

Evaluation of Surface Free Energy for PMMA Films

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Received 17 July 2007; accepted 18 October 2007

DOI 10.1002/app.27687

Published online 28 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Surface free energy (SFE) is a property resulted from the chemical structure and the orientation of the molecules at the surface boundary of the materials. For solids, it can be calculated from the contact angles of liquid drops with known surface tension, formed on the solid surface. There are various SFE evaluation methods based on different theoretical assumptions. In this study, SFE and the dispersive, polar, acidic and basic components of the SFE of a polymeric material, poly(methyl methacrylate) (PMMA), were calculated by using Zisman,

Saito, Fowkes, Berthelot, Geometric mean, Harmonic mean, and Acid–base approaches. The results obtained from various liquid couples or triplets were compared. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 438–446, 2008

Key words: surface free energy; surface tension; acidic-basic components; dispersive component; polar components; contact angle; geometric mean; harmonic mean; Zisman; Saito; Fowkes; Berthelot; PMMA

INTRODUCTION

Surface is the crucial part of a material in various applications, since it contacts first with the environment. Therefore, the properties of the surface such as chemical structure, homogeneity, crystallinity, and the level of cohesive attractions between atoms and molecules, as well as the physical shape, give quite a lot of information about its reactions toward its surroundings. In the field of medicine when materials are used as prostheses, implants, or medical devices, the interactions with blood or with tissue start at the surface and lead to further reactions.^{1,2}

For any material, the molecules in the bulk have no net force acting on them, while the ones at the surface encounter a net force inward. For solids, this force is called as “surface free energy” (SFE) and defined as the amount of energy required to change the surface area of a material by one meter square. Knowing the SFE value of a material, one can predict whether the material is wettable or not by a certain liquid. Solids, which have the similar or higher SFE than that of a liquid’s SFE are wettable by that liquid.³ Contact angle (θ) of a liquid drop is the angle formed by the surface and the tangent of the drop at the point it touches to the surface. Contact angle indicates the strength of noncovalent forces between the liquid and the first monolayer of the material. The liquid drop spreads on the solid and wets the surface, in case of strong interactions between phases.⁴ Zero contact angles mean a strong

interaction between the phases and complete wetting by the liquids.

SFE can be obtained by using different approaches. All these methods are based on contact angle measurements, but they may have discrepancies in the results. Zisman method uses the plots of cosine θ values versus SFE of liquids.^{1,4,5} For accurate results, more than three test liquids data is suggested. Extrapolation to the point where contact angle is zero ($\cos \theta = 1$) indicates complete wetting and gives the critical SFE of the solid. The used test liquids should not interact with the surface, and they need to constitute a homologous series for proper results.¹

Saito¹ proposed another plot, in which $\log(1 + \cos \theta)$ values are plotted versus \log SFE of liquids which is shown as γ_{lv} . The critical SFE of the material is found from the point where θ is zero as in the Zisman plot.

Berthelot³ approximation is based on work of adhesion for a solid–liquid interface obtained from Young’s equation which is given as follows:

$$\gamma_{sv} = \gamma_{sl} + (\gamma_{lv} \cos \theta) \quad (1)$$

where, γ_{sv} , γ_{sl} , and γ_{lv} are the vectors between solid–vapor, solid–liquid, and liquid–vapor, respectively. For low-energy surfaces, γ_{sv} can be shown as γ_s , and γ_{lv} can be shown as γ_l , since the equilibrium film pressures can be neglected.³

Work of adhesion, W_{sl} , for a solid–liquid interface is defined as follows:

$$W_{sl} = \gamma_l + \gamma_s - \gamma_{sl} \quad (2)$$

Combination of 1 and 2 redefines the work of adhesion as follows:

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$$W_{sl} = \gamma_l(1 + \cos \theta) \quad (3)$$

Berthelot³ proposed SFE estimation by approximating the work of adhesion for a solid–liquid interface by a geometric mean as given below:

$$W_{sl} = 2\sqrt{\gamma_l\gamma_s} \quad (4)$$

Combination of eqs. (3) and (4) yields,

$$\cos \theta = -1 + 2\sqrt{\frac{\gamma_s}{\gamma_l}} \quad (5)$$

This equation is a very simple tool to calculate the SFE of a solid, since it requires one data obtained from one liquid. However, use of one liquid's data may not be confident and this equation over-estimates the pair interaction between unlike molecules, therefore largely deviated values are obtained when different liquids are used.³

