

Surface Free Energy Determination by Contact Angle Measurements – A Comparison of Various Approaches

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Abstract. One of the parameters characterizing the surfaces of materials is the surface free energy. The most common way to determine its value is to measure the surface tension by the sessile drop method. In this case a contact angle between the surface and the edge of droplets of liquids is measured.

There are various approaches to calculate the surface free energy from the contact angle measurements. We made a review and a direct comparison of the most widely used methods and testing liquids in order to re-evaluate their advantages and disadvantages.

In the presented work we discuss the limits of applicability of the examined methods. We confirm that methods using a pair of liquids give results dependent on the liquids chosen. Using a pair of non-polar and polar liquid yielded most reliable results. This is even more clear when two-liquid method is transformed into a multiple-liquid method. The algorithms developed during the work will be implemented into liquid contact angle analysis software.

Introduction

It's about 200 years ago since Young described the role of surface tension, i.e. surface free energy (SFE) in wetting. But determination of surface energy of solids from contact angle measurements faces the presence of one more unknown quantity in the Young's equation, the interfacial energy. Many approaches exist to cope with this fact. We have tested a Zisman's approach, which bypasses this problem, and more other ways, that use expressions of work of adhesion to approximate the situation; harmonic mean method, geometric mean method, geometric mean method converted into linear regression, acid-base theory and so called "equation of state" approach.

The presented work was aimed to compare these methods of surface free energy determination on common materials.

Theory

When a droplet of a liquid is formed on a flat solid surface, the balance on the three-phase interface is expressed by Young's equation

$$\gamma_s = \gamma_{sl} + \gamma_l \cos \theta, \quad (1)$$

where γ_l is surface tension of liquid, θ contact angle between the liquid-air interface and the surface, γ_{sl} is interfacial tension and γ_s is surface free energy of a solid. The two last mentioned quantities are both unknown. If we express in (1) γ_{sl} as a sum of facial tensions minus work of adhesion, the work of adhesion can be then written as

$$W_A = \gamma_l (1 + \cos \theta). \quad (2)$$

Many authors like *Fox and Zisman* [1950] say this is incorrect in general case due to effects of vapor adsorption and spreading pressure. The general expression for W_A can be complicated, but the equation (2) is found by those authors to be adequate at least for polymer-liquid systems. W_A is surely additive and it can be divided into contributions of different forces of adhesion. Then it can be assumed, that even SFE can be divided into components representing different surface interactions. For the following calculations SFE is expressed as $\gamma = \gamma^d + \gamma^p$, where d means dispersion and p polar component.

Using this approach, expression of W_A by *Owens and Wendt* [1969] gives the geometric mean method.

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

Considering data for two liquids ($i = 1, 2$), we have a system of two equations. Crucial part of the

solution can be seen in the literature [*Janczuk and Bialopiotrowicz, 1989*].

$$\gamma_s^d = \frac{\left((1 + \cos \theta_2) \gamma_{l2} - \sqrt{\frac{\gamma_{l2}^p}{\gamma_{l1}^p}} (1 + \cos \theta_1) \gamma_{l1} \right)^2}{\left(2\sqrt{\gamma_{l2}^d} - 2\sqrt{\frac{\gamma_{l2}^p \gamma_{l1}^d}{\gamma_{l1}^p}} \right)^2} \quad (4)$$

In order to derive this solution, it's important to treat equations (3) as *linear* in square roots. This feature is also key to convert this method into linear fit to incorporate data for more than two liquids at once (OW fit for short). Dividing (3) by $2\sqrt{\gamma_{li}^d}$ we obtain

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

Left hand side becomes y_i and square root from liquid surface tension components ratio is x_i . Square roots from surface free energy components of the solid become linear regression coefficients.

Wu [1971] developed more complicated harmonic mean method (also for two liquids)

$$(1 + \cos \theta_i) \gamma_{li} = 4 \left(\frac{\gamma_{li}^d \gamma_s^d}{\gamma_{li}^d + \gamma_s^d} + \frac{\gamma_{li}^p \gamma_s^p}{\gamma_{li}^p + \gamma_s^p} \right), \quad (6)$$

that is often solved numerically. Nevertheless, an analytical solution can be found¹ and we present its brief description.

