Evaluation of Surface Energy of Solid Polymers Using Different Models

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ABSTRACT: In the present work, contact angles formed by drops of diethylene glycol, ethylene glycol, formamide, diiodomethane, water, and mercury on a film of polypropylene (PP), on plates of polystyrene (PS), and on plates of a liquid crystalline polymer (LCP) were measured at 20°C. Then the surface energies of those polymers were evaluated using the following three different methods: harmonic mean equation and geometric mean equation, using the values of the different pairs of contact angles obtained here; and Neumann's equation, using the different values of contact angles obtained here. It was shown that the values of surface energy generated by these three methods depend on the choice of liquids used for contact angle measurements, except when a pair of any liquid with diiodomethane was used. Most likely, this is due to the difference of polarity between diiodomethane and the other liquids at the temperature of 20°C. The critical surface tensions of those polymers were also evaluated at room temperature according to the methods of Zisman and Saito using the values of contact angles obtained here. The values of critical surface tension for each polymer obtained according to the method of Zisman and Saito corroborated the results of surface energy found using the geometric mean and Neumann's equations. The values of surface energy of polystyrene obtained at 20°C were also used to evaluate the surface tension of the same material at higher temperatures and compared to the experimental values obtained with a pendant drop apparatus. The calculated values of surface tension corroborated the experimental ones only if the pair of liquids used to evaluate the surface energy of the polymers at room temperature contained diiodomethane. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1831–1845, 2000

Key words: surface energy of polymers; sessile drop method; pendant drop method; polypropylene; polystyrene; LCP

INTRODUCTION

Blending polymers has become an usual method to obtain new materials with improved or even not existing properties. Also, studies using blends involving a liquid crystalline polymer (LCP) and thermoplastics have been conducted[1] recently be-

cause of the interest in obtaining self-reinforced materials and to the ability of the LCP to improve the processing conditions of thermoplastics. The properties of polymer blends are a function of the morphology of the system, which, in turn, depends on the composition of the blend, the processing conditions to obtain the blend, the rheological properties of the components, and the interfacial tension between the components.

Interfacial tension is one of the key parameters that determine the compatibility between the components of a polymer blend; it is also the most accessible parameter that describes the thermo-

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dynamic state and structure of an interface. Interfacial tension between molten polymers can be measured experimentally with extreme difficulty due to their intrinsic high viscosities, using different methods, such as the pendant drop,[2] spinning drop,[3] breaking thread,[4] and imbedded fibers.[5] It could be very valuable to study other methods to obtain surface tension due to the experimental difficulties found in the methods mentioned before. In principle, interfacial tension between molten polymers can be calculated from the surface tensions of the respective molten polymers; also, the surface energy of the polymers at room temperature can be evaluated using the values of contact angles formed by drops of different liquids on the surface of these polymers. Therefore, it is of particular interest to investigate the different methods existing in the literature (harmonic mean equation, geometric mean equation, and Neumann's equation) to evaluate surface energy of polymers at room temperature and verify if it is possible to use the obtained values to evaluate the surface tension at higher temperatures.

The objective of the present study was to evaluate the different models used to obtain the surface energy of solid polymers from contact angle measurements at room temperature and to compare the extrapolated values of surface tension at higher temperatures, obtained from calculations using the values at room temperature, with the ones obtained experimentally using the pendant drop method.

THEORETICAL BACKGROUND

Young's Equation

When a drop of a liquid rests on a solid surface, it forms an angle θ with the surface, called contact angle. In thermodynamical equilibrium conditions, Young[6] showed that

$$\gamma_S = \gamma_{SL} + \gamma_{LV}\cos \theta \qquad (1)$$

where γ_S is the surface energy of the solid, γ_{SL} is the interfacial tension between the solid and the liquid, and γ_{LV} is the surface tension of the liquid.

Many different methods have been proposed to evaluate γ_S using values of contact angles formed by drops of different liquids with known surface tensions; these methods are reviewed below.

Geometric and Harmonic Means

It was proposed by Wu,[7] and it is widely accepted that the intermolecular energy between two ma-

terials results from the summation of a dispersion component and a polar component. Since the surface tension is proportional to the intermolecular energy, the surface tension γ itself can be considered as a sum of a dispersion component γ^d and a polar component γ^p.

The interfacial tension between a liquid and a solid polymer can then be evaluated by the harmonic mean equation,[7] as follows:

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - 4\left(\frac{\gamma_{LV}^d\gamma_S^d}{\gamma_{LV}^d + \gamma_S^d} + \frac{\gamma_{LV}^p\gamma_S^p}{\gamma_{LV}^p + \gamma_S^p}\right) \quad (2)$$

or the geometric mean equation,[7] as follows:

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - 2[(\gamma_{LV}^d\gamma_S^d)^{1/2} + (\gamma_{LV}^p\gamma_S^p)^{1/2}] \quad (3)$$

where γ_S is the surface energy of the solid, γ_{SL} is the interfacial tension between the solid and the liquid, and γ_{LV} is the surface tension of the liquid, γ_S^d and γ_S^p are the dispersion and polar components of the surface energy of the solid, and γ_{LV}^d and γ_{LV}^p are the dispersion and polar components of the surface tension of the liquid.

Using equation (1), equations (2) and (3) transform in equations (4) and (5), respectively.

$$\gamma_{LV}(1 + \cos \theta) = 4\left(\frac{\gamma_{LV}^d\gamma_S^d}{\gamma_{LV}^d + \gamma_S^d} + \frac{\gamma_{LV}^p\gamma_S^p}{\gamma_{LV}^p + \gamma_S^p}\right) \quad (4)$$

$$\gamma_{LV}(1 + \cos \theta) = 2[(\gamma_{LV}^d\gamma_S^d)^{1/2} + (\gamma_{LV}^p\gamma_S^p)^{1/2}] \quad (5)$$

If the contact angles made by two liquids of known γ^d and γ^p are measured, it is possible to solve equation (4) (harmonic mean) or (5) (geometric mean) and infer γ_S^d and γ_S^p for the solid.

Neumann's Equation

The surface energy of a solid polymer can also be calculated using the combination of Young's and Neumann's[8] equation given by

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - 2\sqrt{\gamma_{LV}\gamma_S}\, e^{-\beta}(\gamma_{LV} - \gamma_S)^2 \quad (6)$$

where $\beta = 0.000115$ $(m^2/mJ)^2$, and all the other symbols were defined before, resulting in

$$\cos \theta = -1 + 2\sqrt{\frac{\gamma_S}{\gamma_{LV}}}\, e^{-\beta}(\gamma_{LV} - \gamma_S)^2 \quad (7)$$

In this case, only one liquid is necessary to calculate the surface energy of the solid, but nei-

ther the dispersion nor the polar component can be evaluated.

