

A New Approach to Chemical Characterization of Polymer Surfaces

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SYNOPSIS

The "three-liquid" contact angle procedure of Good et al. was applied to polymer films of varying Lewis acidic and basic nature to test the procedure. Surface energy parameters with the units of mJ/m² are determined for the surfaces. These are γ_s^{LW} (Lifshitz-van der Waals or apolar), γ_s^+ (acidic), and γ_s^- (basic). Very little has yet been published on this new method, and this study found it to be promising. More research on the procedure is warranted. The study included films of basic polymethylmethacrylate (PMMA), and predominately acidic chlorinated polyvinylchloride (CPVC) and polyvinylfluoride (PVF) as well as the series: polyethylene (PE) and PE copolymerized with 1.8% and 7.0% acrylic acid. In some of the experiments receding contact angles were measured, and the surface energy parameters determined in order to cast more light on the mechanism of contact angle hysteresis. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

This article deals with a procedure for quantifying the acidic and basic nature of polymer surfaces which is a relatively new extension of the research and thinking in the field. The approach has been put forward by R. J. Good and collaborators, notably M. K. Chaudhury and C. J. van Oss.¹⁻³ A brief introduction is offered here, but the reader should consult the references for fuller understanding.

Most solid polymers have Lewis acidic and basic sites on their surfaces that are capable of forming complexes with a second phase with which they are in contact. Bond energies are relatively low compared to intramolecular bonds. The term Lewis acid/base is used here in a broad sense where an acid is an electron acceptor or proton donor, as in hydrogen bonding, and a base is an electron donor or proton acceptor. Contact angles of at least three liquids, one apolar and two polar, having known Lewis acidity and basicity are measured. Calculations then reveal the opposite or complementary acid, base, and

apolar nature of the surface. Thus, the new approach is called the "three-liquid procedure."

The present state of thinking that will be applied here is that there are two separate and additive attractive forces operating across an interface. These are the dispersion forces (van der Waals, London, Lifshitz) and acid-base forces. We will use the Good et al. symbol, LW, (apolar) for the first, and AB for the latter. The LW attractive force is primarily due to fluctuating dipoles and the opposite ones induced by them in adjacent molecules (dispersion). However, included in this term are lesser interactions where one or both molecules has a permanent dipole.¹ The dispersion force is universal, relatively long range, and the most important of the LW forces in condensed media.^{4,5} Thus, the work of adhesion of a liquid (L) on a solid (S) is:

$$W_{SL} = W_{SL}^{LW} + W_{SL}^{AB}, \quad (1)$$

where

$$W_{SL} = -\Delta G_{SL}$$

and from the Young-Dupr e relationships⁶ relating W_{SL} to surface tensions (γ),

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$$W_{SL} = \gamma_s - \pi_{sv} + \gamma_L - \gamma_{SL} = \gamma_L(1 + \cos \theta) \quad (2)$$

Equation (2), as used below, assumes the spreading pressure (π_{sv}) is negligible.

The Good-Girifalco-Fowkes combining rule for the LW force between molecules, say across an interface is a geometric mean:

$$W_{SL}^{LW} = 2(\gamma_s^{LW}\gamma_L^{LW})^{1/2} \quad (3)$$

or

$$(W_{SL}^{LW})^2 = 4\gamma_s^{LW}\gamma_L^{LW} = (\gamma_L^{LW}(1 + \cos \theta))^2 \quad (4)$$

Equation (4) is useful in that the γ_s^{LW} of a polymer surface can be assessed by measuring the contact angle of a liquid that has only LW interactions (no acid base) and whose γ_L^{LW} is known. In the work reported below, apolar diiodomethane is used for this purpose.

