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New method of analysis of the surface free energy of polymeric materials calculated with Owens-Wendt and Neumann methods

RAPID COMMUNICATION

Summary — A new method of analysis of differences in the surface free energy (*SFE*) values of a solid, calculated using the methods of Owens-Wendt (OW) and Neumann and two measuring liquids, water and diiodomethane, is presented. The concept of the analysis bases on the differences in *SFE*, which occur objectively and regardless of both the precision and the performing conditions of the contact angle (*CA*) measurements. These differences result from utilizing of different mathematical relations between *CA* and *SFE* in each of the methods. The results obtained with these two methods are compared with one another over the *SFE* range common for polymeric materials (20—50 mJ/m²). It is calculated that the relative difference in *SFE* between the results from the OW and Neumann methods can reach 19.9 % over this range.

Key words: polymeric materials, contact angle, surface free energy, Owens-Wendt method, Neumann method.

NOWA METODA ANALIZY SWOBODNEJ ENERGII POWIERZCHNIOWEJ MATERIAŁÓW POLIMEROWYCH OBLICZANEJ METODAMI OWENSA-WENDTA I NEUMANNA

Streszczenie — Zaprezentowano nową metodę analizy różnic występujących w wartościach swobodnej energii powierzchniowej (*SFE*) materiałów polimerowych, obliczanej metodami Owensa-Wendta (OW) i Neumanna, przy użyciu wody i diiodometanu do pomiarów kąta zwilżania (*CA*). Przedmiotem analizy są obiektywne różnice tych metod, niezależne od sposobu i dokładności wykonywania pomiarów *CA*. Przyczyną tych różnic są odmienne postacie równań matematycznych stosowanych w badanych metodach. Analizę różnic w wartościach *SFE* przeprowadzono w zakresie od 20 do 50 mJ/m², tzn. w przedziale charakterystycznym dla materiałów polimerowych z modyfikowaną i z niemodyfikowaną warstwą wierzchnią. Maksymalna wartość względna tych obiektywnych różnic wynosiła w badanym przedziale 19,9 % (rys. 1 i 2).

Słowa kluczowe: materiały polimerowe, kąt zwilżania, swobodna energia powierzchniowa, metoda Owensa-Wendta, metoda Neumanna.

The Young and Laplace equations, well known for two hundred years, constitute the principles of determination of surface free energy (*SFE*) of solids. However, in the second half of the 20th century a rapid progress in the interface science and wettability processes occurred. As a result, new calculation methods for the *SFE* determination were elaborated, which were very important for polymeric materials surface investigations. These methods are formulated on the basis of a previously measured contact angle (*CA*) or of the drop-shape analysis for various liquids [1, 2].

Many technical restrictions and serious scientific dilemmas occur during *CA* measuring for the *SFE* determina-

tion. Some of these concern all the methods of *SFE* determination and include such problems as thermodynamic equilibrium, metastable state of the shape and *CA* of the examined drop, physical interpretation of advancing and receding contact angles, and origin of differences in the *SFE* values for various liquids applied and different methods used. These problems point out the directions of further interface research of polymeric materials [3, 4].

The main methods of the determination of *SFE* are those of Zisman, Owens-Wendt (OW), Wu, and a relatively new method of van Oss-Chaudhury-Good [2]. The last one is a subject of interest for many researchers and heated scientific discussions [5].

A method based on the so-called *state equation* modified to the Neumann equation [6, 7] is a subject of a detailed analysis in the literature. One of the controversies dealing with this equation is due to the fact that it is impossible to define a nature of β constant. For some authors, it is an universal material constant, whereas for others, it is only an equation parameter [4].

The most often applied method for polymeric materials so far is the OW method, in which water and diiodomethane are used. A growing interest in the Neumann method, based on the results of CA measurements performed with using only one liquid, is an inspiration for new investigations in this field [4].

This work is a continuation of my earlier studies on *SFE* of polymers [8—10]. The aim of this part was to analyze the differences in the values of *SFE* of a solid, calculated by means of the OW and Neumann methods with use of a commonly applied measuring liquids such as water and diiodomethane. The analysis was made in a new way, consisting in separation and determination of some differences between the *SFE* values calculated using these two methods. These differences occur objectively and regardless of the precision and performing conditions of the CA measurements and result from different mathematical formulae valid for each method.

