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Research Article

THE EFFECT OF ACTIVE DILUENT ADDITION ON THE ENERGY AND ADHESIVE PROPERTIES OF EPOXY ADHESIVE

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ABSTRACT
The paper reports values of surface free energy and its components of an epoxy adhesive modified by the addition of an active diluent. Wetting envelopes are determined and they serve as a basis for a wettability analysis and determining the possibility of maximizing the work of adhesion between the liquid and the solid. Static strength tests of adhesive joints made with the analysed adhesive compositions were also conducted. The results are used to determine the effect of active diluent addition on the energy and adhesive properties of the epoxy adhesive.

Keywords: surface free energy, contact angle, epoxy adhesives, adhesive joints,

INTRODUCTION

Compared to other bonding techniques, adhesive bonding offers several advantages. This method can be used to bond materials characterized by different physical and chemical properties. Owing to high properties of joints made by adhesive bonding, this technique is widely used for bonding materials. However, given the specificity of such joints, it is necessary to take into account a number of factors that affect the strength of produced joints. While designing adhesive joints, besides technological and design factors, attention should also be paid to material factors as well as conditions under which these joints will be used (Fig. 1) [1, 2, 3, 4, 6, 12, 15, 16, 18].

The research indicates [5, 8] that producing a durable adhesive joint depends on obtaining a strong adhesive bond. The adhesive properties of an adhesive, in particular its physical and chemical properties, can be maximized by ensuring good wettability of the adherend by the applied bonding composition. It is also important that the surface energy of the adherend is above the surface free energy of the adhesive that wets this material. Also, proper ratios between the surface free energy components of both the liquid and the solid should be maintained.

The current research [11, 13, 17, 19, 20] focuses on determining the effect of different methods of material surface preparation on the wettability, surface free energy and strength of adhesive joints made of thereby prepared material. However, neither the effect of surface free energy of the adhesive nor the impact of maintaining proper ratios of the surface free energy components between the bonded material and the adhesive are taken into consideration.

Having determined the surface free energy components of an adhesive composition, one can conduce a wettability analysis, the results of which can be used to determine which components of surface free energy should be exhibited by the material and what method of surface preparation should be applied in order to produce an adhesive joint with optimal adhesion properties for a given adherend using a particular adhesive composition [9, 10, 14].

