

## Application Note #5:

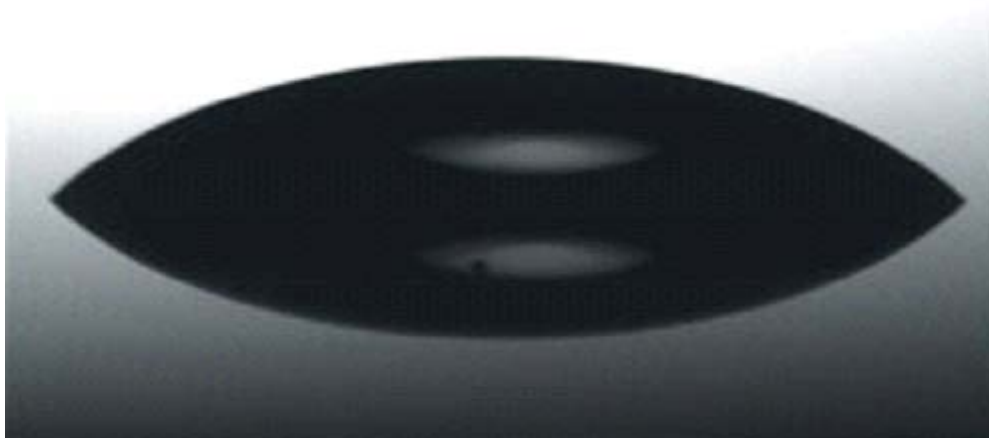
## Surface free energy - Background, calculation and examples by using contact angle measurements



### Summary

Precise characterization of solid material surfaces and fluid interfaces plays a vital role in research, innovation and product development in many industrial and academic areas. Measurement of contact angles and surface/interfacial tensions provides a better understanding of material compatibility. Contact angle and surface/interfacial tension measurement is a rapid and accurate characterization tool for emerging state-of-the-art surface engineering techniques. The present communication explains how such determinations are carried out and brings examples of real applications where this technique has been applied with success:

- Paintability, printability, adhesivity, and water-resistance
- Tribological and wetting properties of hard metal coatings
- Biomedical applications



## Determination of the surface energy of materials by using contact angle measurements

What is surface free energy?

Let's take a piece of a material and try to divide it into two parts. To accomplish this task, some energy needs to be spent in order to overcome interatomic forces holding the parts together. If the separation of the parts is carried out so gently that no deformation is induced in the bulk material, the energy spent can be associated with the excess energy of the two new interfaces formed. In theory, assuming that the above action can be reverted, the same amount of energy should be regained upon putting the two parts back together.

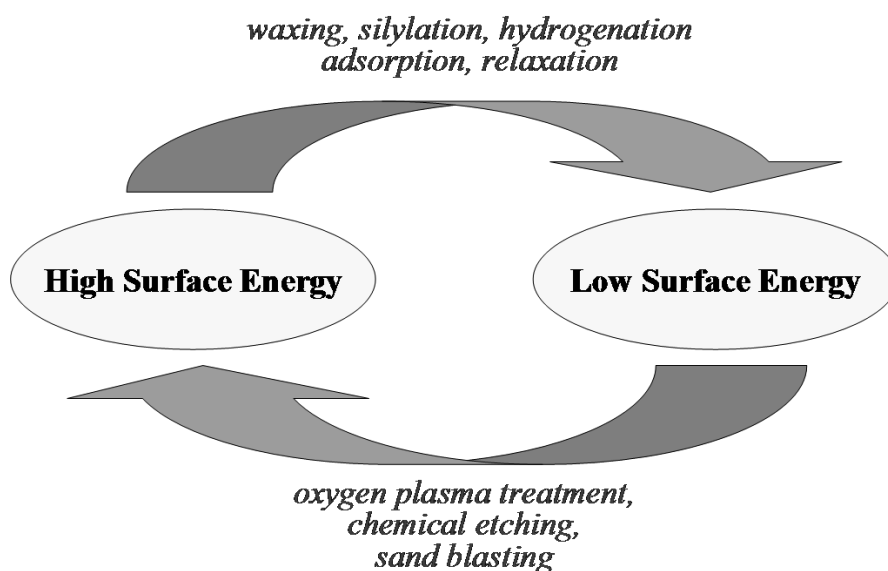
In real systems, the splitting up a material into smaller parts always induces stresses and deformations in each of the parts formed, and therefore some energy is dissipated as heat and some is stored as elastic deformation. As a consequence, the accurate experimental determination of surface energy is only possible for isotropic liquids, in which bulk stresses quickly relax and the excess surface energy coincides with the surface tension. For solids, the true value of the surface energy cannot be measured. When applied to solids, the term "surface energy" acquires a totally different meaning and can be viewed as an "adhesive" parameter characterizing the affinity of the surface to other materials. The higher the surface energy of a solid, the more energy is gained upon bringing this surface into contact with other materials.