Characteristics of the methods analyzed

The set of equations in the OW method, with water and diiodomethane used as measuring liquids, is of the form:

$$(\gamma_{Sd}\gamma_{Wd})^{0.5} + (\gamma_{Sp}\gamma_{Wp})^{0.5} = 0.5 \gamma_W (1 + \cos\Theta_W) \quad (1)$$

$$(\gamma_{Sd}\gamma_{Dd})^{0.5} + (\gamma_{Sp}\gamma_{Dp})^{0.5} = 0.5 \gamma_D (1 + \cos\Theta_D) \quad (2)$$

$$\gamma_S = \gamma_{Sd} + \gamma_{Sp} \quad (3)$$

where: *indexes W and D* — water as a polar liquid and diiodomethane as a dispersion liquid, respectively (for measuring liquids used in the CA measurements); γ_S , γ_{Sd} and γ_{Sp} — calculated values of *SFE* and its polar and disperse components of a solid, respectively; γ_L , γ_{Ld} and γ_{Lp} — known values of *SFE* and its polar and disperse components of a measuring liquid, respectively (*L* refers to *W* or *D*); Θ — contact angle (*L* means the same as above).

The γ_S value of an investigated material is calculated as follows. At first, γ_W , γ_{Wd} , γ_{Wp} , γ_D , γ_{Dd} and γ_{Dp} are to be determined. These values can be measured directly or just be accepted from the literature. The next step is to measure CA, using a set of measuring liquids. These measurements should be done repeatedly (more than 7 times) in order to determine a mean arithmetic value. Values of γ_{Sd} and γ_{Sp} are calculated from eqs. (1) and (2) and γ_S from eq. (3).

The formula for the Neumann method is applied in the following form [6, 7]:

$$\cos\Theta_L = 2(\gamma_S/\gamma_L)^{0.5} \exp[-\beta(\gamma_L - \gamma_S)^2] - 1 \quad (4)$$

with $\beta = 0.0001247$.

In spite of the controversy over eq. (4), this formula is still of the interest of researchers as a very convenient tool for the determination of *SFE*. The main advantage of the method applying this equation is using only one measuring liquid in the CA measurements. It makes the measurements easier to perform and limits the number of errors. The determination of γ_S from eq. (4), when γ_L and Θ_L are known, requires numerical computations.

Assumptions and run of the analysis

Because the *SFE* values obtained with use of the two methods are different, the reasons causing the *SFE* differences should be discussed. Generally, these differences may be due to the four following groups of reasons:

- errors of the CA measurements,
- wrong measuring liquids selected,
- wrong values of *SFE* and its components for measuring liquids, accepted from the literature,
- different mathematical relations between CA and *SFE*, used in each method applied.

The reasons included in first three groups are human-related and also depend on a measuring apparatus, measurement conditions, and measurement precision. As for the fourth group, performing the CA measurements does not influence the differences in the *SFE* values. Since the latter depend on the mathematical relation used, a detailed consideration of these objectively occurring differences is needed.

To discuss the differences in the *SFE* values obtained with the OW and Neumann methods, a new approach to the analysis of the methods was elaborated. In this approach, two commonly used measuring liquids (*W* and *D*) were considered and two basic assumptions were made:

- The analysis should enable to determine the objectively occurring differences in the *SFE* values calculated with use of the two above-mentioned methods, regardless of the kind of the materials studied. The considered *SFE* values of these materials are in the range of 20—50 mJ/m², being typical for a majority of polymeric materials with modified or non-modified surface layer.

- The results obtained using Neumann method and with water as a measuring liquid are considered as reference values, which is based on the fact that this method requires only one measuring liquid for the CA measurements. This has an essential meaning for the determination of CA with other measuring liquids when using the OW method.

The comparative analysis has been based on the results obtained with an appropriate computer program and can be divided into the following steps:

- Determination of characteristic curves from eq. (4) being transformed numerically:

$$\gamma_S = f(\Theta_L) \quad (5)$$

where: *index L is substituted as W or D.*

Value of γ_L needed in calculation was taken from the literature [2].

— Determination of γ_S from eq. (5) for Θ_W varying from 105 to 55° with the decrement of 5°. Thus, the obtained γ_S values vary in the range of 20.0—50.8 mJ/m².

— From eq. (4), calculation of Θ_D relating to each γ_S value determined in the previous step.