One should express for example γ_s^p from equations and compare the results by $\frac{1}{\gamma_s^p}$. The fractions can be simplified then and a solution in the factor form is obtained. To reduce the complexity of formulas we can do following substitutions

$$\begin{aligned} \varphi &= 1 + \left(\gamma_{l2}^d - \frac{1}{4} (1 + \cos \theta_2) \gamma_{l2} \right) \left(\frac{\gamma_{l1}^p - \gamma_{l2}^p}{\gamma_{l1}^p \gamma_{l2}^p} \right) \\ \omega &= \gamma_{l2}^d \left(1 - \frac{\gamma_{l1}^p - \gamma_{l2}^p}{\gamma_{l1}^p \gamma_{l2}^p} \frac{1}{4} (1 + \cos \theta_2) \gamma_{l2} \right) \end{aligned} \quad (7)$$

that act in the coefficients of quadratic equation for γ_s^d . ($A(\gamma_s^d)^2 + B\gamma_s^d + C = 0$)

$$\begin{aligned} A &= \left(\frac{1}{4} (1 + \cos \theta_1) \gamma_{l1} - \gamma_{l1}^d \right) \varphi - \frac{1}{4} (1 + \cos \theta_2) \gamma_{l2} + \gamma_{l2}^d \\ B &= \frac{1}{4} (1 + \cos \theta_1) \gamma_{l1} \gamma_{l1}^d \varphi + \left(\frac{1}{4} (1 + \cos \theta_1) \gamma_{l1} - \gamma_{l1}^d \right) \omega - \frac{1}{4} (1 + \cos \theta_2) \gamma_{l2} (\gamma_{l1}^d + \gamma_{l2}^d) + \gamma_{l1}^d \gamma_{l2}^d \\ C &= \frac{1}{4} (1 + \cos \theta_1) \gamma_{l1} \gamma_{l1}^d \omega - \frac{1}{4} (1 + \cos \theta_2) \gamma_{l2} \gamma_{l1}^d \gamma_{l2}^d \end{aligned} \quad (8)$$

By solving the roots and calculating the other component two results are obtained and the one with physical meaning must be chosen.

Acid-base theory [*van Oss, Chadhury and Good, 1987*] uses non additive relation among total SFE and its components

$$\gamma = \gamma^{LW} + \gamma^{AB} = \gamma^{LW} + 2\sqrt{\gamma^+ \gamma^-}, \quad (9)$$

which are Lifschitz-van der Waals (LW), electron-acceptor (+) and electron-donor (−) components. For three unknown components of the SFE of a solid it needs a system of three equations

$$(1 + \cos \theta_i) \gamma_{li} = 2 \left(\sqrt{\gamma_{li}^{LW} \gamma_s^{LW}} + \sqrt{\gamma_{li}^+ \gamma_s^-} + \sqrt{\gamma_{li}^- \gamma_s^+} \right) \quad (10)$$

Assuming one of the liquids is non-polar, e.g. $\gamma_{l3}^+ = \gamma_{l3}^- = 0$, the corresponding equation simplifies and then γ_s^{LW} can be expressed very easily. Considering γ_s^{LW} no longer an unknown we can incorporate it's

¹Solution presented was calculated by the author. Results were checked by (6).