Interfacial interactions play a key role in all multicomponent materials irrespectively of the number and type of their components or their actual structure. Recognition of the role of the main factors influencing interfacial adhesion and proper surface modification may lead to significant progress in many fields of research and development, as well as in related technologies [1].

Why measure surface free energy?

Ability to measure the surface energy of various materials is essential for ensuring compatibility between the given base material and the top coating one wishes to apply onto it or other materials one wishes to attach to it. The most straight-forward applications include matching a paint to a substrate or matching an adhesive formulation to the materials one expects to be glued together.

In many industrial applications, special tools are used for modifying the surface energy of various materials at will. Thus, to promote adhesion, the surface can be "activated" by plasma treatment or chemical etching, whereby its energy is increased, or on the contrary, it can be passivated by lubrication, silylation, or hydrogenation (see Figure 1). For instance, to ensure good adhesion of printing ink to polyethylene or plastic film, such as used in the production of packaging bags, the surface of the film is plasma-treated prior to printing. The same method can be used to enhance the adhesion of the polyethylene-polypropylene laminate applied to the surface of paperboard, which is an essential operation in the paperboard converting technology, or the adhesion and endurance of a teflon layer on the surface of kitchen items. Dewaxing a metallic surface is needed prior to lacquering to ensure good adhesion of lacquer to metal. Waxing a car does not only adds glance but also reduces the adhesion of dirt to the lacquer. And after teflon-based waxes have become available on the market, care needs to be taken that a paraffin-based wax not be applied over a teflon-based one, while doing it the other way around would work fine.



**FIGURE 1** Common industrial processes for tuning the surface energy of materials to application needs.

This line of examples can be easily extended: adhesion between oil and soil in oil recovery applications, between a surgical implant and a body tissue in medical and dentistry applications, between ink and printed substrate in printing, between fountain solution and fountain roller in flexography, between lubricant and hard coatings in metal-working applications, between cleansing tissue and cleansing liquids used for makeup removal, between hairspray and hair, between absorbents and body fluids, between nail varnish and nails, etc. Obviously, in such applications, the extent of the pre-treatment needs to be optimized and controlled on-line for achieving the best result.

How is the surface free energy of solid materials measured?

(i) Determination of the critical surface energy

The critical surface energy, also known as the critical surface tension, characterizes wettability of the material surface by various liquids. Solids possessing a high critical surface energy are wettable by most liquids, while solids possessing a low critical surface energy are not wettable by most liquids and special means are to be deployed to promote wetting.

The standard determination procedure is outlined in Figure 2. A flat and smooth surface of the material in study is prepared and thoroughly cleaned from possible contamination. Then the contact angle values are determined for a number of liquids (one may choose anything from liquid fluorocarbons having extremely low surface tension, ca 15 mN/m, to mercury, having a very high surface tension of ca 470 mN/m). The measurement procedure is extremely simple: a small liquid drop is deposited onto the surface and the contact angle is determined from the digital image of the sessile drop, or, for small contact angles below 10°, from the drop spreading diameter. The appropriate liquid drop size for such measurements is 0.1 ml. A Zisman plot – type graph is made where the surface tension of the test liquids is plotted on the X-axis, and the cosine of the corresponding contact angle on the Y-axis. The extrapolation of the  $\cos\theta$  vs  $\gamma$  curve to  $\cos\theta = 1$  (corresponding to the zero contact angle, or the complete wetting limit) gives the value of the critical surface energy of the material tested. Some examples are included in the Table in Figure 1.

