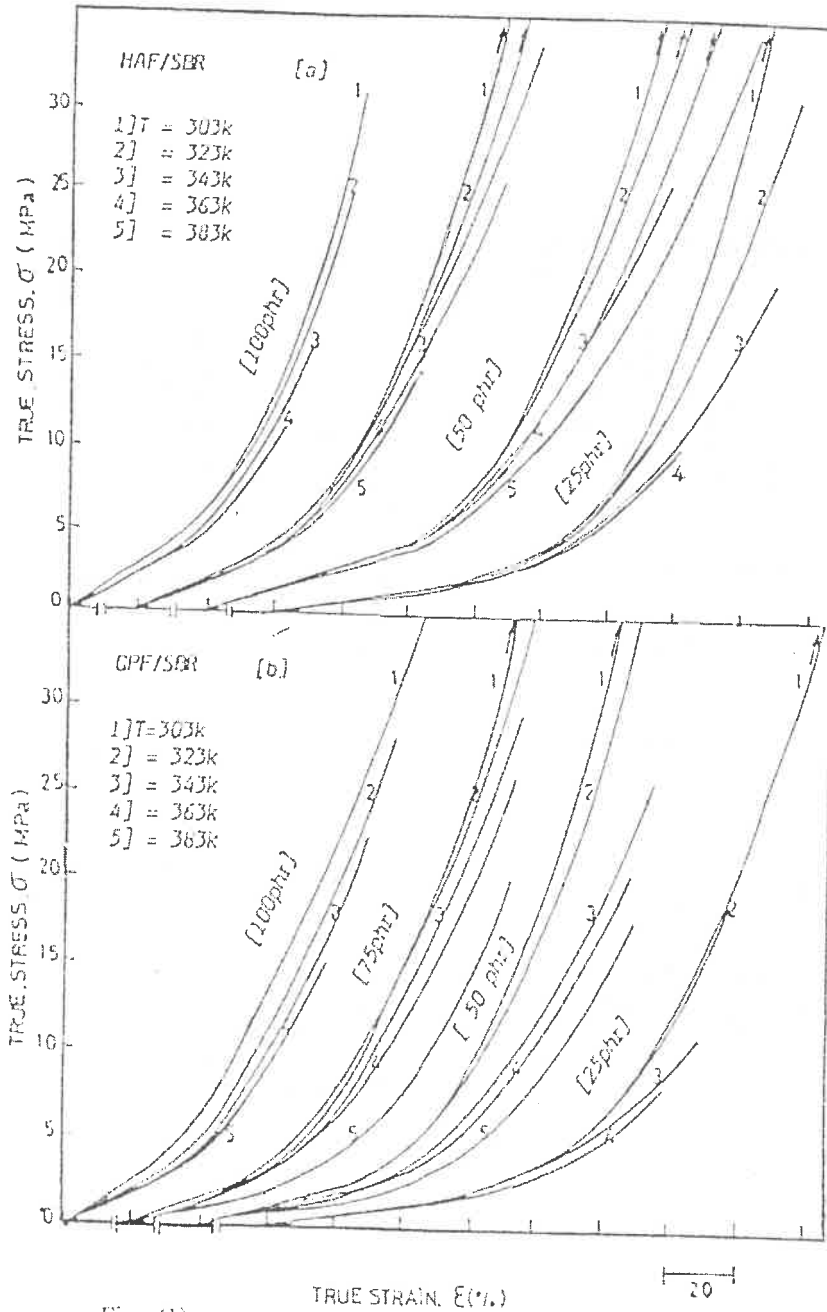
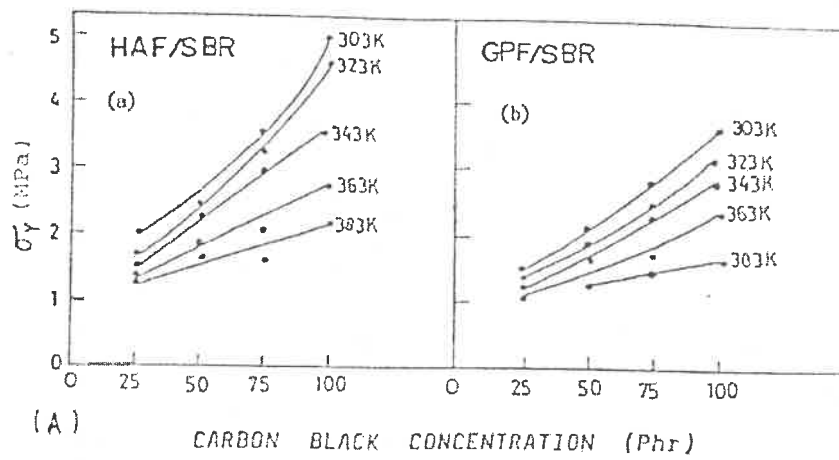
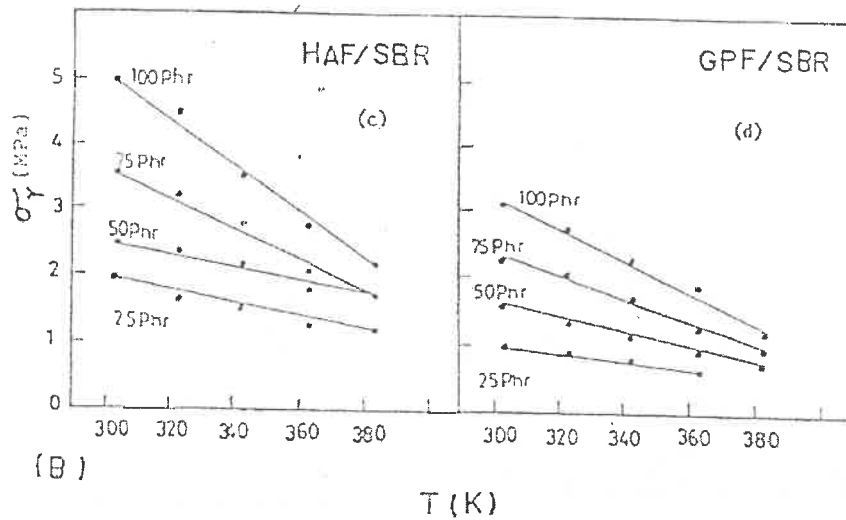