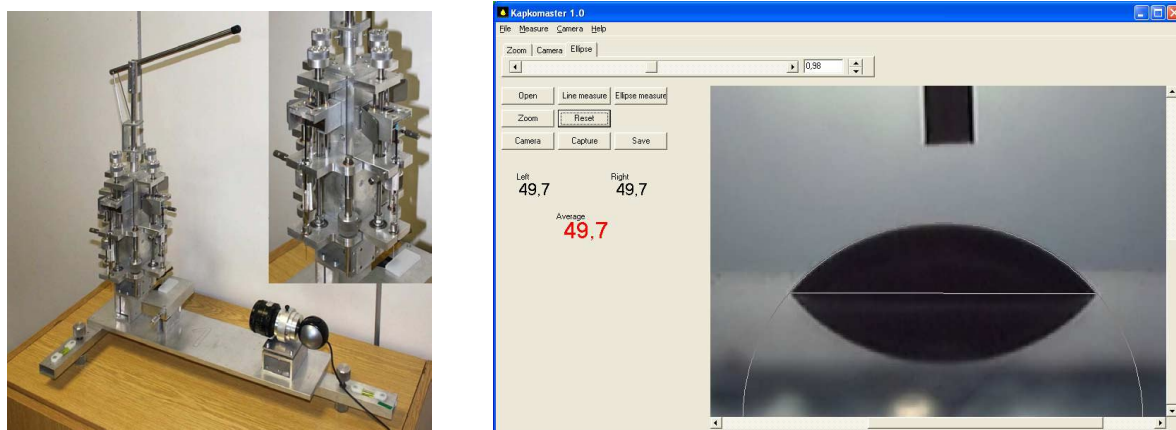


Figure 1. Left: Contact angle measurement device with a detailed view of the head with syringes. Right: Screenshot from the contact angle evaluation software (with ellipse matched to the picture).

terms into left sides of the remaining equations. Then they become *mathematically identical* to geometric mean method and solution is easy and just complex to write.

Undergoing a long development from it's groundwork [Neumann *et al.*, 1974] “equation of state” approach reached it's contemporary form [Kwok *et al.*, 1998]

$$\cos \theta = -1 + 2\sqrt{\frac{\gamma_s}{\gamma_l}} e^{-\beta(\gamma_l - \gamma_s)^2} \quad (11)$$

This method of calculation uses no SFE components. Result can be computed using e.g. Newton's iterative method.

Lastly, we should mention findings by Fox and Zisman [1950], that $\cos \theta$ is a linear function of γ_l . By plotting the points for various liquids and fitting a line through them, we can get a “critical surface tension” (γ_c) by extrapolating the line to $\cos \theta = 1$. γ_c is closely related to SFE of a solid.

Experimental

In this work we have measured contact angles by static sessile drop method. Our device for contact angle measurement includes a holder with four microliter syringes. That allows the user to comfortably form drops of various liquids on a sample positioned on a small movable table. Precise dosing is allowed by screw-driven mechanism. Drops are backlit by LEDs through groundglass and instantly photographed by a camera.

Evaluation of contact angles from the camera data was performed on a software developed by Pavel Sola. Ellipse matching is used instead of direct tangents drawing to obtain more precise results and to avoid a human factor. The liquids we used were diiodomethane, toluene, formamide, glycerol and redistilled water. Data for SFE and it's components of those liquids were mostly taken from the latest work of *ech et al.* [2009]. Test samples of solid materials were thin film prepared by Teflon sputtering, pure bulk polymers (Goodfellow), microscope glass slides and polished silicon wafers. Measurements were done at room temperature.

Results and Discussion

Firstly, we must denote, that all the component-based methods may yield unacceptable results in some cases; solving quadratic equation for harmonic mean may lead to negative or complex numbers, geometric mean, OW-fit and acid-base theory, being problems of square roots, may lead to a demand for square roots to be negative. As we want SFE and it's components to be positive real numbers, we must be careful about these results.

Results for the two-liquid methods are summarised in Tab.1. As an example of the contrast to the measurements for diiodomethane and water in the table stands the result using glycerol and water with geometric mean for Teflon-like layer; $\gamma^d = 4.1 \text{ mJ} \cdot \text{m}^{-2}$ and $\gamma^p = 5.0 \text{ mJ} \cdot \text{m}^{-2}$.

Such large ranges and contradictory inequalities of components may seem drastic. That surely underlines, how strongly the results depend on which liquids were used for calculation. Also Shimizu

and Demarquette [2000] show similar variations and cases when no results were obtained. However, we must at first take into account the positive fact that in all cases total SFE value varied less than it's components, often significantly less. Secondly, we have to point out the conclusion of these authors, that not all of the data are equally relevant. We should take the results for pairs of polar and non-polar liquids as most reliable.

Before we can support these conclusions, we should mention the OW-fits. Resulting SFE values are in Tab.2. Looking at examples of OW-plots in Fig.2 it is clear that connecting the two farthest points would give a good glimpse of entire trend. It is equivalent to the geometric mean calculation for the pair of diiodomethane and water. This confirms that pairs of polar and non-polar liquids are most significant for geometric mean method, as $x (= \sqrt{\gamma_{li}^p/\gamma_{li}^d})$ is related to polarity from definition. Considering the fact that in many cases geometric and harmonic mean methods failed to yield results for the same pairs (e.g. diiodomethane-toluene, both non-polar), it supports the assumption that the same requirement holds for the harmonic mean method.