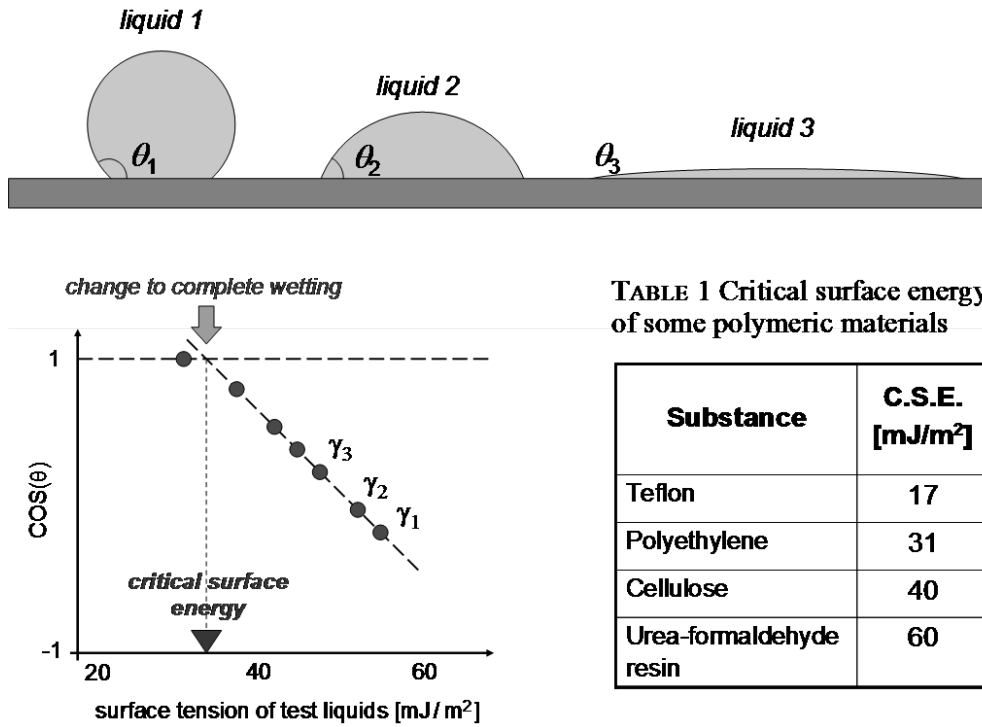


FIGURE 2 Determination of the critical surface energy of solids.

It should be pointed out that the critical surface energy is not really surface energy in a traditional sense; it is rather a wettability benchmark. The critical surface energy shows the maximum surface tension a liquid may have to ensure complete wetting of a given material. In other words, any liquid having a surface tension below the critical surface energy of a given surface will wet that surface completely, forming a uniform surface film. Such behavior is desirable for paints, lacquers, varnishes, lubricants, etc.

(ii) Determination of surface energy for solid materials

To understand how the method works, it is instructive to recall some facts from the thermodynamics of adhesion [2]. Let's estimate the amount of work that needs to be done in order to separate two bodies adhering to each other; let the bodies be designated by letters L and S as shown in Figure 3.

On separating the bodies apart, one interface, body L / body S, disappears and two new interfaces, body L / ambient and body S / ambient, arise. Therefore, the total energy change in such a process, per unit surface area, is

$$E_{\text{adh}} = \gamma_L + \gamma_S - \gamma_{LS} \quad (1)$$

The latter is termed the work of adhesion.

If the body L (which is on the top) is a liquid drop, and body S is a solid substrate, then the contact angle,  $\theta$ , exhibited by the liquid drop at the surface of the substrate is determined by the Young equation,

$$\cos \theta = \frac{\gamma_S - \gamma_{LS}}{\gamma_L} \quad (2)$$

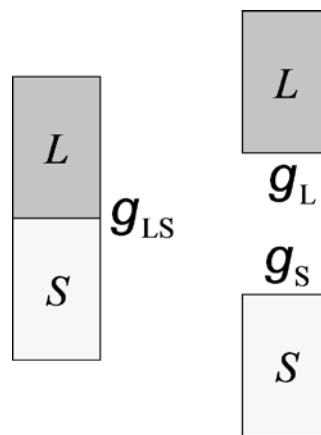


FIGURE 3 Determination of the work of adhesion

By combining the above equations, one arrives at,

$$E_{\text{adh}} = \gamma_L + \gamma_S - \gamma_{LS} = \gamma_L (1 + \cos \theta) \quad (3)$$

Applicability of contact angle measurements for evaluation of the surface energy of solids hinges entirely on a thermodynamic argument that a non-homogeneous interfacial region between two phases in contact with each other can be approximated by a two-dimensional Gibb's dividing surface when at equilibrium. By appropriately choosing the position of this dividing surface, a functional relationship can be established between the three surface tension terms,  $g_{LS} = f(g_L, g_S)$ , referred to as the

equation of state [2]. In fact, what one tries to achieve thereby is to calculate the interaction energy for an asymmetric pair of molecules A and B provided that the interaction energies for the symmetric pairs, A-A and B-B, are known.

Historically, the first concise formulation of this principle, as applied to calculation of interfacial tensions, was given by Giricalco and Good in 1957 [3]. Afterwards, numerous variations of the original concept were proposed by different authors, including van Oss and Good [4], Fowkes [5], Owen and Wendt [6], Kloubek [7], Wu [8], Li and Neumann [9], Schultz et al. [10], and many others. Approximate by their very nature, such calculations provide nonetheless an accuracy level sufficient for material characterization purposes. Once the equation of state has been established,  $\gamma_S$  can be immediately calculated from contact angle exhibited by a test liquid with a known surface tension by solving the equation

$$g_S - f(g_L, g_S) = g_L \cos \theta \quad \text{for } \gamma_S.$$

The mathematical form of the equation of state differs depending of the model assumptions, and in most cases, only empirical relationships are available. For non-polar liquids and non-polar substrates, interacting with each other by means of dispersion forces only, one has

$$\gamma_{LS} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L\gamma_S} \quad (4)$$

The latter equation may be given a meaningful theoretical foundation using the Lifshitz theory of dispersion forces. It also meets the fundamental requirements that (i)

$\gamma_{LS} \rightarrow 0$  if  $\gamma_L \rightarrow \gamma_S$ ; (ii)  $\gamma_{LS} \rightarrow \gamma_L$  if  $\gamma_S \rightarrow 0$ ; and (iii)  $\gamma_{LS} \rightarrow \gamma_S$  if  $\gamma_L \rightarrow 0$ .

