Journal of Engineering Physics and Thermophysics, Vol. 76, No. 3, 2003

INVESTIGATION OF THE STRUCTURE OF POLYMER NETWORKS FROM THE DATA ON DYNAMIC MODULI AT DIFFERENT STATIC DEFORMATIONS

I. P. Borodin,[a] **T. N. Khazanovich,**[b] **and**
V. L. Bodneva[b]

UDC 541:64;539.3

Based on the previously developed molecular theory, we analyze experiments in which a small periodic deformation is applied to a statically extended elastomer and then the dynamic modulus is measured as a function of the static extension ratio λ. *The dependence of the loss modulus on* λ, *which contains three parameters, is investigated, and what information on the network structure is contained in these parameters is elucidated. The accuracy of the information obtained is discussed with the use of the literature experimental data.*

Polymer networks are widely used in industry, medicine, sports, and in many other human activities. At the same time, they represent a fundamental problem for the physics of polymers.

The properties of polymer networks are determined in many respects by their structure, which is characterized by the mean molecular mass of the segments of the chains between the network points and their polydispersity, the presence of defects in the network, i.e., the proportion of dangling chains and loops, and other parameters [1]. For their determination one uses such methods as measurement of the dependence of the equilibrium stresses on the extension ratio λ [1], swelling [1, 2], and birefringence [1–3]; scattering of neutrons [4] and x-rays [5]; the spectroscopy of nuclear magnetic resonance (NMR) [2, 6–8], and others. All these methods have a common disadvantage: their theories are well developed for the model of a network of so-called phantom chains, the permissible configurations of which are limited only by the network points. In reality, the conformations of the chains are additionally limited by their interactions. However, at present there is no universally recognized theory of networks with interacting chains. In this situation, it is necessary to increase the number of approaches to studying the network structure of networks, based on different physical principles, since in them the interactions of chains will manifest themselves differently.

In [9–12], it has been concluded that experiments in which a small oscillating deformation is applied to a constantly extended elastomer can be a new method of determining the network structure. In these experiments, the instantaneous length of a specimen $S(t)$ oscillates with a circular frequency ω near a certain mean value $\overline{S}$ in such a way that

$$\frac{S(t)}{S_0} = \lambda\,(1 + \varepsilon \cos \omega t)\,, \quad \varepsilon << 1\,, \tag{1}$$

where $\lambda = \overline{S}/S_0$. If the dynamic moduli are determined in terms of the true stresses, they will not differ from the moduli measured in standard experiments with viscoelastic bodies. In particular, the loss modulus E'' will be proportional to the dissipation power in a unit volume, averaged over the period, $\overline{W} = \omega\varepsilon^2 E''/2$.

In the present work, we elucidate what information on the network structure can precisely be obtained from the dependences E''–λ.

Molecular theories of the response of extended elastometers to a small oscillating deformation [9–12] dealt with frequencies limited by the transition zone between the glassy and highly elastic states [13]. By now it has been reliably established (see, for example, [14, 15]) that motions whose scale is small in comparison with the dimensions of the chains and large in comparison with the dimensions of the monomers are responsible for the dissipation processes in this zone. Such semilocal motions in nonswollen elastomers and melts are well described by the known Rouse

---

[a] Kostroma State Technological University, Kostroma, Russia; [b] N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia; email: khaz@center.chph.ras.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 76, No. 3, pp. 112–115, May–June, 2003. Original article submitted October 4, 2002.

model [13, 16], which was applied by Mooney to the theory of viscoelasticity of polymer networks. In this model, chains are represented as sequences of beads connected by linear springs with a zero equilibrium length. The beads model the viscous resistance of relatively short segments of the chains, and the potential of extension of the springs is expressed in terms of the logarithm of the distribution of the probabilities for the vectors connecting the neighboring beads. Therefore, these springs are called entropy springs.

According to the Rouse–Mooney model, the loss E'' modulus in networks of any structure is independent of deformation [18]. This conclusion is also true for viscoelastic models of local motions of the type of the Hearst–Harris model [19]. On the other hand, in the majority of experiments (see, for example, [20–22]) it has been revealed that both components of the dynamic modulus (E' and E'') increase when elastomers are extended. The only exception known to us is the investigation carried out in [23], where it has been found that the initial increase in E'' at $\lambda > 4$ gives way to a decrease in this quantity.

