Surface-Free Energy Analysis of Hydrolyzed Ethylene-Vinyl Acetate Copolymers

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Synopsis

Ethylene-vinyl acetate (E-VA) copolymers containing 12, 28, and 40 wt% of vinyl acetate, ethylene-vinyl acetate-vinyl alcohol terpolymers obtained by partial hydrolysis of (E-VA) copolymers and ethylene-vinyl alcohol (E-VOH) copolymers obtained by complete hydrolysis of (E-VA) copolymers were investigated by one-liquid contact-angle method. The polar force component of surface-free energy (γ_{SV}^{p}) of copolymers drastically increased by the substitution of the acetate groups with hydroxyl groups. The dispersion force component (γ_{SV}^{d}) of copolymers increased only slightly with the hydrolysis degree and deviated largely from the additivity law in regards of the surface area functions. The surface-free energy analysis of the cross-linked ethylene-vinyl alcohol and surface-hydrolyzed ethylene-vinyl acetate copolymers was also carried out.

INTRODUCTION

Ethylene-vinyl acetate copolymers have been offered as biomedical polymers in controlled drug-release applications.[1] The recent development of completely hydrolyzed ethylene-vinyl acetate copolymers forming ethylene-vinyl alcohol copolymers (with high vinyl alcohol contents) offers significant promise toward the ultimate development of swelling-controlled, constant-rate delivery systems since these polymers are at once glassy and water swellable, but water insoluble. Moreover, these polymers are easily processed by conventional thermoforming techniques including extrusion and injection molding.[2] The use of partially and fully hydrolyzed ethylene-vinyl acetate copolymers as a hydrophilic contact lens material was also attempted.[3]

The analysis of the surface-free energy of organic polymers by the one-liquid contact-angle method (the air-liquid-solid system) had been proposed by Fowkes,[4,5] Dahlquist,[6] and Wu.[7,8] According to their approach, the surface-free energy of the polymers is the sum of the polar (dipole-hydrogen bonding) and the London dispersion components. A method for estimating these quantities was reported by Owens and Wendt.[9] Another extension of Fowkes' approach has been proposed by Tamai et al.[10,11] from contact angle measurement of water drops on solids in hydrocarbon (the two-liquid contact-angle method). The correlation of the analytical results and the surface concentrations of functional groups has been indicated.[12] The dispersion force component of surface-free energy γ_{SV}^{d} obtained by Tamai et al.[10] seems to be comparatively larger than others as pointed out by Panzer[13] possibly due to the absence of the surface pressure in the one-liquid method resulting in smaller γ_{SV}^{d} values.[11]

Another parameter used as a measure of surface properties of the polymers is the Zisman empirical parameter,[14] the critical surface tension of wetting (γ_c), which is defined by the intercept of the horizontal line $\cos \theta = 1$ with the extrapolated straight line plot of $\cos \theta$ vs γ_{LV} of the liquid drop.[15] Although this intercept is less precisely defined than the critical surface tension of the liquids, nevertheless it is a useful parameter because it is a characteristic of the polymer surface.

The surface-free energy analysis of the molten and solid ethylene-vinyl acetate copolymers by the one-liquid contact-angle method have been published.[16-18] Matsunaga et al.[19] obtained comparatively different results from the two-liquid method. In his paper, the bulk composition of the copolymers was assumed as an approximation to continue to the surface enabling study of the relation between surface energy and its structure in detail. However, γ_{SV}^d value of the copolymers was found to increase drastically almost to that of polyvinyl acetate at only 30 wt % of vinyl acetate containing copolymers, possibly due to the interaction of ethylene and vinyl acetate groups.[19]

In the present study contact-angle measurements were applied for the surface-free energy analysis of the completely and partially hydrolyzed ethylene-vinyl acetate (E-VA) copolymers which are, respectively, ethylene-vinyl alcohol (E-VOH) copolymers and ethylene-vinyl acetate-vinyl alcohol (E-VA-VOH) terpolymers. Surface-free energy analysis of the cross-linked E-VOH and surface-hydrolyzed E-VA copolymers was also carried out.

EXPERIMENTAL

Materials

E-VA copolymers, containing 12, 28, 40 wt% of (VA) were the products of Aldrich Chemical Co. Inc. PE was the low-density polyethylene product of Imperial Chemical Industries Ltd (Alkathene). The cross-linkers, dicumyl peroxide and ethylene dimethacrylate (EGDM) were the products of Hercules Co. and B. D. H. Chemicals Ltd., respectively. The solvents and potassium hydroxide used were the products of B. D. H. Chemicals Ltd. The Melinex sheets used during compression moulding of polymers were supplied from Boyden Data Papers Ltd.

Hydrolysis

E-VA copolymers were dissolved in isopropanol-benzene (30:70) mixture. Potassium hydroxide was dissolved in this solution and the solution was refluxed for 1–3 h. Then, steam distillation was applied to remove benzene and isopropanol. The coagulated product was washed with hot water and dried under vacuum at room temperature for 3 days. The extent of hydrolysis of the products was controlled by the amount of added KOH (2–9 wt%) and the reaction time.

