# Sensitivity of Surface Free Energy Analysis Methods to the Contact Angle Changes Attributed to the Thickness Effect in Thin Films

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**ABSTRACT:** The surface tension of thin, uncured epoxy films spun-cast onto oxidized silica wafers was analyzed as a function of their thickness in the range of 5 to 75 nm. Based on contact angle measurements with polar and apolar liquids, the surface free energies of various films were analyzed and compared using Lifshitz–van der Walls/acid–base (LW/AB), harmonic mean (of Wu), geometric mean, and Zisman approaches. Results of harmonic mean and Zisman surface tension analyses, in spite of significant changes in contact angle attributed to changes in thickness, did not show significant changes. However, geometric mean and LW/AB methods did reveal limited changes in free energy of epoxy surface attributed to variations in thickness. The surface tension components showed a similar trend to that of contact angle changes. It seems that it is better to use surface free energy analysis methods, which use several liquids with different polarities, to reveal the accumulative effect of different group free energy densities on total surface free energy. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1972–1980, 2004

**Key words:** free energy; films; tension; epoxy; surfaces

## INTRODUCTION

Contact angle measurement, using the sessile drop technique, is widely used for investigation of the surface characteristics of various materials. On the other hand, the surface free energies of polymers control their adhesion, adsorption, lubrication, steric stabilization, wettability, and similar surface-related properties.[1,2] In some theories of self-stratification of coatings[3] surface tension is a determinant factor. The macroscopic Young–Dupre equation correlates the contact angle to the surface and interfacial tensions, all of which may be further decomposed into Lifshitz–van der Waals and the polar components of surface energies.[4] The Young–Dupre equation, together with theories of polar and apolar surface tension components, remains the mainstay of measurements of surface properties by the sessile drop measurement. However, different methods of surface free energy analysis, such as Zisman, harmonic mean, geometric mean, and Lifshitz–van der Waals/acid–base (LW/AB) method, yield different results and meanings.

Surface free energy analysis methods suffer from some limitations.[4,5] Through the past years, the above-mentioned approaches have been used by different researchers to analyze surface tension of films. The LW/AB approach has been the focus of increased attention[6–8] during the past few years, in the analysis of surface free energy, because conventional methods, such as Zisman or Neumann method, do not include different surface free energy interactions with the liquid drop. Moreover, in the harmonic or geometric mean methods only two surface tension components, as polar and apolar interactions, are considered, whereas in a polymer chain and the liquids (which are normally used as a drop to measure the contact angle), different groups having different polarities and different physical interactions exist. Therefore, it is apparent that relying on only two components in surface free energy is not sufficient to reveal the exact nature of the surface. Based on this concept, in the LW/AB approach three components are used to analyze the surface free energy, such that it gives the impression that this approach can deal better with the true nature of the surface free energy, especially in multigroup surfaces. The LW/AB method, in some cases, has also encountered some limitations that lead to some unacceptable results.[6,8]

The sessile drop approach itself suffers from some limitations. Most interactions between surfaces are less characterized, so some researchers have argued that this method is unreliable, and the results of ex-

periments largely depend on the sample preparation and test conditions.[9]

As different researchers have mentioned, the most important parameters that affect contact angle measurements are as follows: temperature, material transitions such as glass and crystalline transitions, contaminants and adsorbed materials, polar and apolar interactions, drop dimension, line tension, surface crystallinity, molecular weight, and conformation of chains.[10] Thus for proper measurement of contact angle, such factors must be considered. Nonetheless, there are some new or old experimental problems that reveal the role of unconsidered parameters that need further investigation.

There are a few reports on the effect of thin film thickness on contact angle.[11–13] It is suggested that the surface energy of thin films depends not only on the molecular forces of film material but also on the interactions or attractive forces of substrates. Mate and Wu[12] investigated the dependency of contact angles on the thickness of perfluoropolyether lubricants on silicon wafers and disks coated with amorphous hydrogenated carbon. They characterized a screening length in which the substrate interaction effect decreases exponentially, and thus the contact angle reaches a steady-state condition. This length for alkenes droplets is just a few angstroms, whereas for water droplets the screening length is almost one order of magnitude higher.

Some researchers[13–16] tried to relate this effect with long-range macroscopic interactions between hydrophobic substances, which refer to attractive forces between two or more apolar surfaces or solutes that separate with a liquid. Hato[13] showed that the extent of this long-range interaction is about 5–20 nm. Molecular structuring of the neighboring liquid molecules or interaction of liquid molecules between two surfaces[17] is specified as the result of this attraction.