In [9], the increase in the loss modulus has been explained by the effects of finite tensibility of the chains, for description of which it is agreed in theoretical rheology that the linear (Gaussian) springs in the Rouse model are replaced by nonlinear ones (see, for example, [24, 25]). In [10], it has been proposed to consider only the first three nonvanishing terms of the expansion of the elastic potential of the springs in powers of the ratio of the distance between the neighboring beads a to its value in the maximum extended chain a_{m}:

$$U(a) = \frac{3k_{\text{B}}T}{2\bar{a}^2} a^2 \left[1 + \alpha \left(\frac{a}{a_{\text{m}}} \right)^2 + \beta \left(\frac{a}{a_{\text{m}}} \right)^4 \right]. \tag{2}$$

The expansion coefficients α and β depend on the model of the chain. For example, in the model of freely jointed segments [26] we have

$$\alpha = \frac{3}{10}, \quad \beta = \frac{33}{175}. \tag{3}$$

As in solid bodies, each atom of elastoactive chains in polymer networks has its own mean position in space. For this reason, the micro-Brownian motions of beads are in fact fluctuations near their mean positions. This circumstance makes it possible to replace the model of beads–nonlinear springs by the quasi-Rouse model with anisotropic stiffnesses of the linear springs [9], which are dependent on the mean distances between the neighboring beads and grow when the chains are extended.

The affine model of high elasticity, in which network points are assumed to be immobile and the vectors connecting the points change under deformation much as the dimensions of the sample change, has been adopted in [9–12] following Mooney [17]. In this model, the contributions of individual chains to the dissipation processes are summed.

An increase in the stiffness at constant mobilities of the beads leads to a decrease in the time of relaxation of normal modes. As Gotlib and Darinskii [27, 28] have shown, the mobility of polymer chains can decrease in the case of extension as a result of the decrease in the fraction of rolled isomers and become anisotropic. In this case, the decrease in the relaxation times will be not so large. In [10], based on the model of uncorrelated jumps of Stockmayer and others [29], it has been established that a decrease in the mobility leads to the independence of the relaxation times of the extension, but the introduction of a weak correlation of jumps leads to a small decrease in them. Investigations with the help of computer modeling [30, 31] have shown that the relaxation times of normal modes decrease markedly in the case of extension. Since the results of these works are presented in a form that gives no way of using them in calculating the time correlation functions of the microscopic stress tensor, in terms of which the loss modulus is expressed [9, 11], here we will give the dependences E''–λ obtained in [10, 11] for two limiting cases: constant coefficients of friction of beads (A) and constant times of relaxation of normal modes (B).

The resulting relation that corresponds to potential (2) can be written in the form

$$E''(\omega, \lambda) = (E''_{\text{G}}(\omega) + E''_{\text{d}}(\omega))\,(1 + q_2\Phi_2(\lambda) + q_4\Phi_4(\lambda)). \tag{4}$$

TABLE 1. Structural Parameters of Natural Rubber

T, °C	Variant	q_2	q_4
50	A	0.23±0.05	0.016±0.007
	B	0.14±0.03	0.009±0.001
0	A	0.05±0.04	0.010±0.001
	B	0.03±0.02	0.0055±0.0008
–20	A	0.07±0.06	0.0099±0.0002
	B	0.04±0.03	0.006±0.001

Here $E''_{\mathrm{G}}(\omega)$ is the loss modulus in the Gaussian phantom network, $E''_{\mathrm{d}}(\omega)$ is the contribution of the elastoinactive chains (defects), and

$$q_n = p\,\langle u^n \rangle\,, \tag{5}$$

where the coefficient $p = E''_{\mathrm{G}}/(E''_{\mathrm{G}} + E''_{\mathrm{d}})$ characterizes the perfection of the grid, and $\langle u^n \rangle$ is the nth moment of distribution of the elastoactive chains by the degrees of rolling, i.e., by the ratios of the distances between the ends of the chains in the undeformed state to their contour lengths:

$$\langle u^n \rangle = \frac{1}{N_{\mathrm{c}}} \sum_{1}^{N_{\mathrm{c}}} \frac{L_\nu}{\langle L \rangle} \left(\frac{h_\nu}{L_\nu} \right)^n , \tag{6}$$

$$\langle L \rangle = \frac{1}{N_{\mathrm{c}}} \sum_{1}^{N_{\mathrm{c}}} L_\nu \,. \tag{7}$$

