Study of Elastic and Thermoelastic Properties of Ethylene–Propylene and Ethylene–Vinyl Acetate Copolymers. II. Thermoelastic Properties

V. POLLÁK and A. ROMANOV, *Polymer Institute, Slovak Academy of Sciences, 809 34 Bratislava, Czechoslovakia*

Synopsis

The thermoelastic properties of ethylene–propylene and ethylene–vinyl acetate copolymers crosslinked to different degrees were studied. An equation was proposed for calculating the relative contribution of the internal energy, f_U/f, from the temperature dependence of shear modulus G. Analysis of a relation for calculating f_U/f derived on the basis of the Mooney-Rivlin equation was made.

INTRODUCTION

Numerous papers published so far have shown that the equilibrium retractive force f developed by a deformed real network is not purely entropic in the origin—the change of the internal energy is not negligible.[1] This energy contribution, f_U, to the equilibrium force arises if internal bond rotations are restricted by hindering potentials,[2] i.e., if individual conformations of the polymer chain have different energy.

From the first and second laws of thermodynamics it follows for f_U that

$$f_U = f + T \left(\frac{\partial S}{\partial T}\right)_{T,V} = f - T \left(\frac{\partial f}{\partial T}\right)_{V,L} \tag{1}$$

where $f_U = (\partial U/\partial L)_{T,V}$ and L is the sample length. Because of the experimental difficulties encountered in maintaining the sample volume constant, the values of $(\partial f/\partial T)_{P,L}$ usually obtained are recalculated according[3] to

$$(\partial f/\partial T)_{V,L} = (\partial f/\partial T)_{P,L} + 3f\lambda_L/(\alpha^3 - 1) \tag{2}$$

derived from the Gaussian equation of state.[4] In eq. (2), $\lambda_L = (\partial L/\partial T)_P$, $\alpha = L/L_i$ = relative elongation, and L = the sample length.

For the thermal coefficient of unperturbed chain dimensions according to Flory et al.,[3] we have

$$\frac{d \ln \bar{r}_0^2}{dT} = \frac{f_U}{fT} \tag{3}$$

This coefficient is a characteristic quantity for the given chain and is a function of temperature only.

Shen and Blatz[5] derived for calculation of f_U/f the expression

$$f_U/f = 1 - \frac{d \ln G}{d \ln T} - T\lambda_L \tag{4}$$

(G being the shear modulus), enabling calculation of f_U/f at small elongations, where the computation according to eqs. (1) and (2) is considerably affected by the precision of the α determination.[6]

It is obvious from eq. (3) that f_U/f should be at a given temperature independent of deformation. However, it follows from the analysis of Shen and Croucher[7] that this holds only for an ideal Gaussian network. In the case of non-Gaussian network behavior, f_U/f will be deformation dependent. This is supported also by experimental results[8] which lead to the conclusion that f_U/f generally decreases with increasing deformation.

The purpose of the present paper is to study the thermoelastic properties of ethylene–propylene and ethylene–vinyl acetate copolymers crosslinked to different degrees and to discuss some problems concerning the calculation of the relative energetic contribution f_U/f.

RESULTS AND DISCUSSION

Determination of f_U/f from the Variation of G with T

Equation (4) enables calculation of the values of f_U/f from the temperature dependence of modulus G. Figure 1 shows these dependences for some EPM and EVA samples. The values of dG/dT (if the function of G versus T is approximated by a straight line) and the values of f_U/f calculated from eq. (4) are listed in Table I. This table shows that the values of f_U/f are, within experimental error, independent of the degree of crosslinking of the sample.