Regardless of contact angle measurements, in other research fields the substrate effect on surface properties of thin films has also been observed. Researchers who work on the glass-transition temperature ($T_g$) of thin films have expressed that chain mobility or $T_g$ of polymeric thin films are affected to a gyration radius (Rg) of 15 (according to molecular weight of chains and substrate) thickness from substrate. These effects in length scale are observed at about 10–100 nm.[18–23] Decreasing chain mobility may have some reflections in the contact angle of some liquid drops on the surface.

Furthermore, in IR experiments it has been observed that as the thickness of the $SiO_2$ layer on silicone wafers increases, the frequency of bond stretching vibration ($\nu$) increases.[24] Further, as the oxide thickness approaches 700 Å, the values of $\nu$ begin to approach values characteristic of thick oxides (>1000 Å).

Apparently, a better understanding of the physical and chemical factors that influence surface free energy would have great value for the coatings and adhesives industry, which use contact angle measurement to study their products. Thus, when a coating or adhesive mixture is poured onto a substrate, a thin layer of resin adsorbs onto the attractive substrate and changes the surface free energy. In this article, we concentrated on the relevancy of surface free energy analysis methods with contact angle variations. According to the expressed thickness effect on the contact angle, variations of surface free energy, calculated from different methods with respect to the changes in contact angle that are observed in different thicknesses, was investigated. In this respect, different liquids with different polarities on thin films with different thicknesses were examined to investigate their relationships.

## EXPERIMENTAL

### Materials

Ethylene glycol (for synthesis; extra pure, Merck, Darmstadt, Germany), double distilled water, diethylene glycol (for synthesis; Merck), dipropylene glycol (for synthesis, mixture of isomers; Merck), diiodomethane (Merck), and glycerine (Merck) were used as contact angle measurements drops. Silicon wafers, 5 cm in diameter, were used as the substrate. Oxidized polished silicon wafers were used as received. The thickness of the oxidized layer of wafers was at least 150 nm. According to IR experiments on Si substrates,[24] vibrational frequency increases as the silicon oxide thickness approaches 700 Å, and after 1000 Å it has the value of thick oxide films and does not change with thickness. Normally, silicon oxide has a hydrophilic surface covered by silanols. Above 170°C, SiOH groups condense extensively to form hydrophobic siloxane bridges, Si—O—Si.[25]

Epoxy resins [Araldite GT7014; Huntsman Advanced Materials (formerly Vantico), Everberg, Belgium], dissolved in methyl isobutyl ketone (MIBK), were used to cast thin films.

### Film formation

Thin layers of epoxy film were spin coated (photoresist coater, model 3000; Electronic Microsystems) on silicon wafers by spin casting out of solutions of epoxy resin in MIBK. Silicon wafers were wiped with MIBK before use. The solution concentration and spinning speed varied between 0.25 and 2.5% and between 2000 and 4000 rpm respectively, to achieve different thicknesses. Obviously, for thinner films, higher rates and lower concentrations were better.

## Thickness measurement

Film thickness was measured by microspectrophotometer (MPV-SP; Leitz, Wetzlar, Germany), based on a reflectometric measurement system that can reveal homogeneity of thickness distribution on two- or three-dimensional contour maps. The thickness of films was measured at least at five points and samples with thickness variation >1 nm were rejected. The thickness of the oxide layer on silicon wafers was also measured by this technique.

The refractive index of the epoxy resin was needed for thickness measurement. It was measured in a two-layer system above a layer of $\alpha$-bromonaphthalene (Abbe refractometer, 1T/4T, Atago Co., Kirkland, WA).

## Contact angle measurements

Contact angle measurements were carried out with a contact angle measuring system (G40; Krüss GmbH, Hamburg, Germany). Measurements were performed at room temperature (20°C). The sessile drop method was used to measure the contact angle. For each measurement eight drops (10 mL) of each liquid, except methylene iodide (5 mL), was tested on the surface. Contact angles were measured for each drop after 1 min.

For surface free energy calculation four methods were used: acid–base, harmonic mean, geometric mean, and Zisman method. Data of surface tension components of liquids were obtained from the literature.[26,27]



**Figure 1**  Contact angle (a) and cosine of contact angle (b) of water droplets versus thickness of epoxy film coated on oxidized silicon wafer.

