

# Study of Elastic and Thermoelastic Properties of Ethylene-Propylene and Ethylene-Vinyl Acetate Copolymers. I. Elastic Properties

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## Synopsis

The elastic properties of ethylene-propylene and ethylene-vinyl acetate copolymers crosslinked to different degrees were studied. A correction of the front factor with respect to temperature has been proposed for calculation of the concentration of network chains from shear modulus  $G$ . Deviations from the Gaussian approximation of the dependence of force on deformation were evaluated.

## INTRODUCTION

On the basis of the so-called Gaussian model of polymer chain and polymer network, dependence of the equilibrium force on deformation can be expressed as follows<sup>1-4</sup>:

$$f = GA_i \left( \alpha - \frac{V}{V_i \alpha^2} \right) \quad (1)$$

where

$$G = \frac{N_0 k T}{V_i} \cdot \frac{\bar{r}_i^2}{\bar{r}_0^2} \quad (2)$$

where  $f$  is the equilibrium force,  $\alpha$  is the relative elongation,  $A_i$  and  $V_i$  are, respectively, the area of undeformed sample and its volume in isotropic state,  $N_0$  is the number of network chains,  $\bar{r}_i^2$  and  $\bar{r}_0^2$  are the mean square end-to-end distances in isotropic and reference states,  $k$  is the Boltzmann constant, and  $T$  is temperature.

Unfortunately, eq. (1) describes experimental dependence of force on uniaxial deformation only over the range of very small deformations.<sup>5</sup> The values for the force higher than those corresponding to eq. (1) at high deformations are evidently connected with final extensibility of real polymer chains not considered in the Gaussian approximation. A decrease in the force compared with its theoretical value within the range of medium elongations is ascribed to a number of factors<sup>6</sup>; the reason for these deviations has not yet been explained satisfactorily, and agreement between theories and experiment is only qualitative.

A universal equation depicting the dependence of force on deformation up to 300%–400% is the Mooney-Rivlin phenomenological equation<sup>7,8</sup>:

$$f = 2A_i(C_1 + C_2\alpha^{-1})(\alpha - \alpha^{-2}) \quad (3)$$

The physical sense of the constants  $C_1$  and  $C_2$  is not clear yet and is the subject of an extensive discussion.<sup>9</sup>

The aim of the present paper was to study the elastic properties of ethylene-propylene and ethylene-vinyl acetate copolymers crosslinked to different degrees in the region of small and medium deformations and to evaluate deviations from the Gaussian approximation.

## EXPERIMENTAL

### Materials

Ethylene-propylene copolymer, EPM, product of Montecatini Edison SPA, Milano, Italy, contained 50 mole-% ethylene,  $M_n = 70$  kg/mole, density 861 kg/m<sup>3</sup> (at 298 K).

Ethylene-vinyl acetate copolymer, EVA, product of Bayer AG Leverkusen, BRD, contained 78 mole-% ethylene,  $M_n = 47.3$  kg/mole, density 968 kg/m<sup>3</sup> (at 298°K), crystallinity<sup>10</sup> ~7%, melting point of crystallites 319 K (by DSC).

Dicumyl peroxide, DCP, crystallized from ethanol.

### Methods

DCP employed as a crosslinking agent was mixed with EPM and EVA in the amounts 2.0, 3.0, 4.0, and 5.0 wt-% DCP/100 wt-% EPM and 2.0, 2.5, 3.0, and 4.0 wt-% DCP/100 wt-% EVA. Mixtures were prepared in a laboratory calender at 310°K for 15 min, vulcanized in a laboratory press at 438°K for 45 min as films about 1 mm thick. Samples in the shape corresponding to ASTM-D 1708-59T were cut from the films.