The Critical Surface Tension

Fox and Zisman[9] showed that the cosines of the contact angles formed by drops of homologous liquids on a solid surface vary linearly with their surface tensions. The critical surface tension can then be found extrapolating the linear function to $\cos \theta = 1$. Fowkes[10] showed that the cosines of the contact angles formed by drops of different liquids vary linearly with $\sqrt{\gamma_{LV}^d}/\gamma_{LV}$ (where γ_{LV}^d and γ_{LV} are the dispersion component of the surface tension and the surface tension of the different liquids used for contact angle measurements). Saito[11] showed that $\log(1 + \cos \theta)$ (where θ is the contact angle formed by a liquid on a solid surface) for different liquids vary linearly with $\log(\gamma_{LV})$ (where γ_{LV} is the surface tension of the liquid); the critical surface tension of the solid can be found extrapolating the linear function to $\log(1 + \cos \theta) = \log(2)$. It can be shown that the critical surface tension corresponds to the surface energy of the solid.

EXPERIMENTAL

Materials

Commercially available polypropylene (PP) (PT25E from KOPPOL) and polystyrene (PS) (Lustrex HH-101 from Estireno do Brasil) were used in this work. A liquid crystal polymer was also studied in this work. It was a random copolymer of 4-hydroxybenzoic acid and 6-hydroxy-2-naphtoic acid, namely, VECTRA A-910 from Ticona Polymers.

Methods

For the contact angle determination, pellets of PS and VECTRA A-910 were molded into discs of 25 mm diameter and 1 mm thickness, using a hot-press between sheets of THERPHANE® (Rhodia) or aluminum foil in order to obtain a smooth surface and non-oriented sample, in the case of VECTRA. In the case of PP, a film as obtained from the manufacturer was placed on a smooth steel plate. Sessile drops of diethylene glycol, ethylene glycol, formamide, diiodomethane, water, and mercury were formed on the surfaces of the solid polymers; the contact angles made by the drops of liquids were measured with a Ramé–Hart Contact Angle Goniometer, model 100-10.

Table I Dispersion (γ^d) (mN/m) and Polar (γ^p) (mN/m) Components of Surface Tension (γ) at 20°C of the Liquids Used in This Work

Liquid	γ^d	γ^p	γ
Diethyleneglycol	31.7	12.7	44.4
Ethyleneglycol	30.1	17.6	47.7
Diiodomethane[a]	44.1	6.7	50.8
Diiodomethane[b]	48.5	2.3	50.8
Diiodomethane[c]	50.4	0.4	50.8
Formamide	39.5	18.7	58.2
Water	22.1	50.7	72.8
Mercury	198.0	286.2	484.2

[a–c] Different values of the dispersion and polar components of surface tension found in literature for diiodomethane.

Table I presents the dispersion and the polar component of surface tension of the liquids used in this work for contact angle measurements. For diiodomethane, three different groups of data were available in the literature,[12–14] and all of them were used in the analyses. The experiments were performed at a temperature of 20°C.

The surface tension of molten PS was measured directly with an apparatus based on the pendant drop method. An extensive review of this method to measure surface tension of molten polymers can be found in the literature.[12] The pendant drop method involves the determination of the geometrical profile of a pendant drop of one liquid. The shape of this drop is related to the density and surface tension of the liquid, which can be inferred from the following equation:

$$\gamma = \frac{\rho g a^2}{B} \tag{8}$$

where γ and ρ are the surface tension and the density of the liquid, a is the radius of curvature of the pendant drop at the apex, and B is a shape factor that depends on the geometrical shape of the drop.

The apparatus used in this work is similar to the one used by Demarquette and Kamal.[2] It consists basically of three parts: an experimental cell, where the pendant drop of the molten polymer is formed; an optical system to monitor the evolution of the drop; and a data acquisition system to infer the surface tension from the geometrical profile of the drop. The apparatus used in this work was totally automatic; that is, it would acquire the image of the drop and infer the surface tension on line automatically without the

Table II   Contact Angles θ Made by the Drops of the Different Liquids on the Polymers Surfaces at 20°C

Liquid	PP (°)	PS (°)	VECTRA (°)
Diethyleneglycol	70.3 ± 0.8	53.7 ± 0.7 (52.41 ± 0.61)[b]	39.6 ± 1.1
Ethyleneglycol	76.6 ± 0.5	64.9 ± 0.5 (61.20 ± 0.26)[b]	56.4 ± 0.5
Formamide	79.8 ± 0.7 (86)[a]	70.6 ± 0.3 (74.76 ± 0.41)[b]	64.1 ± 0.5 (63.83)[d]
Diiodomethane	50.0 (56.3)[a]	28.1 ± 0.5 (35)[c] (40–60)[b]	24.5 ± 0.5 (27 ± 2)[e] (26 ± 7)[e] (38.67)[d]
Water	88.6 ± 0.7 (100.3)[a]	90.0 ± 0.5 (91)[c] (88.42 ± 0.28)[b]	75.1 ± 0.8 (80 ± 1)[e] (83 ± 4)[e] (81.68)[d]
Mercury	139.9 ± 1.0	140.1 ± 0.4	132.0 ± 1.2

[a] Schneider.[14]
[b] Kwok et al.[17]
[c] Wu.[7]
[d] Ma et al.[13]
[e] James et al.[18]

input of the user during the whole duration of the experiment. It has been described in details in Arashiro and Demarquette.[15]

In order to extrapolate the values of the surface energy at room temperature to the values at higher temperatures, it was necessary to determine the thermal expansion of PS in the glassy and rubbery state. These parameters were measured using a mercury dilatometer developed in our laboratory.[16]

RESULTS

The contact angles θ formed by drops of the different liquids on the polymers are presented in Table II, together with the values reported in literature.[7,13,14,17,18]

The experimental values of the contact angle were used to calculate the surface energy using the harmonic mean equation, the geometric mean equation, and Neumann's equation and to evaluate the critical surface tension according to Zisman and Saito for the polymers studied in this work.

Tables III to V present the surface energy of PP, PS, and VECTRA, respectively, evaluated using the geometric and harmonic mean equations

for all the different pairs of liquids used in this work. In some cases, no mathematical solution was obtained. Table VI presents the surface energy using Neumann's equation for the different liquids used. In some cases, values from the literature are presented in parenthesis.

Figures 1 to 3 show $\cos \theta$ as a function of γ_{LV} (Zisman), $\cos \theta$ as a function of $\sqrt{\gamma_{LV}^d}/\gamma_{LV}$ (Fowkes), and $\log(1 + \cos \theta)$ as a function of $\log(\gamma_{LV})$ (Saito), respectively, for the three polymers and the liquids used in this work. The lines represent the best fit for the experimental data using the least square regression. In Figure 1 (Zisman's method), the value of the contact angle formed by the drop of mercury was not included in the fitting of the line. Figure 1(a) (Zisman's method) shows $\cos \theta$ as a function of γ_{LV} for $0 < \gamma_{LV} < 500$ mN/m. Figure 1(b) shows $\cos \theta$ as a function of γ_{LV} for $40 < \gamma_{LV} < 80$ mN/m for sake of clarity. Figures 2(a) to (c) show $\cos \theta$ as a function of $\sqrt{\gamma_{LV}^d}/\gamma_{LV}$ using the three different values of γ^d for diiodomethane reported in Table I. Using Zisman's and Saito's methods and Figures 1 and 3, it was possible to infer the critical surface tension. The values are reported in Table VII.