In eq. (4), dG/dT is assumed to be temperature independent. According to relation

$$G = \frac{N_0 kT}{V_i} \cdot \frac{\bar{r}_i^2}{\bar{r}_0^2} \tag{5}$$

the value of the modulus G_{T_0} should be zero at $T_0 = 0$. In our case G_{T_0} deter-
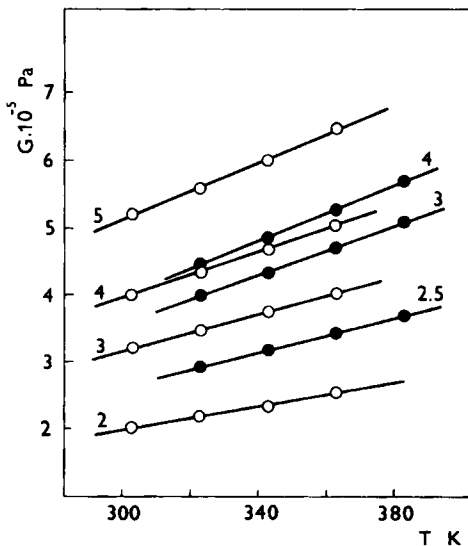

Fig. 1. Plots of G vs temperature for ethylene–propylene (O) and ethylene–vinyl acetate (●) copolymer. Numbers at curves denote DCP content.

TABLE I
Values of dG/dT and f_U/f for Ethylene–Propylene and Ethylene–Vinyl Acetate Copolymer, Calculated According to Eq. (4)

DCP, wt-%	dG/dT, N/m^2 K	f_U/f[a]
EPM		
2	897.5	−0.38
3	1418.5	−0.37
4	1708.5	−0.32
5	2160.0	−0.32
EVA		
2	950.0	−0.40
2.5	1239.5	−0.43
3	1759.0	−0.47
4	1868.7	−0.41

[a] $T = 343.16$ K.

mined by linear extrapolation has the value of the order -10^5 N/m^2, which contradicts eq. (5). If we consider a change of $\bar{r}_i^2$ and $\bar{r}_0^2$ with temperature,[4] we get for dG/dT

$$\frac{dG}{dT} = \frac{N_0 k T}{V_i n l^2 \exp{(\epsilon'/RT)}} \left(\frac{1}{T} - \lambda_L + \frac{\epsilon'}{RT^2}\right) \tag{6}$$

where ϵ' is the chain-folding energy. It is evident from eq. (6) that dG/dT is a function of temperature. The expression of the dependence of G on T by a straight line is only approximate and would be justified only if $\epsilon' = \lambda_L = 0$.

On substituting $\bar{r}_i^2 = \bar{r}_{i0}^2 \exp{(2\lambda_L T)}$, $V_i = V_{i0} \exp{(3\lambda_L T)}$, and $\bar{r}_0^2 = n l^2 \exp{(\epsilon'/RT)}$ into eq. (5) and rearranging, we obtain

$$\lambda_L T + \ln\frac{G}{T} = -\frac{\epsilon'}{RT} + \ln\frac{N_0 k \bar{r}_{i0}^2}{V_{i0} n l^2} \tag{7}$$

where $\bar{r}_{i0}^2$ and V_{i0} are the quantities at $T = 0$. Since the second term on the right-hand side of eq. (7) is temperature independent, the plot of $[\lambda_L T + \ln (G/T)]$ versus $1/T$ should be linear. Application of eq. (7) to the experimental results obtained (Fig. 2) confirmed this assumption.

For f_U/f and $d \ln \bar{r}_0^2/dT$ holds

$$f_U/f = -\frac{\epsilon'}{RT} \tag{8}$$

$$\frac{d \ln \bar{r}_0^2}{dT} = -\frac{\epsilon'}{RT^2} \tag{9}$$

Equations (8) and (9) describe the temperature dependence of f_U/f and $(d \ln \bar{r}_0^2)/dT$ and enable comparison of these values often stated in the literature at various temperatures. Table II contains the values of ϵ', f_U/f, and $(d \ln \bar{r}_0^2)/dT$ for the samples studied.