SFE gives brief information about the attraction forces of the molecules existing on a solid surface. But the types of these attractions, such as dispersive (*d*) and polar (*p*), are also important in compatibility of a material with its surroundings. SFE is the total value of these components.

$$\gamma_{\text{Total}} = \gamma^d + \gamma^p \quad (6)$$

Two approximations, Geometric mean and Harmonic mean, can be used for determination of the components of SFE. These equations are given as follows:

Harmonic mean equation:

$$\gamma_{sl} = \gamma_s + \gamma_{lv} - 4 \left(\frac{\gamma_{lv}^d \gamma_s^d}{\gamma_{lv}^d + \gamma_s^d} + \frac{\gamma_{lv}^p \gamma_s^p}{\gamma_{lv}^p + \gamma_s^p} \right) \quad (7)$$

Geometric mean equation:

$$\gamma_{sl} = \gamma_s + \gamma_{lv} - 2 \left((\gamma_{lv}^d \gamma_s^d)^{1/2} + (\gamma_{lv}^p \gamma_s^p)^{1/2} \right) \quad (8)$$

Combination of eqs. (1) and (7) leads to:

$$\gamma_{lv}(1 + \cos \theta) = 4 \left(\frac{\gamma_{lv}^d \gamma_s^d}{\gamma_{lv}^d + \gamma_s^d} + \frac{\gamma_{lv}^p \gamma_s^p}{\gamma_{lv}^p + \gamma_s^p} \right) \quad (9)$$

Combination of eqs. (1) and (8) leads to:

$$\gamma_{lv}(1 + \cos \theta) = 2 \left((\gamma_{lv}^d \gamma_s^d)^{1/2} + (\gamma_{lv}^p \gamma_s^p)^{1/2} \right) \quad (10)$$

The use of eqs. (9) and (10) would require contact angles as well as dispersive and polar components of SFEs of two test liquids. Solving the equations would lead to γ_s^d and γ_s^p values for the surface. This is possible by using values of liquid pairs. However,

it is also possible to use values of many liquids and obtain a plot. For this purpose, eq. (10) can be rewritten in the following form:

$$\frac{(1 + \cos \theta)\gamma_{lv}}{2\sqrt{\gamma_{lv}^d}} = \sqrt{\gamma_s^d} + \sqrt{\gamma_s^p} \left(\frac{\sqrt{\gamma_{lv}^p}}{\sqrt{\gamma_{lv}^d}} \right) \quad (11)$$

In this equation, the parameters on the left side, $y = [(1 + \cos \theta)\gamma_{lv}] / 2\sqrt{\gamma_{lv}^d}$, can be plotted versus the right side $x = \sqrt{\gamma_{lv}^p} / \sqrt{\gamma_{lv}^d}$.

From the plot of *y* versus *x*, the dispersive and polar components of the solid SFE can be calculated from the intercept and slope.

It is also possible to find SFE from one liquid's data as in the case of Berthelot's equation. However, this time only the dispersive component of the solid SFE is obtained. Fowkes proposed that,

$$W_{sl} = 2\sqrt{\gamma_1^d \gamma_s^d} \quad (12)$$

The combination of eqs. (3) and (12) yields,

$$\cos \theta = -1 + 2\sqrt{\gamma_s^d} \frac{\sqrt{\gamma_l^d}}{\gamma_l} \quad (13)$$

When the contact angle of a liquid on a surface is known, dispersive component can be found by using eq. (13). For using multiple test liquids, a plot of $\cos \theta$ versus $[\sqrt{\gamma_l^d}/\gamma_l]$ can be drawn and this would give the dispersive component from the slope.

A higher value of dispersive component than that of the polar component would mean the surface has apolar character. This apolar character is generally observed for the hydrocarbons, which dominantly have almost zero polar but Van der Waals attractive forces between molecules.