It should be noted that the same requirements can be met by using the harmonic mean instead of the geometric mean,

$$\gamma_{LS} = \gamma_L + \gamma_S - \frac{4\gamma_L\gamma_S}{\gamma_L + \gamma_S} \quad (5)$$

but doing so does not appear to have any meaningful theoretical rationale.

(iii) Partitioning surface tension into dispersive and polar components

The dispersion forces are universal forces acting between any atoms and molecules, both polar and non-polar. However, additional forces may eventually come into play specifically when polar or chemically-interacting substances are dealt with. For instance, if one considers wetting of a mineral surface by water or alcohol, not only dispersive (d) but also dipole-dipole and hydrogen-bonding interactions must be taken into account. The existence of specific interactions translates into stronger adhesion between the liquid and the substrate, as the adhesion energy,  $E_{adh}$ , include now additional contributions due to the polar (p) interactions. The geometric-mean approximation may not be justified in this case, and some correcting terms must be introduced in order to compensate for discrepancies between theory and experiment. A variety of empirical formulas has been proposed by different authors for that purpose [4-9]. Nearly all such formulas can be classified into two categories, viz.:

(a) those in which the correcting term appears as a summand,  $\varphi$ , accounting for polar (dipole-dipole, acid-base, hydrogen-bonding, etc.) interactions,

$$\gamma_{LS} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L^d\gamma_S^d} - \varphi \quad (6)$$

(b) those in which the correcting term appears as an interaction parameter,  $\Phi$ , [3]

$$\gamma_{LS} = \gamma_L + \gamma_S - 2\Phi\sqrt{\gamma_L\gamma_S} \quad (7)$$

The most well-known "equations of state" of the first type are those using a geometric mean polar correction,

$$\gamma_{LS} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L^d\gamma_S^d} - 2\sqrt{\gamma_L^p\gamma_S^p} \quad (8)$$

the latter may be equally credited to Fowkes, Owens and Wendt, and van Oss and Good [4-6], and those using the harmonic mean polar correction,

$$\gamma_{LS} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L^d \gamma_S^d} - \frac{4\gamma_L^p \gamma_S^p}{\gamma_L^p + \gamma_S^p} \quad (9)$$

The harmonic mean representation of both the disperse and the polar components

$$\gamma_{LS} = \gamma_L + \gamma_S - \frac{4\gamma_L^d \gamma_S^d}{\gamma_L^d + \gamma_S^d} - \frac{4\gamma_L^p \gamma_S^p}{\gamma_L^p + \gamma_S^p} \quad (10)$$

was applied by Wu [8].

The best known "equation of state" of the second type is the empirical formula proposed by Li and Neumann [9],

$$\gamma_{LS} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L \gamma_S} \exp\left[-0.0001247(\gamma_L - \gamma_S)^2\right] \quad (11)$$

The exponential term in the latter equation is needed to achieve better accuracy when describing interaction between substances with greatly differing polarity. Let us consider, for instance, wetting of a non-polar substrate, such as polyethylene, by a polar liquid, such as water. In this case,  $\gamma_L$  is substantially greater than its dispersive component,  $\gamma_L^d$ , while  $\gamma_S \approx \gamma_S^d$ . Then, the term  $\sqrt{\gamma_L \gamma_S}$  turns out to be substantially greater than the dispersive part alone,  $\sqrt{\gamma_L^d \gamma_S^d}$ , despite the fact that polar

interactions cannot contribute much to the total interaction between the water and polyethylene because of non-polar nature of the latter. The exponential term provides an empirical correction for this discrepancy.

Eventually, it may happen that a substrate in study has so high a surface energy ( $g_S \geq g_L + g_{SL}$ )

that its surface is completely wettable by most test liquids, and therefore, contact angle measurements cannot be conducted directly. To work around this difficulty, a different experimental setup may be used in which the substrates in study are immersed in some liquid and a drop of another liquid immiscible with the first one is deposited on the substrate surface and its contact angle measured. Thus, one can use octane as ambient and water and mercury as test liquids to measure the surface energy of glass. Such a technique has been developed and successfully applied by Schultz et al. [10]. In principle, any equation of state (8)-(11) can be incorporated into the Schulz method. Once an appropriate equation of state,  $g_{LS} = f(g_L, g_S)$ , has been chosen,  $\gamma_S$  can be immediately calculated from contact angle exhibited by test liquid,  $L_1$ , on the substrate placed in ambient liquid,  $L_2$ , by solving the equation

$f(g_{L_2}, g_S) - f(g_{L_1}, g_S) = g_{L_1 L_2} \cos \theta$  for  $\gamma_S$ ; here  $g_{L_1 L_2}$  is the interfacial tension for the liquid 1 / liquid 2 interface.