The form of the functions $\Phi_n(\lambda)$ depends on the coefficients α and β and on the selected limiting case for the mobility of beads. In case A, for the coefficients of (3) we have

$$\Phi_2^{(\mathrm{A})} = \frac{3}{10}\lambda^2\,; \quad \Phi_4^{(\mathrm{A})} = \frac{3}{7000}(1275\lambda^4 - 370\lambda + 712\lambda^{-2})\,; \tag{8A}$$

in case B, for the coefficients of (3) we have

$$\Phi_2^{(\mathrm{B})} = \frac{4}{15}(2\lambda^2 + \lambda^{-1})\,, \quad \Phi_4^{(\mathrm{B})} = \frac{1}{875}(846\lambda^4 - 24\lambda + 564\lambda^{-2})\,. \tag{8B}$$

Relation (4) was derived under the assumption that elastoinactive chains are extended more weakly than elastoactive chains when an elastomer is deformed and do not come out from the Gaussian (linear) region.

It follows from relations (4) and (8) that the loss modulus must increase when an elastomer is extended, as this took place in many experimental works (see above). It is of interest to note that such an increase was also observed in the case of extension of mixtures of isotactic polypropylene with rubber [32]. The decrease in E'' at $\lambda > 4$, observed in [23], is explained most simply by the ruptures of the most stressed chains in the case of large elongations. Such ruptures decrease the parameter p in (5) and, accordingly, E''. This explanation conforms with the fact that the measured values of E'' at $\lambda > 4$ exceed the values of E'' at $\lambda = 1$. Another possible explanation is the appearance of maximum extended chains at large λ [33], in which there cannot occur semilocal motions. In this case, the value of E''_{G} in (4) and, accordingly, the value of $E''(\omega, \lambda)$ will decrease.

The question arises of whether the choice between limits A and B can be made from a comparison with experiment. The results of Mason [20], obtained for natural rubbers caoutchouc at a frequency of 1 kHz and temperatures of –20, 0, and 50°, are best suited for such analysis since these results are only true for the transition zone. The structural parameters q_2 and q_4 obtained as a result of fitting of the data of [20] by relations (4) and (8) for variants A and B with estimation of errors are presented in Table 1. These data allow the conclusion that the differences between the parameters do not exceed the errors of their determination, which are very large. Thus, the theoretical errors which are explained by the fact that the dependence of the relaxation time of normal modes on the extension of the chains is unknown are comparatively small.

To elucidate the meaning of the structural parameters we assume, following Flory [34], that the distribution of the vectors connecting the ends of the active chains is Gaussian in the nonswollen networks. For chains with a contour length L this distribution can take the form

$$P(\mathbf{h}, L) = \left(\frac{\chi_L}{\pi}\right)^{3/2} \exp(-\chi_L h^2) \; ; \quad \chi_L = \frac{3g}{2 l_K L} \, . \tag{9}$$

The dimensionless coefficient g depends on the network structure. For example, for monodisperse defectless networks with a functionality of the points φ [1, 35] we have

$$g = \frac{\varphi}{(\varphi - 2)} \, . \tag{10}$$

It follows from relations (6) and (9) that

$$\langle u^2 \rangle = \frac{l_K}{g \langle L \rangle} = \frac{1}{g \langle n_K \rangle} \, , \tag{11}$$

$$\langle u^4 \rangle = \frac{5 l_K^2 \langle L^{-1} \rangle}{3 g^2 \langle L \rangle} \, , \tag{12}$$

where the mean length of the chains is determined by relation (7), and $\langle u_K \rangle$ and (L^{-1}) are determined in a similar manner.

According to (11), the quantity $\langle u^2 \rangle$ is close to the parameter in the NMR spectra which determines the value of the residual spin interactions (not averaged by heat motions) in the networks [36, 37]. A difference appears only in polydisperse networks since, in contrast to (11), the second moments of the lines in the NMR spectra are determined by the quantity $\langle n_K^{-1} \rangle$.

The values of the parameter q_2 at 50°C (see Table 1), which are higher than those at the other two temperatures by a value exceeding the determination errors, seem to be strange. This behavior of q_2 is evidently explained by the fact that natural rubbers crystallize in the case of extension.

