Surface free energy of poly(vinyl alcohol) modified with alkyl groups

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The dispersive component of surface free energy $\gamma_S{}^d$ and the nondispersive interactions with polar liquids I_{SW} were determined for poly(vinyl alcohol) (PVA) copolymers having various types of alkyl groups, i.e., four kinds of partly alkyl acetalized PVA's (AlPVA), butyl vinyl ether – vinyl alcohol copolymers (BuVA), ethylene – vinyl alcohol copolymers (EtVA) and BuPVA–PVA mixtures. $\gamma_S{}^d$ and I_{SW} were estimated from the measurements of contact angles by means of a two-liquid method proposed by Matsunaga and Ikada. $\gamma_S{}^d$ and I_{SW} for AlPVA, which were smaller than those for PVA itself, decreased with increases in either content or chain-length of the alkyl side group, while $\gamma_S{}^d$ for EtVA was virtually independent of ethylene content. The dependences of $\gamma_S{}^d$ and I_{SW} on the alkyl side chain content per vinyl repeating unit for BuPVA were smaller than those for BuVA. The result for the polymer blends of PVA and BuPVA showed that both $\gamma_S{}^d$ and I_{SW} fell rapidly even at very small addition of BuPVA. The surface free energy γ_S $(=\gamma_S{}^d+\gamma_S{}^d)$ was found to decrease with increasing alkyl group content except for EtVA.

(Keywords: surface free energy; contact angle; poly(vinyl alcohol) copolymer; hydrophobic group)

INTRODUCTION

Various properties of poly(vinyl alcohol) (PVA) modified with hydrophobic groups have been extensively studied because of their amphiphilic character[1]. Aqueous solution behaviour such as phase separation, viscosity and surface tension have been studied in particular[2]. Surface tension[3] and phase separation[4] for aqueous solutions of PVA having a series of pendant alkyl groups have also been reported previously. However, few systematic studies have been undertaken to estimate surface free energy of such polymer films[5,6]. However, PVA polymers with hydrophobic groups are interesting in application to biomaterials because of their biocompatibility[7]. Recently, the biocompatibility of polymeric materials has been discussed in relation to the surface free energy[8].

It is interesting, therefore, to estimate the surface free energy of the PVA copolymers with both hydrophobic and hydrophilic groups. In this paper, we present the study on the surface free energy of PVA's modified with various alkyl groups. The surface free energy is estimated from contact angles by means of a two-liquid method proposed by Matsunaga and Ikada[9]. The dependences of the dispersive surface free energy and of the non-dispersive interaction on the content and chain-length of the introduced alkyl group are presented. Also, the effect of the bond of alkyl group onto PVA is discussed in relation to the surface free energy of butyralized PVA, butyl vinyl ether–vinyl alcohol copolymer and ethylene–vinyl alcohol copolymer.

EXPERIMENTAL

Materials

Partly n-alkyl acetalized PVA's, i.e. butyralized PVA (BuPVA), octyl acetalized PVA(OcPVA) and lauryl acetalized PVA (LaPVA), were prepared by the reaction of n-alkyl bromide with PVA in dimethyl sulphoxide containing pyridine. The PVA used, PVA-117H, whose degree of polymerization was 1700, was supplied by Kuraray Co. Detailed procedures of synthesis and purification have been described elsewhere[10]. The degree of acetalization x_R was determined from the measurement of the alkali-saponification value for reacetylated acetalized PVA. n-Butyl vinyl ether–vinyl alcohol copolymers (BuVA) were prepared by bulk copolymerization of butyl vinyl ether and vinyl acetate at 50°C, followed by the complete saponification of this polymer. The copolymer composition was calculated from the compositions of the monomer feed and from the monomer reactivity ratios[11]. Ethylene–vinyl alcohol copolymers (EtVA) with 9, 19, 33 and 44 mol% (ethylene content) were supplied by Kurarary Co. and purified by Soxhlet extraction method with methanol.

Contact-angle measurement

Polymer films used for contact angle measurement were prepared by spreading ~10 wt% dimethyl sulphoxide solution on a glass plate, followed by drying under vacuum at 40°C for three days and then at 80°C for two days. The air-side surface was used for the contact-angle measurement.

The contact angle was measured at 25° ± 0.1°C by means of the two-liquid method with a contact angle meter CA-A manufactured by Kyowa Kagaku Co. A polymer film was immersed in a liquid H and kept at a constant temperature. A droplet of a liquid W was introduced onto the film by a needle attached to a syringe. The advancing contact angles on the right and left sides of the droplet were measured for at least five different spots on the same film, and the values were averaged. n-Hexane,

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cyclohexane, n-heptane, n-octane and isooctane were used as a liquid H. As a liquid W, ethylene glycol was used for all samples and formamide was also used in the cases of PVA and BuPVA. These testing liquids were purified by conventional distillation.