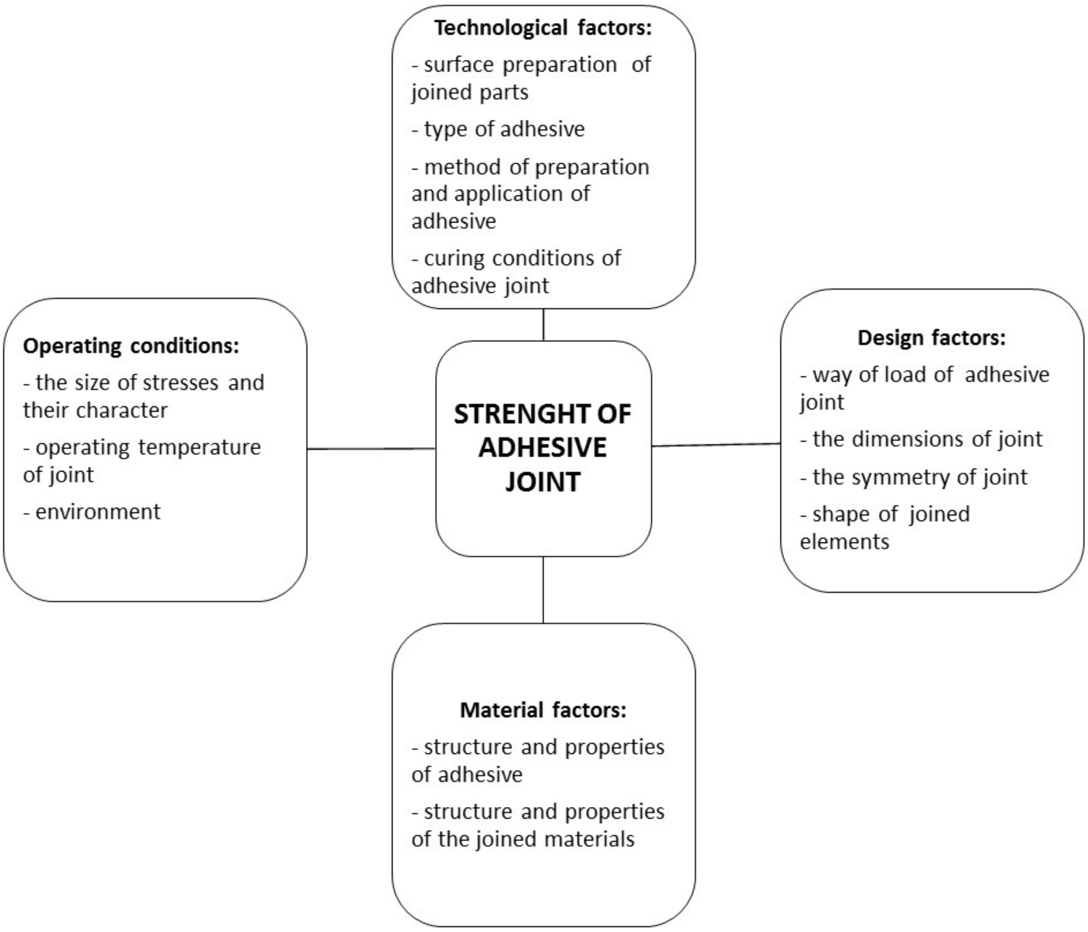

Fig. 1. Factors affecting adhesive joint strength (1)

The main objective of this study is to determine the surface free energy components of an adhesive modified by the addition of different quantities of an active diluent. In addition, an attempt is made to determine the relationship between the surface free energy of the adhesive and the strength of the adhesive joint made with this adhesive.

RESEARCH METHODOLOGY

The study was conducted for chemically setting adhesives which do not penetrate deeply into the material but have a strong chemical affinity to the material surface, thus producing high-strength adhesive joints. The process of setting or curing of such an adhesive takes place due to a chemical reaction of its components. This study involved the use of epoxy adhesives containing the following ingredients:

- Epidian 5 epoxy resin – an epoxy resin derived from the reaction of bisphenol-A with epichlorohydrin,
- IDA hardener – an amine hardener,
- TKB active diluent – a mixture of alcohol and aromatic hydrocarbons used to reduce adhesive viscosity.

The effect of active diluent addition to the epoxy adhesive on its energy properties was determined by examining the capacity of the adhesive to wet the surface of a material with particular energy characteristics. Surface tension of the modified epoxy adhesive was measured to determine its surface free energy. To this end, 15 ml droplets of the epoxy adhesive were metered with a syringe and 20 pedant drop measurements of surface tension were made. The measurements were carried out for each adhesive composition in liquid state and modified by the addition of 10 and 15 parts by weight of the active diluent to 100 parts by weight of the epoxy resin (Table 1).

The values of surface free energy components of the modified adhesive were determined based on the point of intersection of the wetting envelopes plotted on the basis of the contact angles of the tested adhesive compositions on the surface

Table 1. Ratio of diluent and hardener added to tested epoxy adhesive

No.	Symbol	Kind of resin	Kind of diluent	The proportion by weight of a diluent per 100 parts by weight of resin	Kind of hardener	The proportion by weight of a hardener per 100 parts by weight of mixture
1	E5/IDA/ 100:50	Epidian 5	-	-	IDA	50 parts by weight
2	E5/TKB/IDA/ 100:10:50	Epidian 5	TKB	10 parts by weight	IDA	50 parts by weight
3	E5/TKB/IDA/ 100:15:50	Epidian 5	TKB	15 parts by weight	IDA	50 parts by weight

of material with known energy properties with straight characterizing a surface free energy of a suitable adhesive. Droplets of the epoxy adhesive were applied to the surface of the EN AW-2017 aluminium alloy treated with polishing paste with grain size of 1000 using the automatic NICHIRYO Le-20 pipette. The droplet volume was 5±0.02 µl. The application of the drops was followed by measurements of the contact angle. 20 contact angle measurements were performed for each adhesive composition.

