

Study of thermoelastic properties of ethylene-vinyl acetate copolymers and their mixtures with ethylene-propylene copolymer, polystyrene, and poly(vinyl chloride)*

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The thermoelastic properties of the ethylene-vinyl acetate copolymers (EVA) (ethylene content 67—79 weight %) as well as of the mixtures of EVA (ethylene content 55 weight %) with ethylene-propylene copolymer (EPC), polystyrene (PS), and poly(vinyl chloride) (PVC) were studied. In all cases the dependence of equilibrium force (f) on temperature showed a discontinuity caused by the crystallization of polyethylene segments of EVA. The values of relative energy contribution (f_U/f) for EVA (ethylene content 67—79 weight %) in dependence on relative elongation (α) passed through a maximum in the elongation range 1.1—1.3 and reached the value ~ -0.8 at elongation $\alpha \approx 1.5$. The values of f_U/f for the mixtures of EVA with EPC were directly proportional to the composition of the mixtures. f_U/f for the mixtures of EVA with PS or PVC were not significantly influenced by the presence of filler.

Изучались термоэластичные свойства этилен-винилацетатовых сополимеров (ЭВА) (содержание этилена 67—79% вес.), смесей ЭВА (содержание этилена 55% вес.) с этилен-пропиленовым сополимером (ЭПс), полистиролом (ПС) и поливинилхлоридом (ПВХ). Во всех случаях в зависимости равновесной силы (f) от температуры (T), определялась дисконтинуита, вызванная кристаллизацией полиэтиленовых сегментов ЭВА сополимера. Зависимости относительного энергетического вноса (f_U/f) для ЭВА (с содержанием этилена 67—79% вес.) от относительного растяжения (α) переходили через максимум в интервале растяжения 1,1—1,3 и достигали величин пригл. $-0,8$ при растяжении $\alpha \approx 1,5$. Величины f_U/f для смесей ЭВА с ЭПс были прямо пропорциональны составу смесей. Присутствие наполнителя не оказало заметное влияние на величины f_U/f для смесей ЭВА с ПС или ПВХ.

In recent years, a number of papers concerning the thermodynamics of rubber elasticity has been published. From the temperature dependence of the equilibrium force, f , the so-called energy contribution ($f_U = (\partial U/\partial L)_{T, v}$) of the total force f can be determined [1, 2]. The change in the internal energy is related to the changes in conformational energies of polymeric chains; *i.e.* it is assigned to the change in the intramolecular energy of chains. In agreement with statistical theory, the value f_U/f

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should not depend on the density of network and on deformation. For real networks it holds only within the range of small deformations ($\alpha \equiv L/L_0 \doteq 1.4$) [3]. However, it has been observed in many cases that the f_U/f value depends on deformation [4—12]. According to literature, the f_U/f value may be affected by several factors: a non-gaussian behaviour of the network [13], a change in the intermolecular energy as a consequence of the change in the sample volume during deformation [14], or a change in the intermolecular energy due to the orientation of segments during deformation [15] *etc.* The magnitude of changes in the internal energy will be to a high degree influenced by supermolecular structure of the polymer and its changes in the course of deformation as well as by the presence of filler [16, 17].

In this study the thermoelastic properties of ethylene-vinyl acetate copolymers and their mixtures with ethylene-propylene copolymer, polystyrene, and poly(vinyl chloride) were investigated.

Experimental

Materials

Commercially produced ethylene-vinyl acetate copolymers (EVA) were used. They are characterized in Table 1.

Ethylene-propylene copolymer, EPc (trade mark Dutral) contained 40 weight % of ethylene, $M_n = 0.7 \times 10^5$

Polystyrene — powder, particle diameter ~ 0.05 mm.

Poly(vinyl chloride) — powder, particle diameter ~ 0.02 mm.

Dicumyl peroxide (DCP), twice precipitated from ethanol, was used as crosslinking agent. For the mixtures with PVC, benzoyl peroxide (BP), twice precipitated from ethanol, was used as crosslinking agent. Vulcanized mixtures contained 2.5 weight parts of DCP/100 w.p. of polymer or 5.0 w.p. of BP/100 w.p. of polymer. Table 2 presents the composition of mixtures of EVA with EPc, PS, and PVC.