Table 1. Ranges of all results obtained from the two-liquid methods and exemplar values for the pair of diiodomethane and water for (from above): polypropylene (a), Teflon-like layer (b), glass (c) and silicon (d) (all in $\text{mJ} \cdot \text{m}^{-2}$)

	geometric						harmonic					
	range			d-w			range			d-w		
	γ^d	γ^p	γ	γ^d	γ^p	γ	γ^d	γ^p	γ	γ^d	γ^p	γ
a	15.2-34.7	0.7-8.6	23.8-35.3	26.9	1.6	28.5	15.6-27.2	3.0-12.2	27.5-32.2	25.5	5.4	30.9
b	4.1-19.5	0.3-25.1	9.1-34.9	11.9	1.7	13.6	4.8-17.4	1.6-10.6	15.4-20.6	13.5	4.8	18.3
c	3.2-37.9	12.9-68.1	48.4-72.3	27.2	36.0	63.2	11.4-33.8	16.9-53.5	49.1-64.9	26.0	37.9	63.9
d	9.0-40.1	20.8-74.3	53.2-83.3	28.9	26.9	55.8	22.2-31.8	28.2-53.5	55.4-75.7	27.0	30.3	57.3

Table 2. SFE values obtained by multi-liquid component-based methods (all in $\text{mJ} \cdot \text{m}^{-2}$).

sample	acid-base								OW-fit		
	diiodomethane-formamide-water				diiodomethane-glycerol-water				γ^d	γ^p	γ
	γ^{LW}	γ^+	γ^-	γ	γ^{LW}	γ^+	γ^-	γ			
polypropylene	27.8	0.1	1.95	28.7	27.8	0.68	0.79	29.3	26.7	1.8	28.4
Teflon-like layer	12.6	0	2.91	12.8			–		10.5	1.6	12.2
glass	32.7	1.69	45.3	50.1	32.7	1.28	47.5	48.3	18.9	38.9	57.8
silicon	33.7	3.7	25.2	53.0	33.7	6.57	19.2	56.1	23.2	32.4	55.6

Acid-base theory seems to be sensitive to the selection of liquids just like the methods mentioned before. Considering the same modification like from (3) to (5), we can transform solving a system of three acid-base approach equations into plotting a plane through three points in a x, y, z space. Then x, y will be square roots of ratios of surface tension components of a liquid, thus only z will suffer from the uncertainty of experimental data. As these points for triplet of diiodomethane, formamide and glycerol are almost collinear in thought xy plane, it is easy to understand that using this triplet maximises the uncertainty. That is proven by the fact that in most cases this triplet failed to bear results in positive real numbers and in one case the value was obviously incorrect. Results for more useful triplets of diiodomethane, formamide and water and diiodomethane, glycerol and water are listed in Tab.2.

It may be quite misleading that Zisman method is often mentioned in connection with homologous series of liquids. It's true that Zisman's work focused mainly on *organic* liquids varying by the length of the carbon chain – homologous series. But he showed the same linear trend for liquids categorised as “miscellaneous.” That is the most important finding for contemporary use, because we want to combine different kinds of liquids for the reasons mentioned above. Our results in Fig.2 show satisfactory linear trend for polymers. Calculated values of γ_c are $28.5 \text{ mJ} \cdot \text{m}^{-2}$ for polypropylene bulk, $10.3 \text{ mJ} \cdot \text{m}^{-2}$ for Teflon-like layer and $19.1 \text{ mJ} \cdot \text{m}^{-2}$ for Teflon bulk. This value fits in the range published for the same material by *Fox and Zisman* [1950].

Above we mentioned results for glass and silicon. This is one of the special cases included in our work. As these materials are not polymers, assumptions under which (2) is valid are probably not met in this case. As depicted in the example in Fig.2, component based methods yielded self-consistent results for these samples. On the contrary, example in Fig.3 shows how Zisman plots failed in this case. Using different method, *Chibowski et al.* [1989] gives total SFE for glass in the range of $105\text{-}112 \text{ mJ} \cdot \text{m}^{-2}$. Our results clearly do not corroborate with this. But considering the relation given by *Wu* [1982], that spreading pressure is equal to the decrease from SFE in vacuum to SFE in vaporous environment, we can subtract the value of spreading pressure of water given by *Chibowski et al.* [1989] as $35 \text{ mJ} \cdot \text{m}^{-2}$. In this approximation his values become comparable to ours.