## RESULTS AND DISCUSSION

### Contact angle measurements

Contact angles of selected liquids were measured on wafers coated with epoxy resin with different thicknesses. Selection of liquids was according to the requirements of the selected surface free energy analysis methods. Most of the liquids used for contact angle measurements were capable of interacting by hydrogen bonds with epoxy resin (ethylene glycol, diethylene glycol, dipropylene glycol, glycerin, and water). Among the selected liquids, diiodomethane has a nearly apolar nature. The liquid sets for surface free energy analysis in different routes were as follows: EG, DEG, and DPG for the Zisman approach; water and methylene iodide for the harmonic mean method. For the geometric mean method, we used the MI and water plus glycerin and the same set as usual for the LW/AB method.

Epoxy chains can interact by polar, apolar, and hydrogen bond attractive forces. Although the range of interactive forces is rather complicated, it allows one to verify simultaneously the interaction behavior of apolar and polar liquids.
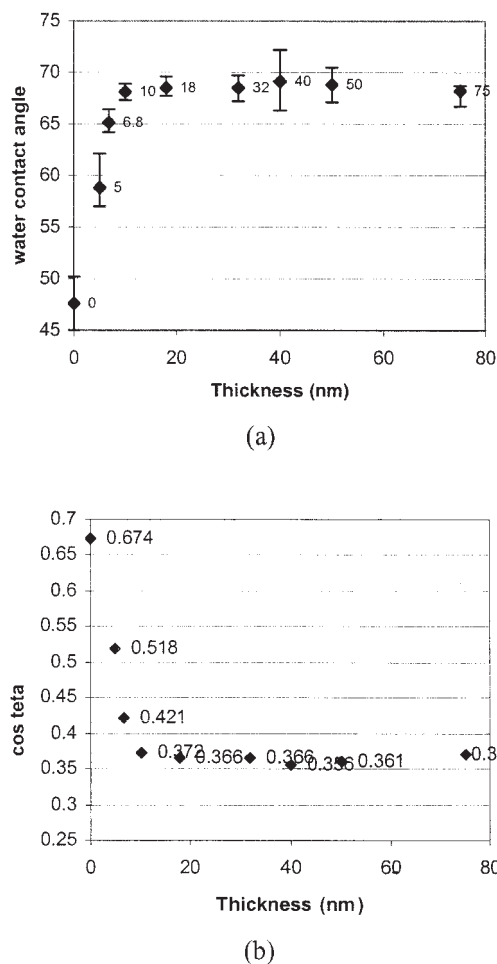
The variation of contact angles against thickness of the epoxy film for three liquids is shown in Figures 1–3. As can be seen there is a similar trend in these graphs and the trends of variation for other tests were approximately analogous to the above results. In addition, the cosines of contact angles versus thickness in Figures 1 and 2 also show an inclination similar to that of the contact angle. The curves show an ascending or descending behavior with a steep increase or decrease for thicknesses about 5 to 10 nm, after which the curves plateau. It seems that when the thickness of the epoxy film exceeds 18 nm, the contact angles of these liquids become independent of thickness. Water and glycerin contact angles on the epoxy-coated wafers are increased concomitantly (pseudoexponentially) with the thickness of epoxy film, whereas with diiodomethane, the contact angle is decreased in the same way. The substrate is supposed to have an effect on the contact angle of test liquids, which is attenuated by
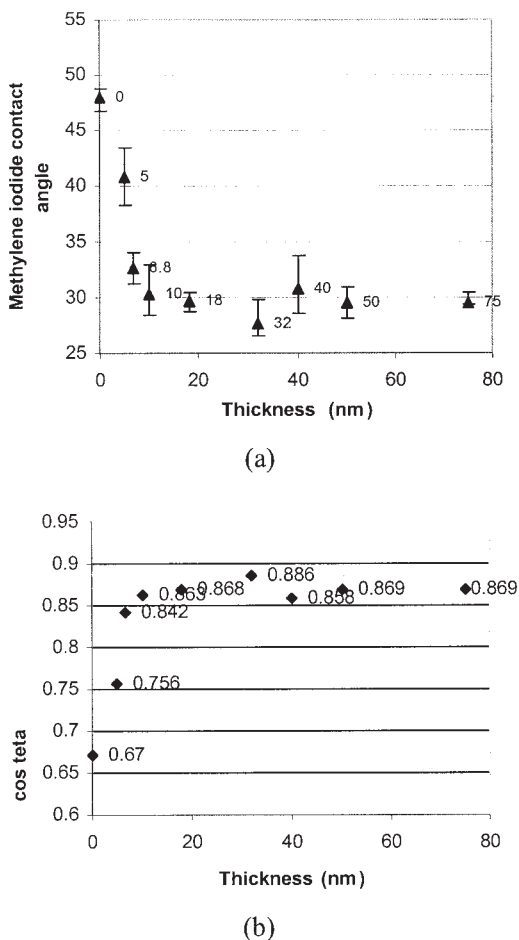
(a)



