

CONTRIBUTION TO THE DETERMINATION OF RELATIVE INCREMENT OF INTERNAL ENERGY AT LOW DEFORMATIONS OF CROSS-LINKED RUBBER

Vladimír POLLÁK and Andrej ROMANOV

Institute of Polymers,

Slovak Academy of Sciences, 809 34 Bratislava

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The relative change of the internal energy, f_U/f , during deformation of cross-linked elastomers, poly(ethylene-co-propylene) and poly(ethylene-co-vinyl acetate), was determined at various temperatures. Anomalies in the dependence of f_U/f on relative dilatation in the region of small deformations (<35%) are to a large extent besides other factors due to the sensibility of the formula used to calculate f_U/f to temperature changes.

During deformation of cross-linked rubber, nonnegligible changes of the internal energy take place besides entropy changes¹. The relative change of the internal energy is given as

$$f_U/f = 1 - (\partial \ln f / \partial \ln T)_{V,L}, \quad (1)$$

where $f_U = (\partial U / \partial L)_{T,V}$, f denotes equilibrium force, V volume, L length, and T temperature of the sample. The quantity f_U/f is related to the change of the end-to-end distance of the polymeric chain with the temperature according to the equation²

$$d \ln \bar{r}_0^2 / dT = f_U / fT, \quad (2)$$

where \bar{r}_0^2 is the mean square end-to-end distance of the chain in the reference (unperturbed) state. The temperature coefficient of the unperturbed chain dimensions (2) is a characteristic quantity for a given polymer and depends only on the temperature.

The use of Eq. (1) is connected with difficulties due to the condition of constant volume of the sample. In practice, therefore, the ratio of f_U/f is usually determined from the equation derived by Flory and co-workers²:

$$f_U/f = 1 - (\partial \ln f / \partial \ln T)_{P,L} - \beta T / (\alpha^3 - 1), \quad (3)$$

where β is the volume thermal expansion coefficient, P pressure, and α relative dilatation of the sample.

Eq. (2) shows that f_U/f is at a given temperature a constant independent of the deformation. Experimental results treated by Eq. (3) show, however, that mainly in the region of small deformations the dependence of f_U/f on α is considerably curved^{3,4}. Our aim was to reinvestigate the dependence of f_U/f on α at various temperatures in the region of small deformations for cross-linked ethylene-propylene and ethylene-vinyl acetate copolymers.

EXPERIMENTAL

Poly(ethylene-co-propylene) was product of the firm Montecatini-Edison and contained 50 mol% ethylene, $M_n = 70$ kg/mol, density 861 kg/m³ at 25°C. Poly(ethylene-co-vinyl acetate) was product of Bayer AG, contained 75 mol% ethylene, $M_n = 473$ kg/mol, density 968 kg/m³ at 25°C, crystallinity⁵ about 7%, melting point of crystallites about 319 K (determined by differential scanning calorimetry). Copolymers were precipitated from a toluene solution into methanol. Bis(α, α' -dimethylbenzyl peroxide) (Perkadox SB)-product Akzochemie GmbH (m.p. 312.2 K), used as a cross-linking agent was recrystallized from ethanol. It was added to the copolymers in the weight ratios 4 : 100 and 2 : 100 and mixed on a laboratory stirrer at 310 K for 15 min. The mixtures were vulcanized in a laboratory press at 438 K for 45 min in the form of sheets of 1 mm thickness, from which samples were cut in the form corresponding to the norm ASTM-D1708-59T.

The dependences of the equilibrium force on deformation and temperature in the range between 300 and 400 K were obtained on an apparatus of own construction equipped with a tensometric force detector and a digital voltmeter. The samples were annealed by heating under nitrogen, their temperature was maintained within a range of ± 0.3 K. The force was measured with an accuracy to within $\pm 5 \cdot 10^{-3}$ N. The sample length and the temperature coefficient β

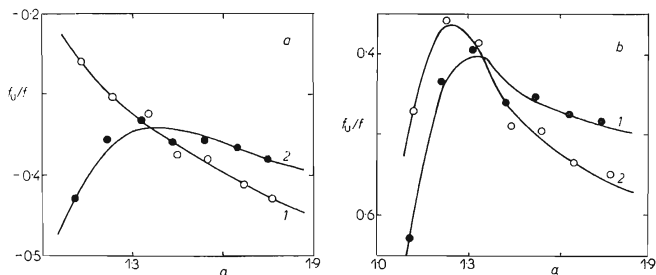


FIG. 1

Dependence of Relative Increment of Internal Energy f_U/f on Deformation α for Cross-Linked Poly(ethylene-co-propylene) a and Poly(ethylene-co-vinyl Acetate) b

