

Methods for the calculation of surface free energy of solids

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Materials

ABSTRACT

Purpose: The main purpose of this paper is the analysis of the most common methods for the calculation of the surface free energy (SFE) of solids, utilising the results of the contact angle measurements. The calculation deals also with the SFE at the interface, especially that at the surface of polymers and polymeric materials. The survey has been meant to ease the understanding of physical processes occurring at the solid-liquid interface and to help to find proper measuring methods with respect to various physical systems.

Design/methodology/approach: The presented analysis has been based on the papers of the fundamental nature as well as on the specialised literature reports. The results of the experimental and theoretical studies of the author of this article are also considered.

Findings: Different assumptions have been made in the individual methods for calculating the SFE of polymeric materials. Thus, the SFE values for a given material, obtained by various methods and with use of different measuring liquids, are not consistent. The method for the calculation of the SFE of porous or granulated materials, powders, and fibres, in which the Washburn equation is utilised, is very useful in practice. Currently, there is no appropriate alternative to this method.

Research limitations/implications: The method for calculating the SFE with use of the equation of state requires further investigation, both experimental and theoretical. Further studies on the phenomena associated with penetration of the measuring liquids into the bulk of an examined material and on the relevant changes concerning this material, including the changes in its SFE, have also to be carried out.

Practical implications: The presented results of the investigations may be applied in optimisation of the current and derivation of the new methods for calculating the SFE of solids and liquids, including mainly the SFE of polymers in the solid state.

Originality/value: Because of differences in the assumptions made in most of the methods for the SFE calculation and of differences in the interactions between the individual measuring liquids and the examined material, the SFE values for various polymer materials may be compared with one another only when the contact angle measurements have been made using the same measuring liquids and when the SFE calculations have been performed by the same method.

Keywords: Engineering polymers; Surface free energy analysis; Methods of calculations

1. Introduction

A proper choice of a material for making a product is a very important part of the engineering design. This choice affects not only the product properties, but also the nature and course of the

relevant technological process. Thus, it constitutes an essential element of the engineering design of new products and products being modernised [1,2].

Dynamic development and steadily increasing scope of applications of polymeric materials in various areas of life

stimulate a better recognising of their physicochemical properties and improving of their functional qualities. Wettability and, related to it, the surface free energy (SFE) belong to these qualities. The wettability is crucial to the production of composite materials with the polymeric warp, reinforced with fibres, which play a more and more important role in such vital areas as the automotive or aviation industries [3]. Also, the wettability of solids with various liquids is of a great practical importance for many industrial processes, such as catalysis, flotation, making protective coatings, varnishing, gluing, and printing. Studies on the properties of the surface layer (SL) of various materials, including the wettability and SFE, are the subject of intensive scientific research for over forty years. These quantities are being assumed as important criteria for evaluation of adhesion properties of solid polymers. They are especially useful for the analysis of the effects of modification of the SL of polymeric materials. The wettability and SFE are of a great interest to the scientists working in various fields of knowledge, especially in physics, chemistry, materials engineering, and biology. The *surface engineering*, connecting cognitive and utility aspects of the surface phenomena, is now considered as an independent field, separated just recently [4-8].

Studies on the composition and structure of a material constituting the SL, on interfacial phenomena, and structure of the geometrical surface of polymeric materials are of special importance. A distinct differentiation between the terms of *surface* and *surface layer* is intentional because of the formal and methodological reasons. The surface is one of the basic terms of geometry, which means an ensemble of points or straight lines and, thus, has no physical thickness. On the other hand, the SL is an outer layer of a material, limited by its surface and comprising the region of space that ranges from the surface to the inside and differs in properties from the bulk of this material. The thickness of the SL defined this way depends on the chosen physical and chemical properties characteristic of this layer. It can equal from a fraction of nanometer (e.g., in case of atomic monolayers occurring in adsorption processes) to several hundreds or even more micrometers (e.g., in case of a surface layer of a polymeric product made by the techniques of injection or extrusion). Defining the surface similarly as in the surface analysis, which concerns the instrumental determination of the qualitative and quantitative compositions of the outer atomic layers of solids and adsorbates, may be a compromising solution. According to this definition, an examined surface is associated with a layer of the thickness equal to 1-4 outer atomic layers. The term a *subsurface layer* [7-9] is also used to indicate that the considerations deal with a very thin SL.