Comparison of Tables I and II shows that the values of f_U/f calculated according to eqs. (4) and (7) are close, indicating that the expression of G as a function of temperature by a straight line is a good approximation. From a theoretical point of view it is better to use eq. (7) for calculating f_U/f.
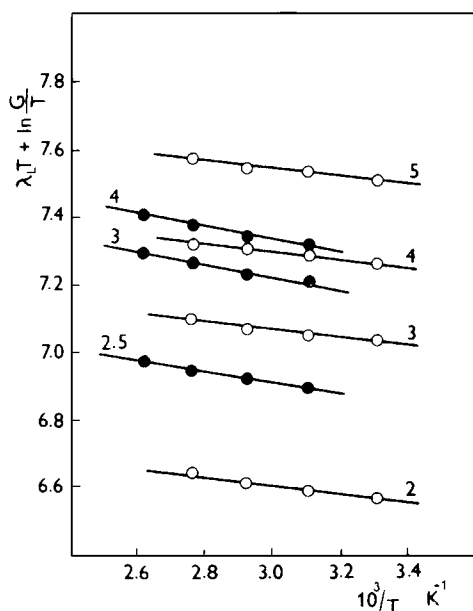
Fig. 2. Plots of $\lambda_L T + \ln (G/T)$ vs $1/T$ for ethylene–propylene (O) and ethylene–vinyl acetate (●) copolymer. Numbers at curves denote DCP content.

Determination of f_U/f from the Variation of f with T

Equations (1) and (2) make calculation of f_U/f possible on the basis of the dependence of f on T. Variations of f with T for EPM and EVA crosslinked by 2.5 wt-% DCP have already been described.[9,10] The shape of these curves is not influenced by a change in the degree of crosslinking over a range investigated.

In Figures 3 and 4, the f_U/f values are shown as a function of α calculated from eqs. (1) and (2). Despite the scatter of experimental points, it is seen from the figures that the f_U/f values exhibit a tendency to decrease with increasing α, which is marked especially with EVA copolymer. A decrease in f_U/f with increasing α can take place as a consequence of both the non-Gaussian behavior of networks studied[11,12] and the interactions of chain segments oriented during

TABLE II
Values of ϵ', f_U/f, and $d \ln \bar{r}_0^2/dT$ for Ethylene–Propylene and Ethylene–Vinyl Acetate Copolymer, Calculated from Eq. (7)[a]

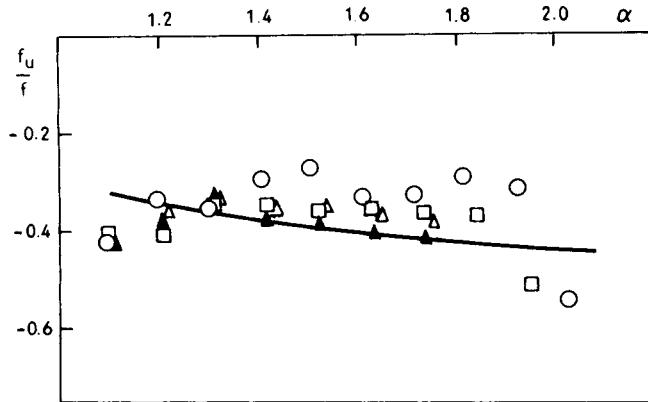| DCP, wt-%	ϵ', J/mole	f_U/f	$d \ln \bar{r}_0^2/dT \times 10^3$, K^{-1}
EPM			
2	1016	−0.356	−1.038
3	1035	−0.363	−1.056
4	911	−0.319	−0.930
5	916	−0.321	−0.935
EVA			
2	1113	−0.390	−1.137
2.5	1164	−0.408	−1.189
3	1315	−0.461	−1.343
4	1141	−0.400	−1.165

[a] $T = 343.16$ K.

Fig. 3. Plot of f_U/f vs α for ethylene–propylene copolymer. Points calculated from eqs. (1) and (2): (O) 2; (□) 3; (▲) 4; (△) 5 wt-% DCP/100 wt-% EPM. Curve calculated from eq. (10) for EPM + 3 wt-% DCP. Curves for other samples are close to the curve outlined. $T = 343.16$ K.
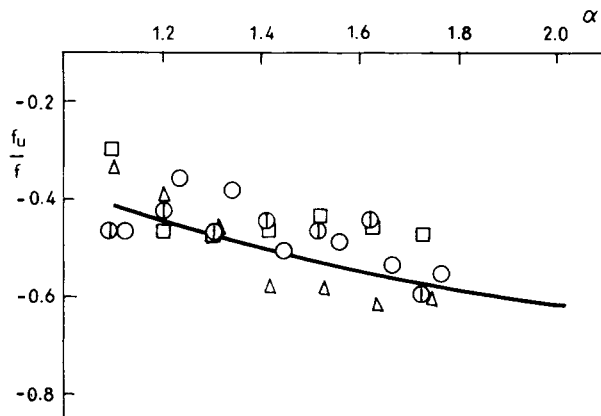

