Comparison of Surface Energies Using Various Approaches and Their Suitability

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ABSTRACT: The surface chemistry and surface energies of materials are important to performance of many products and processes—sometimes in as yet unrecognized ways. This article has been written for the researchers who wish to calculate solid surface energy (SE) from contact angle data. In this article, we describe various methods of calculations and their assumptions. The theoretical and experimental approaches for understanding the solid surface free energy using various methods are discussed in this article. Researchers concerned with many fields such as printing, dyeing, coating, adhesion, pharmaceuticals, composite materials, textiles, polymers, and ceramics should have interest in this topic. SE calculated by various methods for polyethylene surface treated in air plasma is discussed. Using contact angle data, the values of surface roughness using Wenzels equation, have been obtained and correlated to surface roughness calculated from AFM data. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3707–3717, 2008

Key words: contact angle; surface energy; plasma; polyethylene; AFM; surface roughness

INTRODUCTION

The origin of surface tensions arises from the existence of unbalanced intermolecular forces among molecules at the interface. The characterization and quantitative description of forces at interfaces constitute one of the most important problems in materials surface interfacial science.[1] Solid surface tension is an important thermodynamic quantity governing many technological processes. However, because of the absence of surface mobility, a solid phase is very different from a liquid phase; hence, one cannot measure the surface tension of a solid phase directly as is case for a liquid phase. The possibility of estimating solid surface tension from contact angle relies on a relation which was recognized by Young in 1805.

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \tag{1}$$

where γ_{lv} is the liquid–vapor surface tension or simply surface tension of a liquid, γ_{sv} is the solid surface tension, γ_{sl} is solid–liquid interfacial tension, and θ is angle of contact. Knowledge of interfacial free energy is necessary for a better understanding and modeling of interfacial processes such as wetting, spreading, and floatation. Among the different indirect approaches in determining solid surface tensions, contact angle is believed to be the simplest and hence widely used approach.[2,3] One can measure contact angle experimentally and liquid surface tension γ_{lv} can be accurately measured using Dunouy ring method. It means Young's equation contains only two measurable quantities, γ_{lv} and θ. To determine γ_{sv} and γ_{sl}, an additional expression/relation relating these quantities must be sought. Nevertheless, Young's equation suggest that the observation of the equilibrium contact angles of liquids on solids may be a starting point for investigating the solid surface tensions, γ_{sv} and γ_{sl}. This has inspired many studies in an attempt to develop methodologies for determining solid surface tensions. A common feature of these approaches is the assumption that contact angle measurement is a trivial task.

In most of the instances the liquids do not spread indefinitely across solid surfaces. Instead a drop with some angle of contact between the solid surface and liquid is formed. The angle thus formed is referred as the angle of contact (θ). Young's equation describes the equilibrium between various interfacial tension and contact angle θ as shown in Figure 1.

Surface chemistry is important to processes involving spreading, wetting, liquid penetration, and adhesion.[1] Such process might include printing, drug formulation, painting, and gluing. The phenomenon

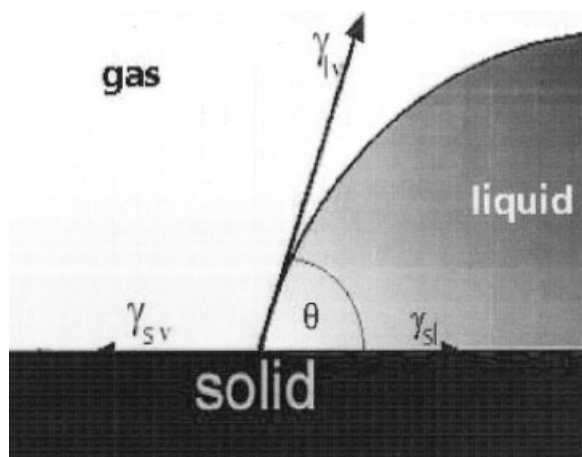*Correspondence to:* R. R. Deshmukh (rajedeshmukh@rediffmail.com).

Figure 1 A balance between three phases.

of wetting and adhesion between a liquid and a solid phase are very important because of their technological importance. Wetting is characterized by the contact angle formed when a liquid drop rests on a solid surface. Wetting is important in many industrial processes, such as cleaning, dying, painting, coatings, adhesion, and pesticide application. The most common method of evaluating wetting is contact angle measurement, where a small liquid drop is deposited on a solid surface. As contact is made, molecular interactions between the liquid and solid surface take place, advancing the contact line. The stronger is the interaction, greater is the wetting.

Several contact angle approaches of current interest, which are largely inspired by the idea of using Young's equation for the determination of surface energy (SE) are discussed.[4–8] While these approaches are, logically and conceptually, mutually exclusive, they share, nevertheless, the following basic assumptions:

1. All approaches rely on validity of Young's equation for surface energies from experimental contact angles.
2. Pure liquids are always used; surfactant solution or mixture of liquids should not be used, since they would introduce complications due to preferential adsorption.
3. The values of γ_{lv}, γ_{sv}, and γ_{sl} are assumed to be constant during the experiment, i.e., there should not be physical/chemical reaction between the solid and the liquid.
4. The surface tensions of the test liquids should be higher than the anticipated solid surface tension.
5. The values of γ_{sv} in going from one liquid to another are also assumed to be constant, i.e., independent of the liquids used.

6. It has been observed that evaporation of liquid affects the measured contact angle profoundly. Thus it is necessary to measure contact angles instantaneously.

To assure that the experimentally measured contact angles do not violate any of the above assumptions, one requires careful experimentation and suitable methodology. It is observed that after taking proper care in the experimentation, the variation in the measurement of contact angle is around ±1–2.

MATERIALS AND EXPERIMENTAL

Polyethylene (PE) films having thickness of 40 μm were supplied by Reliance India. Before treatment the films were cleaned with acetone in an ultrasonic bath for 6 min and then dried in air. PE films were partially crystalline in nature. A typical bell jar type plasma reactor having height of 30 cm and diameter of 30 was used. The two electrodes were capacitively coupled to the RF source capable of giving power output up to 100 W. Various ports were fitted on the base plate for gas and monomer inlet. Pirani gauge was fitted onto the top plate. To confine the glow discharge to the specific volume, the magnetron was mounted on the base plate. Because of magnetron, the plasma could be confined to a volume 500 cm^3 and the maximum sample that can be uniformly treated in our plasma chamber is 10 cm × 10 cm. However, PE films of size 8 cm × 8 cm were used in the present work. The working pressure was adjusted to 0.2 mbar and gas flow rate to 15 SCCM. Liquids used for contact angle measurement were of AR grade and were obtained from S. D. Fine chemicals (India).

