

Surface Free Energy Analysis of Ethylene-Vinyl Acetate Copolymers

TOSHIAKI MATSUNAGA* and YASUKATSU TAMAI, *Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira 2-1-1, Sendai 980, Japan*

Synopsis

Ethylene-vinyl acetate copolymers containing 4, 11, and 19 wt. % of vinyl acetate (VAc), polyethylene, and poly(vinyl acetate) were investigated by the two-liquid contact-angle method at 20°C. The dispersion force component of surface free energy γ_s^d increased drastically with the increase of VAc content, and deviated largely from the additivity law in regards of the surface area fractions of ethylene and VAc. On the other hand, the nondispersive (i.e., mainly due to hydrogen bonding) interaction free energy between solid and water I_{sw}^n increased linearly with the concentration of VAc on the surface.

INTRODUCTION

The analysis of the surface free energy of organic polymers by the two-liquid contact-angle method (the hydrocarbon-water-solid system) have been already reported.^{1,2} Recently, the correlation of the analytical results and the surface concentrations of functional groups has been indicated.³

As the extension of this proposition, ethylene-vinyl acetate random copolymers (PEVAc) are investigated, expecting to change regularly the surface concentrations of polar groups with the content of vinyl acetate in the bulk.

Although surface tensions of molten EVAc copolymers^{4,5} and of the solid PEVAc by the one-liquid contact-angle method (the air-liquid-solid system)⁶ have been already published, comparatively different results may be obtained from the two-liquid method as has been shown for other polymers.² As discussed there, the differences between these methods may be attributable to the neglect of the surface pressure of adsorbed film on the solid surface in the analysis of the one-liquid method.

EXPERIMENTAL

Three ethylene-vinyl acetate copolymers, containing 4, 11, and 19 wt % of vinyl acetate (VAc), polyethylene (PE), and poly(vinyl acetate) (PVAc) were investigated. PEVAc and PE are hot-pressed plates without additives, ca. 2 mm thick. PVAc samples are films of ca. 0.1 mm thickness which were formed on slide glass from 40% methanol solution and evacuated for 15 hr at maximum 50°C. The degree of polymerization of PVAc $\bar{M}_n = 1700$. Some properties of these polymers are listed in Table I.

Surface preparation has been done by the same method as reported.³ Mea-

* Present address: Department of Fuel Chemistry, Mining College, Akita University, Akita 010, Japan.

TABLE I
 Polymers and Their Properties

Polymer	VAc content (wt %)	Density (g/cm ³)	Melt index ^a (g/10 min)	Supplier
PE	0	0.93	—	Mitsubishi Petrochem. Co.
PEVAc (a)	4	0.90 ₉	0.3	Mitsui Polychem. Co.
(b)	11	0.92 ₇	1.3	
(c)	19	0.94 ₅	2.5	
PVAc	100	1.2	—	Kuraray Co.

^a 190°C, 2160 g loaded.

surement of contact angles has been carried out with a goniometer-telescope system at 20° ± 0.5°C in two combinations, cyclohexane(*c-hex*)-water-solid and isooctane(*i-oct*)-water-solid.

RESULTS AND DISCUSSIONS

The dispersion force components of surface free energies γ_S^d and the nondispersion interaction free energies between water and solid I_{SW}^n can be obtained from the contact angles of the two-liquid method as previously described.^{1,3} The contact angles of water drops in hydrocarbon and the analytical results are listed in Table II, under which the surface and interfacial tensions of liquids used are also shown. In Table II the nondispersive components of the surface free energy γ_S^s are also included, which were calculated on the basis of the geometrical mean law, assumed to be applicable even to the interaction energy between water and solid.

Except PE, the γ_S^d values here obtained seem to be larger than γ values from other methods, for example, 36.5 dyn/cm for PVAc at 20°C.⁷ There may be some reasons for this discrepancy, such as possible discontinuity between solid and molten polymers, or the neglect of surface pressure in the one-liquid method as discussed in the previous paper.² However, in this paper we will only consider the relation between the results of the two-liquid method and the composition of copolymers.