The copolymer compositions were determined by elemental analysis of carbon, hydrogen, and oxygen (Perkin Elmer 240 C Elemental Analyzer). The extent of hydrolysis of E-VA copolymers was monitored qualitatively by infrared spectroscopy (Perkin Elmer 177 Grating IR) and quantitatively by saponification titration.

The hydrolyzed copolymers were pressed in metal moulds containing metal gasket and Melinex (a heat-resistant type of polyester) sheets on both faces at 150°C under 14 kg/cm^2 pressure. The thickness of the cylindrical mouldings were 2 $\pm$ 0.1 mm and their diameters were 20 $\pm$ 1 mm. The densities of these discs were pycnometrically measured.

Surface Hydrolysis

E-VA copolymer having 40 wt % VA content was moulded at 150°C under 13 kg/cm^2 pressure to form cylindrical discs of the above-mentioned size. The surface hydrolysis of these discs were carried out in stoppered flasks containing varying amounts of KOH in methanol solution at room temperature and at 50°C in water bath.

Crosslinking

E-VOH copolymer obtained by fully hydrolyzing E-VA copolymer containing 28 wt% VA content was mixed with varying amounts of dicumyl peroxide on the two-roll mill at 50°C. Each sample was cured by compression moulding at 140–180°C for 40–60 min under 14 kg/cm^2 pressure. Melinex sheets used in the inner faces of the metal moulds prevented the copolymer from sticking to the metallic surface.

Some samples having varying amounts of dicumyl peroxide were swollen in ethylene dimethacrylate for 2 days and were moulded at 160°C for 15 min under 15 kg/cm^2 pressure for efficient crosslinking of the copolymer.

Surface Preparation and Measurement of Contact Angles

Prior to contact-angle measurements, the polymer surfaces were cleaned by washing with a detergent solution followed by a thorough rinsing with distilled water and finally drying in a vacuum dessicator at room temperature.

The water used for the contact-angle measurements was doubly distilled. Drops of each liquid 5 μL in size were deposited onto the polymer surface with a hypodermic syringe. The readings on the drop were directly taken using a cathetometer fitted with a goniometer eyepiece at 20°C. Each value reported for the contact angle was the average of at least four measurements on either side of the sessile drop. Variation in the contact-angle measurement was not greater than $\pm 2°$.

THEORY

Surface-Free Energy Components

The Young equation[20] describes the thermodynamic equilibrium of the three surface tensions γ_{SV}, γ_{SL}, γ_{LV} existing at the phase boundaries of a drop of liquid at rest on a solid surface:

$$\gamma_{LV}\cos \theta = \gamma_{SV} - \gamma_{SL} \qquad (1)$$

Where γ_{LV}, γ_{SV}, γ_{SL} are, respectively, the free energies of liquid, solid against their saturated vapor, and of the interface between solid and liquid. Sub-

scripts L, S, and V refer to liquid, solid, and vapor, respectively. In this equation, the phases are supposed to be mutually in equilibrium and the equilibrium film pressure of the adsorbed vapor of the liquid on the solid (π_e) is neglected.

The work required to pull the liquid away from the surface leaving the equilibrium-adsorbed film is given by Dupré equation:[21]

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{2}$$

Eliminating γ_{SL} from eqs. (1) and (2), the well-known Young-Dupré equation is obtained:

$$W_A = \gamma_{LV}(1 + \cos\theta) \tag{3}$$

Fowkes[4] proposed that the free energy of adhesion of a solid in contact with a liquid can be represented by the equation:

$$W_A = 2\left(\sqrt{\gamma_{SV}^d \, \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \, \gamma_{LV}^p}\right) \tag{4}$$

based on the assumptions

$$\gamma = \gamma^d + \gamma^p \tag{5}$$

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\left(\sqrt{\gamma_{SV}^d \, \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \, \gamma_{LV}^p}\right) \tag{6}$$

Equation (5) states that the surface-free energy of liquids and solids consists of dispersion and polar (mainly hydrogen bonding) components as shown by the superscripts d and p, respectively.

Owens and Wendt[13] described the calculation of the interfacial tension components of a polymer surface from contact-angle measurements using liquids with known γ_{LV}^d and γ_{LV}^p values:

$$\gamma_{SV}^d = \left(\frac{D}{2}\right)^2 \tag{7}$$

$$\gamma_{SV}^p = \left(\frac{P}{2}\right)^2 \tag{8}$$

where

$$D = \frac{(1 + \cos\theta_1)\gamma_{LV_1}\sqrt{\gamma_{LV_2}^p} - (1 + \cos\theta_2)\gamma_{LV_2}\sqrt{\gamma_{LV_1}^p}}{\sqrt{\gamma_{LV_1}^d \, \gamma_{LV_2}^p} - \sqrt{\gamma_{LV_2}^d \, \gamma_{LV_1}^p}} \tag{9}$$

$$P = (1 + \cos\theta_1)\frac{\gamma_{LV_1}}{\sqrt{\gamma_{LV_1}^p}} - \left(\sqrt{\frac{\gamma_{LV_1}^d}{\gamma_{LV_1}^p}}\right)D \tag{10}$$

Subscripts LV_1 and LV_2 refer to surface-free energy of water and methylene iodide, respectively.