Fig. 4. Plots of f_U/f vs α for ethylene–vinyl acetate copolymer. Points calculated from eqs. (1) and (2): (O) 2; (⊕) 2.5; (□) 3; (▲) 4 wt-% DCP/100 wt-% EVA. Curve calculated from eq. (10) for EVA + 2.5 wt-% DCP. Curves for other samples are close to the curve outlined. $T = 343.16$ K.

deformation.[13]   A decrease in f_U/f with increasing α caused by the interaction of segments of polyethylene sequences is very probable for EVA copolymer mainly with respect to its tendency to crystallize. The interaction effect of the polar groups of vinyl acetate units cannot be excluded. A smaller decrease in f_U/f with increasing α for EPM is probably due to lower ethylene content and to the nonpolar character of this copolymer.

Description of Plots of f_U/f Versus α by the Mooney-Rivlin Equation

One of the possible ways for describing a plot of f_U/f versus α is to express the coefficient $(\partial \ln f/\partial T)_{P,L}$ by the Mooney-Rivlin equation.[4] Differentiation of this equation with respect to temperature at constant P and L and substitution into eqs. (1) and (2) give for f_U/f

$$f_U/f = 1 - T\frac{\dfrac{d(2C_1)}{dT} + \dfrac{d(2C_2)}{dT} + 2C_2\lambda_L\alpha^{-1}}{2C_1 + 2C_2\alpha^{-1}} - \lambda_L T \qquad (10)$$
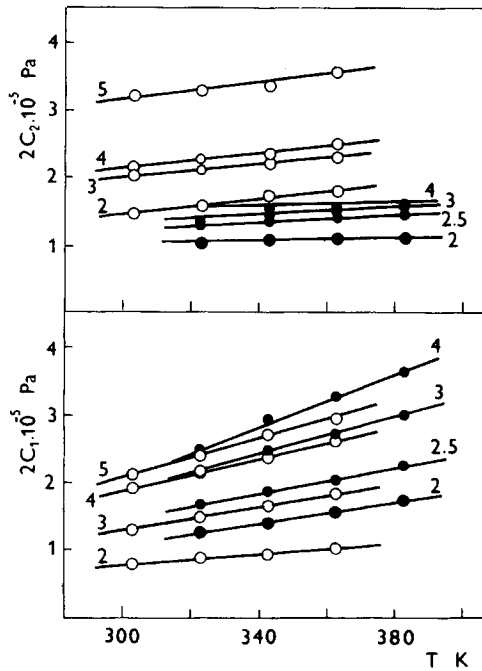
Fig. 5. Plots of constants $2C_1$ and $2C_2$ of Mooney-Rivlin equation vs temperature for ethylene–propylene (O) and ethylene–vinyl acetate (●) copolymer. Numbers at curves denote DCP content.

Figure 5 shows the values of $2C_1$ and $2C_2$ as a function of T for EPM and EVA samples and Table III contains the values of $d(2C_1)/dT$ and $d(2C_2)/dT$. The curves in Figures 3 and 4 calculated from eq. (10) indicate that this equation describes well the trend of the dependences of f_U/f on α.

Equation (10) may be rearranged to

$$f_U/f = 1 - T\frac{\dfrac{d(2C_1)}{dT} + \dfrac{d(2C_2)}{dT}}{2C_1 + 2C_2} - \lambda_L T - \frac{\lambda_L T}{\dfrac{2C_1\alpha}{2C_2} + 1}$$

$$- T\frac{2C_2\dfrac{d(2C_1)}{dT} - 2C_1\dfrac{d(2C_2)}{dT}}{(2C_1 + 2C_2)(2C_1 + 2C_2\alpha^{-1})}(1 - \alpha^{-1}) \quad (11)$$