(b)

**Figure 2** Contact angle (a) and cosine of contact angle (b) of methylene iodide droplets versus thickness of epoxy film coated on oxidized silicon wafer.

increasing the film thickness and is completely screened out after about 18 nm. The data show that the interaction of water, glycerin, and ethylene glycol with silicon oxide is stronger than that with the epoxy film, whereas diiodomethane interacts with epoxy film more strongly does than silicon oxide. Droplets of glycols on bare wafers rapidly flattened, so it was considered as zero.

There are a few studies in this area, although there are some complications in interpreting some of the presented data; different researchers have thus chosen different points to discuss about this phenomenon. Mate and Wu[12] performed some experiments with alkane liquids on PFPE-coated disks and they observed an exponential increase of contact angles before reaching a plateau around 2 nm. For water, however, they observed the change of contact angle with film thickness up to about 8 nm. The interaction of alkane droplets with the coated surface is considered (in their theory) to split into a direct contact term with the coating and a term that represents the interaction of the alkane with the substrate, mediated by the

intervening coating film. However, their results for water contact angle did not have an exponential trend with thickness, and its curve reached a plateau at higher thicknesses. In other words, the water still interacts with the underlaying substrate, either through the thick film or, as they stated, it displaces a significant number of the coating molecules in the layer.

In a different investigation, Hato[13] found that the long-range attractive forces, between two hydrophobic surfaces across water, are effective at most to 15–20 nm. In his experiments at surface separations < 15 nm, the rapidly increasing attraction emerges and the surfaces rapidly merge with each other. Therefore, the attractive force increases exponentially. Hato was the first who proposed the long-range attraction as the mechanism of contact angle effect; Mate also proposed a mechanism like that of Hato, but not with the same terms.

In the present work, the liquid drops (except diiodomethane) have a polar nature. Moreover, in spite of Hato's work, the epoxy chain is not an inert medium with respect to the surfaces and it can interact with different groups of liquid droplets and also silicon dioxide layer on the wafer.

Surprisingly, in Figures 1–3 we observed that there is a pseudoexponential trend for both polar and apolar liquids, although it is believed that the nature of long-range attraction between polar or apolar groups is different.[15] The decaying length of different interactive forces between polar or apolar groups through epoxy film is not known to us at this time and needs to be determined in future investigations with homogeneous materials. In addition, it must be said that contact angle differences in these experiments cannot simply be split into a constant and an exponential component.[12] Attractive forces of the substrate not only have effects on the liquid droplets but also, as shown in this work, exert some effects on the chains of medium in the vicinity of the droplet, such that they can
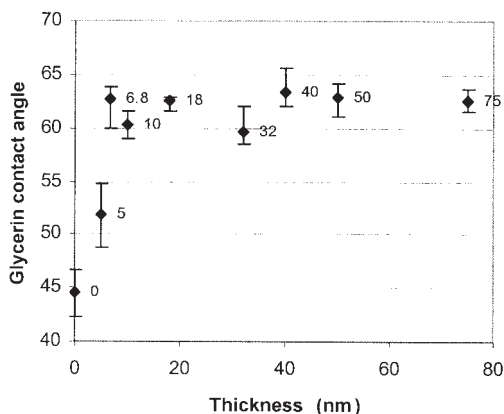


**Figure 3** Contact angle of glycerin droplets versus thickness of epoxy film coated on oxidized silicon wafer.

manipulate the contact angle. Therefore, we think that the mentioned pseudoexponential trend may not really be pseudoexponential but that it is the result of the interaction of polar/apolar interactions and reconformation of chains that finally dictate the trend of variation, and with other materials the trend may not be pseudoexponential. Adsorptive interactions between chain segments and sites on the surface and entropic constraints imposed on the motion of chains at a phase boundary strongly influence the conformation, mobility, and relaxation of epoxy chains. All these aspects vary with distance from the solid surface on a length scale comparable to the chain dimension of epoxy resins.