The polar component of SFE also has two sub-groups as acidic and basic components. In the acid–base approach, the perception is such that molecules at the solid–liquid interface can interact through electron donor/acceptor manner.³ Consequently according to acid–base approach SFE is divided into Lifshitz-van der Waals (γ^{LW}) and acid–base (γ^{AB}) components corresponding to dispersive and polar components, respectively. The acid–base (polar) component is composed of acidic (γ^+) and basic (γ^-) components. Acidic component is the electron acceptor parameter and basic component is the electron donor parameter. The acidic component of the solid interacts with the basic component of the liquid, and the basic component of the solid interacts with the acidic component of the liquid. If the acid–base component is zero then both the acidic and

TABLE I
Contact Angle, SFE, Dispersive and Polar Components of Test Liquids

Symbol	Liquids	Average contact angle (θ)	γ_L^d (mJ/m ²)	γ_L^p (mJ/m ²)	γ_{Total} (mJ/m ²)
W	Water	63.51 \pm 0.86	21.8	51	72.8
G	Glycerol	53.02 \pm 2.04	34	30	64
F	Formamide	49.11 \pm 2.13	39.5	18.7	58.2
Dm ^a	Diiodomethane	32.46 \pm 2.01	44.1	6.7	50.8
Dm ^b	Diiodomethane	32.46 \pm 2.01	50.8	0	50.8
E	Ethylene glycol	40.36 \pm 0.91	29	19	48
B	Bromonaphthalene	26.63 \pm 1.33	44.4	0	44.4
De	Diethylene glycol	33.25 \pm 1.96	31.7	12.7	44.4
DMSO	Dimethyl sulfoxide	32.32 \pm 1.92	36	8	44
T	Tricresylphosphate	25.84 \pm 1.73	36.2	4.5	40.7

^a From Ref. 1.

^b From Ref. 8.

basic components are also zero, and the surface is said to be apolar. When acidic or basic components have a value, then the surface is considered as monopolar, and if both have significant values then bipolar.

In the acid-base approach, the work of adhesion is given as follows:

$$W_{sl} = 2 \left(\sqrt{\gamma_l^{LW} \gamma_s^{LW}} + \sqrt{\gamma_l^+ \gamma_s^-} + \sqrt{\gamma_s^+ \gamma_l^-} \right) \quad (14)$$

This leads to eq. (15).

$$(\cos \theta + 1) \gamma_l = 2 \left(\sqrt{\gamma_l^{LW} \gamma_s^{LW}} + \sqrt{\gamma_l^+ \gamma_s^-} + \sqrt{\gamma_s^+ \gamma_l^-} \right) \quad (15)$$

To solve eq. (15), data obtained from at least three liquids are essential. Depending on the choices of these liquid triplets, quite different results can be obtained. Use of at least one liquid with no polar component is suggested.³

The evaluation of SFE is still an uncompleted discussion of the science community.^{6,7} This study aims to find SFE and its components for PMMA by using different approaches and compares the obtained results.

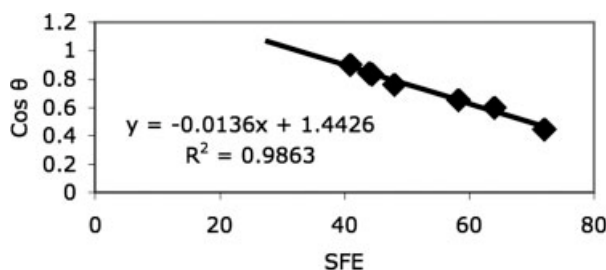


Figure 1 Zisman plot.

MATERIALS AND METHODS

Test liquids and polymer

Poly(methyl methacrylate) (PMMA), $[-CH_2C(CH_3)(CO_2CH_3)-]_n$, with a molecular weight of 120 kDa, was purchased from Aldrich, Steinheim, Germany and used to prepare films. Chloroform ($CHCl_3$) was purchased from Lab-Scan, Dublin, Ireland and used as a solvent for PMMA. Tricresyl phosphate ($(CH_3C_6H_4O)_3PO$) and bromo naphthalene ($C_{10}H_7Br$) were products of Aldrich (Steinheim, Germany), aniline ($C_6H_5NH_2$) and formamide ($HCONH_2$) were products of Merck (Darmstadt, Germany). Diiodomethane (CH_2I_2), glycerol ($CH_2OHCHOHCH_2OH$), ethylene glycol ($HOCH_2CH_2OH$), and dimethyl sulfoxide (C_2H_6OS) were products of Acros (NJ), and diethylene glycol ($O(CH_2CH_2OH)_2$) was a product of Fischer (Fair Lawn, NJ). In all the experiments deionized triple distilled water was used. All the liquids were of reagent grade.

