

Stress Relaxation in Carbon Black Loaded Butyl Rubber

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Received 12 July 1999; accepted 15 November 1999

ABSTRACT: The dependence of equilibrium force (F^*) on the strain ratio (α) of carbon black loaded butyl rubber was studied. The relation between elastic constant and volume fraction of carbon black was found in good agreement with that obtained by Guth and Gold relation at low concentrations using the shape factor ($f = 6.5$). The relaxation time and viscosity (η) were calculated by using stress relaxation of these samples at different compression strains. The same agreement was observed in the relation between viscosity and volume fraction of carbon black concentration. The results are discussed according to the dispersion mechanism of carbon black in rubber.

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INTRODUCTION

One of the major problems of polymer science is to set up a complete analysis of the composition, structure, and correlation between the structure and physical properties of a given polymer. The effect of fillers on the mechanical properties of elastomers is of great interest because fillers can be used very effectively to enhance the ultimate properties. The reinforcement effect of carbon black (HAF) and the effect of accelerator were studied by Kontov and Spathis.¹ The Mooney–Rivlin relation was used to describe the behavior of the rubber matrix. Moreover, the effect of reinforcing HAF on the network structure, technical properties, and failure of ethylene propylene diene monomer (EPDM) rubber vulcanizates was studied.² Extensive research^{3,4} was carried out on the effect of type and concentration of HAF on the elastic modulus of butyl rubber. The time of vulcanization and its effect on the elastic modulus

and the tensile strength of isobutylene isoprene rubber were also investigated. Eberhard and Mansour⁵ studied the effect of HAF on the mechanical properties of elastomers. The relationships between the structure of networks and mechanical properties of rubber vulcanizates were studied by Mingshi.⁶ On the other hand, the static and dynamic elastic moduli of particulate composites, consisting of two phases, one of which has isotropic elastic and the other of which has linear viscoelastic properties, were studied by Theocaris and Sideridis.⁷ A model defining the approximate equations for determining the elastic modulus of a composite from the properties of the constituent material was used. Further problems of stress relaxation in butyl rubber HAF systems are tackled in the present work.

EXPERIMENTAL

Pereparation of Rubber Samples

Samples of butyl rubber (IIR) were prepared according to standard methods with the compositions shown in Table I.

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Journal of Applied Polymer Science, Vol. 77, 1067–1076 (2000)
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Table I Composition of the Composite

Ingredients	Phr ^a
IIR	100
Stearic acid	2
Zinc oxide	5
Processing oil	10
HAF	0, 15, 25, 35, 45, 65, 85, 105
MBTS ^b	2
PBN ^c	1
Sulfur	2

^a Parts per hundred weight of rubber.

^b Dibenzthiazyle disulphide.

^c Phenyl- β -naphthylamine.

The test samples were cut in the form of discs of with a surface area of 0.78 cm^2 and a thickness of 0.3 cm. All samples were vulcanized at $153 \pm 2^\circ\text{C}$ under a pressure of 40 kg wt/mm^2 for 20 mm. They were thermally aged at 90°C for 35 days to attain reasonable stability and reproducibility of measured quantities.⁸

Stress-strain isotherms at 25°C were obtained for discs cut from sheets, using standard techniques. The apparatus used for the stress-strain measurements is illustrated in Figure 1.

The sample was put between two disc ends (load cell). The lower end was fixed and the upper end was suspended from a strain gauge (Stathem Model GJ-16-350). A constant voltage dc power supply (Hewlett-Packard 6217) was used to supply approximately 14 V to the transducer, which was frequently calibrated using a set of standard weights. Its output was found to remain constant over the usual time span of an experiment. The sample was subjected to compression strains by turning the screw different turns. The potential from the stress gauge was calibrated in terms of newtons per square meter. Stress-strain measurements were made by using a sequence of increasing numbers of turns. The values of the elastic force (F^*) were recorded only after they became constant. To measure the stress relaxation, a certain number of turns of the screw were fixed and the stress recorded with time.

