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Symmetric expressions of surface tension components

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ABSTRACT

Surface tensions of solid materials have been studied over 200 years and widely used for industrial or engineering applications. The surface tensions and surface tension components can be calculated using measured contact angles, for example, by the model studied by Owens and Wendt. The model is often represented in an asymmetric linear form, called the Owens-Wendt-Rabel-Kaelble method, with the use of the linear least squares method. However, due to the practical preference not to use many types of test liquids, the existing statistical analysis is unsuitable, especially when the data measured are scattered. The present work proposes symmetric linear and circular expressions of the model of the two surface tension components. The symmetric linear expression can be used for obtaining the polar and dispersion components of surface tension of a solid; it enables appropriate choices for test liquids, physically meaningful screening of measured values, and clear validation of deduced surface tension components of solids. The symmetric circular expressions can be applied to deduce polar and dispersion components of liquids by using test solids. In conjunction with this, appropriate choices of test solids can be determined.

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1. Introduction

Evaluating the wetting characteristics of a material surface is useful for both practical and industrial applications. It is essential for establishing optimal adhesion between dissimilar substances. One of the easiest methods for evaluation is to measure the contact angles that a liquid makes with a given solid surface. On the other hand, the concept of surface tension or surface tension components is advantageous for understanding a material's wetting characteristics since it can give a clear idea about the interaction of a liquid to a solid surface.^[1] The total surface tension is the sum of the different intermolecular interactions. The component of surface tension corresponding to the non-specific London dispersion interactions is called the dispersion component.^[2] Here, the London dispersion interactions are temporary attractive interactions that are induced when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. In the two-component model,

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the polar component is defined as the component corresponding to a non-dispersion component, that is, collectively as a component associated with the intermolecular interactions other than the London dispersion interactions. There are some attempts to further divide the polar component into different components or add a third component.^[3] For example, Kitazaki and Hata propose the model including the dispersion component, the hydrogen bonding component, and the polar (dipole-dipole) interaction component.^[4] Van Oss et al. proposes Lewis acid and Lewis base subcomponents to establish the three-component model.^[5] Another example of the three-component model includes Hansen solubility parameters (HSP), consisting of parameters of dispersion, polar, and hydrogen bonds.^[6] HSP are thermodynamic quantities, describing physical interactions among molecules, and have been used for a variety of applications.^[6,7] In general, the three-component models require at least three test liquids to obtain unknown three surface tension components of a solid. Despite theoretical support for the three-component models, the two-component model is widely used for practical industrial applications, probably due to simple measurements of contact angles and easy calculation to estimate the surface tension components.

The surface tension of solids can be obtained in various ways, including the use of measured contact angles.^[8] However, there are critical issues when calculating the surface tension using the measured contact angles. For one, measuring the static contact angle can be problematic.^[9] This is due to the contact angle slowly advancing after the liquid is initially dropped onto the surface, which makes whatever succeeding calculation for the surface tension increasingly inaccurate. Another problem is that the calculation of the surface tension assumes a perfectly flat and smooth solid surface, which is unrealistic. Furthermore, it is reported that even the dynamic contact angle measurement can show difficulties in obtaining meaningful results, indicating that considerable experimental care and suitable methodology are required.^[10] Furthermore, the measurement of the contact angles can be unreliable since any specific test liquid may behave poorly.^[11] Nevertheless, the measurement of contact angles and calculation of the surface tension are widely employed.^[12] In addition, from a previous work about the “cohesion of fluids”^[13] to the most recent endeavours on hydrophobicity,^[3] surface tension, surface tension components and contact angles have been explored and discussed thoroughly by researchers for the past two centuries. There are a number of ways of calculating the surface tension components of a solid by measuring contact angles in the two-component model. While their approaches are different, essentially a similar idea is proposed based on simplified relations between the surface tension components and the contact angle [for example 1, 14]. More specifically, the surface tension components of a solid can be obtained through the measuring the contact angles with two or

more different liquids. One could say that the only difference between these two representative references is that while ref.^[1] uses the geometric equation:

$$(\gamma_{li}^d + \gamma_{li}^p)(1 + \cos\theta) = 2(\gamma_s^d \gamma_{li}^d)^{\frac{1}{2}} + 2(\gamma_s^p \gamma_{li}^p)^{\frac{1}{2}} \quad (1)$$

ref.^[14] uses the following harmonic expression instead:

$$\gamma_{li}(1 + \cos\theta) = 4 \frac{\gamma_s^d \gamma_{li}^d}{\gamma_s^d + \gamma_{li}^d} + 4 \frac{\gamma_s^p \gamma_{li}^p}{\gamma_s^p + \gamma_{li}^p} \quad (2)$$

where $\gamma_{li}^d, \gamma_{li}^p$ are the dispersion and polar components of the liquid's surface tension, γ_s^d, γ_s^p are the dispersion and polar components of the solid's surface tension, and θ is an equilibrium contact angle defined by Young.^[13] Equation (1) was obtained through geometric analysis of a solid-liquid system and can be used generally for any such system.^[15] On the other hand, the focus of ref.^[14] is on organic macromolecular compounds and is deemed to be more suitable for such materials than the general equations proposed in refs.^[1,15] Fundamentally speaking, it is clear that Equations (1) and (2) can be solved in a similar way. When the values of $\gamma_{li}^d, \gamma_{li}^p$ are known for two different liquids, the contact angle between these liquids and the solid in question can be measured. Once the measurement is done, the values of γ_s^d, γ_s^p can be obtained through solving a system of two equations with two unknowns of γ_s^d, γ_s^p . This method of approach, especially for Equation (1), wherein contact angle data are obtained and applied in an equation, is called the Owens-Wendt method.^[16] This method can be carried out with two or more liquids.