Preparation of PMMA films

Thin films were prepared by solvent casting method. Solutions containing 20% (w/w) PMMA in chloroform were prepared at room temperature and placed on microscope slides and let to dry. Solvent evaporation was achieved in an oven at room temperature

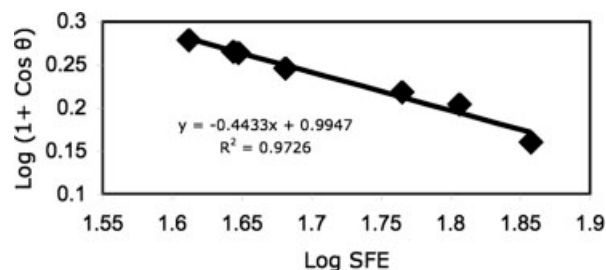


Figure 2 Saito plot.

TABLE II
Dispersive and Polar Components of SFE of PMMA Obtained from Geometric and Harmonic Mean Equations

Liquid couple	Geometric mean			Harmonic mean		
	γ_L^d (mJ/m ²)	γ_L^p (mJ/m ²)	γ_{Total} (mJ/m ²)	γ_L^d (mJ/m ²)	γ_L^p (mJ/m ²)	γ_{Total} (mJ/m ²)
W-G	23.37	17.73	41.1	20	23.07	43.07
W-F	21.83	18.61	40.44	21.6	22.6	44.2
W-E	15.98	22.62	38.6	15.68	25.94	41.62
W-De	19.27	20.25	39.52	19.7	23.4	43.1
W-DMSO	22.62	18.15	40.77	24.3	20.92	45.22
W-T	25.52	16.74	42.26	27.6	19.6	47.2
G-F	21.63	19.4	41.03	23	19.7	42.7
G-De	16.28	25.61	41.89	19.7	23.41	43.11
G-DMSO	22.34	18.71	41.05	25	17.91	42.91
G-T	25.58	15.78	41.36	28.2	15.47	43.67
F-DMSO	23.54	16.47	40.01	26	14.84	40.84
F-T	26.8	13.3	40.1	28.7	12.7	41.4
E-De	25.49	11.97	37.46	24.8	13.16	37.96
E-DMSO	27.55	10.35	37.9	27.8	10.95	38.75
E-T	29	9.26	38.26	29.4	9.98	39.38
De-DMSO	28.94	8.65	37.59	29.2	8.76	37.96
De-T	30	7.74	37.74	30.2	8.02	38.22
DMSO-T	29.4	8.12	37.52	30.6	7.07	37.67
B-W	39.82	10.52	50.34	39.93	16.05	55.98
B-G	39.82	6.97	46.78	39.93	9.58	49.51
B-F	39.82	3.88	43.7	39.93	5.49	45.42
B-E	39.82	3.63	43.45	39.93	5.63	45.56
B-De	39.82	0.38	40.2	39.93	3.45	43.38
B-DMSO	39.82	0.93	40.75	39.93	1.65	41.58
B-T	39.82	0.11	39.93	39.93	0.38	40.31
Dm-W ^a	43.17	9.45	52.63	43.44	15.35	58.79
Dm-G ^a	43.17	5.58	48.75	43.44	8.38	51.82
Dm-F ^a	43.17	2.55	45.72	43.44	4.2	47.64
Dm-E ^a	43.17	2.51	45.68	43.44	4.68	48.12
Dm-De ^a	43.17	1.12	44.29	43.44	2.45	45.89
Dm-DMSO ^a	43.17	0.17	43.34	43.44	0.66	44.1
Dm-W ^b	31.46	13.72	45.18	32	17.85	49.85
Dm-G ^b	33.87	9.99	43.86	33.7	12.1	45.8
Dm-F ^b	39.11	4.2	43.31	36.6	6.96	43.56
Dm-E ^b	39.79	3.64	43.43	36.9	6.6	43.5
Dm-B ^b	39.81	3.62	43.43	39.93	3.89	43.82
Dm-De ^b	45.57	0.59	46.16	41.3	3.03	44.33
Average	32.50 ± 9.03	9.81 ± 7.27	42.31 ± 3.63	32.76 ± 8.47	11.51 ± 7.46	44.27 ± 4.66

^a Dm having $\gamma^d = 50.8$ and $\gamma^p = 0$.

^b Dm having $\gamma^d = 44.1$ and $\gamma^p = 6.70$.

for 5–7 days, and then placed in vacuum oven at room temperature to remove the residual solvent-if exist.