The relations of γ_S^d and I_{SW}^n values to the VAc contents in the bulk copolymers are indicated in Figure 1. The γ_S^d value increases drastically as the VAc content

 TABLE II
 Contact Angles and the Analytical Results

Polymer	Contact angles (deg) ^a		γ_S^d (erg/cm ²)	I_{SW}^n (erg/cm ²)	γ_S^s (erg/cm ²)
	<i>c-hex</i>	<i>i-oct</i>			
PE	172.8 ± 1.0	171.3 ± 1.0	29 ± 2	0.3 ± 0.2	0.00
PEVAc (a)	169.0 ± 0.5	158.9 ± 1.0	49 ± 4	1.5 ± 0.2	0.01
(b)	161.2 ± 1.0	151.8 ± 0.6	58 ± 5	3.6 ± 0.2	0.06
(c)	157.0 ± 0.5	147.2 ± 0.5	67 ± 6	5.1 ± 0.2	0.13
PVAc	109.7 ± 1.1	103.5 ± 1.0	77 ± 8	34.4 ± 0.4	5.9

^a $\gamma_{c-hex} = 25.0$, $\gamma_{c-hex/W} = 50.0$, $\gamma_W = 72.7$, $\gamma_{i-oct} = 18.9$, $\gamma_{i-oct/W} = 49.3$, $\gamma_W^d = 23.0$ erg/cm² at 20°C.

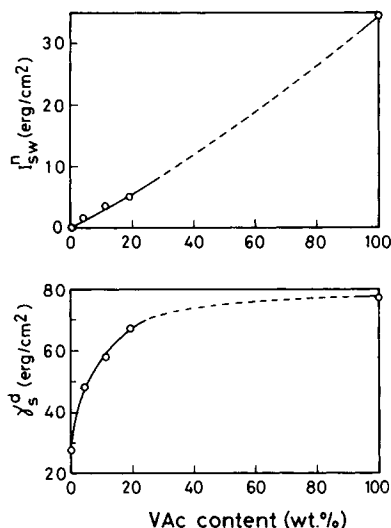


Fig. 1. γ_S^d and I_{SW}^n values of ethylene-vinyl acetate copolymers.

increases so that γ_S^d reaches almost that of PVAc at only 30 wt % of VAc. On the other hand, the I_{SW}^n value increases rather mildly with the increase of VAc content.

Since the knowledge about the composition of the real surface region, which is required to study the relation between surface energy and its structure in detail, is quite inadequate, the bulk composition was assumed as an approximation to continue to the surface. This assumption may be admitted in case of solids. Furthermore, these copolymers have various degrees of crystalline parts of PE. The crystallinities calculated according to the method of Kamath and Wakefield⁸ from x-ray diffraction diagrams shown in Figure 2 agree well with those from their equation

$$\chi(\%) = 63.0 - 1.47 \times (\text{VAc wt \%}) \quad (1)$$

However, since we do not know exactly the fractions of crystalline and amorphous parts on the surface, and additionally since the densities of PEVAc could be calculated from the reasonable density values of PVAc and PE on the basis of the assumption that the copolymer volume can be expressed as the sum of those of its constituents, ethylene and VAc parts, as shown in Appendix, the surface compositions were estimated as follows.

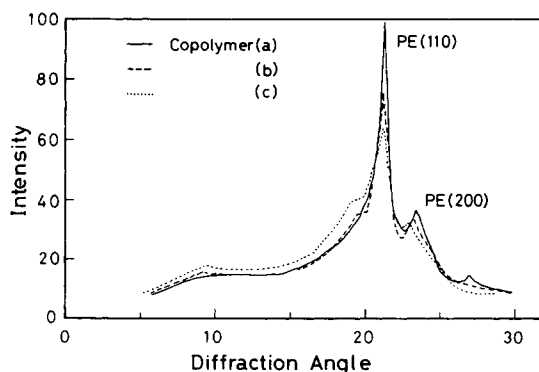


Fig. 2. X-Ray diffraction patterns of ethylene-vinyl acetate copolymers. ($\text{Cu } K\alpha$).

