

Step-Strain Stress Relaxation of Carbon Black-Loaded Natural Rubber Vulcanizates

Tarek M. Madkour

Department of Chemistry, UAE University, P.O. Box 17551, Al-Ain, United Arab Emirates

Received 10 April 2003; accepted 17 November 2003

ABSTRACT: Step-strain stress relaxation experiments were performed on natural rubber vulcanizates of various carbon black (HAF) concentrations by subjecting the samples to a very rapid strain and fixing its length at the deformed state. Time-temperature superposition in the viscoelastic region was evaluated to investigate the effect of temperature on the relaxation times of the rubbery composites. Remarkably, it was observed that, at higher HAF concentrations, increasing the temperature had a lesser effect on decreasing the overall stress values. That was attributed to the lower number of elastomeric chains per unit volume due to the agglomeration of the carbon black particles. The energy barrier resulting from the adsorption of the rubbery chains on the filler particles was insufficient to drastically reduce the diffusion and rearrangement of the polymer

chains. The activation energy of the rubber-like deformation calculated from the time-temperature superposition was shown to be independent of temperature. Interestingly, the viscosity coefficients showed a large increase with a modest addition of the carbon black. This is due to the long-range nature of the temporary bonds formed between the polymer molecules and the surface-active carbon black. The stress-strain of the rubbery composites was shown to behave in a Gaussian manner in accordance with the Mooney-Rivlin relationship. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3387-3393, 2004

Key words: stress; rubber; carbon black; time-temperature superposition; viscoelastic properties

INTRODUCTION

The stress relaxation of crosslinked filled elastomers is a very interesting problem since it contains much information about the internal physics of random polymer networks.^{1,2} Currently, significant experimental and theoretical studies are dedicated to the evaluation of the stress-strain convolution^{3,4} and the change in its behavior as a function of the change in temperature.^{5,6} It is also well documented that carbon black fillers impart strength and toughness to elastomers and thus improve the rubber's resistance to tearing, abrasion, and flex fatigue by increasing its traction and durability as was shown by Madkour and Hamdi⁷ and Yuan and Mark.⁸ In addition, high abrasion furnace carbon black (HAF) influences to a great degree the electrical conductivity and the dielectric properties of the elastomers giving rise to various applications in the rubber industry.⁹ Lawandy and Abdelnour¹⁰ have explained the apparent conduction of the reinforced rubber samples on the basis of the percolation concept tunneling mechanism.

Extensive research has been carried out on the effect of type and concentration of HAF on the stress-strain behavior of filled rubber.^{9,11,12} The static and dynamic elastic moduli of particulate composites were shown to consist of two phases, namely isotropic elastic and linear viscoelastic.^{13,14} Designing optimal materials for specific applications requires an estimation of the effects of time and temperature on the viscoelastic moduli of crosslinked polymers. Jonas et al.¹⁵ and Ploehn and Simon¹⁶ have developed separately a molecular-level model for the temperature dependence of the viscoelasticity of linear monodispersed and crosslinked polymers, respectively. The model consists of a time-dependent momentum balance of representative polymer segments of the crosslinked network and phenomenological expressions for forces acting on the segments. These forces include a cohesive force that accounts for the long-range van der Waals attraction between molecules, an entropic force describing the thermodynamics governing chain conformations, and a frictional force that captures the temperature dependence of the relative chain motion. Madkour and Ebaid¹⁷ and Madkour¹⁸ also modeled the stress-strain behavior of linear and model networks. The modeling results indicated that the maximum atomic-level forces were those exerted on the atoms of the short crosslinking chains rather than on the atoms at the junction points between the short crosslinking chains and the long elastomeric chains of

Correspondence to: T. M. Madkour (tarek.madkour@uaeu.ac.ae).