After equilibrium was established, forces were measured between 290 and 400 K with an apparatus with a tensometric force transducer with an accuracy of  $\pm 5 \times 10^{-3}$  N. The sample was annealed by heating under nitrogen, the temperature of which was kept within a range of  $\pm 0.2$  K. The longitudinal thermal expansion coefficients determined by a cathetometer were:

$$\lambda_{L \text{ EPM}} = (2.25 \pm 0.05) \times 10^{-4}$$

$$\lambda_{L \text{ EVA}} = (2.55 \pm 0.05) \times 10^{-4} \text{ K}^{-1} \quad \text{at 343 K}$$

## RESULTS AND DISCUSSION

Figures 1 and 2 show the experimental data of  $f/A_i$  versus  $(\alpha - \alpha^{-2})$  for the samples studied. The measured dependences were presented by the polynomial of third degree using the least-squares method computer program (LSMCP). The values of  $G$  (identical with the shear modulus<sup>11</sup>) obtained as the slope of the curves at  $f/A_i = 0$  are listed in Table I.

Plots of  $f/A_i$  versus  $\alpha$  can be described very well in the interval investigated by eq. (3) (Figs. 3 and 4). The straight lines in the figures were computed by LSMCP. Table I shows also the values of  $2C_1$  and  $2C_2$  obtained as an intercept and the slope of these lines.

For small deformations the following holds<sup>12</sup>:

$$G = 2C_1 + 2C_2 \quad (4)$$

It is evident from Table I that agreement between experiment and eq. (4) is very good.

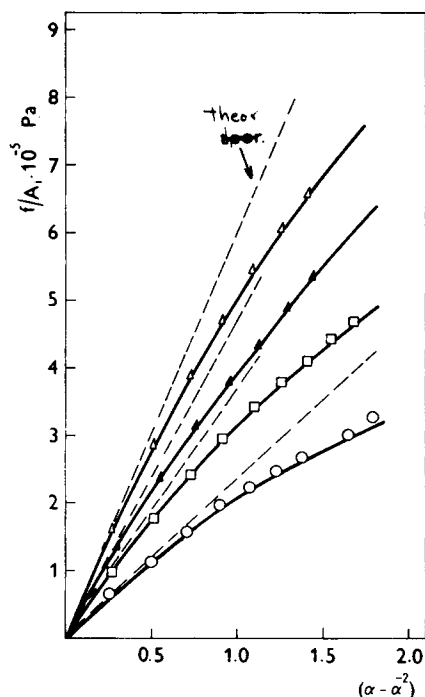


Fig. 1. Plot of  $f/A_i$  vs  $(\alpha - \alpha^{-2})$  for EPM copolymer ( $T = 343.16$  K): (○) 2; (□) 3; (▲) 4; (Δ) 5 wt-% DCP per 100 wt-% EPM; (—) exper. (polynomial 3rd degree-LSMCP); (- - -) theor. (slope at  $f/A_i = 0$ ).

The dependence of  $2C_1$  and of  $2C_2$  on the concentration of network chains can be expressed by straight lines with positive slope, which is consistent with most of the literature data.<sup>9</sup> The values of  $2C_1$  are almost equal to the same degree of crosslinking for both copolymers, the values for  $2C_2$  being higher for EPM (Fig. 5).

TABLE I  
Values of  $G$ ,  $2C_1$ , and  $2C_2$  for EPM and EVA<sup>a</sup>

DCP	$G \times 10^{-5}$ , Pa	$2C_1 \times 10^{-5}$ , Pa	$2C_2 \times 10^{-5}$ , Pa	$(2C_1 + 2C_2)$ $\times 10^{-5}$ , Pa	$2C_2/(2C_1 + 2C_2)$
EPM					
2	2.35	0.91	1.70	2.62	0.651
3	3.75	1.65	2.16	3.81	0.567
4	4.71	2.37	2.30	4.67	0.493
5	5.99	2.71	3.34	6.05	0.552
EVA					
2	2.46	1.39	1.05	2.44	0.430
2.5	3.18	1.85	1.33	3.18	0.418
3	4.35	2.47	1.90	4.37	0.434
4	4.81	2.93	1.97	4.89	0.403

<sup>a</sup>  $T = 343.16$  K.