Since the area fraction of VAc on the surface S_A^{area} should be equal to the volume fraction in the bulk copolymer C_A^{vol} ,

$$S_A^{\text{area}} = C_A^{\text{vol}} = w_A \rho / \rho_A \quad (2)$$

where w_A is the weight fraction of VAc, ρ is the density of each copolymer, and ρ_A is that of VAc constituent which was verified to be equal to that of PVAc, as given in the Appendix. Then the surface area fraction of ethylene S_E^{area} is

$$S_E^{\text{area}} = 1 - S_A^{\text{area}} \quad (3)$$

Now, if the additivity law of γ_S^d in regard to the surface area fractions holds, γ_S^d will be

$$\gamma_S^d = S_A^{\text{area}} \gamma_A^d + S_E^{\text{area}} \gamma_E^d = S_A^{\text{area}} (\gamma_A^d - \gamma_E^d) + \gamma_E^d \quad (4)$$

where γ_A^d and γ_E^d are the γ^d values of PVAc and PE, respectively. However, the relation of γ_S^d values vs. S_A^{area} deviates largely from linearity, as seen in Figure 3.

When the degree of heterogeneity of surface is in the order of sufficiently larger ones than molecular dimensions, the additivity law will be valid as usually adopted.⁹ But when the degree of heterogeneity is in the order of molecules, as in this case, the additivity law should not be expected, because interaction forces between ethylene and VAc groups may not be neglected and must have some definite additional contribution to γ_S^d values.

In a previous paper,³ it has been proposed that I_{SW}^n values can be calculated by summation of hydrogen bonding contribution of each functional group to I_{SW}^n values, as

$$I_{SW}^n = \sum_x S(x) I_{SW}^n(x) \quad (5)$$

where $S(x)$ is the number of a functional group x on the unit surface area and $I_{SW}^n(x)$ is the contribution of each x .

If the cross area of the vinyl acetate monomer unit a_A is approximated as $a_A = (v_A)^{2/3}$, where v_A is the volume of the monomer unit, $S(\text{ester})$ can be obtained from eq. (2):

$$S(\text{ester}) = S_A^{\text{area}} / a_A = w_A \rho / a_A \rho_A \quad (6)$$

$S(\text{ester})$ values are listed in Table III, and $I_{SW, \text{obs}}^n$ values are plotted vs. $S(\text{ester})$ in Figure 4. Including PVAc a rather good linear relation was obtained. From this line, an average $I_{SW}^n(x)$ value for the ester group is calculated as 8.4×10^{-14} erg/group. The previously reported value $I_{SW}^n(\text{ester}) = 4.5 \times 10^{-14}$ erg/group

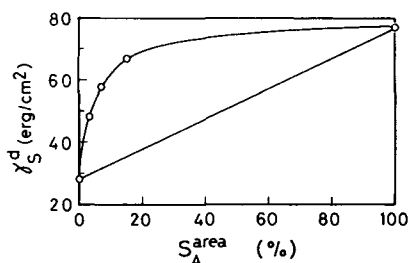


Fig. 3. Change of γ_S^d with the area fractions of vinyl acetate on the surface, S_A^{area} .

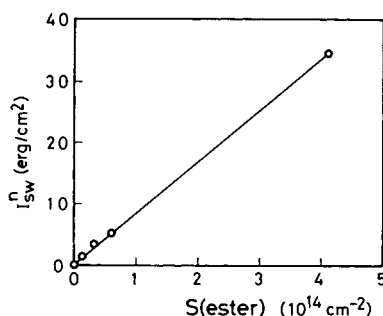


Fig. 4. Correlation of I_{SW}^n with the surface concentration of ester groups, $S(\text{ester})$.