(iv) A calculation example

Let's demonstrate how to determine the polar and the non-polar dispersive components of the surface energy of a solid based on the contact angle measurements for two different liquids. We will choose the Fowkes equation as our equation of state. In this case, the adhesion energy is a sum of two partial contributions, each of which is expressed as the geometric mean of two adhesion parameters,  $\gamma_L$  and  $\gamma_S$ , the first of which characterizes the "adhesive power" of the liquid, and the second, of the solid,

$$\gamma_L (1 + \cos \theta) = 2[\sqrt{\gamma_L^d \gamma_S^d} + \sqrt{\gamma_L^p \gamma_S^p}] \quad (12)$$

The adhesion parameters of some common test liquids are known (see Table 2). Therefore, by measuring the contact angles for two different liquids, the remaining two parameters - those of the solid in study - can be found.

TABLE 2 Adhesion parameters for some test liquids [4]

Test Liquid	$\gamma_L$ (mJ/m <sup>2</sup> )	$\gamma_L^d$ , (mJ/m <sup>2</sup> )	$\gamma_L^p$ , (mJ/m <sup>2</sup> )
Water	72.8	21.8	51.0
Ethylene glycol	48.0	29.0	19.0
Diiodomethane	50.8	50.8	0.0

Let's assume that, for the material the surface energy of which we want to determine, the contact angles with water and diiodomethane were found to be 49.6° and 75.2°, respectively. In this case, the following algebraic system of equations needs to be solved,

$$\begin{cases} 72.8 \times (1 + \cos 49.6^\circ) = 2[\sqrt{21.8 \times \gamma_S^d} + \sqrt{51.0 \times \gamma_S^p}] \\ 50.8 \times (1 + \cos 75.2^\circ) = 2\sqrt{50.8 \times \gamma_S^d} \end{cases} \quad (13)$$

whence we get  $\gamma_S^d = 20$  and  $\gamma_S^p = 30$  mJ/m<sup>2</sup>.

Eventually, the polar part can be further sub-divided into acid and base parts, in which case one gets [4],

$$\gamma_L (1 + \cos \theta) = 2[\sqrt{\gamma_L^d \gamma_S^d} + \sqrt{\gamma_L^{\text{acid}} \gamma_S^{\text{base}}} + \sqrt{\gamma_L^{\text{base}} \gamma_S^{\text{acid}}}] \quad (14)$$

The physical meaning of the acid and base adhesion parameters is rather vague, though.

Table 3 gives a brief summary of all the methods described above:

TABLE 3 Methods most commonly used for determination of the surface energy of solids

Method	Characteristics it provides	Application notes
Critical surface energy (aka the Zisman or Fox-Zisman method)	Maximum surface tension a liquid may have to ensure complete wetting	Used as a wettability benchmark; solids possessing a high critical surface energy are readily wettable by most liquids
Geometric mean (aka the Fowkes, extended Fowkes, Owens and Wendt, or OWRK method)	Total surface energy and surface energy components derived using the geometric mean equation (eq.(8)).	Suitable for characterization of non-polar and moderately polar substrates such as plastics, rubber, polymer films, paper, etc. Hydrogen bonding, coulomb, donor-acceptor and other specific interaction may be added in the same fashion.
van Oss-Good (aka the acid-base method)	Total surface energy, its dispersive and polar components, as well as the acid and base adhesion parameters obtained using eq.(14).	A modification of the above method better suited for the characterization of polar substrates, e.g. polyacrylamides, proteins, mineral surfaces, and alike, which are likely to be engaged in acid-base interactions with certain highly polar test liquids such as amines, carboxylic acids, water, etc.
Harmonic mean (aka the Wu method)	Total surface energy and surface energy components derived using the harmonic mean equation (eq.(10)).	The same as the above. From a theoretical viewpoint, the geometric mean formula (8) is better justified.
Li-Neumann (aka the equation of state method)	Total surface energy derived using the equation of state in the form of eq.(11).	Suitable for characterization of non-polar and moderately polar substrates such as plastics, rubber, polymer films, paper, etc. Should be preferred if the polarities of the substrate and of the test liquids differ significantly.
Schultz	Total surface energy and surface energy components derived using any appropriate equation of state; e.g. eq.(8) or (11).	Suitable for characterization of high-energy substrates, such as ceramics, metals and metal oxides, chemically grafted protein films, etc., for which the contact angle with common test liquids cannot be measured in a traditional way.

