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Adhesive Properties

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1. Introduction

Adhesive joints function in multiple branches of technical engineering in which the phenomenon of adhesion appears: creating adhesive joints, sealing, applying protective or decorative coating (paint or varnish), printing, decorating and many others. Among adhesive bonding techniques these are adhesive joints which are used most often in various machine structure joints.

Surface phenomena, such as adhesion, cohesion and wettability, play an exceptionally important role in creating adhesive joints, as they influence the possibility of creating such a joint and its quality. Adhesive properties are fundamental in processes in which the phenomenon of adhesion appears. These properties are referred to as the whole of physical-chemical properties heavily influencing adhesion. Adhesive properties are a crucial indicator determining, for instance, whether the surface layer is properly prepared for permanent or temporary adhesive joints to be formed. The surface layer is the external layer of the material, limited by the real surface of the object, including this surface and the outer part of the material together with its real surface. It demonstrates different physical and chemical properties or qualities when compared with the core of the material.

When analysing the issue of constituting adhesive properties, exceptional importance is ascribed to the first two groups of technological operations aimed at preparing and obtaining specific properties of the surface and the surface layer of the material, as well as a special improvement (modification) of the aforementioned. They allow, for instance, obtaining proper energy and geometric properties of the surface layer of joined materials, which positively influence adhesion.

These operations are considered crucial in terms of constituting these properties in reference to forming and the quality of hybrid adhesive joints, as they are composed of materials of different physical, mechanical and chemical properties.

Surface preparation, conducted according to the requirements, is one of the methods of constituting adhesive properties of a surface. Depending on the characteristics and required properties of adhesive joints it is possible to increase or decrease adhesion, i.e. to improve or lower adhesive properties.

The selection of a surface preparation method (including appropriate technological operations allowing to achieve desired structure and energy properties) depends on many

factors, among which the most important ones is the type of materials creating the adhesive joint.

2. Surface layer

In geometry, the surface is a two-dimensional geometric figure that limits the space filled with matter, i.e. surface in a theoretical sense. In mechanics, the surface is defined as the edge of a material body, which may be analysed in a molecular scale, micro- and macroscale, at the same time distinguishing different surfaces: material, nominal, real, observed, under machining, machined (Burakowski & Wierzchoń, 1995; Sikora, 1997). The real surface may be defined as the surface separating the object from the surrounding environment. However, from the point of view of adhesion, the most important concept of surface is presented in the physical-chemical sense, as it involves the phases. In physical chemistry, surface is a boundary of two touching phases, i.e. interfacial surface or an interface, where an abrupt change of properties occurs together with the phase transition. Interfacial surfaces are surfaces between bodies of different states of aggregation (Hebda & Wachal, 1980). Surface in physical-chemical sense is analysed in three dimensions, despite the difficulties in determining the thickness/depth of the interface due to its small dimensions.

The physical space is not a homogenous area between two phases. Atomically clean surface is extremely active physically and chemically, therefore, each contact with another body results in the adsorption of the substances. Newly adsorbed substances may initiate formation a new phase. Another aspect is that under a physically clean surface there may be various deformations and defects resulting from surface formation. Consequently, different properties may be observed in the physically clean surface compared to the core of the object. As a result, different layers constituting the surface layer may occur: below the surface, surface and above the surface.

2.1 The surface layer structure

At present a number of definitions of the surface layer exist (Sikora, 1996, 1997; Roźniatowski, Kurzydłowski, & Wierzchoń, 1994). One of the alternatives states that the surface layer is the external layer of the material, limited by the real surface of the object, including this surface and the outer part of the material under its real surface, which demonstrates different physical and, occasionally, chemical properties when compared with the core of the material. The articles (Kuczmazewski, 2006; Sikora, 1996, 1997) contain the description and the model of the surface layer of the material resulting from the adhesive failure. The surface layer has zonal structure. The proportions and the thickness of different zones vary, in addition the zones may interpenetrate, changing into one another or occupying the same space.

The structure and properties of the surface layer depend on the type and course of multiple phenomena and processes, including physical-chemical phenomena, such as adhesion.

2.2 The non-saturated surface force field

The surface of any body consists of atoms, particles or ions, which are in different conditions than the ones inside the body. In the volume phase the particles are subject to equal forces of

interaction. In the interface, however, the particles come into contact with their own phase as well as another one, which leads to the occurrence of asymmetric forces of interaction (Fig. 1, Burakowski & Wierzchnoń, 1995). The particles on the surface are more forcefully drawn into the volume phase, and as a result the surface has higher energy than the inside of the body. Such a surface is active and is able to adsorb other atoms or particles in its vicinity (Burakowski & Wierzchnoń, 1995; Dutkiewicz 1998).

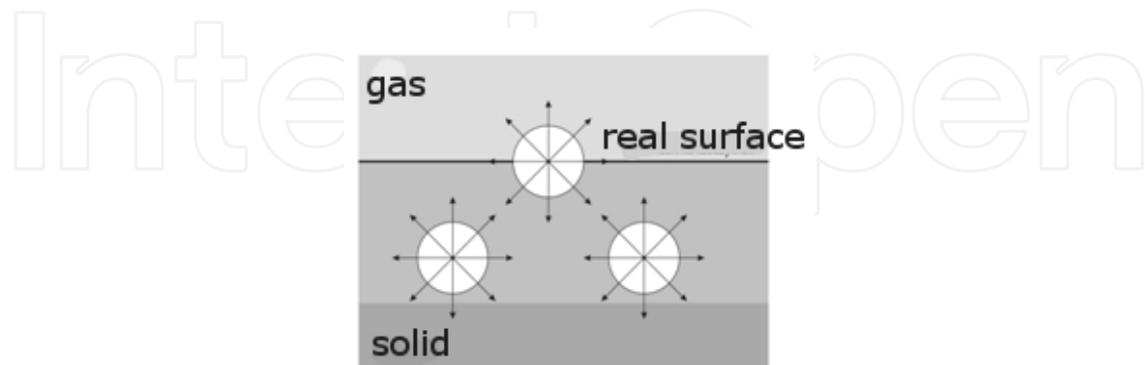


Fig. 1. A model of forces interacting with particles inside the solid and on its surface

What is equally important is the degree to which the surface particles are surrounded by other particles, i.e. whether the surface is flat or porous (Fig. 2, Dutkiewicz, 1998). The degree of non-saturation of forces is higher for a porous surface than for a flat one, therefore, the former is more active physically and chemically.

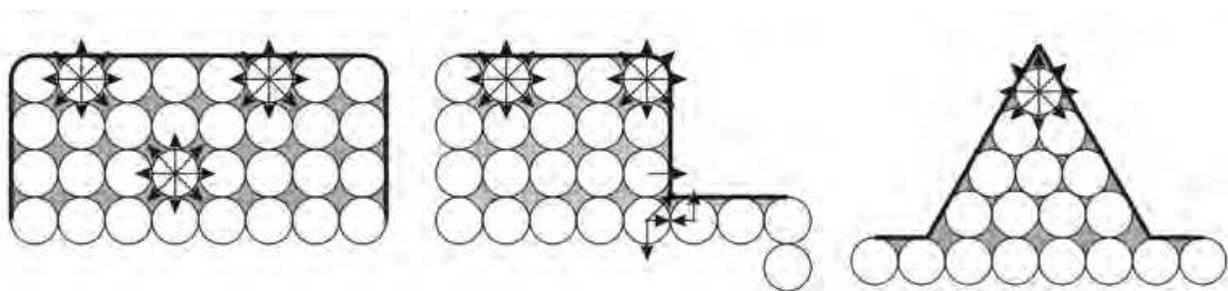


Fig. 2. The influence of porosity on the force field of various surfaces

It is the surface free energy, characteristic of solids, which is the measure of the interactions between the particles on the surface and inside the body.

3. Adhesion

3.1 Adhesion and adhesive properties definitions

The literature on the analysed subject is to some extent inconsistent in terms of contradicting terminology defining adhesion. Etymologically, 'adhesion' is derived from Latin *adhaesio* and stands for clinging or linkage. The adhesion is defined as a surface phenomenon, consisting in binding bodies in close contact as a result of force field interactions (Harding & Berg, 1997; Kuczmaszewski, 2006; Mittal, 1978, 1980; Żenkiewicz, 2000). The force field, induced by the charges of atoms constituting the surface layer (particles, ions), decreases exponentially with the distance to the surface (van der Waals interaction forces are

negligible for the gap over 1-2 nm). Therefore for the adhesion to take place, the close contact of surfaces is required.