THEORY

Measurement of the contact angle at the solid–liquid–vapor interface has been used extensively for the study of the surface properties of both solids and liquids. Many different techniques have been developed for the measurement of contact angle. In the present work we have used sessile drop method. The contact angles measured for probe liquids on solids of interest are used to calculate surface free energies using a suitable method. The use of contact angle measurements to determine SE relies on the use of Young's equation. For contact angle measurements to comply with Young's equation certain conditions must apply.[9] Again, equilibrium contact angle measurements which satisfy this relationship can be made on ideal solid surfaces that are homogeneous and flat, and have properties which do not change appreciable due to interactions with the liquid or vapor phases. In practice, the measured
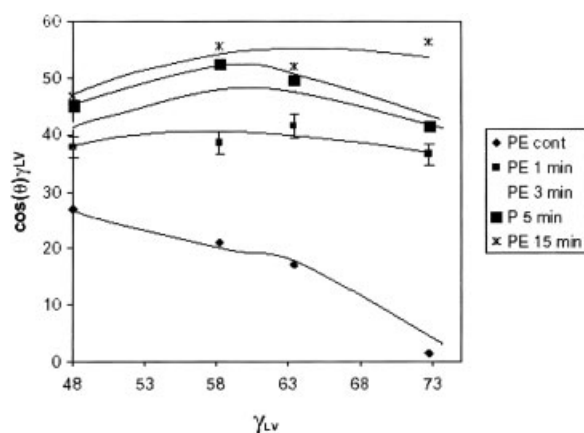
Figure 2 Graph of $\gamma_{lv}\cos(\theta)$ versus γ_{lv}.

contact angle may not fully satisfy the assumptions implicit in Young's equation.

Historically, the interpretation of contact angle in terms of solid surface energies started with pioneering work of Zisman[4] the key observation they made was that for a given solid the measured contact angles did not vary randomly as the liquid was varied; rather, $\cos\theta$ changed smoothly with the liquid surface tension γ_{lv} with in a band in a fashion that may suggest a straight line relationship.

Figure 2 shows these contact angle results in a plot of $\gamma_{lv}\cos\theta$ versus γ_{lv} for different pure liquids increasing surface tension, ethylene glycol (EG), formamide (F), glycerol (G), and water (W). The curves are the best-fits of experimental data to a simple quadratic equation. The choice of plotting $\gamma_{lv}\cos\theta$ in Figure 2 instead of $\cos\theta$ reflects our intension to follow Young's equation as closely as possible. It can be seen that for a given solid surface, $\gamma_{lv}\cos\theta$ changes smoothly and systematically with γ_{lv}. Since the surface tension, γ_{sv}, of a given solid is expected to be constant, i.e., independent of the choice of the test liquid used, Figure 2 implies that $\gamma_{lv}\cos\theta$ depends only on γ_{lv} at constant γ_{sv}. Changing the solid surface from hydrophobic surface to hydrophilic surface (may be by suitable technique), shifts the curve in a very regular manner. Increase in hydrophilicity of PE film surface (after plasma treatment) shifts the curve to the right as shown in Figure 2 (of plot of $\gamma_{lv}\cos\theta$ vs. γ_{lv}) These results suggest that the value of $\gamma_{lv}\cos\theta$ depends on γ_{lv} and γ_{sv}. Thus, contact angle can be changed simply by changing either γ_{lv} or γ_{sv}. While the specific intermolecular forces (e.g., dipole–dipole moment and hydrogen bonding) determine that primary surface tensions of liquids and solids, they do not appear to have any additional and independent effects on the contact angles, in context of Young's equation.

However, the actual curves are not smooth as that of theoretical one.[10] In our case, since the values of $\gamma_{lv}\cos\theta$ do not appear to give a smooth and systematic change with γ_{lv}, one might argue that the contact angle (or $\gamma_{lv}\cos\theta$) cannot be a simple function of only γ_{lv} and γ_{sv}, but has to depend also on the various specific intermolecular forces (such as polarities) of the liquids and solids and surface roughness. It is well-known that surface becomes rougher after the plasma treatment.[11] In addition to this there can be variety of causes for different materials. Accurate contact angle measurements require extreme experimental care. Even minor vibrations can result in error of several degrees; surface roughness can also change the value of contact angle significantly. Swelling of a solid by a liquid[12] can also change the chemistry of solid and hence the values of γ_{sl} and θ in an unpredictable manner. The disagreement of theoretical values with respect to the experimental contact angle patterns arises from the fact that contact angle phenomena are often complex. In addition to the solid surface tensions given by Young's equation, experimental contact angles often contain a variety of other information about a given solid surface, such as molecular orientation at the surface or surface topography.

Choice of a liquid for SE measurement is a crucial thing. If $\gamma_{lv} \leq \gamma_{sv}$, complete wetting occurs; such liquids cannot be used to find contact angle and hence SE, because liquid drop becomes flat immediately and generally there is large % error in the measurement of angle of contact. It is therefore advised that we should start with high surface tension (e.g., water, 72.8 mJ/m^2), the values of $\gamma_{lv}\cos\theta$ increase as γ_{lv} decreases, reaching a global maximum. Further decreases in γ_{lv} causes the data points to fall 45° straight line where the contact angles are zero. Thus the liquid surface tensions of the test liquids should be higher than that of the anticipated solid surface tension, by the appropriate choice of the liquids. Another possible effect of $\gamma_{lv} < \gamma_{sv}$ is liquid adsorption, which could cause γ_{sv} to be different from liquid to liquid. Therefore, the test liquids used in this study were selected to fulfill the condition $\gamma_{lv} > \gamma_{sv}$. A recent contact angle study has confirmed that contact angles should be measured for $\gamma_{lv} > \gamma_{sv}$ and that the measurements with $\gamma_{lv} < \gamma_{sv}$ contains no information about γ_{sv}.[13] Dalal noted that the calculated values for surface free energy components depended upon the choice of liquids.[14] The use of dissimilar liquid pairs (e.g., water and methylene iodide) minimized the dependence of the calculated results upon the precise choice of probe liquids.