The material to which the adhesive was applied has the total surface free energy of 22.3 mJ/m^2 and the non-polar component of 21.8 mJ/m^2. These values were determined using the Owens-Wendt method. The study was conducted using diiodomethane and water as measuring liquid, and the volume of dispensed droplets was 4 µl. For each measuring liquid 30 measurements of the contact angle were performed. The measurements of surface tension, contact angles of adhesive drops on the aluminium alloy samples as well as the measurements of the contact angle of two liquids for the base material were made with the DSA30 device manufactured by KRÜSS using an automatic module of data collection and results analysis.

The impact of modification of the epoxy adhesive by adding an active diluent on its adhesive properties was investigated by static shear strength testing of the samples combined with the use of the analysed adhesive compositions. Experimental studies were conducted on EN AW-2017 aluminium alloy samples described by the following dimensions: length l = 100 mm, width b = 25 mm, thickness of the bonded samples g = 2 mm. The samples were bonded to make a lap of 25 mm. 5 joints were made for each of the tested adhesive compositions. After curing (24 hours) and seasoning (7 days), the samples were subjected to experimental studies on the Zwick/Roell Z150 testing machine. The strength tests were performed under the axial mounting of the samples and uniform static load at the constant peeling speed of 5 mm/min.

RESULTS

The following terms and abbreviations were used in the study:

- pendant drop method – the pendant drop is a drop suspended from a needle in a bulk liquid or gaseous phase. The shape of the drop results from the relationship between the surface tension or interfacial tension and gravity. The pendant drop method consists in calculating surface tension or interfacial tension based on the shadow image of a pendant drop using drop shape analysis,
- wetting envelope – a wettability profile of the solid created by determining the surface free energy and its polar and disperse parts,
- E5/IDA/100:50 – an epoxy adhesive based on epoxy resin mixed with IDA hardener; 50 parts of the hardener to 100 parts of the epoxy resin by weight,
- E5/TKB/IDA/100:10:50 – an epoxy adhesive based on epoxy resin mixed with TKB active diluent and IDA hardener; 10 parts of the active diluent to 100 parts of the epoxy resin by weight; 50 parts of the hardener to 100 parts by weight of the epoxy resin composition with diluent,
- E5/TKB/IDA/100:15:50 – an epoxy adhesive based on epoxy resin mixed with TKB active diluent and IDA hardener; 15 parts of the active diluent to 100 parts of the epoxy resin by weight; 50 parts of the hardener to 100 parts by weight of the epoxy resin composition with diluent.

The surface free energy of the tested adhesive compositions was determined by measuring surface tension using the pedant drop method. Approximate values of the surface free energy components of the adhesive compositions were measured as the point of intersection of the wetting envelopes that were determined based on the surface free energy components of aluminium alloy EN AW-2017 and the contact angles of the adhesives on this material. The straight line in the chart denotes the value of surface free energy. The research method is described in detail in [10]. Table 2 and Figure 2 list average values of the contact angle and the total surface free energy and its components obtained for the tested adhesive compositions.

The diagram in Fig. 2 shows that the highest value of total surface free energy is attained by the adhesive containing 15 parts of a TKB diluent to 100 parts of Epidian 5 epoxy resin by weight. The total surface free energy of this adhesive is 41.4 mJ/m^2. As a result of the adhesive's modification by the addition of active diluent, the distribution of the surface free energy components changes. The adhesive composition containing 10 parts by weight of the TKB diluent has the highest polar component equal to 30.3 mJ/m^2, which is 84.2% of total surface free energy. With increasing the diluent content by 5 parts by weight the polar component decreases to 5.7 mJ/m^2.

The next stage of the research involved an analysis of wettability of the adhesive on the surface of a material with known energy properties. The analysis was performed using EN AW-2017 aluminium alloy samples with a surface free energy of 37.2 mJ/m^2 and its components: polar – 18.2 mJ/m^2 and nonpolar – 19.0 mJ/m^2. The curves in Fig. 3 illustrate the wetting envelopes describing the tested epoxy adhesives and the corresponding curves illustrating the work of adhesion. They served as a basis for determining the maximum work of adhesion between the solid and the liquid that forms a given contact angle on the surface of the material.