Figure 4 shows the surface tension of polystyrene in the rubbery state as a function of temper-

Table III   Surface Tension (mN/m) and Its Dispersion, γ^d and Polar γ^p Components at 20°C for PP Calculated with the Harmonic Mean and the Geometric Mean Equations for Different Pairs of Liquids

Pair of Liquids	Harmonic			Geometric		
	γ^d	γ^p	γ	γ^d	γ^p	γ
Diethyleneglycol–ethyleneglycol	21.1	2.64	23.7	23.8	0.392	24.2
Diethyleneglycol–formamide	8.88	20.9	29.8	10.4	10.4	20.8
Diethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Diethyleneglycol–diiodomethane[b]	—	—	—	40.6	3.00	43.6
Diethyleneglycol–diiodomethane[c]	—	—	—	35.7	1.24	36.9
Diethyleneglycol–water	10.7	14.7	25.4	11.3	9.10	20.4
Ethyleneglycol–formamide	—	—	—	—	—	—
Ethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Ethyleneglycol–diiodomethane[b]	—	—	—	39.0	1.36	40.4
Ethyleneglycol–diiodomethane[c]	—	—	—	35.4	0.599	36.0
Ethyleneglycol–water	7.23	17.8	25.0	7.43	11.8	19.2
Formamide–diiodomethane[a]	—	—	—	—	—	—
Formamide–diiodomethane[b]	—	—	—	39.0	1.33	40.3
Formamide–diiodomethane[c]	—	—	—	35.3	0.510	35.8
				$(31.9)^d$	$(0)^d$	$(31.9)^d$
Formamide–water	11.9	13.9	25.8	11.5	9.02	20.5
				$(14.2)^d$	$(3.0)^d$	$(17.2)^d$
Diiodomethane–water[a]	28.9	6.97	35.9	32.6	2.15	34.7
Diiodomethane–water[b]	31.7	6.32	38.0	32.1	2.24	34.3
Diiodomethane–water[c]	34.5	5.76	40.3	33.1	2.08	35.2
				$(30.4)^d$	$(0.3)^d$	$(30.7)^d$

[a–c] Using the different values of the dispersion and polar components of surface tension of diiodomethane indicated in Table I.
[d] Schneider et al.[14]

ature. The symbols represent the experimental data points and the straight line, the best fit obtained by linear least square regression.

Table VIII shows the thermal expansion coefficient of polystyrene in the glassy state and rubbery state obtained by mercury dilatometry.

DISCUSSION

Contact Angles

It can be seen from Table II that the values of contact angles found in this work for PS and VECTRA are in reasonable agreement with the values published in the literature. For PP, however, some deviations were observed. This could be due to the presence of additives since commercial samples were used.[19]

Surface Energy Using Geometric Mean, Harmonic Mean, and Neumann's Equation

It can be seen from Table IV and VI that the values of surface energy of PS found in this work

using the harmonic mean equation and Neumann's equation corroborate with the ones published in the literature.[7,17] Also, the values of the surface energy of VECTRA evaluated in this work using the harmonic and geometric mean equations and using the pair of liquids formamide and water and diiodomethane and water are in reasonable agreement with data published in the literature.[13,18] It can be seen from Table III that the values of surface energy of PP found in this work using the geometric mean equation corroborate the ones published.

It can be seen from Tables III to VI that the surface energy values calculated using the harmonic mean, the geometric mean, and Neumann's equation depend on the liquids used for contact angle measurements. For PP, the surface energy varied 70% (harmonic), 127% (geometric), and 71% (Neumann) with respect to the minimum value obtained; for PS, the values varied 81% (harmonic), 111% (geometric), and 72% (Neumann) with respect to the minimum value obtained; and for VECTRA, the surface energy values varied 63% (harmonic), 72% (geometric), and

Table IV Surface Tension (mN/m) and Its Dispersion γ^d and Polar γ^p Components at 20°C for PS Calculated with the Harmonic Mean and the Geometric Mean Equations for Different Pairs of Liquids

Pair of Liquids	Harmonic			Geometric		
	γ^d	γ^p	γ	γ^d	γ^p	γ
Diethyleneglycol–ethyleneglycol	—	—	—	33.9	0.474	34.4
Diethyleneglycol–formamide	—	—	—	—	—	—
Diethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Diethyleneglycol–diiodomethane[b]	—	—	—	51.5	2.00	53.5
Diethyleneglycol–diiodomethane[c]	—	—	—	46.4	0.705	47.1
Diethyleneglycol–water	20.5	8.90	29.4	27.3	2.76	30.1
Ethyleneglycol–formamide	35.4	0.758	36.2	35.5	0.0910	35.6
Ethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Ethyleneglycol–diiodomethane[b]	—	—	—	50.9	1.52	52.4
Ethyleneglycol–diiodomethane[c]	—	—	—	46.3	0.645	47.0
Ethyleneglycol–water	15.3	11.2	26.5	21.2	4.30	25.5
Formamide–diiodomethane[a]	—	—	—	—	—	—
Formamide–diiodomethane[b]	—	—	—	51.7	2.19	53.9
Formamide–diiodomethane[c]	—	—	—	46.5	0.892	47.4
Formamide–water	20.0	9.09	29.1	23.6	3.63	27.2
Diiodomethane–water[a]	41.4	4.09	45.5	49.1	0.234	49.3
	(38.3)[d]	(4.26)[d]	(42.6)[d]			
Diiodomethane–water[b]	41.8	4.05	45.9	45.1	0.459	45.6
Diiodomethane–water[c]	44.2	3.72	47.9	44.5	0.501	45.0

[a–c] Using the different values of the dispersion and polar components of surface tension of diiodomethane indicated in Table I.
[d] Wu.[7]

53% (Neumann) with respect to the minimum value obtained. Larger variations were obtained for the dispersion and polar components of the surface energy. It should be noted that there is a reasonable agreement among the results whenever the contact angle formed by a drop of diiomethane is considered in the calculations. Tables IX to XI show the surface energy of PP, PS, and VECTRA calculated using the harmonic and the geometric mean equations using the values of contact angles formed by drops of diiodomethane and another liquid; it can be seen that the variation among the results is much lower in this case, with values of 38.1 ± 1.3 (harmonic) and 37.5 ± 1.1 (geometric) for PP, 46.5 ± 0.7 (harmonic) and 49.0 ± 1.1 (geometric) for PS, and 49.1 ± 1.4 (harmonic) and 48.0 ± 0.5 (geometric) for VEC-TRA. With the exception of diiodomethane, all the liquids used here for contact angle measurements are polar. Thus, it seems that in order to obtain reliable values of surface energy, using harmonic mean and geometric mean equations, pair of polar–non polar liquids should be used.

Similar conclusions have already been reached in the literature.[13,18,20] Ma et al.[13] studied the surface energy of commercial thermotropic LCPs measuring the contact angle formed by drops of water, glycerol, formamide, and diiodomethane on LCP films. They analyzed their data with various methods: Good–Girifalco, geometric mean equation, harmonic–mean equation, and the Lifshitz–van der Waals Acid–Base Theory.[21] They observed that their results depended on the liquids they used to make the calculations, but that better consistency was obtained whenever two polar and one nonpolar liquid was used with the Lifshitz–van der Waals Acid-Base Theory. Kano and Akiyama[20] applied Saito's method for a group of polar and a group of nonpolar testing liquids on a poly(ethyl acrylate)–poly(vinilidene fluoride-*co*-hexafluoroacetone) blend. When plotting log(1 + cos θ) as a function of the surface tension of the different liquids, those researchers obtained two straight lines of different slopes, leading to different values of critical surface tension.

