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Investigation of selected properties of adhesive compositions based on epoxy resins

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This paper reports the results of research on selected properties of adhesive compositions containing two types of epoxy resin: Epidian 5 and Epidian 6, and two types of polyaminoamide curing agents. The resins and curing agents were mixed in different stoichiometric ratios. This led to the production of 20 adhesive compositions which were then subjected to single-stage cold curing. Specimens were made from the compositions to examine their structure as well as thermal and mechanical properties in the cured state. Changes in the structure of the specimens were examined by FTIR-ATR spectroscopy, their thermal properties were determined by thermogravimetric analysis, whereas strength was measured by static tensile tests. The results demonstrate that the properties of the adhesive compositions are affected by the type of both epoxy resin and curing agent, as well as by the ratio in which they are mixed. It has been found that the variation of curing agent contents (in terms of the stoichiometric ratio of resin to curing agent) influence both the strength and elasticity of the tested material.

1. Introduction

The use of adhesives offers a number of advantages, including the possibility of bonding different materials, e.g. polymers with metals or elements of varying thicknesses [1–4]. The use of this method enables producing structures that have a considerably lower weight than those produced by riveting. Due to their properties, epoxy adhesives (often two- and multi-component adhesives) are among the most widely used types of structural adhesives [5–8].

The main component of epoxy adhesives are epoxy resins [5,9–12]. Some of them can be cured at ambient temperature, while others are cured at an elevated temperature (up to 100 °C) [12]. The adhesive properties of a resin are shaped by mixing it with a suitable chemical compound to cause spatial cross-linking of the resin. Cross-linking is caused by a chemical reaction of functional groups, which are present in an epoxy containing a cross-linking agent (curing agent) [12–16]. Curing agents are chemical compounds which can react both with the epoxy group (e.g. first- and second-order diamines, polymercaptans, aromatic and aliphatic polyamines, organic acids) and with hydroxyl groups (acid anhydrides) [5,12,15]. This process can be described as a polyaddition reaction, leading to the production of hard and infusible resins; moreover, no side products are produced, which is typical of this kind of reaction [9]. The curing process of epoxy resins can also be performed by microwave radiation, electron beam, x-ray, γ and UV radiation [17–26].

The choice of a resin or curing agent depends on the required properties of an adhesive [12,27–30]. Aliphatic polyamines are used as curing agents at ambient temperature. Adhesive compositions produced with these compounds have low thermal strength. The hot curing process (below 80°C-100 °C) is performed using third-order amines and first-order aromatic amines. In the case of first-order aromatic amines, high thermal strength of an adhesive is ensured by the application of an additional curing operation at a higher temperature. The curing process

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at 120°C-180 °C is generally performed with the use of acid anhydrides. Thereby, the produced adhesive has very good dielectric properties and high thermal strength. When Lewis acids are used as a curing agent, the curing process – depending on the applied complex – is performed under different conditions than is the case with amino curing agents [9,15].

Physical properties of adhesive compositions change during the curing process, that is an exothermic process [10,25,31–33]. Because an increase in the temperature of the system accelerates the curing reaction, to prevent an undesired increase in temperature, a curing agent is added to the resin to absorb heat. On mixing the resin with the curing agent, small particles merge to form branched macro-particles which have not yet undergone cross-linking, which leads to increasing the system's viscosity. After a specified period of time, the viscosity rapidly increases until it reaches the gel point. When cross-linked spatial structures are formed, the system becomes infusible and partly insoluble in organic solvents. It is also worth mentioning that a volume of the reaction mixture decreases during the curing process. This phenomenon is generally described as chemical curing shrinkage [12].

During the curing process, after a longer period of time, one can observe that parameters such as glass transition temperature and strength reach their limit values. If the curing process is continued without increase in temperature the above properties do not increase. However, the use of an after-bake at a higher temperature can enhance performance including increased strength and higher glass transition. It should also be mentioned that the curing of epoxy resins can be performed faster at a lower temperature if suitable accelerating agents are used.