While two liquids are often used in finding the solid surface tension components of solids, one can also deal with multiple (i.e. more than two) liquids to the same effect with statistically more reliable results.^[11] One of the commonly used plots for the Owens-Wendt-Rabel-Kaelble (OWRK) method takes either of the two following equations as linear expressions derived from Equation (1).

$$\frac{(\gamma_{li}^p + \gamma_{li}^d)(1 + \cos\theta)}{2(\gamma_{li}^d)^{\frac{1}{2}}} = (\gamma_s^p)^{\frac{1}{2}} \left(\frac{\gamma_{li}^p}{\gamma_{li}^d} \right)^{\frac{1}{2}} + (\gamma_s^d)^{\frac{1}{2}} \quad (3)$$

$$\frac{(\gamma_{li}^p + \gamma_{li}^d)(1 + \cos\theta)}{2(\gamma_{li}^p)^{\frac{1}{2}}} = (\gamma_s^d)^{\frac{1}{2}} \left(\frac{\gamma_{li}^d}{\gamma_{li}^p} \right)^{\frac{1}{2}} + (\gamma_s^p)^{\frac{1}{2}} \quad (4)$$

In case $\gamma_{li}^p = 0$, which is not an unusual occurrence, Equation (4) cannot be used. Plotting $\left(\left(\frac{\gamma_{li}^p}{\gamma_{li}^d} \right)^{\frac{1}{2}}, \frac{(\gamma_{li}^p + \gamma_{li}^d)(1 + \cos \theta)}{2(\gamma_{li}^d)^{\frac{1}{2}}} \right)$ or $\left(\left(\frac{\gamma_{li}^d}{\gamma_{li}^p} \right)^{\frac{1}{2}}, \frac{(\gamma_{li}^p + \gamma_{li}^d)(1 + \cos \theta)}{2(\gamma_{li}^p)^{\frac{1}{2}}} \right)$ for more than one test liquid and fitting a straight line can give the estimates of $(\gamma_s^p)^{\frac{1}{2}}, (\gamma_s^d)^{\frac{1}{2}}$ obtained as a slope and an intercept of the straight line. Although these equations are widely used, there are problems associated with these. First, γ_s^d and γ_s^p are weighted asymmetrically. Namely, in Equation (3), $(\gamma_s^p)^{\frac{1}{2}}$ is the gradient of the straight line and $(\gamma_s^d)^{\frac{1}{2}}$ is the ordinate intercept, and vice-versa for Equation (4). In either case, this means that the two are weighted asymmetrically, when linear regression (least squares method) analysis is employed, which is not ideal. It is demonstrated for a different linear model that the presentation of a linear expression significantly affects the accuracy of the linear fitting.^[17] Second, the test liquids appropriate for a specific solid need to be selected experimentally or via trial and error.^[18,19] Third, the straight lines are not interpolated but extrapolated from a few coordinates to obtain the intercept, which could be argued to be an inadequate estimate. Finally, but most importantly, the linear least squares method is used for fitting the straight lines of Equations (3,4). However, the application of the linear least squares method assumes that the data to be handled should be corrected to follow Poisson distribution, and that the number of the data is assumed to be 10 or more.^[20] This is also the case of the non-linear least squares method.^[20] It is generally true that the non-linear least squares method gives more reliable results,^[21,22] but it is based on the fundamental assumption that the data to be handled is corrected, and the number of the data is large enough for the statistical analysis. The problems in the contact angle measurement are that the number of test liquids is desirably small to avoid liquids which are difficult to handle. As a result, purely statistical analysis is not suitable for determination of surface tension components based on the contact angle measurements. Furthermore, the least squares methods do not provide a direct understanding of the data correction. A different approach rather than a purely statistical analysis is needed so that the data can be more reliably assessed even when the number of the data sets is small.

Meanwhile, Equation (1) is applicable not only for deducing the surface tension components of a solid surface, but also for that of a liquid. This can be demonstrated in a similar way to the Owens-Wendt method. For example, through the known surface tension components of distilled water and glycerol, the surface tension values of polyester and high-density polyethylene (HDPE) were calculated using Equation (1).^[23] Then, through these values, the surface tension components of different concentrations of saltwater were calculated, again through Equation (1).

The existing graphical representation of obtained data, for example the OWRK method using Equations (3,4), can hardly give a sensible understanding of the measured results. In addition, a “wetting envelope for complete wetting” is demonstrated in ref.^[24] that plots the dispersion component against the polar component of the surface tension, which is graphically unintuitive. Interpreting the consequences of what would occur if the values of certain variables were changed is almost impossible, because the governing equations are nonlinear and asymmetric.

The present work proposes symmetric linear and circular expressions of Equation (1) to establish clear interpretation and understanding of the estimated results. In other words, the present work proposes that, for ease of graphical representation and visualization, Equation (1) be reorganized to 1) a symmetric linear expression in the standard form, with variables $\left((\gamma_s^p)^{\frac{1}{2}}, (\gamma_s^d)^{\frac{1}{2}} \right)$ for the estimation of surface tension components of solids, and 2) a relation in the form of equation of a circle, with variables $\left((\gamma_{li}^p)^{\frac{1}{2}}, (\gamma_{li}^d)^{\frac{1}{2}} \right)$ for the estimation of surface tension components of liquids. Hereinafter, due to the uncertainty of the obtained surface tension, the present work calls them the “estimated surface tension” or the like,^[9] when appropriate, and does not discuss the issues of reliability and accuracy of contact angle measurements.

It is true that the result of the estimated surface tension component values is the same if the data measured are correct and reliable. This issue will be extensively discussed later, exhibiting the advantage in using the newly proposed symmetric expressions. Essentially, these new expressions can be used to screen the data and exclude any obviously inaccurate data points, by observing the distribution of the intersections in the diagram. It is not easily done with the existing linear or non-linear least squares, which are prone to producing faulty results. This is because these squares methods rely on statistical analysis, which assumes that all the data are correct, following Poisson’s distribution, and that there are 10 or more data points.^[20] However, these assumptions are unrealistic in the contact angle measurement process since some undesirable test liquids in terms of toxicity will be inevitably involved.

2. Experimental methods

Polar and nonpolar polymers were selected as solid substances. As a polar polymer, polyester in the form of glass-fibre reinforced polyester (GFRP. G-Etronax PM. Elektro-Isola, Denmark) was used. The specimen was covered with the matrix of polyester, and hence it is simply referred to as polyester. As a nonpolar polymer, high-density polyethylene (HDPE. varenr. 1185, Knud

E. Dan A/S, Denmark) was used. All polyester and HDPE surfaces were cleaned using ethanol and then dried.

As test liquids, deionized water and analytical grade glycerol (minimum 99.5% purity, Merck KGaA, Germany) were selected. The values of the polar and dispersion components of the surface tension used for the evaluation were 51.0 mJ m^{-2} and 21.8 mJ m^{-2} for deionized water,^[17] and 30.0 mJ m^{-2} and 34.0 mJ m^{-2} for glycerol at room temperature.^[25]

From the deionized water, saltwater solutions with different concentrations were prepared. Saturated saltwater was made by mixing an excess of salt ('Siciliansk Middelhavssalt' product of the FORNAIO brand) with deionized water. It is assumed that the saturated saltwater has a concentration of 26 wt% at room temperature.^[26] Solutions with lower salt concentrations were then prepared by mixing the saturated saltwater with predetermined amounts of deionized water.