RESULTS AND DISCUSSION

The strain dependence of stress during the mechanical compression process of butyl rubber loaded with different concentrations of HAF [0,

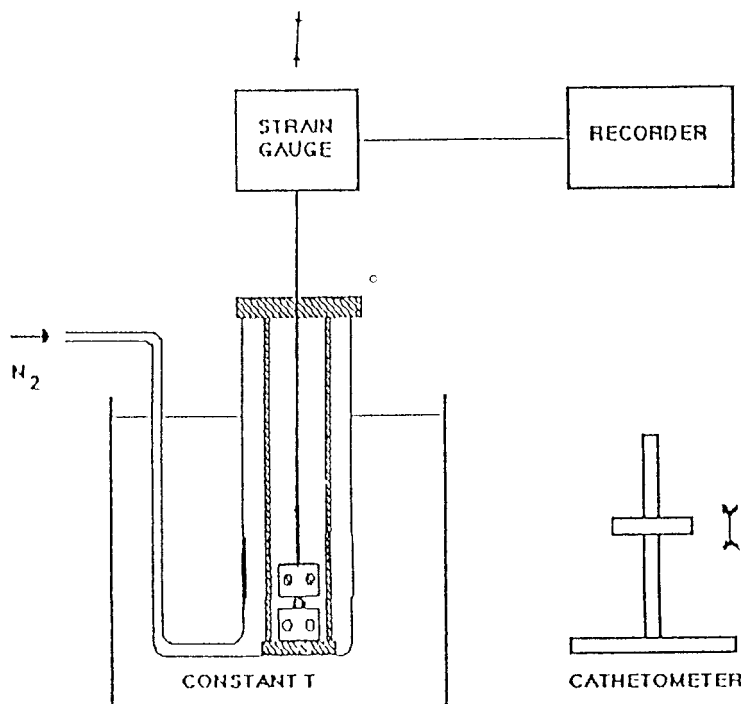


Figure 1 Schematic diagram of the apparatus used for the stress-strain measurements.

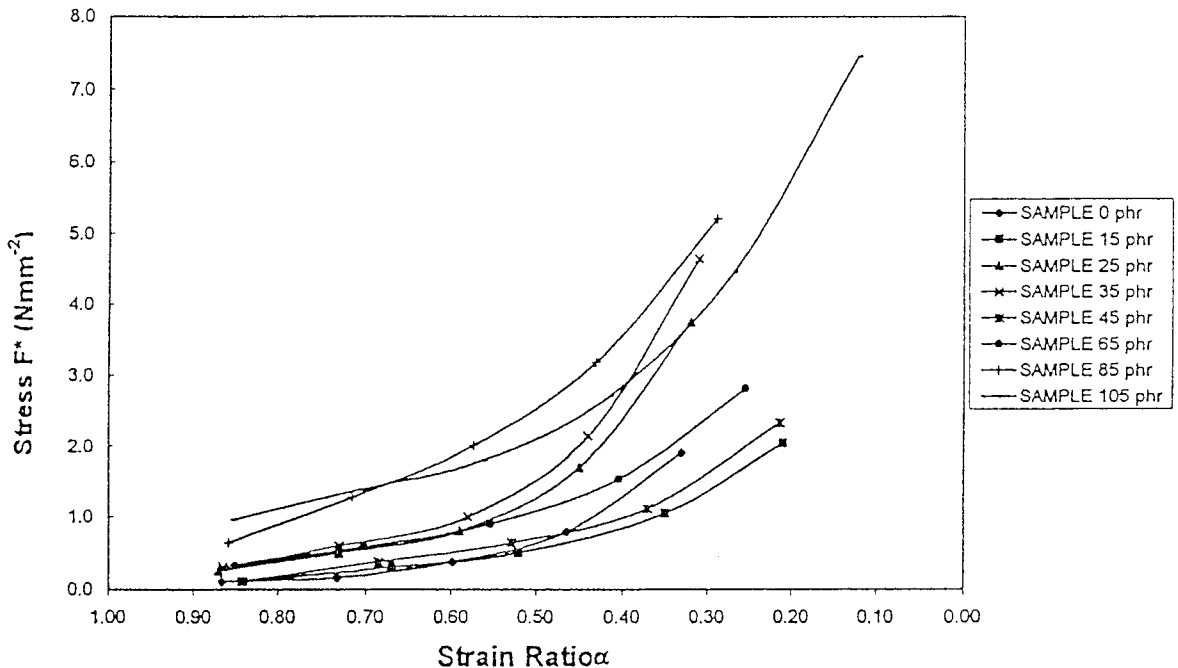


Figure 2 The stress-strain ratio dependence of butyl rubber loaded with different carbon black concentrations.