Table 2. Average contact angle and total surface free energy and its components for selected epoxy adhesives

The adhesive composition	The average contact angle [°]	The total surface free energy [mJ/m^2]	Polar part [mJ/m^2]	Non-polar part [mJ/m^2]
E5/IDA/ 100:50	73.8	40.8	16.0	24.8
E5/TKB/IDA/ 100:10:50	99.4	36.0	30.3	5.7
E5/TKB/IDA/ 100:15:50	64.6	41.4	5.7	35.7

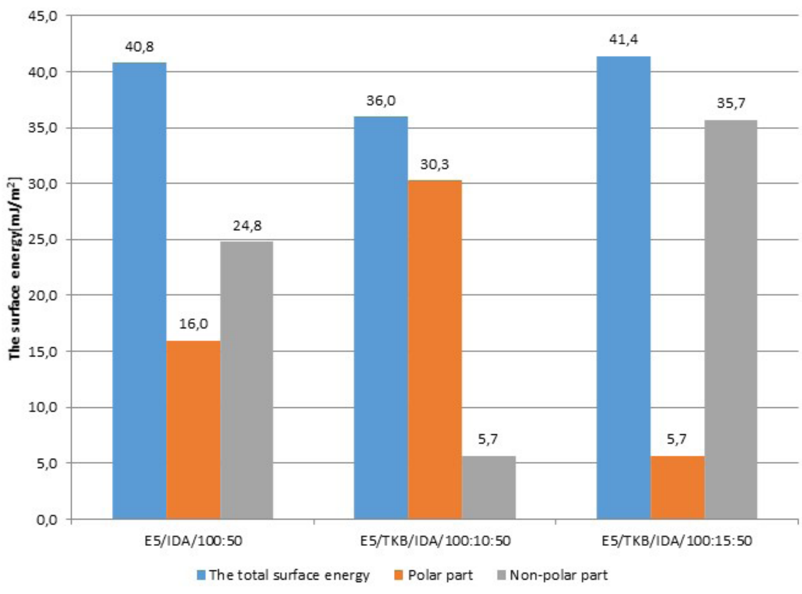

Fig. 2. Values of total surface free energy and its components obtained for the tested epoxy adhesives (prepared by the authors)