Curing agents (with the exception of ionic polymerization initiating curing agents) generally react with epoxy resins in stoichiometric ratios. For this reason, they are used in quantities which are similar to the contents of epoxy groups in the resin and of functional groups with active hydrogen atoms in the curing agent.

It is important to add a precise quantity of curing agent to the resin. A two-component (or multi-component) product must be specially selected to achieve the desired result when mixed in the correct proportion. It is recommended that the mixing of the two-component products takes place in the correct proportions, and that the finished product exhibits certain properties. If the curing agent is not properly added, the composition will not achieve its predicted properties.

The strength of cured resins is significantly affected by the chemical composition of a curing agent [5,13,16,31]. In order to obtain products with high strength properties, i.e., with a rigid structure and high cross-linking density, it is necessary to use curing agents which consist of many functional groups and contain aromatic rings. One example of such curing agents is m-phenylenediamine. If the functional groups in a curing agent are bonded by short hydrocarbon chains, products have low thermal strength and exhibit brittleness at ambient temperature. Such products include triethylenetetramine. Curing agents which show elastic properties contain a small number of functional groups separated from one another by long hydrocarbon chains. Examples of such compounds include polyaminoamides and polyanhydrides of aliphatic dicarboxylic acids.

Adhesive joint strength is also affected by the conditions under which the curing process is conducted, such as external curing pressure, load, temperature and duration of the process [31]. Load among other things is applied to prevent an adhesive from spreading over a low energy surface. Load depends on the type of both adhesive and materials being bonded. To prevent the adhesive compound from flowing out of the joint, the load should not be too high.

The curing time depends by the temperature of the curing process [17,30–33]. In cold curing, longer the curing time lead to an increase of the joint strength up to an upper asymptotic value; in hot curing, on the other hand, joints have the highest strength after the optimum curing time.

The objective of this paper is to investigate the properties of epoxy adhesive compositions obtained using varying contents of curing agents and a constant content of epoxy resins. These tests are based on information on the applicability of the specific curing agents for curing resin data. The bibliographic data (and technical data of the adhesive manufacturers) [15,16,29,31,34] provide for some curing agents, the compositions range that can be used. They result by the stoichiometric ratio of the specified combination of resin and curing agents. This also applies to the properties, but also to the cost of the obtained epoxy compositions and the cost of making adhesive joints or epoxy resin components and epoxy elements. Therefore, the purpose of the research was to: (1) determine the properties of the adhesive compositions (in cured state) containing different resin and curing agent ratios (within the range recommended by the manufacturers), (2) assess whether use of the smallest and the largest amounts contribute to significant differences in properties, which may be important in the design of both adhesive bonding and epoxy forming technologies, (3) pay attention to the cost of the adhesive compositions prepared, which is related to the amount of added curing agents. Increasing the amount of curing agents contributes to the greater cost of the adhesive composition itself, which may affect the final costs of the production process.

The compositions were prepared using two types of epoxy resin, i.e. Epidian 5 and Epidian 6, as well as two types of polyaminoamide curing agents, i.e. PAC and PF. The thermal stability of individual adhesive compositions was measured by thermogravimetric analysis (TGA). FTIR-ATR spectroscopy was used to identify chemical groups produced in the adhesives. In addition, the adhesive compositions in the cured state were subjected to tensile testing.

2. Methods

2.1. Description of the materials

The epoxy resins used in the experiments were manufactured by Organika-Sarzyna-Ciech (Nowa Sarzyna, Poland) [35]. Adhesive compositions were made using two types of non-modified epoxy resin: Epidian 5 and Epidian 6 (their properties are given in Table 1), and two types of curing agent: PAC and PF (Table 2).

The structure of Epidian 5 epoxy resin is presented in Fig. 1 and the structure of Epidian 6 epoxy resin is presented in Fig. 2.