Table 1

EVA copolymers and their characterization

Sample	Ethylene content weight %	M_n 10^5	% cryst. ^c	T_m , K DSC	T_c , K from $f = f(T)$
1 L ^a	55.0	0.47	7	319	313
2 M-1 ^b	67.8	0.75	17	341	324
3 M-2 ^b	68.6	1.05	18	341	324
4 M-3 ^b	79.7	0.32	32	350	335

a) Levapren, product of Bayer AG, Leverkusen.

b) Miravithen, product of VEB Leuna Werke.

c) According to *Andreas et al.* [18].

Table 2

Composition of the polymer mixtures			
EVA-L w.p.	EPc w.p.	PS w.p.	PVC w.p.
80	20		
60	40		
50	50		
40	60		
20	80		
100		5	
100		10	
100		15	
100		25	
100			10
100			25

Methods

The mixtures were prepared in a laboratory calender. The samples were crosslinked to obtain foils *ca.* 1 mm in thickness in a laboratory press. The crosslinking by DCP was carried out at 438 K for 45 min and by BP at 403 K for 15 min.

The temperature dependences of the equilibrium force were obtained as described in [11, 12, 19]. The coefficient of thermal longitudinal expansion (obtained by cathetometer KM-6) varied between $1.8\text{--}2.5 \times 10^{-4} \text{ K}^{-1}$ in the temperature range from 333 to 353 K depending on the sample.

The values of thermodynamic quantities were obtained from equations [1]

$$f = (\partial U / \partial L)_{T, V} - T(\partial S / \partial L)_{T, V} = f_U + f_S, \quad (1)$$

$$-(\partial S / \partial L)_{T, V} = (\partial f / \partial T)_{V, L} \quad (2)$$

where f , U , S , L , V , and T are the equilibrium force, internal energy, entropy, sample length, sample volume, and temperature, respectively. The coefficient $(\partial f / \partial T)_{V, L}$ was calculated from the coefficient $(\partial f / \partial T)_{p, L}$ determined experimentally according to the relation [1]

$$(\partial f / \partial T)_{V, L} = (\partial f / \partial T)_{p, L} + \frac{3\lambda f}{\alpha^3 - 1}, \quad (3)$$

where $\lambda = L_0^{-1}(\partial L_0 / \partial T)_p$ and $\alpha = L / L_0$, *i.e.* relative elongation.

The f_U / f value was calculated from the relation

$$f_U / f = 1 - (\partial \ln f / \partial \ln T)_{p, L} - \frac{3\lambda T}{\alpha^3 - 1} \quad (4)$$

Melting temperatures, T_m , of the individual samples were established by Perkin—Elmer Differential Scanning Calorimeter.

Results and discussion

EVA Copolymers

Dependence of the equilibrium force, f , on the temperature, T , in the range from 293 to 388 K at both decreasing and increasing temperature can be represented by straight lines with an intersection (break) at temperatures T_{c1} and T_{c2} which are characteristic of the given sample (Fig. 1). This phenomenon was observed also

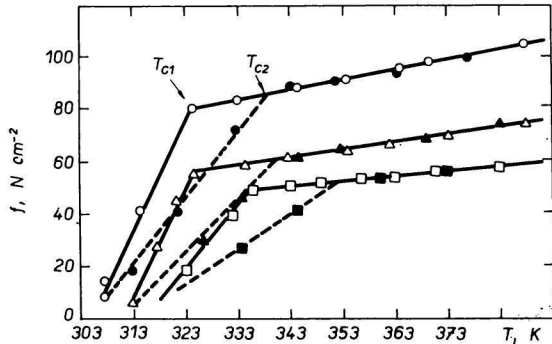


Fig. 1. Temperature dependence of the equilibrium force for the crosslinked ethylene-vinyl acetate copolymers with various ethylene content.

○ ● 67.8 weight % E; △ ▲ 68.8 weight % E; □ ■ 79.7 weight % E; elongation $\alpha \doteq 1.34$;
△ ○ decreasing temperature; ▲ ● increasing temperature.