Because of the dependence on the liquids used to evaluate surface energy shown above, methods taking into account the values of the contact angles formed by all the different liquids were tested here for the three different

Table V   Surface Tension (mN/m) and Its Dispersion γ^d and Polar γ^p Components at 20°C for VECTRA Calculated with the Harmonic Mean and the Geometric Mean Equations for Different Pairs of Liquids

Pair of Liquids	Harmonic			Geometric		
	γ^d	γ^p	γ	γ^d	γ^p	γ
Diethyleneglycol–ethyleneglycol	—	—	—	—	—	—
Diethyleneglycol–formamide	—	—	—	—	—	—
Diethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Diethyleneglycol–diiodomethane[b]	45.7	1.01	46.7	48.4	0.00131	48.4
Diethyleneglycol–diiodomethane[c]	45.9	0.981	46.9	46.4	0.0736	46.5
Diethyleneglycol–water	20.8	16.0	36.8	25.1	9.73	34.8
Ethyleneglycol–formamide	34.8	2.75	37.6	33.1	1.71	34.8
Ethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Ethyleneglycol–diiodomethane[b]	—	—	—	49.7	0.152	49.9
Ethyleneglycol–diiodomethane[c]	46.1	0.319	46.4	46.8	0.0143	46.8
Ethyleneglycol–water	12.8	20.9	33.7	13.8	15.8	29.6
Formamide–diiodomethane[a]	—	—	—	—	—	—
Formamide–diiodomethane[b]	—	—	—	50.6	0.444	51.0
	(39.58)[d]	(1.28)[d]	(40.86)[d]	(41.12)[d]	(0.14)[d]	(41.26)[d]
Formamide–diiodomethane[c]	—	—	—	47.1	0.0912	47.2
Formamide–water	16.6	18.2	34.8	16.7	13.9	30.6
	(19.99)[d]	(13.07)[d]	(33.06)[d]	(23.34)[d]	(7.16)[d]	(30.50)[d]
Diiodomethane–water[a]	36.9	11.0	47.9	41.8	4.66	46.5
	(37)[e]	(9)[e]	(46)[e]			
Diiodomethane–water[b]	41.6	10.1	51.7	42.3	4.56	46.9
	(36.45)[d]	(8.37)[d]	(44.82)[d]	(37.11)[d]	(3.43)[d]	(40.54)[d]
Diiodomethane–water[c]	45.4	9.53	54.9	44.3	4.14	48.4

[a–c] Using the different values of the dispersion and polar components of surface tension of diiodomethane indicated in Table I.
[d] Ma et al.[13]
[e] James et al.[18]

Table VI   Surface Tension (mN/m) at 20°C Calculated with Neumann's Equation for Different Liquids and Polymers

Liquids	PP	PS	VECTRA
Diethyleneglycol	22.5	30.1	36.1
		(30.45)[a]	
Ethyleneglycol	21.5	27.1	31.3
		(29.32)[a]	
Formamide	26.1	31.3	35.0
		(29.36)[a]	
Diiodomethane	36.8	46.7	48.0
Water	30.0	29.1	39.0
		(30.15)[a]	

[a] Kwok et al.[17]

equations (geometric mean equation, harmonic mean equation, and Neumann's equation). These are reviewed below.

Surface Energy Using the Values of the Contact Angles of All the Liquids

Geometric Mean Equation

Equation (5) can be rewritten as

$$y = (\gamma_S^d)^{1/2} + (\gamma_S^p)^{1/2}x \qquad (9a)$$
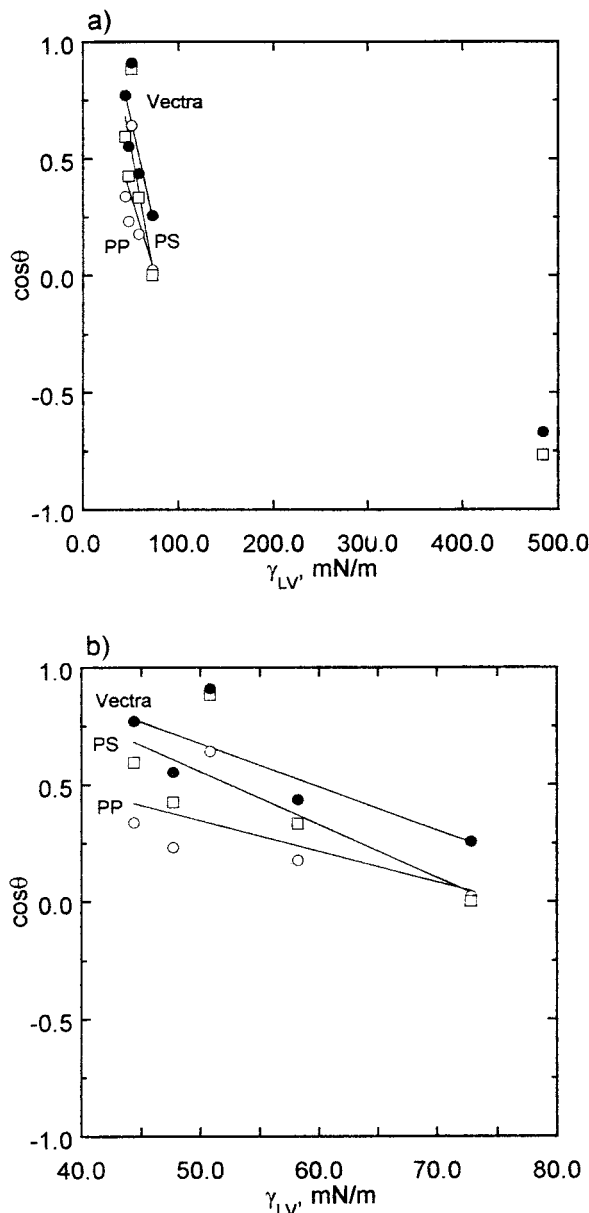
where

$$y = \frac{(1 + \cos\theta)\gamma_{LV}}{2(\gamma_{LV}^d)^{1/2}} \qquad (9b)$$

$$x = \sqrt{\frac{(\gamma_{LV}^p)}{(\gamma_{LV}^d)}} \qquad (9c)$$

The symbols were defined before.

If the contact angle made by various liquids on the polymer surface are measured, γ^d, γ^p, and,

a)

b)

Figure 1   Zisman's method for the determination of the critical surface tension: Cosines of the contact angles θ, formed by the drops of the testing liquids on the surface of the solid polymers at room temperature against the surface tension γ_{LV} of the testing liquids. Part (b) shows the range of γ_{LV} from 40 to 80 mN/m.

consequently, γ of the polymer can be obtained from the plot of y against x defined above.