A contact angle measuring system (CAM100, CreLab Instruments AB, Sweden) was used to measure static contact angles on polyester and HDPE at room temperature. All measurements were taken within 5 seconds after initial contact of the droplet. Using the CAM100 program, one angle was measured from each side of the drop. This was repeated an appropriate number of times for each liquid. When recording results, obvious outliers were omitted if they were imprecise and had a significant effect on the accuracy of the averaged value. At least 23 measurements were taken for each condition, and averaged values were taken as the measured contact angles. Detailed experimental procedures are presented in ref.^[23]

3. Results and discussion

To obtain a simple symmetric relation between the polar and dispersion components of a given solid, both sides of Equation (1) are divided by $(\gamma_{li}^d + \gamma_{li}^p)(1 + \cos\theta)$:

$$\frac{2(\gamma_{li}^p)^{\frac{1}{2}}}{(\gamma_{li}^d + \gamma_{li}^p)(1 + \cos\theta)} (\gamma_s^p)^{\frac{1}{2}} + \frac{2(\gamma_{li}^d)^{\frac{1}{2}}}{(\gamma_{li}^d + \gamma_{li}^p)(1 + \cos\theta)} (\gamma_s^d)^{\frac{1}{2}} = 1 \quad (5)$$

Here, Equation (1) has been expressed as a symmetric linear expression in the standard form with variables $\left((\gamma_s^p)^{\frac{1}{2}}, (\gamma_s^d)^{\frac{1}{2}} \right)$, and can be graphed as

a straight line. A similar expression as "the more general form" is presented by Owens and Wendt,^[16] but is not further studied to reveal the usefulness of the symmetric expression. There are several benefits to formatting Equation (1) this way, apart from the ease at which it can be graphed – since all the

coordinates, namely $(\gamma_s^p)^{\frac{1}{2}}$ and $(\gamma_s^d)^{\frac{1}{2}}$, are positive, the graph is always a straight line graphed in the first quadrant. The slope of the equation is defined purely by the surface tension components of the test liquid, which means that the slope is always the same no matter the solid being tested, if the test liquid is the same. The slope is:

$$\text{Slope} = - \left(\frac{\gamma_{li}^p}{\gamma_{li}^d} \right)^{\frac{1}{2}} \quad (6)$$

The implication therefore is that the nature of the solid has an impact on not the slope of the graph, but rather the intercepts. This can be determined from the equation to the graph, as each coefficient is dependent on $(1 + \cos\theta)$, which does not influence the slope but does influence the intercepts. In other words, the slope and the intercept of the straight line are determined by selecting a test liquid, and by measuring a contact angle of the test liquid on a solid surface, respectively. The point corresponding to the surface tension components of the solid is somewhere on the straight line, and can only be determined after (a) subsequent line(s) is/are drawn. The ratio of the surface tension components of the solid can be between zero and infinity, independent of the slope, and undefined if only one test liquid is used. There are two limits to consider for the value of the angle θ : one at $\theta = 0$ and the other at $\theta = \pi$.

Equation (5) at $\theta = 0$ becomes:

$$\frac{(\gamma_{li}^p)^{\frac{1}{2}}}{(\gamma_{li}^d + \gamma_{li}^p)^{\frac{1}{2}}} (\gamma_s^p)^{\frac{1}{2}} + \frac{(\gamma_{li}^d)^{\frac{1}{2}}}{(\gamma_{li}^d + \gamma_{li}^p)^{\frac{1}{2}}} (\gamma_s^d)^{\frac{1}{2}} = 1 \quad (7)$$

Equation (7) is a straight line representing characteristics of a specific liquid, for which the contact angle $\theta = 0$. When the contact angle $\theta = 0$, the estimated surface tension of the solid at this condition is called “critical tension”.^[27]

One must consider, however, that there are some limitations to this method of calculation. For example, this method relies on the assumption that $|\cos\theta| \leq 1$. In other words, the surface tension components of a solid can only be estimated when the point $\left((\gamma_s^p)^{\frac{1}{2}}, (\gamma_s^d)^{\frac{1}{2}} \right)$ is in the region surrounded by $(\gamma_s^p)^{\frac{1}{2}}$ axis, $(\gamma_s^d)^{\frac{1}{2}}$ axis, and the straight line where $\theta = 0$ (Equation (7)).

On the other hand, to graph anything above and to the right of this line, $|\cos\theta| > 1$ must hold, which is impossible. Physically, this is represented by perfect wetting. This limitation therefore requires that one considers different test liquids to estimate the surface tension components of a solid most appropriately. Different relations for different liquids are illustrated in [Figure 1](#) when the contact angle $\theta = 0$. Here, the symmetric linear expression can

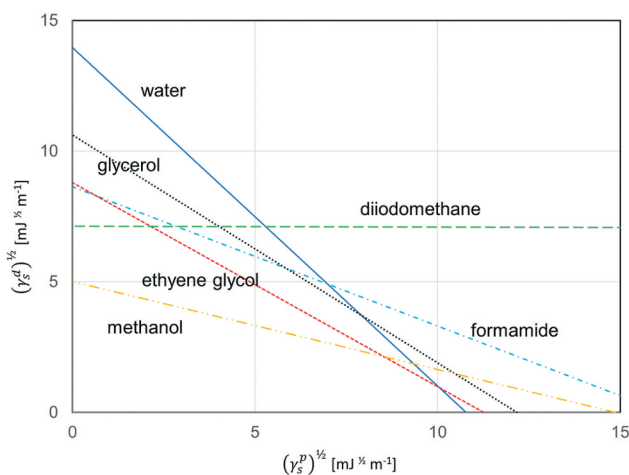


Figure 1. Characteristic straight lines of Equation (7) for representative liquids (data from refs.-[25,28]). Solid line: water, dotted line: glycerol, short-dashed line: ethylene glycol, long-dashed line: diiodomethane, dashed-dotted line: formamide, and dashed-double-dotted line: methanol.

present additional advantage in the sense of simple indication of total wetting conditions in the linear expression. It is a good comparison with the asymmetric expression of so-called “wetting envelope”, which is neither linear nor circular.^[24,29]

While this at first seems to indicate a vast array of different choices of liquid, one must be considerate in different ways. Water is commonly chosen as a test liquid, as is glycerol.^[11,23,25,28,30,31] Both can be handled safely, and both cover a large area on the plane, which conversely guarantees that the probability of perfect wetting will be smaller. Diiodomethane, often considered a representative dispersion liquid, is a viable option^[25,28,31] since it covers a large area, but its toxicity makes it unfavourable. Liquids such as alcohols are not often considered as test liquids since they cover far less area than water, for example. On the other hand, when good wetting is required, for example for a solvent of adhesives or paints, an appropriate liquid can be selected among liquids covering small areas in Figure 1.