Based on (5), (11), and (12), we obtain for the quantity $p_{\text{low.b}} = 5q_2^2/3q_4$

$$p = p_{\text{low.b}} \langle L \rangle \langle L^{-1} \rangle \, . \tag{13}$$

Since $\langle L \rangle \langle L^{-1} \rangle > 1$, $p_{\text{low.b}}$ is the lower bound of the possible values of the coefficient p. There is no point to give the values of $p_{\text{low.b}}$ calculated from the table data, since larger errors in the parameters q_2 and q_4 lead to even larger (exceeding 100%) errors in the lower bound of the coefficient p. These errors are explained by the fact that the minima of the sum of the squares of the differences between the calculated and experimental values are very "small," although there is excellent agreement between theory and experiment on the graphs. In this situation, the requirements on the accuracy of experiment and the number of experimental data increase. In all probability, we should improve the accuracy of the theory, going beyond approximation (3).

In closing, we discuss the role of the interactions of chains in the proposed method of investigating the network structure. The approximate proportionality of the loss modulus to the frequency to power 1/2, observed in the transition zone [13], points to the fact that the interactions of chains, responsible for the appearance of topological restrictions, have no influence on the processes of energy dissipation in this zone. Interactions in the networks can also produce effective orienting fields [38]. An effective field was introduced in [39]. This field markedly changed the equilibrium dependence of the stress on the extension and weakly influenced the deformation dependence of the loss modulus. Consequently, the dependences E''–λ are sensitive only to the forces extending the chains; in this sense, the method considered is unique.

NOTATION

a, distance between the neighboring beads; $\overline{a^2}$, mean square of the distance between the neighboring beads in a free chain; E' and E'', accumulation and loss moduli, MPa; E''_{G}, loss modulus in the network of Gaussian chains; E''_{d}, contribution of elastoinactive chains to the loss modulus; g, coefficient dependent on the network structure; h, distance between the ends of the elastoactive chain; k_{B}, Boltzmann constant; L, contour length of the elastoactive chain; l_{K}, length of the Kuhn segment; N_{c}, number of elastoactive chains in the network; n_{K}, mean number of the Kuhn segments in the elastoactive chains; $P(\mathbf{h}, L)$, probability density for the distances between the ends of the chains with a contour length L; q_2, q_4, structural parameters; $S(t)$, instantaneous length of the specimen; S_0, length of the undeformed specimen; $\langle u^n \rangle$, n-th moment of distribution of the chains by the degrees of their rolling; $U(a)$, entropy potential; T, absolute temperature; t, time; $\overline{W}$, dissipation power averaged over the period in a unit volume; α and β, coefficients dependent on the chain model; λ, extension ratio of the specimen; χ_L, parameter of the Gaussian distribution; ε, amplitude of the periodic deformation; φ, functionality of the network points; Φ_2^{A}, Φ_4^{A}, Φ_2^{B}, and Φ_4^{B}, functions of the extension ratio determined from formulas (8A) and (8B); ω, circular frequency, sec^{-1}. Subscripts: over-bar, mean value; $\langle\,\rangle$, value averaged over the network; A and B, limiting cases; c, chain; d, defect; G, Gaussian; K, Kuhn; L, contour length; low.b, lower bound; m, maximum; ν, ordinal number of the chain in the network; 0, undeformed state.