— By means of OW methods [eqs. (1—3)], calculation of *SFE* using appropriate sets of *CA* accepted in the second step and computed in the third step. Values of γ_L and its disperse and polar components were taken from the literature [2].

— Comparison of the results obtained using these methods.

The intervals between neighboring measurement points (5°), accepted in the second step, seem to be sufficient in view of both the aim of the calculations and the course of each characteristic curve [eq. (5)].

RESULTS AND DISCUSSION

The characteristic curves for each measuring liquid (W and D) are presented in Fig. 1. Clearly, the plots are similar in shape to one another and the γ_S values decrease monotonically with increasing Θ_L . Moreover, the values of *SFE* increase with Θ_L of each liquid ($\gamma_W > \gamma_D$) over the entire range of Θ_L considered.

Table 1. Surface free energy (*SFE*) of a solid, calculated using the Neumann method, for contact angles of water (Θ_W) and diiodomethane (Θ_D)

<i>SFE</i> , mJ/m ²	Contact angle, deg	
	Θ_W	Θ_D
20.0	105	83
23.0	100	77
26.1	95	71
29.2	90	64
32.4	85	58
35.5	80	51
38.6	75	45
41.7	70	37
44.8	65	30
47.8	60	20
50.8	55	1

The *SFE* values calculated for varying Θ_W and the corresponding values of Θ_D are listed in Table 1, with the accuracy of 0.1 mJ/m² for *SFE* and 1° for Θ_L . The values in Table 1 are the starting data for calculations conducted with use of the OW method and for comparing of the results obtained.

The obtained *SFE* values are compared in Fig. 2. The data calculated using Neumann method are based on

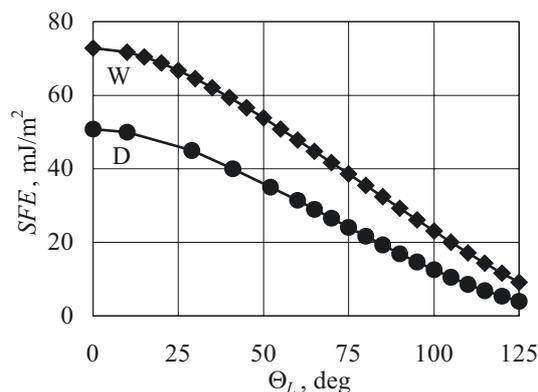


Fig. 1. Surface free energy (*SFE*) of a solid versus the contact angle (Θ_L) of water (W) and diiodomethane (D), calculated using Neumann method

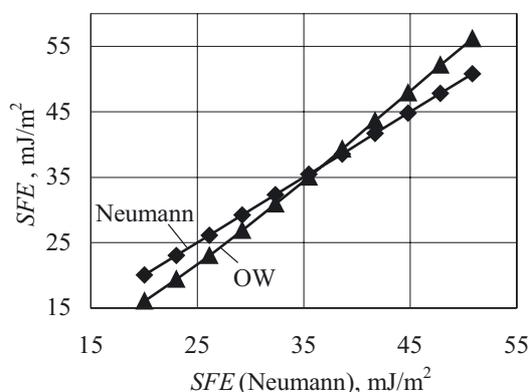


Fig. 2. Comparison of surface free energy (*SFE*) values of a solid, calculated using the Neumann or Owens-Wendt (OW) methods

the *CA* measurements carried out with use of W (parameters for chemically pure water were applied), while those calculated with using OW method, on the *CA* measurements with use of W and D. A reference scale of the horizontal axis refers to the *SFE* values computed by the Neumann method; therefore, it is denoted as *SFE* (Neumann). The plot corresponding to this method is a straight line at a slope of 45° to the horizontal axis. The smallest differences in the results obtained with use of these methods are in the middle of the *SFE* range analyzed, *i.e.*, between 32 and 42 mJ/m².

CONCLUSIONS

— The *SFE* values calculated with use of various methods differ not only due to the errors and different performing conditions of the *CA* measurements, but also due to objectively existing differences in the mathematical formulae used.

— In the *SFE* range of 20—50 mJ/m², being characteristic for most polymeric materials, the differences between the *SFE* values calculated using Neumann and OW methods reach 19.9%.

— Because of an indirect way of the *SFE* values calculation and of occurring differences in the results obtained using various methods, surface free energy of a polymeric material cannot be accepted as an independent physical quantity that determines exactly a thermodynamic state of the surface layer of the material.

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