Equation (11) is formally identical with the equation derived by Shen and Blatz,[15] eq. (13) in their paper. However, it is necessary to take into account an error in the sign of eq. (26b). Since[4]

$$G = 2C_1 + 2C_2$$

and thus

$$\frac{dG}{dT} = \frac{d(2C_1)}{dT} + \frac{d(2C_2)}{dT} \quad (12)$$

TABLE III
Values of $d(2C_1)/dT$ and $d(2C_2)/dT$ for Ethylene–Propylene and Ethylene–Vinyl Acetate
Copolymer

DCP, wt-%	$d(2C_1)/dT$, N/m² K	$d(2C_2)/dT$, N/m² K
EPM		
2	359.0	559.0
3	789.3	520.0
4	1049.0	525.0
5	1388.5	714.5
EVA		
2	805.0	105.0
2.5	1026.5	154.0
3	1307.5	380.0
4	1772.5	320.0

the first three terms on the right-hand side of eq. (11) correspond to eq. (4), and the last two terms express the deviation from the Gaussian approximation dependent on α. Figure 6 shows the course of the sum of the last two terms of eq. (11) $[\Delta(f_U/f)^{MR}]$ as a function of α. The absolute values of $\Delta(f_U/f)^{MR}$ increase with α more rapidly for EVA than for EPM. Analysis of the relation for $\Delta(f_U/f)^{MR}$ shows that the value of $\Delta(f_U/f)^{MR}$ at given α will be most influenced by the value of the last term in eq. (11) which will be conditioned by the ratio $2C_2/2C_1$ and $[d(2C_1)/dT]/[d(2C_2)/dT]$. The numerical analysis showed that the change in the ratio $2C_2/2C_1$ between 0.8 and 1.2 affects only slightly the value of $\Delta(f_U/f)^{MR}$, which strongly depends on the magnitude of the coefficient $d(2C_2)/dT$. As $d(2C_2)/dT$ decreases, $\Delta(f_U/f)^{MR}$ increases rapidly. This fact can be accounted for by an idea of partially energetic origin of $2C_2$. According to van der Hoff[8], the entropic and energetic parts of this constant can be determined from the temperature dependence of $2C_2$. The energy contribution to $2C_2$ is ~15% for EPM and about 55% for EVA. Accordingly, $\Delta(f_U/f)^{MR}$ is, at given α, much larger for EVA than for EPM.
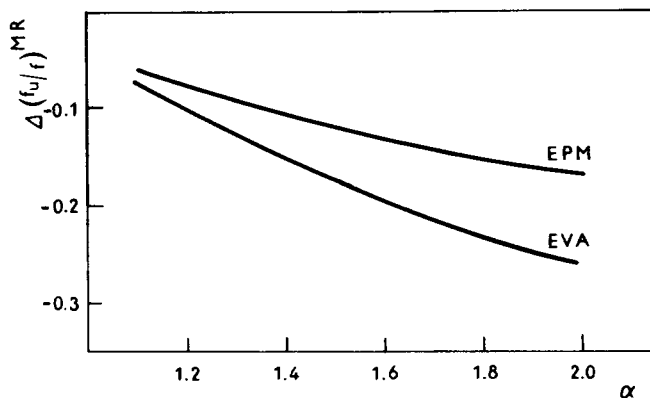

Fig. 6. Plots of $\Delta(f_U/f)^{MR}$ vs α for ethylene–propylene and ethylene–vinyl acetate copolymer calculated from eq. (11): EPM + 3 wt-% DCP; EVA + 2.5 wt-% DCP. Curves for other samples are close to the curves outlined.

CONCLUSIONS

The analysis of the relation for the shear modulus G showed that the plot of G versus temperature represented by a straight line is only approximate. A new equation was proposed for calculation of f_U/f and $d \ln \bar{r}_0^2/dT$ from the temperature dependence of G taking into account the change of the front factor $\bar{r}_i^2/\bar{r}_0^2$ with temperature.

The study of the variations of f_U/f with deformation showed that f_U/f tends to decrease with increasing α.

For describing the course of f_U/f versus α, an equation was derived on the basis of the Mooney-Rivlin equation. It was shown that the deviation $\Delta(f_U/f)^{MR}$ from the Gaussian approximation greatly depends on the magnitude of the coefficient $d(2C_2)/dT$.

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