Adhesive properties and adhesive joints strength of graphite/epoxy composites

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Abstract. The article presents the results of experimental research of the adhesive joints strength of graphite/epoxy composites and the results of the surface free energy of the composite surfaces. Two types of graphite/epoxy composites with different thickness were tested which are used to aircraft structure. The single-lap adhesive joints of epoxy composites were considered. Adhesive properties were described by surface free energy. Owens-Wendt method was used to determine surface free energy. The epoxy two-component adhesive was used to preparing the adhesive joints. Zwick/Roell 100 strength device were used to determination the shear strength of adhesive joints of epoxy composites. The strength test results showed that the highest value was obtained for adhesive joints of graphite-epoxy composite of smaller material thickness (0.48 mm). Statistical analysis of the results obtained, the study showed statistically significant differences between the values of the strength of the confidence level of 0.95. The statistical analysis of the results also showed that there are no statistical significant differences in average values of surface free energy (0.95 confidence level). It was noted that in each of the results the dispersion component of surface free energy was much greater than polar component of surface free energy.

1. Introduction

Adhesive joints are used in many fields of engineering where surface processes, particularly adhesion, wettability and adsorption, play a significant role [1-4]. The knowledge about adhesion and adhesive properties, particularly information about methods for shaping adhesive properties of surface layer of specified materials, enables forming strong adhesive bonds which will lead to producing high-strength adhesive joints [1,3,5]. Adhesive properties can be assessed by surface free energy which describes specific properties of surface layer of a material [7]; surface free energy is affected by surface treatment methods applied [7-13]. One example of adhesive joints is adhesive joints used in a variety of structures in the machine design, automotive, aircraft and building industries [13-17]. Composite materials are nowadays widely used constructional materials due to their properties, including high strength and rigidity as well as resistance to brittle cracking [1,3,15, 18-23]. Different
forms and types of composite reinforcements and matrixes with varying properties enable formation of composites with desired properties [15, 25-27]. One of the ways of forming polymer composites is adhesive bonding [1,2, 17, 28-30]. The popularity of this technique stems from numerous advantages of adhesive-bonded joints [17], including their high strength if specified conditions for producing such joints are observed. Among others, the adhesive bonding technique does not change the structure of a material in the place of a joint.

This paper investigates the strength of adhesive joints of graphite/epoxy composites with varying thicknesses produced at constant composite production and adhesive-bonding conditions. Experimental tests involved determining surface roughness parameters of the adherends and their mechanical properties, shear strength of graphite/epoxy composites, and surface free energy of the composite adhesive joints.

2. Experimental test

2.1. Characteristics of the tested materials

The tests were conducted on specimens made of two types of graphite/epoxy composite: GR-EP 199-45-005 with a thickness of 0.48 mm and GR-EP 199-45-003 with a thickness of 0.66 mm (figure 1 and figure 2). Each composite had two layers of fabric with 90° orientation subjected to curing (in compliance with a relevant technology).

![Figure 1. Thickness of fabrics and produced graphite/epoxy composites (0.48 mm).](image1)

![Figure 2. Thickness of fabrics and produced graphite/epoxy composites (0.66 mm).](image2)

In the first case, the fabric thickness was 0.24 mm, and in the other - it was 0.33 mm. The above composites are manufactured by an aircraft production plant and used to make different aircraft components.

2.2. Microscopic analysis of the investigated composites surfaces

The tests involved performing a microscopic analysis of the graphite/epoxy composites to determine the structure of the adherends and chemical composition of the tested composite materials. Surface morphology and chemical composition of the study was performed using scanning electron microscopy (SEM) - TESLA BS-340 analyzer [31] equipped with an element EDX (Energy Dispersive X-ray Spectroscopy) Thermo-NORAN. Scanning electron microscope with EDX detector can identify the elemental composition of the material for all elements with atomic number greater than boron.