Temperature: a 1 303.16 K; 2 343.16 K; b 1 343.16 K; 2 383.16 K.

of linear dilatation were measured with a cathetometer. The coefficients β for cross-linked copolymers were determined as $(2.25 \pm 0.05) \cdot 10^{-4} \text{ K}^{-1}$ for poly(ethylene-co-propylene) and $(2.55 \pm 0.05) \cdot 10^{-4} \text{ K}^{-1}$ for poly(ethylene-co-vinyl acetate).

RESULTS AND DISCUSSION

Eq. (3) enables to calculate f_U/f from the dependence of f on T . These dependences were for the studied copolymers already described^{6,7}. The values of f_U/f for the studied samples as functions of α are shown in Fig. 1 for two different temperatures. It is seen that for $\alpha < 1.35$ the mentioned function is anomalous. One of the possible explanations is that the last term of the right side of Eq. (3) is extremely sensitive to errors in the determination of α (ref.⁴). However, in determining the dependence of f_U/f on α at various temperatures we found that their course for $\alpha < 1.35$ is variable, the values of f_U/f being lower at higher temperatures. In contrast, at higher deformations the values of f_U/f are higher at higher temperatures. The temperature dependence of f_U/f can be calculated from the equation⁸

$$\bar{r}_0^2 = nl^2 \exp(\varepsilon'/RT), \quad (4)$$

where n is the number of segments of a model chain, l their length, and ε' intramolecular interaction energy. The equation was derived for a simple model, which is related to the physical model of the hydrocarbon chain with *trans* and *gauche* position of rotation isomers. On logarithming and differentiating Eq. (4) with respect to temperature we obtain

$$d \ln \bar{r}_0^2 / dT = -\varepsilon'/RT^2. \quad (5)$$

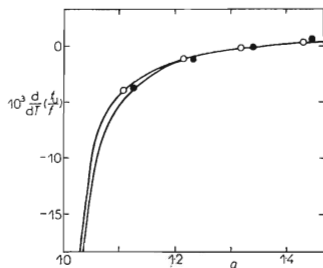


FIG. 2
Dependence of $d(f_U/f)/dT$ on α for Poly(ethylene-co-propylene) (○) and Poly(ethylene-co-vinyl acetate) (●)

By combining this result with (2) we obtain the relation

$$f_U/f = -\varepsilon'/RT, \quad (6)$$

which gives the temperature dependence of f_U/f . Since ε' is a constant for a given polymer, the value of f_U/f should approach zero with increasing temperature, which is at variance with experimental results. To explain this phenomenon, we shall analyse Eq. (3) by differentiating with respect to temperature:

$$d(f_U/f)dT = (\partial \ln f/\partial T)_{P,L} [T(\partial \ln f/\partial T)_{P,L} - 1] - 3\beta/(\alpha^3 - 1) - 9\alpha^3\beta^2T/(\alpha^3 - 1)^2. \quad (7)$$

A plot of $d(f_U/f)/dT$ against α is shown in Fig. 2. The points were obtained from experimental values, the curve was constructed from the values of $(\partial \ln f/\partial T)_{P,L}$ obtained from the equation

$$(\partial \ln f/\partial T)_{P,L} = -3\beta/(\alpha^3 - 1) + 1/T + \varepsilon'/RT^2 \quad (8)$$

and the value of ε' was determined as a mean value from four differently cross-linked samples⁹. Eq. (8) was obtained from (3) and (6). The values of ε' for cross-linked copolymers are 962 and 1120 J/mol for poly(ethylene-co-propylene) and poly(ethylene-co-vinyl acetate), respectively. It is seen from Fig. 2 that the ratio of f_U/f drops considerably with increasing temperature for $1 < \alpha < 1.2$. The zero value of $d(f_U/f) : dT$ corresponds to $\alpha \approx 1.35$ in accord with the fact that at about this elongation there is an intersection of the plots of f_U/f against α determined from Eq. (3) at different temperatures (Fig. 1). Hence, besides inaccuracy in determining the value of α , the dependence of f_U/f on α will be in the region of small deformations ($\alpha < 1.3$) to a large extent influenced by the sensitivity of Eq. (3) to temperature changes.

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