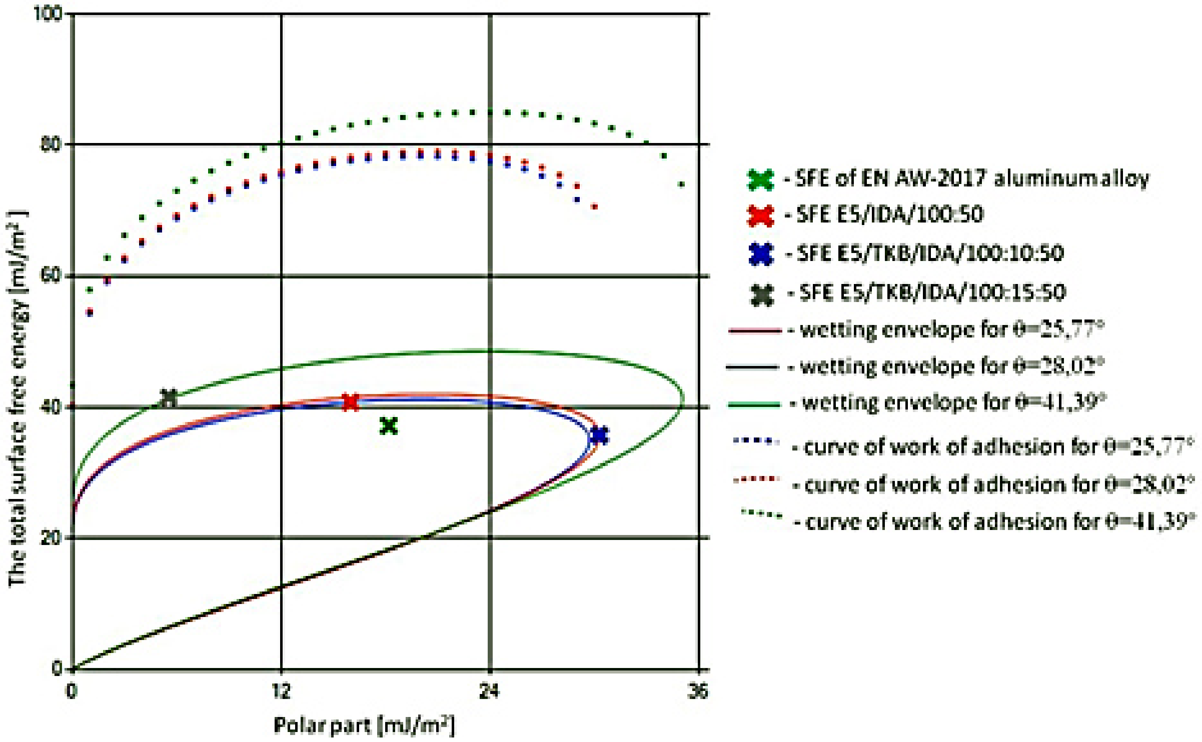

Fig. 3. Wetting envelopes and curves of work of adhesion determined for EN AW-2017A aluminium alloy and surface free energy values of selected adhesive compositions (prepared by the authors)

As the curves in the figure show, the best wetting conditions for EN AW-2017 aluminum alloy samples are obtained for the adhesive composition of Epidian 5 epoxy resin and IDA hardener without the addition of active diluent. The value of surface free energy and polar component of the adhesive mark a point that lies closer to the point representing the surface free energy of aluminum alloy. The adhesive containing 15 parts of the diluent to 100 parts of epoxy resin by weight has the highest contact angle value of 41.39°.

The diagram can also be used to determine whether the adhesive can be modified to increase the value of work of adhesion such that it corresponds to the maximum value of work of adhesion for a specified contact angle. The maximum work of adhesion corresponds to the minimum value of interfacial tension at the same time. The work of adhesion between aluminum alloy EN AW-2017 and the drops of the tested epoxy adhesives does not reach its maximum value for a specified contact angle. The work of adhesion determined for the adhesive without the addition of active diluent is the closest to the maximum value of work of adhesion and is equal to 77.54 mJ. The maximum work of adhesion for the angle of 25.77° is 78.3 mJ.

The impact of modification of the epoxy adhesive by the addition of an active diluent on its adhesive properties is shown in Fig. 4.

The results of shear strength prove the positive effect of the active diluent. Its application changes the viscosity of the adhesive, contributing to the improvement of the wetting process, which, in turn, increases the strength of mechanical adhesion. In comparison to the compositions containing the diluent, the strength of the joints made with the adhesive based on Epidian 5 epoxy resin and IDA hardener is lower and amounts to 0.78 MPa.

CONCLUSIONS

Ideally, in the adhesive bonding process the surface free energy of the adhesive that wets the surface of a material should be lower than the surface free energy of the wetted body. Considering that the epoxy adhesive is a polar substance, it is important to maintain the minimum difference between the value of surface free energy value of the adhesive and the solid, and to maintain an appropriate proportion between the components of surface free energy. This will ensure the best adhesion properties.

