COMPARISON OF THE INITIAL MODULI OF POLY(ALKYL ACRYLATE) NETWORKS IN EXTENSION AND COMPRESSION

J. HASA

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6

Received July 11th, 1973

The tensile and compression deformation behaviour of networks based on poly(methyl acrylate), poly(ethyl acrylate), poly(butyl acrylate) and poly(octyl acrylate) with different degrees of network density has been measured. It has been found that the initial compression modulus coincides with the initial tensile modulus only if the former has been corrected for the influence of the shape factor of the sample.

According to the kinetic theory of rubberlike elasticity, the tensile and compression stress-strain curves of polymeric networks should satisfy the equation

$$f/A = G(\alpha - \alpha^{-2}) , \qquad (1)$$

where f is force, α is relative elongation, A is the cross-section of the sample in undeformed state, and G is modulus of elasticity. In actual fact, however, it is difficult to compare both types of deformation, because Eq. (*1*) describes only stress-strain curves in compression, while in the case of tensile measurements the modulus G depends on deformation; it holds $G = C_1 + C_2/\alpha$, where C_1 and C_2 are constants[1]. Attention has therefore been devoted predominantly to the question of agreement between the initial modulus G_0 in tensile and compression measurements determined in the region of small deformations or calculated from the sum of constants C_1 and C_2 (ref.[2-10]). Determination of G_0^c in extension does not meet with experimental difficulties, but its magnitude in compression, G_0^c, is affected by friction between the sample surface and the deformation device. The experimentally determined value of G_0^c depends on the dimensions of the sample according to a semiempirical relationship[11,12]

$$\overline{G}_0^c = G_0^c(1 + Bs^2) , \qquad (2)$$

where s is the diameter-to-height ratio of the sample and B is a factor depending on the friction coefficient between the plate and the sample. For a sample with a circular cross-section glued on the surface of the deforming areas B varies from 0·1 to 0·2 and increases with decreasing G_0^c. The value of G_0^c does not depend on the dimensions of the sample only in absence of friction ($B = 0$), which is fulfilled to a great extent if swollen samples immersed in a solvent are taken for measurements. It follows from the data published so far that under these circumstances the values of compression and tensile initial moduli coincide[2-5]. The results for dry samples are not so unequivocal; some authors have obtained compression values higher than the tensile ones[6,7], others indicate an approximative agreement of both types of data[8-10]. The differences

observed have been interpreted as a consequence of friction on contact surfaces[6] or as a consequence of different role played by network topology in both types of deformation[7].

This paper is devoted to the investigation of the effect of the sample dimensions and of network topology on the tensile and compression moduli for various polyacrylate networks measured in dry state.

EXPERIMENTAL

A mixture of the respective monomer, of a small amount of 3,6,9-trioxaundecamethylene diacrylate as the crosslinking agent and of azobisisobutyronitrile ($c = 3 \cdot 10^{-3}$ mol/l) was heated in a teflon mould thermostated to 60°C for 24 h. Copolymers based on methyl acrylate, ethyl acrylate, butyl acrylate and octyl acrylate with various degrees of crosslinking were obtained; the samples used for measurements were cut out from plates thus obtained. Strips. 60× 10× 3 mm in size were used for tensile measurements; their cross-section was determined from their weight, density and undeformed length. Compression measurements were performed with cylinders, 10 mm in diameter and 3 mm high, the cross-section of which was calculated from the dimensions of the die and fitted the value determined from the weight, density and undeformed height of the sample. Various diameter-to-height ratios of the sample were attained by stacking several cylinders. Preliminary results showed that for the deformation range investigated the above procedure does not affect the results obtained.

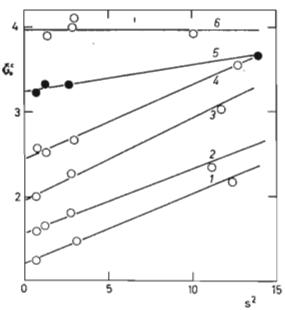

FIG. 1

Dependence of Values of Initial Modulus in Compression G_0^c (kg cm^{-2}) on Shape Factor for Poly(butyl acrylate)

Content of crosslinking agent (c, mol/l): *1* 0·0106, *2* 0·0212, *3* 0·0384, *4* 0·0596, *5* 0·0936, *6* 0·1357.

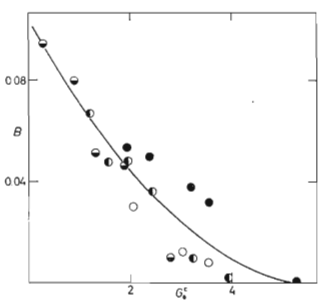

FIG. 2

Dependence of Parameter B on Initial Modulus G_0^c (kg cm^{-2})

Alkyl: ○ methyl, ● ethyl, ◐ butyl, ◒ octyl.