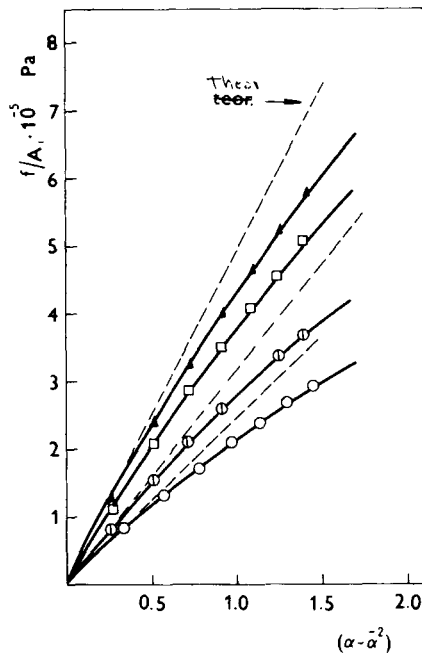


Fig. 2. Plot of  $f/A_i$  vs  $(\alpha - \alpha^{-2})$  for EVA copolymer ( $T = 343.16$  K): (○) 2; (⊙) 2.5; (□) 3; (▲) 4 wt-% DCP/100 wt-% EVA; (—) exper. (polynomial 3rd degree-LSMCP); (- - -) theor. (slope at  $f/A_i = 0$ ).

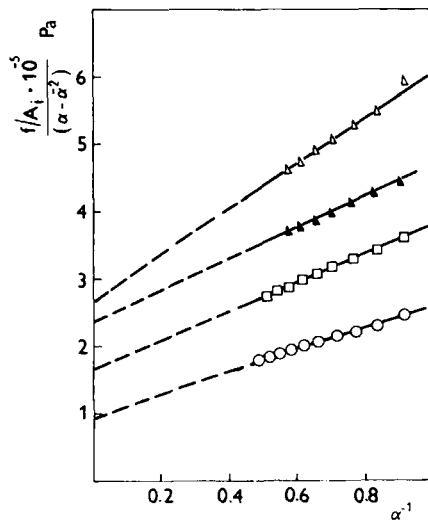


Fig. 3. Plot of  $(f/A_i)/(\alpha - \alpha^{-2})$  vs  $\alpha^{-1}$  for EPM copolymer ( $T = 343.16$  K): (○) 2; (□) 3; (▲) 4; (Δ) 5 wt-% DCP/100 wt-% EPM.

### Determination of the Concentration of Network Chains

The concentration of network chains  $N_0/V_i$  ( $\text{m}^{-3}$ ) was calculated from the experimental values of  $G$  according to relation (2). In a first approximation it was assumed that  $\rho = \bar{r}_i^2/r_0^2 = 1$ . The values of  $N_0/V_i$  calculated on this basis increase with temperature (Table II, column 3). This is contrary to the expectation that  $V_i$  increases with temperature. Therefore, the temperature dependence of  $\rho$  must be considered.

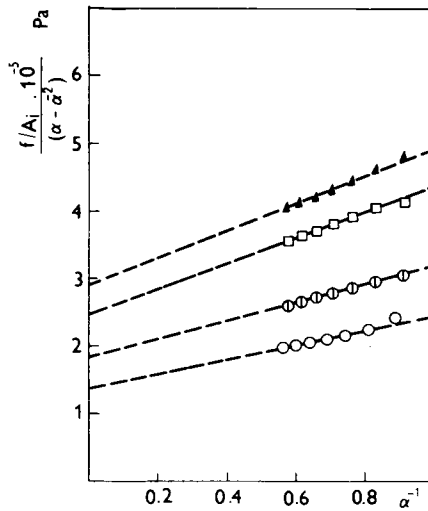


Fig. 4. Plot of  $(f/A_i)/(\alpha - \alpha^{-2})$  vs  $\alpha^{-1}$  for EVA copolymer ( $T = 343.16$  K): (○) 2; (◐) 2.5; (◻) 3; (▲) 4 wt-% DCP/100 wt-% EVA.