Harmonic Mean Equation

In the case of the harmonic mean equation, the separation of variables is not as possible as it is for the geometric mean equation. Therefore, in order to evaluate the surface energy of the poly-

mer using the values of the contact angles made by the different liquids, a value of γ_S^d of the polymer was assumed, and γ_S^p was calculated for each testing liquid with equation (4). The average value for γ_S^p, that is, $\overline{\gamma_S^p}$ was then calculated using equation (10); and the quadratic dispersion of γ_S^p in relation to the average value, E^2, was calculated using equation (11) shown below

$$\overline{\gamma_S^p} = \frac{\sum\limits_i (\gamma_S^p)_i}{n} \tag{10}$$

$$E^2 = \frac{\sum\limits_i (\gamma_S^p - \overline{\gamma_S^p})_i^2}{n} \tag{11}$$

where n is the number of testing liquids, and all the other symbols were defined before.

The value of γ_S^d, which minimized the quadratic dispersion of γ_S^p, was considered as the dispersion component and the corresponding average value of γ_S^p; that is, $\overline{\gamma_S^p}$ was adopted as the polar component of the surface energy of the polymer.

Neumann's Equation

Neumann's equation can be rewritten in a self-consistent form as

$$\frac{1}{2\beta\gamma_{LV}}\left[\ln\left(\frac{1 + \cos\theta}{2}\sqrt{\frac{\gamma_{LV}}{\gamma_S}}\right) + \beta(\gamma_{LV}^2 + \gamma_S^2)\right] = \gamma_S^* \tag{12}$$

where all the parameters have been defined previously. The * symbol is used for differentiating the iterative γ_S and the resulting γ_S^* parameters.

In order to calculate the surface energy using the values of contact angles formed by the different liquids, a value for γ_S was assumed, and γ_S^* was calculated for each liquid using equation (12). A quadratic error defined in equation (13) was then calculated for each testing liquid.

$$E^2 = \frac{\sum\limits_i (\gamma_S^* - \gamma_S)_i^2}{n} \tag{13}$$

where n is the number of testing liquids, and all the other symbols were defined before.

The value of γ_S that minimized the quadratic error E^2 (the average error considering all the
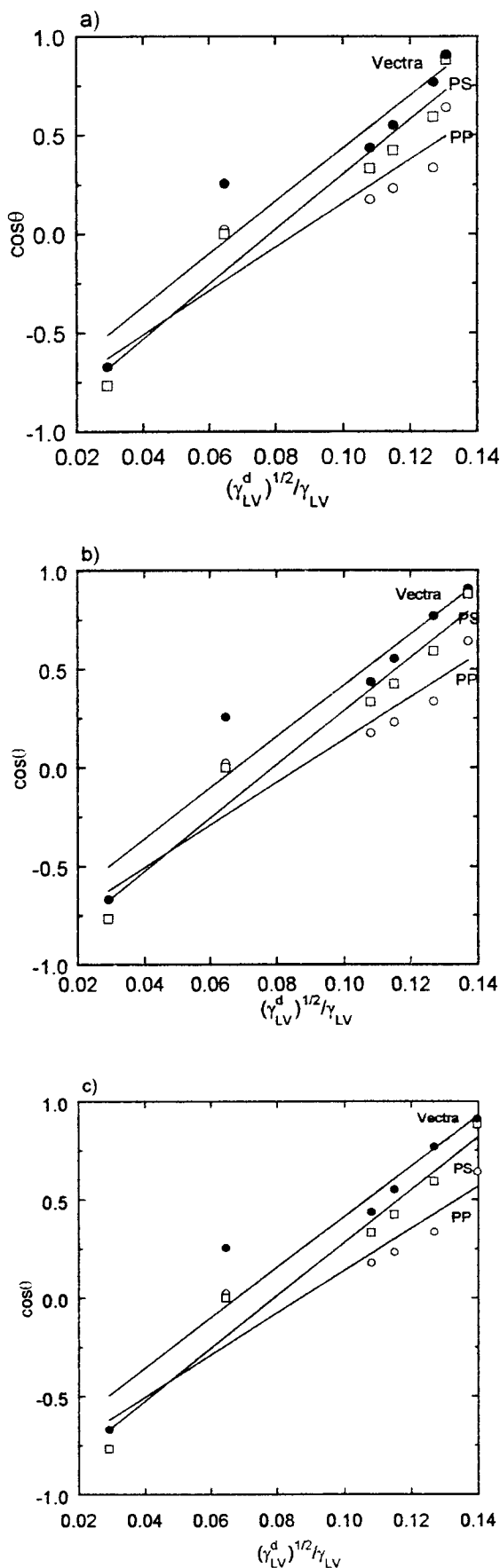
testing liquids) was adopted as the surface energy of the polymer.

Figures 5(a) to (c) show $y = [(1 + \cos\theta)\gamma_{LV}/2(\gamma_{LV}^d)^{1/2}]$ as a function of $x = \sqrt{(\gamma_{LV}^p)/(\gamma_{LV}^d)}$ for the three different values of γ^d and γ^p of di-iodomethane reported in Table I. The lines represent the best fit of the experimental data using linear least square regression, although no perfect fitting was obtained for any of the polymers studied here. The linear least square regression coefficients were used for the calculation of γ_S^d and γ_S^p, which are reported in Table XII. The values obtained using the harmonic mean and Neumann's equation when considering all the liquids are also reported in Table XII. Also shown in Table XII is the polarity of the different polymers, x^p, defined as

$$x^p = \gamma^p/\gamma \qquad (14)$$

where γ^p and γ have been defined before.

It can be seen from Table XII that there is a good agreement between the values obtained using the geometric mean equation and the ones obtained using Neumann's equation. However, a large scatter was obtained for the results originated from the harmonic mean equation.

The values reported in Table XII show that the polarity of PP and VECTRA are similar ($x_{PP}^p \approx 0.08$ to 0.18 and $x_{\text{VECTRA}}^p \approx 0.11$ to 0.19) and that the polarity of PS is in the range of 0.02 to 0.05. PP is normally a nonpolar polymer, and x_{PP}^p should be zero. The results shown here could be explained by the presence of some additives since commercial samples were used. The results could be also due to the variation of γ^p, depending on the liquids used for the calculation, as shown in Tables III to V.

Wu[7] reported a value of 42.6 mN/m for the surface energy of PS at 20°C when using the harmonic mean equation and a value of 42.0 mN/m when using the geometric mean equation. Wu reported values for polarity of $x^p = 0.10$ (harmonic) and of $x^p = 0.02$ (geometric). These values

Figure 2 Fowkes' method for the determination of the critical condition for liquid spreading on the polymer: Cosines of the contact angles θ, formed by the drops of the testing liquids on the surface of the solid polymers at room temperature against the ratio $\sqrt{\gamma_{LV}^d}/\gamma_{LV}$, of the testing liquids. Different values of γ^d for diiodomethane ([a-c] in Table I) were used in (a), (b), and (c), respectively.
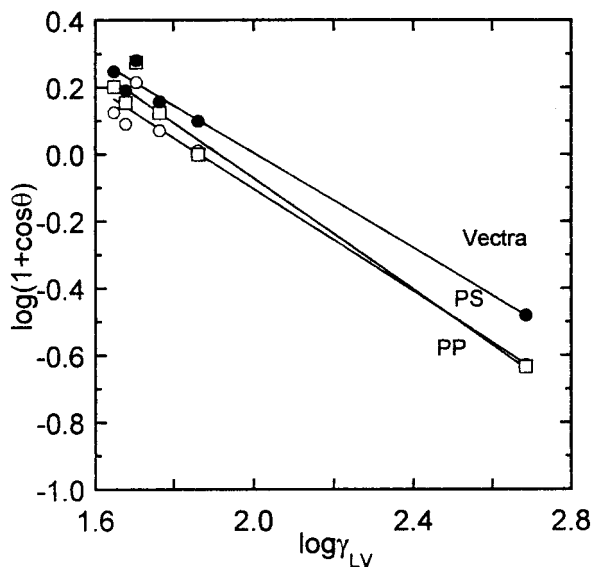
Figure 3 Saito's method for the determination of the critical surface tension plot of the $\log(1 + \cos\theta)$ against the logarithm of the surface tension γ_{LV} of the testing liquids.