(v) The solution stability issue

From a mathematical viewpoint, a system of equations such as the one in the above example may not have a real solution at all or may have an ill-defined solution, which shows great sensitivity to small variations in experimental data. Proper mathematical tools are needed to deal with such problems. In practice, it is always advisable to carry out contact angle measurements for a greater number of liquids than the number of surface tension components one wants to evaluate, and to employ an appropriate mathematical regression procedure to obtain the best-fit solution. In general, it boils down to a minimization problem, which may be stated as follows: to find non-negative parameters

$(g_S^d, g_S^p, \dots)$  such that the mean-square residual deviation be a minimum,

$$\min_{\{g_S^d, g_S^p, \dots\}} \sum_i \{q_i^{\text{calcd}}(g_S^d, g_S^p, \dots) - q_i^{\text{exp}}\}^2 \quad (15)$$

Here the subscript "exp" marks the experimental contact angle value measured for the test liquid, and "calcd" marks the corresponding theoretical value calculated using a chosen equation of state,

$g_S - f(g_L, g_S) = g_L \cos q$ . A solution is said to be stable if a small variations in the experimental

input,  $q_i \mapsto q_i + dq$ , causes only small variations in the best-fit parameters

$(g_S^d \mapsto g_S^d + dg_S^d, g_S^p \mapsto g_S^p + dg_S^p, \dots)$ .

For instance, if changing the contact angle values in the system (13) by  $0.1^\circ$  entails a change of  $0.1 \text{ mJ/m}^2$  or so in the surface energy components, the solution stability is satisfactory. However, if the same small variation in the contact angle data entailed a change of  $10 \text{ mJ/m}^2$  in the surface energy components, the reliability of the determination would not be acceptable.

(vi) Concluding remarks

Accuracy and reliability of results of the surface energy determinations depends on the following conditions:

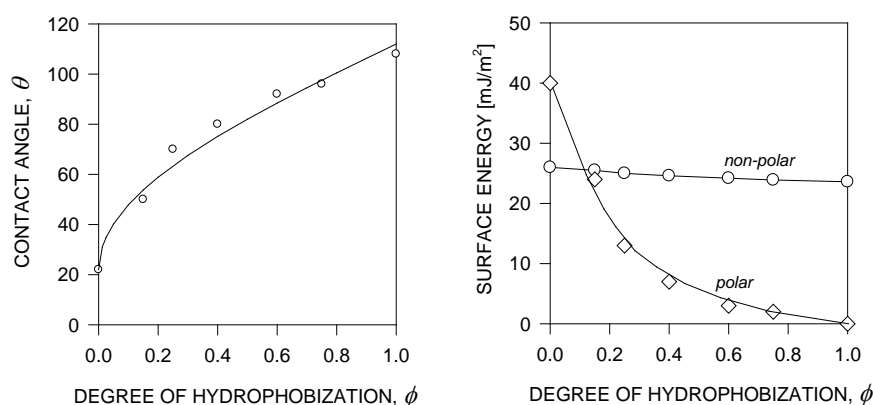
- Substrate is sufficiently smooth so that there is no contact angle hysteresis; the reliability of results being contingent on the possibility to measure the equilibrium contact angle;
- Surface is sufficiently clean or the degree of contamination can be controlled if reproducibility of results is sought;
- Surface is homogeneous so that sessile drops of test liquids assume a hemispherical shape;
- No absorption, swelling or dissolution occur when the substrate is brought into contact with test liquids.

It should be realized that for real-life applications, these conditions may be too straightening, and hence, the credibility of results obtained may often be dubious.

## Application examples

### (i) Paintability, printability, adhesion, and water-resistance

Adsorption of surface-active components, deposition of surface films, silylation, chemical etching, plasma cleaning and plasma modification are the standard tools for modifying the surface energy of materials according to specific application needs. To demonstrate how it works, and what results can be achieved, let's consider the changes in hydrophobicity of a metallic surface coated by monomolecular film assembled from a mixture of alkyl and hydroxyalkyl thiols (see Figure 4). Terminal hydroxyalkyl thiol is the bearer of hydrophilic functionality, while the normal alkyl thiol is the bearer of hydrophobic functionality. For such a surface, different degrees of hydrophobization can be attained by varying the thiol ratio [11].



**FIGURE 4** Changes in the contact angle of water and the surface energy for mixed  $\text{HS}(\text{CH}_2)_{16}\text{OH}/\text{HS}(\text{CH}_2)_{16}\text{CH}_3$  thiol-coated gold substrates with varying thiol ratio.

Similar phenomena occur in the process of sizing of paper and paperboard widely used in the papermaking industry [12,13]. The sizing process can be depicted as "waxing" the surface of cellulose fibre with certain chemicals, such as alkylketene dimer or alkenyl succinic anhydride, whereby a part of highly polar hydroxyl groups is substituted by less polar ester group. The bulky alkyl moieties of the ester groups sterically hinder hydrogen-bonding and polar interactions with water, rendering paper water-repellent, as explained in Figure 5.