γ_{LV}^d, γ_{LV}^p for a liquid of known surface tension on a solid surface with known γ_{SV} components, is calculated from:[22]

$$\gamma_{LV}^p = (\alpha \gamma_{LV})^2 \tag{11}$$

$$\gamma_{LV}^d = (\beta \gamma_{LV})^2 \tag{12}$$

where

$$\alpha = \left\{ \frac{P(1 + \cos \theta_I)}{D^2} + \left[\frac{1}{\gamma_{LV}} \left(1 + \frac{P^2}{D^2} \right) - \left(\frac{(1 + \cos \theta_I)}{D} \right)^2 \right]^{1/2} \right\} \left(1 + \frac{P^2}{D^2} \right)^{-1} \tag{13}$$

$$\beta = \frac{(1 + \cos \theta_I) - P\alpha}{D} \tag{14}$$

where θ_I = Contact angle of the liquid on the solid surface.

Area Fractions of Vinyl Acetate and Vinyl Alcohol on the Copolymer Surface

On the assumption that the volume of the copolymer can be expressed as the sum of those of its constituents ethylene and vinyl acetate, ethylene and vinyl alcohol, the density of the copolymer is given as:[19]

$$\frac{1}{\rho} = \frac{W_{VA}}{\rho_{PVA}} + \frac{1 - W_{VA}}{\rho_{PE}} = \left(\frac{1}{\rho_{PVA}} - \frac{1}{\rho_{PE}} \right) W_{VA} + \frac{1}{\rho_{PE}} \tag{15}$$

$$\frac{1}{\rho} = \frac{W_{VOH}}{\rho_{PVOH}} + \frac{1 - W_{VOH}}{\rho_{PE}} = \left(\frac{1}{\rho_{POVH}} - \frac{1}{\rho_{PE}} \right) W_{VOH} + \frac{1}{\rho_{PE}} \tag{16}$$

where W_{VA} and W_{VOH} are the weight fractions and ρ_{PVA}, ρ_{PVOH}, ρ_{PE} are the densities of the VA, VOH and ethylene constituents of the copolymers respectively.

Since the area fraction of vinyl acetate and vinyl alcohol on the surface should be equal to the volume fraction in the bulk copolymer,[19]

$$S_{VA}^{area} = C_{VA}^{vol} = \frac{W_{VA}\rho}{\rho_{PVA}} \tag{17}$$

$$S_{VOH}^{area} = C_{VOH}^{vol} = \frac{W_{VOH}\rho}{\rho_{PVOH}} \tag{18}$$

then, the surface area fraction of ethylene constituent of the copolymer is:

$$S_E^{area} = 1 - S_{VA}^{area} \tag{19}$$

$$S_E^{area} = 1 - S_{VOH}^{area} \tag{20}$$

RESULTS AND DISCUSSIONS

The contact-angle results of the water, glycerol, formamide, methylene iodide, and ethylene glycol drops on E-VA and E-VOH copolymers are listed in Tables I–III. A typical Zisman plot which was used in the determination of critical surface tension of the copolymers is shown in Figure 1. The surface-free energy components of E-VA and E-VOH copolymers are calculated using the values reported by Owens and Wendt[9] (H_2O : $\gamma_{LV} = 72.8$ erg, cm^{-2}, $\gamma_{LV}^p = 51.0$ erg, cm^{-2}, $\gamma_{LV}^d = 21.8$ erg, cm^{-2}, CH_2I_2 : $\gamma_{LV} = 50.8$ erg, cm^{-2}, $\gamma_{LV}^p = 1.3$ erg, cm^{-2}, $\gamma_{LV}^d = 49.5$ erg, cm^{-2}) in the eqs. (7)–(10) and are listed in Tables IV–VI.

The surface-free energy components of glycerol and formamide are calculated from the contact-angle results in Table I for each particular copolymer using eqs. (11)–(14) and data in Table IV. The averages of these results are listed in Table VII. Then, the surface-free energy components of the copolymers are recalculated from glycerol and formamide, glycerol and methylene iodide contact-angle results using data in Table I and VII, eqs. (7)–(10) and are listed in Tables VIII and IX. The comparison of Tables IV, VIII, and IX shows that the order of the surface-free energy components of the copolymers agrees well, however, the individual values vary beyond the experimental error.

Since, the whole calculations are based on the values of the surface-free energy components of water and methylene iodide reported by Owens and Wendt,[9] the determination of the experimentally verified values of γ_{LV}^d and γ_{LV}^p of the used liquids is necessary to eliminate the discrepancy in the γ_{LV}^d and γ_{LV}^p values of the polymers. Such a computation will be the subject of a later paper.

The relations of γ_{SV}^p, γ_{SV}^d, and γ_{SV} values of the E-VA copolymers to their VA contents are indicated in Figures 2 and 3. The γ_{SV}^p value increases with the increase of VA content and the slopes of the lines obtained independently from water-methylene iodide, glycerol-formamide, glycerol-methylene iodide pairs are approximately equal in Figure 2.

The increase in γ_{SV}^d values (from data in Table IV) reaches a maximum almost at 30 wt% of VA in Figure 3, similar to the results of Matsunaga and Tamai[19] with nearly half of their γ_{SV}^d values. The γ_c values obtained from Zisman plot are in the same order with γ_{SV} values in Table IV as expected.