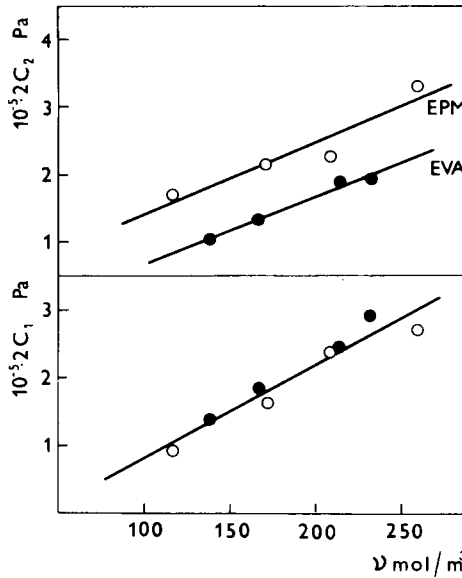


Fig. 5. Plots of  $2C_1$  and  $2C_2$  constants vs concentration of network chains  $\nu$ : (○) EPM; (●) EVA.

According to Flory et al.,<sup>13</sup>  $r_i^2$  is proportional to the macroscopic dimensions of the sample and varies with temperature in the same manner as  $V_i^{2/3}$ . Thus,

$$\bar{r}_{i2}^2 / \bar{r}_{i1}^2 = \exp[2\lambda_L(T_2 - T_1)] \tag{5}$$

where subscripts 1 and 2 refer to temperatures  $T_1$  and  $T_2$ . The temperature dependence of  $\bar{r}_0^2$  for the model of the so-called one-dimensional chain is given by<sup>14</sup>

$$\bar{r}_0^2 = nl^2 \exp(\epsilon'/RT) \tag{6}$$

TABLE II  
Comparison of  $N_0/V_i$  Values Uncorrected and Corrected with Respect to Temperature  
Dependence of the Front Factor<sup>a</sup>

$T, K$	$G \times 10^{-5}, Pa$	$(N_0/V_i) \times 10^{-25}, m^{-3}$ (uncorrected)	$(N_0/V_i) \times 10^{-25}, m^{-3}$ (corrected)	$\rho$
303	4.02	9.61	11.50	0.836
323	4.40	9.87	11.42	0.864
343	4.71	9.95	11.18	0.890
363	5.05	10.08	11.02	0.915
383	5.40	10.21	10.87	0.939

<sup>a</sup> Values were calculated from the sample of EPM + 4 wt-% DCP ( $\epsilon' = 970$  J/mole, see part II of this work). Similar results were obtained for all samples studied.

where  $n$  is the number of chain segments,  $l$  is their length, and  $\epsilon'$  is the chain folding energy. Then

$$\bar{r}_{02}^2 / r_{01}^2 = \exp \left[ \frac{\epsilon'}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right] \quad (7)$$

For the ratio  $\rho_2/\rho_1$  by combining eqs. (5) and (7) we get

$$\rho_2/\rho_1 = \exp \left[ 2\lambda_L(T_2 - T_1) - \frac{\epsilon'}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right] \quad (8)$$

Recently, the assumption that the chain dimensions in noncrystalline polymers are very close to the unperturbed chain dimensions was confirmed experimentally.<sup>15</sup> During crosslinking, the crosslinks can be considered as chain ends. These are fixed at the distance corresponding to the crosslinking temperature. It can then be assumed that at the crosslinking temperature,  $\rho_C = 1$ . On substituting  $T_1 = T_C$  and  $\rho_1 = \rho_C = 1$ , eq. (8) gives directly the value of  $\rho$  as a function of temperature and  $\epsilon'$ . As is obvious from Table II, the values  $N_0/V_i$  corrected for the temperature dependence of  $\rho$  on the basis of eq. (8) decrease with temperature as theoretically expected.