Knowledge of the adhesive propriety plays important role in processes in which appears the occurrence of the adhesion. To such processes we can number the bonding, the painting, the decoration, the printing, the lacquer finish, etc. The adhesive properties characterise the surface of the materials taking into account their applicability in the adhesive processes. Good adhesive properties have a positive influence on the strength of the adhesive joint obtained, low properties significantly lower this strength or even prevent the bonding. Knowing the properties allows as well to constitute them properly by means of required surface preparation treatment of the analysed materials (Rudawska, 2010).

3.2 Geometric structure and SEM technique

Geometric structure and adhesive properties are extremely important in the technology of creating adhesive joints. The geometrical structure of the material surface has an influence on the adhesive joints strength obtained, and that is the reason why it should be carefully analysed before bonding. Surface roughness is important in view of the part the mechanical adhesion plays in general adhesion; consequently, it is beneficial to know the structure of the material surface layer that will be used in the adhesion process.

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample (http://en.wikipedia.org/wiki/Scanning_electron_microscope). Scanning electron microscopy (SEM) is generally considered micro-analytical techniques which are able to *image* or *analyze* materials we can not generally observe with the resolution offered by visible techniques. By *image* we mean photograph an object much smaller than we can see, even with the aid of an optical microscope (<http://epmalab.uoregon.edu/epmatext.htm>). SEM technique is very useful to analysis geometric structure of material for which is described adhesive properties (for example wettability or surface free energy).

Below there are some of example of materials for which it was determined the geometric structure (Rudawska, 2009 b, 2010).

The tests were conducted on aramide-epoxy composite samples. The composite consisted of two layers (2 x 0.3 mm) of aramide material marked KV-EP 285 199-46-003. The materials were arranged at 90 degree angle and subjected to the polymerisation process.

The geometric structure of the analysed composite was defined by means of SEM images. The results are shown in Fig. 3.

SEM images of the surface of analysed composite, show distinct differences in the surface structure, that are the result of specific character of the surface of the measures composites.

The pleat and the direction of the materials arranged at 90 degrees angle can be easily noticed.

The next tests were conducted on CP1 and CP3 titanium sheets samples. The samples of titanium sheets are made from:

1. CP1 (Grade 1- ASTM B265) and thickness 0.4 mm,
2. CP3 (Grade 3 - ASTM B265) and thickness 0.8 mm.

The results of SEM images of titanium sheets geometric structure are shown in Fig. 4 and Fig. 5.

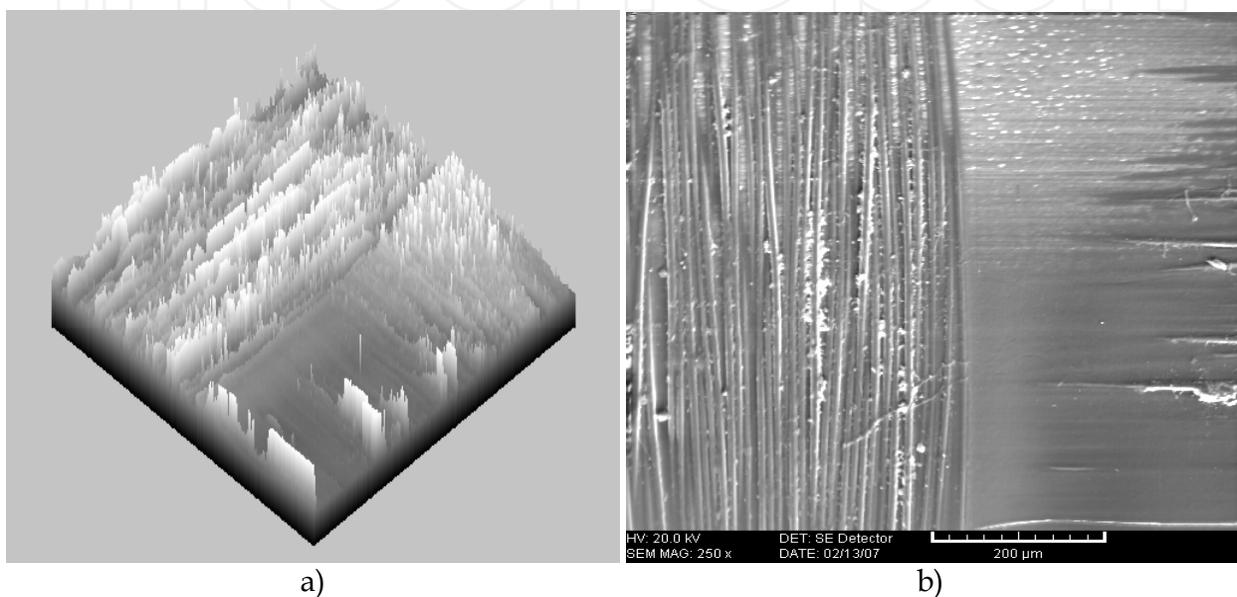


Fig. 3. Example of a surface topography SEM of the aramid/epoxy composite, magnification x250, a) spatial view, b) surface view (Rudawska, 2010)

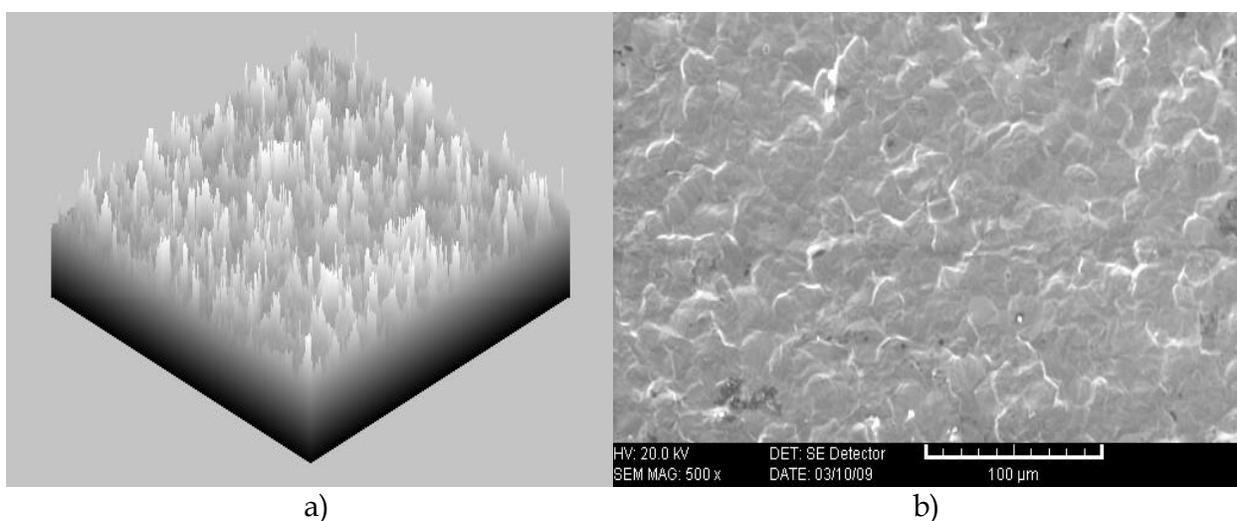


Fig. 4. Example of a surface topography SEM of CP1 titanium sheets surface, magnification x500, a) spatial view, b) surface view (Rudawska, 2009 b)