RESULTS AND DISCUSSION

According to the two-liquid method proposed by Matsunaga and Ikada[9], we can obtain the following relation between the dispersive-force component of the surface free energy γ_S^d of a solid S and the contact angle θ_{SW} of a droplet of the liquid W on the solid S under the liquid H:

$$\gamma_W-\gamma_H+\gamma_{WH}\cos\theta_{SW}=2[(\gamma_W^d)^{1/2}-(\gamma_H)^{1/2}](\gamma_S^d)^{1/2}+I_{SW}+\pi_e \tag{1}$$

where γ_W and γ_H are the surface free energies of the liquids W and H, respectively, γ_{WH} is the interfacial free energy between the liquids W and H, I_{SW} is related to all the nondispersive interactions between the solid S and the liquid W and π_e is the surface spreading pressure. On the approximation that π_e can be neglected, measuring the contact angles of the liquid W under several liquids H such as saturated hydrocarbons (whose surface free energy is assumed to be $\gamma_H=\gamma_H^d$), $(\gamma_S^d)^{1/2}$ and I_{SW} can be obtained from the plot of $Y=\gamma_W-\gamma_H+\gamma_{WH}\cos\theta_{WH}$ against $X=2[(\gamma_W^d)^{1/2}-(\gamma_H)^{1/2}]$, as intercept and slope, respectively, of the resulting straight line.

The observed contact angles are listed in the Appendix. Examples of the *X–Y* plot for a series of BuPVA are presented in *Figure 1*. In this study, the values of γ_W, γ_W^d, γ_H and γ_{WH} for the testing liquids were cited from the work of Matsunaga and Ikada[9]. The values of γ_S^d and I_{SW} obtained from such *X–Y* plots are summarized in the third and fourth columns of *Table 1*, respectively.

The values obtained for PVA were in fair agreement with the reported values[9] ($\gamma_S^d=29$ erg.cm^{-2}, $I_{SW}=28$ erg.cm^{-2} by ethylene glycol; $\gamma_S^d=29$ erg.cm^{-2}, $I_{SW}=37$ erg.cm^{-2} by formamide). Also, the values of γ_S^d determined by use of ethylene glycol and by formamide for a series of BuPVA agree well, though I_{SW} is affected by the liquid W as pointed out by Matsunaga and Ikada[9].

Figure 2 shows the dependence of γ_S^d on the nature and the content of the alkyl group for the alkyl acetalized PVA. The value of γ_S^d for the longer side chain is smaller.

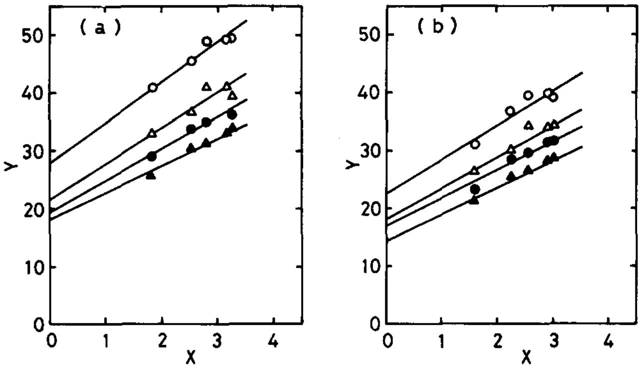

Figure 1 *X–Y* plot for a series of BuPVA: (○), BuPVA-1; (△), BuPVA-2; (●), BuPVA-3; (▲), BuPVA-4. (a) formamide in alkanes, and (b) ethylene glycol in alkanes

Table I Components of surface free energy*

Sample†	x_R (mol%)‡	γ_S^d	I_{SW}	γ_S^p	γ_S
PVA	–	32	27	11.9	44
		(34)	(34)	(12.6)	(46)
BuPVA-1	12.8	28	22	8.3	36
		(29)	(32)	(10.7)	(40)
BuPVA-2	19.3	27	18	5.6	33
		(28)	(24)	(6.2)	(34)
BuPVA-3	30.8	24	17	4.7	17
		(26)	(20)	(4.4)	(30)
BuPVA-4	36.1	23	14	3.3	26
		(26)	(17)	(3.0)	(29)
OcPVA-1	14.9	24	8.9	1.3	25
OcPVA-2	23.4	20	8.5	1.2	21
OcPVA-3	32.7	18	7.0	0.8	18
LaPVA-1	13.6	16	7.0	0.8	17
LaPVA-2	22.1	14	6.5	0.7	15
LaPVA-3	31.1	14	6.0	0.6	14
BuVA-1 (P=2100)	4.0	27	24	9.1	36
BuVA-2 (P=550)	10.0	21	18	5.2	26
EtVA-1 (P=1200)	9	29	13	2.7	32
EtVA-2 (P=1100)	19	28	19	5.8	34
EtVA-3 (P=1200)	33	30	23	9.1	39
EtVA-4 (P=960)	44	30	18	5.3	36
Mixture-1	0.5	27	22	7.7	35
Mixture-2	1.0	22	17	4.6	27
Mixture-3	5.0	23	11	2.1	25
Mixture-4	10.0	23	11	2.1	25