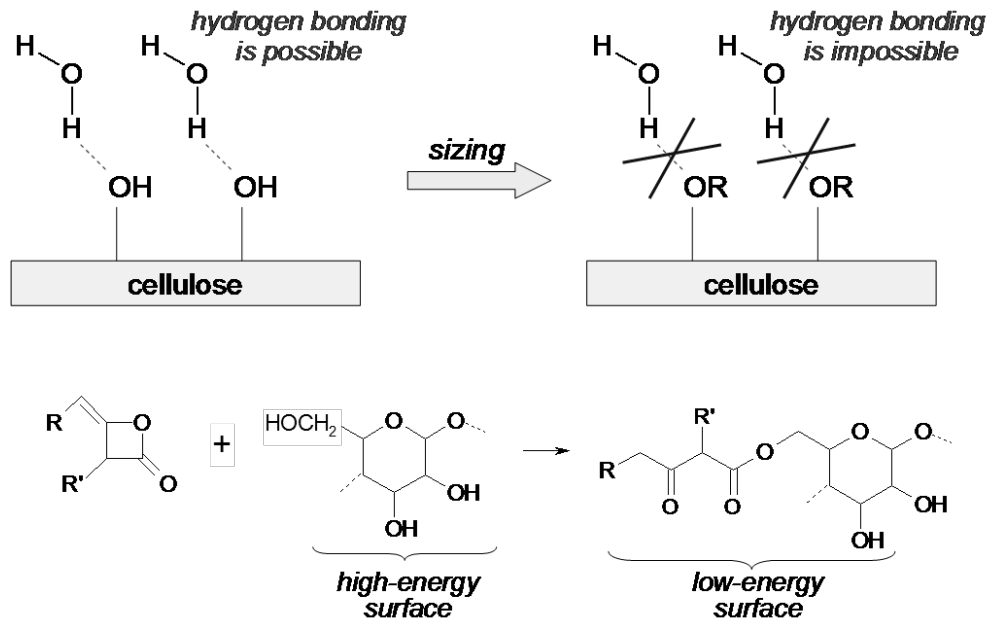


FIGURE 5 Effect of sizing on the surface energy of paper and paperboard.

The sizing efficiency increases with increasing the charge of the sizing agent, but upto a certain limit, above which a plateau is reached or even sizing reversion may occur. By measuring the changes in the surface energy of sized paper versus the size charge, the optimal addition level can be found (see Figure 6).

A decrease in the surface energy of paper brought about by sizing is beneficial in terms of improved water-resistance, but it may incur certain problems in printing, converting, or sheet-feeding operations [14-17]. Therefore, it is expedient that the surface energy of supplied paper stock be monitored as one of the key parameters ensuring the flow of the said processes.

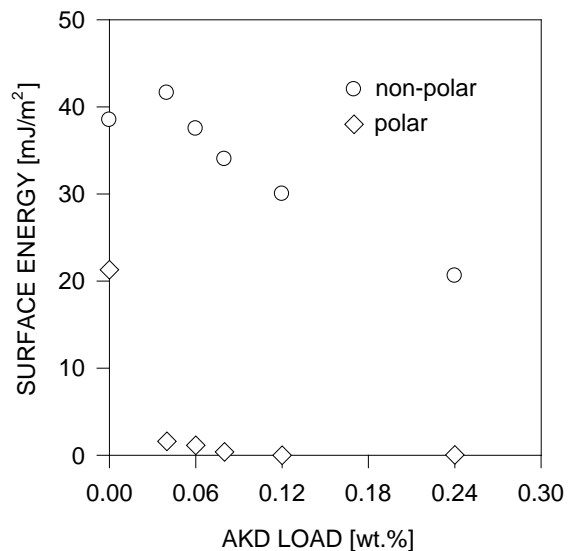


Figure 6 Changes in the surface energy of paper with varying the degree of AKD sizing [12].

(ii) Tribological and wetting properties of hard metal coatings

Hard coatings are used in various industries for minimizing friction and improving wear-resistance and of metal surfaces under heavy tribological load (e.g. in magnetic storage disks, metalworking tools, etc.) Their composition, deposition technologies and properties vary from application to application. Diamond-like coatings (DLC) are most common when smooth surfaces with a very low friction coefficient are needed [18]. Recently, it has been observed that hydrogenated DLC coatings exhibit significantly lower friction coefficients than their non-hydrogenated analogues [19-21]. The hydrogenation does not only alters the tribological behaviour of the coatings, but also affects their interaction with lubricants. For instance, mineral oils will spread faster over hydrogenated DLC's because of reduced significance of the contact-line pinning effect [22] (Figure 7).