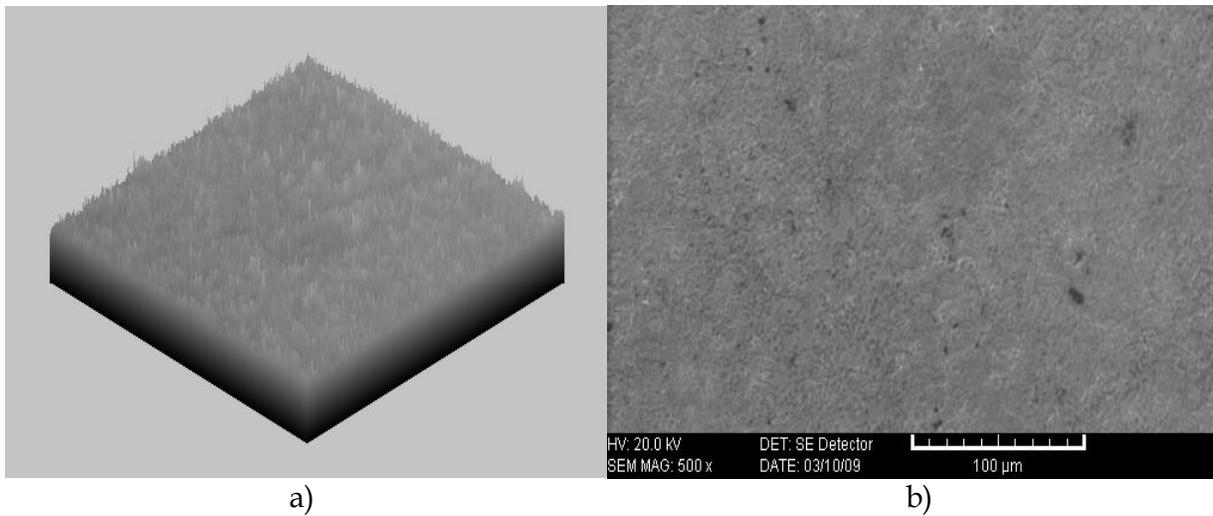


Fig. 5. Example of a surface topography SEM of CP3 titanium sheets surface, magnification x500, a) spatial view, b) surface view (Rudawska, 2009 b)

SEM images of the titanium sheets surface show differences in the surface structure of analysed titanium sheets.

The following samples are concern the SEM images of aluminium sheets surface. The samples used were aluminium clad (plated) sheets type 2024-T3 (sheet thickness: 0.64 mm) The results of SEM images of aluminium sheets geometric structure are shown in Fig. 6 (own research).

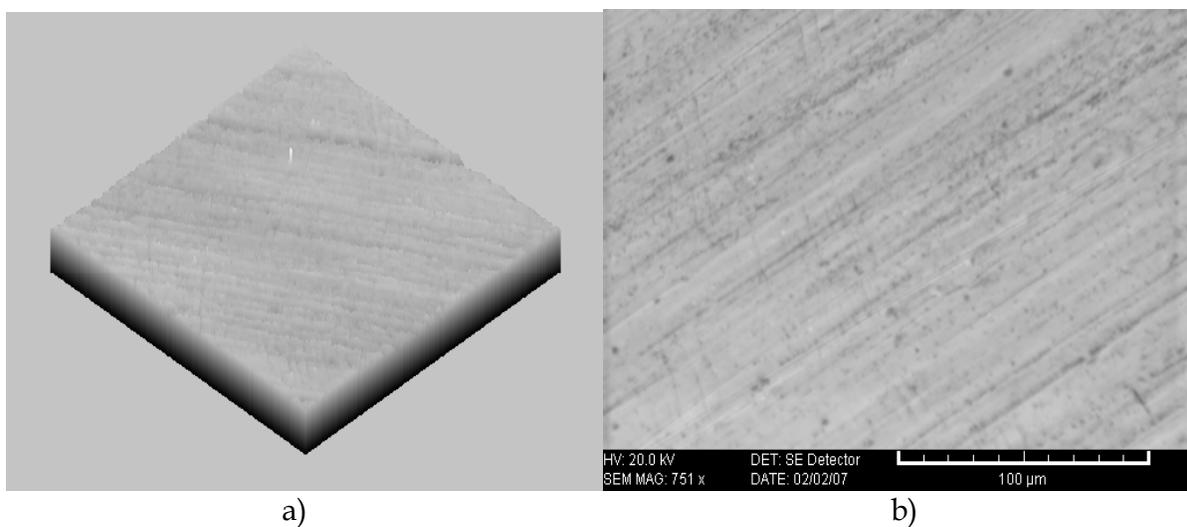


Fig. 6. Example of a surface topography SEM of aluminium 2024-T3 sheets surface, magnification x750, a) spatial view, b) surface view

The analysis of geometric structure of the analysed sheets considered in relation to adhesion technology is extremely important since these factors influence the obtained the adhesive joints strength.

4. Wetting phenomenon and contact angle

4.1 Wettability

The wetting phenomenon is a significant issue in various technological processes (Birdi & Vu, 1993; Norton, 1992; Parsons, Buckton & Chacham, 1993; Sommers & Jacobi, 2008; Qin & Chang, 1996). Wetting is a surface phenomenon consisting in substituting the surface of the solid and the liquid with a boundary surface, characterised by certain tension (σ), which results from the difference in the surface tension between the solid and liquid in the gaseous medium (Fig. 7), (Hay, Dragila & Liburdy 2008; Żenkiewicz, 2000).

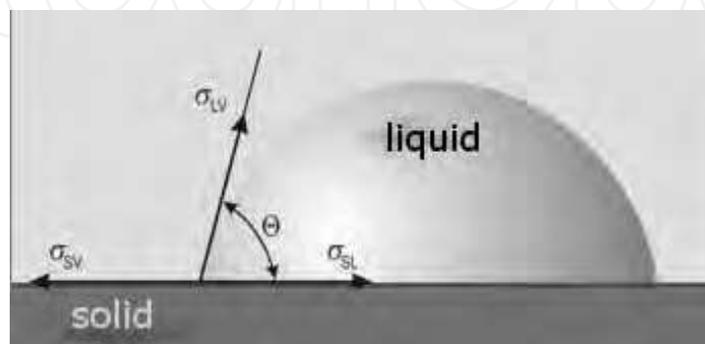


Fig. 7. Wetting a solid by a liquid

Wetting is a procedure that determines the diffusion of a liquid (adhesive) over a solid surface (substrate), creating an intimate contact between them. The air displacement caused by this physical attraction minimises the interfacial flaws. Good wettability of a surface is a prerequisite for a good adhesive bonding. Wettability is a crucial issue in the case of forming adhesive joints, because it directly affects the phenomenon of adhesion, increasing or decreasing adhesion forces.

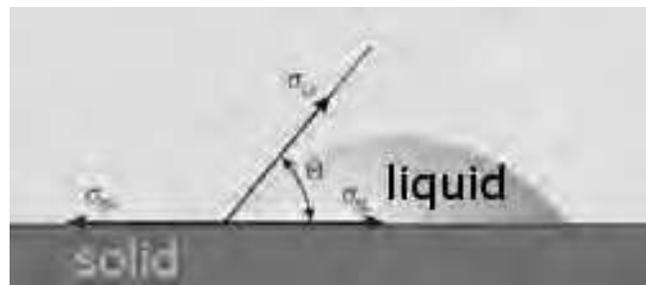
4.2 Contact angle

The contact angle Θ provides the measure of wettability. This is the angle formed between the wetted solid surface and the tangent to the wetting liquid surface (to the meniscus of the wetting liquid), at the contact point of the liquid and the solid surface (Comyn, 1992; Hebda & Wachal 1980; Lee, 1993; McCarthy, 1998; Żenkiewicz, 2000).

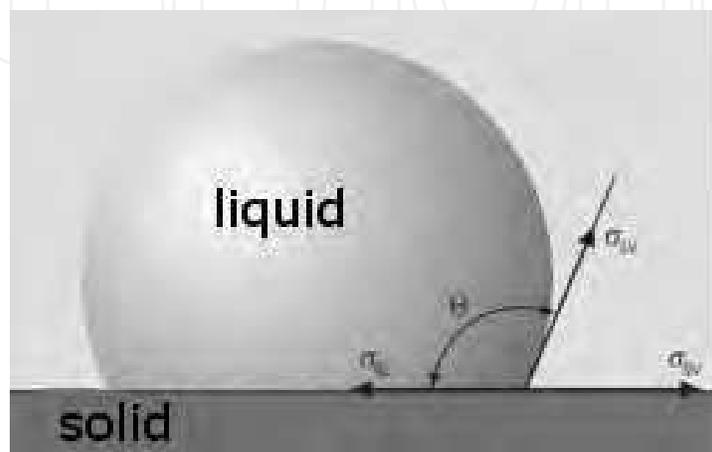
When wetting the surface of a solid, the contact angle value will be lower than 90° (Fig. 8). The case when the contact angle $\Theta = 0^\circ$, indicates that the liquid spreads over the surface evenly and, furthermore, represents complete wetting of a solid surface by a liquid. If the contact angle $\Theta = 180^\circ$, then the result is absolute non-wetting (McCarthy, 1998).