*Units in erg. cm^{-2}. Values in parentheses were obtained by using formamide as a liquid W

†The degrees of polymerization for PVA and alkyl acetalized PVA's are 1700, and those for BuVA and EtVA series are shown in parentheses

‡Values for mixtures are the content (wt%) of BuPVA with x_R = 18.1 mol%

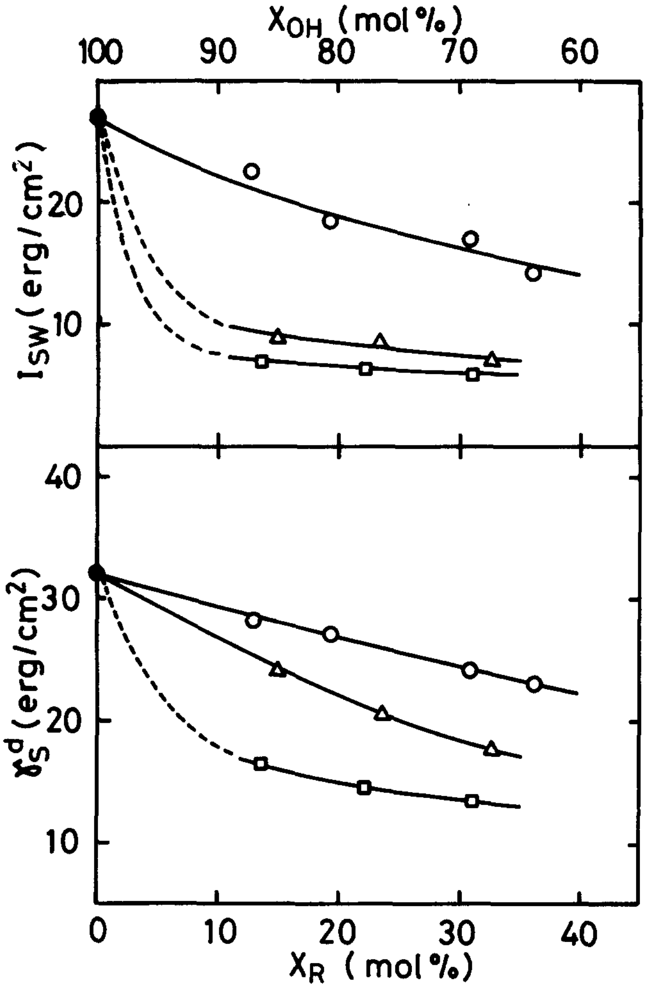

Figure 2 The dependence of $\gamma_S{}^d$ and I_{SW} on the degree of acetalization for alkyl acetalized PVA's: (●), PVA; (○), BuPVA; (△), OcPVA; (□), LaPVA

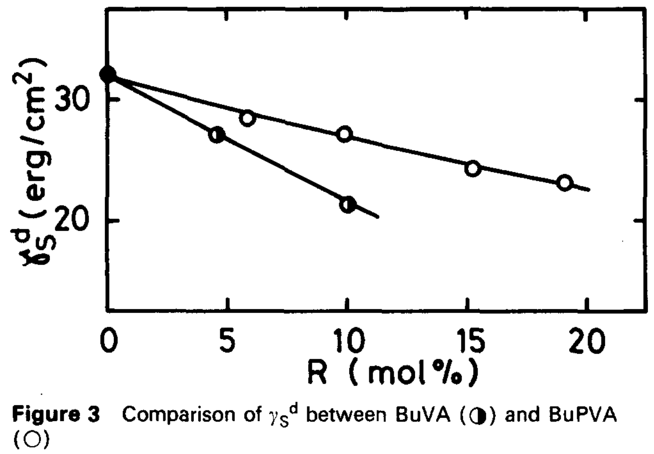

Figure 3 Comparison of $\gamma_S{}^d$ between BuVA (◑) and BuPVA (○)

Also, γ_S^d decreases with increasing substitution degree x_R despite a decrease in the hydroxyl-group content. These may be due to the following reason: the surface entropy increases with the uptake of the pendant alkyl-group on the film surface and with the distortion of regular arrangement of crystalline PVA molecules by the side chain. Their influence on the surface entropy is larger for the larger content and the longer side chain of the alkyl group. Ko *et al.*[5] also reported the similar result that γ_S^d decreased with decreasing the hydrophilic-group content for 2-hydroxyethyl methacrylate/ethyl methacrylate grafted polyethylene films.

