

Specific Diluent Effects on the Elastic Properties of Polymeric Networks

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Introduction

At present the elastic properties of rubber-like materials are rather well understood. The form of the stress-strain curve and the temperature dependence of the stress at fixed strain can be explained on a molecular basis. Recent theoretical work^{1,2} on the chain dimensions as a function of intramolecular forces has been related to thermoelastic properties of idealized models of networks. However, real networks may deviate from those models in several important aspects. The present status may be summarized as follows.

All theories assume that the chains are Gaussian in the unconstrained state. This assumption is not severely restrictive and appears to be a good approximation for networks of chains consisting of many links.

A second assumption is that interactions between chains are independent of deformation. This assumption has not yet been evaluated theoretically, although some recent experimental evidence³ suggests that effects of this nature are not large.

A third assumption is that the unperturbed chain dimensions of free unperturbed chains are independent of specific diluent effects. These diluent effects may be important in a study of the elastic properties of swollen networks. Contrary to the former two assumptions, the third one may be relaxed from a theoretical point of view. The consequences of this more general approach are investigated below.

Flory⁴ has given the following equation for a network in the unswollen state

$$f = \nu k T (\langle \alpha \rangle^2 / L_{10}) (\alpha - \alpha^{-2}). \quad (1)$$

For a network at force zero in swelling equilibrium with a diluent, he obtained⁴

$$(\nu V_1 / N_a V_0) [\langle \alpha \rangle^2 v_2 - v_2 / 2] = -[\ln(1 - v_2) + v_2 + \chi_1 v_2^2] \quad (2)$$

and for a force f ,

$$(\nu V_1 / N_a V_0) [\langle \alpha \rangle^2 (v_2')^{2/3} (L_{10} / L) - v_2' / 2] = -[\ln(1 - v_2') + v_2' + \chi_1 (v_2')^2], \quad (3)$$

combined with

$$f = \nu k T (\langle \alpha \rangle^2 / L_{10}^2) (v_2')^{2/3} L (1 - L_{10}^3 / v_2' L^3). \quad (4)$$

ν is the number of chains in the sample; k and N_a are respectively Boltzmann's constant and Avogadro's number. T is the absolute temperature. L_{10} and L_1 are the lengths of the isotropic sample in the unswollen and swollen state respectively, and L is the length corresponding to the force f , either for the swollen or unswollen sample. By definition $\alpha = L/L_1$. v_2 and v_2' are the volume fractions of polymer in the swollen sample in respectively the isotropic state and the deformed state, corresponding to f . χ_1 is the interaction parameter for diluent-polymer interaction. V_1 is the molar volume of the diluent and V_0 is the volume of the unswollen polymer. $\langle \alpha \rangle^2 = \langle r_1^2 \rangle / \langle r_0^2 \rangle$, where $\langle r_1^2 \rangle$ is the mean square end-to-end distance of the polymer chains in the isotropic sample at the volume, corresponding to f , and $\langle r_0^2 \rangle$ is the mean square end-to-end distance for uncross-linked chains.

Earlier theories have assumed that $\langle r_0^2 \rangle$ is constant, independent of temperature and specific diluent effects. However, it has recently^{3,5} been shown that the temperature dependence of $\langle r_0^2 \rangle$ may be introduced in rubber elasticity theory. In fact, at present, this theory is successfully used to evaluate $d \ln \langle r_0^2 \rangle / dT$ for various polymers.

We will critically examine the implicit assumption that $\langle r_0^2 \rangle$ is independent of diluent effects. The relative probabilities of different conformations may conceivably depend on the diluent, as has been observed for 1,2 dichloroethane⁶ in different solvents. If these effects also exist for polymeric chains, $\langle r_0^2 \rangle$ depends on the diluent. It follows then that $\langle \alpha \rangle^2$, and through eq. 4 the force on an elongated swollen sample, is a function of the diluent.

Experimental

Linear polyethylene ("Super Dylan", low pressure polyethylene, obtained from the Koppers Company) was chosen as the polymer. The diluents chosen were paraffin, melting range 65-70°C, n-hexadecane, α -chloronaphthalene and di-2-ethylhexyl azelate (DEHA). The latter three solvents were "Reagent Grade" and no attempt was made to purify them further.

