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Non-Gaussian Optical Properties of Bimodal Elastomeric Networks

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Introduction

Most molecular theories of rubberlike elasticity are based on a Gaussian function for the required distribution of end-to-end distances r of the network chains.[1,2] In the case of very large deformations, however, the Gaussian distribution becomes seriously inadequate. Specifically, stretching the chains close to the limits of their extensibility results in probabilities significantly lower than those given by the usual Gaussian exponential in $-r^2$.[3] As a result, there are upturns in the elastic stress,[3-10] and this "non-Gaussian behavior" is of interest both for the evaluation of non-Gaussian theories[2,3,11] and for the reinforcement effect it provides.

Very little has been done to characterize the corresponding non-Gaussian effects on the optical properties of networks.[2,12] The present investigation therefore addresses this issue, using elastomeric networks of poly(dimethylsiloxane) (PDMS). The focus is on PDMS networks having a bimodal distribution of network chain lengths since such elastomers have very high extensibilities (relative to their moduli), and the non-Gaussian characteristics of their stress–strain isotherms in elongation have been well documented.[3-10]

Experimental Details

The two PDMS samples employed were hydroxyl terminated, with the short chains having a number-average molecular weight of 880 and the long ones 21.3×10^3 g mol^{-1}. Their polydispersity indices would be expected to be in the vicinity of 2. The three compositions investigated corresponded to 60.0, 70.0, and 93.4 mol % short chains and 5.84, 8,79, and 36.9 wt %. The synthesis of the networks was carried out in the usual manner.[13,14] The required amounts of long and short chains were first thoroughly mixed with the stoichiometric amount of cross-linking agent (tetraethyl orthosilicate) and with the catalyst (stannous 2-ethylhexanoate, 0.1 wt%) and then cured for 2 days at room temperature. The resulting elastomers were extracted to remove the soluble material (~3 wt %) which they contained. They were then dried in vacuo to constant weight.

A strip of the appropriate dimensions was cut from each (unswollen) network and placed in the sample cell of the strain-birefringence apparatus, which was of conventional design.[2] The light source was a He-Ne laser (632.8 nm), the optics included Glan-Thompson prisms (polarizer and analyzer), and the detector was a photometer/radiometer using a silicon light probe. The glass sample cell had a double-walled jacket, thus permitting temperature control (at 25 °C) by means of water circulation through the parts of the cell not in the path of the laser beam. The elastic force was measured by using a Statham "strain" gauge, the signal of which was monitored by a Hewlett-Packard chart recorder.

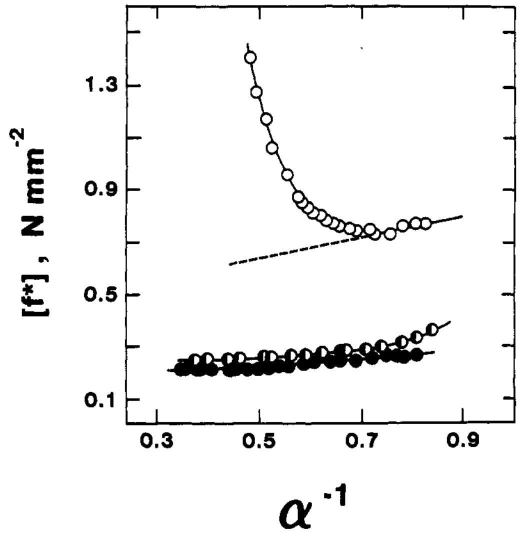

Figure 1. Stress–strain isotherms at 25 °C for the bimodal poly(dimethylsiloxane) networks[10] in the Mooney–Rivlin representation.[2,19] The elastomers consisted of network chains having number-average molecular weights of 880 and 21.3×10^3 g mol^{-1}, and the short-chain concentrations were 60.0 (●), 70.0 (◐), and 93.4 mol % (○). In this and the following figures, the linear portions of some of the curves are extended by dashed lines to facilitate characterization of the departures from linearity.

The quantities of interest were (i) the reduced stress or modulus defined by[15,16]

$$[f^*] \equiv f/A^*(\alpha - \alpha^{-2}) \tag{1}$$

where f is the equilibrium elastic force, A^* is the cross-sectional area of the unstretched sample, and $\alpha = L/L_i$ is the elongation (where L and L_i are the stretched and unstretched lengths, respectively) and (ii) the birefringence $\Delta n = R/t$, where t is the sample thickness and R is the measured relative retardation. The relationship[13]

$$C = \Delta n/\tau \tag{2}$$

defines the stress-optical coefficient C, where τ is the true stress (relative to the existing cross-sectional area). It is thus simply the slope of the line in a plot of Δn against τ. Finally, the optical-configuration parameter is defined by[17]

$$\Delta a = (45kT/2\pi)[n/(n^2 + 2)^2](\Delta n/\tau) \tag{3}$$

where k is the Boltzmann constant, T is the absolute temperature, and n is the index of refraction of the (unstretched) network. This parameter is particularly important with regard to the rotational isomeric state analysis[18] of the optical properties of a polymer.