the network. According to the theory of linear viscoelasticity,¹⁹ stress, σ , is related to strain, ϵ , by

$$\sigma/\epsilon = f(t) \quad (1)$$

i.e., Young's modulus, $E = \sigma/\epsilon$, is time (t) dependent. Maxwell²⁰ showed that the rate of change of stress could be expressed in terms of

$$\frac{d\sigma}{dt} = E \frac{d\epsilon}{dt} - \frac{\sigma}{\tau} \quad (2)$$

where τ is known as the relaxation time. At constant stress, $d\sigma/dt = 0$, and,

$$\sigma = E\tau d\epsilon/dt \quad (3)$$

Comparison of eq. (3) and Newton's law given by

$$\sigma = \eta d\gamma/dt \quad (4)$$

where η is the viscosity coefficient and γ is the relative stress, indicates that

$$\eta = E\tau \quad (5)$$

In case of constant strain, $d\epsilon/dt = 0$, eq (2) is reduced to

$$\frac{d\sigma}{dt} = -\frac{\sigma}{\tau} \quad (6a)$$

or

$$\text{or } \frac{d\sigma}{\sigma} = -\frac{dt}{\tau} \quad (6b)$$

Integration of eq. (6b) results in

$$\ln \frac{\sigma}{\sigma_0} = -\frac{t}{\tau} \quad (6c)$$

i.e.,

$$\text{i.e., } \sigma = \sigma_0 e^{-t/\tau} \quad (7)$$

where σ_0 is the initial stress at time $t = 0$ characterizing the nonequilibrium state of the polymer and σ is the stress after a certain interval of time t during the stress relaxation experiments. If a polymer sample is subjected to a very rapid (theoretically instantaneous) strain and was fixed at this deformed state, the stress arising in the sample would be greater than the equilibrium stress since the sample would not have enough time to reach the equilibrium strain. After a given time, the relaxation time, the polymeric sample

at the fixed deformed state would have developed a rubber-like strain corresponding to a low modulus as a result of the changes in the chain conformations. The difference in the energies of the active and initial states is the activation energy of the rubber-like deformation. The rate of establishing equilibrium is related to the probability of transition of the system from one state of equilibrium to another under the influence of the thermal motion. The probability of this process is expressed by Boltzmann's law:

$$W = v_0 e^{-\Delta U/RT} \quad (8)$$

where v_0 is the intrinsic frequency of molecular vibration, which is similar for liquids and solids (10^{13} to 10^{14} vibrations/s), ΔU is the activation energy of the rubber-like deformation, R is the gas constant, and T is the temperature. The reciprocal of the probability of the changes in the chain conformations, i.e., the relaxation time is given by

$$\tau = \tau_0 e^{\Delta U/RT} \quad (9)$$

where τ_0 is the period of vibration of atoms and equals 10^{-13} s. The smaller the value of ΔU and the higher the temperature, the smaller the relaxation time and the faster the stress relaxation are expected to be.

In this article, we investigate the effect of concentration of carbon black (HAF) on the step-strain stress relaxation of natural rubber vulcanizates as a function of time. Our investigation parallels that of Urayama et al.²¹ for triblock (PS/PI) copolymers. We also focus on the relaxation time-temperature relationship to deduce the activation energy of the relaxation process as a function of the filler concentration. The study is also extended to evaluate the viscosity coefficients in the viscoelastic region for the carbon black-loaded natural rubber vulcanizates at the various concentrations and temperatures.

Experimental

Preparation of the elastomeric composites

Samples of natural rubber vulcanizates were prepared according to standard methods as described earlier⁹ with the compositions shown in Table I, resembling a standard recipe commonly used by the Transport and Engineering Co. (Alexandria, Egypt) for the production of automobile tires. Sheets of the polymer were vulcanized at 153°C under a pressure of 40 kg wt/mm² for 20 min. They remained unattained for 14 days before testing at room temperature to acquire reasonable stability and reproducibility of the measured quantities.

TABLE I
Composition of the Natural Rubber Composites Under Study

Ingredients	phr ^a
Natural rubber	100
HAF	0, 35, 65, 105
PBN ^b	1
Zinc oxide	5
Stearic acid	2
Processing oil	10
Sulfur	2
MBTS ^c	2

^a Parts per hundred weight of rubber.