The purpose of this paper is to analyse the most common methods for the calculation of the surface free energy (SFE) of solids, utilising the results of the contact angle measurements. The calculation comprises the SFE at an interface, especially that at the surface of polymers and polymeric materials. The survey has been meant to ease the understanding of physical processes occurring at the *solid-liquid* interface and to help to find proper measuring methods with respect to various physical systems. Because it deals equally with *polymers*, *plastics*, and *polymeric materials*, these terms are considered as synonyms, in spite of the differences existing between them.

2. Interfacial interactions

2.1. The Young equation

The Young equation [10] is known for over two hundred years. Its modified form is as follows:

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\Theta \quad (1a)$$

or

$$\gamma_{sl} = \gamma_s - \gamma_l \cos\Theta \quad (1b)$$

where γ_s is the SFE of a solid, γ_{sl} – the SFE corresponding to the solid-liquid interface, γ_l – the SFE of a measuring liquid, and Θ – the contact angle between the solid and the measuring liquid.

This equation and the measured value of the contact angle are still being used as the basis for calculating the SFE of polymeric materials. However, the studies on the phenomena occurring at the interface, especially adsorption, catalysis, and wetting, began to develop quickly as late as in mid the twentieth century. As part of the results of these studies, theoretical and empirical fundamentals of various methods for the determination of the SFE of solids, including mostly the SFE of polymeric materials, have been elaborated. Among these methods, those based on the contact angle measurements are essential because of a relative ease of performing the measurements and high accuracy of the results obtained [4,6,7].

The quantities γ_l and Θ , appearing in Eq. 1a, can easily be measured. However, the quantity γ_{sl} remains unknown. In general, the effect of adsorption of the measuring liquid on the surface of a solid should also be taken into account [11,12]. Nevertheless, most of the researchers neglect this phenomenon because its influence in the systems containing a solid polymer and a measuring liquid is insignificant. Thus, in order to solve Eq. 1a, some additional assumptions concerning the relations between γ_s , γ_l , and γ_{sl} have to be made. The essence and physical interpretation of these assumptions determine the directions of the scientific research in this field and constitute a base of the methods for calculating the SFE of polymeric materials.

2.2. Equations of state

The basic assumption made in the above-mentioned research area is that γ_{sl} is a parameter the value of which depends on the properties of a solid and measuring liquid. This is reflected in the so-called equation of state:

$$F(\gamma_s, \gamma_l, \gamma_{sl}) = 0 \quad (2a)$$

or

$$\gamma_{sl} = f(\gamma_s, \gamma_l)$$

which is the subject of numerous studies, being carried out mostly by Neumann et al. [13-20].

Berthelot initiated this direction of studies at the end of the 19th century. He assumed that the interfacial adhesion work (W_{sl})

was equal the geometric mean of the cohesion work of a solid (W_{ss}) and the cohesion work of a measuring liquid (W_{ll}):

$$W_{sl} = (W_{ss}W_{ll})^{0.5} \quad (3)$$

Then, using the relation:

$$W_{ss} = 2\gamma_s, W_{ll} = 2\gamma_l \quad (4a)$$

and the Dupre equation [21]:

$$W_{sl} = \gamma_s + \gamma_l - \gamma_{sl} \quad (4b)$$

he formulated a hypothesis, called later after him the Berthelot hypothesis, in the form of the following equation [18]:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s\gamma_l)^{0.5} \quad (5)$$

Eq. 5 is essential as a starting point for deriving relations that enable to determine γ_s .

Independently of Berthelot, Antonow attempted to determine γ_s and presented the following formula [19]:

$$\gamma_{sl} = |\gamma_l - \gamma_s| \quad (6)$$

However, unlike Eq. 5 that is partially justified by the theory of the London intermolecular interactions, Eq. 6 is not adequately based on the scientific approach and, thus, is not being applied commonly.

Girifalco and Good [22] attempted to formulate the equation of state as well. They modified Eq. 5 by introducing the parameter Φ , characterising the interfacial interactions, as follows:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\Phi(\gamma_s\gamma_l)^{0.5} \quad (7)$$

In case of an interfacial system, in both parts of which interactions of the same type occur, $\Phi = 1$ was assumed.