To express this dimension in terms of gyration radius (Rg), a rough approximation from the data of SANS experiments on polymeric chains was used. To estimate the Rg value of our epoxy chains, we chose the bulk constant of polycarbonate chain from Sperling,[28] given that these two polymers have approximately similar chain structures. The calculated Rg was about 1.7 nm, and because our resin was not monodisperse, this number was considered as a mean and approximate value. Thus in 5, 6.8, and 10 nm points, the thickness is at least equal to 3–6 Rg. As researchers who worked on $T_g$ depression (or increase) in thin films have expressed, normally in the range of 1–13 Rg, chain mobility is affected from the substrate. Tsui[20] measured the thickness dependency of $T_g$ on his experiments up to about 15 nm, but some other researchers report $T_g$ depression up to 100 nm.[22] Therefore, it is plausible to examine chain mobility variation through the tested thickness. It must be noticed that, depending on the instrument, which is used to investigate properties of thin films on any substrate, the screening thickness may have different values because sensitivity of the equipment and the nature of materials are not similar.

It should be noticed that in each epoxy chain (Araldite 7014) on average there are about four hydroxyl (OH) groups, 10 ether linkages, and two epoxide groups. Also the benzene rings of bisphenol-A in the epoxy chains are an electron-donor source, which interact with polar groups, and also there are many methyl and methylene groups, which are apolar in nature. Thus, it would be possible for chains to flip-flop to decrease interfacial tension between the liquid drops and the epoxy surface, if there were not serious restrictions for their motion.

By this approach we cannot be sure that atoms or different groups of the epoxy chains with varying thicknesses have the same or different decaying length attractive forces on liquid drops on the surface. One should thus be attentive to treat these data, such as the care that should be followed for patchy surfaces.[14,16] Contact angle or surface tension on heterogeneous surfaces is the result of a combination of the effect of

**TABLE I**
**Surface Energy Components (in mJ/m$^2$) for Test Liquids**

| Liquid | $\gamma$ | $\gamma^d$ | $\gamma^p$ |
|---|---|---|---|
| Water | 72.8 | 22.1 | 50.7 |
| Methylene iodide | 50.8 | 44.1 | 6.7 |

different surface patches according to the Cassie formula. It is thus reasonable to expect that the influence of silica substrate on different groups (liquid droplet or epoxy chains) up to a specific distance is effective and the combination of these different decaying lengths and the outcome surface free energies of different groups can be treated like patchy surfaces.

However, because the contact angle of liquid on the film is attributed to interactions of different groups of epoxy chains and substrate, it is plausible to suggest that the effect of some groups of epoxy chains and substrate can interact with each other so that the effect of some groups seems stronger or weaker. However, we cannot tell that the interaction of all of different groups decay exponentially (or in a different trend) but they attenuated more or less in a definite thickness, and thus the curve of thickness versus contact angle is primarily a cumulative curve that consists of curves of different interactions versus thickness. Now we do not intend to treat the origins of changes in contact angle with the thickness of epoxy film (this is the subject of another article by the authors): here the main point is to investigate the correlation of contact angle changes with the surface free energies calculated from different routes.
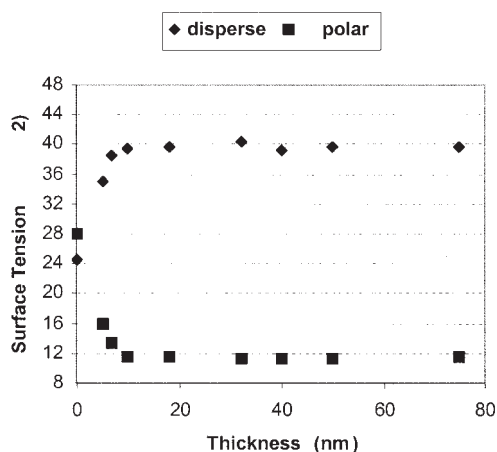
## Surface tension

A substantial amount of work has been done on the evaluation of the surface tension of low-energy surfaces such as polymers. Even though until now it seems impossible to measure directly the surface tension of a solid, several approaches exist that correlate the contact angle of a liquid droplet on a solid with its surface free energy. A few of the important methods that have normally been used to analyze surface free energy are harmonic mean, geometric mean, Lifshitz–van der Waals/acid–base, and Zisman approaches.