Fig. (1)



(A)



(B)

Fig. (2)

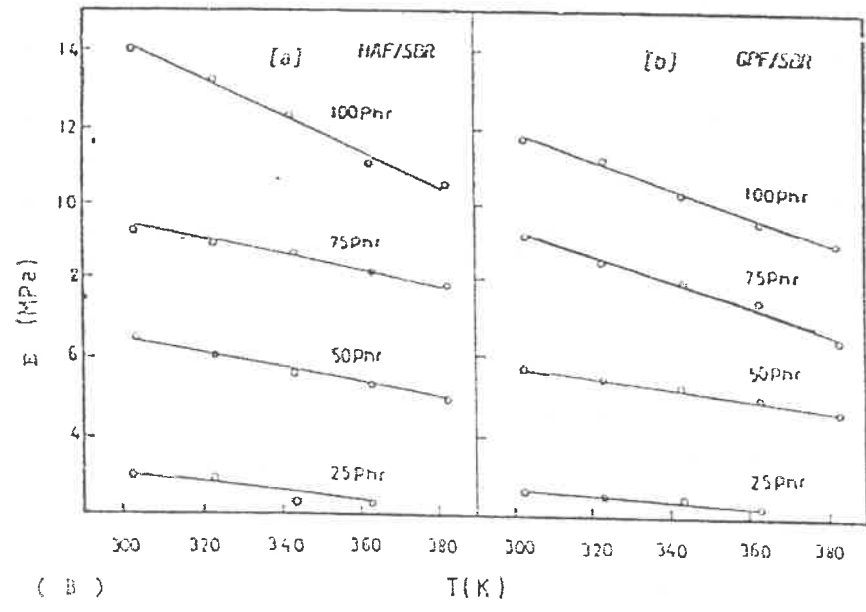
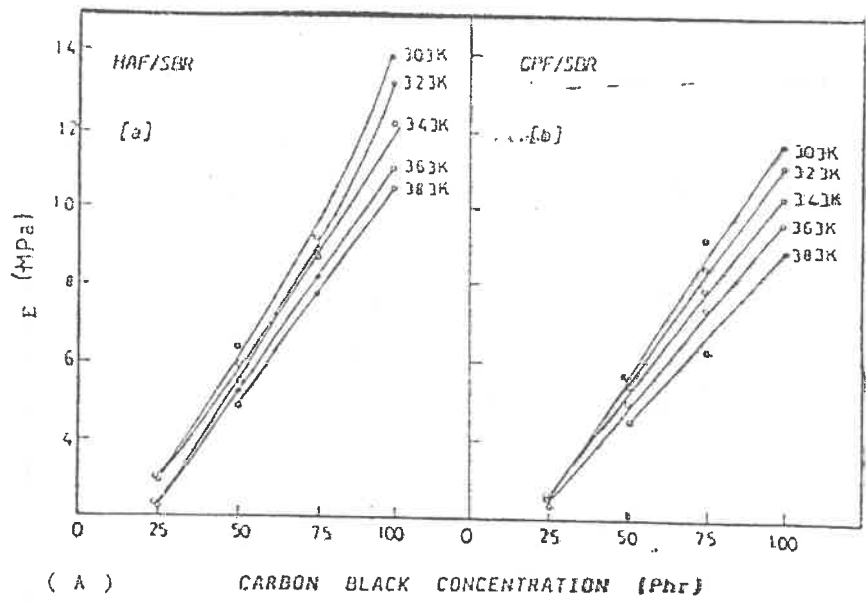


Fig. (3)