The test liquids are so chosen that their polar and disperse components of a liquid surface tension are known. One may then calculate the SE components of the solid by measuring contact angles, θ, for few liquids.[15] Water has been commonly chosen as a probe liquid since its properties are well established.
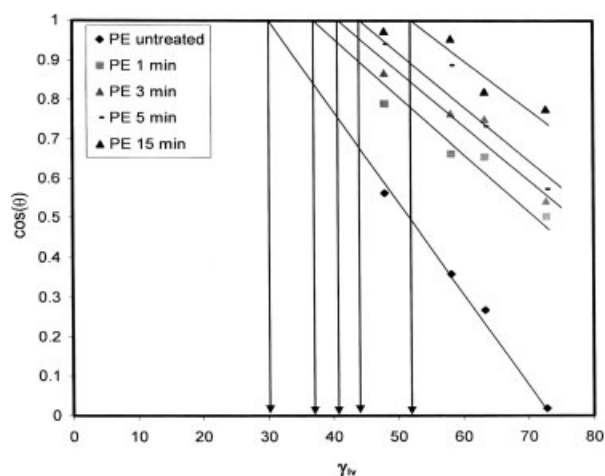
Figure 3 Zismans plot of cos(θ) versus γ_{lv}.

VARIOUS APPROACHES FOR THE ESTIMATION OF SURFACE FREE ENERGY OF SOLIDS

Zisman's critical tension

The concept of critical surface tension was first introduced by Fox and Zisman in 1950.[16] Zisman[4] made pioneering investigations of the thermodynamics of wetting and adhesion. They observed a quasi-linear relationship between cosine of contact angle and liquid surface tension for a series of homologous liquids. If nonhomologous liquids are used, experimental points formed a narrow rectilinear band. The plot of cosine of contact angle as a function of liquid surface tension is usually called the Zisman plot. The experimental contact angle patterns in the plot of $\cos\theta$ versus γ_{lv} as shown in Figure 3. We see that for a given solid surface, as γ_{lv} decreases, cosine of the contact angle ($\cos\theta$) increases, intercepting at $\cos\theta = 1$ with a ''limiting'' γ_{lv} value. We identify this limiting value as γ_{lv}^c. As γ_{lv} decreases beyond this γ_{lv}^c value, contact angle becomes more or less zero ($\cos\theta \approx 1$), representing the case of complete wetting. The trend described here appears to change systematically to the right for a more hydrophilic surface (plasma treated PE film) and to the left for relatively more hydrophobic surface (untreated PE film). Changing the solid surfaces in this manner change the limiting γ_{lv}^c value, suggesting that γ_{lv}^c might be of indicative value as a solid property. Infact, Zisman labeled this γ_{lv}^c value as the critical surface tension of the solid surface γ_c. Zisman's relation is empirical. In many cases this critical surface tension is less than that of the actual surface tension of a solid. It is the minimum SE. However, determination of γ_c is an adequate measure of solid SE for many practical problems. Zisman's model for estimating surface free energies provides a number of

insights into the relation between surface chemistry and contact angle. Water and other hydrogen-bonding liquids usually appreciably deviate from linearity when the surface that is measured contains functional group which can establish hydrogen bonding with the liquid. Furthermore, the Zisman's model can be of importance to practical applications including wettability, painting, printing, coating, etc. The critical surface tension met great success, in cracking the problem mentioned in Young's equation.

Several investigators, including Fowkes,[17–20] have constructed statistical thermodynamic models for wetting and adhesion. These models may be considered as statistical thermodynamic in the sense that they offer molecular interpretations for origins of wetting and adhesion. Intermolecular forces between molecules result from interaction between their corresponding electron orbitals.

Good and Girifalco model

In the second half of the 1950s, Good et al. formulated a theory of interfacial tension using microscopic (statistical mechanics) consideration. They tried to relate the interfacial tension between two phases (1 and 2) to the geometric mean of the surface tension of each phase. It is a particular case of a more general equation, now known as Good-Girifalco equation namely:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi(\gamma_1\gamma_2)^{1/2} \qquad (2)$$

where Φ is the interaction parameter, but a characteristic of a given system that can be evaluated from molecular properties of the two phases. The interaction parameter was found very close to unity when dominant cohesive and adhesive forces were of the same kind. Interfaces satisfying these requirements were called regular interfaces. To a good approximation, the interaction parameter is given in this case by:

$$\Phi = 4(V_1 V_2)^{1/3} \Big/ \left(V_1^{1/3} + V_1^{1/3}\right)^2 \qquad (3)$$

where V is the molar volumes.

If eq. (2) is substituted in the Young eq. (1) the following relationship results

$$\gamma_s = [\gamma_1(1 + \cos\Theta) + \pi_e]^2 / 4\Phi^2\gamma_1 \qquad (4)$$

Or, neglecting spreading pressure

$$\gamma_s = \gamma_1(1 + \cos\Theta)^2 / 4\Phi^2 \qquad (5)$$

In this way it is possible to calculate the value of solid surface tension from a single contact angle measurement and the knowledge of interaction

TABLE I
Values of Surface Energy (in mJ/m^2) for Various Liquids
on Control PE Surface by Many Methods

Liquids	Mean Θ (C.A)	Methods used to determine surface energy for control PE film			
		Good and Girifalco	Neumann	Fowkes[a]	Zisman[a]
Water	88.93	18.88	32.98		
Glycerol	74.47	25.47	32.02		
Formamide	68.92	24.41	30.07		
Ethylene glycol	55.75	29.12	27.38		
Avg		24.47	30.61	30.44	30.12

[a] It requires contact angle w.r.t. minimum three liquids and for other methods we can get surface energy by one liquid.

parameter of the system. The Good-Girifalco theory stimulated much work on the real meaning of Zisman's critical surface tension, its relationship with the true solid surface tension[21,22] and how to express the interaction parameter in terms of molecular properties.[23] Wu exploited the critical surface tension and the Good-Girifalco theory and proposed an equation of state[24] that gives accurate values of surface tension.[25] By substituting the definition of critical surface tension in eq. (4) and expanding in a power series a rapidly converging expression was obtained, so that:

$$\gamma_C = \Phi^2 \gamma_s - \pi_e \quad (6)$$

where the second subscript of the critical surface tension indicates its dependence on interacting parameter.