TABLE III
Calculated Values of Surface Concentrations of Vinyl Acetate Groups^a

Polymer	$S_A^{\text{area}} = C_A^{\text{vol}}$	$S(\text{VAc})$ (10^{14} cm^{-2})
PEVAc (a)	0.031	0.13
(b)	0.068	0.28
(c)	0.151	0.62
PVAc	1.000	4.1

^a $\rho_A = 1.20 \text{ g/cm}^3$, $a_A = 2.4 \times 10^{-15} \text{ cm}^2$.

was applicable to polycarbonate or polyester,³ in which ester groups are contained in the polymer chains. On the other hand, since ester groups of PVAc are in side chains and are estimated to be more movable and more freely interactable with water molecules, $I_{SW}^n(\text{ester})$ may well be a larger value. This interpretation may be verified, when we consider that the agreement of I_{SW}^n between the observed 27.6 erg/cm² for poly(methylmethacrylate) (PMMA) and its calculated 31.1 erg/cm² with 8.4×10^{-14} erg/group as the value of $I_{SW}^n(\text{ester})$ is much better than previously reported,³ where the value of $I_{SW}^n(\text{ester})$ 4.5×10^{-14} erg/group was adopted even for PMMA which has its ester groups in side chains.

Appendix

On the assumption that the volume of the copolymer can be expressed as the sum of those of its constituents, ethylene and VAc, the density of copolymer is given as

$$\frac{1}{\rho} = \frac{w_A}{\rho_A} + \frac{1-w_A}{\rho_E} = \left(\frac{1}{\rho_A} - \frac{1}{\rho_E} \right) w_A + \frac{1}{\rho_E} \quad (7)$$

With the values of ρ and w_A for three copolymers indicated in Table I, and by application of the method of least squares, the values of ρ_A and ρ_E were obtained as 1.20 and 0.90, respectively. The densities of copolymers calculated from these ρ_A and ρ_E values agree very well with the observed ones: copolymer (a) $\rho_{\text{calc.}} = 0.909$ (0.90₉), (b) $\rho_{\text{calc.}} = 0.925$ (0.92₇), (c) $\rho_{\text{calc.}} = 0.945$ (0.94₅) g/cm³ (the values in parentheses are the observed ones). Moreover, $\rho_A = 1.20$ agrees with the reported value 1.19 g/cm³ at 25°C* and $\rho_E = 0.90$ is within the limits of 1.00 for crystalline PE and 0.84 g/cm³ for amorphous PE.*

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* *Encyclopedia of Polymer Science and Technology*, Interscience, New York, 1968, Vol. 9, p. 404; and *ibid.* 1971, Vol. 15, p. 618.

References

1. Y. Tamai, K. Makuuchi, and M. Suzuki, *J. Phys. Chem.*, **71**, 4176 (1967).
2. Y. Tamai, T. Matsunaga, and K. Horiuchi, *J. Colloid Interface Sci.*, **60**, 112 (1977).
3. T. Matsunaga, *J. Appl. Polym. Sci.*, **21**, 2847 (1977).
4. R. J. Roe, *J. Colloid Interface Sci.*, **31**, 228 (1969).
5. T. Nose, *Polym. J.*, **3**, 196 (1972).
6. T. Matsumoto, K. Nakamae, Y. Nakano, and K. Nonaka, *Sen-i Gakkaishi*, **30**, T559 (1974).
7. S. Wu, *J. Macromol. Sci., Rev. Macromol. Chem.*, **10**, 1 (1974).
8. P. M. Kamath and R. W. Wakefield, *J. Appl. Polym. Sci.*, **9**, 3153 (1965).
9. R. E. Johnson, Jr. and R. Dettre, in *Surface and Colloid Science*, Vol. 2, E. Matijejevic, Ed., Wiley-Interscience, New York, 1969, p. 85.

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