The literature offers various tips on surface wetting, which account for the differences in size and interdependencies (as for the contact angle). In order for the liquid to wet the surface of the solid favourably, its surface tension should be lower than the surface tension of the liquid.

The contact angle can provide the measure of wettability of solids by liquids, it can determine critical surface tension, moreover, it can be used for determining surface free energy, as well as for the analysis of surface layer changes occurring when the surface is modified (Żenkiewicz, 2000).



a)



b)

Fig. 8. Wetting of a solid surface by the liquid in the case of: a) favourable wettability $\Theta < 90^\circ$ and insufficient wettability $\Theta > 90^\circ$

There are a number of factors significantly influencing the value of contact angle and the correctness of the angle measuring process, which include: the longitudinal modulus of elasticity (surface rigidity), surface porosity, chemical and physical homogeneity of the surface (and the surface layer), surface contaminants, the type of a measuring liquid, drop volume or humidity.

The aforementioned factors contribute to disturbing the measuring of the contact angle, hinder the interpretation of results and are the cause of various metastable states of the drop itself. What is more, these phenomena result in the contact angle hysteresis (Chibowski & González-Caballero, 1993; Diaz, M. Fuentes, Cerro & Savage, 2010; Żenkiewicz, 2000).

The hysteresis is assumed to consist of two basic components: thermodynamic and dynamic. The sources of the former can be found in porosity and heterogeneity of the surface and the surface layer of the analysed material. This component of the hysteresis is independent of the surface age of the drop, provided the volume of the drop remains unchanged throughout. The other component, the dynamic hysteresis, results from the wetting liquid – test material chemical interaction, as well as from penetration of the gaps in the material by the measuring liquid. The dynamic hysteresis depends on the surface age of the drop (Żenkiewicz, 2000).

There are a number of methods for measuring the contact angle, and the most common include such techniques as: the bubble measure method, geometric method (where the contact angle is measured from the dimensions of the drop), the capillary rise method (such

as Wilhelmy plate method) or the direct measurement method (Ahadian, Mohseni & Morawian, 2009; Shang, Flury, Harsh & Zollars, 2008; Mangipudi, Tirrell & Pocius, 1994; Volpe & Siboni, 1998; Żenkiewicz, 2000).

At present, this is the direct measurement of the contact angle which is a commonly applied method, and the measurement is conducted by means of specialised instruments called goniometers or contact angle analysers (Żenkiewicz, 2000).

4.3 Factors influencing the contact angle

There is a number of factors substantially affecting the contact angle and the correctness of its measurements, which include: the longitudinal modulus of elasticity (surface rigidity), surface porosity, surface (and surface layer) physical and chemical homogeneity, surface contamination, the type of measuring liquid, drop volume, humidity, etc (Ajaev, Gambaryan-Roisman & Stephan 2010; Brown, 1994; Chibowski & González-Caballero, 1993; Extrand, 1998; Thompson, Brinckerhoff & Robbins, 1993; Żenkiewicz, 2000).

One of the factors influencing the contact angle is the *drop volume*. The impact of this factor is by no means certain, since there are no prevailing conclusions, due to the fact that the contact angle measurement methods and calculating models applied in tests were different. In his work (Żenkiewicz, 2000) M. Żenkiewicz included a lot of information both on the measuring drop volumes as well as contact angle measuring methods. M. Zielecka (Zielecka, 2004) observed the influence of the size of the drop on the contact angle measurement, and arrived at a drop volume range of 2-6 mm, within which the size of the drop bears no influence on the measurement of the contact angle. X. Tang, J. Dong, X. Li (Tang, Dong & Li, 2008). conducted contact angle measurements for distilled water drops in the volume range of 3-6 μl . In their tests, K. B. Borisenko and others (Borisenko, Evangelou, Zhao & Abel, 2008). used the diiodomethane drop volume of 5 μl . Although, in the tests conducted by M. Żenkiewicz (Żenkiewicz, 2005), Q. Bénard, M. Fois and M. Grisel (Bernard, Fois, & Grisel, 2005). the measuring liquids applied were different (distilled water, glycerol, formamide, diiodomethane, α -bromonaphthalene), the volume of the drop was identical - 3 μl . In the case of many works (Holysz, 2000; Serro, Colaço & Saramago, 2008; Żenkiewicz, 2000) the measuring drop volume ranges from 2-5 μl (2 μl , 4 μl), e.g. J. Shang and others (Shang, Flury, Harsh & Zollars, 2008). apply a 2 μl drop for static contact angle measurements and larger - 5 μl in the case of dynamic contact angle measurements. According to the data collected from the literature (Żenkiewicz, 2000), the size of the drop should range between 28mm³ and 0.5 mm³.

The surface age of the drop, i.e. the time between the application of a drop and the measurement, is one another contact angle affecting factor. M. Żenkiewicz (Żenkiewicz, 2000) notes that the time between the application and the measurement should be as short as possible, and moreover, identical for all the drops of the test series. Following this procedure should ensure a small influence of the drop-surface interaction and reduction of the drop volume as a result of evaporation.

X. Tang, J. Dong and X. Li (Tang, Dong & Li, 2008) deal with the phenomena of wetting and contact angle and additionally present test results of the influence of the surface age of the drop on the contact angle volume for different (wet and dry) surface states.

Another factor taken into consideration is *temperature*. M. Żenkiewicz (Żenkiewicz, 2000) mentions in his paper that within the range of 80°C, any changes in temperature only to a small degree trigger changes in the surface free energy, and natural temperature fluctuations, possible during laboratory tests, have a negligible impact on the samples contact angle measurements results. N. Zouvelou, X. Mantzouris, P. Nikolopoulos (Zouvelou, Mantzouris & Nikolopoulos, 2007) compared their tests observations with the literature data and drew a linear dependence of the surface free energy and the contact angle of certain materials on the temperature (nevertheless for high temperatures of approx. 800°C - 1173 K, 1500°C - 1773 K).

The longitudinal modulus of elasticity (surface rigidity) is yet another factor which should be considered when measuring the contact angle. M. Żenkiewicz, J. Gołębiowski and S. Lutomirski (Żenkiewicz, Gołębiowski & Lutomirski, 1999). stress that the surface of the test material where measuring drops are placed should be appropriately rigid. Therefore, the longitudinal modulus of elasticity of the material should be higher than 10 kPa, as it would prevent any drop deformations, resulting from the weight of the measuring drop.

One of the components of the thermodynamic hysteresis, *surface porosity*, is the next factor in question. R.D. Hazlett (Hazlett, 1992) describes and presents opinions of other researchers on the influence of surface porosity on the hysteresis of the contact angle, to conclude that the influence of porosity is beyond a shadow of a doubt. It can be, however, assumed that if $Ra < 0,5 \mu\text{m}$, then the impact of porosity on the contact angle is insignificant.

A.P. Serro, R. Colaço and B. Saramago (Serro, Colaço & Saramago, 2008) present test results for two samples made of UHMWPE (ultra-high-molecular-weight polyethylene) of different porosity, characterised by the Ra parameter of 3.9 and 1.0 nm, and the distance between the micropores of 23 and 6 nm respectively. They note that the wettability for given cases is irrespective of surface porosity, and that the contact angles measured for water and hexadecane are identical. However, J. Xian (Xian, 2008) points out that the wettability and the contact angle for a porous surface, e.g. analysed steel and polymers, is different for a smooth surface, adding that the change of the contact angle on a porous surface depends on the contact angle of a smooth surface of the analysed materials.

The physical and chemical homogeneity of the surface (and the surface layer) – i.e. physio-chemical homogeneity, which is the second source of the thermodynamic hysteresis, is another aspect taken into consideration when measuring the contact angle. Moreover, a considerable influence on the contact angle value may be observed on the part of the following: additive migration, diverse supermolecular structure, along with surface inhomogeneity – the result of different functional groups of different size and character formed on that surface.

What cannot be disregarded when measuring the contact angle is the analysis of *the type of the measuring liquid*. The measuring liquid penetration of the gaps in the surface layer of the material as well as of the intermolecular spaces is one of the causes of the dynamic hysteresis. The molar volume of the liquid plays an important role in the process as well – the rate of water penetration processes becomes slower and limited when the volume rises. Owing to its low molar volume water easily penetrates the structure of certain materials, therefore the importance of proper measuring liquid selection.

Other factors significantly disturbing the measurement of the contact angle are the *surface contaminants* and *air humidity* at the time of a test. Furthermore, *the sample should be firmly fixed* in order to prevent any measuring drop deformations as a result of vibrations.