15, 25, 35, 45, 65, 85, 105 phr] are illustrated in Figure 2. It is noted that, at low values of strains, the stresses are nearly independent of it up to strain ratio of 0.5. The regular effects of HAF concentrations appear where there are slight increases in stress with HAF concentrations in this region of strain. At high values of strain (low values of strain ratio), a sharp rise in stress with strain takes place. The rise in stress with HAF concentrations appears clearly at higher values of HAF. Between 45 and 65 phr of HAF, there are some fluctuation in stress (see Fig. 3). It is noticed that, at both low and high HAF concentrations, the elastic constant increases with HAF. However, at moderate concentrations, a peak centered at about 30phr is clearly observed. This peak is thought to be the result of redistribution of HAF from a dispersed⁹ system to an attached one. In fact, a dispersed system is one in which the spherical carbon particles are individually dispersed in the host material. An attached system, on the other hand, implies the occurrence of contacts between particles, thus forming aggregates, which favor the rise in the composite stiffness. The process of redistribution would introduce some air gaps between carbon particles, which lowers the elastic constant until these gaps are filled again.

The low concentration part of Figure 3 is more thoroughly understood by constructing a relation between the volume fraction and the calculated elastic constant E , as in Figure 4. The results are adapted to a relation of the form,

$$E = E_0(1 + 0.67fc + 1.62f^2c^2)$$

where E_0 is the elastic constant of the unloaded rubber sample, and f is the shape factor taken in most cases as the ratio between the length and width of the test sample; its value ranges from 4 to 7 in many reports. For our results, the value of $f = 6.5$ yields satisfactory agreement between experimental and calculated values of the elastic constant.

The second part of this investigation deals with the stress relaxation phenomenon at different values of strain for different loadings of samples. For most samples, the stress decreases exponentially at early times and is time-independent after a short time, as in Figure 5. At an early time (10 s), if we plot a relation between stress ($\ln F^*$) and time (t) at different HAF concentrations for different strains, we obtain a spectrum of lines (Fig. 6). From these lines that obey the relation $F = F_0 \exp(-t/\tau)$, we can cal-