REFERENCES

1. J. E. Mark and B. Erman, *Rubberlike Elasticity. A Molecular Primer*, Wiley, New York–Chichester–Briston–Toronto–Singapore (1988).
2. D. J. P. Harrison, W. R. Yates, and J. F. Johnson, *J. Macromol. Sci. C*, **25**, No. 4, 481–549 (1985).
3. P. M. Mott and C. M. Roland, *Macromolecules*, **29**, No. 26, 8492–8496 (1996).
4. S. Westermann, W. Pichout-Hintzen, D. Richter, E. Straube, and R. May, *Macromolecules*, **34**, No. 7, 2186–2194 (2001).
5. T. Kawamura, K. Uruyama, and S. Kohjiva, *J. Chem. Phys.*, **112**, No. 20, 9105–9111 (2000).
6. J. P. Cohen Addad, in: J. P. Cohen Addad (ed.), *Physical Properties of Polymeric Gels*, Chichester (1996), pp. 39–88.
7. E. Fisher, F. Grinberg, R. Kimmich, and S. Hafner, *J. Chem. Phys.*, **109**, No. 2, 846–854 (1998).
8. L. P. Smirnov, *Vysokomolek. Soed. A-B*, **42**, No. 10, 1775–1792 (2000).
9. I. P. Borodin and T. N. Khazanovich, *Vysokomolek. Soed. A*, **15**, No. 9, 2121–2127 (1973).
10. I. P. Borodin, *Vysokomolek. Soed. A*, **22**, No. 6, 1302–1310 (1980).
11. I. P. Borodin and T. N. Khazanovich, *Polymer*, **27**, No. 7, 1044–1049 (1986).
12. I. P. Borodin and T. N. Khazanovich, in: *Structure and Dynamics of Molecular Systems* [in Russian], Ioshkar-Ola (2001), pp 7–10.
13. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd edn., Wiley, New York (1980).
14. Yu. Ya. Gotlib and K. M. Salikhov, *Akust. Zh.*, **9**, No. 2, 301–312 (1963).
15. A. Kloczkowski, J. E. Mark, and H. L. Frish, *Macromolecules*, **23**, No. 14, 3481–3490 (1990).
16. M. Mondello, G. S. Grest, E. B. Webb, III, and P. Peczak, *J. Chem. Phys.*, **109**, No. 2, 798–805 (1998).
17. M. Mooney, *J. Polym. Sci.*, **34**, No. 127, 599–626 (1959).
18. T. N. Khazanovich, *Mekh. Polimer.*, No. 6, 980–986 (1969).
19. R. A. Harris and J. E. Hearst, *J. Chem. Phys.*, **44**, No. 7, 2595–2602 (1966).
20. P. Mason, *J. Appl. Polym. Sci.*, **5**, No. 16, 428–435 (1961).
21. E. A. Meinecke, *Rheol. Acta*, **10**, No. 2, 302–309 (1971).

22. N. Sasaki, T. Uchiumi, Y. Sugo, and N. Nishida, *Polym. Bull.*, **12**, No. 3, 215–222 (1984).
23. R. Diaz Calleja, E. Riande, and J. Guzmaʹn, *Polymer*, **29**, No. 12, 2203–2207 (1988).
24. R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, Vol. 2, *Kinetic Theory*, 2nd edn., Wiley, New York (1987).
25. H. C. Öttinger, *Stochastic Processes in Polymeric Fluids*, Berlin–Heidelberg–New York (1966).
26. P. J. Flory, *Statistical Mechanics of Chain Molecules*, New York (1969).
27. Yu. Ya. Gotlib and A. A. Darinskii, *Vysokomolek. Soed. A*, **16**, No. 10, 2296–2302 (1974).
28. Yu. Ya. Gotlib and A. A. Darinskii, *Vysokomolek. Soed. A*, **18**, No. 1, 77–84 (1976).
29. W. H. Stockmayer, W. Gobush, Y. Chikahisa, and D. K. Carpenter, *Disc. Faraday Soc.*, No. 49, 182–192 (1970).
30. A. A. Darinskii, Yu. Ya. Gotlib, A. V. Lyulin, and I. M. Neelov, *Vysokomolek. Soed. A*, **36**, No. 7, 1148–1153 (1994).
31. I. M. Neelov, A. V. Lyulin, F. I. Torchinskii, A. A. Darinskii, and R. Kuk, *Vysokomolek. Soed. A*, **38**, No. 8, 1394–1402 (1996).
32. A. Amash and P. Zugenmaier, *J. Polym. Sci. B, Polym. Phys.*, **35**, No. 9, 1439–1448 (1997).
33. D. J. K. Taylor, R. F. T. Stepto, R. A. Jones, and I. Ward, *Macromolecules*, **32**, No. 6, 1978–1989 (1999).
34. P. J. Flory, *Proc. Roy. Soc. London A*, **351**, No. 1666, 351–380 (1976).
35. D. S. Pearson, *Macromolecules*, **10**, No. 3, 696–701 (1977).
36. Yu. Ya. Gotlib, M. I. Lifshits, V. A. Shevelev, I. S. Lishanskii, and I. V. Balanina, *Vysokomolek. Soed. A*, **18**, No. 10, 2299–2303 (1976).
37. A. A. Lundin and T. N. Khazanovich, *Vysokomolek. Soed. A*, **31**, No. 2, 363–368 (1989).
38. M. E. Ries, M. G. Brereton, P. G. Klein, I. M. Ward, P. Ekanayake, H. Menge, and H. Schneider, *Macromolecules*, **32**, No. 6, 4461–4468 (1999).
39. I. P. Borodin and T. N. Khazanovich, *Vysokomolek. Soed. A*, **17**, No. 6, 1353–1359 (1975).