2.3. Surface roughness

In order to determine parameters of geometrical structure of the adhesive-bonded composites, a selection of surface roughness parameters were measured. The measurements were performed on two batches of 5 specimens each. In each batch the specimens had their surface cleaned by degreasing.
Next, each specimen underwent three measurements, in total 15 measurements per each tested type of composite material. The measurements were made in compliance with the standard PN-EN ISO 4287 [32]. The measurements of the selected surface roughness parameters were made using a Perthometer 2 surface finish measurement instrument from Mahr.

2.4. Surface free energy
Surface free energy of the adhesive bonded materials was measured by the Owens-Wendt method described in numerous publications [6, 8, 11, 33, 34]. In the tests, two measurement liquids were used: distilled water and diiodomethane, the properties of which are listed in Table 1 [1].

| Measuring liquids | The surface free energy and its components |  |
|------------------|-----------------------------------------|---|
|                  | $\gamma_L$ (mJ/m$^2$) | $\gamma_L^d$ (mJ/m$^2$) | $\gamma_L^p$ (mJ/m$^2$) |
| Distilled water  | 72.8 | 21.8 | 51.0 |
| Diiodomethane    | 50.8 | 48.5 | 2.3 |

Table 1. The surface free energy $\gamma_L$ and its components of the measuring liquids [7].

The measurements of the contact angle were performed at a temperature of 20±1°C and air humidity of 30±2%. The volume of drops of the measuring liquids ranged from 1.6 to 2.0 μl. To every sample surface (there were 7 samples per each batch) 6 drops of the measuring liquids were applied. After that, 8-12 measurements were made and the mean per each sample batch was calculated. The contact angle was measured after a few seconds following the application of a drop of the measuring liquid. The measurements were made using a PGX goniometer manufactured by Fibro System (Sweden) and a PG programme for computer image analysis Surfaceware. The relations between SFE and its components as well as a detailed description of contact angle measurements are given in the literature [7,8,11].

2.5. Adhesive joints
The strength tests were performed on shear-loaded single-lap polymer composite adhesive joints. The shape and dimensions of the tested graphite/epoxy composite adhesive joints are illustrated in figure 3 and figure 4.

In the tests, the surface finish treatment of the composites involved degreasing with the Loctite 7063 degreasing agent. This degreasing method is described in [8]. The adhesive joints were made using Loctite 3430 epoxy adhesive which was subjected to single-stage curing for 48 hours in an ambient temperature of 20±2°C, under a load of 0.02 MPa and a humidity of 39±1%.
2.6. Adhesive joints
The strength tests were performed on:
- adherends, i.e. graphite/epoxy composite materials,
- single-lap adhesive joints of graphite/epoxy composites.

The tests were performed on 10-11 test pieces per each batch. The tests were performed using the Zwick/Roell testing machine in compliance with the standard DIN EN 10002-1. The tests were conducted at the following parameters: modulus of elasticity: 60 MPa/s, yield point: 60 MPa/s, flow rate: 0.00025 1/s, test speed: 0.008 1/s. The following strength test results of the graphite/epoxy composite specimens were examined: E – modulus of elasticity in MPa, \( R_{p0,2} \) – yield strength in MPa, \( R_m \) – tensile strength in MPa. The adhesive joints of graphite/epoxy composites were also subjected to strength testing using the Zwick/Roell 150 testing machine, in compliance with the standard DIN EN 1465. The test speed was set to 5 mm/min. Then, the fixed adhesive joints were subjected to strength testing until specimen failure. The tests helped determine the failure force for the examined adhesive joints and hence the shear strength of these joints. The strength tests were performed at an ambient temperature of 21±2°C and humidity ranging between 36% and 38%.

3. Experimental results

3.1. Description of the tested adherends
Representative images of surfaces of the tested composites obtained with the scanning electron microscope (SEM) and stereoscopic microscope are shown in figure 5. Surface morphology and chemical composition of the study was performed using scanning electron microscopy (SEM) with EDX detector (point 2.2) - figure 6 and figure 7.

![Figure 5](image1.png)
**Figure 5.** SEM images of the graphite/epoxy composite surface: a) 0.48 mm thickness, b) 0.66 mm thickness, magnified by 55 times.