The new procedure uses a combining rule for the AB interaction that is not a geometric mean. (A "polar" geometric mean combining rule: $W_{SL}^p = 2(\gamma_s^p\gamma_L^p)^{1/2}$ has been used by many workers but is not correct.⁸ However, in certain limited cases, it has found empirical use in spite of its lack of specificity.)

$$W_{SL}^{AB} = -\Delta G_{SL}^{AB} = 2(\gamma_s^+\gamma_L^-)^{1/2} + 2(\gamma_s^-\gamma_L^+)^{1/2} \quad (5)$$

A nongeometric form of a similar equation for H-bonding was proposed in 1953 by Small.⁷ When combined with eqs. (1) and (2), the overall combining rule of both apolar and acid-base interfacial forces is:

$$\begin{aligned} W_{SL}^{Total} &= \gamma_L^{Total}(1 + \cos \theta) \\ &= 2[(\gamma_s^{LW}\gamma_L^{LW})^{1/2} + (\gamma_s^+\gamma_L^-)^{1/2} \\ &\quad + (\gamma_s^-\gamma_L^+)^{1/2}] \end{aligned} \quad (6)$$

We seek to determine γ_s^{LW} , γ_s^+ , and γ_s^- , and first, γ_s^{LW} is evaluated using liquid #1 (apolar) and eq. (4). Because two unknowns remain, eq. (6) is used for liquids #2 and #3 and solved simultaneously. The γ_L^+ and γ_L^- for a series of liquids that can serve as #2 and #3 were established by assuming for water $\gamma_w^+ = \gamma_w^- = 25.5 \text{ mJ/m}^2$ ($\gamma_w^{AB} = 51.0 \text{ mJ/m}^2$). The contact angles of this series of polar liquids were measured on monopolar solids (having only γ_s^+ or γ_s^-) along with water and eq. (6) applied to determine γ_L^+ and γ_L^- for each liquid. In this procedure, the surface parameters for the solid cancel out.^{10,11}

We agree with Good et al. that water should be included as one of the polar liquids. Indeed, using three or more polar liquids allows for the determination of two or more values each for γ_s^+ and γ_s^- . These can be averaged, but see ref. 2, page 1292-93, for precautions to be taken.

The reader should consult the comments of Berg⁹ on the role of acid-base interactions in wetting, especially pp. 131-133. Here, he points out the need for checking the internal consistency of the method. We are presently involved in improving the internal consistency of the method and plan to measure the enthalpy of interaction of the polar liquids with the polymers reported below.

MATERIALS AND PROCEDURES

Flat polymer films were prepared using polymethylmethacrylate, PMMA (Plexiglas V-100, $\overline{M}_n \sim 110,000$, polydispersity 1.65, Rohm and Haas); chlorinated polyvinylchloride, CPVC (623 \times 563, 67% chlorine, $\overline{M}_n \sim 122,000$, polydispersity 1.53, B. F. Goodrich); and polyvinyl fluoride, PVF (Tedlar type 30, untreated, transparent, \overline{M}_n known, DuPont). The PMMA and CPVC were cast onto glass slides from purified toluene and tetrahydrofuran, respectively, and dried thoroughly. The CPVC was washed with methanol. The clear PVF film was used as received after cleaning with methanol and acetone. The Tedlar film is processed with dimethylacetamide, and residual amounts of this solvent are present in the film.

The earlier work done in this laboratory by Maruchi and Fowkes¹² used films dip coated onto polished and cleaned silicon disks from solution in boiling xylene that had been purified by passage through silica and alumina columns. The polymers were polyethylene, PE (LK-30, Mitsubish-Yuka) and ethylene-acrylic acid copolymers, EAC-1.8 and EAC-7.0 (Dexon XEA-6, 1.8% acrylic acid, and XEA-7, 7.0% acrylic acid, Exxon). These polymers were purified by dissolving (2%) in purified decahydronaphthalene at 100°C, passing through silica (100°C) and precipitating in pure methanol, washing with hot methanol, and drying under vacuum (7 days).

Contact angles of pure liquids on PMMA, CPVC, and PVF were measured at 23°C using an automated goniometer (Connelly Applied Research, Nazareth, PA). This device introduces, or withdraws, the liquid with a computer-controlled syringe pump, stores video images from the long-range microscope, and determines the advancing, or receding, contact angle

using a subpixel interpolation method. Data is stored and calculations made in a spread sheet. A number of math procedures to determine the contact angle from the profile of the drop were tested to find one that was consistent with the manual goniometer (Ramé–Hart). Also, known shapes were used for calibration. A given sessile drop was advanced four to seven times, and the angle measured on both sides after each (θ_a). Liquid was pumped in at 1.0 $\mu\text{L/s}$ until an advance was detected optically from the ~ 5 mm diameter original drop, or subsequent enlarged diameters. Images were stored just before the liquid advanced to its new diameter and 60 s later. The latter “advanced” data are averaged for the drop and for two or three other drops on different locations of the given surface. For each drop the first receded angle (θ_r) averages were used because subsequent ones tended to decline in value. The lowering angles may be due to lengthening contact time. However, the contact time for the first recede, drop to drop, was essentially constant.