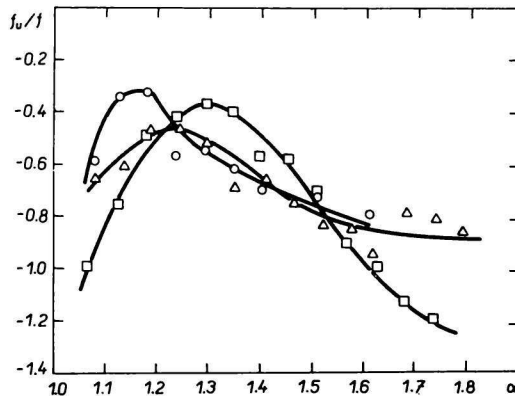


Fig. 2. Relationship between relative contribution of the energy component of the equilibrium force f_u/f and elongation α for ethylene-vinyl acetate copolymer with various ethylene content.

○ 67.8 weight % E; △ 68.6 weight % E; □ 79.7 weight % E; $T = 343$ K.

with EPc [10, 20] and it was ascribed to the crystallization of the sample under the given conditions. Temperatures, at which a break occurs on the dependences f vs. T increase with increasing ethylene content (and crystallinity) of samples. With increasing temperature the break appears at higher temperature (T_{c2}) which is approximately the same as T_m determined by DSC. Above T_{c2} , the f values are identical at both decreasing and increasing temperatures, this providing evidence for the reversibility of the process and amorphous nature of the samples.

The course of dependences of f_U/f on α at 343 K is shown in Fig. 2. In the range of small elongations, the dependences show a maximum which shifts to higher elongations with increasing ethylene content in samples. Relatively high negative values of f_U/f in the region of elongations from 1.05 to 1.20 were observed also for EPc with the ethylene content 60 weight % [10]. In addition to the inaccuracy of determination of α at small elongations [3], this may be caused also by other factors, the effect of which has not yet been discussed thoroughly. A decrease in f_U/f after passing through the maximum is probably due to a gradual parallel arrangement of polyethylene segments in the direction of deformation [15]. Deformation can also lead to a change in the intermolecular forces ensuing from the polar groups of vinyl acetate. The presented results show the considerable departure of the thermoelastic properties of the studied EVA-M copolymers from the statistical elasticity theory.

EVA-L + EPc mixtures

The thermoelastic properties of individual components were studied previously [11, 12]. In the case of their mixtures the temperature of the break on the force-temperature curve is practically not affected by the EPc content and varies between 305 and 307 K (at $\alpha \doteq 1.33$). Above 323 K the f values are identical at both increasing and decreasing temperature. Table 3 presents the f_U/f values

Table 3
Values f_U/f for EVA-L + EPc mixtures

EVA-L: EPc weight	f_U/f^a at 343 K	$(\partial f/\partial T)_{p,L}$ (303 K) ^b
		$(\partial f/\partial T)_{p,L}$ (343 K)
100: 0	-0.469 ± 0.016	7.71
80: 20	-0.426 ± 0.020	7.26
60: 40	-0.416 ± 0.038	7.16
50: 50	-0.397 ± 0.015	5.35
40: 60	-0.365 ± 0.021	4.64
20: 80	-0.331 ± 0.025	2.74
0: 100	-0.312 ± 0.011	1.00

a) In the range $1.20 < \alpha < 1.85$; b) at $\alpha \doteq 1.35$.

calculated at 343 K and shows that the quantity f_U/f is directly proportional to the composition of the mixture so testifying the absence of the specific interactions between components. The presence of EPc is reflected also on the course of dependence of f on T over the temperature range below T_i as shown by the values of ratio of coefficients $(\partial f/\partial T)_{p,l}$ at 303 and 343 K (Table 3), decreasing rapidly with increasing EPc content in the mixture.

EVA-L + PS or PVC mixtures

Polymer fillers introduced into polymer matrix complicate the interpretation of thermoelastic measurements. The following measurements are concerned solely with the qualitative comparison of the possible changes.