Combining eqs. (5) and (6)

$$\gamma_C = (1/4)(1 + \cos \Theta)^2 \gamma_l \quad (7)$$

In this way a spectrum of critical surface tension can be straightforwardly calculated. The advantage of eq. (7) is that the surface tension of a given solid can be obtained by simply measuring the equilibrium contact angle of single liquid of known surface tension. Since, it uses single probe liquid, it has strong dependence on the liquid. Our work shows that there is a variation in solid SE from liquid to liquid for control PE film as depicted in Table I. The trend we observed in this case is that as liquid surface tension is decreased, solid surface tension increases.

Acid–base surface free energies of solids: Some basics concepts

The most important concept in the theory of interfacial acid–base interactions is certainly the definition itself. Among the different definitions of acids and bases, the Lewis theory is the most satisfactory for applications to polymers, and it is the theory that all experimental approaches naturally refer to calculate the acid–base components of polymer surface. In general, the sites that can act as electron acceptors are acidic: metal atoms of organomatallic compounds, electrophilic carbons (i.e., carbon atoms covalently linked to a more electronegative element, such as oxygen or fluorine), hydrogen atoms in hydroxyl or carboxyl groups. In contrast, Lewis bases are electron donors: atoms containing lone-pair electrons (such as oxygen) or aromatic rings, where the π electron acts as basic site. This broader definition best describes the kind of acid–base interactions of interest in polymer surface and interfacial science. And it is within the same notion that the terms ''electron donor'' and ''electron acceptor'' fit, and are frequently used in the literature as synonyms for ''Lewis base'' and ''Lewis acid,'' respectively.

It is worthy of note that many compounds contain both acidic and basic sites and are, therefore, self associated substances: water provides an important example, because of balanced basicity of oxygens and the acidity of hydrogens. The water example suggests further comments on the term ''polar'': it is obviously correct to define water as a ''polar'' compound, owing to the polarity of —OH bond, but the associated dipole, as measured, for instance, by the relative dipole moment, does not contribute to the intermolecular interactions in the condensed phase.[26] The correct interpretation of ''polar'' (i.e., nondispersive) interactions of water molecules comes from the coexistence of electron rich (i.e., basic) and electron poor (acidic) sites. They will interact with neighboring molecules in a Lewis acid–base way, and this particular acid–base interaction constitutes hydrogen bonding.

The calculation of acid–base properties by wetting measurements involves estimating the fundamental acid–base properties of solid surfaces by their ability to interact with liquids, as manifested through wetting phenomena. The basic idea of this approach[17,26–28] consists in the assumption that the surface free energy splits into components describ-

ing, respectively, the contribution γ^{LW} due to electrodynamic interactions (dominated by dispersion forces) and the acid–base contribution γ^{AB} (polar components)

$$\gamma = \gamma^{LW} + \gamma^{AB} \tag{8}$$

where the superscript LW stands for Lifshitz-van der Waals. The above equation basically states that the ''dispersive'' and acid–base interaction are independent of each other, and is formally similar to the dispersive/polar approach widely used before the role of acid–base properties was recognized.

According to Good, van Oss, and Chaudhury model[20,29,30] the Lewis acid–base parameter is modeled as follows:

$$\gamma^{AB} = 2(\gamma^+\gamma^-)^{1/2} \tag{9}$$

where γ^+ is the Lewis acid parameter and γ^- the Lewis base parameter. Lewis acid–base interactions encompass hydrogen bonding, electron donor–acceptor, and organic nucleophile–electropile interactions.

Good, van Oss and Chaudhury further choose,

$$\gamma^+ = \gamma^- \equiv 0$$

for alkanes, methylene iodide, and α-bromonaphathalene which presumably interact only through Lifshitz-van der Waals (γ^{LW}) ractions.

For Water, $\gamma_{H_2O}^+ = \gamma_{H_2O}^- \equiv 25.5 \ mJ/m^2$.

The complementarity of acid–base interactions explicitly appears in the expression introduced by Good, van Oss and Chaudhury (GvOC) to describe acid base components of the surface free energy of solids or liquids of.[7,27,30]

$$\gamma_{l,s} = \gamma_{l,s}^{LW} + 2\left(\gamma_{l,s}^+\gamma_{l,s}^-\right)^{1/2} \tag{10}$$

which, combined with the Young's equation, leads to the following relationship for work of adhesion between a liquid and a solid:

$$W_{adh} = \gamma_l(1 + \cos\theta)$$
$$= 2(\gamma_l^{LW}\gamma_s^{LW})^{1/2} + 2(\gamma_l^+\gamma_s^-)^{1/2} + 2(\gamma_l^-\gamma_s^+)^{1/2} \tag{11}$$

Here γ^{LW} is the previously defined Lifshitz-van der Waals contribution, whereas γ^+ and γ^- are electron-acceptor (Lewis acid) and electron donor (Lewis base) parameters, respectively. The subscripts l and s refer to solid and liquid, respectively. Equation (11) is referred as GvOC. If GvOC parameters are known for at least three liquids and then contact angles of these liquids on a solid are measured, then eq. (11) can be used to determine GvOC parameters for the

surface free energy of the solid. The GvOC equation is, in principle, the tool which allows us to measure the acid–base properties of polymer surfaces, to account for the result of interfacial interactions, and to design a given surface modification treatment for a given application.

Moreover, in spite of the relatively simple mathematical form (the set of GvOC equations is linear in the square roots of polymer acid–base and dispersive parameters). However, the results obtained from GvOC method strongly depends on the choice of the three liquids used for contact angle measurements and in some cases, these roots assume negative values, which obviously cannot be justified.[31] In our opinion, one can simply ignore the difficulties and keep applying GvOC approach for comparative study.