The relations of γ_{SV}^p, γ_{SV}^d, and γ_{SV} values of the E-VOH copolymers to their VOH contents are indicated in Figures 4 and 5. The γ_{SV}^p value increases drastically with the increase of VOH content nearly three times of the increase of γ_{SV}^p with VA contents due to the strong H-bonding property of the hydroxyl group. However, γ_{SV}^d value is nearly constant as shown in Figure 5. The γ_{SV} increase of the E-VOH copolymer with VOH content is mainly due to the increase of its γ_{SV}^p component.

The relations of γ_{SV}^p, γ_{SV}^d, γ_{SV} values of the E-VA copolymer having 28 wt% VA content with the hydrolysis degree are indicated in Figures 6 and 7. Since partially hydrolyzed E-VA copolymers are ethylene-vinyl acetate-vinyl alcohol terpolymers, the increase of γ_{SV}^p and γ_{SV}^d with hydrolysis degree exhibits the effect of the substitution of acetate groups with hydroxyl groups, that means more rapid increase of γ_{SV}^p than γ_{SV}^d.

TABLE I
Contact-Angle Results of E-VA and E-VOH Copolymers

	PE	EVA-12	EVA-28	EVA-40	EVOH-12	EVOH-28	EVOH-40	82% Hydrolyzed EVA-28	94% Hydrolyzed EVA-28
Water	92 ± 2	83 ± 2	80 ± 2	79 ± 2	68 ± 2	63 ± 2	60 ± 2	70 ± 2	66 ± 2
Glycerol	82 ± 2	73 ± 2	71 ± 2	70 ± 2	59 ± 2	56 ± 2	55 ± 2	60 ± 2	57 ± 2
Formamide	76 ± 2	65 ± 2	63 ± 2	62 ± 2	52 ± 2	48 ± 2	48 ± 2	53 ± 2	50 ± 2
Methylene iodide	57 ± 2	49 ± 2	47 ± 2	46 ± 2	37 ± 2	35 ± 2	34 ± 2	40 ± 2	37 ± 2
Ethylene glycol	51 ± 2	45 ± 2	43 ± 2	42 ± 2	33 ± 2	31 ± 2	31 ± 2	34 ± 2	32 ± 2

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TABLE II
Contact-Angle Results of Surface-Hydrolyzed E-VA Copolymers Having 40 wt% (VA) Content

Sample no.	% KOH	Temp. (°C)	Time (days)	Contact θ				
				Water	Glycerol	Formamide	Methylene iodide	Ethylene glycol
1	0.2	20	4	79 ± 2	72 ± 2	62 ± 2	44 ± 2	43 ± 2
2	0.5	20	4	77 ± 2	69 ± 2	61 ± 2	45 ± 2	41 ± 2
3	1	20	4	76 ± 2	67 ± 2	59 ± 2	42 ± 2	40 ± 2
4	10	20	4	59 ± 2	52 ± 2	47 ± 2	35 ± 2	33 ± 2
5	1	50	4	69 ± 2	60 ± 2	53 ± 2	37 ± 2	35 ± 2
6	1	50	7	67 ± 2	59 ± 2	52 ± 2	38 ± 2	34 ± 2

TABLE III
Contact-Angle Results of Cross-linked E-VOH Copolymers Having 16.6 wt% (VOH) Content

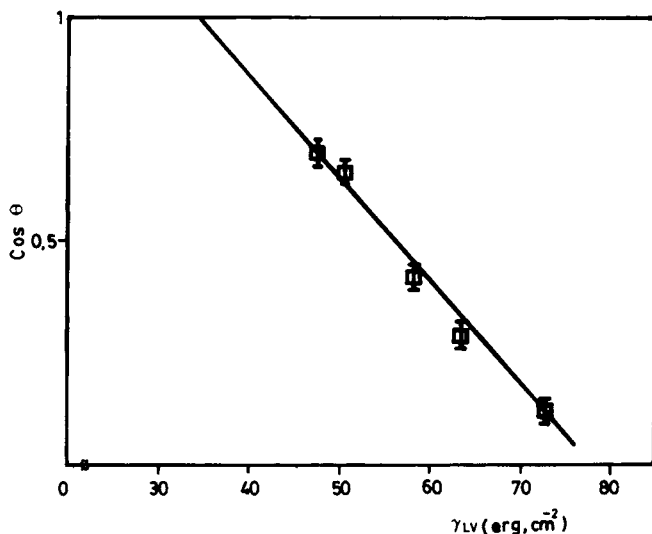| Sample no.	Dicumyl peroxide (wt%)	Swelling in EGDM	Contact θ				
			Water	Glycerol	Formamide	Methylene iodide	Ethylene glycol
1	5	—	57 ± 2	52 ± 2	47 ± 2	37 ± 2	34 ± 2
2	10	—	60 ± 2	55 ± 2	51 ± 2	40 ± 2	37 ± 2
3	20	—	66 ± 2	59 ± 2	54 ± 2	42 ± 2	40 ± 2
4	5	+	70 ± 2	61 ± 2	57 ± 2	44 ± 2	40 ± 2
5	10	+	70 ± 2	62 ± 2	56 ± 2	44 ± 2	38 ± 2

Fig. 1. Zisman plot for E-VA copolymer having 12 wt% VA content.