In the harmonic mean method, to obtain a good result, two liquids with large differences in their polarity should be used. Water and methylene iodide are two convenient testing liquids, whose surface tension components are listed in Table I. Most experiments[10,27] revealed that if other liquids, except water and diiodomethane are used, the results would not remain constant and with each liquid pair, we would encounter different values for surface free energy. Thus most investigators normally prefer to work with these two liquids. Results of surface free energy anal-
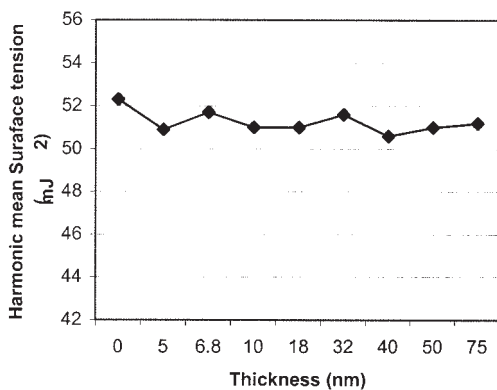
(a)



(b)

**Figure 4** Surface tension (a) and its components (b) based on harmonic mean method and their components versus thickness.

ysis, based on the harmonic mean method, and its components are presented in Figure 4. As it is observed, there was no sensible variation for surface free energy versus thickness, although its components, like contact angle data, show a pseudoexponential trend. It seems that in this method, the combination of polar and disperse components in our samples hide the true nature of the surface. Therefore, that one component can cause the effect of other component to be so weak that the net result of both components shows insignificant changes. It can be concluded here that the conventional liquid set for the harmonic mean method (water and MI) is not suitable for multigroup surfaces.

The geometric mean method is also based on the contact angle of two or three liquids. In this research, three liquids are used. In addition, here also, different sets of liquids give different surface tensions. In this method, like the harmonic mean approach, two components of surface free energy (polar and disperse) are calculated. Here it was decided to use a liquid set similar to the liquids normally used for the LW/AB method until we can compare their results. The ana-

lyzed results based on this method are shown in Figure 5. The fitness accuracy for the three-liquid system was between 89 and 99%. As can be seen, the surface free energy results, like surface tension components, show pseudoexponential behavior akin to the contact angle data up to the thickness of 6.8, but after that point the surface tension does not show any effect from the substrate (thickness effect), whereas contact angle data show the thickness effect up to 18 nm. In addition, its components trends are not as smooth as the harmonic mean components. It seems that in spite of the harmonic mean, the selection of three liquids in this method can better reveal the true nature of surface free energy changes. In other words, the combination of interactions of liquids with different polarities can better present the free energy density changes on the surface, with the thickness.

The LW/AB approach, developed by Van oss and colleagues, presents a useful method for surface free energy formulation. According to this approach, the



(a)

**Geometric mean surface tension**
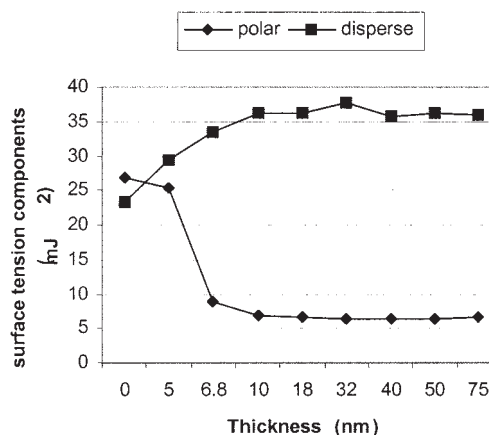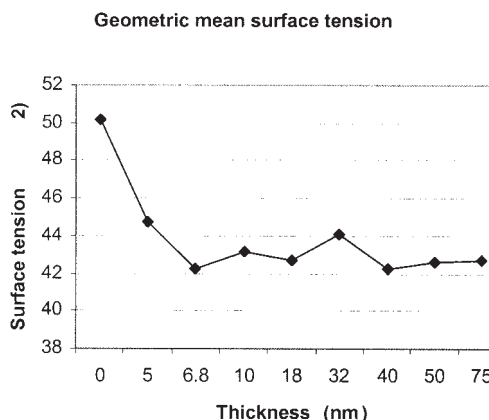


(b)

**Figure 5** (a) Surface tension components according to geometric mean approach of epoxy film with different thicknesses. (b) Geometric mean surface tension versus thickness of epoxy film.