^b Phenyl-*B*-naphthylamine.

^c Dibenzthiazyle disulphide.

Step-strain stress relaxation experiments

The stress-strain isotherms as well as the step-strain stress relaxation data at various temperatures were obtained on strips cut from the crosslinked sheets using standard techniques. The strips had cross-sectional areas A^* of approximately 4 mm^{-2} and the lengths of the central portions of the strips were approximately 12 mm. The apparatus used for the stress-strain measurements is described elsewhere.²² The sample, held vertically between two clamps, was placed into a double-jacket Pyrex glass cell attached to thermostatted water bath. The temperature of the sample cell was controlled to a precision of 0.1°C by means of a Neslab circulating bath (with ethylene glycol as the bath fluid). A stream of nitrogen through the chamber protected the sample against oxidative degradation at the higher temperatures. Measurements were made at 30, 50, 70, and 100°C . The lower clamp was fixed and the upper clamp was suspended from a strain gauge (Statham model G1-16-350). A constant voltage DC power supply (Hewlett-Packard 6217) was used to supply approximately 14 V potential to the transducer. The transducer was frequently calibrated using a set of standard weights. Its output was found to remain constant over the usual time span of an experiment.

Prior to attaching the clamps to a sample, two thin lines were drawn on it by means of a white powder. The sample clamps were lined with thin sheets of rubber to minimize premature rupture or slippage of the samples at the contact points. The exact length of the thus-demarcated section of the sample was measured precisely at the desired temperature by means of a cathetometer (Gaertner Scientific Corp., Model M940-303P, precision $1 \mu\text{m}$), and the thickness and width were determined with a micrometer. Three measurements each along the thickness and width of the strip were taken, and the average cross-sectional area, A^* , was determined.

The upper clamp was raised to a position giving the desired elongation of the strip in a step-wise fashion,

hence the step-strain notation. The distance between the two lines was measured with a cathetometer and recorded as the length L . The ratio of L to L_0 (initial length) presents the elongation (strain), ϵ . The potential from the stress gauge was calibrated in terms of Newtons (N). The stress relaxation measurements were made using a sequence of increasing values of the elongation (strain steps). The values of the elastic force σ were recorded at every strain step for the duration of the initial 30 min of the relaxation experiment. The equilibrium elastic force, σ_e , was noted after the force reading had become sensibly constant for at least 15 min.

The elastic quantity of interest for the stress-strain investigation portion was the reduced stress or modulus defined by²²

$$[\sigma_e^*] = \sigma_e / [A^*(\epsilon - \epsilon^{-2})] \quad (10)$$

whereas the elastic quantity of interest for the step-strain stress relaxation investigation portion was the nominal stress, $\sigma^* = \sigma / A^*$, as related to the elapsed time of the relaxation experiment by

$$\sigma^* = (\sigma_0 / A^*) e^{-t/\tau} \quad (11)$$

RESULTS AND DISCUSSION

Stress relaxation measurements

The representation of the stress-strain data is based on the Mooney-Rivlin equation:

$$[\sigma_e^*] = 2C_1 + 2C_2\epsilon^{-1} \quad (12)$$

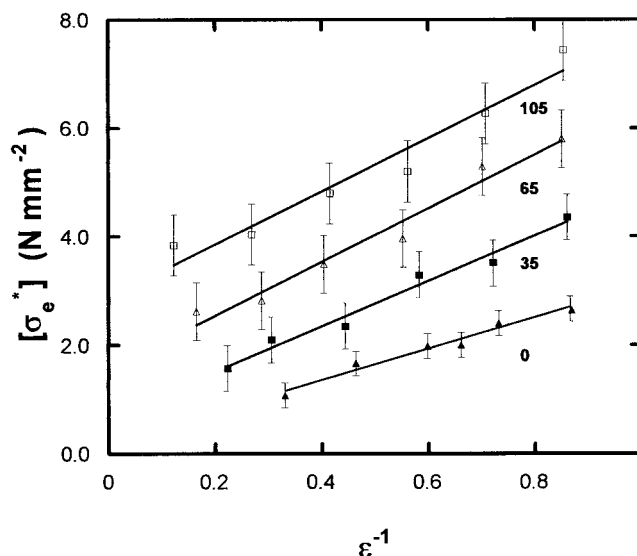


Figure 1 Mooney-Rivlin isotherms for the natural rubber composites filled with different portions of carbon black (HAF).