![Figure 6](image2.png)
**Figure 6.** The chemical composition of graphite-epoxy composite of 0.48 mm thickness: a) SEM micrograph, b) chemical composition in area 1 from SEM micrograph.
The chemical composition of graphite-epoxy composite of 0.66 mm thickness: a) SEM micrograph, b) chemical composition in area 1 from SEM micrograph.

In figure 6a the Base [2] it means the second research samples among 10 tested samples and pt1 (figure 6 b) it means the first point during analysis. In figure 7a the Base [1] it means the first research samples among 10 tested samples and pt1 (figure 7 b) it means the first point during analysis. The tested composites contain the following elements:
- graphite/epoxy composite with g=0.48 mm: S (highest concentration), Na, Au, Cl,
- graphite/epoxy composite with g=0.66 mm: Si (highest concentration), Na, Nb, Au.

Some differences in their compositions probably result from a slightly different chemical concentration of the fabrics that the two composites are made of.

3.2. Surface roughness

The surfaces of the tested graphite/epoxy composites significantly differ with respect to their geometrical structure due to the properties and design of the composite materials (and the fabrics they are made of). Table 2 lists the mean values of selected amplitude parameters of the composites measured in three measuring points (10 measurements on one point). One can immediately notice a high scatter of the results.

| Graphite-epoxy composite, thickness, mm | Ra (µm)      | Rz (µm)     | Rk (µm)     | Rpk (µm)     | Rvk (µm)     |
|---------------------------------------|--------------|-------------|-------------|--------------|--------------|
| 0.48 mm                               | 1.30 (± 0.78)| 5.45 (± 2.58)| 2.83 (± 0.74)| 2.13 (± 1.78)| 7.68 (± 6.87)|
| 0.66 mm                               | 1.09 (± 0.20)| 5.88 (± 1.01)| 2.88 (± 0.55)| 1.13 (± 0.52)| 3.71 (± 1.03)|

Examining the surface roughness parameters and surface profilograms we can observe significant variations in the composites’ surface geometry. The numerous cavities and surface irregularities are predominantly caused by the type of the applied components (fabrics) for making the composites (figure 5). Probably this is the reason for high scatter in surface roughness. Such a structure is probably advantageous for the making of adhesive joints because the adhesive can penetrate deep into these irregularities and form mechanical fixings, which leads to higher adhesive strength of these joints. It is important that the adhesive has suitable viscosity to fill in all surface irregularities, so the real surface of adhesive joint will be higher than the theoretical one, which will also lead to higher strength.

3.3. Surface free energy

Table 3 lists the values of surface free energy \( \gamma_S \) and its components (\( \gamma_S^d \) and \( \gamma_S^p \)) determined based on the measurements of the angle of contact of surfaces of the tested polymer composites according to relevant dependencies. The contents of individual components of surface free energy are illustrated in a graphic form in figure 8.
**Table 3.** The surface free energy $\gamma_S$ and its components of the graphite-epoxy composites

| Measuring liquids | The surface free energy and its components |
|------------------|------------------------------------------|
|                   | $\gamma_S$ (mJ/m$^2$) | $\gamma^d$ (mJ/m$^2$) | $\gamma^p$ (mJ/m$^2$) |
| Graphite-epoxy composite, 0.48 mm | 45.4 | 39.7 | 5.7 |
| Graphite-epoxy composite, 0.66 mm | 45.0 | 41.4 | 3.6 |

The results of the statistical tests demonstrate that there are no significant differences in the mean SFE values (confidence level: 0.95). It can be observed that in each investigated case the dispersive component is much higher than the polar component.

### 3.4. Strength tests of the graphite/epoxy composites

The strength results of the tested polymeric graphite/epoxy composites are given in figures 9 and 10.