Contact angle measurements

Ten microliters of liquids were placed on samples by a microsyringe, and the images of droplets were obtained instantaneously by using a digital camera (Fujifilm F FX-6900 Zoom-E). Static contact angles were detected from the images of droplets by using Windows Excel and Paint computer programs. For this purpose the tangent lines to the droplets from both sides and the baseline were drawn in the paint program to obtain the intersection coordinate values. These values were used in Windows Excel program to calculate contact angles. For statistical approach,

for each liquid at least five (mostly 8) values were measured. Drops which had unsymmetrical forms (difference between the angles of both sides being higher than 5°) were excluded. The temperature of the environment was fixed at 20°C. The contact angle results, as well as the polar and dispersive component values of the liquids are given in Table I.

Surface free energy determination

Different methods, namely Zisman, Saito, Fowkes, Berthelot, Geometric and Harmonic mean, and Acid–base approach, were used to find the SFE and components of SFE for PMMA. In the calculations, Windows Excel program and Mathpad (Mark Widholm) program, working in the MAC OS environment were used.

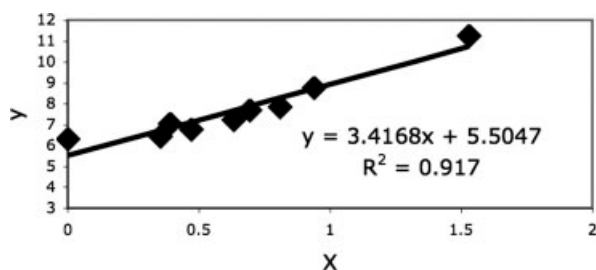


Figure 3 The plot obtained from eq. (11) using all the test liquids data.

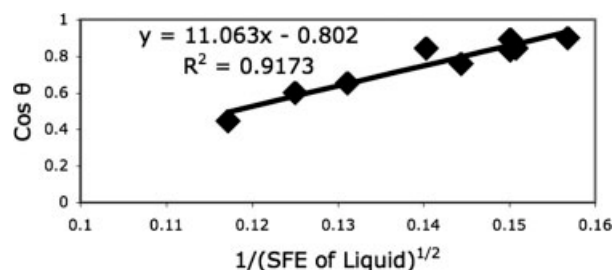


Figure 4 Application of data using Berthelot's approach.

RESULTS AND DISCUSSION

Zisman and Saito approaches

Contact angle values obtained from different liquids were used in Zisman (Fig. 1) and Saito (Fig. 2) plots, and SFE values of 32.5 and 36.7 mJ/m^2 were obtained, respectively. The values are quite close, but still about 4 mJ/m^2 difference was resulted.

Geometric and harmonic mean approaches

Geometric mean equation was applied for all possible combinations of nine test liquids (Table II). Three of the pair-combinations (glycerol-ethyleneglycol, formamide-ethyleneglycol, and formamide-diethyleneglycol) were deviated quite a lot and not shown in the table. The common property of these three pairs is the presence of hydroxyl functionality in one of the liquids. These groups might interact with acrylate groups of PMMA surfaces causing deviated results. However, they gave in-range results when used with other liquids. In the literature, it was defined that use of a pair-liquid in which one is highly polar and the other is almost nonpolar gave better results in the calculations.¹ Keeping in mind the effect of difference in polarity, it can be assumed that water-formamide pair gave the most accurate value, since the polarity difference is high when

compared with other pairs. By using this pair, dispersive and polar components of PMMA were found as 21.83 and 18.61 mJ/m^2 , respectively, and the total SFE was found as 40.44 mJ/m^2 . Even though, this SFE is close to literature values of PMMA, the ratio of polar to dispersive components is found to be higher than the literature, where PMMA was given as a highly apolar polymer.^{5,6} For Dm, two different literature data (one considers Dm as a completely dispersive liquid) were applied.^{1,6} The polar components of Dm were taken as 6.7 and 0 mJ/m^2 , and the SFE values were found in the ranges of 43.31–46.16 mJ/m^2 and 43.34–52.63 mJ/m^2 depending on the partner liquid, respectively. When all pairs are considered, the average values for total SFE, for polar, and for dispersive components are calculated as 42.31, 9.81, and 32.50 mJ/m^2 , respectively.

Geometric mean approach, when applied for all liquids graphically, SFE of PMMA was obtained as 41.97 mJ/m^2 having γ_s^d and γ_s^p components as 30.30 and 11.67 mJ/m^2 , respectively, (Fig. 3).