Tensile measurements were carried out with an Instron apparatus at a constant rate of deformation of 0·5 mm/min and at a temperature higher by 85°C than the glass transition temperature of each poly(alkyl acrylate) (Me 90°C, Et 55°C, Bu and octyl 25°C). The values of the initial modulus G_0^e and of the initial length l_0 were calculated from the dependence of fl^2 on l^3 by the least squares method within the interval $l_0 < l < 1{\cdot}2\,.\,l_0$. The G_0^e values thus determined agreed within the limits of experimental error with those determined on a relaxometer by using the same procedure as in the compression measurements; the deformation was measured from the distance between two points on the sample in order to rule out the effect of fixation in the clamps. The compression measurements were carried out at the same temperatures as tensile measurements on a relaxometer of our own design. The sample was deformed between two teflon plates, 20 mm in diameter, the distance between which was measured by an indicator with an accuracy of a hundredth of millimeter. The time dependence of the force was measured by a transducer connected with a bridge (Hottinger Baldwin Messtechnik, FRG) and recorded with a recorder (accuracy ± 1 g). In the modulus calculations, force values after two minutes of relaxation were employed, since the time dependence of the force was unpronounced in all samples[13]. Each time after two minutes the deformation was raised by the same interval up to a maximum value ($l_n = 0{\cdot}81_0$). The $\bar{G}_0^e$ and l_0 values were calculated by the same procedure as in the tensile experiments.

RESULTS AND DISCUSSION

The $\bar{G}_0^e$ values obtained from the compression measurements depend on the shape factor, s, similarly to the values published for natural rubber[11,12]. The G_0^e values independent of the dimensions of the sample and thus comparable with the results of the tensile measurements of G_0^e were obtained by extrapolation according to Eq. (2) for $s = 0$ by using the least squares method. An example of the dependence of $\bar{G}_0^e$ on s^2 for Bu is shown in Fig. 1; the dependences obtained for the remaining three polymers were similar. The B values calculated from the slope of these dependences decrease with increasing G_0^e in the same way for all polymers, which is in accordance

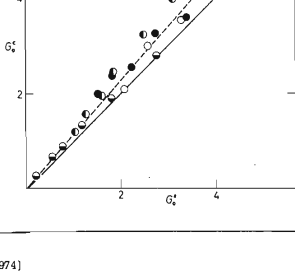

FIG. 3

Dependence of Initial Compression Modulus G_0^e (kg cm^{-2}) Values on Initial Tensile Modulus G_0^e (kg cm^{-2}) for Various Poly(alkyl acrylates)

——— Dependence for $G_0^e = G_0^e$, – – – – – experimental dependence.

Points designated as in Fig. 2.

with the finding that the surfaces of the samples were similar. The B values are much lower than for natural rubber ($B < 0{\cdot}1$, Fig. 2), probably because the samples were not firmly connected with the friction surfaces.

All the G_0^c values are higher than the G_0^e values, and their ratio is approximately the same for all polymers ($G_0^c/G_0^e = 1{\cdot}1$, *cf.* Fig. 3). It may be inferred, therefore, that the effect of the structure parameters of the network (concentration of crosslinks and entanglements) has a negligible effect on the ratio G_0^c/G_0^e. The fact that the tensile modulus decreases with increasing deformation while the compression modulus is independent of deformation probably contributes to the finding that the above ratio is greater than unity. Since G_0 has been calculated in both cases on the basis of measurements of the modulus G within a certain interval of the deformation values one may expect, when using Eq. (*1*), that $G_0^c/G_0^e > 1$. In our case, when the deformation interval was $1{\cdot}0-1{\cdot}2$ and $C_1 \geqq C_2$ (ref.[13]), it may be expected that the ratio $G_0^c/G_0^e \leqq 1{\cdot}05$. Taking into account that the G_0^e values were obtained by extrapolation and that the time conditions for both types of deformation were different (although the effect of time was unimportant in the majority of cases), the agreement observed here may be regarded as satisfactory. It is possible to conclude, therefore, that the results of the tensile and compression measurements of the initial modulus obtained by the procedure described above agree also for dry samples.

The author is indebted to Professor van der Hoff, University of Waterloo, Waterloo, Canada, for kindly supplying the samples.

REFERENCES

1. Dušek K., Prins W.: Advan. Polymer Sci. *6*, 1 (1969).
2. Gluff E. F., Glading E. K., Pariser R.: J. Polymer Sci. *45*, 341 (1960).
3. Smith D. A.: J. Polymer Sci. C, *16*, 525 (1967).
4. Kay E., Moore B. B., Thomas D. K.: Polymer *10*, 55 (1969).
5. Melley R. E., Stuckey J. E.: J. Appl. Polymer Sci. *14*, 2327 (1970).
6. Blockland R., Prins W.: J. Polymer Sci. A-2, *7*, 1559 (1969).
7. van der Hoff B. M. E., Glynn P. A. R.: J. Macromol. Sci. *A3*, 991 (1969).
8. de Candia F., Amelino L.: J. Polymer Sci. A-2, *10*, 715 (1972).
9. Wolf F. P.: Polymer *13*, 347 (1972).
10. Treloar L. R. G.: *The Physics of Rubber Elasticity*. Oxford University Press, 1958.
11. Payne A. R., Scott J. R.: *Engineering Design with Rubber*. Mc Laren, London 1960.
12. Payne A. R.: Ind. Eng. Chem., Prod. Res. Devel. *1*, 86 (1962).
13. Hasa J., van der Hoff B. M. E.: J. Polymer Sci., Polymer Phys. Ed. *11*, 297 (1973).

Translated by L. Kopecká.