Meanwhile, as θ approaches π , Equation (5) approaches the origin. This means that as θ increases, the graph is displaced towards the origin, until $\theta \rightarrow \pi$, at which point the graph vanishes.

Below, the fundamental use of the symmetric linear expression (5) is presented using two test liquids. Specifically, the way to estimate the polar and dispersion components of the surface tension of any solid is demonstrated, when two liquids with different polar and dispersion components are given. This does not mean that two test liquids should be used for this method, but more than two test liquids can be used, which will be described later.

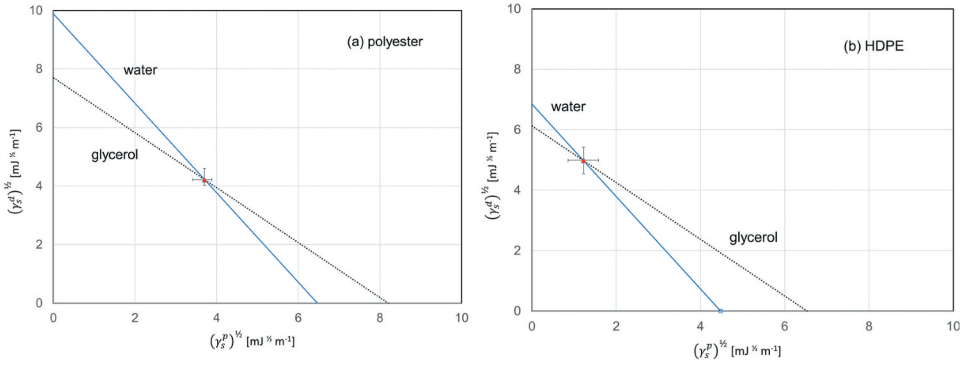


Figure 2. Experimental plots of Equation (5) for estimating surface tension components of polyester (a), and HDPE (b). Solid line: water, and dotted line: glycerol.

The different polar and dispersion components of test liquids ensure that they have different gradients. Graphically, this can be represented by two straight lines in the form of Equation (5), and the coordinate corresponding to the point of intersection gives square roots of the polar and dispersion components of the solid in question – as shown in Figure 2. On Figure 2, Equation (5) has been plotted for water (solid line) and glycerol (dotted line). Figure 2a marks the intersection of these two lines when the liquids are tested on polyester, while Figure 2b is that for HDPE.

Additionally, the slopes obtained from the two liquids aid with the selection of test liquids. For example, if the slopes are close to each other in value, a small change in one of the measured contact angles would lead to a large change in the coordinate of intersection. Hence, it is recommended that two equations with similar slopes are not selected as test liquids.

For the case of using two liquids 1 and 2, the solutions of Equation (5) can be expressed as:

$$(\gamma_s^p)^{\frac{1}{2}} = \frac{(\gamma_{li1}^d + \gamma_{li1}^p)(1 + \cos\theta_1)(\gamma_{li2}^d)^{\frac{1}{2}} - (\gamma_{li2}^d + \gamma_{li2}^p)(1 + \cos\theta_2)(\gamma_{li1}^d)^{\frac{1}{2}}}{2\left\{(\gamma_{li1}^p\gamma_{li2}^d)^{\frac{1}{2}} - (\gamma_{li2}^p\gamma_{li1}^d)^{\frac{1}{2}}\right\}^{\frac{1}{2}}} \quad (8)$$

$$(\gamma_s^d)^{\frac{1}{2}} = \frac{-(\gamma_{li1}^d + \gamma_{li1}^p)(1 + \cos\theta_1)(\gamma_{li2}^p)^{\frac{1}{2}} + (\gamma_{li2}^d + \gamma_{li2}^p)(1 + \cos\theta_2)(\gamma_{li1}^p)^{\frac{1}{2}}}{2\left\{(\gamma_{li1}^p\gamma_{li2}^d)^{\frac{1}{2}} - (\gamma_{li2}^p\gamma_{li1}^d)^{\frac{1}{2}}\right\}^{\frac{1}{2}}} \quad (9)$$

It is noted that the measurable polar and dispersion components of surface tensions will not exceed certain values. If the estimated surface tension components exceed them, it suggests that this measurement itself may have

a problem. If for any experimental or analytical reason, the intersections of the two linear graphs appear in the second or fourth quadrant, it is clear that the given solution is not an appropriate one. However, let it also be noted that since the values obtained on the right-hand sides of Equations (8) and (9) are squared to find γ_s^p and γ_s^d , it is possible that during the calculation the negative sign is overlooked. In short, a presence of a negative value for $(\gamma_s^p)^{\frac{1}{2}}$ or $(\gamma_s^d)^{\frac{1}{2}}$ is a result of a measurement error, a calculation error, or an inappropriate application of the underlying theory.

This method is further applied to four different data sets reported in the literature, as listed in Table 1, in order to clarify the usefulness of the method. As is demonstrated below, this method is useful to screen the measured datasets in a physically meaningful way to omit any outliers and obtain correct results. It is noted that three data sets are taken from ref.^[25] In all cases, either Equation (3) or (4) is used and the linear least squares method was applied in the literature.

Ref.^[11] uses six different test liquids (water, glycerol, ethylene glycol, dimethyl sulfoxide, formamide, and benzyl alcohol) to examine the polar and dispersion components of the surface tension of polydimethylsiloxane (PDMS). In Figure 3, the demonstration of Equation (5) is illustrated, together with the plot of the surface tension components obtained by the OWRK method, Equation (4) (polar component: 1.2 mJ m^{-2} , dispersion component: 9.8 mJ m^{-2}). The representation in Figure 3 provides several suggestions for the reported data.^[11]

Apart from the line corresponding to benzyl alcohol, five of the linear graphs intersect at nearly the same coordinates; therefore, the data for benzyl alcohol should be omitted for the evaluation, since it is most likely erroneous. Additionally, the slopes of ethylene glycol and formamide are close to each other in value. Simultaneous use of these test liquids can pronounce scatter of the intersections even with a small error in either measurement, so it is suggested that one of them, for example ethylene glycol, is omitted. After omitting these data points, any known techniques can be used for the re-estimation of the surface tension components, since the remaining data set can be considered as correct data. Here, by using the OWRK method with

Table 1. Examples of reported contact angle measurements and evaluation of polar and dispersion components of surface tension using the OWRK method by the linear least squares method.