Polyethylene films of a uniform thickness of 1-2 mm. were pressed at about 150°C and samples were cut at room temperature with a mold in the shape of a dumbbell. These samples are of uniform width of 3.1 mm. over a length of 25 mm. In order to crosslink the samples, they were irradiated at room temperature in evacuated glass containers by γ -radiation from a cylindrical Co^{60} source with a uniform dose rate of 0.61 megarep/hr. The samples investigated below received doses of 10 to 40 megarep. The dumbbell shape enabled the samples to be clamped in and stretched without breakage at the clamps. The clamps consisted of a pair of small metal plates, held together by screws. The lower clamp was fixed, while the upper clamp was suspended from a strain gauge which could be

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adjusted vertically. The strain gauge (Statham Instrument Company, Transducer Model G-1) had a capacity of 750 g. and a linear response of 0.05 mv. per g. under a supplied e.m.f. of 12 v. The output of the strain gauge was displayed on a Leeds and Northrup recorder, giving a full scale deflection of 10 mv. The instrument was calibrated by addition of known weights before and after each experiment.

The length of the sample was measured with a cathetometer. Two thin metal pins, perforating the uniform section 20 mm. apart, served as markers.

A stream of high purity nitrogen was passed through the sample chamber in order to prevent oxidative degradation. Samples were swollen by diluent in the sample chamber. After the stress-strain experiment, the polyethylene sample was extracted with boiling xylene and evaporated to dryness at 150°C in vacuum. The stress-strain curve in the unswollen state after this treatment was usually identical, within experimental error, to that before swelling; otherwise the experiment was discarded.

The liquid thermostat (containing Silicone Oil DC-550, Dow Corning Corporation) maintained a constant temperature of $150 \pm 0.1^\circ\text{C}$.

Stress-strain curves were obtained by stretching the sample at intervals to an extension ratio of about 1.3 and decreasing the length in similar intervals until the relaxed, isotropic state was reached. At each interval the length was kept constant for 15 minutes before the force was read.

The procedure for obtaining the ratio R , defined as $\langle r_0^2 \rangle_{\text{swollen}} / \langle r_0^2 \rangle_{\text{unswollen}}$, was as follows. From the stress-strain curve in the unswollen state $\nu < \alpha >$ was obtained through eq. 1. Substituting this value and the measured value of ν_2 in eq. 2, we obtained χ_1 . Subsequently ν_2 corresponding to the length L was calculated with the aid of eq. 3 and with this value f was calculated according to eq. 4. During this procedure $\langle r_0^2 \rangle$ was assumed to be equal to $\langle r_0^2 \rangle_{\text{unswollen}}$. On comparing the calculated value of the force with that measured at the same L , we have that $R = f_{\text{calculated}} / f_{\text{measured}}$.

Results and Discussion

Table I

$$\text{Ratio } R = \frac{\langle r_0^2 \rangle_{\text{swollen}}}{\langle r_0^2 \rangle_{\text{unswollen}}}$$

for different diluents

Solvent	α	$f_{\text{unswollen}}$	f_{swollen}	v_2'	calculated	R
		g.	g.		f_{swollen}	
DEHA	1.35	60.0	75.8	0.394	74.0	0.98
α -Cl. n.	1.275	55.5	95.5	0.217	81.3	0.86
α -Cl. n.	1.32	61.3	104.5	0.230	90.3	0.86
n-hexad.	1.35	63.5	103.0	0.221	89.8	0.87
n-hexad.	1.31	56.4	96.0	0.196	82.2	0.86

The results obtained are given in Table I. It is to be remarked, however, that the data are preliminary and need further confirmation. Eqs. 1-4 are valid for measurements performed in equilibrium. It was apparent from the stress-strain curves for the unswollen samples, however, that the force was not constant after a period of 15 minutes. This results in hysteresis loops in the stress-strain curves. Attempts to increase this period showed that the time required would be impractically long. The results for the dry state are therefore open to doubt.

The measurements performed in the swollen state are more reliable, since hysteresis is small in this case. We are inclined to believe that the value of $\langle r_0^2 \rangle$ in n-hexadecane is close to that in polyethylene in the bulk, in view of the similarity of the molecules. If this is accepted, the value of $\langle r_0^2 \rangle$ in α -chloronaphthalene is the same as that in polyethylene in the bulk, but $\langle r_0^2 \rangle$ would be about 15 percent greater in di-2-ethylhexyl azelate.

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From our theoretical calculations it has become apparent that $\langle r_0^2 \rangle$ is very sensitive to slight changes in intramolecular interactions. Nevertheless, as is apparent from Table I, the chain dimensions are remarkably invariant with respect to such great changes in solvent from an aliphatic to an aromatic medium, or to molecules containing ester groups. Therefore, the implicit assumption adopted in rubber elasticity theory that unperturbed chain dimensions are independent of solvent medium, seems justified at least to a first approximation.

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