Figure 4 Surface tension of PS as a function of temperature.

do not corroborate the results shown in Table XII. However, it should be noted that Wu used only two liquids to infer the surface energy of PS; in this case, the two liquids used were water and diiodomethane. Kwok et al.[17] used the Neumann's equation and obtained $\gamma = 29.8$ mN/m as an average value for PS at 23.0°C corroborating our results.
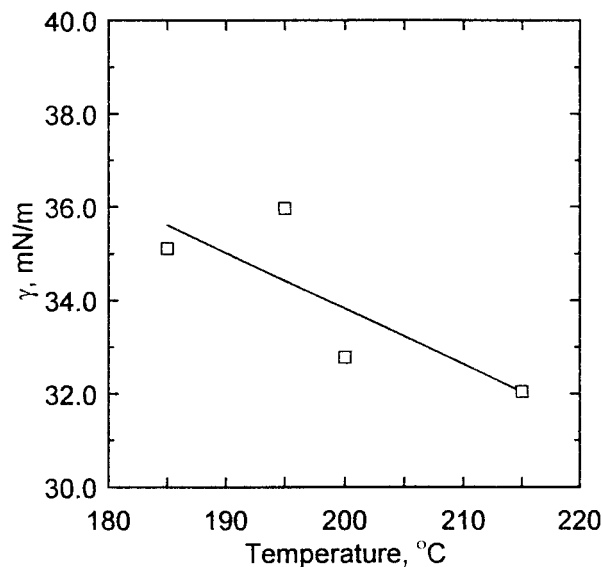
The values of surface energy of VECTRA at 20°C shown in Table XII are lower than the ones reported in the literature. James et al.[18] reported $\gamma = 46.1$ mN/m and $x^p = 0.20$ at 20°C using the harmonic mean equation and the pair of liquids water–diiodomethane. Ma et al.[13] studied the surface energy of commercial thermotropic LCPs and concluded that for VECTRA A950, $\gamma = 41$ mN/m at 25°C. Both values reported by Ma and James are much higher than the ones shown in

Table XII, although the contact angles for diiodomethane, water, and formamide obtained here showed good agreement with the reported ones in literature, as can be seen in Table II.

The discrepancy observed between our results and the results reported by Wu (in the case of PS) and those of Ma et al. and James et al. (in the case of VECTRA) clearly shows the dependence on the liquids chosen for contact angle measurement when using the harmonic mean, the geometric mean, and Neumann's equations.

Critical Surface Tension

It can be seen from Table VII that the results for critical surface tension using Zisman or Saito's methods differed, depending slightly on the method used. For PP, Zisman's method led to a negative value. It should be noted, however, that the liquids used in this work for contact angle measurement were not as homogeneous as they should be when using Zisman's method.

Table VII Critical Surface Tension γ_{crit} (mN/m) of the Polymers Studied in This Work at 20°C

Polymer	γ_{crit} [a]	γ_{crit} [b]
PP	—	29.5
PS	30.3	35.6
VECTRA	32.3	38.3

[a] Zisman's method.
[b] Saito's method.

Table VIII Volumetric Thermal Expansion Coefficient of PS in the Glassy α_g (25°C) and Rubbery α_r (200°C) States Obtained by Mercury Dilatometry

Temperature (°C)	$\alpha \times 10^4$ (K^{-1})
25	4.8
200	31

Table IX   Surface Tension (mN/m) and Its Dispersion γ^d and Polar γ^p Components at 20°C for PP Calculated with the Harmonic Mean and the Geometric Mean Equations for Different Pair of Liquids, Involving Diiodomethane

Pair of Liquids	Harmonic			Geometric		
	γ^d	γ^p	γ	γ^d	γ^p	γ
Diethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Diethyleneglycol–diiodomethane[b]	—	—	—	40.6	3.00	43.6
Diethyleneglycol–diiodomethane[c]	—	—	—	35.7	1.24	36.9
Ethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Ethyleneglycol–diiodomethane[b]	—	—	—	39.0	1.36	40.4
Ethyleneglycol–diiodomethane[c]	—	—	—	35.4	0.599	36.0
Formamide–diiodomethane[a]	—	—	—	—	—	—
Formamide–diiodomethane[b]	—	—	—	39.0	1.33	40.3
Formamide–diiodomethane[c]	—	—	—	35.3	0.510	35.8
Water–diiodomethane[a]	28.9	6.97	35.9	32.6	2.15	34.7
Water–diiodomethane[b]	31.7	6.32	38.0	32.1	2.24	34.3
Water–diiodomethane[c]	34.5	5.76	40.3	33.1	2.08	35.2
Average	31.7	6.35	38.1	35.9	1.61	37.5
Error	1.6	0.35	1.3	1.0	0.27	1.1

[a]–[c] Using the different values of the dispersion and polar components of surface tension of diiodomethane indicated in Table I.

Also, the fitting in the case of the Zisman plot (Fig. 1) is much poorer than in the case of Saito plot (Fig. 3), even if cos θ for mercury is excluded. Wu[7] reported a value of critical surface tension of PS at room temperature of 33 mN/m, which corroborates the values shown in Table VII.

Comparing the values of critical surface tension shown in Table VII to the results reported in Table XII, it can be seen that the values calcu-

Table X   Surface Tension (mN/m) and Its Dispersion γ^d and Polar γ^p Components at 20°C for PS Calculated with the Harmonic Mean and the Geometric Mean Equations for Different Pair of Liquids, Involving Diiodomethane

Pair of Liquids	Harmonic			Geometric		
	γ^d	γ^p	γ	γ^d	γ^p	γ
Diethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Diethyleneglycol–diiodomethane[b]	—	—	—	51.5	2.00	53.5
Diethyleneglycol–diiodomethane[c]	—	—	—	46.4	0.705	47.1
Ethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Ethyleneglycol–diiodomethane[b]	—	—	—	50.9	1.52	52.4
Ethyleneglycol–diiodomethane[c]	—	—	—	46.3	0.645	47.0
Formamide–diiodomethane[a]	—	—	—	—	—	—
Formamide–diiodomethane[b]	—	—	—	51.7	2.19	53.9
Formamide–diiodomethane[c]	—	—	—	46.5	0.892	47.4
Water–diiodomethane[a]	41.4	4.09	45.5	49.1	0.234	49.3
Water–diiodomethane[b]	41.8	4.05	45.9	45.1	0.459	45.6
Water–diiodomethane[c]	44.2	3.72	47.9	44.5	0.501	45.0
Average	42.5	3.95	46.5	48.0	1.02	49.0
Error	0.9	0.12	0.7	0.9	0.24	1.1

[a]–[c] Using the different values of the dispersion and polar components of surface tension of diiodomethane indicated in Table I.