Harmonic mean approach results are as given: the total SFE values varied between 37.67 and 58.79 mJ/m^2 resulting in an average value of 44.27 mJ/m^2 (Table II). The pair liquids having high polar components (e.g., W and G) demonstrated very high γ_s^p for PMMA (in the range of 15–25 mJ/m^2), which may not be accepted as correct values. The lowest polar and the highest dispersive components were

TABLE III
The SFE Results Obtained from Berthelot's Method Using Single Liquid Data

Liquid	PMMA SFE (mJ/m^2)
W	38.06
G	41.04
F	39.84
D	43.17
E	37.25
De	37.43
B	39.82
DMSO	37.44
T	36.73
Average	38.98 \pm 2.15

TABLE IV
The Results Obtained from Fowkes Method Using Single Liquids

Liquid	Dispersive component (mJ/m^2)
W	127.09
G	77.25
F	59.45
D	49.73
E	61.66
De	52.42
B	39.82
DMSO	45.77
T	41.30
Average	61.61 \pm 27.16

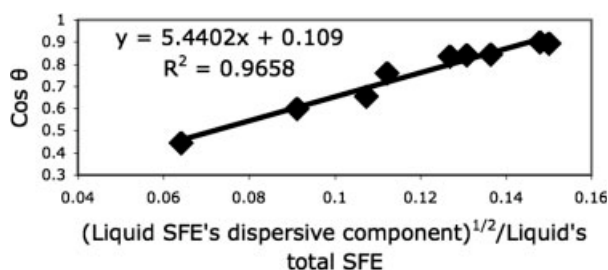


Figure 5 Application of data using Fowkes approach.

obtained as 0.38 and 43.44 mJ/m², respectively for PMMA.

The results obtained from Geometric and Harmonic mean approaches, demonstrated large deviations and were significantly different from each other. Also in literature, highly scattered values are reported when measurements were carried out with various liquids. For polypropylene, by using five liquids (water, mercury, formamide, diiodomethane, and ethyleneglycol), the reported values obtained from Harmonic mean method, were given in the range of 7.23–34.5 mJ/m² for dispersive component, 5.76–20.9 mJ/m² for polar component, and 23.7–40.3 mJ/m² for total SFE.¹ On the other hand, the same values obtained from Geometric mean method were reported as 7.43–40.6 mJ/m² for dispersive component, 0.392–11.8 mJ/m² for polar component, and 19.2–40.3 mJ/m² for total SFE.

In our study, nine liquids were used and all the possible combinations were estimated. Therefore, it is very logical to obtain such a variation in the results since SFE estimation depends on the choice of liquid pairs or triplets and the applied methods. The important point here is that, the science community still needs to improve SFE estimation methods that would

give precise results and would be in good agreement so that all the work would be simplified.

Berthelot's approach

Berthelot's approach was applied by using single liquids and the obtained results are given in Table III. The results are relatively precise and accurate compared with other methods. The average SFE value was found as 38.9 mJ/m².

On the other hand, when all the liquids data are plotted (Fig. 4), the total SFE was found to be 30.60 mJ/m² which is even lower than Zisman plot result.

Fowkes approach

Fowkes approach gives only the dispersive component of SFE, and no convenient results were obtained from Fowkes, neither when the liquids were applied individually (Table IV) nor when all liquids were used in one plot (Fig. 5).

The values of γ_s^d ranged from 39.82 to 127.09 mJ/m². The average value was obtained as 61.61 ± 27.16 mJ/m² with a very high standard deviation, indicating the inapplicability of this method to PMMA surfaces. When all the liquids data are applied in the plot, γ_s^d was calculated as 7.39 mJ/m².

Acid–base approach

In acid–base approach calculations, values obtained from literature^{3,5,6,9} were used for the test liquids as shown. These values of acidic basic components are given in Table V.