The liquids used were diiodomethane (99% Aldrich) purified through an alumina column and stored over copper turnings in the dark, distilled water, glycerol (99% Aldrich), ethylene glycol (certified, Fisher) and formamide (98%, Aldrich) used as received.

Contact angles on the PE, EAC-1.8, and EAC-7.0 films were measured at 20°C with a Ramé–Hart goniometer. Only advancing angles were measured. The liquids were diiodomethane as above, distilled water, 0.1 N NaOH in water, and dimethylsulfoxide (certified ACS, Fisher) purified through an alumina column and distilled. Drops of 10 μL were measured after 1 min for three or more drops per surface. The angle remained essentially constant even up to 1 day.

RESULTS AND DISCUSSION

The results will be presented in two sections: first, the newer experiments wherein the automated goniometer was used and, second, the older ones using the manual goniometer. In both cases, surfaces varying in acidity and basicity were assessed with the three-liquid procedure of van Oss et al.¹

AUTOMATED GONIOMETER

Table I lists the average θ_a and θ_r for the PMMA, CPVC, and PVF surfaces. Table II gives the values of the three surface energy parameters γ_s^{LW} , γ_s^+ (acidity), and γ_s^- (basicity) for the polymer surfaces calculated from Table I angles.

We note that when advancing angles are used, PMMA is the most basic of the polymers and has no acidity, as expected. Again, as expected, CPVC and PVF exhibit acidity, but both have a slight degree of basicity. These low values of γ_s^- for CPVC and PVF are possibly due to the weak basicity of the halogen atoms or to a slight diffusion of the basic solvents from the bulk to the surface of the CPVC and PVF films. In any event, both the acid parameter, γ_s^+ , and the basic one, γ_s^- are relatively low. These results are consistent with data reported by Good and van Oss.¹ These authors give values for PMMA cast film of $\gamma^+ = 0$ and $\gamma^- = 9.5$ to 22.4 mJ/m² and poly(vinylchloride) $\gamma_s^+ = 0.04$, $\gamma_s^- = 3.5$ mJ/m². Thus, these polymer surfaces are relatively inactive chemically.

To illustrate, the low activity of the PVF surface was increased by plasma treatment in helium. The results, using θ_a of diiodomethane, water, and formamide are given in Table III. θ_r was not measured. Note that the corona treatment had little effect on the surface energy parameters. ESCA showed that the plasma treatment was far more oxidative than corona. It may also have been less prone to surface reconstruction upon storage.

The γ_s^{LW} values, using advancing angles, in Tables II and III fall into the same 35–45 mJ/m² range as a varied group of polymers reported in ref. 2. Reference 2 reports values for coal (a polymer) in this range. Indeed, 13 coals gave about the same γ_s^{LW} (39 mJ/m²), despite variations in oxygen and ash content. In this laboratory γ_s^{LW} for a series of pigmented inks ranged from 27 to 40 mJ/m², based on θ_a . Thus, this surface energy of polymers, which is based on long-range forces, seems to vary very little over a wide range of polymer types.

In Table I we see that the receding angle, θ_r , is always lower than the advancing one, θ_a , i.e., there is hysteresis. Thus, using θ_r for diiodomethane, for example, results in higher values of γ_s^{LW} than when θ_a is used. Because acid–base interactions are negligible with this liquid (although not for the polymers), we can develop a model in which the surface retains a film of the receding diiodomethane. This gives the “solid + liquid film” a higher surface energy, γ_s^{LW} , than for the solid alone, consistent with the finding that cohesive LW forces exceed interfacial LW forces. The reason for this hysteresis is generally thought to be heterogeneity of the surface, either roughness or chemical patchiness, which leads to metastable states at the solid–liquid–vapor three-phase line. Differentiation between these two types of heterogeneity is difficult at best, and will not be dealt with here. See Johnson and Dettre’s discussion

Table I Contact Angles (°) for Various Liquids on Polymers

	CH ₂ I ₂	Water	Glycerol	Ethylene Glycol	Formamide
	θ_a				
PMMA	48.9	75.8	73.0	57.7	62.1
CPVC	27.7	87.5	75.3	63.5	—
PVF	49.1	84.9	75.0	61.6	60.8
	θ_r				
PMMA	27.8	64.2	62.9	39.3	43.3
CPVC	22.9	76.0	63.9	43.8	—
PVF	34.8	71.8	63.2	49.2	50.4

of low-energy surfaces.¹³ However, the receding angle probably better represents the energetic situation in the rupture of adhesive bonds.

