Stress – strain isotherms and thermoelastic properties of crosslinked amorphous polyoxyethylene in compression

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Stress—strain isotherms at a number of temperatures in the range 45–85°C have been determined for a compressed, amorphous polyoxyethylene network swollen with a constant amount of non-volatile diluent. The observed isotherms showed much smaller departures from the form indicated by the molecular theories of rubberlike elasticity than is generally the case for polymer networks in elongation. The thermoelastic behaviour of the network was characterized by the dependence of the stress on temperature at constant deformation. The value of the temperature coefficient of the unperturbed dimensions of polyoxyethylene calculated from these data is in good agreement with values obtained both from thermoelastic measurements on polyoxyethylene networks in elongation, and from viscosity—temperature studies on isolated polyoxyethylene chains in a thermodynamically good solvent.

INTRODUCTION

It has recently been demonstrated that it is quite feasible to use compression measurements to study both stress–strain relationships and stress–temperature coefficients of amorphous polymer networks[1]. In such studies, it is frequently most convenient to determine stress–strain isotherms, at a number of temperatures. One thereby immediately obtains information on the degree to which the observed isotherms differ from the form indicated by the statistical or molecular theories of rubberlike elasticity[2]. In addition, such a series of isotherms directly provides values of the stress as a function of temperature at fixed deformation. As has now been well established, such 'thermoelastic' data may be used to calculate both the fraction f_e/f of the stress which is due to energetic effects, and the temperature coefficient d $\ln\langle r^2 \rangle_0/dT$ of the unperturbed dimensions of the network chains[3].

In the present study, compression measurements were carried out on polyoxyethylene (POE) $[CH_2-CH_2-O-]_x$, a particularly important polymer to be studied in this way because some serious disagreements[4–6] regarding the value of d $\ln \langle r^2 \rangle_0/dT$ for this chain molecule have only recently been resolved[7], and this temperature coefficient plays a crucial role in the understanding of the configuration-dependent properties of polyoxide chains in general[7,8].

EXPERIMENTAL

Preparation of networks

The sample of POE (Polyox WSR-205, Union Carbide) employed had a molecular weight of approximately 600 000 and a melting point of approximately 65°C (in the undiluted, uncrosslinked state). A portion of this material was moulded, under pressure and at approximately 68°C, into a cylindrical pellet having a diameter of 1.76 cm and a length of 3.50 cm. This sample was then crosslinked

under vacuum at room temperature, using approximately 16.4 Mrad of γ-radiation. After the small amount of soluble material present in the sample was extracted, approximately 8% of the antioxidant N-phenyl-2-naphthylamine was incorporated into the network by means of a swelling—deswelling technique[4]. Sufficient m-cresol, a non-volatile diluent, was then incorporated into the network to decrease the volume fraction v_2 of polymer to 0.75, thus further decreasing the melting point of the POE network. The thermal expansion coefficient $\beta = (\partial \ln V/\partial T)_p$ of the swollen network in the vicinity of 65°C was obtained from dilatometric measurements; it was found to be 0.509 x 10^{-3} K^{-1}.

Stress—compression measurements

Stress—strain isotherms were obtained for this swollen POE network in compression, at 45, 55, 65, 75, and 85°C, in the manner described in detail elsewhere[1,9]. A slurry of graphite in low molecular weight dimethylsiloxane fluid applied to the Teflon compression plates aided in preventing non-uniform deformation of the network. Values of the relative length or compression $\alpha = L/L_i$ of the sample were in the range 1.00–0.80. The isotherms were found to be reversible and there was no evidence of crystallization under the conditions employed in these measurements.

RESULTS AND DISCUSSION

The experimental data were used to calculate values of the 'reduced force' $[f^*]$ defined by:

$$[f^*] = f v_2^{1/3}/A^*(\alpha - \alpha^{-2}) \tag{1}$$

where f is the elastic force or stress, and A^* is the cross-sectional area of the unswollen, undistorted sample at 45°C. Values of the deformation or compression, α, were
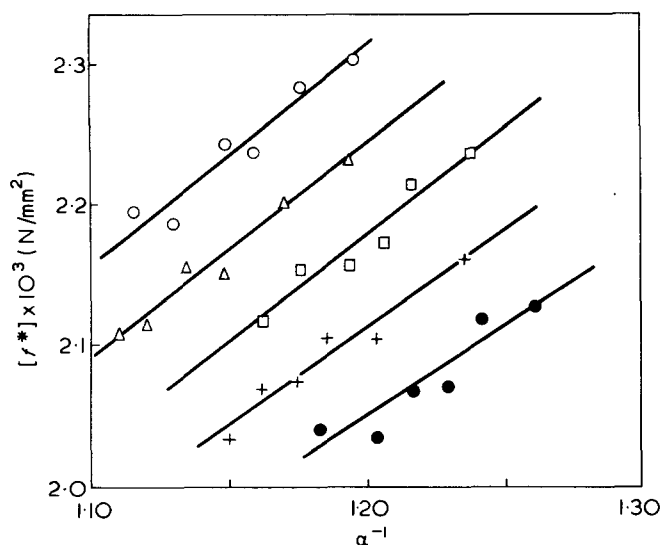
Figure 1 Stress—strain isotherms for polyoxyethylene in compression. The deformation α is defined by $L(T)/L_i(T)$, i.e., the length of the sample at the specified temperature relative to the undeformed length at the same temperature. ●, 45°; +, 55°; □, 65°; △, 75°; ○, 85°C

of the Table. They are seen to vary only slightly with α, and give the average results $f_e/f = 0.06 (\pm 0.01)$ and $\mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T = 0.19 (\pm 0.03) \times 10^{-3} \, \mathrm{K}^{-1}$.