The results of the surface-free energy components of surface-hydrolyzed E-VA copolymers having 40 wt% VA content calculated from H_2O and CH_2I_2 contact-angle results and γ_c values obtained from Zisman plot are listed in Table V. As seen from Tables II and V, mainly γ_s^p components of the copolymers increase with the increase of the KOH concentration, reaction

TABLE IV
Surface-free Energy Components of E-VA and E-VOH Copolymers Calculated
from Water and Methylene Iodide Contact-Angle Results and
γ_c Values Obtained from Zisman Plot

Polymer	γ_{SV}^d erg, cm^{-2}	γ_{SV}^p erg, cm^{-2}	γ_{SV} erg, cm^{-2}	γ_c erg, cm^{-2}
PE	28.6	2.0	30.6	31.2
E-VA-12	31.9	4.1	36.0	34.0
E-VA-28	32.6	5.1	37.7	35.0
E-VA-40	33.0	5.4	38.4	35.5
E-VOH-12	35.9	9.5	45.4	38.0
E-VOH-28	36.0	12.2	48.2	38.5
E-VOH-40	36.0	13.9	49.9	39.0
% 82 hydrolyzed E-VA-28	34.7	8.9	43.6	38.1
% 94 hydrolyzed E-VA-28	35.6	10.7	46.3	38.4

TABLE V
Surface-Free Energy Components of Surface-Hydrolyzed E-VA Copolymers
Having 40 wt% VA Content Calculated from Water and Methylene Iodide
Contact-Angle Results and γ_c Values Obtained from Zisman Plot

Sample no.	γ_{SV}^d erg, cm^{-2}	γ_{SV}^p erg, cm^{-2}	γ_{SV} erg, cm^{-2}	γ_c erg, cm^{-2}
1	34.1	5.1	39.2	38.5
2	33.2	6.1	39.3	38.5
3	34.7	6.1	40.8	39.0
4	35.4	14.7	50.1	39.5
5	36.1	9.0	45.1	39.2
6	35.2	10.3	45.5	39.0

TABLE VI
Surface-Free Energy Components of Cross-linked E-VOH Copolymers
Having 16.6 wt% VOH Content, Calculated from Water and Methylene Iodide
Contact-Angle Results and γ_c Values Obtained from Zisman Plot

Sample no.	γ_{SV}^d erg, cm^{-2}	γ_{SV}^p erg, cm^{-2}	γ_{SV} erg, cm^{-2}	γ_c erg, cm^{-2}
1	34.1	16.5	50.6	38.5
2	33.0	15.1	48.1	34.0
3	32.9	11.7	44.6	33.5
4	32.5	9.7	42.2	34.0
5	32.5	9.7	42.2	35.0

temperature, and time. The shape deformation of the discs begin after 1%
KOH concentration due to the molecular structure difference between the
surface and the inside of the copolymer. The surface hydrolysis renders the
surface of the copolymer more hydrophilic, however, it is difficult to obtain
reproducible results with the same procedure.

TABLE VII
Average Surface-Free Energy Components of Glycerol and Formamide
Calculated from Data in Tables I and IV

	γ_{LV}^{d} erg, cm^{-2}	γ_{LV}^{p} erg, cm^{-2}	γ_{LV}^{a} erg, cm^{-2}
Glycerol	21.8 ± 5.6	41.6 ± 5.6	63.4
Formamide	23.3 ± 5.9	34.9 ± 5.9	58.2

[a] The surface-free energy (γ_{LV}) values of glycerol and formamide were taken from CRC, *Handbook of Chemistry and Physics.*

TABLE VIII
Surface-Free Energy Components of E-VA and E-VOH Copolymers
Calculated from Glycerol and Formamide Contact-Angle Results
by Using Data in Tables I and VII

Polymer	γ_{SV}^{d} erg, cm^{-2}	γ_{SV}^{p} erg, cm^{-2}	γ_{SV} erg, cm^{-2}
PE	31.0	2.4	33.4
E-VA-12	49.6	1.6	51.2
E-VA-28	48.3	2.2	50.5
E-VA-40	47.6	2.6	50.2
E-VOH-12	30.3	12.0	42.3
E-VOH-28	28.2	14.6	42.8
E-VOH-40	27.5	15.5	43.0
% 82 hydrolyzed E-VA-28	30.9	11.2	42.1
% 94 hydrolyzed E-VA-28	28.9	13.7	42.6

TABLE IX
Surface-Free Energy Components of E-VA and E-VOH Copolymers Calculated
from Glycerol and Methylene Iodide Contact-Angle Results
by Using Data in Tables I and VII