Neumann et al. derived three other forms of the equation of state. The first one was obtained from the fundamental thermodynamic relations concerning the intermolecular interactions [13]:

$$\gamma_{sl} = \{(\gamma_s)^{0.5} - (\gamma_l)^{0.5}\} / \{1 - 0.015(\gamma_s\gamma_l)^{0.5}\} \quad (8)$$

The second one was a modified Berthelot hypothesis expressed by Eq. 5 [15]:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s\gamma_l)^{0.5} \exp\{-\beta_1(\gamma_l - \gamma_s)^2\} \quad (9)$$

The third one was a further modification of the Berthelot hypothesis [18]:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s\gamma_l)^{0.5} \{1 - \beta_2(\gamma_l - \gamma_s)^2\} \quad (10)$$

The coefficients $\beta_1 = 0.0001247$ and $\beta_2 = 0.0001057$, appearing in Eqs. 9 and 10, have been determined experimentally. There was measured the contact angle for several standard solids (fluorocarbon-covered mica, fluorinated copolymer of polyethylene and polypropylene, poly(ethylene terephthalate)) and for various measuring liquids. Then, some iterative procedures, adjusted to the automated axisymmetric drop shape analysis (ADSA), were used [23, 24].

The results of these investigations were consistent to a great extent, which, according to the authors, validated Eqs. 9 and 10. However, the literature reports are not unequivocal with respect to the meaning of the coefficients β_1 and β_2 [25]. The controversy deals with the question whether they are universal constants of a material or just quantities obtained as a result of the iterative procedures applied.

2.3. Partition of surface free energy into components

The idea of the partition of the SFE into individual components includes the assumption that the quantity γ_{sl} is determined by various interfacial interactions that depend on the properties of both the measuring liquid and the SL of the studied solid. Fowkes [26,27] was a pioneer of such an approach. He assumed that the SFE of a solid (and of a liquid) is a sum of independent components, associated with specific interactions:

$$\gamma_s = \gamma_s^d + \gamma_s^p + \gamma_s^h + \gamma_s^i + \gamma_s^{ab} + \gamma_s^o \quad (11)$$

where γ_s^d , γ_s^p , γ_s^h , γ_s^i , and γ_s^{ab} are the dispersion, polar, hydrogen (related to hydrogen bonds), induction, and acid-base components, respectively, while γ_s^o refers to all remaining interactions.

According to Fowkes, the dispersion component of the SFE is connected with the London interactions, arising from the electron dipole fluctuations. These interactions occur commonly in the matter and result from the attraction between adjacent atoms and molecules. The London forces depend on the kind of mutually attracting elements of the matter and are independent of other types of interactions. The remaining van der Waals interactions, i.e., the Keesom and Debye ones, have been considered by Fowkes as a part of the induction interactions.

Fowkes investigated mainly two-phase systems containing a substance (solid or liquid) in which the dispersion interactions appear only. Considering just such systems, Fowkes determined the SFE corresponding to the solid-liquid interface as follows:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d\gamma_l^d)^{0.5} \quad (12)$$

Eq. 12 is of the form of the Berthelot hypothesis (Eq. 5), limited to the interfacial London interactions.

Zettlemoyer [28] modified Eq. 12 by replacing the geometric mean of the interfacial interactions with the arithmetic one and obtained the following relationship:

$$\gamma_{sl} = \gamma_s + \gamma_l - (\gamma_s^d + \gamma_l^d) \quad (13)$$

However, like Eq. 6, Eq. 13 has not widely been applied, mostly because of insufficient theoretical and experimental justification.

Owens and Wendt [29] significantly changed the Fowkes idea while assuming that the sum of all the components occurring on the right-hand side of Eq. 11, except γ_s^d , can be considered as associated with the polar interaction (γ_s^p). Consequently, the following equation was obtained:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d\gamma_l^d)^{0.5} - 2(\gamma_s^p\gamma_l^p)^{0.5} \quad (14)$$

Because the polar interaction definition by Fowkes differs from that by Owens and Wendt, the meanings of γ_s^p and γ_l^p in Eq. 11 are different than those in Eq. 14.

Wu [30,31] accepted the idea by Owens and Wendt to divide the SFE into two parts, but used the harmonic means of the interfacial interactions instead of the geometric ones in Eq. 14 and derived the following equation:

$$\gamma_{sl} = \gamma_s + \gamma_l - 4 \{ \gamma_s^d \gamma_l^d / (\gamma_s^d + \gamma_l^d) + \gamma_s^p \gamma_l^p / (\gamma_s^p + \gamma_l^p) \} \quad (15)$$

In spite of only slight differences between the values of γ_{sl} , calculated with Eqs. 14 and 15, the approach by Wu has not widely been used in the studies on the wettability and SFE of polymeric materials.