One can calculate LW component of a purely dispersive solid from the contact angle of purely dispersive liquids on the solid, and vice versa.

$$i.e \quad \gamma_{l,s}^+ = \gamma_{l,s}^- = 0$$

Therefore, eq. (11) reduces to

$$\gamma_l(1 + \cos\theta) = 2\left(\gamma_l^{LW}\gamma_s^{LW}\right)^{1/2} \tag{12}$$

Squaring and rearranging the above equation,

$$\gamma_s^{LW} = \frac{\gamma_l^2(1 + \cos\theta)^2}{4\gamma_l^{LW}} \tag{13}$$

and,

$$\gamma_l^{LW} = \frac{\gamma_l^2(1 + \cos\theta)^2}{4\gamma_s^{LW}} \tag{14}$$

Thus, one can determine Lifshitz-van der Waals i.e., LW parameter (disperse component) of a solid or a liquid if all other parameters are known.

The SE characteristics such as γ_{lv}, γ^{LW}, γ^{AB}, γ^+, and γ^- various pure liquids are compiled from the literature[15,20,32–35] and is reproduced here in Table II. The SE (S.T.) of a liquid can be determined by the Du Nouy ring method. The polar (γ_l^p) and disperse (γ_l^d) components of a liquid can be calculated using contact angle measurements of that liquid on PTFE, which is considered to be completely nonpolar ($\gamma_s^p = 0$) and have a surface free energy ($\gamma_s = \gamma_s^d$) of 19 mJ/m^2 at 20°C.[32]

The Fowkes approach

To calculate the surface free energy of the substrate a set of minimum three liquids of known polar and disperse components are used. To minimize the

TABLE II
Surface Tension Parameters for Various Liquids
at 20°C in mJ/m²

Liquid	γ_l	γ^{LW}	γ^{AB}	γ^+	γ^-
Water	72.8	21.8	51	25.5	25.5
Glycerol	64	34	30	3.92	57.4
Formamide	58	39	19	2.28	39.6
Thiodiglycol	54.0	38.5	15.5	–	–
Ethylene glycol	48	29	19	1.92	47.0
Dimethyl sulfoxide	44	36	8	0.5	32
Nitrobenzene	43.9	41.3	2.6	0.26	6.6
Chlorobenzene	33.6	32.1	1.5	0.9	0.61
Diiodomethane	50.8	50.8	0	0	0
Trichlorobiphenyl	45.0	45.0	0	0	0
α-Bromonaphthalene	44.4	44.4	0	0	0
Nonadecane	28.59	28.59	0	0	0
Hexadecane	27.47	27.47	0	0	0
Pentadecane	27.07	27.07	0	0	0
1,1,2,2-tetrabromoehatane	49.70	49.70	0	0	0
Pyridine	37.5	37.5	0	0	0

error involved, it is better to use more number of liquids. A set of large number of liquids is given in Table II.

The equation to calculate surface free energy by using Fowkes approximation[15,36,37] is as follows:

$$\left[\frac{1+\cos\theta}{2}\right] \times \left[\frac{\gamma_l}{\sqrt{\gamma_l^d}}\right] = \sqrt{\gamma_s^p} \times \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \quad (15)$$

The equation is of the form

$$Y(LHS) = mX(RHS) + C \quad (16)$$

where value of LHS can be obtained by calculating θ for the liquid used. Value of γ_l and γ_l^d can be obtained from Table II. Similarly, RHS can be calculated by using polar and disperse components of liquid used. Here it is demonstrated the method of calculation of polar and disperse component of solid SE from Fowkes plot for control PE film using four liquids. Plot of LHS versus RHS gives straight line with intercept on Y-axis as shown in Figure 4. Slope and intercept obtained from the plot is squared and added up to give total SE.

As discussed earlier, Fowkes[18,19] first suggested that free energy could be considered as a sum of components resulting from different classes of intermolecular interactions. Thus,

$$\gamma = \gamma^P + \gamma^d \quad (17)$$

where γ^p is polar component because of dipole–dipole (Debye) interactions and γ^d is disperse component.

While it is generally recognized that $\gamma^p = \gamma^{AB}$ and $\gamma^d = \gamma^{LW}$.

Therefore, above equation can be rewritten as,

$$\gamma = \gamma^{AB} + \gamma^{LW}$$

Neumann's approach

Neumann and coworkers[38–44] have discussed the surface tension of solids from purely thermodynamic point of view. Their view contrasts with the statistical thermodynamic approaches used by Good and Fowkes. Because Neumann's approach does not consider the molecular origins of surface tension no statistical mechanical insight is gained. Kwok and Neumann[9] correctly remind us that the contact angle measurements could be difficult. Measured contact angles can deviate from the true Young's contact angle which satisfies Young's fundamental equation.

According to Kowk and Neumann,[9] the contact angle can be expressed as a function of γ_{lv} and γ_{sv} only. Thus,

$$\gamma_{lv}\cos\theta = f(\gamma_{lv}, \gamma_{sv}) \quad (18)$$

Kowk and Neumann have observed smooth monotonic dependence of $\gamma_{lv}\cos y$ with γ_{lv} consistent with equation[18] when liquid solid pair closely to the assumptions of Young's equation. For arbitrary solid–liquid pairs such a plot may show considerable scatter because the measured contact angles deviate significantly from the true Young's contact angle. Neumann has derived the following equation for the determination of solid SE from single liquid contact angle measurement.

$$1 + \cos\theta = 2\left(\frac{\gamma_{sv}}{\gamma_{lv}}\right)e^{-\beta(\gamma_{lv}-\gamma_{sv})^2} \quad (19)$$

Empirically it has been shown that,

$$\beta \approx 0.0001247$$
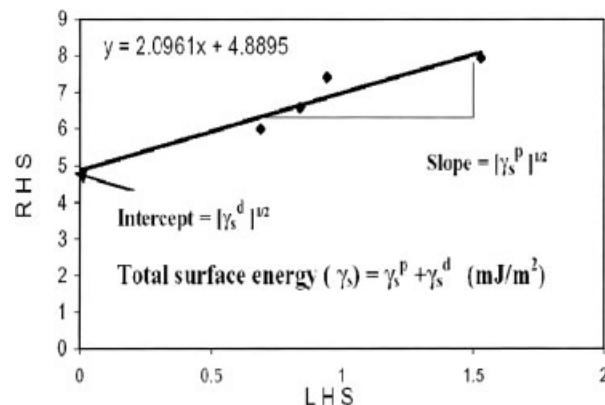
Figure 4 Determination of SE for control PE film by Fowkes method.