Publications include plenty of information on the aspects of drop dispersion, along with the model of phenomena occurring when the contact angle measurement is taken for different liquid contact models, not to mention the characteristics of static and dynamic contact angle measurements. Some articles highlight the practical importance of wetting and wettability of different liquids in various processes, such as impregnation.

The factors mentioned in the preceding paragraphs hinder the measurement of the contact angle and the analysis of tests results, in addition they lead to different metastable states of the drop itself. These phenomena result in the contact angle hysteresis.

4.4 The contact angle hysteresis

Among many issues connected with the contact angle (the type of angle, measurements and values used in calculations) special importance is attributed to *the contact angle hysteresis*, which is the result of phenomena associated with metastable states of the measuring drop placed on the analysed surface of a solid (Bayer, Megaridis, Hang, Gamota & Biswas, 2007; Vedantam & Panchagnula, 2008; Zielecka, 2004; Żenkiewicz, 2000).

The first significant research on the contact angle hysteresis began in the middle of the 1970s and was conducted for example by R.J. Good (Good, 1979). E. Chibowski and F. González-Caballero (Chibowski & González-Caballero, 1993). presented theoretical information on the contact angle hysteresis, factors causing it and the description of the observed contact angle hysteresis connected with chemical interactions. C.W. Extrand (Extrand, 1998). characterised some of the contact angle hysteresis theoretical models and presented the study of the contact angle hysteresis thermodynamic model based on the research on polymers.

The Young equation constitutes the basis for theories related to the phenomenon of wettability. This equation comprises a measurable geometric parameter – the contact angle with three thermodynamic indices, which allow explaining the properties of interactions in the interface. The Young equation (also called Young-Laplace equation) was formed in 1805 and since then its principles and description have been used in multiple publications (Diaz, Fuentes, Cerro & Savage 2010; Faibish, Yoshida & Cohen, 2002; Żenkiewicz, 2006, 2000).

The Young equation describes an ideal system, which meets specific requirements of the contact angle measurement, geometric properties and qualities of the analysed surfaces (e.g. porosity, rigidity, physical and chemical homogeneity or the lack of surface contaminants). These requirements have been described in subsection 4.3.

If the surface meets the Young equation principles, the drop placed on it remains in equilibrium, which is accompanied by the lowest energy state. In such a situation, the contact angle is referred to as an equilibrium contact angle and its value does not depend on the changes of the drop volume. If the surface fails to meet the principles of Young equation, the measuring drop placed on it is in a metastable state, and then the contact angle of this drop may be higher or lower than the equilibrium angle. Initially, the gradual increase of the drop volume causes the increase of the contact angle until it reaches the limit, called *the advancing contact angle* Θ_A (Chibowski & González-Caballero, 1993; Żenkiewicz, 2000).

After this volume has been exceeded, an abrupt change of the drop position occurs - an abrupt change of the drop contour (decrease in height, increase in the contact area) and decrease in the volume of the contact angle. If the volume of the drop is gradually decreased, the value of the contact angle will initially decrease until it reaches the value called the *receding angle* Θ_R . After this value has been exceeded, the contour of the drop abruptly recedes (the height increases, the contact area decreases) and the value of the contact angle increases. A new metastable state of the drop location is, characterised by the contact angle is higher than the receding angle. Therefore, the contact angle hysteresis is defined as the difference between the advancing angle Θ_A and the receding angle Θ_R on the three-phase contact line (Chibowski & González-Caballero, 1993; Faibish, Yoshida & Cohen, 2002; Vedantam & Panchagnula, 2008; Volpe & Siboni 1998; Żenkiewicz, 2000).

The contact angles Θ_A and Θ_R , along with their corresponding drop volumes: maximum (for Θ_A) and minimum (for Θ_R) with a constant diameter (D) of the circle created by the drop lying on the tested material, are shown in the Fig. 9 (Żenkiewicz, 2000).

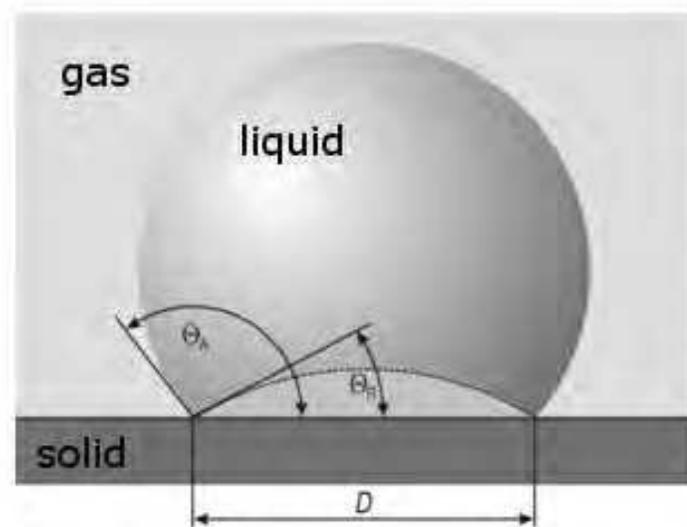


Fig. 9. The contact angles with a constant diameter D ($D=\text{const}$): Θ_A - the advancing angle, Θ_R - the receding angle, 1 - the maximum volume drop, 2 - the minimum volume drop

The hysteresis is assumed to consist of two basic components. First is the so called *thermodynamic hysteresis*, which results from porosity and heterogeneity of the surface and the surface layer of the tested material. This component is independent of the surface age of the drop (provided that the drop volume remains unchanged while measured). The other component is *the dynamic hysteresis*. It results from, among other things, chemical interactions of the measuring liquid with the tested material, and the measuring liquid penetration of the gaps in the material. The dynamic hysteresis depends on the surface age of the drop (Żenkiewicz, 2000).

The research on the hysteresis is extremely important from the practical point of view of, for instance, the surface free energy calculations. It is mostly connected with the question of which contact angle should be adopted in the simplified equation (3) in order to obtain the correct result. The contact angle used in calculations is the angle θ_A called the advancing angle.

5. Surface free energy

Surface free energy (SFE) is one of the thermodynamic quantities describing the state of atom equilibrium in the surface layer of materials (Hołysz, 2000; Żenkiewicz, 2000,2005). This quantity is characteristic for each substance. It reflects the specific state of unbalance in intermolecular interaction which is present at the phase boundary of two mediums.

Surface free energy is of equal number to the work necessary for creating a new surface unit while separating two phases in equilibrium, in a reversible isothermal process. It is measured in [mJ/m²] (Żenkiewicz, 2000).

5.1 Young equation

The basis for methods of calculating surface free energy from the measurements of the contact angle is the Young equation (Fig. 7) (Chibowski & González-Caballero, 1993; Lee, 1993; Thompson, Brinckerhoff & Robbins, 1993; Żenkiewicz, 2000).

It was derived from the condition of equilibrium of forces which represent surface tensions at the contact point of three phases – solid, liquid and gas.

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \Theta_V \quad (1)$$

where Θ_V is the equilibrium contact angle, and σ_{LV} , σ_{SV} , and σ_{SL} are the surface free energies of liquid–vapour, solid–vapour and solid–liquid interfaces, respectively.

The Young equation may also be derived from the energy balance for the triple point (Chibowski & González-Caballero, 1993; Michalski, Hardy & Saramago, 1998; Zouvelou, Mantzouris & Nikolopoulos, 2007). In this case, the equation is of the following form (Żenkiewicz, 2000):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \Theta_V \quad (2)$$

where: γ denotes surface free energy and the other symbols have the same meaning as in the equation (1).

It is impossible to determine surface free energy directly from the equation (2) because of the two unknowns: γ_{SV} and γ_{SL} . For calculation purposes, the following form of the equation (2) is commonly used to determine the surface free energy of solids (Chibowski & González-Caballero, 1993; Żenkiewicz, Gołębiewski & Lutomirski, 1999):

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \Theta \quad (3)$$

where: γ_S – surface free energy of solids in a vacuum,
 γ_{SL} – surface tension on the solid – liquid phase boundary,
 γ_L – surface free energy of the measured liquid,
 Θ – contact angle measured on the examined true surface.

The main drawback of the equation (1) is that it refers to an ideal system because it has been based on theoretical considerations, to a large extent not confirmed empirically. Still, this is the contact angle measurement which is the most often used method to determine energy properties of solids.