TABLE II
Ultimate Properties of Natural Rubber Vulcanizates

HAF concentration (phr)	ϵ_m^a	$(\sigma/A^*)_m^b$ (N mm ⁻²)	$10^3 E_m^c$ (J mm ⁻³)
0	3.561	2.832	4.316
35	3.924	4.903	7.852
65	3.876	6.284	11.151
105	4.020	7.002	18.260

^a Maximum strain.

^b Maximum nominal stress.

^c Maximum required energy.

where $2C_1$ and $2C_2$ are constants. Typical isotherms of this type are shown in Figure 1. Every isotherm in the figure represents the stress–strain behavior at 25°C of a natural rubber composite loaded with a different HAF content. The stress–strain relationship as shown in the figure follows the Gaussian behavior depicted by the Mooney-Rivlin equation [eq. (12)]. It is obvious from the figure that natural rubber composites with a higher loading of the carbon black filler exhibit a higher level of toughness. This is because the filler particles in the polymer network increase the network's modulus by increasing the number of effective network chains per unit volume. This will enhance the elastic properties of the individual chains close to the filler particles since the excluded volume of the filler particles itself will naturally change the distribution function of the end-to-end vectors of the nearby chains.¹⁸ The ultimate properties obtained for these composites are shown in Table II. They are the maximum strain, ϵ_m , the maximum nominal stress, σ_m , and the energy required to reach the maximum nominal stress at the maximum strain, E_m . The maximum required energy was calculated by considering the area under the nominal stress–strain isotherms. The marked increase in the maximum required energy with the increase in the filler content is due to the adsorption of the polymer chains on the surface of the filler particles, thus effectively increasing the crosslink density of the polymer networks. By performing the stress relaxation procedures at a constant strain value of $\epsilon = 2$ and observing the relaxation of the nominal stress by time (t), the effect of temperature on the stress relaxation was evaluated. Figures 2–5 illustrate the dependence of the nominal stress of the various natural rubber composites on the elapsed time of the measurements at the different temperatures. In all of the figures, it is obvious that, during the relaxation process, the stress has decreased by time as the released energy within the rubbery sample enables the recoiling and rearrangement of the molecular chains. Depending on the topology of the polymer network and the amount of the released energy, the relaxation process behaves differently at different temperatures and various HAF loadings. This is since the stress

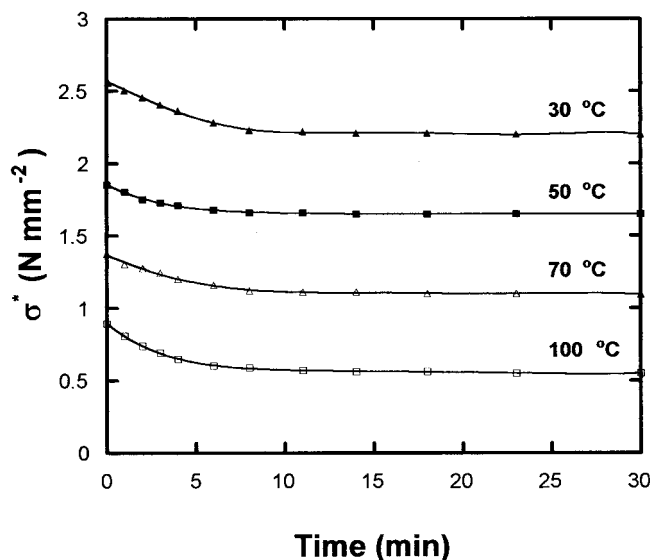


Figure 2 Stress relaxation curves in the viscoelastic region for unfilled natural rubber networks at the various temperatures.