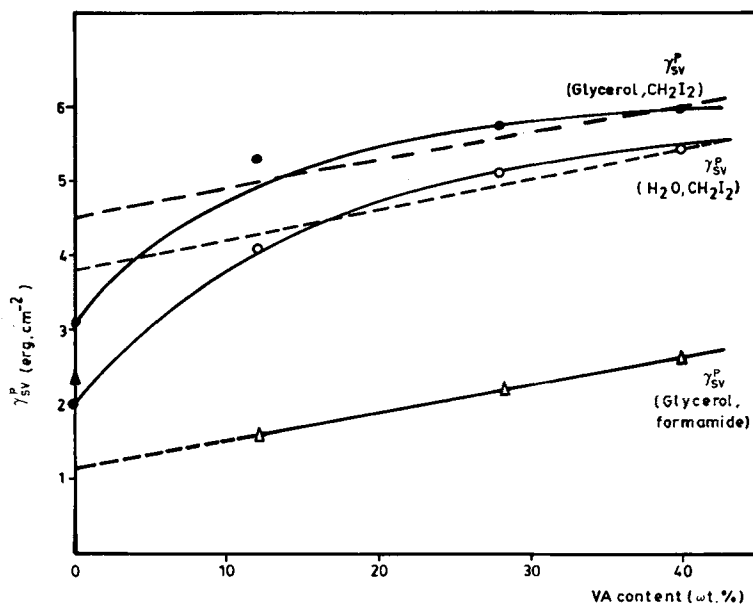| Polymer	γ_{SV}^{d} erg, cm^{-2}	γ_{SV}^{p} erg, cm^{-2}	γ_{SV} erg, cm^{-2}
PE	28.0	3.1	31.1
E-VA-12	31.4	5.3	36.7
E-VA-28	32.3	5.8	38.1
E-VA-40	32.7	6.0	38.7
E-VOH-12	35.9	9.7	45.6
E-VOH-28	36.4	10.9	47.3
E-VOH-40	36.7	11.2	47.9
% 82 hydrolyzed E-VA-28	34.5	9.8	44.3
% 94 hydrolyzed E-VA-28	35.6	10.7	46.3

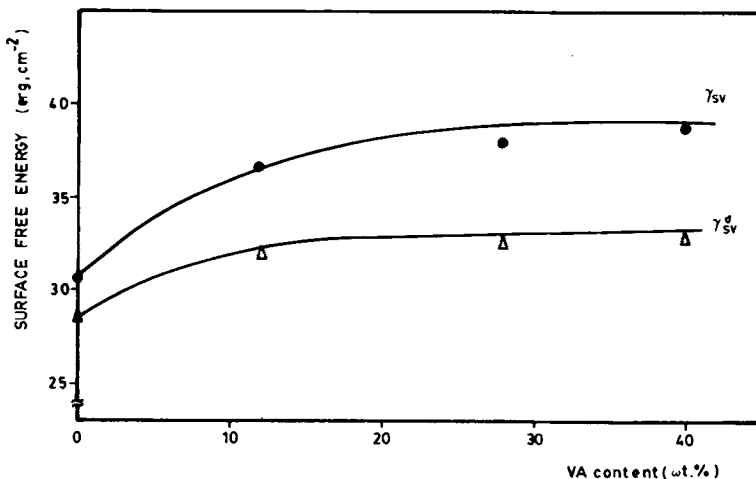Fig. 2.   Change of γ_{SV}^{P} with the vinyl acetate content of the E-VA copolymers.

Fig. 3.   Change of γ_{SV} and γ_{SV}^{d} with the vinyl acetate content of the E-VA copolymers.

The results of the surface-free energy components of cross-linked E-VOH copolymers obtained from E-VA-28 are listed in Table VI. Since the sample which was mixed with 5 wt% dicumyl peroxide was sticky and could be difficult to release from Melinex sheet due to the poor cross-linking efficiency, high dicumyl peroxide percentages and a cross-linking coagent, ethylene dimethacrylate, were used to increase crosslinking of the copolymer. The cross-linked copolymers with dicumyl peroxide exhibited slightly lower γ_{SV}^{d} values than uncross-linked E-VOH-28. The γ_{SV}^{P} and γ_{SV}^{d} values decreased with the increased dicumyl peroxide percentage due to the decrease of polar and intermolecular dispersion forces by crosslinking of the polymer chains. The
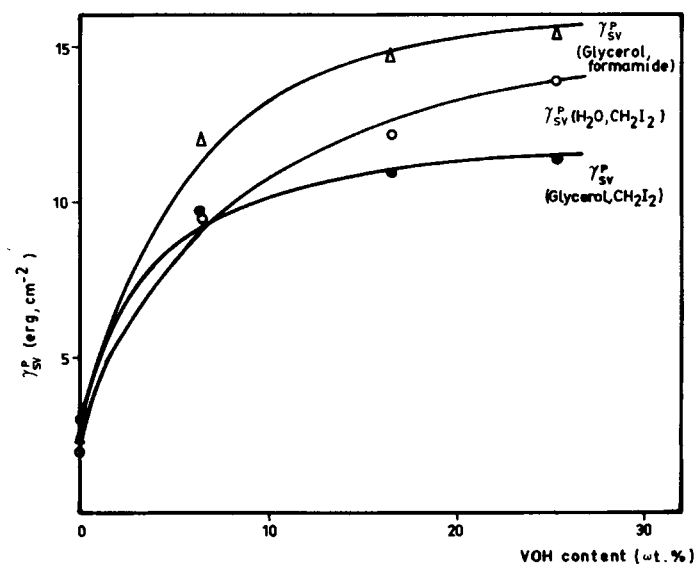
Fig. 4.   Change of γ_{SV}^p with the vinyl alcohol content of the E-VOH copolymers.
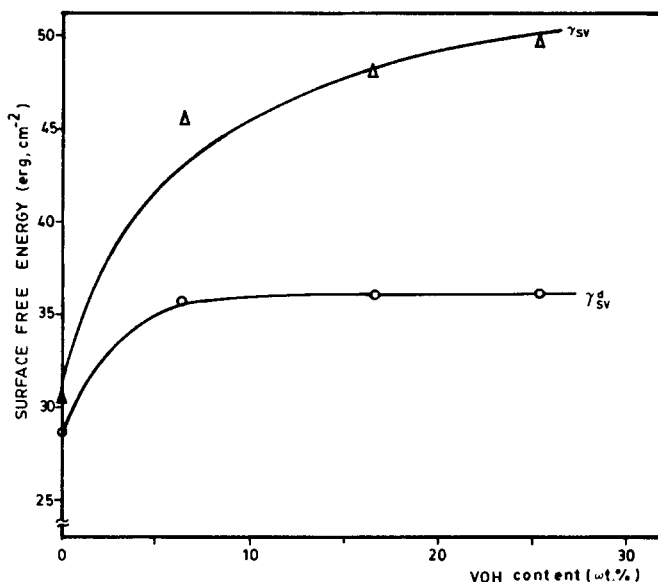