TABLE III
### Values of Surface Energy (in mJ/m^2) and Contact Angle Obtained by Neumaans Method

C.A	S.E	C.A	S.E	C.A	S.E
0	72.8	51	53.182	101	22.435
1	72.789	52	52.599	102	21.829
2	72.756	53	52.012	103	21.225
3	72.7	54	51.423	104	20.624
4	72.623	55	50.831	105	20.026
5	72.525	56	50.236	106	19.431
6	72.405	57	49.639	107	18.839
7	72.264	58	49.04	108	18.251
8	72.102	59	48.439	109	17.667
9	71.92	60	47.836	110	17.088
10	71.719	61	47.231	111	16.512
11	71.499	62	46.624	112	15.942
12	71.26	63	46.015	113	15.376
13	71.003	64	45.405	114	14.816
14	70.729	65	44.793	115	14.261
15	70.438	66	44.179	116	13.713
16	70.132	67	43.565	117	13.17
17	69.809	68	42.948	118	12.635
18	69.472	69	42.331	119	12.106
19	69.121	70	41.713	120	11.585
20	68.756	71	41.093	121	11.071
21	68.378	72	40.472	122	10.566
22	67.987	73	39.851	123	10.069
23	67.585	74	39.228	124	9.582
24	67.171	75	38.605	125	9.103
25	66.746	76	37.981	126	8.635
26	66.311	77	37.357	127	8.177
27	65.866	78	36.732	128	7.729
28	65.412	79	36.107	129	7.292
29	64.949	80	35.481	130	6.867
30	64.478	81	34.855	131	6.454
31	63.998	82	34.229	132	6.053
32	63.51	83	33.603	133	5.664
33	63.016	84	32.976	134	5.288
34	62.514	85	32.35	135	4.926
35	62.005	86	31.724	136	4.577
36	61.491	87	31.098	137	4.242
37	60.97	88	30.473	138	3.92
38	60.443	89	29.848	139	3.613
39	59.911	90	29.224	140	3.321
40	59.374	91	28.601	141	3.042
41	58.832	92	27.978	142	2.778
42	58.285	93	27.356	143	2.529
43	57.733	94	26.736	144	2.294
44	57.178	95	26.117	145	2.073
45	56.618	96	25.499	146	1.866
46	56.054	97	24.882	147	1.673
47	55.487	98	24.267	148	1.494
48	54.916	99	23.655	149	1.327
49	54.341	100	23.044	150	1.174
50	53.763				

and the measured solid surface free energy using this choice for β is nearly independent of the choice of liquid. Therefore, Neumann's method for determining SE from single liquid contact angle is advisable. Table I shows that the SE calculated from this method for control PE film is in close resemblance with that of Zisman and Fowkes method. Whereas,

in case of Good's approximation, SE is dependant on probe liquids. Above equation can be used in two ways. First, β can be chosen as 0.0001247 and a suitable contact angle can be used to determine γ_{sv}. Second, β and γ_{sv} can be treated as adjustable parameters. Least-square analysis using contact angles measured for several liquids is then used to determine the best fit of values for β and γ_{sv}. The second approach would seem to be preferable. An alternate combining rule has been suggested recently by Kowk and Neumann.[10] We have solved the Neumann's equation using computer software (Mu PAD Pro 3.1), and have calculated the value of SE assuming various contact angles (from 0 to 150) for water and is given in Table III. This data could be useful to the researchers who wish to know the SE of their materials if angle of contact with respect to water is known. Neumann's equation has two solutions i.e., it gives two values of solid SE for a given contact angle. We observed that out of the two values, lower value refers to the correct SE. Using this data, a graph of SE versus contact angle was plotted and is shown in Figure 5. From this plot, we have developed a general equation using ORIGIN 6.0 software for the solid SE for water as a probe liquid and are given below:

$$S.E = 2.9 \times 10^{-5}(\theta)^3 - 0.00652(\theta)^2 - 0.1326(\theta) + 72.8$$

Similarly, Glycerol (G), Formamide (F), Ethylene Glycol (EG), and Diiodomethane (DIM) are also used as a probe liquids because they have high surface tension and less volatile in comparison with other liquids mentioned in Table II. Therefore, the general equations for these liquids are also given below for the researchers who wish to calculate SE by Neumann's method using the above-mentioned liquids.
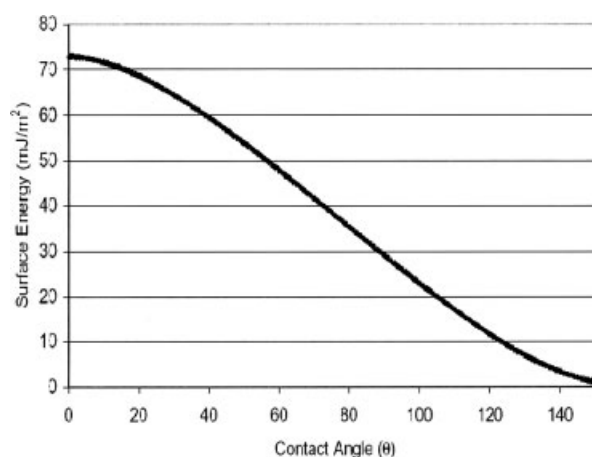
Figure 5 A plot of SE versus contact angle for water as a probe liquid.

$$S.E = 2.9 \times 10^{-5}(\theta)^3 - 0.00648(\theta)^2 - 0.101(\theta) + 63.4$$
$$\text{For G}$$

$$S.E = 2.9 \times 10^{-5}(\theta)^3 - 0.00631(\theta)^2 - 0.089(\theta) + 58.2$$
$$\text{For F}$$

$$S.E = 2.9 \times 10^{-5}(\theta)^3 - 0.00569(\theta)^2 - 0.072(\theta) + 48.0$$
$$\text{For EG}$$

$$S.E. = 2.9 \times 10^{-5}(\theta)^3 - 0.00585(\theta)^2 - 0.076(\theta) + 50.8$$
$$\text{For DIM}$$

The general form of the above five equations is a third order polynomial and is given below.

$$S.E = A(\theta)^3 - B(\theta)^2 - C(\theta) + \gamma_L \qquad (20)$$

where A, B, and C are constants, needs to be determined for individual liquid.