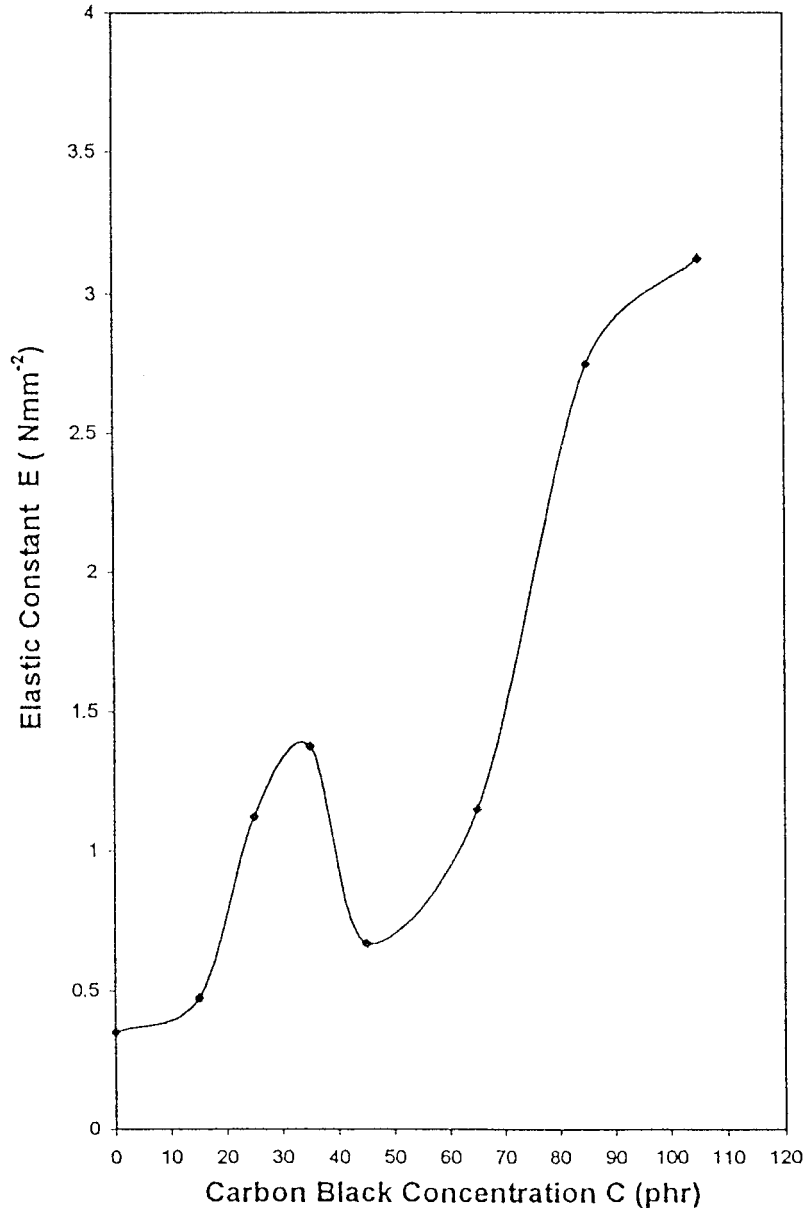


Figure 3 The dependence of the elastic constant on the carbon black concentration.

culate the relaxation times, where F_0 is the stress at zero time, and τ is the relaxation time at which $F = (1/e)F_0$.

Table II represents the relaxation times of samples containing different concentrations of HAF at different values of strains. From this table we notice that: first, for unloaded samples (unfilled), the relaxation time is very long, which means that the property is an irrecoverable one. However, at high-compression strain the relaxation time is relatively short, which means that some lateral ordering is formed, so

it becomes a recoverable process. Second, for the loaded samples, HAF assists the recoverable process [i.e., HAF acts as a hard phase that links the soft phases (rubber)]. Also, the strains increase the relaxation time for these samples.

The viscosity (η) can be calculated from the relation $\eta = E\tau$. It is plotted against the volume fraction of HAF concentration in Figure 7. It is found that the viscosity increases with volume fraction at low concentrations and obeys the relation:

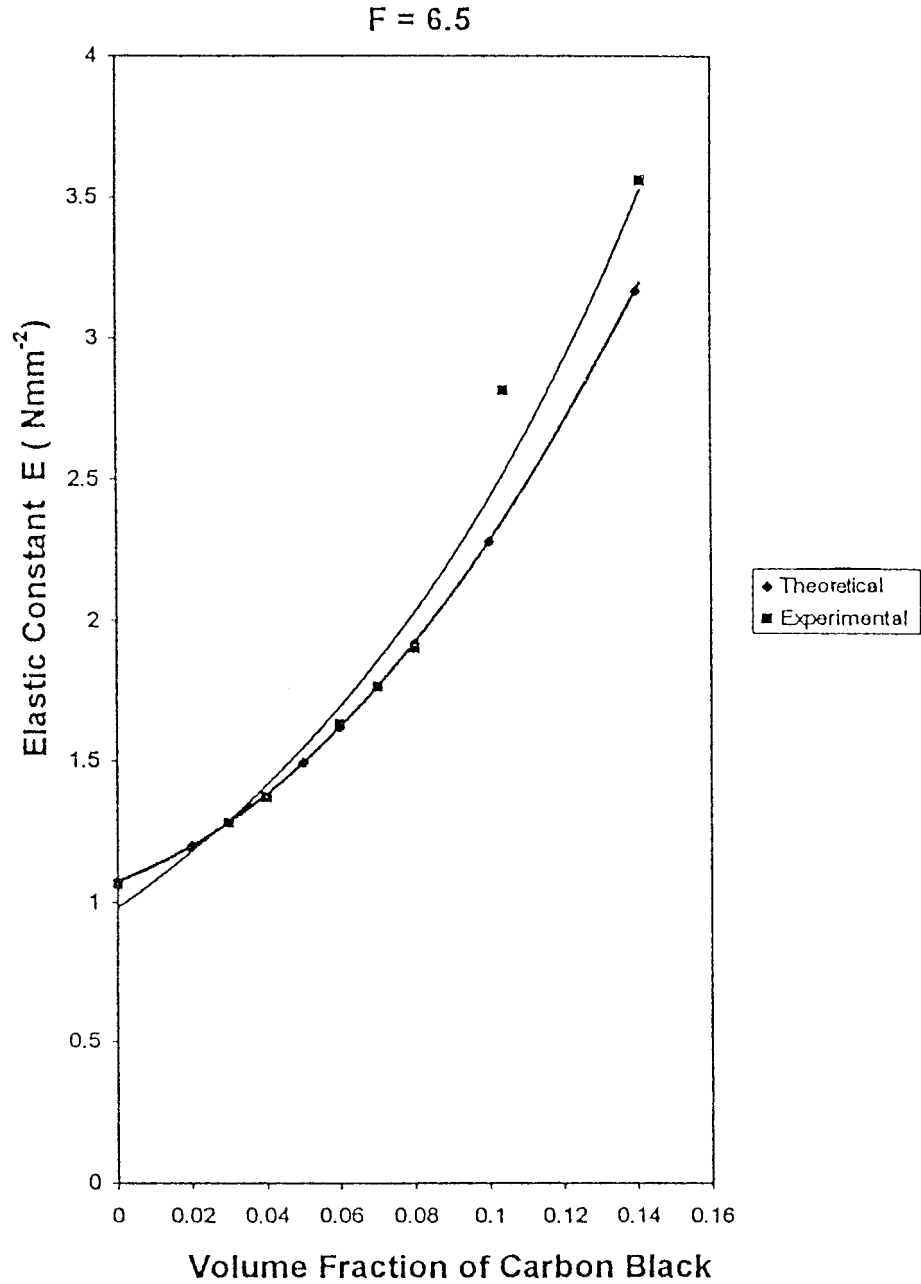


Figure 4 The experimental as well as theoretical dependence of the elastic constant on the volume fraction of carbon black.

$$\eta = \eta_0(1 + 2.5c + 14.1c^2)$$

$$\eta_{sp} = 2.5c + 14.1c^2$$

If we calculate the specific viscosity

and

$$\eta_{sp} = \eta - \eta_0/\eta_0$$

$$\eta_{sp}/c = 2.5 + 14.1c$$

we find that

If we plot a relation between η_{sp}/c against HAF concentrations (Fig. 8), we obtain a straight line;