Results and Discussion

The representation of the stress–strain data was based on the Mooney–Rivlin equation[2,19]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{4}$$

where $2C_1$ and $2C_2$ are constants. These plots, of the reduced stress against reciprocal elongation, are shown in Figure 1. They also appear in an earlier publication,[10] where they are analyzed in detail. In brief, the values of $[f^*]$ increase with increase in short-chain concentration, since this corresponds to an increase in cross-link density. Only the network containing the largest concentration of short chains (93.4 mol %) shows the upturn in modulus, at an elongation of approximately 1.4. This is consistent with earlier results[6] which show that a minimum concentration of short chains is required to observe this non-Gaussian effect. It also confirms that the deformation is

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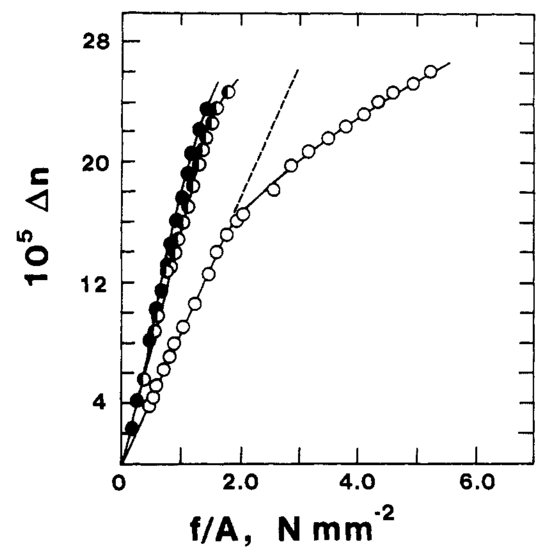

Figure 2. Dependence of the birefringence on the true stress at 25 °C for the bimodal networks; see legend to Figure 1.

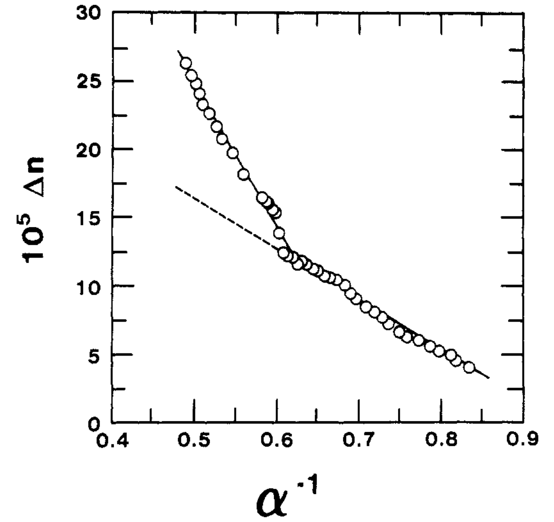

Figure 3. Mooney–Rivlin type of representation of the birefringence–strain data for the network containing 93.4 mol % short chains.

markedly nonaffine, in that the strain within the network structure is being reapportioned in such a way as to delay as long as possible the deformation of the difficultly deformable short chains.

The dependence of the birefringence Δn on the true stress $\tau = f/A$ is shown in Figure 2. The curves for all three networks pass through the origin, as expected.[2] Very little curvature at high elongation is seen in the curves for the two lower short-chain concentrations. For these two bimodal networks, $10^{24} \times \Delta a$ was found to be 0.50 ± 0.04 cm^3, in excellent agreement with the literature values for unimodal PDMS networks, 0.52 cm^3.[17] At 93.4 mol % short chains, however, there is a marked change in slope at $\alpha \simeq 1.7$. This can also be seen, at $\alpha \simeq 1.6$, in a Mooney–Rivlin-type plot of birefringence against reciprocal elongation, as shown in Figure 3. The plot is quite similar to the corresponding representation of the stress–strain data, in Figure 1. Under these conditions, the stress–optical coefficient would be expected to be very dependent on elongation and this is confirmed in Figure 4. As in the case of the mechanical properties,[3-10] the limited extensibility of the very short chains is obviously the origin of the non-Gaussian behavior.

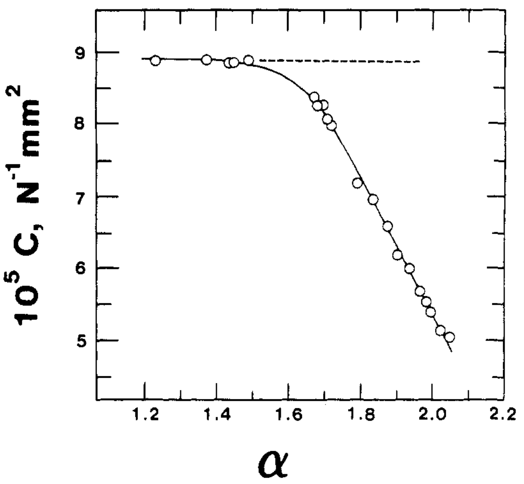

Figure 4. Strain dependence of the stress–optical coefficient for the network containing 93.4 mol % short chains.

Although there is some molecular theory for the mechanical properties of bimodal networks,[20,21] there is none yet for the optical properties. For unimodal networks, however, theory predicts that the magnitude of the non-Gaussian effects should depend strongly on both the lengths of the network chains and the extent of the deformation.[2] This is clearly supported by the present experimental results.

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