Table XI   Surface Tension (mN/m) and Its Dispersion γ^d and Polar γ^p Components at 20°C for VECTRA Calculated with the Harmonic Mean and the Geometric Mean Equations for Different Pair of Liquids, Involving Diiodomethane

Pair of Liquids	Harmonic			Geometric		
	γ^d	γ^p	γ	γ^d	γ^p	γ
Diethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Diethyleneglycol–diiodomethane[b]	45.7	1.01	46.7	48.4	0.00131	48.4
Diethyleneglycol–diiodomethane[c]	45.9	0.981	46.9	46.4	0.0736	46.5
Ethyleneglycol–diiodomethane[a]	—	—	—	—	—	—
Ethyleneglycol–diiodomethane[b]	—	—	—	49.7	0.152	49.9
Ethyleneglycol–diiodomethane[c]	46.1	0.319	46.4	46.8	0.0143	46.8
Formamide–diiodomethane[a]	—	—	—	—	—	—
Formamide–diiodomethane[b]	—	—	—	50.6	0.444	51.0
Formamide–diiodomethane[c]	—	—	—	47.1	0.0912	47.2
Diiodomethane–water[a]	36.9	11.0	47.9	41.8	4.66	46.5
Diiodomethane–water[b]	41.6	10.1	51.7	42.3	4.56	46.9
Diiodomethane–water[c]	45.4	9.53	54.9	44.3	4.14	48.4
Average	43.6	5.49	49.1	46.4	1.57	48.0
Error	1.5	2.12	1.4	1.0	0.72	0.5

[a–c] Using the different values of the dispersion and polar components of surface tension of diiodomethane indicated in Table I.

lated with the geometric mean and Neumann's equations corroborate reasonably well the critical surface tensions calculated with the Zisman's and the Saito's methods.

The $(\gamma^d)^{1/2}/\gamma$ ratios for the different polymers studied here were calculated using the values reported in Table XII following the method suggested by Fowkes; the values of $(\gamma^d)^{1/2}/\gamma$ are shown in Table XIII with the values at the critical condition of spreading obtained from Figure 2 (Fowkes' method); the agreement among all the values is reasonably good.

Surface Tension of PS in the Rubbery State

It can be seen from Figure 4 that the surface tension of PS decreases linearly as a function of temperature; this behavior is expected according to considerations from thermodynamics. The equation of the straight line obtained by fitting the surface tension as a function of temperature is

$$\gamma = -0.12t + 57.68 \qquad (15)$$

where t is the temperature in °C.

$(d\gamma/dT)_r$, the surface tension temperature coefficient in the rubbery state, is -0.12 mN m^{-1} K^{-1}, which compares well to values obtained for other PS.[22] The value of $(d\gamma/dT)_r$ is slightly higher than the values published by Wu.[23] Wu

published a value of $-0,072$ mN m^{-1} K^{-1} for a PS of $M_v = 44,000$. The difference between our results and the results published by Wu could be due to the difference of polydispersity of the PS samples used in both studies. The temperature coefficient corresponds to the entropy change of interface formation per unit area at constant volume, which decreases when polydispersity increases.[24]

The values of surface energy of PS obtained at 20°C from the geometric mean, harmonic mean, and Neumann's equations reported in Tables VI, X, and XII were used to evaluate the surface tension of PS at higher temperatures, using the relation that exists between $(d\gamma/dT)$ in the glassy and rubbery states, given by

$$\left(\frac{d\gamma}{dT}\right)_g = \frac{\alpha_g}{\alpha_r}\left(\frac{d\gamma}{dT}\right)_r \qquad (16)$$

where α_g and α_r are the isobaric volumetric thermal expansion coefficient in the glassy region and rubbery region, respectively, measured by mercury dilatometry, and $(d\gamma/dT)_g$ is the surface energy temperature coefficient in the glassy state.

The values of surface tension of PS calculated and obtained experimentally, for the different temperatures, are presented in Table XIV. It can be seen that when using the value of the surface
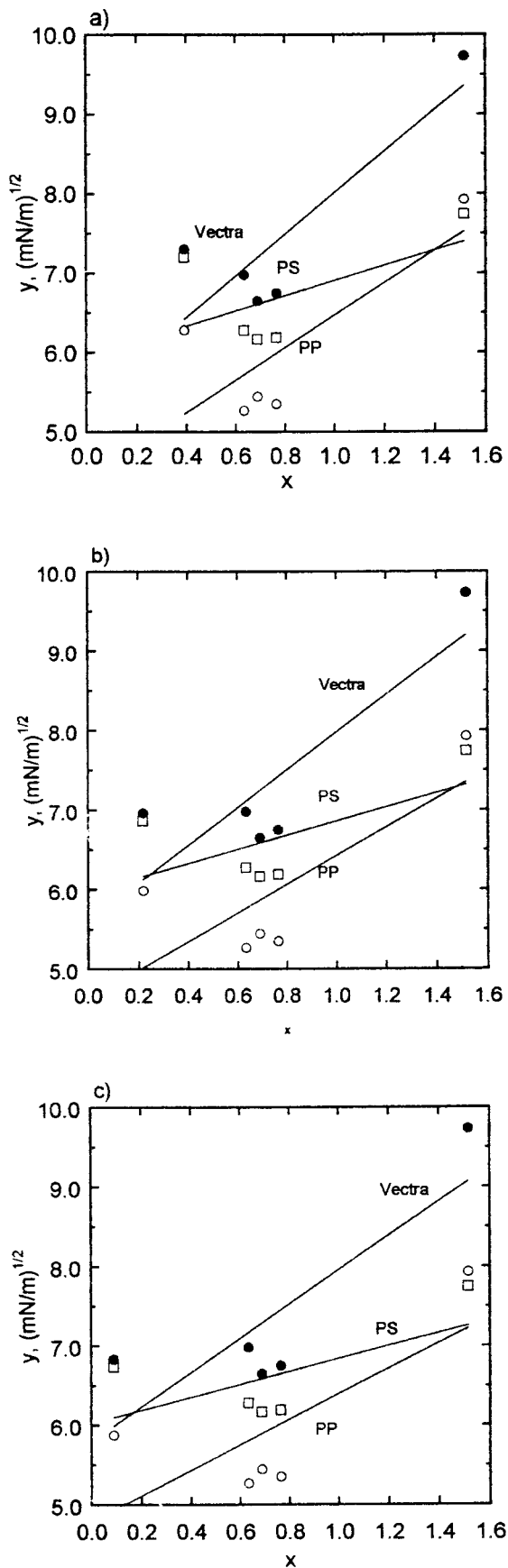
energy of PS in the solid state reported in Table XII, taking into consideration the contact angles obtained for all the liquids studied here, the calculated values of surface tension do not corroborate the ones obtained experimentally with the pendant drop apparatus. This behavior cannot be just due to experimental error. The discrepancy between the experimental and calculated results of surface tension indicates that the surface energy values obtained in this work using the harmonic mean, geometric mean, or Neumann's equations are underestimated. It can be also seen from Table XIV that when using the values of the surface energy of PS reported in Table X, taking into consideration the contact angles made by one drop of diiodomethane and one drop of another liquid, the extrapolated values corroborate the ones measured directly with the pendant drop method. The results shown in Table XIV confirm the conclusion from the surface energy analysis reported above (see the section entitled "Surface Energy Using Geometric Mean, Harmonic Mean, and Neumann's Equation"). In order to obtain reliable values of surface energy using harmonic mean and geometric mean equations, a pair of polar-non polar liquids should be used.