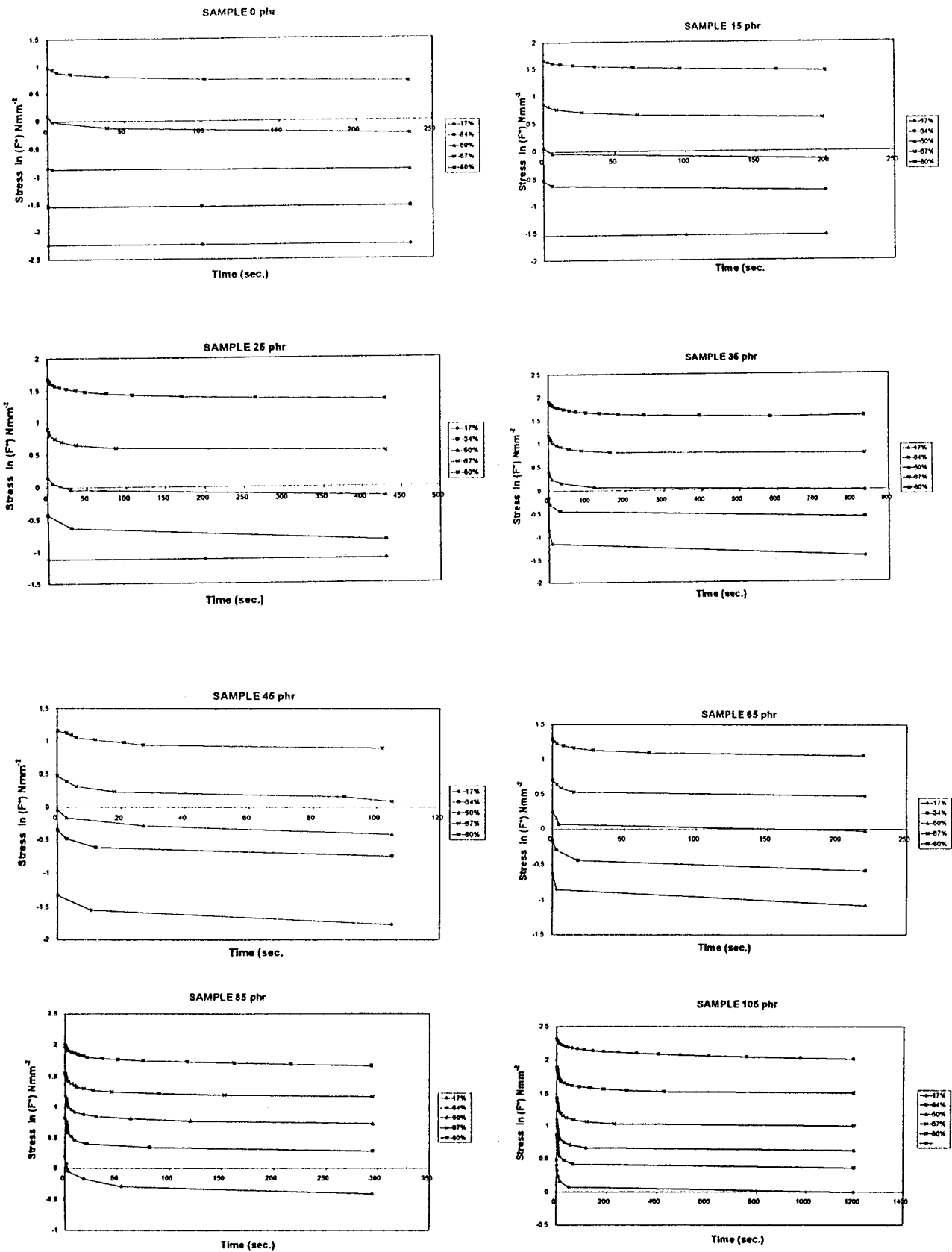


Figure 5 The time dependence of mechanical stress (ln F*) at different compressive strains, for Butyl rubber loaded with different Carbon black concentrations.