The latest idea of the partition of the SFE of solids and liquids into components is that presented by van Oss, Chaudhury, and Good [32,33]. The authors divided γ_s into two components, one including the long-range interactions (London, Keesom, and Debye), called the Lifshitz-van der Waals component (γ^{LW}), and the other that contains the short-range interactions (acid-base), called the acid-base component (γ^{AB}). The latter component is considered to be equal $2(\gamma^+ \gamma^-)^{0.5}$, where γ^+ and γ^- mean the acidic and basic constituents, respectively, which are associated with the acid-base interactions. As a result, the following relationship was formulated:

$$\gamma_s = \{ (\gamma_s^{LW})^{0.5} - (\gamma_l^{LW})^{0.5} \}^2 + 2 \{ (\gamma_s^+)^{0.5} - (\gamma_l^+)^{0.5} \} \cdot \{ (\gamma_s^-)^{0.5} - (\gamma_l^-)^{0.5} \} \quad (16)$$

Derivation of Eq. 16 has been initiated by the results of the studies on interactions between proteins (biopolymers) and hydrophobic solids and by the attempts to explain the then unclear term a *hydrophobic bond* [32].

3. Methods for calculation of SFE, based on partition of this quantity into independent components

3.1. Fowkes method

According to Fowkes [26-28], the combination of Eq. 1a with Eq. 12 yields the formula that enables to calculate the SFE of a nonpolar solid, i.e., the solid for which $\gamma_s = \gamma_s^d$ is valid:

$$\gamma_s = \gamma_s^d = \gamma_l^2 (1 + \cos\Theta)^2 / (4\gamma_l^d) \quad (17a)$$

If the measuring liquid is a dispersion one, i.e., the one that can be characterised by the dispersion interaction only, then $\gamma_l = \gamma_l^d$ and Eq. 17a simplifies to the following formula:

$$\gamma_s = \gamma_s^d = 0.25\gamma_l (1 + \cos\Theta)^2 \quad (17b)$$

Using Eq. 17a, the dispersion component of the measuring liquid can be determined. In this case, polytetrafluoroethylene as totally nonpolar material with $\gamma_s^d = 18 \text{ mJ/m}^2$ is being applied as a

reference compound. After introducing this value of γ_s^d to Eq. 17a, the relation can be transformed into the following one:

$$\gamma_l^d = \gamma_l^2 (1 + \cos\Theta)^2 / 72 \quad (17c)$$

The Fowkes method can also be applied to determine γ_s of any solid. In this case, the equalities $\gamma_s = \gamma_s^d + \gamma_s^p$ and $\gamma_l = \gamma_l^d + \gamma_l^p$ are assumed to be valid while using Eqs. 1b, 12, and 17b. At first, the contact angle for the solid is measured using the dispersion liquid. Then, γ_s^d is calculated from Eq. 17b. Next, the contact angle (Θ_p) is measured using a liquid, for which $\gamma_l = \gamma_l^d + \gamma_l^p$. Using Eq. 14 and the determined values of γ_s^d and Θ_p , the quantity γ_s^p can be calculated from the following formula:

$$\gamma_s^p = \{ 0.5\gamma_l (1 + \cos\Theta_p) - (\gamma_s^d \gamma_l^d)^{0.5} \}^2 / \gamma_l^p \quad (18)$$

When applying the Fowkes method, it is recommended to use water and diiodomethane as the measuring liquids: water is considered as the liquid with the dominant polar component ($\gamma_l^d = 21.8 \text{ mJ/m}^2$ and $\gamma_l^p = 51.0 \text{ mJ/m}^2$) and diiodomethane, as the dispersion liquid ($\gamma_l = \gamma_l^d = 50.8 \text{ mJ/m}^2$). It has to be noted that the data on the SFE of diiodomethane, reported in the literature, are inconsistent; some authors give the values: $\gamma_l^d = 48.5 \text{ mJ/m}^2$ and $\gamma_l^p = 2.3 \text{ mJ/m}^2$ [34].

The Fowkes method is being used at some specialized laboratories for the determination of the SFE of polymeric materials [35]. It is especially convenient when applied to the nonpolar polymers and polymeric materials. One has to bear in mind, however, that this method is based on the independence and additivity of the dispersion and polar interactions.