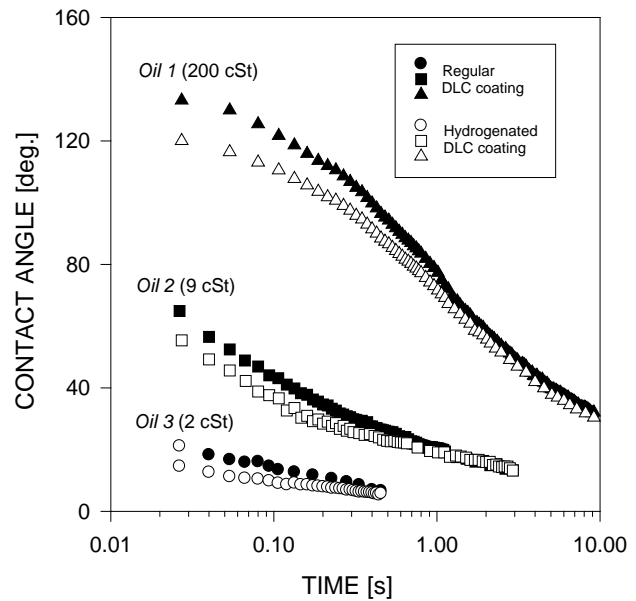


Figure 7 Dynamic contact angle exhibited by drops of lubricating mineral oils of varying viscosity grades spreading over the surface of DLC-coated steel substrates.

The importance of proper optimization of the surface energy component of various mechanical parts in the motor industry is not paid due attention, where production costs, fuel economy, and mechanical durability are given primary consideration [23]. At the same time, general experience suggests that, by lowering the surface energy of many engine parts, such as piston rings, cylinder linings, and intake valves, the risk of deposit formation and adhesion-related wear can be reduced and the overall engine performance improved.

(iii) Biomedical applications

Consistency in frictional, wetting and adsorption characteristics of various surgical implants, ranging from dental and orthopedic devices to heart valves and aortic grafts, is of paramount importance for patient well-being. For instance, the use of metallic grafts in the past was associated with increased thrombogenicity and erythrocyte damage. The drawbacks of metallic implants are primarily associated with a high surface energy of metals, a factor favoring blood protein adsorption on the graft surface. Introduction of polymeric, pyrolytic carbon and teflon grafts has significantly alleviated the aforesaid problems associated with the use of metallic grafts. In those cases where a substitute for metallic devices cannot be easily found, surface modification can be attempted [24, 25].

The response of biological tissue to implanted materials in vivo is one of the most fundamental and complex challenges of modern restorative medicine. Whether a material is biocompatible or not is determined partly by the properties of the material surface that interact with the surrounding cells.

To promote tissue formation and integration, a surface which enables cell adhesion, proliferation, and migration, is needed [26]. In a recent study by Lynch et al. [27] dealing with the adhesion of human epithelial cells on polymer films, it has been demonstrated, by using the contact angle measurements, that there exists a direct correlation between the surface energy and cell adhesion. Figure 8 shows the changes in the contact angle for three test liquids with the surfaces of polymer film with varying polarity. In the case in study, the modest decrease in the surface energy resulting from the substitution of isopropylacrylamide by bulkier *tert*-butylacrylamide groups causes a significant increase in cell adhesion.

Surface energy considerations may serve valuable guidelines in a variety of other applications, e.g. in optimizing the dental filling adhesion to the tooth surface [28], etc.

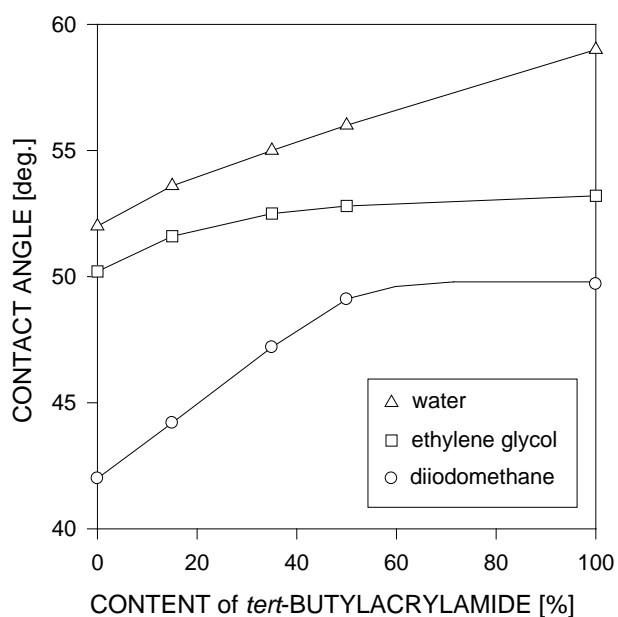


FIGURE 8 Changes in contact angle of test liquids with varying the composition of isopropyl-/*tert*-butyl-acrylamide copolymer film [27].

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