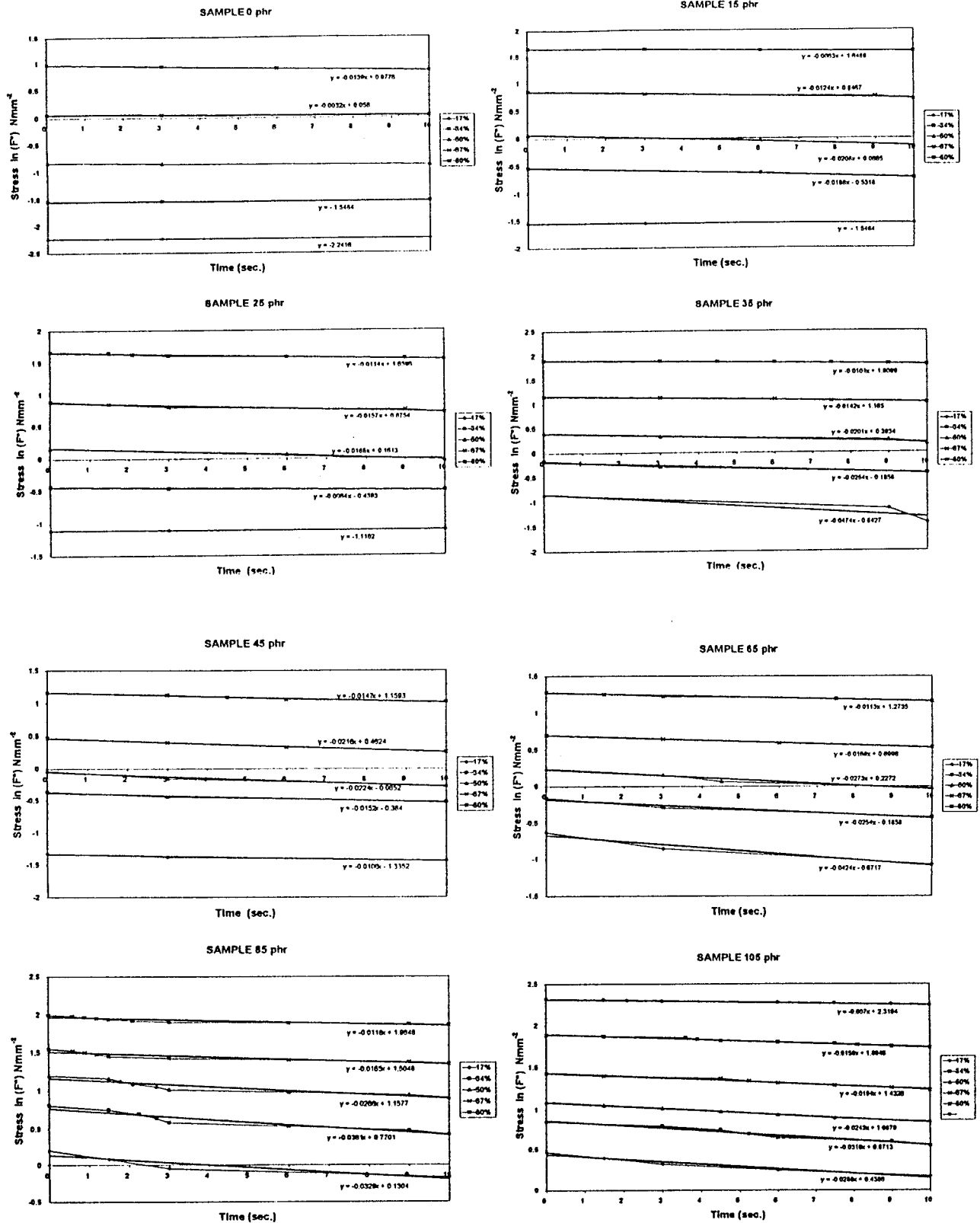
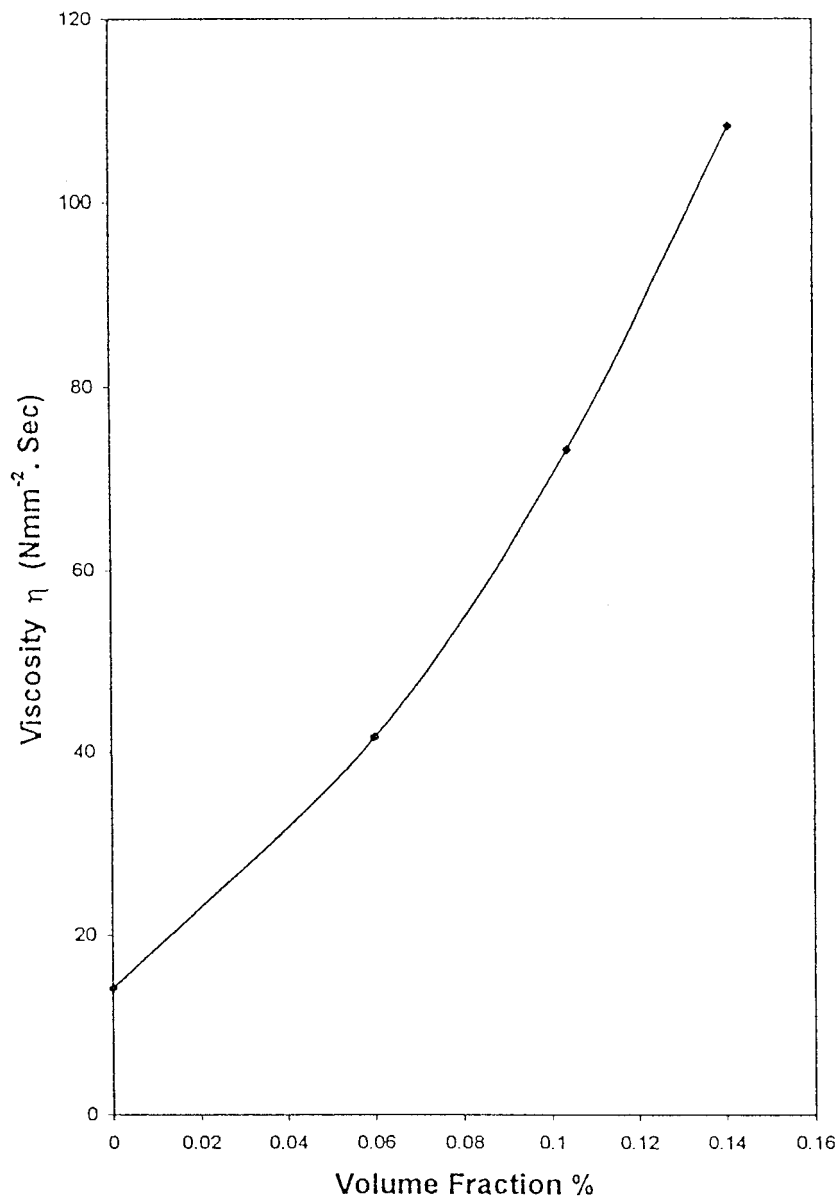


Figure 6 Mechanical stress in F^* against time t in the first 10 s at different compressive strains, for butyl rubber loaded with different carbon black concentrations.