The value of $\mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T$ for POE which is obtained in the present study is in very good agreement with the value $0.23 (\pm 0.02) \times 10^{-3} \, \mathrm{K}^{-1}$ resulting from a thermoelastic study of a POE network in elongation[4], and with the value $0.2 (\pm 0.2) \times 10^{-3} \, \mathrm{K}^{-1}$ obtained from viscosity—temperature measurements on isolated POE chains in a thermodynamically good solvent[7]. (Other thermoelastic results[5,13] of lower reliability[6,13] are in fair agreement with the results cited above. Values calculated from viscosity—temperature studies on POE chains of low molecular weight[5] have been shown to be unreliable[7], and are therefore not presented here.)

The fact that there is good agreement between values of $\mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T$ obtained in compression and elongation has some bearing on the alleged existence of intermolecularly ordered domains[14,15] or 'supermolecular structures'[5] in polymers in the amorphous state. Since any such ordering would reasonably be expected to respond differently to (uniaxial) elongation and compression (mechanically equivalent to biaxial elongation[11]), the absence of any difference between the values of $\mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T$ obtained using these two different types of deformation would seem to represent yet another piece of evidence[16] against the existence of ordered regions in amorphous polymers.
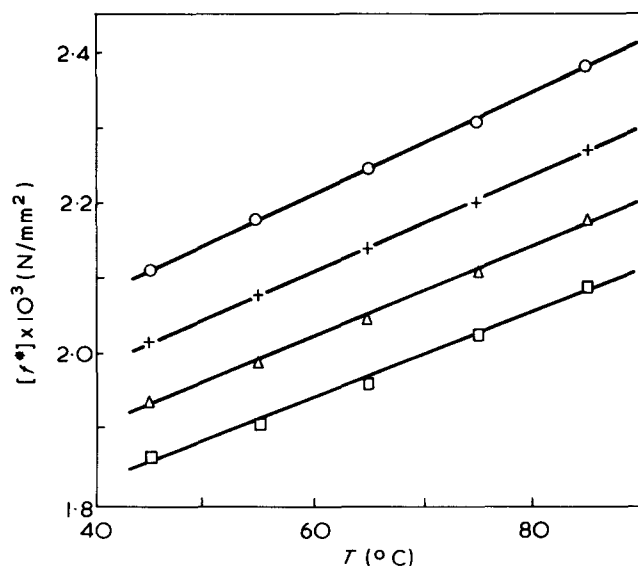
calculated relative to the initial length, L_i, at the particular temperature of measurement, and values of the reduced force were expressed in N/mm^2. (In order to facilitate comparison of these results with others already in the literature, it may be helpful to point out that 1 $N/mm^2 = 1 \, MN/m^2 = 10.20 \, kg/cm^2$.) The values of $[f^*]$ thus calculated were plotted against the reciprocal of the compression, α, as suggested by the semi-empirical Mooney—Rivlin equation[10]:

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \qquad (2)$$

The results are shown in *Figure 1*; each line, representing a stress—strain isotherm, was located by the method of least squares. The slopes of these lines represent values of the constant $2C_2$, which is a measure of the departure of the observed stress—strain relationship from the theoretical prediction that $[f^*]$ be independent of α^{11}. From these results, $2C_2 = 0.0014 (\pm 0.0002) \, N/mm^2$, a result very much smaller than the values of this correction generally obtained for networks in elongation[11]. Similarly small values of $2C_2$ have been reported for several other polymers which have been studied in compression[1].

Values of the reduced force at selected values of α in the range 0.95—0.80 were obtained from each stress—strain isotherm by means of interpolation and limited extrapolation. The values of $[f^*]$ thus obtained were found to vary linearly with temperature. Typical results are presented in *Figure 2*, where the lines shown were again located by least-squares analysis. The slopes of these lines were used to calculate[1] values of the coefficient $[\partial \ln ([f^*]/T)/\partial T]_{p,\alpha}$ at the average temperature, 65°C, employed in this study; these results are given in the second column of *Table 1*. The quantities f_e/f and $\mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T$ were then calculated from the equations[1,12]:

$$f_e/f = T \, \mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T$$

$$= -T[\partial \ln ([f^*]/T)/\partial T]_{p,\alpha} + \beta T/3 \qquad (3)$$

Values of these quantities are given in the last two columns

Figure 2 Reduced force shown as a function of temperature for selected values of the deformation, α. These results were obtained from *Figure 1*, in which $\alpha = L(T)/L_i(T)$, and thus pertain to constant deformation rather than constant length. ○, $\alpha = 0.80$; +, $\alpha = 0.85$; △, $\alpha = 0.90$; □, $\alpha = 0.95$

Table 1 Thermoelastic results on polyoxyethylene in compression

α	$[\partial \ln ([f^*]/T)/\partial T]_{p,\alpha}$ $\times 10^3$	f_e/f	$\mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T$ $\times 10^3$
0.950	−0.0658	0.08	0.24
0.925	−0.0501	0.07	0.22
0.900	−0.0335	0.07	0.20
0.875	−0.0169	0.06	0.19
0.850	−0.0008	0.06	0.17
0.825	0.0167	0.05	0.15
0.800	0.0346	0.05	0.14

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