**TABLE II**
**Surface Energy Components (in mJ/m² ) for Test Liquids**

| Liquid | $\Gamma$ | $\gamma^{LW}$ | $\gamma^{+}$ | $\gamma^{-}$ |
|---|---|---|---|---|
| Water | 72.8 | 21.8 | 25.5 | 25.5 |
| Glycerin | 64.0 | 34.0 | 3.9 | 57.4 |
| Methylene iodide | 50.8 | 50.8 | 0.7 | 0.0 |

surface free energy splits into components describing the contribution attributed to dispersion forces ($\gamma^{LW}$) and the acid–base contribution ($\gamma^{AB}$). Acid–base forces are also analyzed by two components, electron-donor and electron-acceptor components, which enables one to investigate more precisely important parameters that exert an effect on surface tension. The values of three surface energy components of the test liquids used in this study are listed in Table II.[27] The results of surface tension analysis based on LW/AB and its components are illustrated in Figure 6 The results for the Lifshitz component show a trend similar to that of contact angle data, but despite an abnor-

mality at a thickness around 6.8, a roughly smooth trend, similar to that of contact angle data, can be observed for the acid–base component. The abnormality is akin to the abnormality that can be observed in contact angle data of glycerin. It seems that in this method the proposed values of the acid–base components of the liquids can lead to errors in the calculation results. Even though the increase and decrease of the components with thickness did not overlap each other completely, the total obtained surface tension showed some changes with thickness. As shown in Figure 6, the decrease of $\gamma^{AB}$ was attributed to a decrease in both $\gamma^{+}$ and $\gamma^{-}$ components. It is notable that the decreasing trend for both of these parameters was also similar.

The Zisman approach is based on an empirical rectilinear relation between the cosine of contact angle and the surface tension of a series of testing liquids on a given surface. When homologous liquids are used as the testing liquids, a straight line is often obtained. When nonhomologous liquids are used, however, the
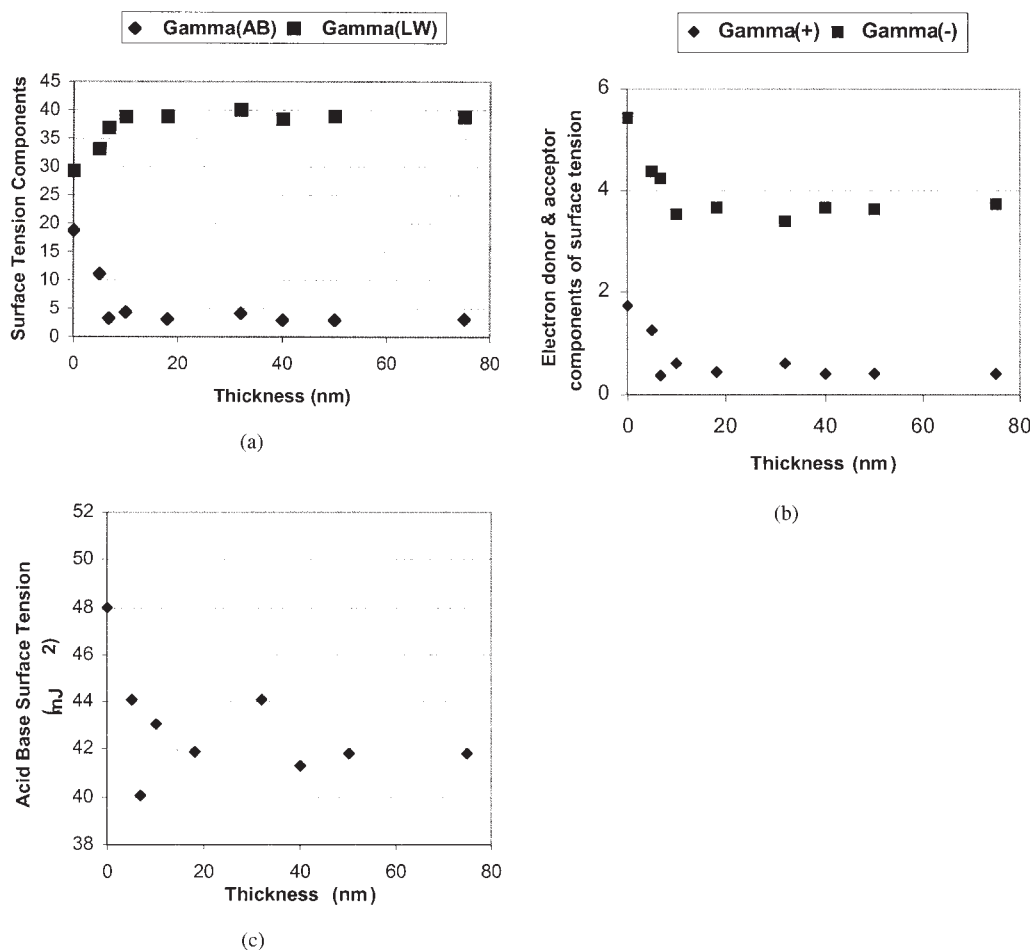