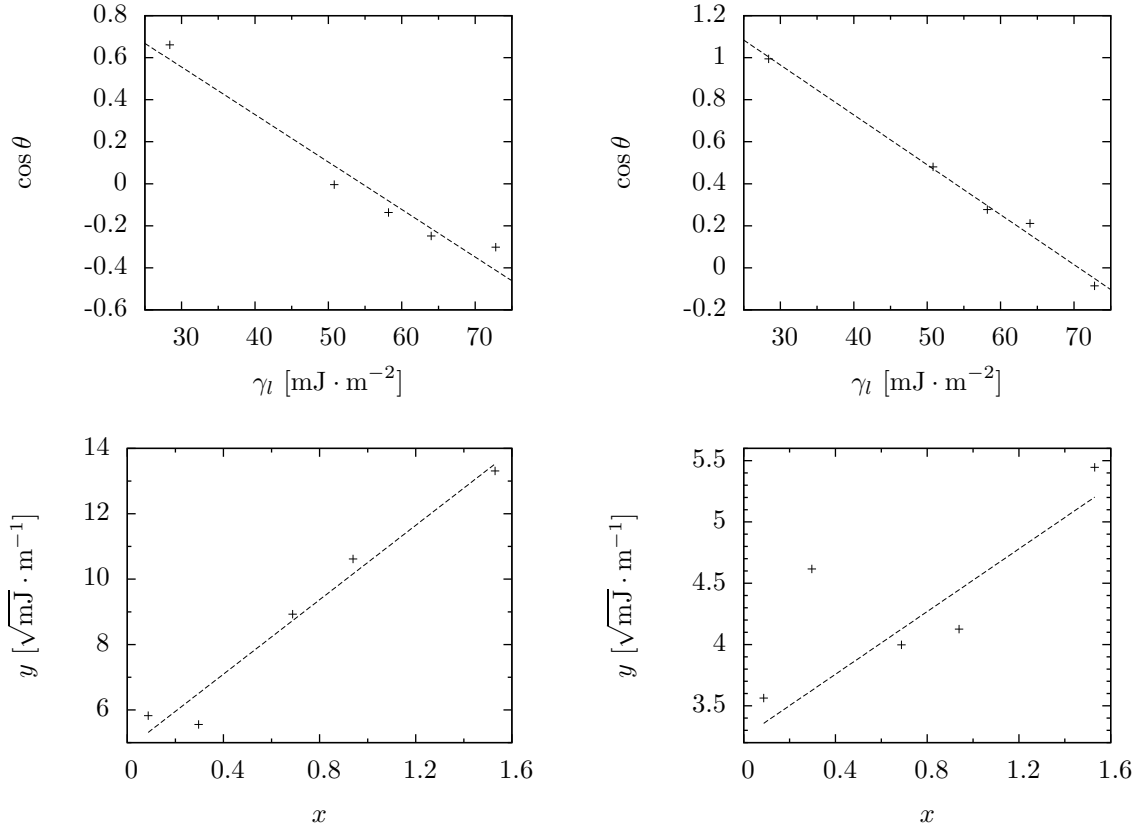


Figure 2. Above: Zisman plots for Teflon-like layer (left) and polypropylene bulk (right). Test liquids from left to right: toluene, diiodomethane, formamide, glycerol, water. Below: Self-consistent result for silicon sample (left) and quite satisfactory plot for Teflon-like layer (right) both using OW fit. Test liquids from left to right: diiodomethane, toluene, formamide, glycerol, water.