Owens–Wendt model

Owens–Wendt model[6] has only two parameters, it is necessary to measure contact angles for two liquids.

$$W_{adh} = \gamma_l(1 + \cos\theta) = 2\left(\gamma_l^{LW}\gamma_s^{LW}\right)^{1/2} + 2\left(\gamma_l^{AB}\gamma_s^{AB}\right)^{1/2} \qquad (21)$$

Equation (21) and data from measurements using polar and nonpolar liquids can be used to determine γ_s^{LW} (disperse component) and γ_s^{AB} (polar component) of solid surface free energy.

The models by Zisman[4] and Kwok and Neumann[9] yield total surface energies. As the models are thermodynamic (classical) in nature, no direct and detailed information is given on the molecular origins of the observed contact angles. Zisman's approach is operationally simple and adequate for some product quality applications. Because Neumann's approach is theoretically more rigorous, it would seem more suitable, particularly when the contact angles from several liquids are used to determine the surface free energy of the solids under study.

Calculation of surface roughness from contact angle measurement

To control wettability and adhesion of polymers numerous surface modification techniques are used, such as exposure to flames, plasma, and chemical modification (grafting).[45–47] In many cases, the wettability is regulated by changes in the chemical composition of the surfaces. But, it has also been long recognized that surface roughness can be important for wettability. Wenzel was the first who discussed the influence of surface roughness on contact angle.[32] He introduced the roughness factor, r_w, into
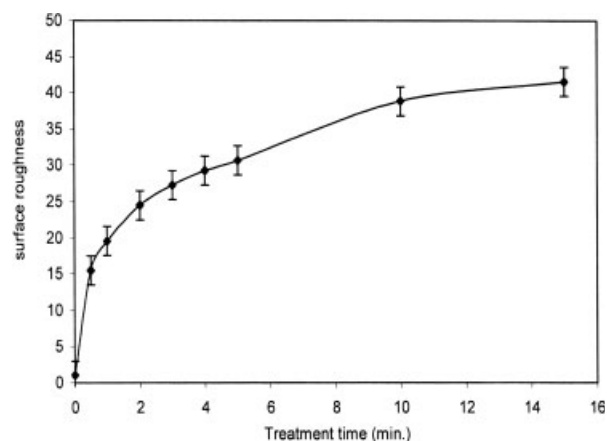
Figure 6 Variation of surface roughness with time for air plasma treated PE films.

the Young's equation because he argued that in case of a rough solid surface, the interfacial tensions γ_{sv} and γ_{lv} should not be referred to the geometric area, but to the actual surface area. Thus,

$$r_w = \frac{\text{true surface area}}{\text{geometric surface area}}$$

or

$$r_w(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv}\cos\theta_w$$

For the contact angle on a rough surface he obtained
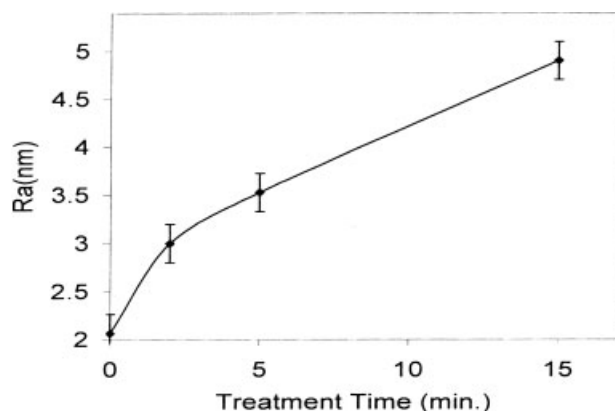
$$\cos\theta_w = r_w\cos\theta$$

where the Wenzel contact angle, θ_w, is, therefore, the equilibrium contact angle on a rough solid surface having the intrinsic angle θ. Thus, the surface roughness of PE films treated in air plasma calculated from above equation is given in Figure 6. It was thought interesting to study surface morphology and surface roughness using AFM of air plasma treated PE films for different durations of time. AFM photographs are given in Figure 7. The mean surface roughness obtained from AFM for different plasma treatment time is given in Figure 8. It can be clearly seen from Figures 6 and 8 that the trend in change in surface roughness with time of treatment is similar.