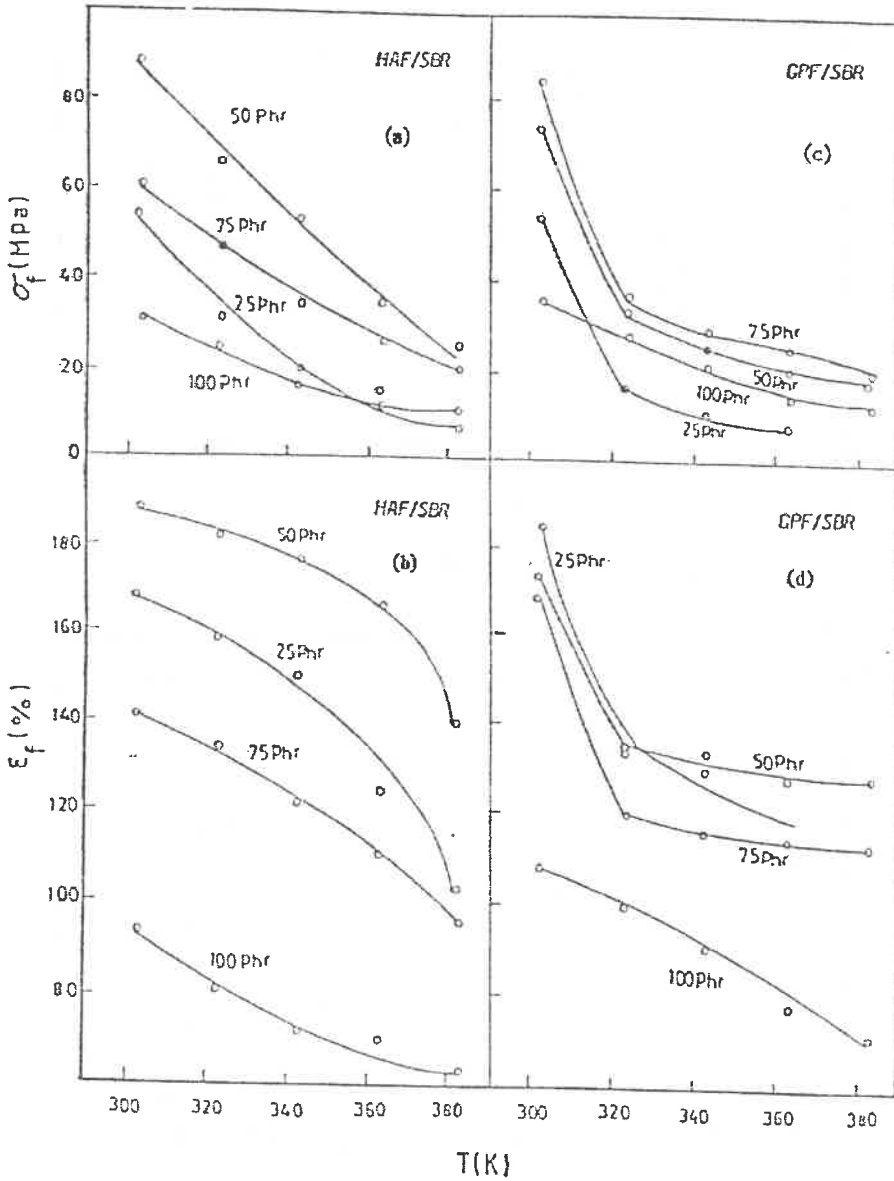


Fig. (4)