The results obtained for PMMA surfaces by using these different liquids data are shown in Table VI. It is clearly seen that the choice of liquid triplets and

TABLE V
Acidic, Basic Components of Surface Free Energies of Test Liquids
Obtained from Literature^{3,5,6,9}

Liquid	γ_L (mJ/m ²)	$\gamma^{LW} (\gamma^d)$ (mJ/m ²)	γ_L^- (mJ/m ²)	γ_L^+ (mJ/m ²)	γ_L^{AB} (mJ/m ²)
Water	72.8	26.25	11.16	48.5	46.55
Water ^a	72.8	21.8	25.5	25.5	51
Glycerol	64	35.05	7.33	27.8	28.55
Glycerol ^a	64	34	57.4	3.92	30
Formamide	58	35.5	11.3	11.3	22.5
Formamide ^a	58	39	39.6	2.28	19
Diiodomethane	50.8	50.8	0	0	0
Ethylene glycol	48	33.9	51.6	0.97	14.1
Ethylene glycol ^a	48	29	47	1.92	19
Bromonaphtalene	44.4	44.4	0	0	0
Dimethyl sulfoxide	42.93	32.3	763	0.037	10.63
Dimethyl sulfoxide ^a	44	36	32	0.5	8

^a From Refs. 3 and 5.

TABLE VI
Surface Free Energy Components of PMMA Surface
Calculated by Acid-Base Approach

Liquid triplets	γ_s (mJ/m ²)	γ_s^{LW} (γ_s^d) (mJ/m ²)	γ_s^- (mJ/m ²)	γ_s^+ (mJ/m ²)	γ_s^{AB} (mJ/m ²)
W-G-F	40.113	28.909	6.491	4.835	11.205
W-G-E	36.267	30.016	9.200	1.062	6.251
W-G-DMSO	32.553	30.748	11.218	0.073	1.805
W-F-Dm	44.206	43.173	7.918	0.034	1.032
W-F-E	41.643	39.28	7.486	0.186	2.363
W-F-B	41.714	39.818	7.546	0.119	1.896
W-F-DMSO	41.921	41.419	7.724	0.008	0.501
W-Dm-E	44.23	43.173	6.895	0.04	1.056
W-Dm-B	46.634	41.592	5.155	1.233	5.042
W-Dm-DMSO	43.513	43.173	7.257	0.004	0.34
W-E-B	41.991	39.818	7.423	0.159	2.173
W-E-DMSO	46.546	46.479	6.432	0	0.068
W-B-DMSO	40.479	39.818	8.182	0.013	0.661
G-F-Dm	45.623	43.173	4.103	0.366	2.45
G-F-B	43.894	39.818	4.578	0.907	4.076
G-Dm-E	44.314	43.173	4.882	0.067	1.141
G-Dm-B	45.543	41.592	3.847	1.014	3.951
G-Dm-DMSO	43.477	43.173	5.329	0.004	0.303
G-E-B	41.947	39.818	5.797	0.195	2.129
G-E-DMSO	48.333	48.296	3.693	0	0.037
G-B-DMSO	40.423	39.818	6.627	0.014	0.605
F-Dm-E	44.288	43.173	5.75	0.054	1.115
F-Dm-B	45.641	41.592	2.025	2.025	4.049
F-Dm-DMSO	43.502	43.173	6.586	0.004	0.329
F-E-B	41.988	39.818	7.228	0.163	2.17
F-E-DMSO	48.111	48.084	3.971	0	0.027
F-B-DMSO	40.501	39.818	8.865	0.013	0.683
Dm-E-B	41.707	41.592	0.008	0.419	0.115
Dm-E-DMSO	43.587	43.173	13.563	0.003	0.414
Dm-B-DMSO	41.592	41.592	0	0.011	0
E-B-DMSO	40.81	39.818	23.944	0.010	0.992
Using ^a values in Table V					
W-G-F	37.83	18.114	16.488	5.894	19.716
W-G-Dm	48.702	43.173	12.78	0.598	5.529
W-G-B	46.783	39.818	13.174	0.921	6.965
W-G-DMSO	37.338	11.554	17.98	9.243	25.783
W-F-Dm	45.305	43.173	20.984	0.054	0.054
W-F-E	37.289	26.158	19.726	1.57	11.132
W-F-B	40.12	39.818	20.756	0.001	0.302
W-Dm-E	44.518	43.173	17.537	0.026	1.344
W-Dm-B	51.54	41.592	4.974	4.974	9.948
W-E-B	42.832	39.818	17.919	0.127	3.014
W-E-DMSO	36.718	24.166	20.036	1.966	12.551
G-F-DMSO	41.063	20.237	43.393	2.499	20.826
G-Dm-B	43.077	41.592	0.194	2.842	1.485
F-Dm-E	45.677	43.173	6.796	0.231	2.503
F-Dm-B	42.237	41.592	0.077	1.344	0.645
F-Dm-DMSO	55.242	43.173	61.193	0.595	12.068
F-E-B	43.015	39.818	16.272	0.157	3.197
F-E-DMSO	35.603	32.612	53.464	0.042	2.991
Dm-E-B	42.045	41.592	0.046	1.122	0.453
Dm-B-DMSO	41.619	41.592	0.002	0.109	0.027

the data of the liquids extremely affect the results. Some results indicate that PMMA has a significant polarity with considerable acidic and basic components implying that it is bipolar, while some results indicate that the polymer has mainly dispersive character with a very small polarity.