Wetting is governed by molecular interactions in the outermost surface layer of a few angstroms. Consequently, the forces dictating the wetting behavior of organic substances do not originate from the organic molecule as a whole, but rather from the outermost surface groups. Furthermore, for interfacial-energy minimization reasons, the molecules tend to arrange themselves in the surface layer in such a way that only their low-energy or high-energy portions come into contact with the surrounding phase.
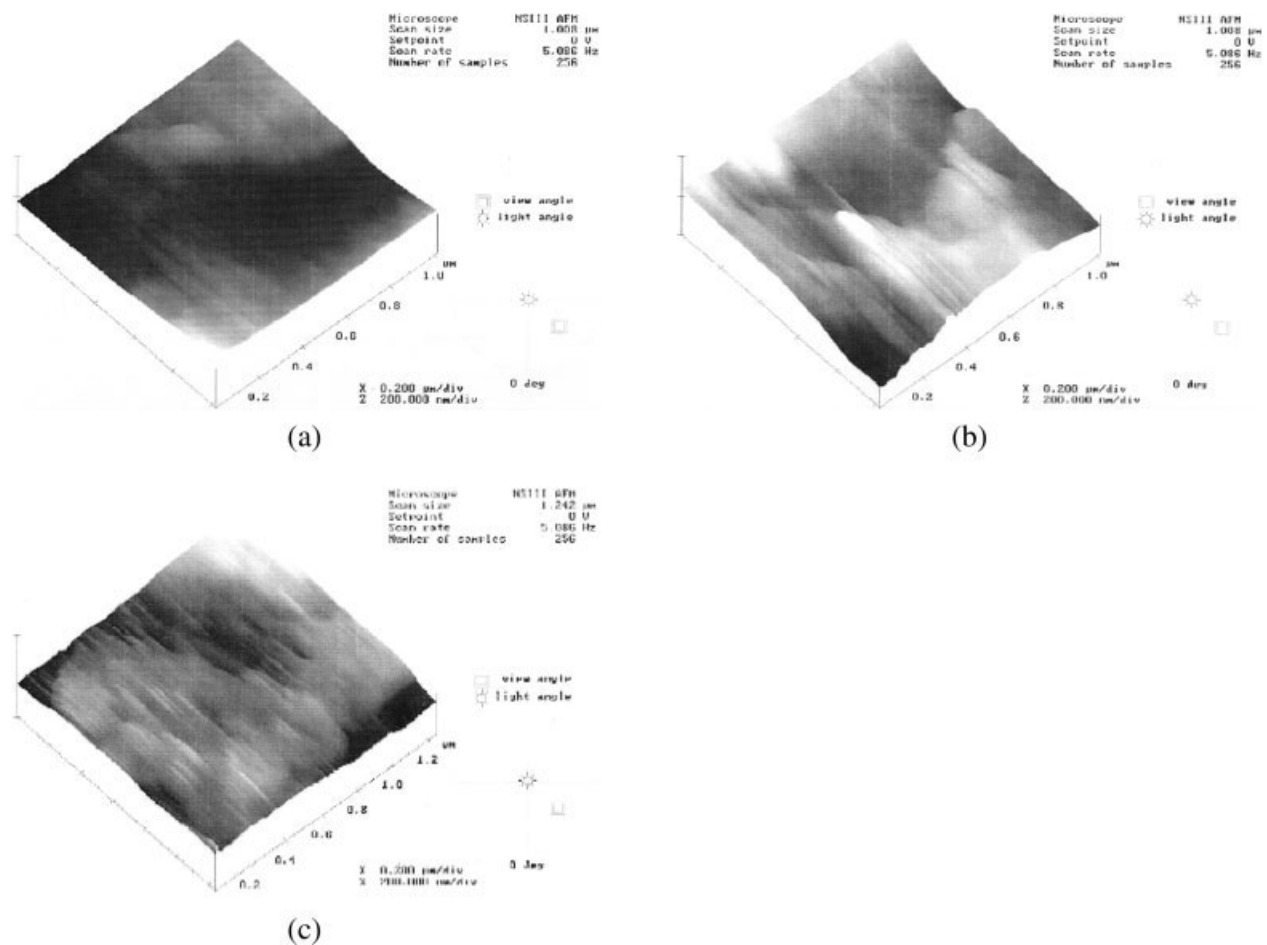
Figure 7 AFM photographs of (a) control PE film. (b) PE film treated in air plasma for 5 min. (c) PE film treated in air plasma for 15 min.

As a result, the wettability of an organic material is not related to its overall chemical structure, but depends on the chemical nature of energetically favored functional groups and the extent to which these are exposed at the material surface.

Calculation of work of adhesion from contact angle measurement

The general adhesion pattern (of plot W_{adh} vs. γ_{lv}) is that W_{adh} increases with γ_{lv}. Increase in hydropilicity of the surface (after plasma treatment) shifts the curve in Figure 9 (of plot W_{adh} vs. γ_{lv}) to the higher

Figure 8 Surface roughness study of air plasma treated PE film by AFM.
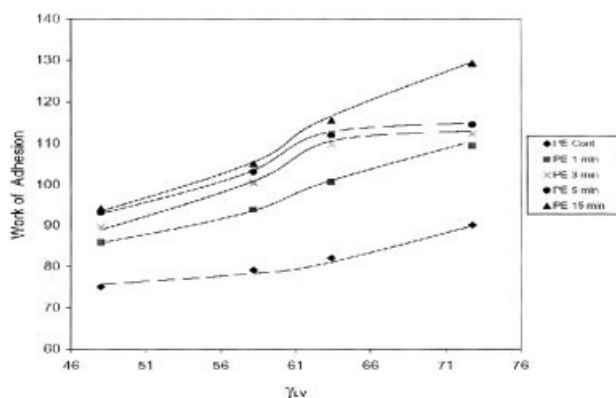
Figure 9 Graph of work of adhesion versus γ_{lv} for various time duration.

side. The work of adhesion of a liquid on a solid surface (W_{adh}) was calculated using following formula,

$$W_{adh} = \gamma_{lv}(1 + \cos\theta)$$

From the figure we can see that as the liquid surface tension is increased the work of adhesion is increased.

Contact angles of different liquids on one and the same solid surface can be employed to study the systematic effect of changing γ_{lv} on W_{adh} through θ.

CONCLUSIONS

Our article describes that the SE determined by all these methods is in good agreement with each other. However, Fowkes and Zisman's methods are found to be more reliable, because it gives value of SE from more than three liquids and minimizes error. It makes the use of graph to calculate the SE, graph represents the overall trend and hence minimizes error. In addition to this, Fowke's method gives us the break up of solid SE in terms of polar and disperse components. Polar components are basically due to intermolecular forces (e.g., dipole–dipole interactions, hydrogen bonding, etc). Measurement of contact angle with one liquid (preferably water) is sufficient for Good and Girifalco approximation and Neumann's formula to calculate SE. Neumann's approach is purely thermodynamic and does not depends on the test liquid i.e., γ_{lv} unlike Goods approximation. However, Neumann's equation is exponential and very difficult to calculate SE. Therefore, we have simplified it from the values obtained by his equation. Our equation seems to be simple for calculation purpose. The constants in our equations are different for different liquids. Hence we have proposed different equations for different liquids. We strongly feel that our equation would be useful to the researchers concerned with many fields such as printing, adhesion, pharmaceuticals, composite materials, textiles polymers, and ceramics, who are using single probe liquid.

Thus contact angle measurements give us the value of solid surface free energy. It is also useful to determine surface roughness and work of adhesion.

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