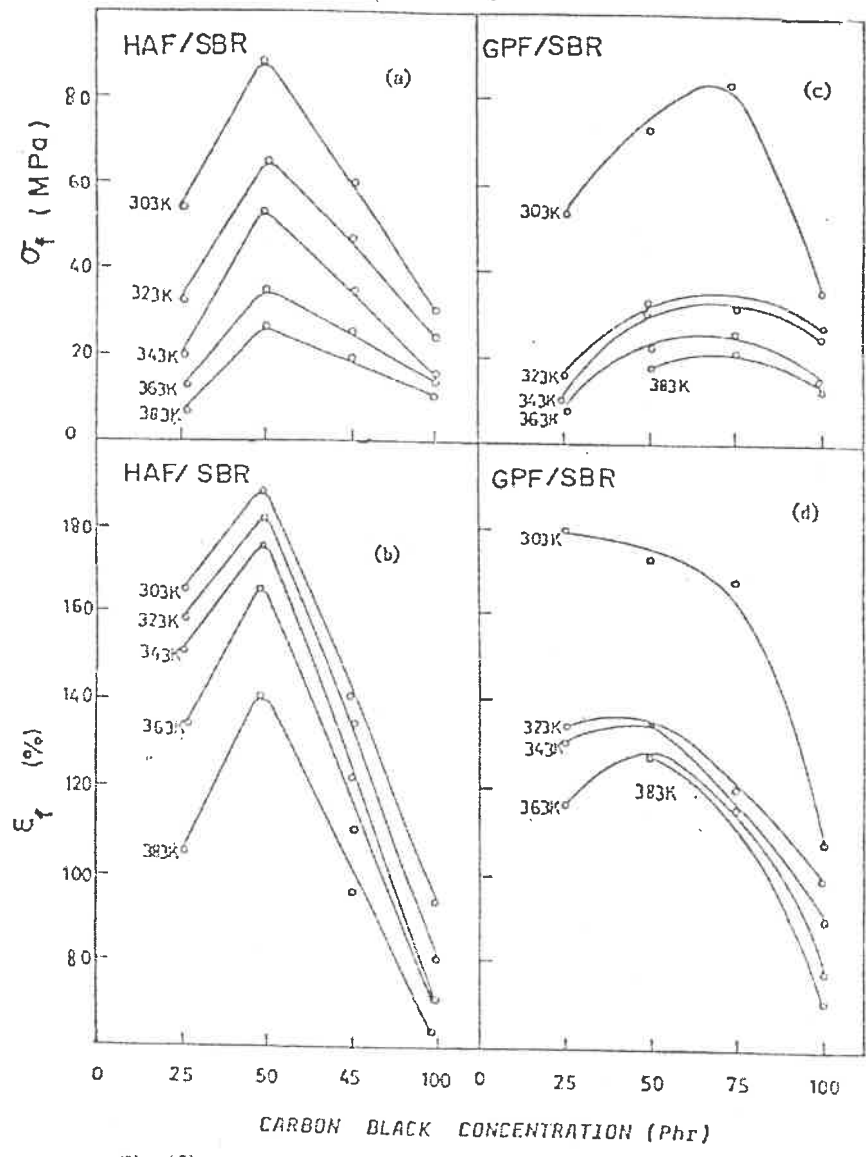


Fig.(5)