Table II The Calculated Relaxation Times for Samples Containing Different Carbon Black Concentrations and at Different Strains

Strain	0 phr	15 phr	25 phr	35 phr	45 phr	65 phr	85 phr	105 phr
17	∞	∞	∞	21.09	94.33	23.58	30.39	34.72
34	∞	53.19	156.25	39.37	65.78	39.37	27.70	31.34
50	∞	48.07	53.19	49.75	44.64	36.63	37.59	41.15
67	315.1	80.64	63.69	70.42	46.29	59.52	60.60	63.29
80	71.94	166.6	87.71	99.00	68.02	88.49	84.74	142.85

**Figure 7** The dependence of viscosity of butyl rubber on the volume fraction of carbon black.

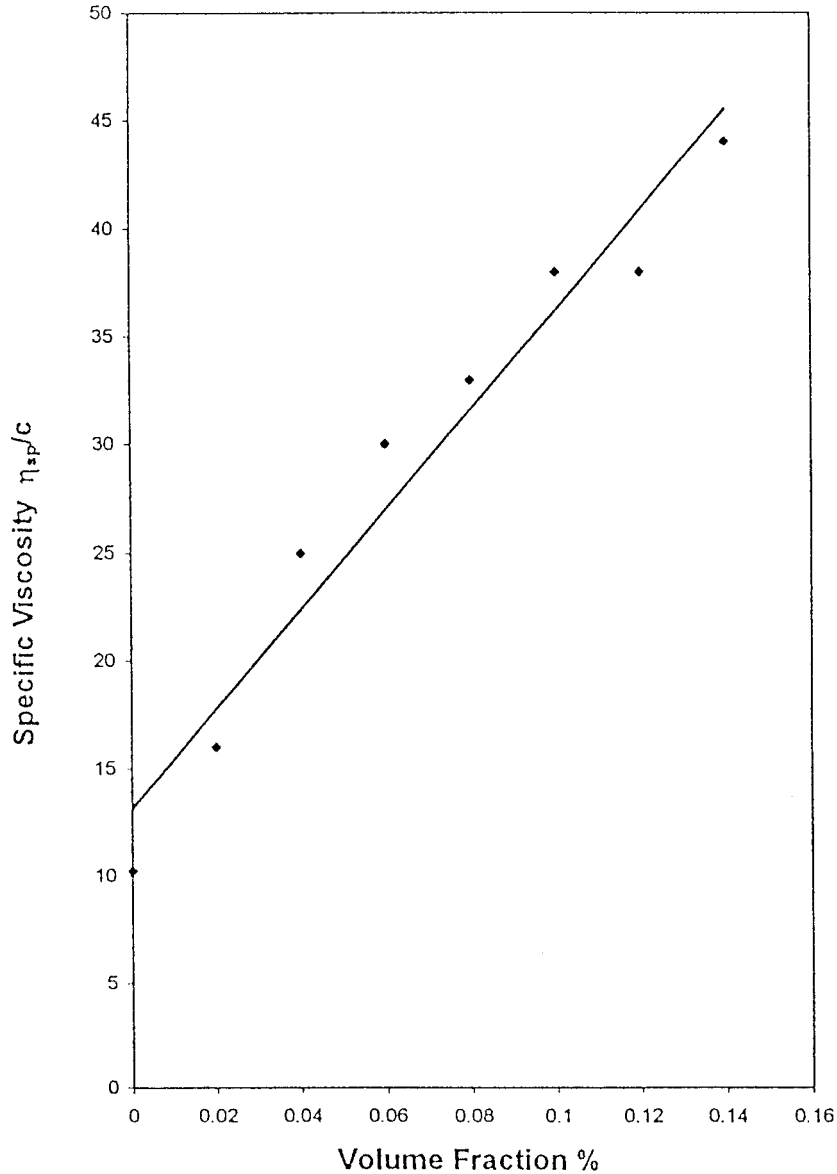


Figure 8 The dependence of specific viscosity per volume fraction on the volume fraction concentration of carbon black.

the intercept of this line at zero concentration is >2.5 . This is due to the solvation process¹⁰ at the surface of the carbon sphere embedded in the rubber matrix.

CONCLUSION

The elastic constant E increases with increasing HAF concentrations in butyl rubber according to

the relation

$$E = E_0(1 + 0.67fc + 1.62f^2c^2)$$

and a satisfactory experimental agreement is obtained for $f = 6.5$. The anomaly in E with HAF concentration at moderate concentrations of HAF is a clear indication of a transition from a dispersed system to an attached one. The relaxation time that is calculated from the stress relaxation relation (in F^* with time t) depends on HAF concentrations.

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