3.2. Owens-Wendt method

In the Owens-Wendt method [29], there have been made the assumptions similar to those in the Fowkes method. The two methods, being identical in the mathematical aspect, differ slightly in the way of calculating the SFE. The combination of Eq. 1b with Eq. 14 leads to the following relationship:

$$(\gamma_s^d \gamma_l^d)^{0.5} + (\gamma_s^p \gamma_l^p)^{0.5} = 0.5\gamma_l (1 + \cos\Theta) \quad (19)$$

Because two unknowns, γ_s^d and γ_l^p , appear in Eq. 19, this formula is insufficient to determine the SFE of a polymer. Thus, the contact angle has to be measured using *two* measuring liquids, which would yield *two* equations in the form of Eq. 19, with different values of the constant coefficients. As a result, a system of two linear equations is obtained:

$$\begin{aligned} x + ay &= b(1 + \cos\Theta_1) \\ x + cy &= d(1 + \cos\Theta_2) \end{aligned} \quad (20)$$

where $x = (\gamma_s^d)^{0.5}$, $y = (\gamma_s^p)^{0.5}$, Θ_1 and Θ_2 are the contact angle values for the two measuring liquids, and a, b, c, d are the coefficients dependent on the kinds of these liquids. The liquid with a dominant polar component should be chosen as one of the measuring liquids and the dispersion liquid as the other one. Then, the solution of the system of Eqs. 20 would be affected as slightly as possible by the errors accompanying the determination of the components γ_l^d and γ_l^p . Such conditions are well fulfilled by the

pairs of liquids selected from the following set: water (W), glycerol (G), formamide (F), diiodomethane (D), and α -bromonaphthalene (B). For example, the pairs of liquids like WD, WB, GD, GB, FD, and FB can be used for the contact angle measurements. The values of the coefficients appearing in the system of Eqs. 20 for these pairs of liquids have been given elsewhere [36].

The Owens-Wendt approach is one of the most common methods for calculating the SFE of polymeric materials, water and diiodomethane being used most frequently as the measuring liquids.

3.3. Van Oss-Chaudhury-Good method

Taking into account that the component γ^{AB} is equal $2(\gamma^+\gamma^-)^{0.5}$ and combining Eq. 1b with Eq. 16, van Oss, Chaudhury, and Good obtained the following relationship [33]:

$$(\gamma_s^{LW}\gamma_l^{LW})^{0.5} + (\gamma_s^+\gamma_l^-)^{0.5} + (\gamma_s^-\gamma_l^+)^{0.5} = 0.5(1 + \cos\Theta) \quad (21)$$

Since *three* unknowns, γ_s^{LW} , γ_s^+ , and γ_s^- , appear in Eq. 21, the solution of a system of *three* independent linear equations, analogous to the system of Eqs. 20, is needed to determine these quantities. Such a system is obtained when *three* different liquids are used to measure the contact angle of a studied polymeric material. One nonpolar and two bipolar liquids should constitute the set of the three measuring liquids. The values of the coefficients appearing in such a system of equations, for several sets of these liquids, have been given elsewhere [36].

The solution of the system of three equations represented by Eq. 21, as used in the van Oss-Chaudhury-Good method, cannot always be proper and unequivocally interpreted. This follows from the assumed conditions and limitations, associated with both the kinds of selected measuring liquids and the ways of determination of the SFE components such as γ_l^{LW} , γ_l^+ , and γ_l^- .

The effect of wrong conditions relating to the system of linear equations on its solution may be discussed considering the following example. The solution of the system of two linear equations, $x + 20y = 21$ and $2x + 41y = 43$, consists in a pair of numbers, $x = 1$ and $y = 1$. If the coefficient at 'y' in the first equation is changed from 20 to 19.99 (i.e., by 0.05%), then the pair of numbers, $x \approx 1.41$ and $y \approx 0.98$, is the solution of a new system of equations, $x + 19.99y = 21$ and $2x + 41y = 43$. It means that a very small change in the value of only one coefficient may cause many times larger changes in the solution ('x' increases by ca. 41% and 'y' decreases by ca. 2%). If four coefficients in the two equations are changed, each by 0.01, then a new system of equations, $x + 19.99y = 21.01$ and $2x + 41.01y = 42.99$, is obtained, the solution of which consists in a pair of numbers, $x \approx 2.18$ and $y \approx 0.94$. In this case, very small changes in the values of the coefficients (by 0.05, 0.0476, 0.0244, and 0.0233%, respectively) cause very large changes in the solution ('x' increases by ca. 118% and 'y' decreases by ca. 6%).