Solid	Test liquids	Equation	Ref.
Poly-dimethylsiloxane	water, glycerol, ethylene glycol, dimethyl sulfoxide, formamide, and benzyl alcohol.	(4)	[11]
Graphene	water, glycerol, ethylene glycol, and diiodomethane	(3)	[31]
Graphene oxides	water, glycerol, ethylene glycol, benzyl alcohol, chlorobenzene, and diiodomethane	(3)	[25]

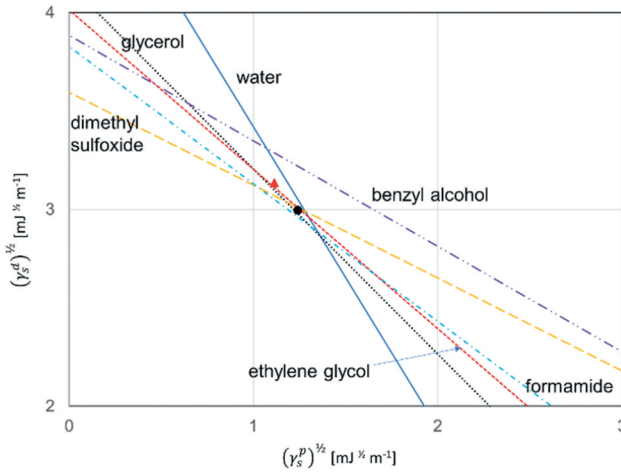


Figure 3. Symmetric linear presentation of the contact angle measurement results reported in ref.^[11] The estimated surface tension components using OWRK method (Equation (4)) from these measurements in ref.^[11] and those after data correction are plotted by a solid triangle and a solid circle, respectively. Solid line: water, dotted line: glycerol, short-dashed line: ethylene glycol, long-dashed line: dimethyl sulfoxide, dashed-dotted line: formamide, and dashed-double-dotted line: benzyl alcohol.

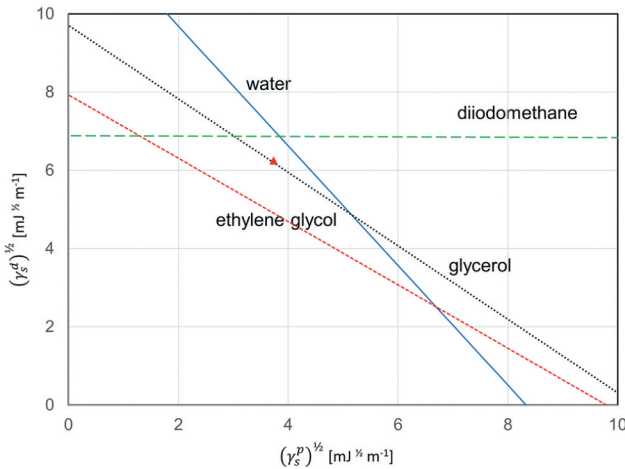


Figure 4. Symmetric linear presentation of the contact angle measurement results reported in ref.^[31] The estimated surface tension components using the OWRK method from these measurements in ref.^[31] are plotted by a solid triangle. Solid line: water, dotted line: glycerol, short-dashed line: ethylene glycol, and long-dashed line: diiodomethane.

Equation (4) for the re-estimation, the polar and dispersion components are found to be 1.54 and 8.97 mJ m^{-2} , respectively. The corresponding point is plotted with a solid circle in Figure 3.

Ref.^[31] studies the surface tension components of graphene by contact angle measurements. In Figure 4, the demonstration of Equation (5) is exemplified

for a graphene surface using four test liquids of water, glycerol, ethylene glycol, and diiodomethane, together with the plot of the surface tension components obtained by the OWRK method using Equation (3) reported in ref.^[31] In this case, the coordinates of the intersections scatter significantly, indicating that the measured data could be reconsidered.

Ref.^[25] studies the surface tension components of graphene oxides by contact angle measurements. In Figure 5a, the demonstration of Equation (5) is exemplified for a fresh graphene oxide surface using six test liquids of water, glycerol, ethylene glycol, benzyl alcohol, chlorobenzene, and diiodomethane, together with the plot of the surface tension value obtained by the OWRK method using Equation (3).

What is interesting to note in Figure 5a is that although the lines for water, glycerol, ethylene glycol, and benzyl alcohol all intersect at roughly the same coordinate, the lines representing diiodomethane and chlorobenzene cross the