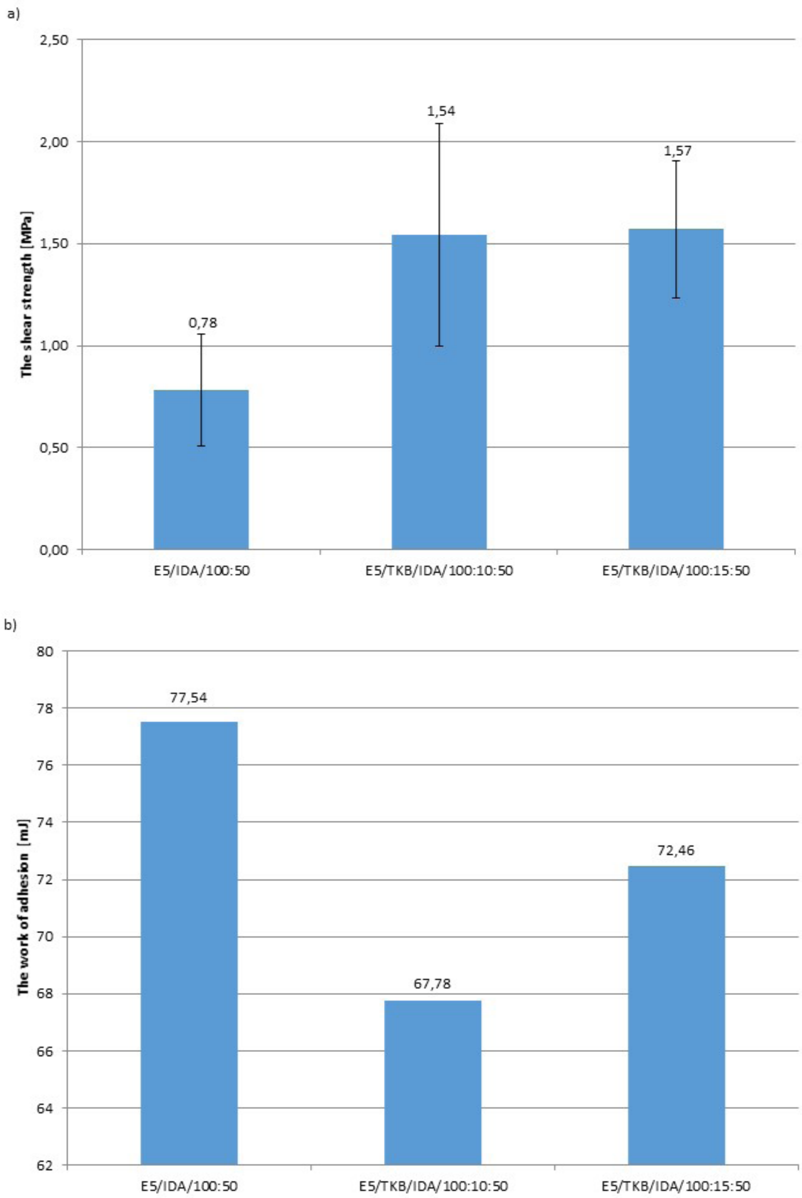

Fig. 4. Diagrams of: a) average shear strength b) work of adhesion of the adhesive joints made using the epoxy adhesive modified by the addition of an active solvent (prepared by the authors)

The research has shown that the highest values of surface free energy were obtained for the adhesive compositions containing a 15% TKB active diluent, and not for the modified adhesive. At the same time, however, these compositions exhibit the highest values of work of adhesion – 72.46 mJ and 77.54 mJ, respectively. It should be noted that in the case of E5/TKB/IDA/100:15:50 composition, the polar component of surface free energy is significantly lower than the non-polar component.

The high value of work of adhesion of an adhesive composition containing 15% of TKB active diluent results in a higher strength of the joint, which can be accounted for by the increased strength of chemical, hydrogen, dipole and inductive bonds. For compositions with addition of 10% TKB active diluent, high relative strength of the joint was observed, which in turn is associated with an increase in the non-polar component of the Van der Wals forces and the increase in the share of mechanical adhesion in the adhesion balance of the joint.

Taking into account the above results, it has been demonstrated that the modification of epoxy adhesive created using Epidian 5 epoxy resin mixed with the IDA hardener by adding an active diluent makes a significant difference in the ratio between surface free energy components of the adhesive composition, causing a slight change in total surface energy. As can be seen from Fig. 3, depending on the type of bonded material, it is possible to modify the properties of the adhesive composition using a suitable amount of active diluent to obtain optimum wetting properties while at the same time maintaining the strength parameters of the joint. As is clear from Fig. 4, the measurement of energy itself cannot fully determine the strength properties of the joint for the modified adhesive compositions because the analysis does not take account of the mechanical, electrical and diffusion components of interactions included in the Fowkes model [7].

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