When the values of the coefficients at the unknowns in an improperly conditioned system of linear equations are determined from independent measurements and calculations, then an even very small measurement or calculation error of only one of these values may totally distort the solution (see the first part of the example above). Also, the measurement or calculation errors

made during the determination of the remaining coefficients at the unknowns as well as the experimental errors relating to the values of the coefficients that appear on the right-hand side of the transformed equations represented by Eq. 21, may cause the obtained solution to be inconsistent with the current state of knowledge and with the expected result. It means that this solution may be wrong. Proper conditions relating to the system of equations represented by Eq. 21 are secured by, e.g., the following sets of liquids: WGD, WFD, and GFB.

A detailed discussion on the above conditions and limitations has been presented elsewhere [37]. The van Oss-Chaudhury-Good method is undoubtedly one of the recent achievements in the studies on the SFE of polymeric materials. In spite of many disputes and controversies over the results obtained by this method, it enables to learn better the examined phenomena, especially the interfacial acid-base interactions.

4. Other methods for determination of SFE of polymeric materials

4.1. Zisman method

This method is used to determine the so-called critical surface free energy (γ_c) that differs from the quantity γ_s , appearing in Eq. 1a. According to Zisman [38,39], the value of γ_c of a solid is equal the value of γ_l of a liquid being in contact with this solid and for which the contact angle is zero. The γ_c value is determined from empirical investigations, consisting of the contact angle measurements for the studied solid and the liquids of a homologous series of organic compounds. Then, a plot is constructed in a coordination system with the y axis corresponding to the cosine values of the contact angle (Θ) and the x axis relating to the γ_l values for the applied liquids. The values of $\cos\Theta$ for the liquids of a series of *n*-alkanes form approximately a straight line. Extrapolation of this line to the point of $\cos\Theta = 1$ yields the value of γ_c equal to γ_l at this point.

The measurement results can be described with a following relationship, being a straight line in the coordination system discussed:

$$\cos\Theta = 1 + b(\gamma_c - \gamma_l) \quad (22)$$

where *b* is the tangent of an angle between the x axis and the straight line being the approximation of the measurement results. Combining Eq. 1a with Eq. 22 and making relevant transformations, one may obtain a relationship between γ_c and γ_s of the studied solid as follows:

$$\gamma_s = (b\gamma_c + 1)^2/(4b) \quad (23)$$

The way of deriving Eq. 23 indicates that another solution is also possible: $\gamma_s = \gamma_c$.

At the time it was elaborated, the Zisman method made a significant progress with respect to understanding the phenomena associated with the wettability and determination of the SFE of polymeric materials. At present, however, it is not commonly applied, mainly because of insufficient theoretical justification and time-consuming investigation procedures.

4.2. Neumann method

The Neumann method consists in suitable transformation of Eq. 1b and combining the resulting formula with Eq. 2b. Many researchers were trying to find a proper form of the equation of state (Eq. 2). Consequently, they derived various versions of it, expressed, e.g., by Eqs. 8-10. When combined with Eq. 1b, each of these formulae enabled to obtain an implicit dependence of γ_s on γ_l and Θ . Unlike in the methods for the SFE determination, based on partition of γ_s into independent components (Eqs. 18, 19, and 21) and in which use of two or three measuring liquids is required, in the Neumann method, independently of its version, only one measuring liquid is applied.

Out of three hitherto existing versions of the Neumann equation, the following two formulae, resulting from Eqs. 9 and 10, are widely discussed:

$$(\gamma_s/\gamma_l)^{0.5} \exp\{-\beta_1(\gamma_l - \gamma_s)^2\} = 0.5(1 + \cos\Theta) \quad (24a)$$

and

$$(\gamma_s/\gamma_l)^{0.5} \{1 - \beta_2(\gamma_l - \gamma_s)^2\} = 0.5(1 + \cos\Theta) \quad (24b)$$

The principal questions concerning the Neumann method arise from the fact that Eqs. 24a and 24b have been derived using the iterative procedures, in which the results of the contact angle measurements for various polymers are considered as the input data [16,18]. Our studies indicate that significant differences between the SFE values determined by the methods of Owens-Wendt and Neumann occur in the energy range of 20-50 mJ/m², characteristic of most polymeric materials, including those with the modified SL [40,41].