Fig. 5.   Change of γ_{SV} and γ_{SV}^d with the vinyl alcohol content of the E-VOH copolymers.

rapid decrease of γ_{SV}^p with the application of EGDM swelling procedure may be due to the expenditure of more hydroxyl groups during crosslinking with this bifunctional monomer.

The measured densities and the calculated area fractions of the constituents of the copolymers used in Table IV are listed in Table X. The $(\rho_{PVA}, \rho_{PVOH}, \rho_{PE})$ values were calculated as 1.10, 0.75, 0.90, respectively, by the application of least-squares method to Eqs. (15) and (16). Then,
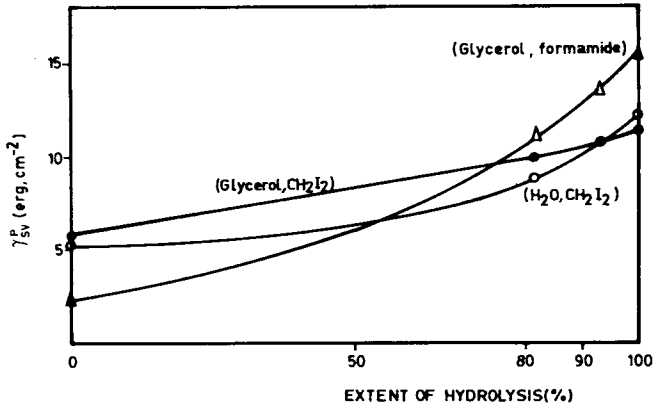
Fig. 6.   Change of γ_{SV}^p of the E-VA copolymer having 28 wt% VA content with the hydrolysis degree.
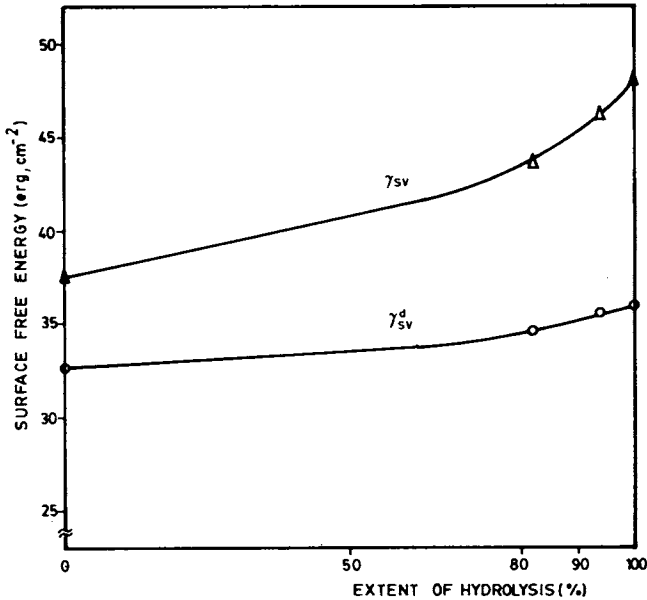

Fig. 7.   Change of γ_{SV} and γ_{SV}^d of the E-VA copolymer having 28 wt% VA content with the hydrolysis degree.

S_{VA}^{area}, S_{VOH}^{area}, S_{PE}^{area} values were calculated by using Eqs. (17)–(20). The change of $(\gamma_{SV}, \gamma_{SV}^d$ and $\gamma_{SV}^p)$ values of E-VA and E-VOH copolymers with $1 - S_{PE}^{area}$ values are shown in Figure 8. The curves deviates largely from the additivity law of γ_{SV}^d and γ_{SV}^p in regard to the surface area fractions such as:

$$\gamma_{SV}^{d,p} = S_{PVA, PVOH}^{area}\gamma_{PVA, PVOH}^{d,p} + S_{PE}^{area}\gamma_{PE}^{d,p} \qquad (21)$$

which $33.0, 36.0, 5.5, 18.5$ erg, cm^{-2} values used for $\gamma_{PVA}^d, \gamma_{PVOH}^d, \gamma_{PVA}^p, \gamma_{PVOH}^p$, respectively.