relaxation of the adsorbed chains is a function of the filler size and concentration and can vary for a given volume fraction of the carbon black if agglomeration of the particles occurs. At higher HAF concentrations, the relaxation time was observed to increase dramatically. Remarkably, increasing the temperature had a lesser effect on decreasing the overall stress values at the higher concentrations compared to the lower ones. The increase in the relaxation times and the decrease in the stress decline at the higher HAF concentrations can be attributed to the lower number of the elasto-

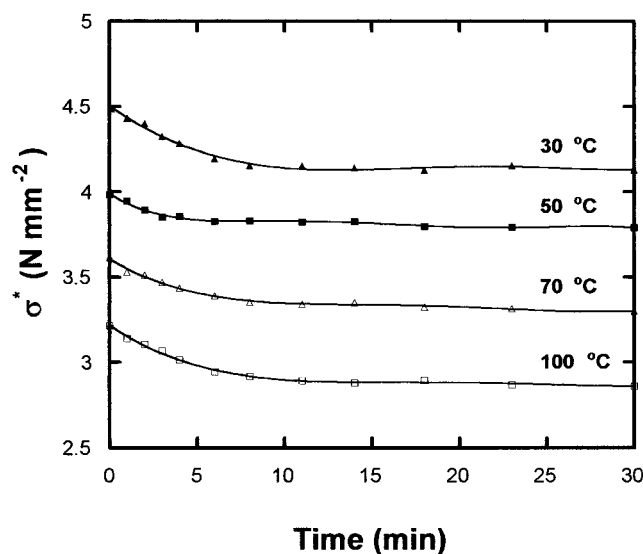


Figure 3 Stress relaxation curves in the viscoelastic region for natural rubber composites filled with 35 phr HAF at the various temperatures.

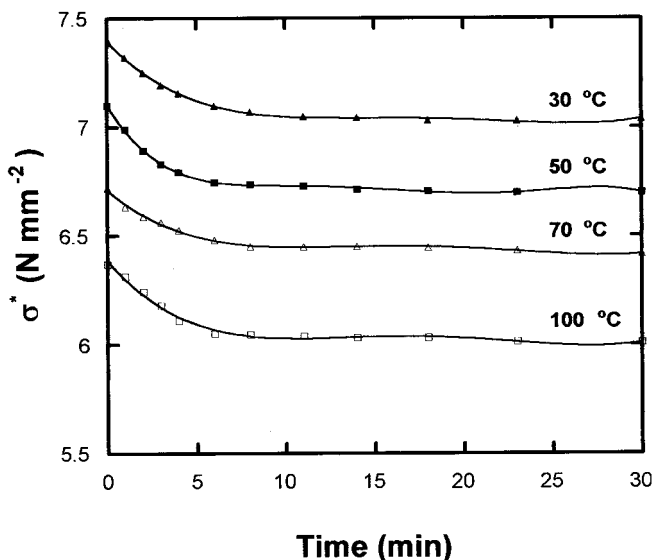


Figure 4 Stress relaxation curves in the viscoelastic region for natural rubber composites filled with 65 phr HAF at the various temperatures.

meric chains per unit volume as the HAF concentration increases. The thermal motion of the elastomeric chains in this case will become less sensitive to the increase in the temperature as the energy barrier resulting from the adsorption of the rubbery chain segments on the filler particles becomes insufficient to drastically reduce the diffusion and the rearrangement of the polymer chains.