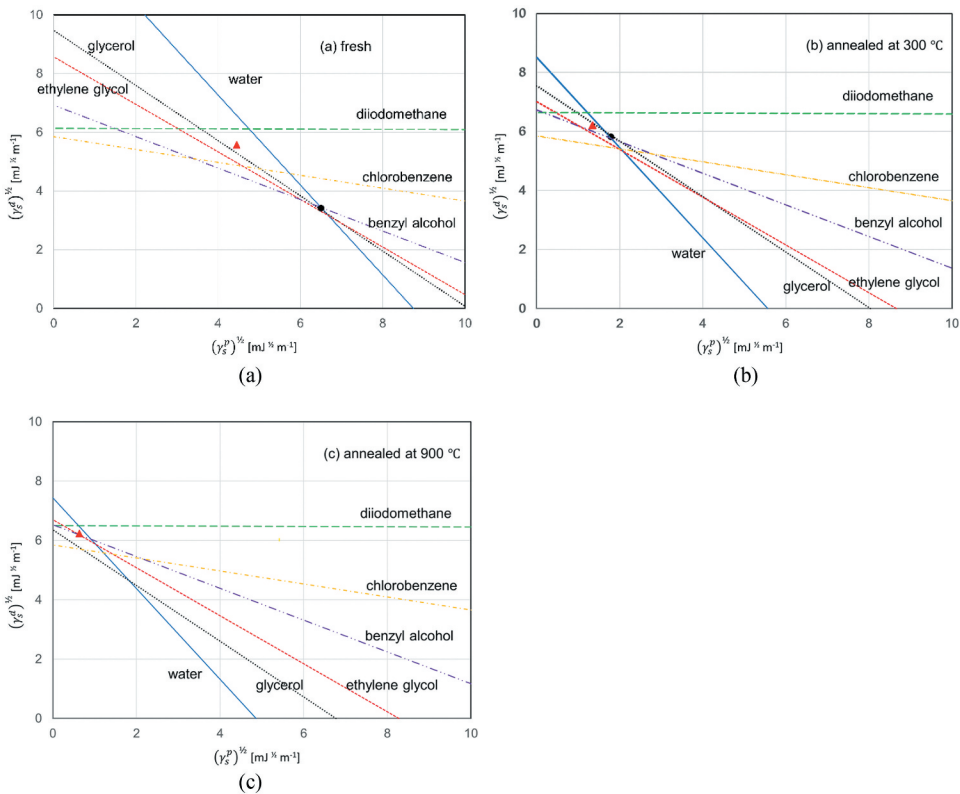


Figure 5. Symmetric linear presentation of the contact angle measurement results for fresh graphene oxide (a), graphene oxide annealed at 300°C (b), and graphene oxide annealed at 900°C (c) reported in ref.^[25] The estimated surface tension components using the OWRK method from these measurements in ref.^[25] and those after data correction are plotted by a solid triangle and a solid circle, respectively. Solid line: water, dotted line: glycerol, short-dashed line: ethylene glycol, long-dashed line: diiodomethane, dashed-dotted line: chlorobenzene, and dashed-double-dotted line: benzyl alcohol.

other lines at much higher locations. Ref.^[25] applies the OWRK method to estimate the surface tension components of the fresh graphene surface (polar component: 19.8 mJ m^{-2} , dispersion component: 31.1 mJ m^{-2}), which is indicated by a solid triangle in Figure 5a. The polar component is smaller, and the dispersion component is larger than at the more likely coordinate, which is where the four other lines converge. This is likely due to using diiodomethane and chlorobenzene as test liquids. It is suggested that the measurements using diiodomethane and chlorobenzene in ref.^[25] are omitted to obtain a more reliable estimation of the surface tension components of the fresh graphene surface. Also, the slopes of glycerol and ethylene glycol are close in value. As discussed above, this could potentially lead to large inaccuracies in the final measurement. Hence, it is suggested that glycerol and ethylene glycol are not selected together as test liquids, and test liquids with large differences in slopes should be chosen instead. Here, for example, the data for the ethylene glycol can be omitted. Accordingly, the symmetric linear presentation can give a clear insight about the estimation of surface tension values of solids. Here, by using the OWRK method with Equation (3) for the re-estimation, the polar and dispersion components are found to be 42.29 mJ m^{-2} and 11.64 mJ m^{-2} , respectively.

Similar analysis was carried out for the graphene oxides annealed at 300°C and 900°C , reported in ref.^[25] Each of the graphical representations are shown in Figure 5b,c. The linear functions in Figure 5b are more scattered than in Figure 5a. Using the same reasoning as before for Figure 5a, one can omit diiodomethane chlorobenzene, and ethylene glycol. The OWRK method reports that the polar and dispersion components for graphene oxide at 300°C are 1.8 mJ m^{-2} and 38.5 mJ m^{-2} respectively, whereas the “corrected” estimations with the appropriate omissions are 3.18 mJ m^{-2} and 33.74 mJ m^{-2} , respectively. Upon observing Figure 5c, one can see that the intersections between the linear functions are all quite scattered. Hence, it is most likely not advisable to use this data set.

In summary, the symmetric linear expressions are useful in various ways. For example, as seen previously, it can be used to estimate the surface tension components of a given solid in a concise way as demonstrated in Figure 2. However, especially when four or more test liquids are used and the data is scattered, the symmetric linear expression shows obvious usefulness for the initial data screening. Specifically, first, the symmetric linear functions for test liquids are plotted to screen for outliers of the straight lines as shown in Figures 3–5, and then any known method is employed to calculate the surface tension components of a solid. In this way, more reliable values of the surface tension components can be obtained.

There are generally two possibilities that cause outliers. The first is errors induced by contact angle measurements or data-processing. Second is errors of surface tension components of test liquids, which are taken from literature.

The above-mentioned screening technique does not directly provide an indication of the types of errors. However, in the case of [Figure 5a](#), for example, the contact angle of diiodomethane from the data in ref.^[25] is 43.9°. On the other hand, for the straight line of diiodomethane with the literature values of the surface tension components to pass the common intersection, the contact angle to be measured is estimated to be 92°. It is therefore unlikely that measurement errors would be the cause of the outliers. In [Figure 5b](#), diiodomethane is again listed again as the outlier. As a result, it is realistic to suspect that the materials properties of the diiodomethane in the calculation in ref.^[25] may be deviated from the literature value. In this way, the type of errors can be speculated in some specific cases. A method to estimate a real surface tension values in ref.^[25] will be discussed using the circular symmetric form later.

As another approach to present Equation (1), one can work the other way around – using known surface tension components of two (or more) solids, one can obtain the unknown surface tension components of liquid. For this, Equation (1) is used to evaluate the surface tension components of a liquid when the known surface tension components of two solids are used.

From Equation (1):

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

It is a circle of a radius of $\frac{(\gamma_s^p + \gamma_s^d)^{\frac{1}{2}}}{1 + \cos\theta}$, centred at $\left(\frac{(\gamma_s^p)^{\frac{1}{2}}}{1 + \cos\theta}, \frac{(\gamma_s^d)^{\frac{1}{2}}}{1 + \cos\theta} \right)$ in the $(\gamma_{li}^p)^{\frac{1}{2}} - (\gamma_{li}^d)^{\frac{1}{2}}$ plane, as demonstrated in [Figure 6](#). The centre of the circle lies on a straight line passing the origin with the slope $\left(\frac{\gamma_s^d}{\gamma_s^p} \right)^{\frac{1}{2}}$.

The proposition is that one can measure contact angles between the liquid in question and two different solid surfaces. Thereafter, two circular expressions corresponding to the two different solid surfaces and their respective contact angles can be drawn. The intersection of these two circles gives the estimated surface tension components of the liquid. The centre of each circle is

at $\left(\frac{(\gamma_s^p)^{\frac{1}{2}}}{1 + \cos\theta}, \frac{(\gamma_s^d)^{\frac{1}{2}}}{1 + \cos\theta} \right)$ as mentioned before, and characteristically each circle

derived from Equation (10) passes through the origin. The varying radius of the circle is dependent on the contact angle between the solid and liquid, and the minimum radius occurs when the contact angle $\theta = 0$.