Table III contains the values for the concentrations of chains for the copolymers studied corrected according to eq. (8) and those corrected in addition for free chain ends.<sup>16</sup>

TABLE III  
Concentration of Network Chains for EPM and EVA<sup>a</sup>

DCP		$(N_0/V_i) \times 10^{-25}, m^{-3}$	$\nu, moles/m^3$
wt-%	moles/m <sup>3</sup>		
EPM			
2	61.9	5.58	116.4
3	92.6	8.90	171.5
4	123.5	11.18	209.4
5	154.4	14.20	259.5
EVA			
2	69.3	5.96	138.4
2.5	86.6	7.71	167.4
3	103.8	10.55	214.4
4	138.4	11.66	232.9

<sup>a</sup>  $T = 343.16$  K.

### Deviations of the Deformation Dependence of Force From the Gaussian Approximation

The deviation of the experimentally found force  $f$  from the Gaussian approximation as a function of deformation was evaluated on the basis of the relation

$$H = \frac{f_{\text{exp}}}{GA_i(\alpha - \alpha^{-2})} \quad (9)$$

where the value of  $GA_i(\alpha - \alpha^{-2})$  is taken as a theoretical value of the force, at the given elongation. Figure 6 shows a plot of  $H$  versus deformation for the samples investigated. A decrease in the force found experimentally compared with the Gaussian approximation is, in the range of elongations studied, evident. The dependence of  $H$  on  $\alpha$  for a given copolymer can be expressed by one curve. This means that the deviation is, within experimental error, independent of the degree of crosslinking over the region investigated.

The Mooney-Rivlin equation contains a term expressing the deviation from the Gaussian approximation. In order to express  $H$  in terms of the Mooney-Rivlin equation, this equation was modified as follows:

$$f/A_i = (2C_1 + 2C_2)(\alpha - \alpha^{-2}) - 2C_2(1 - \alpha^{-1})(\alpha - \alpha^{-2}) \quad (10)$$

The first term of the right-hand side of eq. (10) [see eqs. (1) and (4)] corresponds to the Gaussian equation for rubber elasticity, the second term expresses deviation as a function of  $2C_2$  and  $\alpha$ . By substituting eq. (10) into eq. (9) we obtain for  $H$

$$H = 1 - \frac{2C_2}{2C_1 + 2C_2} (1 - \alpha^{-1}) \quad (11)$$

The curves in Figure 6 were calculated from eq. (11). The variation of  $H$  with  $\alpha$  is represented by single curves, one for each type of copolymer. The scatter of  $H$  values does not exceed 2% at a given  $\alpha$ . It follows from Figure 7 that the deviation from the Gaussian behavior is greater for EPM than for EVA copolymer.

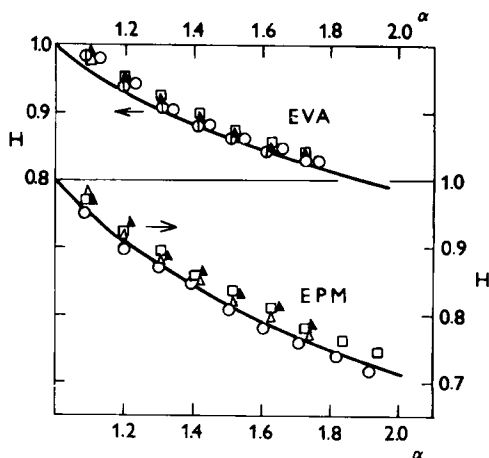


Fig. 6. Plots of  $H = f/GA_i(\alpha - \alpha^{-2})$  vs  $\alpha$  for EPM and EVA ( $T = 343.16^\circ\text{K}$ ): (○) 2; (◐) 2.5; (◑) 3; (▲) 4; (△) 5 wt-% DCP/100 wt-% polymer. Curve calculated from eq. (11).