The relaxation times calculated using eq. (7) are plotted in Figure 6 as a function of the temperature at

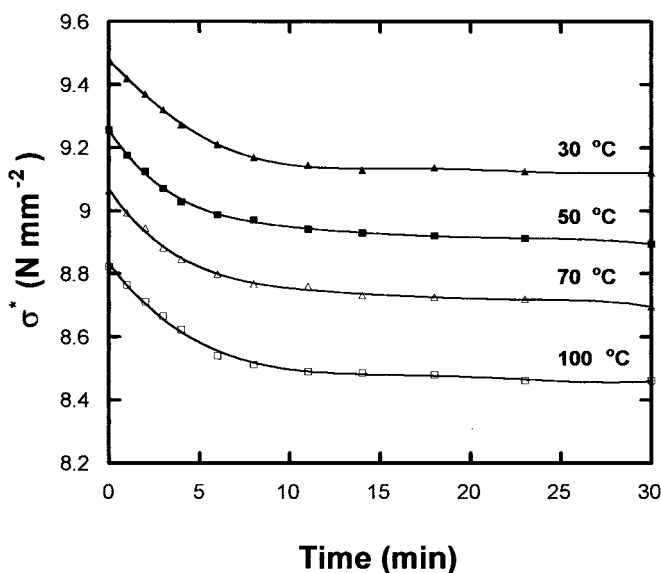


Figure 5 Stress relaxation curves in the viscoelastic region for natural rubber composites filled with 105 phr HAF at the various temperatures.

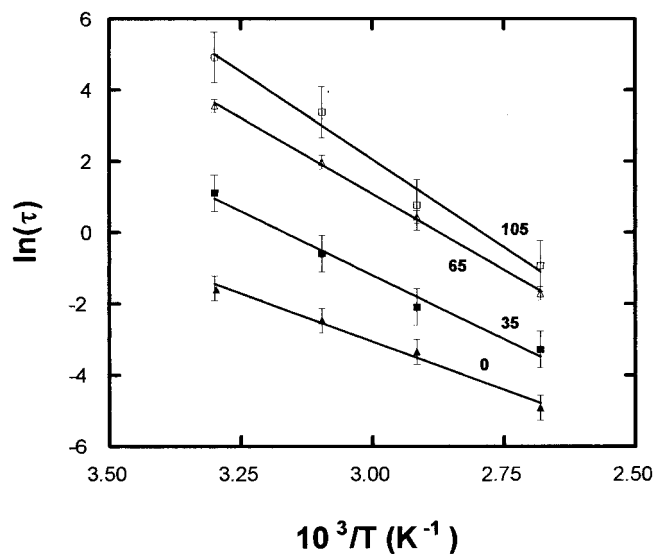


Figure 6 The dependence of the relaxation times of the various natural rubber vulcanizates on the inverse temperature.

the various HAF loadings. The figure clearly illustrates the decline in the relaxation times of the polymer composites with the increase in temperature, as the aforementioned energy barrier becomes considerably weak. At the higher temperatures, more and more segments are able to break free and could, in fact, participate in the recoiling and rearrangement process. The higher the HAF content, the slower the relaxation process and the greater the relaxation times will be. It is interesting in this context to consider the ultimate cases of very low and very high temperatures in light of the behavior illustrated in Figure 6. It could be elaborated that, at low temperatures, the deformation of the polymeric samples would be quite small and therefore would be independent of the time of force action. At these temperatures, the relaxation time is much greater than the time of the deformation and any time intervals would be insufficient for the polymeric chains to rearrange themselves. Alternatively, at quite high temperatures, the relaxation time of the sample would be very small and rubber-like deformation could develop irrespective of the loading time. By applying eq. (9) and taking into account the relaxation time estimates at the various temperatures, the activation energy of the rubber-like deformation, ΔU , could be estimated. This is shown in Figure 7 for the various rubbery composites. It is important to demonstrate here that the activation energy of the rubber-like deformation is independent of the temperature during the stress relaxation experiments. This is since the temperature only affects the rate of attainment an equilibrium. The higher the temperature, the faster the stress relaxation process will be as a result of the increase in the thermal motion related to the changes

in the chain conformation as explained by Vanden Eynde et al.²³ The apparent increase, however, in the activation energy of the rubber-like deformation as a function of the carbon black concentration highlights the increase in the cooperativity in the intermolecular coupling between the local segmental motions in the different chains during the relaxation process.