The dependence of f on α for EVA-L + PS or PVC mixtures measured at 343 K is shown in Fig. 3. In contrast to PVC, PS shows a reinforcing effect on polymeric

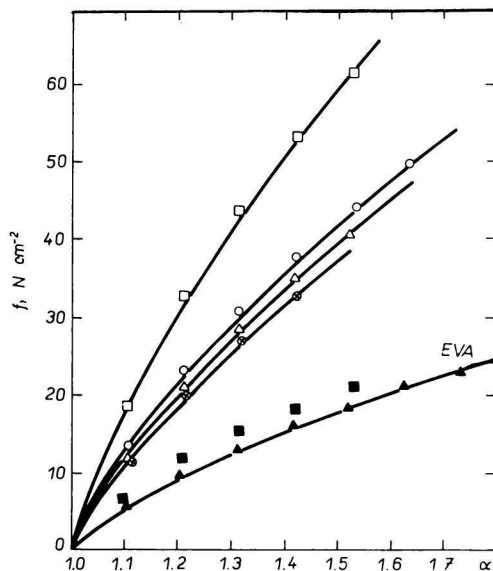


Fig. 3. Relationship between equilibrium force f and elongation α for the mixtures ethylene-vinyl acetate copolymer (EVA-L, ethylene content 55 weight %) with polystyrene or poly(vinyl chloride).

⊗ 5 w.p. PS; △ 10 w.p. PS; ○ 15 w.p. PS; □ 25 w.p. PS; ▲ 10 w.p. PVC; ■ 25 w.p. PVC; $T = 343$ K.

— Pure EVA-L (cf. [11, 12]).

matrix, which can be related to the measure of interactions of the system components [21].

Variations of f with T were linear for both systems EVA between 323 and 373 K. The f_U/f values were computed at 343 K and for the EVA-L + PS mixtures they are plotted in Fig. 4. The quantities f_U/f decrease slightly with increasing PS content in

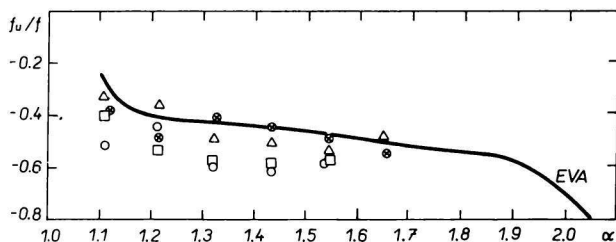


Fig. 4. Relationship between relative contribution of the energy component of the equilibrium force f_u/f and elongation α for the mixtures ethylene-vinyl acetate copolymer (EVA-L, ethylene content 55 weight %) with polystyrene.

⊗ 5 w.p. PS; Δ 10 w.p. PS; \circ 15 w.p. PS; \square 25 w.p. PS; $T=343$ K.
— Pure EVA-L (cf. [11,12]).

the sample. This may be a result of several simultaneously operating factors (volume and size of the filler particles, orientation of the elastomer molecules in the immediate neighbourhood of the filler, the existence of interphases, etc.); but in principle they can be reduced to interfacial interactions between elastomer and the filler. Fig. 5 shows a relation between f_u/f values and α for the EVA-L+PVC

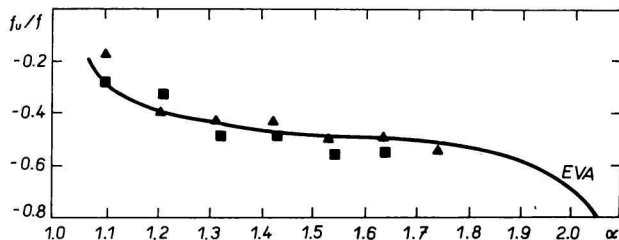


Fig. 5. Relationship between relative contribution of the energy component of the equilibrium force f_u/f and elongation α for the mixtures ethylene-vinyl acetate copolymer (EVA-L, ethylene content 55 weight %) with PVC.

\blacktriangle 10 w.p. PVC; \blacksquare 25 w.p. PVC; $T=343$ K.
— Pure EVA-L (cf. [11, 12]).

mixtures. As obvious from this figure, the presence of PVC does not affect the dependence of f_u/f on α .

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