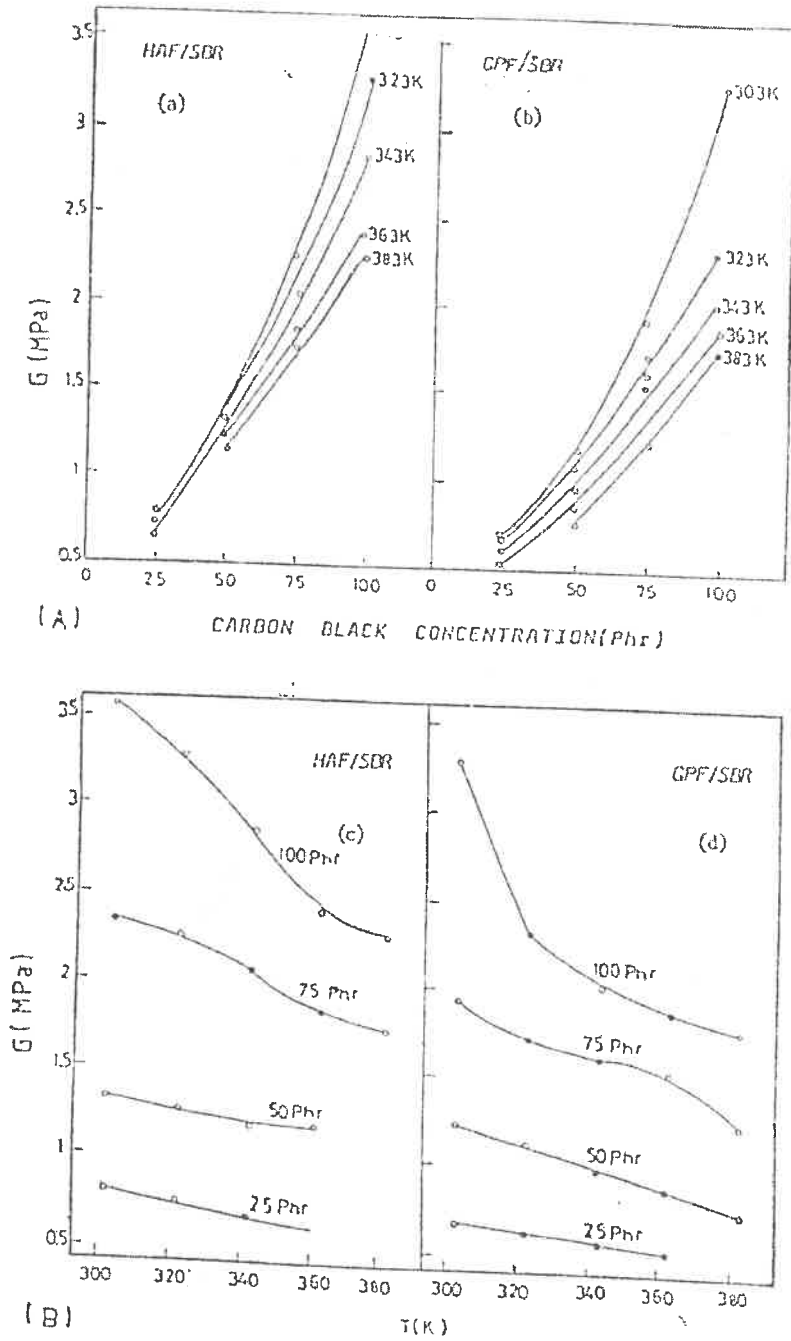


Fig. (6)