4.3. Method based on determination of the contact angle hysteresis

This approach is one of the latest methods for calculating the SFE of polymeric materials, which has been elaborated a few years ago [42,43]. It consists in the measurements of both the advancing contact angle (Θ_a) and the receding one (Θ_r) with use of the same measuring liquid of a known value of γ_l . The SFE of a studied solid can then be calculated from the following equation:

$$\gamma_s = \gamma_l (\cos\Theta_r - \cos\Theta_a) \{ (1 + \cos\Theta_a)^2 / [(1 + \cos\Theta_r)^2 - (1 + \cos\Theta_a)^2] \} \quad (25)$$

Unlike the approaches presented above, Eq. 25 takes into account adsorption at the interface. Other assumptions are as follows:

- The contact angle appearing in Eq. 1a is the advancing contact angle. Thus, this equations transforms into the following one:

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\Theta_a \quad (26a)$$

- The SFE of a solid (γ_{sf}), which takes into account adsorption occurring during the measurement of Θ_r , can be expressed by the following relationship:

$$\gamma_{sf} = \gamma_{sl} + \gamma_l \cos\Theta_r \quad (26b)$$

- The following relation is valid:

$$\gamma_{sf} = \gamma_{sl} + \pi \quad (26c)$$

where π is the equilibrium pressure of a spreading film of the measuring liquid.

- The adhesion work can be determined from Eq. 4b, in which Θ_a or Θ_r is used, depending on the kind of the interfacial system.

When applying the Young and Dupre equations and the parameter Φ defined by Girifalco and Good [22] as well as making suitable substitutions in and transformations of Eqs. 26a-26c, one can derive Eq. 25. While obtaining this relationship, its authors did not question nor verify the fundamentals of the current knowledge in this area. Finding new relations between the quantities that characterise the wetting processes and deriving Eq. 25 that is a new approach to the SFE determination are unquestionable contribution of the authors of this method. Its usefulness has been confirmed by the results of our investigations on a filled polyolefine film, modified by the corona treatment [44].

The determination of the SFE of a polymeric material with use of Eq. 25 requires the measurements of Θ_a and Θ_r and knowledge of γ_l of the measuring liquid. However, as the authors of the method emphasise, the calculated values of the SFE depend on the kind of the applied measuring liquid. Thus, they confirm the results of our studies concerning other methods for calculating the SFE of polymeric materials [45-47].

5. Wettability and SFE of porous, granulated, powder, and fibre materials

The contact angle measurements for porous, granulated, and powder materials and fibres cannot be carried out with a goniometer. It is because of a rapid penetration of a measuring liquid into the porous structure of a material, on which a drop of the liquid is placed. In case of the granulated and powder materials, a drop cannot be deposited because of geometrical reasons relating to these materials. Only very small drops can be placed on thin fibres, which in addition requires specialized dosing and measuring devices and is associated with large errors.

A measurement technique, in which the Washburn theory and equation [48] are utilised, is one of the possibilities to overcome the above-mentioned hindrances. This equation in its original form expresses the dependence between the rate (v) of entry of a liquid into a capillary and other quantities:

$$v = r \gamma_l \cos\Theta / (2\eta x) \quad (27)$$

where r is the radius of the capillary, γ_l – the SFE of the penetrating liquid, Θ – the contact angle between the liquid and the capillary, η – the viscosity of the liquid, and x – the depth of penetration.

While assuming that a liquid penetrates porous materials in a similar way, Eq. 27 may be adjusted to measure the contact angle

in case of such materials. The mass (m) of a liquid entering a capillary may be expressed as:

$$m = \pi r^2 \rho x \quad (28)$$

where ρ is the specific mass of the liquid and the remaining symbols mean the same as in Eq. 27. The penetration rate may be replaced with the penetration time that can be determined from a commonly known formula: $v = x/t$. Then, the following relationship is obtained:

$$t = 2 \eta m^2 / (\pi^2 r^5 \rho^2 \gamma_l \cos\Theta) \quad (29)$$

Hence,

$$\cos\Theta = (m^2/t) (\eta/\rho^2\gamma_l) (2/\pi^2r^5) \quad (30)$$

Eq. 30, derived through the transformation of Eq. 27, describes the entry of a liquid into a single capillary. Assuming that n pores of similar sizes are present on the surface of the studied material, which can be represented by n capillaries of a mean radius r , and making the transformation as above, one can derive the following equation:

$$\cos\Theta = (m^2/t) (\eta/\rho^2\gamma_l) (2/\pi^2r^5n^2) \quad (31)$$

and, finally:

$$\cos\Theta = (m^2/t) A B \quad (32)$$

Using Eq. 32, the contact angle of porous materials can be calculated and, then, their SFE. One measures gain in the mass of the studied sample, which is equal the mass (m) of the liquid penetrating this sample during time (t) of the measurement. The constant A is associated with the kind of the measuring liquid. The constant B depends on the material properties and has to be determined experimentally.