The viscosity coefficients (η) of the various rubber composites in the viscoelastic region were calculated using eq. (5). The viscosity dependence on the carbon black (HAF) content (Fig. 8), was noted to obey the power law:⁹

$$\eta = \eta_0(1 + fc + f^2c^2) \quad (13)$$

where η_0 is the viscosity coefficient of the unfilled rubber sample, c is the carbon black concentration, and f is the shape factor taken in most cases as the ratio of the length of the test sample to its width. Interestingly, the viscosity calculations showed a large increase in the viscosity coefficients with a modest addition of the carbon black to the rubber samples, indicating the long-range nature of the temporary bonds²⁴ formed between the polymer molecules and the surface-active carbon black (HAF).

CONCLUSION

The adsorption of the polymer chains on the surface of the filler particles in natural rubber composites effectively increases the crosslink density of the polymer networks. The stress relaxation of these composites at a constant strain value can vary for a given volume fraction of the carbon black if agglomeration of the

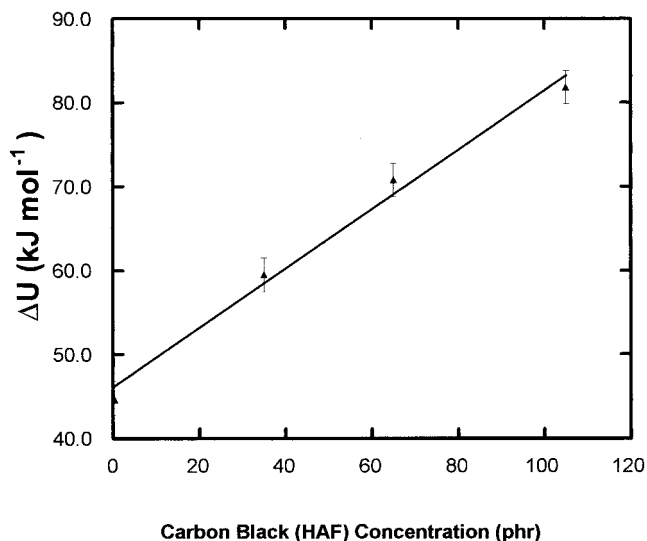


Figure 7 The dependence of the activation energy of the rubber-like deformation of the various natural rubber vulcanizates on the carbon black concentration.

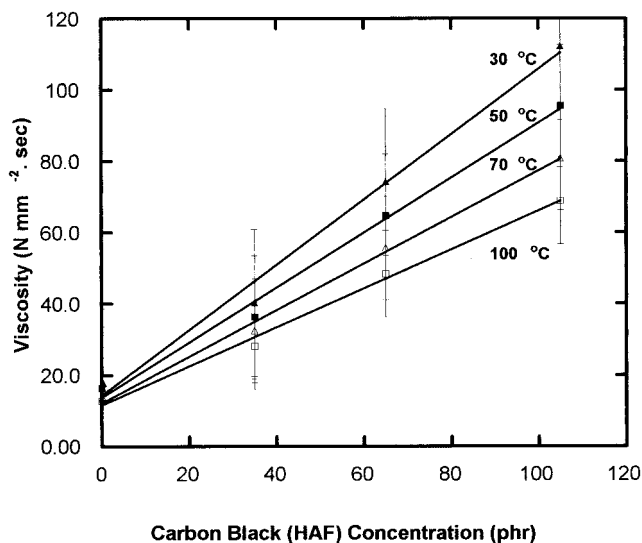


Figure 8 The dependence of the viscosity coefficients of the various natural rubber vulcanizates on the carbon black concentration at the different studied temperatures.