One must also consider the possibility of perfect wetting. Perfect wetting means that the contact angle cannot be determined. This implies that the coordinate $\left((\gamma_{li}^p)^{\frac{1}{2}}, (\gamma_{li}^d)^{\frac{1}{2}} \right)$ belongs inside the smallest possible circle that can

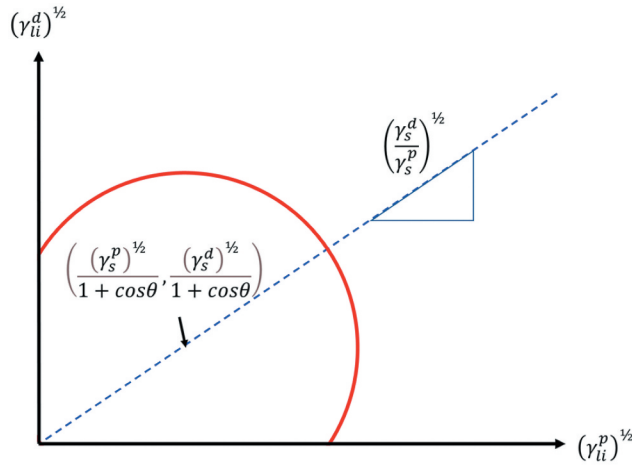


Figure 6. Equation (10) – A symmetric circular expression of Equation (1) (solid circle). The short, dashed line passes through the centre of the circle.

be drawn. Therefore in this case, the surface tension components of the liquid cannot be estimated.

Using the method proposed, the surface tension components of diiodomethane used in ref.^[25] are estimated. Specifically, the fresh graphene oxide and the graphene oxide after annealing at 300°C are used as the test solids. The estimated surface tension components after data correction and the estimated contact angles of the diiodomethane in ref.^[25] are summarized in Table 2.

Using equation (10), two circles are plotted as shown in Figure 7. The coordinates of the intersection are (2.42, 6.03). Therefore, the surface tension components of the diiodomethane used in ref.^[25] are estimated to be 5.9 (polar), and 36.4 (dispersion) mJ m^{-2} . On the other hand, the surface tension components of diiodomethane used for the calculation in ref.^[25] are 0 and 50.8 mJ m^{-2} . The difference is not negligible. If the estimation of the present work and the measurement in ref.^[25] are correct, the result indicates that the test liquid used as diiodomethane in ref.^[25] may have different surface tension components than a general diiodomethane, for example, due to degradation.

Using the method proposed as another example, the estimated surface tension components of various concentrations of saltwater^[23] have been

Table 2. Corrected surface tension components of graphene oxides and contact angles of diiodomethane calculated from the datapoints in.^[25]

Graphene oxide	Surface tension [mJ m^{-2}]		Contact angle of diiodomethane [°]
	Polar component	Dispersion component	
Fresh	42.29	11.64	43.9
After 300°C annealing	3.18	33.74	30.3

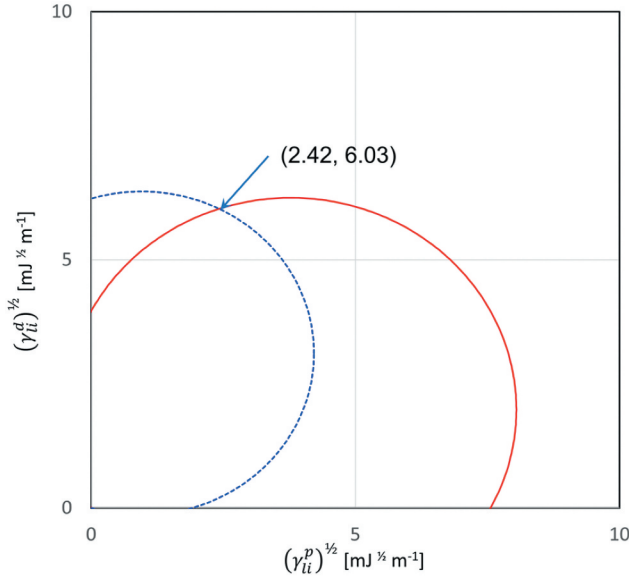


Figure 7. Symmetric circular presentation of the contact angle measurement results for the fresh and 300°C-annealed graphene oxides.^[25] Solid line: fresh graphene oxide, dotted line: graphene oxide annealed at 300°C. The intersect of the circles corresponds to the surface tension components of diiodomethane used for the measurement, estimated in the present work.

plotted in [Figure 8](#), using polyester and HDPE as test solid surfaces. The aim of the plots is to demonstrate the visual understanding of the estimation method for surface tension components of a liquid using the symmetric circular expression (Equation (10)).

The polar and dispersion components of the estimated surface tension components of polyester and HDPE, determined by the contact angle measurements with deionized water and glycerol, are as follows:

$$\gamma_{polyester}^p = 13.29 \pm 0.06 \text{ mJ m}^{-2}$$

$$\gamma_{polyester}^d = 18.16 \pm 0.53 \text{ mJ m}^{-2}$$

$$\gamma_{HDPE}^p = 1.48 \pm 0.07 \text{ mJ m}^{-2}$$

$$\gamma_{HDPE}^d = 24.89 \pm 0.68 \text{ mJ m}^{-2}$$

As reported in ref.^[23], the surface tension of the saltwater tends to increase as the salt concentration increases, the trend agreeing with literature,^[32–34] though only results at low concentrations are reported, except in ref.^[23] The trend of increasing surface tension is due to the surface excess of saltwater.^[23] The selection of these surfaces is well justified in [Figure 8](#), as they have different enough slopes as demonstrated. This highlights another important