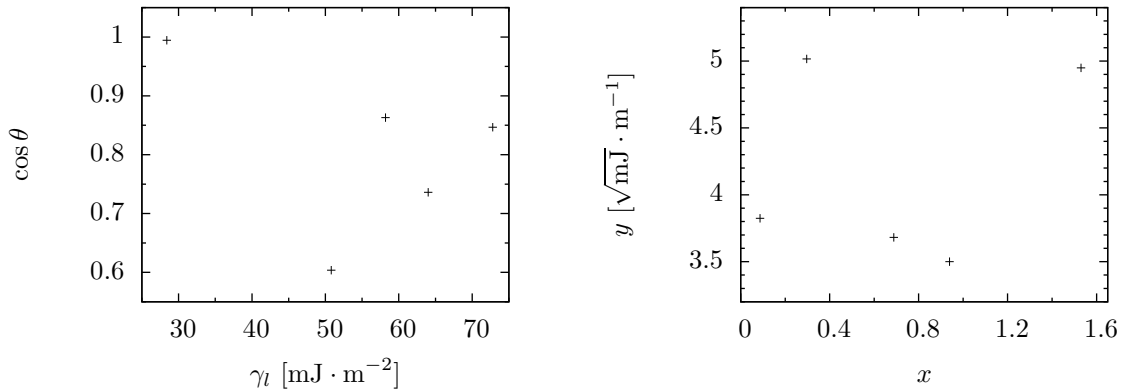


Figure 3. Examples of negative results. Left: Zisman plot for glass and broken linear trend for Teflon bulk for OW fit.

All the calculations of SFE are of course based on the approximation of perfectly smooth surface (as well as the Young's equation is) what is almost never true. The second special case we studied was macroscopically rough bulk Teflon sample. It can be seen in Fig.3 that shifts in contact angle values due to the roughness resulted in loss of the linear trend for OW-fit. This is also reflected by the fact that for most pairs of liquids harmonic and geometric mean methods failed. For the pair of diiodomethane and water harmonic mean yielded $\gamma^d = 16.3 \text{ mJ} \cdot \text{m}^{-2}$, $\gamma^p = 2.3 \text{ mJ} \cdot \text{m}^{-2}$ and $\gamma = 18.6 \text{ mJ} \cdot \text{m}^{-2}$, geometric mean yielded $\gamma^d = 14.1 \text{ mJ} \cdot \text{m}^{-2}$, $\gamma^p = 0.6 \text{ mJ} \cdot \text{m}^{-2}$ and $\gamma = 14.7 \text{ mJ} \cdot \text{m}^{-2}$. However, Zisman plot was almost unaffected by the surface roughness.

In the dependence on the liquid used, the SFE values calculated using “equation of state” approach varied as 24.8-30.4 mJ · m⁻² for polypropylene, 11.6-23.3 mJ · m⁻² for Teflon-like layer and 15.0-19.9 mJ · m⁻² for Teflon bulk (28.2-63.3 mJ · m⁻² for glass and 28.4-60.1 mJ · m⁻² for silicon). Minimum/maximum value was not related to the particular liquid throughout the materials. The fact, that SFE values obtained by this method are different for different liquids agrees with results of *Shimizu and Demarquette* [2000] and contrasts with an opinion of authors of the method [*Kwok et al.*, 1998]. But we must consider that in their work developers of the method exceptionally cared about conditions of the experiment and surface smoothness.

To discuss the selection of liquids, it must be said that suitability of further use of toluene and glycerol is debatable. Glycerol is hygroscopic, so its properties may change with time. Toluene has overall low surface energy what leads to trivial (near 0°) contact angles. That also violates the assumption pointed-out by some authors like *Janczuk and Bialopiotrowicz* [1989] that the liquids used should have a higher surface energy than the solid. Furthermore, toluene can chemically interact with the surface.

Conclusions

Our results show that values of the surface energy components calculated by the methods using a pair of liquids depend strongly on liquids used, but the total value of SFE varies much less than components. Considering the OW-plots we agree that using data from a pair of diiodomethane and water (or to be more general a pair of a polar and non-polar liquid) gives the most reliable results. These liquids are viewed as most distant in the plot so the effect of the measurement uncertainty is maximally suppressed.

The acid-base theory which aims to deliver more information about SFE components is also vulnerable to choice of combination of liquids with inadequate properties (e.g. diiodomethane-formamide-glycerol). Component-based methods are generally sensitive; to the selection of liquids used for calculations and to the surface roughness. On the other hand, these methods give self-consistent results for samples with higher SFE.

Zisman plot yielded satisfactory results for all polymer samples and it was not significantly affected by the surface roughness. But this method failed for high-energy samples where no linear trend in the plots was observed.

“Equation of state” approach seems to be impractical. In our laboratory conditions results of this method were dependent on the liquids used for calculations. But unlike for the component-based methods there is no way how to discuss which values are most plausible.

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