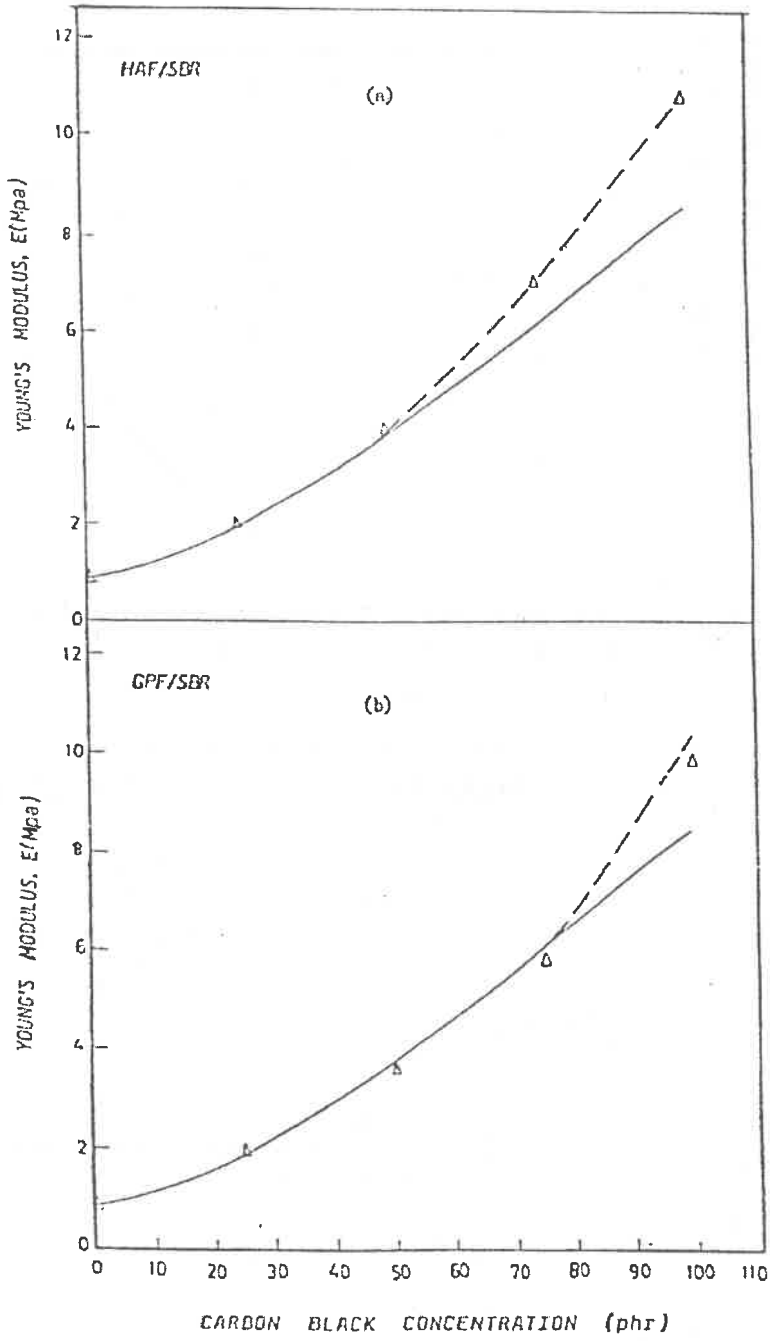


Fig. (7)