The results reveal that the tested graphite/epoxy composites have a similar modulus of elasticity $E$ (difference is 1%) and tensile strength $R_m$ (difference is about 3%). On the other hand, they differ significantly with respect to yield strength ($R_{p0.2}$). The specimens of the graphite/epoxy composite with a higher thickness exhibit a higher yield strength (137 MPa), while the yield strength $R_{p0.2}$ of the composite with a lower thickness (0.48 mm) is 65% of the value of $R_{p0.2}$ of the composite with a thickness of 0.66 mm.
3.5. **Strength tests of the graphite/epoxy composite adhesive joints**

The strength results of the examined polymer composite adhesive joints are given in figure 11. The results demonstrate that the graphite/epoxy composite with a smaller thickness of the joined materials has a higher strength of the shear-loaded adhesive joints amounting to 19.09 MPa. The shear strength of the adhesive joints of the graphite/epoxy composite with a higher thickness is 94% of the strength of the adhesive joints made of the 0.48 mm thick graphite/epoxy composite.

![Figure 11. Shear strength of adhesive joints of the tested polymer composites: 1) graphite/epoxy composite (0.48 mm), 2) graphite/epoxy composite (0.66 mm).](image)

The statistical analysis results reveal that there are significant differences regarding strength at a confidence level of 0.95. This can be attributed to the effect of the thickness of the joined materials on the strength of composite adhesive joints. This factor could lead to a higher bending moment resulting from a higher load eccentricity due to joining elements with higher thicknesses.

3.6. **Results and discussion**

Examining the geometrical structure (microscopic analysis results and surface roughness parameters) and mechanical properties (strength results) of the joined materials, the following was observed:

- graphite/epoxy composites have a similar geometrical structure, and the differences in their thickness do not lead to producing differences in the geometrical structure,
- surface roughness significantly differs over the entire area of the examined specimen in both composites, which is reflected in the microscopic images (figure 2 and figure 3) and surface roughness parameters of these composites,
- most mechanical properties of both composites are similar,
- thicker graphite/epoxy composite specimens have a higher yield strength.

The geometrical structure results suggest that such a structure is advantageous for making adhesive joints since combined with other technological factors, e.g. an adhesive with suitable properties, it can result in strong mechanical fixing of the adhesive, which will in turn lead to a higher adhesive strength of the adhesive joints due to mechanical adhesion.

Comparing the results of surface free energy (table 4) and shear strength of adhesive joints of the tested composites (figure 11), the following observations can be made:

- there is a relation between the surface free energy $\gamma_S$ of the joined composites and the shear strength of adhesive joints of the tested graphite/epoxy composites. The coefficient of correlation between these quantities equals 1. This means that higher adhesive properties (defined by surface free energy) of surface of the joined materials lead to a higher strength of the adhesive joints;
- a similar relation was observed for the polar component $\gamma_S^p$ of surface free energy;
- comparing the dispersive component $\gamma_S^d$ of surface free energy and the shear strength of adhesive joints of the tested composites, it was possible to determine the coefficient of correlation which is equal -1. This means that there is a correlation between the examined...
quantities yet the relation is inverse, i.e. with an increase in $\gamma_S$ the shear strength of the adhesive joints decreases. The differences in the values of surface free energy components of the tested composites can result from a slightly different chemical composition of the fabrics used for making these composites, as shown in figures 4 and 5. Although the statistical analysis results demonstrate that the mean values of $\gamma_S$ of surfaces of both composites are statistically equal, there are difference in the values of surface free energy components, and they can lead to obtaining a statistically significant difference in strength of adhesive joints of the tested composites. It must however be noted that the strength is also affected by the structural factors.

4. Summary
Comparing the strength test results of graphite/epoxy composite adhesive joints and the surface free energy results for these composites, it can be observed that the strength of the adhesive joints of these composites significantly differ in spite of lack of statistically significant differences in the obtained SFE results. Moreover, it was observed that the thickness of the joined elements has an effect on the strength of the adhesive joints, which also results from the occurrence of bending moment due to the fact that in the tested adhesive joints the tensile forces (in strength testing) are not located in one plane while, additionally, the adhesive layer is loaded by the bending moment. This moment increases with an increase in thickness of the adhesive-bonded elements. The adhesive joints strength is also affected by the geometrical structure of the joined materials; it was observed that the structure of the tested composites enables mechanical adhesion to a significant extent, thereby increasing the adhesive strength of the joints. The tests have therefore confirmed the synergic impact of material, technological as well as structural factors. Given the peculiar nature of the adhesive bonding technique, these problems require further research and examination.

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