CONCLUSIONS

In this work, contact angles formed by drops of diethylene glycol, ethylene glycol, formamide diiodomethane, and water and mercury on surfaces of polypropylene, polystyrene, and a liquid crystaline polymer were obtained at 20°C. The values reported corroborated well the values published in the literature.

The surface energy of polypropylene, polystyrene, and the liquid crystal polymer were evaluated using the following three methods: harmonic mean equation and geometric mean equation, using the values of the different pairs of contact angles obtained here; and Neumann's equation, using the different values of contact angles obtained here. It was shown that the values of surface energy generated by those three methods

Figure 5   Determination of the dispersion γ^d and the polar γ^p components of the surface tension of the polymers at room temperature considering all the testing liquids and using the geometric mean equation. Different values of γ^d for diiodomethane ([a-c] in Table I) were used in (a), (b), and (c), respectively.

Table XII   Surface Tension (mN/m) and Its Dispersion γ^d and Polar γ^p Components at 20°C for the Different Polymers Calculated with the Harmonic Mean, Geometric Mean, and Neumann's Equations Considering All the Testing Liquids at Once

Polymer	Harmonic				Geometric				Neumann (γ)
	γ^d	γ^p	γ	x^p	γ^d	γ^p	γ	x^p	
PP[a]	12.5	7.35	19.9	0.37	19.6	4.17	23.8	0.18	26.4
PP[b]	23.6	1.99	25.6	0.08	21.4	3.24	24.6	0.13	—
PP[c]	35.0	0.362	35.4	0.01	23.0	2.58	25.6	0.10	—
PS[a]	18.0	6.20	24.2	0.26	35.4	0.914	36.3	0.03	32.1
PS[b]	30.8	1.69	32.5	0.05	35.6	0.794	36.4	0.02	—
PS[c]	39.6	0.688	40.2	0.02	36.3	0.663	37.0	0.02	—
VECTRA[a]	19.9	9.82	29.7	0.33	29.1	6.84	35.9	0.19	37.2
VECTRA[b]	32.1	4.10	36.2	0.11	31.4	5.63	37.0	0.15	—
VECTRA[c]	64.0	0.186	64.2	0.0029	33.6	4.67	38.3	0.12	—

[a–c] Using the different values of the dispersion and polar components of surface tension of diiodomethane indicated in Table I.

depend on the choice of liquids used for the contact angle measurements, except when a pair of liquids containing diiodomethane was used. The results indicated that in order to obtain reliable values of surface energy using the harmonic and geometric mean equations, a pair of polar and nonpolar liquids should be used. The average values of surface energy obtained when diiodomethane was used as one of the testing liquids, considering the harmonic mean, the geometric mean, and Neumann's equations were, respectively, 38.1, 37.5, and 36.8 mN/m for PP; 46.5, 49.0, and 46.7 mN/m for PS; and 49.1, 48.0, and 48.0 mN/m for the LCP.

Table XIII $(\gamma^d)^{1/2}/\gamma$ Ratio in $(mN/m)^{-1/2}$ Calculated Using the Results in Table XII for the Different Polymers Compared to the Value Obtained from the Fowkes' Method

Polymer	Harmonic $(\gamma^d)^{1/2}/\gamma$	Geometric $(\gamma^d)^{1/2}/\gamma$	Fowkes $(\gamma^d)^{1/2}/\gamma$
PP[a]	0.18	0.19	0.18
PP[b]	0.19	0.19	0.18
PP[c]	0.17	0.19	0.18
PS[a]	0.18	0.16	0.15
PS[b]	0.17	0.16	0.15
PS[c]	0.16	0.16	0.15
VECTRA[a]	0.15	0.15	0.14
VECTRA[b]	0.16	0.15	0.14
VECTRA[c]	0.12	0.15	0.15

[a–c] Using the different values of the dispersion and polar components of surface tension of diiodomethane indicated in Table I.

Different methods, taking into account the values of contact angles formed by drops of all the different liquids studied here, were also tested for the three equations (geometric mean equation, harmonic mean equation, and Neumann's equation). The results generated by the geometric mean and Neumann's equations were in good agreement. However, a large scatter was obtained for the results generated by the harmonic mean equation.

The critical surface tensions of PP, PS, and the VECTRA were evaluated at 20°C according to the methods of Zisman and Saito, using the values of contact angle obtained here. It was shown that the values of critical surface tensions for each polymer obtained according to methods of Zisman and Saito corroborated the results of surface energies found using the geometric mean and Neumann's equation methods.

The values of surface energy of PS at 20°C obtained from the harmonic mean, the geometric mean, and Neumann's equations were used to evaluate the surface tension of the same material at higher temperatures using the relation that exists between $d\gamma/dT$ in the glassy and rubbery states. These values were compared to experimental data obtained using a pendant drop apparatus. It was shown that, when using the value of surface energy of PS calculated from the contact angles formed by one drop of diiodomethane and one drop of another liquid, the extrapolated values of surface tension in the rubbery state compared well with the ones measured directly with the pendant drop apparatus; the same behavior

Table XIV   Surface Tension (mN/m) Extrapolated to Different Temperatures (°C) Compared to Those Measured with the Pendant Drop Method for PS

Temperature	Table	Harmonic	Geometric	Neumann	Experimental
185	10/6	34.9	37.4	35.1	35.1
185	12[a]	12.6	24.7	20.5	35.1
185	12[b]	20.9	24.8	—	35.1
185	12[c]	28.6	25.4	—	35.1
195	10/6	33.7	36.2	33.9	36.0
195	12[a]	11.4	23.5	19.3	36.0
195	12[b]	19.7	23.6	—	36.0
195	12[c]	27.4	24.2	—	36.0
200	10/6	33.1	35.6	33.3	32.8
200	12[a]	10.8	22.9	18.7	32.8
200	12[b]	19.1	23.0	—	32.8
200	12[c]	26.8	23.6	—	32.8
215	10/6	31.3	33.8	31.5	32.1
215	12[a]	9.01	21.1	16.9	32.1
215	12[b]	17.3	21.2	—	32.1
215	12[c]	25.0	21.8	—	32.1

[a–c] Using the different values of the dispersion and polar components of surface tension of diiodomethane indicated in Table I.

was not seen when the values of surface energy of PS used in the extrapolation was calculated using all the values of contact angle formed by drops of all the different liquids.

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