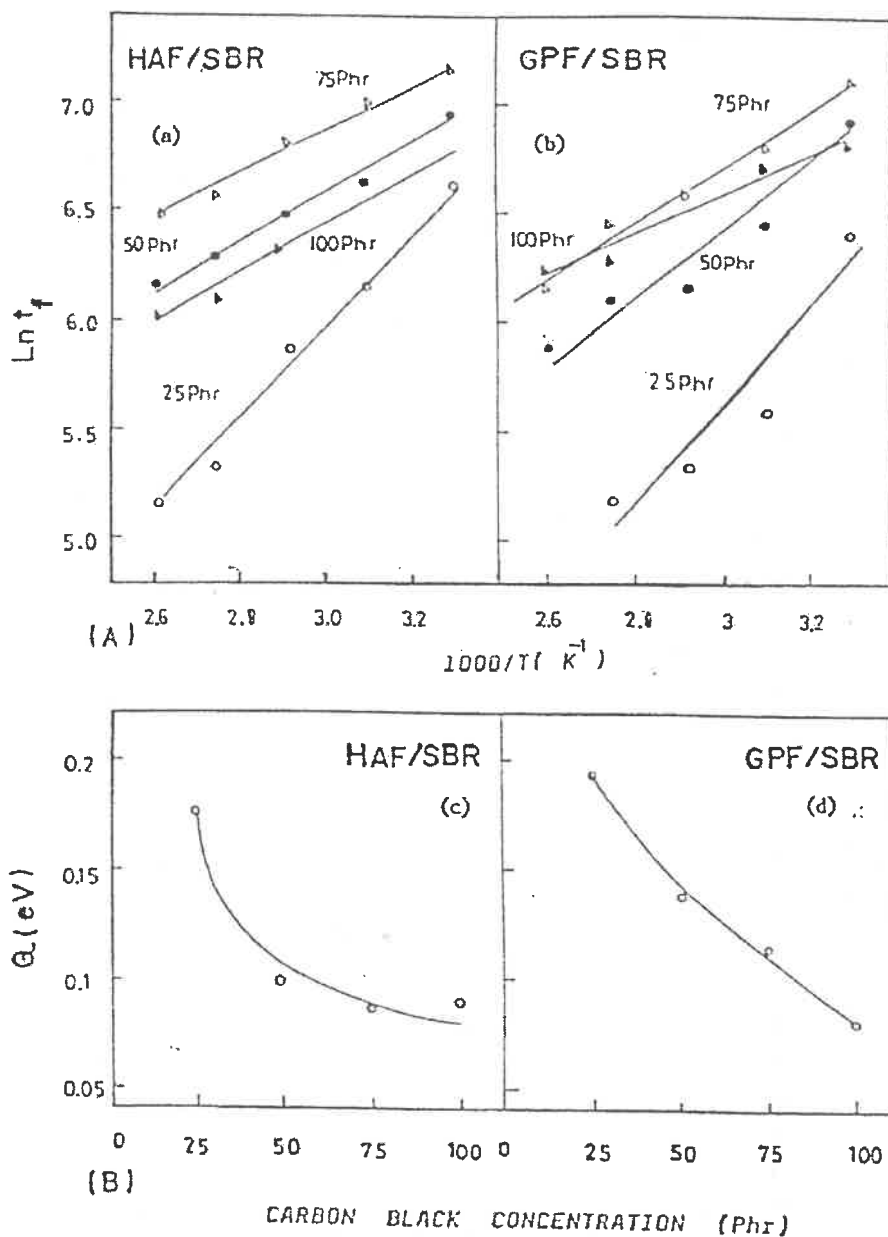


Fig. (8)