The hysteresis encountered when the polar liquids were used resulted in small and about equal increases in γ_s^- for all three polymers. That is, they all became more basic as a result of being wet by the probe liquid. On the other hand, the slightly acidic CPVC declined in acidity (lower γ_s^+ using θ_r) as did acidic PVF (to a lesser extent). The basic PMMA appeared not to have changed, i.e., did not gain in acidity if the water-formamide value is disregarded.

The lower acid parameter using θ_r than θ_a was surprising, so literature values were collected and are given in Table IV. These parameters were all calculated using angles of diiodomethane, water, and glycerol. Four of the five surfaces from ref. 14 show that θ_r gives a lower γ_s^+ than does θ_a , as was seen for CPVC in Table II. Reference 14 also listed formamide angles on the polymers, and all but one

showed the decline as seen for PVF in Table II (but not PMMA). Why γ_s^+ values are generally lower than γ_s^- is not known but, because they are, it is possible that the effect we are seeing with γ_s^+ is due to error. That the γ_s^+ values are low compared to γ_s^- is a point that is discussed on page 16 of ref. 3. The authors give three possible explanations for this. We will not discuss the point here except to point out that higher γ_s^+ values, ranging from 5 to 10 mJ/m², have been reported for a glass surface cleaned in various ways. γ_s^- values were 2.9 times the γ_s^+ values.¹⁵

ETHYLENE-ACRYLIC ACID SERIES

In an effort to explore γ_s^+ for polymers where activity would be expected to vary, some unpublished data from this laboratory¹² were calculated according to the new combining rule. Contact angles were measured for diiodomethane, water, dimethylsulfoxide,

Table II Surface Energy Parameters (mJ/m²) of the Polymers

Polymer	Pair, Water Plus	Using θ_a			Using θ_r		
		γ_s^{LW*}	γ_s^+	γ_s^-	γ_s^{LW*}	γ_s^+	γ_s^-
PMMA	Glycerol	35.0	0	12.5	43.9	0	18.5
	Ethylene glycol		0	12.2		0	16.3
	Formamide		0	11.9		0.15	13.9
CPVC	Glycerol	45.2	0.11	2.6	46.9	0.02	8.1
	Ethylene glycol		0.36	3.7		0.04	6.0
PVF	Glycerol	34.8	0.05	4.9	42.6	0.08	10.0
	Ethylene glycol		0.04	5.5		0.01	12.1
	Formamide		0.47	3.1		0.22	7.2
PMMA	Average	35.0	0	12.2	43.9	0.03	16.2
CPVC	Average	45.2	0.24	3.1	46.9	0.03	7.0
PVF	Average	34.8	0.19	4.5	41.2	0.10	9.8

* γ_s^{LW} determined by use of diiodomethane.

Table III Effect of Plasma on Surface Energy Parameters

	γ_s^{LW}	γ_s^+	γ_s^-	ESCA, Atom %	
				O	F
PVF untreated	38	0.02	13.2	1.8	35.0
PVF plasma	45	1.38	32.9	13.1	22.0
PVF corona	39	0.07	19.2	5.8	31.7

and 0.1 N NaOH on polyethylene containing different levels of acrylic acid as copolymer (see Materials and Procedures). In Table V we see the advancing angles that were used to calculate the surface energy parameters in Table VI. The diiodomethane angles showed that all three polymers were equal in $\gamma_s^{LW} = 31.1 \text{ mJ/m}^2$.

None of the polymers showed any basicity (Table VI), although there was a slight increase in $\sqrt{\gamma_s^-}$ as the acrylic acid content increased. This was true for both polar liquid pairs. We will discuss the negative values of $\sqrt{\gamma_s^-}$ and $\sqrt{\gamma_s^+}$ below.