5.2 Surface free energy determination methods

The various SFE determination methods are based on specific relations, and involve the measurement of contact angles of various liquids. A number of factors have a substantial influence on the correctness of the contact angle measurement (subchapter 3.3). Some issues related to contact angle measurements and wettability have been highlighted shown in the literature.

Determination of surface free energy of solid objects involves indirect methods - direct methods can only be used in the case of liquids. Among the various indirect methods are the approaches due to Fowkes, Owens-Wendt, van Oss-Chaudhury-Good, Zisman, Wu, and Neumann (Ahadian, Mohseni & Morawian, 2009; González-Martín, Labajos-Broncano, Jańczuk & Bruque, 1999; Greiveldinger & Shanahan, 1999; Hołysz, 2000; Jańczuk, Białopiotrowicz & Zdziennicka, 1999; Lee, 1993; Lugscheider & Bobzin, 2001; Żenkiewicz, 2000, 2006).

5.2.1 The Owens-Wendt (Kaelble-Owens-Wendt) method (OW)

The Owens-Wendt method (sometimes referred to as Kaelble-Owens-Wendt method) is a frequently applied method for determining the surface free energy of, e.g. polymers (Jańczuk & Białopiotrowicz, 1987; Rudawska & Kuczmazewski, 2006; Rudawska, 2008). This method consists in determining dispersive and polar components of SFE based on Berthelot principle (Żenkiewicz, 2000), which assumes that interaction between molecules of two bodies in their surface layers equals the geometric mean of the cohesion work between the molecules of each body.

This method assumes that the surface free energy (γ_s) is a sum of two components: polar (γ_s^p) and dispersive (γ_s^d), and that there is a relation between the three quantities:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (4)$$

The dispersive element is the sum of components derived from such intermolecular interactions as: polar, hydrogen, induction and acid-base, with the exception of dispersive interactions. Dispersive interactions constitute the dispersive component of the surface free energy.

The work of adhesion between the solid and the liquid can be described by means of the Dupré equation:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (5)$$

By combining the equations 2 with 3, the Young-Dupré equation is obtained:

$$W_a = \gamma_{LV}(1 + \cos\Theta) \quad (6)$$

However, Owens and Wendt propose the following form of the work of adhesion between interacting solid and liquid.

$$W_a = 2(\gamma_s^d \gamma_{LV}^d)^{0.5} + 2(\gamma_s^p \gamma_{LV}^p)^{0.5} \quad (7)$$

If we compare and combine equations (6) and (7), the following equation is obtained:

$$\gamma_{LV}(1+\cos\Theta) = 2(\gamma_S^d \gamma_{LV}^d)^{0,5} + 2(\gamma_S^p \gamma_{LV}^p)^{0,5} \quad (8)$$

This equation allows determining the surface free energy of a solid and its SFE components.

In order to determine the polar and the dispersive components of the surface free energy, the measurements of the contact angle of the analysed samples need to be conducted with two measuring liquids. The surface free energy of the measuring liquids used in test is known, including its polar and dispersive components. One of the liquids is non-polar and the other is bipolar. Most frequently, the tests include distilled water as the polar liquid and diiodomethane as the non-polar one.

The SFE γ_S is calculated using the adjusted dependence describing the dispersive component of the surface free energy (Jańczuk & Białopiotrowicz, 1987; Rudawska & Kuczmaszewski, 2005; Rudawska, 2008; Rudawska & Jacniacka 2009).

$$\left(\gamma_S^d\right)^{1/2} = \frac{\gamma_d(\cos\Theta_d + 1) - \sqrt{\frac{\gamma_d^p}{\gamma_w^p} \gamma_w(\cos\Theta_w + 1)}}{2\left(\sqrt{\gamma_d^d} - \sqrt{\gamma_d^p \frac{\gamma_w^d}{\gamma_w^p}}\right)} \quad (9)$$

and the polar component of the surface free energy

$$\left(\gamma_S^p\right)^{0,5} = \frac{\gamma_w(\cos\Theta_w + 1) - 2\sqrt{\gamma_S^d \gamma_w^d}}{2\sqrt{\gamma_w^p}} \quad (10)$$

where: γ_S^d – the dispersive component of the test material surface free energy, γ_S^p – the polar component of the test material surface free energy, γ_d – the surface free energy of diiodomethane, γ_d^d – the dispersive component of the surface free energy of diiodomethane, γ_d^p – the polar component of the surface free energy of diiodomethane, γ_w – the surface free energy of water, γ_w^d – the dispersive component of the surface free energy of water, γ_w^p – the polar component of the surface free energy of diiodomethane, Θ_d – the contact angle of diiodomethane, Θ_w – the contact angle of water.

There is one of example of materials for which it was determined the surface free energy after various surface treatment (Rudawska, 2008, 2009).

The surface free energy of the material presented below was calculated with the Owens-Wendt method. This is a structural material applied in e.g. aircraft industry. The tests were to determine the influence of a surface preparation method on the SFE of the sample material.

The tests were conducted on glass-epoxy composite samples consisting of two layers (2x0.30 mm) of glass fibre 3200-7781. The fabric layers were arranged at a right angle and cured conforming to the technology standards.

The composite samples were tested for four surface preparation variants:

1. variant I – no surface preparation;
2. variant II – degreasing with Loctite 7036 (a detailed description of this method can be found in e.g. (Rudawska & Kuczmaszewski, 2005));

3. variant III – mechanical surface preparation with P320 abrasive tool;
4. variant IV – mechanical surface preparation with P320 abrasive tool, followed by degreasing with Loctite 7036.

The surface free energy values as well as the components of the SFE for four tested glass-epoxy composite surface preparation variants are presented in Fig. 10-13 (Rudawska, 2008, 2009).

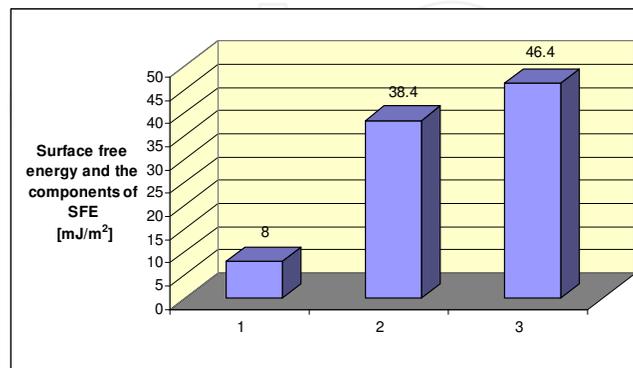


Fig. 10. Surface free energy and the components of SFE - the surface of glass/epoxy composite without surface treatment (variant I): 1 – polar component of SFE, 2 – dispersive component of SFE, 3 – surface free energy (SFE)

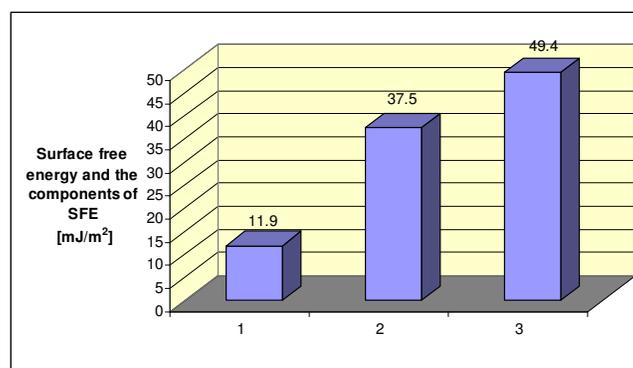


Fig. 11. Surface free energy and the components of SFE - the surface of glass/epoxy composite after degreasing (variant II): 1 – polar component of SFE, 2 – dispersive component of SFE, 3 – surface free energy (SFE)

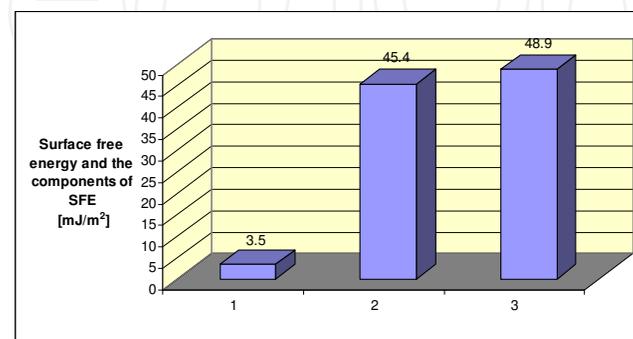


Fig. 12. Surface free energy and the components of SFE - the surface of glass/epoxy composite after the P320 grinding tool processing (variant III): 1 – polar component of SFE, 2 – dispersive component of SFE, 3 – surface free energy (SFE)