Figure 6 (a) Lifshitz–van der Waals (LW) and polar components of acid–base (AB) surface tension versus thickness. (b) Electron-acceptor and –donor components of acid–base surface tension versus thickness. (c) LW/AB surface free energy of epoxy film versus thickness.
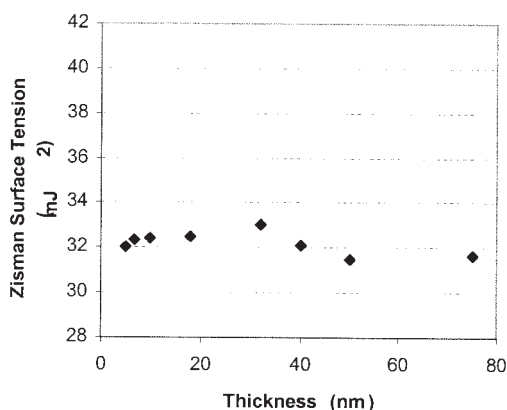
**Figure 7** Surface tension of epoxy film based on Zisman method versus thickness.

data are often scattered within a rectilinear band or give a curved line. The fitness accuracy for the liquids selected in this study was 96% and, as was expected, the critical surface tension had different values related to the data obtained by other methods (Fig. 7). It should be noted that the selected liquids can generate hydrogen bonds with epoxy film, and if a different series of liquids with different polarities is chosen, other values for critical surface free energy could be obtained.

As can be seen in Figures 4–7, surface tensions calculated by the mentioned routes have different values and trends. It is plausible to say that geometric mean and acid–base method are more sensitive in disclosing some of the small differences among other methods, which are shown by contact angle measurements, such that as the thickness increases, the contact angle and the cosine of contact angle (which is more relevant to surface free energy) steeply increase or decrease up to about 10 nm. However, in surface free energy values calculated by the other two methods, the curves did not progress with such a trend. Although there is no established rule for the necessity of this relationship, the differences in values of surface tension between the methods can demonstrate that the calculated numbers are neither a good picture of the true nature of such a surface phenomenon, nor a good representative of what is (the trend) displayed by the contact angle. It seems that collective interactions of different groups on surface free energy can be determined only by testing several liquids with different polarities, and if fewer liquids are used, less-accurate results will be obtained.

Furthermore, for each thickness there are substantial differences in the exact values of surface free energy. Thus as others stated about surface tension analysis methods, it is not yet possible to rely on a single value as a universal surface free energy for a material by these methods. In other words, it seems that we could compare different calculated surface free ener-

gies only with each other, when similar experimental and preparation procedures are used.

By increasing the epoxy film thickness up to about 18 nm, the polar components in different surface tension analysis methods were decreased, whereas the disperse components were increased. If the amount of increase and decrease of the components is almost the same, the total surface tension cannot show changes with thickness; otherwise, the surface tension results could show the trends of contact angle data.

## CONCLUSIONS

In this work, we concluded that the contact angle of epoxy resin thin films would change by increasing or decreasing the film thickness below about 18 nm. Adsorption of epoxy chains on substrate and their interactions with other chains are also other important parameters in restricting the chain mobility that can finally affect the surface properties of thin films. The results show that the nature of the surface of epoxy films changes to a more hydrophobic state as its thickness increases.

It is strongly suggested that, in addition to other parameters that affect the contact angle measurement and surface free energy analysis of polymers (e.g., drop volume, surface roughness, molecular weight, etc.), the film thickness in nanometric scale also be considered as an important factor.

Results of surface tension analysis showed that various methods yield different values, and they are affected in different ways from contact angle data. Surface free energy components could reveal more details of the nature of the surface. Our results revealed that the calculated surface free energies from geometric mean and acid–base methods show increasing hydrophobicity of the epoxy surface with increasing film thickness. Because the harmonic mean and Zisman methods could not show the increasing hydrophobicity of epoxy surface with thickness, it is readily apparent that the methods that use more liquids with different polarities can better determine the true nature of the surface.

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