The acidic parameters were of greatest interest with both liquid pairs showing the expected increase in $\sqrt{\gamma_s^+}$ with increasing acrylic acid, although the values are low. The 0.1 N NaOH-DMSO pair was more definitive, for when $\sqrt{\gamma_s^+}$ was squared to get γ_s^+ , we still see the trend. Not so for the water-DMSO pair. Other liquid pairs might be more sensitive, but we believe that bases strong enough to swell the EAC polymers should be avoided. For instance, 1 N NaOH showed a swelling, more pronounced with EAC 7.0 than with EAC 1.8.

Negative values of $\sqrt{\gamma_s^+}$ and/or $\sqrt{\gamma_s^-}$ have been encountered, usually for $\sqrt{\gamma_s^+}$, and would seem to be

real and useful from this brief experiment. Good and van Oss³ point out that the form:

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+} \sqrt{\gamma_s^-} \quad (7)$$

should be used when negative values of the square root are encountered. Thus, γ_s^{AB} can be negative and the surface can be stable as long as γ_s^{LW} is positive enough to make the total positive

$$\gamma_s^{\text{Total}} = \gamma_s^{LW} + \gamma_s^{AB}.$$

Experiments of this sort need to be done on other surfaces graded in acidity and in basicity. Also, other polar liquid pairs should be tried. We are exploring the choice of polar liquid pairs, and have evidence that liquids should be paired which have considerable differences in

$$\left(\frac{\gamma_s^-}{\gamma_s^+}\right)^{1/2}.$$

Indeed, checking the results calculated with one liquid pair with one or more other pairs is desirable.

CONCLUSION

The new combining rule for quantifying the surface energy of polymers acidic and basic sites gives encouraging results for basic PMMA, and acidic CPVC and PVF. Further testing of this hypothesis is warranted. The receding contact angle reveals higher γ_s^{LW} and γ_s^- than the advancing angle calculations, as expected. However, γ_s^+ was lower in some cases using θ_r . This situation also needs a larger data base in order to explain the cause, if real.

Table IV Surface Parameters for Polymer Surfaces Using θ_a and θ_r , mJ/m²

Polymer	Using θ_a			Using θ_r			Reference No.
	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{LW}	γ_s^+	γ_s^-	
Polypropylene	32.6	0	0	37.0	1.3	0.9	2
Corona-treated polypropylene	41.1	1.3	8.0	44.6	1.8	25.4	2
Corona-treated polyethylene	33	0	0.1	42	2.1	30	3
Anthracite coal	39.3	0	5.8	47.7	2.2	29.1	2
Bituminous coal	39.8	0.1	8.2	50.2	1.7	41.1	2
PMMA	42.5	0.19	11.3	49.5	0.07	32.3	14
Polyhexamethyladipamide	38.6	0.64	9.8	46.5	0.31	35.3	14
Polylaurinlactam	37.5	0.52	6.0	45.4	0.46	22.4	14
Polypropylene oxidized	39.1	0.26	33.2	46.5	0.06	54.5	14
Polytetrafluoroethylene	19.6	0.28	3.2	32.0	0.42	11.4	14

Table V Contact Angles for Various Liquids on Polymer Surfaces

Polymer	% Acrylic Acid	Average θ_a (°)			
		Diiodomethane	Water	Dimethylsulfoxide	0.1 N NaOH
PE	0	52.0	106.3	55.9	106.3
EAC 1.8	1.8	52.0	104.6	54.6	104.3
EAC 7.0	7.0	51.9	102.9	52.3	101.3

Table VI Acidic and Basic Parameters of the Polymer Surfaces

Polymer	Polar Liquids	$\sqrt{\gamma_s^+}$	γ_s^+	$\sqrt{\gamma_s^-}$	γ_s^-	γ_s^{AB}
PE	Water/DMSO	-0.18	0.03	-0.01	0	0.002
EAC 1.8		0.03	0	0.03	0	0.001
EAC 7.0		0.13	0.02	0.04	0	0.005
PE	0.1 N NaOH/DMSO	0.05	0	-0.04	0	-0.002
EAC 1.8		0.004	0	0.04	0	0
EAC 7.0		0.49	0.24	0.10	0	0.05

Oxidation of the polymer surface is unequivocally described by the new procedure. However, when acidity increase was more subtle in the case of the ethylene acrylic acid copolymers, the parameter $(\gamma_s^+)^{1/2}$ was more revealing than γ_s^+ .

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