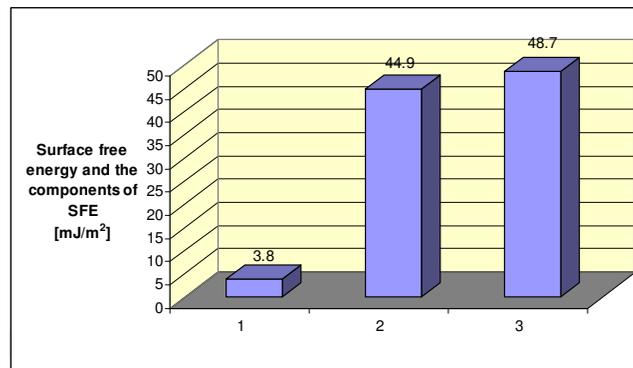


Fig. 13. Surface free energy and the components of SFE - the surface of glass/epoxy composite after the P320 grinding tool processing and degreasing (variant IV):
1 - polar component of SFE, 2 - dispersive component of SFE, 3 - surface free energy (SFE)

The results demonstrate that the highest values of the surface free energy were obtained in the case of degreasing, while the lowest were observed for variant I, with no surface preparation. Consequently, it appears that mechanical surface preparation and mechanical surface preparation followed by degreasing both increase the surface free energy. Additionally, no statistically relevant difference in the γ_s values of the two variants in question was observed.

Taking into consideration the polar component of the SFE, its highest value was noted in the case of surface preparation variant II, in which the surface free energy value was the highest as well. Additionally, the polar component constituted 24% of the total SFE. In the case of variant I, with the lowest γ_s value in the tests, the polar component constitutes 17% of the SFE. For the other two variants, III and IV, the polar component represented scant 7% and 8% respectively.

The analysis of the SFE values leads to the observation that degreasing the surface of the glass-epoxy composite has beneficial effect on the surface free energy value. It results in the increase of the SFE as compared to the surfaces with no prior surface preparation.

To conclude, it must be mentioned that, firstly, forming an adhesive joint should be preceded by certain surface preparation methods, and secondly, that this is degreasing which produces the best results in terms of adhesive properties of the analysed glass-epoxy composite.

5.2.2 The van Oss-Chaudhury-Good method (OCG)

In the case of the van Oss-Chaudhury-Good method the surface free energy is a sum of two components (Adão, Saramago & Fernandes, 1999; Żenkiewicz, 2000). While the first component γ^{LW} is connected with long-range interactions (dispersive, polar and inductive, referred to as Lifshitz-van der Waals electrodynamic interactions), the second component γ^{AB} describes the acid-base interactions (Holysz 2000; Jansen, 1991):

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (11)$$

Good R.J. and van Oss C.J. (Good & van Oss, 1992) separate the acid component (electron-acceptor: γ_L^+, γ_S^+) and the base component (electron-donor: γ_L^-, γ_S^-) of the surface free energy.

Moreover, the γ^{AB} component can be described by means of equation for bipolar compounds (showing properties of both Lewis acids and bases), (Elftonson, Ström, Holmberg & Olsson, 1996):

$$\gamma_i^{AB} = 2(\gamma_i^+ \gamma_i^-)^{0,5} \quad (12)$$

where: γ^+ - Lewis acid surface free energy component, γ^- - Lewis base surface free energy component, index i - subsequent measuring solids or liquids.

Determining the SFE of test materials will consist in measuring their surfaces contact angle with three different measuring liquids and calculating the γ s of the system of three equations:

$$(\gamma_S^{LW} \gamma_{Li}^{LW})^{0,5} + (\gamma_S^+ \gamma_{Li}^-)^{0,5} + (\gamma_S^- \gamma_{Li}^+)^{0,5} = \gamma_{Li} (1 + \cos\Theta_i) / 2 \quad (13)$$

where: $i=1,2,3$.

Measuring the contact angle requires the application of two polar and one non-polar liquids; nevertheless, solving the equation (3) requires additional information - particular values for the applied measuring liquids. Polar liquids applied in tests are water, glycerol, formamide or ethylene glycol, and non-polar liquids (not showing properties of either Lewis acids or bases) diiodomethane or α -bromonaphthalene.

A detailed description of this method is provided in the publications (Shen, Sheng, & Parker, 1999; Żenkiewicz, Gołębiewski & Lutomirski, 1999; Żenkiewicz 2000).

Determining the SFE with the van Oss-Chaudhury-Good method is uncomplicated, nevertheless, the test results should be carefully analysed. This method is burdened with a few problems, including e.g. the fact that the test results depend heavily on the applied measuring liquids configuration. This issue has been described by e.g. C. Della Volpe and S. Siboni (Volpe & Siboni, 1998). who in addition present the Drago theory, concerning, among other issues, the properties of Lewis acids and bases.

5.2.3 The comparison OW and OCG methods

Due to the fact that the methods of calculating the surface free energy presented in the previous chapters are most frequently applied, a comparison of selected structural materials SFE values calculated with the Owens-Wendt and the van Oss-Chaudhury-Good methods should be conducted (Kuczmazewski & Rudawska, 2002).

The structural material under analysis was electrolytic zinc coated and hot dip zinc coated sheets, which find application in such industries as automotive, construction or machine-building. The zinc coated sheets were 0.7 mm thick, the hot dip zinc coating equalled 18 μ m and electrolytic zinc coating equalled 7.5 μ m (following the PN-89/H-92125 and PN-EN 10152 standards).

The sample material surface was degreased with degreasing agents: Loctite 7061 and acetone. Degreasing was conducted in ambient temperature between 18 and 20 $^{\circ}$ C with relative humidity oscillating between 38% and 40%.

The method applied for measuring the contact angle was the direct measurement of the angle between the measuring drop and the tested surface.

For calculating the surface free energy with the Owens-Wendt method relationships (9) and (10) were applied. The values of both the surface free energy and its components for the applied measuring liquids are presented in Table 1 (Jańczuk & Białopiotrowicz, 1987).

No.	Measuring liquid	Surface free energy and its components [mJ/m ²]		
		γ_L	γ_L^p	γ_L^d
1	Distilled water	72.8	21.8	51.0
2	Diiodomethane	50.8	2.3	48.5

Table 1. The values of the surface free energy and its components for the applied measuring liquids

The SFE components values used in the van Oss-Chaudhury-Good method are presented in Table 2 (Żenkiewicz, Gołębiowski & Lutomirski, 1999).

No.	Measuring liquid	Surface free energy and its components [mJ/m ²]				
		γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-
1	Distilled water	72.8	21.8	51.0	34.2	19.0
2	Glycerol	64.0	34.0	30.0	5.3	42.5
3	Diiodomethane	50.8	50.8	0	0	0

Table 2. The values of the surface free energy and its components for the applied measuring liquids

The values of the surface free energy and its components were calculated with the van Oss-Chaudhury-Good method using the data presented in Table 2 as well as relationships (3) and (4).

The surface free energy values of the electrolytic zinc coated and hot dip zinc coated sheets calculated with the Owens-Wendt method are presented in Table 3 (Kuczmaszewski & Rudawska, 2002).

No.	The type of zinc coated sheets	The type of the degreasing agent	Surface free energy and its components [mJ/m ²]		
			γ_s	γ_s^p	γ_s^d
1	Electrolytic zinc coated sheets	Loctite 7061	42.0	17.8	24.2
		Acetone	35.4	10.7	24.7
2	Hot dip zinc coated sheets	Loctite 7061	44.7	9.7	35.0
		Acetone	43.8	11.6	32.2

Table 3. The zinc coated sheets surface free energy calculated with the Owens-Wendt method

The results demonstrate that the dispersive component of the surface free energy for hot dip zinc coated sheets is higher (even three times) than its polar component. In the case of electrolytic zinc coated sheets degreased with Loctite7061, this difference is less significant.

The values of the surface free energy of the electrolytic zinc coated and hot dip zinc coated sheets calculated with the van Oss-Chaudhury-Good method are presented in Table 4 (Kuczmaszewski & Rudawska, 2002). The results were obtained from the tested sheet surface layer contact angle measurement taken with distilled water, glycerol and diiodomethane as measuring liquids.