In *Figure 2* are also shown the dependences of I_{SW} on x_R. I_{SW} decreases with increasing alkyl-group content, i.e. decreasing OH-group content. I_{SW} decreases more rapidly for OcPVA and LaPVA than for BuPVA, because the OH groups on the surface are concealed behind the long side-chain of the formers.

In *Figures 3* and *4*, the dependences of γ_S^d and I_{SW} on the alkyl-group content R per vinyl repeating unit for BuVA are compared with those for BuPVA. Both γ_S^d and I_{SW} appear more sensitive for BuVA than for BuPVA. This is attributed to the flexibilities of the side chain of BuVA and BuPVA. The former is bonded by the ether bond and the latter by the ring structure of the acetal bond. The more flexible side chain of BuVA has the greater ability to increase the surface entropy and to conceal the OH groups.

As mentioned above, alkyl side groups have a significant influence on γ_S^d and I_{SW} of the polymer surface. Such effects of the alkyl group were reported for the surface tension of the aqueous solutions of the same PVA copolymers[3].

Figure 5 shows γ_S^d and I_{SW} for EtVA. γ_S^d is not dependent on the ethylene content, compared to that for the PVA copolymers with the alkyl side chain. This tendency of γ_S^d may be due to the absence of the hydrophobic side chain

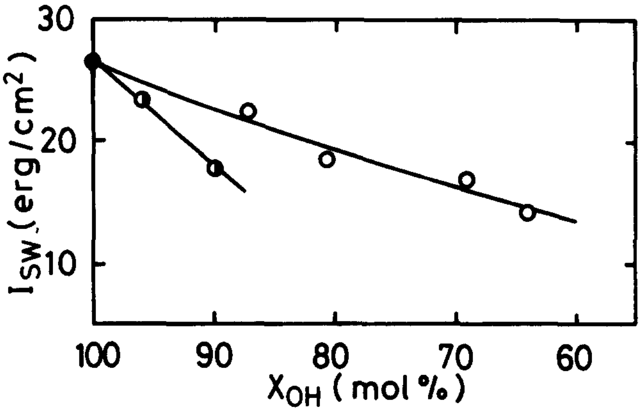

Figure 4 Comparison of I_{SW} between BuVA (◑) and BuPVA (○)

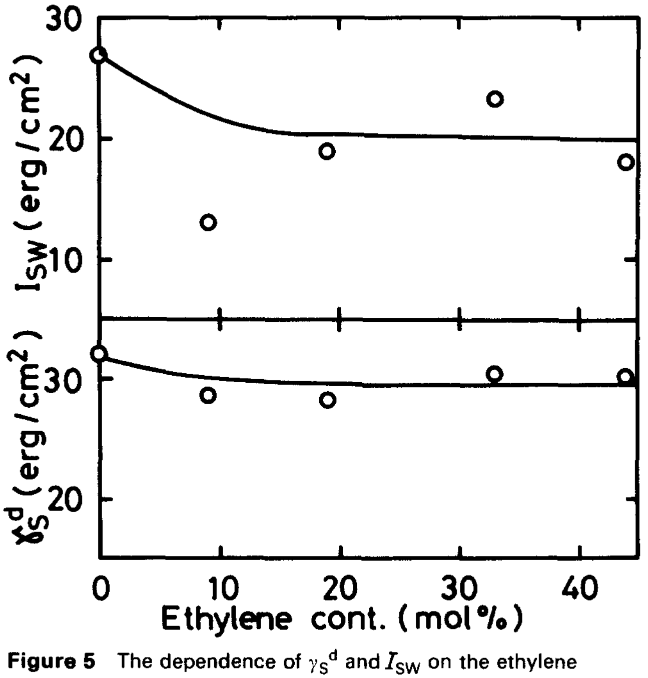

Figure 5 The dependence of $\gamma_S{}^d$ and I_{SW} on the ethylene content

and to the crystalline nature of both PVA and polyethylene.