particles occurs. This was shown to be related to the released energy, which enables the recoiling and rearrangement of the molecular chains. The time-temperature superposition results showed that, as the temperature increases, the relaxation times of the polymer composites decrease. This is natural since the energy barrier resulting from the adsorption of the rubbery chain segments on the filler particles becomes weak and insufficient to drastically reduce the diffusion and the rearrangement of the polymer chains. Nevertheless, the higher the HAF content, the slower the relaxation process and the greater the relaxation times will be. This was explained in terms of the activation energy of the rubber-like deformation. The activation energy is independent of the temperature during the stress relaxation experiments, as the temperature affects only the rate of attainment of an equilibrium through the increase in the thermal motion of the chains. Increasing the temperature, however, had a lesser effect on decreasing the overall stress values at high carbon black concentrations, indicating that the thermal motion at these concentrations is less sensitive to the increase in temperature. The increase in the activation energy as a function of the increase in the carbon black concentration is due to the extra temporary bonds formed between the polymer molecules and the surface-active carbon black, which subsequently increases the viscosity coefficients of the various rubber composites in the viscoelastic region.

The author expresses deep thanks to the Transport and Engineering Co. (Alexandria, Egypt) for providing the necessary materials used throughout this study.

References

1. Madkour, T. M. In *Polymer Data Handbook*; Mark, J. E., Ed.; Oxford University Press: New York, 1999.
2. Kloczkowski, A.; Mark, J. E.; Frisch, H. L. *Macromolecules* 1990, 23, 3481.
3. Hotta, A.; Clarke, S. M.; Terentjev, E. M. *Macromolecules* 2002, 35, 271.
4. Apostolov, A. A.; Fakirov, S.; Mark, J. E. *J Appl Polym Sci* 1998, 69, 495.
5. Kleppinger, R.; van Es, M.; Mischenko, N.; Koch, M. H. J.; Reynaers, H. *Macromolecules* 1998, 31, 5805.
6. Madkour, T. M.; Mohamed, S.; Barakat, A. M. *Polymer* 2002, 43, 533.
7. Madkour, T. M.; Hamdi, M. S. *J Appl Polym Sci* 1996, 61, 1239.
8. Yuan, Q. W.; Mark, J. E. *Macromol Chem Phys* 1999, 200, 206.
9. Osman, M.; Abdel Ghani, S. A.; Madkour, T. M.; Mohamed, A. R. *J Appl Polym Sci* 2000, 77, 1067.
10. Lawandy, S. N.; Abdelnour, K. N. *J Appl Polym Sci* 1986, 31, 841.
11. Abo-Hashem, A.; Sattar, A. A.; Elshokrofy, K. M. *Polym Degrad Stab* 1992, 36, 5.
12. Eatah, A. I.; Chani, A. A.; Hashem, A. A. *Angewandte Makromolekulare Chemie* 1989, 165, 69.
13. Theocaris, P. S.; Sideridis, E. *J Appl Polym Sci* 1984, 29, 2997.
14. Sharaf, M. A.; Kloczkowski, A.; Mark, J. E. *Rubber Chem Technol* 1995, 68, 601.
15. Jonas, A.; Legras, R.; Scherrenberg, R.; Reynaers, H. *Macromolecules* 1993, 26, 526.
16. Ploehn, H. J.; Simon, P. P. *J Rheol* 1997, 41, 641.
17. Madkour, T. M.; Ebaid, A. H. *J Mol Modeling* 2001, 7, 392.
18. Madkour, T. M. *Angew Makromol Chem* 1999, 266, 63.
19. Atkins, P. W. *Physical Chemistry*; Oxford University Press, Oxford, 1986.
20. Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
21. Urayama, K.; Yokoyama, K.; Kohjiya, S. *Macromolecules* 2001, 34, 4513.
22. Mark, J. E.; Erman, B. *Rubberlike Elasticity: A Molecular Primer*; Wiley-Interscience, New York, 1988.
23. Vanden Eynde, S.; Mathot, V. B. F.; Koch, M. H. J.; Reynaers, H. *Polymer* 2000, 41, 4889.
24. Madkour, T. M.; Soldera, A. *Eur Polym J* 2001, 37, 1105.