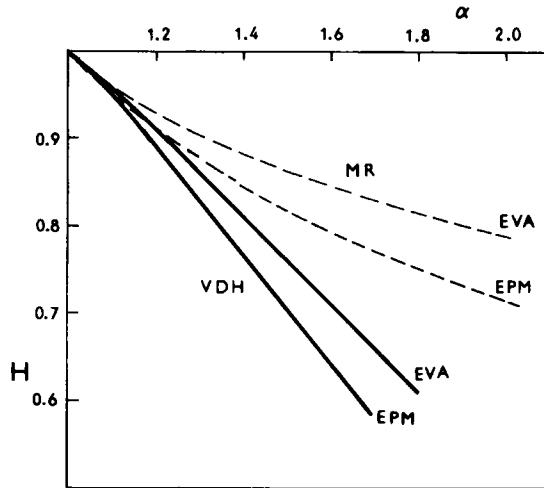


Fig. 7. Plot of  $H$  vs  $\alpha$  for EPM and EVA. Dashed curves: calculated according to eq. (11); heavy curves: calculated according to eq. (13).

One of the interesting theories expressing quantitatively the deviation of the experimental data from the Gaussian approximation is the van der Hoff theory.<sup>17</sup> According to van der Hoff, the force compared with its theoretical value in the range of medium deformations decreases as a result of the interaction of chain segments tending to become parallel during extension. In this case the force can be expressed as follows<sup>17</sup>:

$$f = GA_i(\alpha - \alpha^{-2})[1 - CT(\alpha)] \quad (12)$$

where  $T(\alpha)$  is the degree of orientation of the end-to-end vectors of network chains calculated on the basis of Treloar's distribution function<sup>18</sup> and  $C$  is the constant obtainable from thermoelastic data.\* Values for  $C$  are 0.31 for EPM and 0.25 for EVA copolymer. On the basis of eq. (12), we have for  $H$

$$H = 1 - CT(\alpha) \quad (13)$$

The values of  $H$  as a function of  $\alpha$  for our two copolymers are shown in Figure 7. Equation (13) evidently describes the experimental dependence only over the range of very low deformations. At higher elongations the values for  $H$  are lower than the experimental ones. This is probably due to the shape of the function  $T(\alpha)$  derived for ideal polymer networks.

On rearranging expression for  $H$  to

$$H = 1 - C\alpha^K T(\alpha) \quad (14)$$

eq. (12) describes very well the course of the force at deformations and temperatures studied ( $K$  is the empirical parameter). It is interesting that  $K$  is  $-1.2$  for both copolymers.

\* For calculation of  $C$  and  $T(\alpha)$ , see ref. 17.



## CONCLUSIONS

The study of the elastic properties of ethylene-propylene (EPM) and ethylene-vinyl acetate (EVA) copolymers showed that deviations from the Gaussian approximation of the dependence of the force on deformation cannot be neglected already in the range of very small deformations.

The equilibrium force as a function of deformation over the range studied is described well by the Mooney-Rivlin equation. The sum of the constants of this relation is, within experimental error, identical with the shear modulus  $G$  obtained as a slope of the experimental curve  $f/A_i$  versus  $(\alpha - \alpha^{-2})$  at  $f = 0$ .

We found that in calculating the concentration of network chains  $N_0/V_i$  from the modulus  $G$  it is necessary to correct the front factor with respect to the temperature change. A method was proposed for this correction.

The evaluation of the deviations  $H$  of the experimental dependence of  $f$  on  $\alpha$  from the Gaussian approximation showed that at the deformations investigated,  $H$  is independent of the degree of crosslinking. We compared the functions  $H$  obtained from the Gaussian approximation, Mooney-Rivlin equations, and van der Hoff equation. Probably the interaction of chain segments tending to become parallel during deformation affects considerably the force-deformation dependence.

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Received February 17, 1977

Revised November 9, 1977