In order to determine the value of B, a measurement should be performed with a liquid, for which the contact angle (with respect to the studied sample) is zero. Then, the following relation is valid:

$$B = t/(m^2A) \quad (33)$$

The value of B, determined this way, may be used in further investigations, provided that the samples of the porous materials are of the same size and of a uniform geometrical structure of their surface.

The measurement of the mass of a liquid penetrating the studied porous material is being carried out as follows. A sample of the material is fastened to a pull rod connected to a sensor enabling to measure mass and placed over a vessel containing the measuring liquid. The surfaces of the sample and liquid should be parallel to each other. Then, the vessel with the liquid is raised until the liquid touches the sample. From this moment on, the measurement time and the sample mass gain are recorded. The measurement is concluded after a specified time has elapsed or the sample mass has stopped to gain. The determination of the B value is performed in a similar way. The value of A is calculated using the parameters (η , ρ , and γ_l) characteristic of a given

measuring liquid. Finally, the contact angle can be calculated from Eq. 32. The SFE of the studied material may then be determined using one of the various methods presented above.

The contact angle measurements for the granulated, powder, and fibre materials are carried out similarly. In this case, there is used a container equipped with a sieve bottom, in which a granulated or powder sample is placed or a holder to keep a fibre bundle is mounted. The measurements are restricted by the requirement that the contact angle between the measuring liquid and the studied material cannot exceed 90° otherwise the liquid could not enter capillaries of the material. The other requirements are that the mass of the penetrating liquid and the penetration time are to be measured with a high accuracy, the constant B is to be determined with an error as small as possible, and the material samples are to be prepared in the same manner. These requirements result from the fact that the relevant factors significantly influence the contact angle value to be calculated.

The transformed Washburn equation (Eq. 32) is a useful tool for the determination of the contact angle of porous materials, powders, and fibres. Special instruments have already been constructed to perform the relevant measurements with a high accuracy [49]. Nevertheless, as in case of the other methods for the SFE determination, many attempts to modify this method are being made, mainly because some authors believe that the contact angle determined by this method is not the same as that appearing in Eq. 1a [50,51].

6. Summary

In spite of over two hundred years since its formulation, the Young equation still constitutes a base of many methods for calculating the SFE of polymeric materials in the solid state. The calculations are made while utilising the results of the contact angle measurements for these materials with use of various measuring liquids. The Dupre equation and Berthelot hypothesis are also of a great importance. These three outstanding researchers have elaborated the theoretical fundamentals of all of the methods discussed in the present article (except the Zisman method).

Because the Young equation contains two unknowns (γ_s and γ_{sl}), the authors of various methods for the determination of γ_s focused on finding the formulae that would express the γ_{sl} value with γ_s , γ_l , and their components and sometimes with other quantities and numerical coefficients. They also used widely the Dupre equation and Berthelot hypothesis.

The phenomena of interfacial interactions in the systems of various liquids and polymeric materials and, especially, mathematical relationships describing quantitatively these interactions are still not fully known. In the individual methods for the calculation of the SFE of polymeric materials, in which the contact angle measurements are applied, various assumptions have been made. Thus, the SFE values of a given material, determined by various methods and with use of different measuring liquids, are not equal to one another. When the SFE of a material with a modified SL is to be determined, the situation is even more complicated. Various extents of the modification lead to differences in the chemical composition and structure of the surface layer, which causes changes in the interfacial interactions and, thus,

in the SFE values calculated using the individual methods. Hence, only the results obtained by the same method with use of the same measuring liquids may mutually be compared.

In spite of some limitations, the method for calculating the SFE of porous, granulated, powder, and fibre materials with use of the Washburn equation is practically very useful. At present, there is no other, equally convenient, alternative to this method. The proper determination of constant B of the transformed Washburn equation and preparation of the successive samples, which would not cause changes in the values of the constant B, constitute the most difficult part of this technique.

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