It was observed that, quite high deviations appear when W-G or E-DMSO are present as couples in the triplets. In the choice of liquid triplets it was suggested to use at least one completely dispersive liquid,³ however, this was not the trend in this study. It was observed that, having one purely

TABLE VII
SFE Results and the Ranges of Results of Different Liquid Combinations

Method	γ_s^{LW} (γ_s^d) (mJ/m ²)	γ_s^{AB} (γ_s^p) (mJ/m ²)	γ_s^- (mJ/m ²)	γ_s^+ (mJ/m ²)	γ_s (mJ/m ²)
Zisman					32.50
Saito					36.70
Geometric mean	15.98–45.57 Av = 32.50 ± 9.03	0.11–25.61 Av = 9.81 ± 7.27			37.46–52.63 Av = 42.31 ± 3.63
Harmonic mean	15.68–43.44 Av = 32.76 ± 8.47	0.38–25.94 Av = 11.51 ± 7.46			37.67–58.79 Av = 44.27 ± 4.66
Acid–base approach	28.91–48.30 Av = 40.91 ± 4.34	0.00–11.21 Av = 1.90 ± 2.35	0.00–13.56 Av = 6.77 ± 4.24	0.00–4.84 Av = 0.42 ± 0.95	32.55–48.33 Av = 42.81 ± 3.19
Acid–base approach (using ^a values in Table V)	11.55–43.17 Av = 35.23 ± 11.10	0.02–25.78 Av = 7.86 ± 8.83	0.00–61.19 Av = 18.61 ± 20.86	0.00–9.24 Av = 1.96 ± 2.72	35.60–55.24 Av = 43.10 ± 5.20
Berthelot (all liquids together)					30.60
Berthelot (single liquid results)					36.73–43.17
Fowkes (all liquids together)	7.39				
Fowkes (single liquid results)	39.82–127.09				

dispersive liquid (e.g., Dm or B) in the triplets resulted in either similar values or no results. As a result, the ranges and the average values for SFE and the components of SFE for PMMA surface calculated from different approaches are summarized in Table VII.

CONCLUSION

Surface properties of the polymers are very important for their compatibility with their environments, and the one important parameter is SFE. SFE and its dispersive and polar (acidic–basic) components are affected by crystallinity, thickness, ratio of the functional groups, etc.^{8,10,11} However, the evaluation methods are not clearly defined and they may result in deviated values for the same material. The results obtained in this study, clearly indicates this point. SFE values given in literature are generally based on the data obtained from few liquids. Actually, the given value may not be the real value, since the result depends on the type of the liquids. Therefore, if the surface and the SFE are important parameters, it is advisable to search suitable liquids and methods for a specific surface. This would be particularly useful when surface is going to be modified. Even though, the work of Shimizu and Demarquette¹ proposed that better results would be obtained when polar and nonpolar liquids are used as a couple in the geometric mean equation, in this study it is demonstrated that liquids with similar polarities may also give good results.

Most of the methods are well approximations of the total SFE. However, when it comes down to component's estimation, the methods are in question. It is evident that the result of SFE is more affected by the choices of liquid couples, when geometric mean or harmonic mean equation is applied. For SFE components evaluation, acid–base approach is observed as the more precise and accurate method when the correct liquids are chosen.

Results of acid–base approach can be improved by considering the theoretical approaches given by Della Volpe and Siboni.^{6,12} In addition, it is also mentioned that better results can be obtained when liquid combinations are chosen according to the condition number, which is a coefficient whose quantitative knowledge is related to the reliability of the liquid combinations. However in our study, the aim was to compare the results of the basic acid–base equation obtained from different liquid combinations.

When all the data in this article are considered, the prepared PMMA surface appears to have higher polarity than the literature values.^{5,6} This may be explained by conformational changes of the molecules, which differ by the type of solvent and the surface used in the solvent casting method.

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