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TABLE X

Densities and Area Fractions of the Constituents of the Copolymers

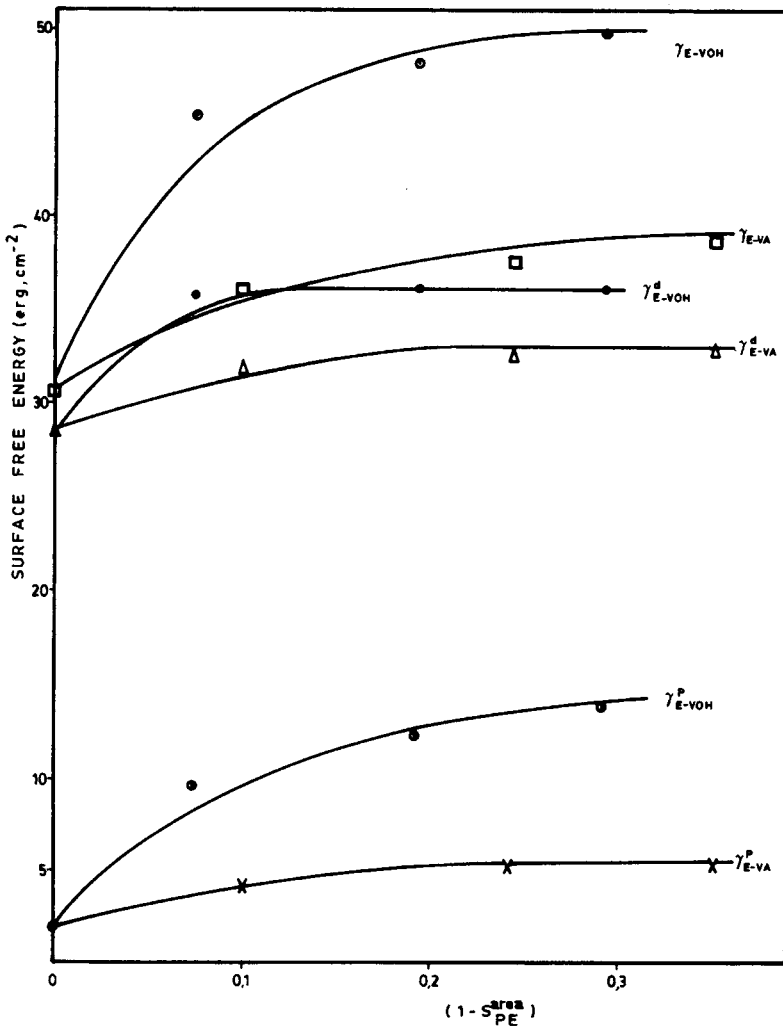| Polymer	ρ g, cm^{-3}	$W_{VA,VOH}$	S_{VA}	S_{VOH}	S_{PE}
PE	0.921	0	0	0	1
E-VA-12	0.917	0.120	0.100	—	0.900
E-VA-28	0.948	0.280	0.241	—	0.759
E-VA-40	0.967	0.400	0.352	—	0.648
E-VOH-12	0.882	0.065	—	0.076	0.924
E-VOH-28	0.873	0.166	—	0.193	0.807
E-VOH-40	0.861	0.254	—	0.292	0.708

Fig. 8. Change of γ_{SV}, γ_{SV}^{d} and γ_{SV}^{p} of E-VA and E-VOH copolymers with $1 - S_{PE}^{area}$.

The deviation of the additivity law may arise from two facts: (1) the assumption of the volume additivity of the copolymer constituents on the surface is inadequate and the bulk composition can not be expected to continue to the surface or (2) the interaction forces between ethylene and vinyl acetate, ethylene and vinyl alcohol groups should have definite additional contribution to γ_{SV}^d, γ_{SV}^p values.

CONCLUSIONS

The substitution of the acetate groups present in ethylene-vinyl acetate copolymer with the hydroxyl group by hydrolyzing the copolymer increases (γ_{SV}^p) of the product drastically as expected. The (γ_{SV}^d) values increase only slightly and reach a maximum of approximately 10 wt% VOH content. The hydrolysis degree is a measure of this substitution and may be used to estimate the surface-free energy components of the produced copolymer.

The surface hydrolysis of E-VA copolymers produces more hydrophilic and rigid surfaces having high γ_{SV}^p values, however it is difficult to control the degree of hydrolysis.

The cross-linking of E-VOH copolymers with dicumyl peroxide and ethylene dimethacrylate decreases γ_{SV}^d and γ_{SV}^p values due to the decrease of intermolecular dispersion and polar forces.

The determination of the experimentally verified values of γ_{LV}^d and γ_{LV}^p of the liquids used in contact-angle measurements is required for more accurate calculations of γ_{SV}^d and γ_{SV}^p of polymer surfaces enabling better understanding of the relation of surface free energy with the chemical structure of the polymer surface.

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