Figure 6 presents γ_S^d and I_{SW} for the mixtures of PVA and BuPVA with $x_R = 18.1$ mol%. It should be noted that both γ_S^d and I_{SW} fall rapidly and come close to the values for pure BuPVA at the very small content of BuPVA. This reflects the result that the BuPVA molecules with the hydrophobic groups are selectively concentrated on the air-side surface in the course of preparation of the film.

I_{SW} in equation (1) has often been assumed to be expressed by the following equation and used to estimate the polar component γ_S^p of the surface free energy:

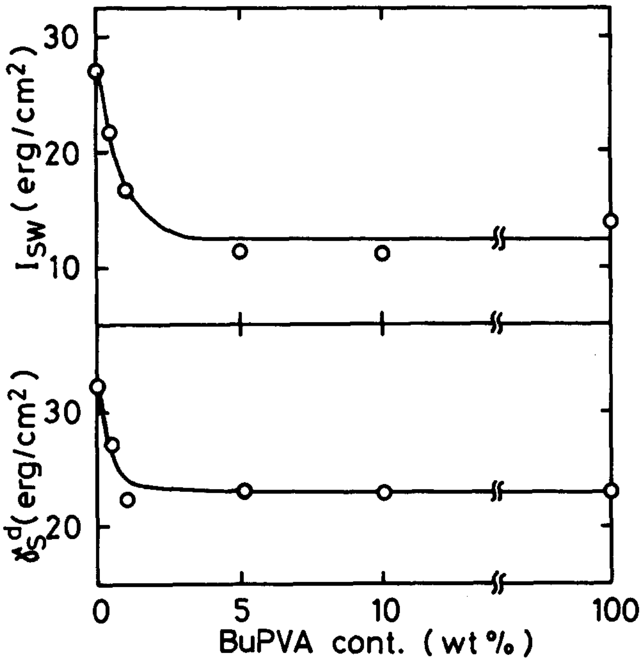

Figure 6 The dependence of $\gamma_S{}^d$ and I_{SW} on the content of BuPVA for the PVA–BuPVA mixtures

$$I_{SW} = 2(\gamma_S^p \cdot \gamma_W^p)^{1/2} \qquad (2)$$

where γ_W^p is the polar component of the surface free energy of the liquid W. This equation was tentatively applied to the present systems to estimate γ_S^p and $\gamma_S (= \gamma_S^d + \gamma_S^p)$, nevertheless equation (2) does not always hold for systems containing hydrogen bonds[9,12]. The obtained values are summarized in the fifth and sixth columns of *Table 1*, respectively. γ_S's for all samples except EtVA decrease by introducing the alkyl groups to PVA.

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APPENDIX

The observed contact angles are as follows:

Table 2 Contact angles* of ethylene glycol (formamide)† under alkane

Sample	n-hex	c-hex	n-hep	n-oct	iso-oct
PVA	48.8	52.6	43.2	42.2	41.0
	(58.6)	(62.8)	(58.9)	(56.6)	(55.4)
BuPVA-1	56.0	60.6	48.4	54.0	53.6
	(68.8)	(72.8)	(65.4)	(70.6)	(67.8)
BuPVA-2	74.6	78.8	67.4	78.4	75.2
	(91.8)	(90.6)	(83.2)	(90.0)	(86.8)
BuPVA-3	84.4	91.0	84.8	84.0	83.8
	(98.4)	(100.4)	(96.8)	(96.6)	(–)
BuPVA-4	94.4	98.1	95.2	94.4	94.4
	(103.0)	(110.0)	(105.6)	(103.8)	(104.0)
OcPVA-1	112.4	111.4	95.4	111.8	111.0
OcPVA-2	123.1	129.6	125.4	123.7	124.4
OcPVA-3	129.0	131.3	129.4	–	–
LaPVA-1	127.4	131.0	128.8	130.2	128.4
LaPVA-2	132.8	137.2	135.4	135.0	135.8
LaPVA-3	136.0	139.8	136.3	–	–
BuVA-1	57.6	64.0	57.8	58.9	57.0
BuVA-2	80.5	85.5	81.2	79.5	79.4
EtVA-1	84.9	93.6	92.6	86.8	83.8
EtVA-2	75.5	76.8	76.2	75.4	74.7
EtVA-3	50.2	54.2	62.4	53.6	49.4
EtVA-4	79.9	78.8	71.2	76.8	77.7
Mixture-1	66.8	74.8	66.6	63.0	60.4
Mixture-2	90.4	82.2	83.2	86.4	93.0
Mixture-3	104.3	110.3	102.2	104.3	102.2
Mixture-4	105.5	110.2	103.3	105.6	103.4

*Units in degrees
†Values in parentheses