No.	The type of zinc coated sheets	The type of the degreasing agent	Surface free energy and its components [mJ/m ²]				
			γ_s	γ_s^{LW}	γ_s^{AB}	γ_s^+	γ_s^-
1	Electrolytic zinc coated sheets	Loctite 7061	43.7	32.5	11.2	13.8	2.3
		Acetone	38.6	30.5	8.1	4.3	3.9
2	Hot dip zinc coated sheets	Loctite 7061	45.0	41.5	3.5	0.3	11.6
		Acetone	41.4	39.2	2.2	0.1	15.8

Table 4. The zinc coated sheets surface free energy calculated with the van Oss-Chaudhury-Good method

It can be observed that the component of the surface free energy connected with long range interactions γ_s^{LW} (polar, dispersive and inductive) is higher than the component describing acid-base interactions γ_s^{AB} . The γ_s^{AB} component is scant in hot dip zinc coated sheets. Drawn from the analysis of the acid-base interactions component γ_s^{AB} , certain regularity may be observed. Lewis acid (γ_s^+) surface free energy component is higher than Lewis base (γ_s^-) surface free energy component for electrolytic zinc coated sheets, whereas for hot dip zinc coated sheets the γ_s^+ value was negligible when compared with the γ_s^- component. Owing to the insignificant γ_s^{AB} value it may be presumed that these surfaces will show properties of monopolar or non-polar substances.

A comparison of the surface free energy calculated with both the Owens-Wendt method and the van Oss-Chaudhury-Good method for hot dip zinc coated and electrolytic zinc coated sheets degreased with Loctite 7061 is presented in Fig.14 (Kuczmaszewski & Rudawska, 2002).

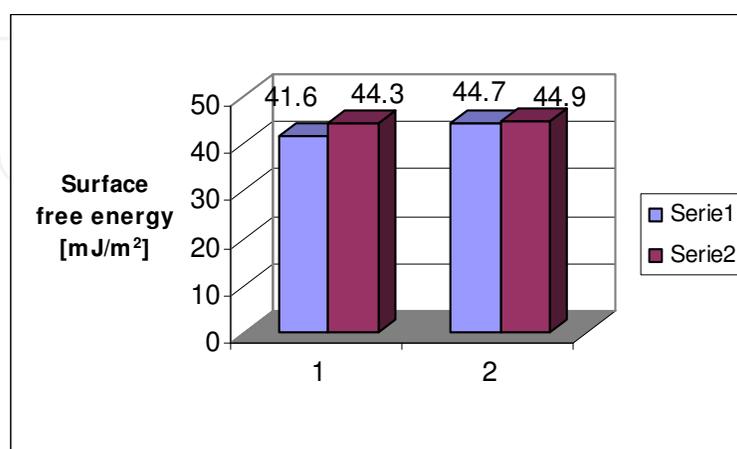


Fig. 14. The surface free energy values calculated with the Owens-Wendt method (series 1) and the van Oss-Chaudhury-Good method (series 2) for: 1- electrolytic zinc coated sheets, 2- hot dip zinc coated sheets after degreasing with Loctite 7061

A comparison of the surface free energy calculated with the Owens-Wendt method and the van Oss-Good method for hot dip zinc coated and electrolytic zinc coated sheets degreased with acetone is presented in Fig. 15 (Kuczmazewski & Rudawska, 2002).

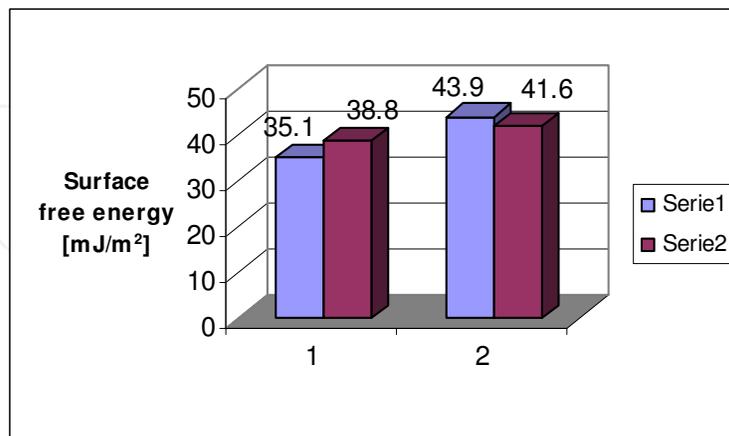


Fig. 15. The surface free energy values calculated with the Owens-Wendt method (series 1) and the van Oss-Chaudhury-Good method (series 2) for: 1- electrolytic zinc coated sheets, 2- hot dip zinc coated sheets after degreasing with acetone

The research results were subsequently analysed statistically using statistical models used for statistical verification (Krysicki et al., 1999). The statistical model – Student’s t-test consisted in comparing means when the test variances were equal (Fisher - Snedecor distribution), with a predetermined level of significance $\alpha = 0.05$. The statistical analysis provided basis for formulating the following conclusions.

The analysis proved that there are no statistically significant differences in the values of the SFE calculated with either the Owens-Wendt or the van Oss-Good method when the sheets are degreased with Loctite 7061. This holds true for both electrolytic zinc coated sheets and hot dip zinc coated sheets.

When degreasing with acetone operation was applied on the sheet surface, statistically significant differences in the SFE calculated for the hot dip zinc coated sheets were observed. The γ_s value calculated with the van Oss-Chaudhury-Good method was higher. However, this difference is not too significant (lower than 10%). Still, there were no statistically significant differences in the SFE calculated with the van Oss-Good method for electrolytic zinc coated sheets.

When analysing the SFE values calculated with the Owens-Wendt method, it may be assumed that the surface layer of the electrolytic zinc coating would most likely demonstrate higher affinity with the polar substance than the hot dip zinc coating would.

6. Conclusion

Adhesion and concurrent phenomena, e.g. wettability, are present in numerous fields of engineering and life in general. Determining the factors influencing the quality of adhesion and finding technology that can increase or decrease it is of utmost importance when it comes to constituting adhesive joints. What cannot be disregarded is the structure of the

surface layer of analysed materials or methods of determining adhesive properties, which assess materials suitability for adhesive processes. The existence of many methods for measuring the surface free energy stems from the fact that certain methods are suitable in particular circumstances. Existing methods describe the thermodynamic state of the surface layer differently yet all, through subsequent analyses of the surface free energy and its components, expand our knowledge of the phenomenon of adhesion.

SEM technique is very useful to analysis geometric structure of material for which is described adhesive properties. SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. The information of geometric structure is extremely important for the progress of adhesive processes like gluing, sealing, painting, coating.

In the subchapter devoted to a comparative analysis of the surface free energy measuring methods, the selection of the OW and the OCG methods was dictated by the fact that, on the one hand, these are the most frequently applied methods for measuring the surface free energy, on the other hand, due to relatively uncomplicated measurement of the contact angle with standard measuring liquids. The statistical analysis of the results evidences that, in most of the analysed cases, there are no statistically relevant differences between the values of surface free energy measured with either the Owens-Wendt or van Oss-Chaudhury-Good method.

Based on the statistical analysis it may be concluded that the choice of the surface free energy measurement method in the case of the analysed zinc coated sheets is basically of no relevance. Nevertheless, in ordinary working conditions it is the Owens-Wendt method which should be selected as a more efficient and less complicated tool for measuring the surface free energy of materials. The van Oss-Chaudhury-Good method, however, could be applied when a more detailed evaluation of the thermodynamic state of a surface (or a surface layer) is required.

Recent developments in the field of materials engineering contribute to creating structural materials or coatings, which are increasingly modern and specific – designated for particular applications. This creates the demand for continuous research into determining and describing their adhesive properties when adhesively bonding or joining such materials.

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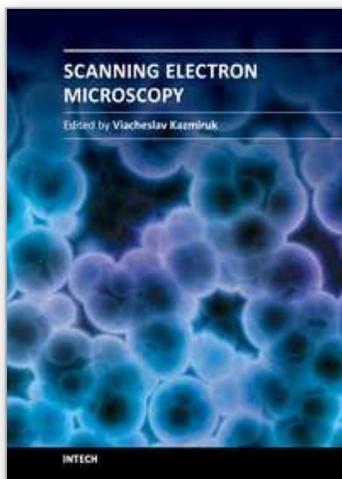
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