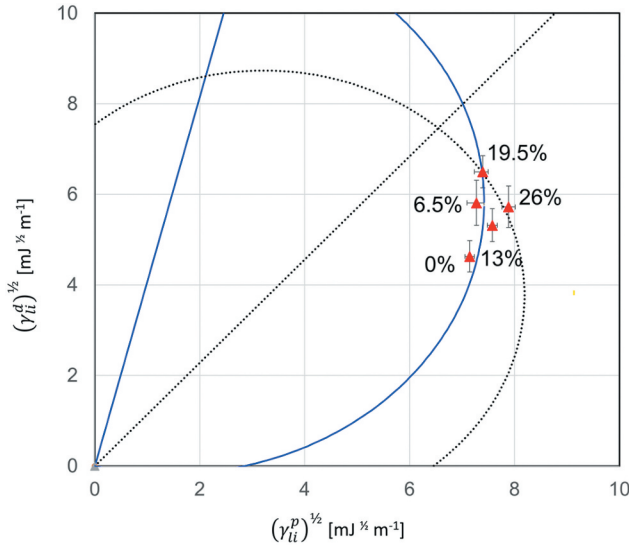


Figure 8. Experimental plots of Equation (10) for estimating surface tension components of salt water at different concentrations. The condition for the circles corresponds to the concentration at 19.5 wt%. Solid circle: HDPE, dotted circle: polyester, the centres of the circles of HDPE and polyester are on the solid straight line and the short-dashed straight line, respectively.

aspect of estimating surface tension components of liquids. In other words, one must make an adequate selection of test solid surfaces. A large enough difference between the slopes of the solids must exist, and additionally the radii of the obtained circle must be small. Thus, sample data from ref.^[35] regarding the different surface tension components of solids has been processed and plotted on Figure 9, relating the minimum radius $\frac{(\gamma_s^p + \gamma_s^d)^{\frac{1}{2}}}{2}$ with the slope $\left(\frac{\gamma_s^d}{\gamma_s^p}\right)^{\frac{1}{2}}$. Here, solid materials selected are polyvinyl fluoride (PVF), polyimide (PI), polyethylene terephthalate (PET), polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and polyethylene (PE).

Upon selecting two solids, it is favourable to choose those that have a large difference in slope $\left(\frac{\gamma_s^d}{\gamma_s^p}\right)^{\frac{1}{2}}$. Also, having a smaller value for the minimum radius is better so that the circle can potentially span a larger area, but the usefulness of its magnitude is limited by whichever radius is larger. For example, if there is a requirement for PVF to be selected, the two most viable options for the second solid would be PTFE or PE, as the slopes of these two are not so different. Although PE has a smaller radius than PTFE, since PVF has a large radius, the choice between PE or PTFE does not give a noticeable difference.

Finally, the symmetric circular expression is compared to the generally used asymmetric expression of the wetting envelopes^[29] in Figure 10. If the surface tension components of a given liquid lie on the envelope, the liquid will form

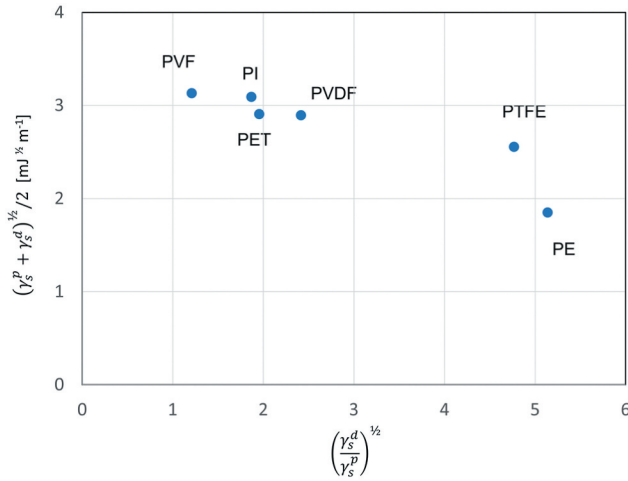


Figure 9. Comparison of the minimum radius with the slopes for representative solids (data from^[35]).

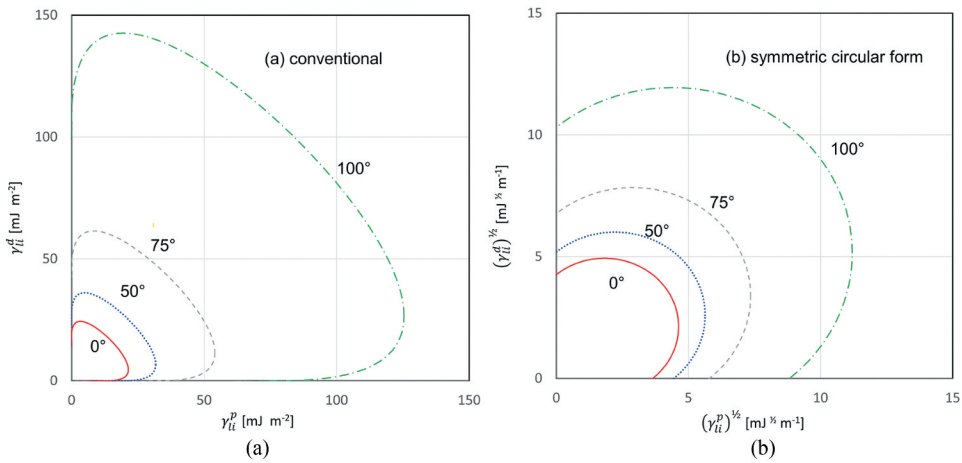


Figure 10. Conventional (a) and symmetric circular expression (b) of wetting envelopes of polyester plates at the contact angles of 0, 50, 75, and 100°.

a specific contact angle with a specific solid surface. If the surface tension components for the liquid are located inside the envelope, the contact angle is lower than the specific value obtained from the envelope. The wetting envelope is widely used to help visual understanding of the relation between surface tension components of solid and liquids. The wetting envelopes for the polyester plates at the contact angles of 0, 50, 75, and 100° are plotted in [Figure 10a](#) for the conventional asymmetric wetting envelopes, and [Figure 10b](#) for a symmetric circular expression. Apart from the simplicity and beauty of the symmetric circular expression in [Figure 10b](#), there is another advantage.

The wetting envelopes are usually used for investigating good wetting at lower contact angles. Looking at [Figure 10a](#), there is a larger spacing between the envelopes for 50° and 100°, compared to the envelopes for 0° and 50°. This means that data points for lower contact angles will be more difficult to observe. However, because square roots are taken in [Figure 10b](#), the spacing between the envelopes with the different angles is more uniform than in [Figure 10a](#), which makes observation of these lower contact angles easier.

4. Conclusions

Using symmetric linear and circular expressions for representing and estimating surface tension components has proven to be advantageous. While Equation (1) is not easy to visualize graphically, using its reorganized expressions can immediately highlight problematic data, regardless of whether they are raw or processed. By utilizing these expressions one can make an educated selection of different test liquids and test solids for measurements of surface tension components. Furthermore, the symmetric expressions can be used for an appropriate choice of solvents for adhesives and paints.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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