The curing agents are used in amounts resulting from stoichiometric ratios, i.e., based on the number of resin epoxide groups, there are corresponding amounts of active crosslinking groups. Reducing or

Table 1
Properties of non-modified epoxy resins produced in Poland [35–37].

Type of epoxy resin	Characteristic	Properties		
		Viscosity (mPas) 25 °C	Density (g/cm^3) 20 °C	Number of epoxy
Epidian 5	Unmodified epoxy resin based on bisphenol A, which is the starting point for a series of compositions used as screeds, adhesives.	Max. 30000	1.17	0.49–0.52
Epidian 6	Unmodified epoxy resin based on bisphenol A, a lower viscosity than Epidian 5, which is the starting point for a series of compositions used as screeds.	10000–15000	1.17	0.51–0.54

Table 2
Properties of PAC and PF curing agents [38].

Type of curing agent		Properties			
Designation	Chemical base	Gelation time with Epidian 5 epoxy resin (100 g sample) in 20 °C (min)	Viscosity (mPas) 25 °C	Density (g/cm³) 20 °C	Amine number (mg KOH/g)
PAC	Polyaminoamide -fatty acid adduct of triethylenetetramine	180	10000–25000	1.10–1.20	290–360
PF	Polyaminoamide-dimer fatty acid adduct of triethylenetetramine	70	10000–20000	1.15–1.20	350–400

increasing the proportion of curing agent relative to the amount resulting from the stoichiometric calculations reduces the crosslinking density, leading to softening, tackiness or swelling of the entire adhesive [39].

Typical amounts of curing agent per 100 g of epoxy resin are presented in Table 3.

PAC is a modified polyamide curing agent produced by the polycondensation of polyamine with dimers of unsaturated fatty acid methyl esters [24,35]. It is predominantly used for modifying and curing small-particle epoxy resins and adhesive compositions based on these resins. This curing agent ensures elasticity and impact strength of cured structures. PAC is a high viscosity and brown fluid. At ambient temperature the pot life (i.e. time available to use the adhesive before it starts to gel) of PAC-based adhesive compositions is several hours long and total curing takes place within 4–7 days. The curing process can be accelerated by running the curing process for 6–8 h at a temperature of approx. 60 °C. Adhesive compositions with higher PAC contents have a quite high elasticity and impact strength. These compositions are used for the adhesive bonding of tenuous structures which are exposed to considerable strains. Such adhesive joints are characterized by high strength properties at temperatures below 0 °C [38]. Nonetheless, adhesive compositions containing PAC have a lower hardness and chemoresistance and are less resistant to elevated temperatures than the compositions containing other curing agents.

PF is a curing agent used for curing liquid resins and epoxy compositions at ambient temperature. This curing agent is used whenever lower viscosity and shorter gelation time are required. Although epoxy products containing PF are less elastic than those based on PAC, they have a higher thermal strength and compression strength (by approx. 25%), as well as higher chemoresistance [38].

2.2. Specimen preparation

Each resin was subjected to curing using both curing agents in ratios specified in Table 4.

The specimens of adhesive compositions in the cured state were prepared in elastic silicone moulds. Their preparation also involved the use of POLSILFORM (Chemical Plant ”Polish Silicones” producer, Nowa Sarzyna, Poland) [35] a colourless, odourless and solvent-free silicone agent which ensures that adhesive compositions are separated from the mould. When sprayed on the mould, the agent produces a thin layer of silicone oil with anti-adhesive properties. The agent was sprayed onto the surface of the mould from the distance of about 30 cm. Adhesives with the addition of the curing agent were weighed using an electronic scales (with accuracy of ± 0.001 g). Each composition was mechanically mixed in a polymer container for 90 s with the shear rate of 128 m/min until a uniform mass was obtained. Gas cavities produced during the mixing were removed from the compositions using degassing pump. Each fluid composition was then distributed over the mould surface. The specimens of the adhesives in the cured state were prepared under the following conditions:

- temperature: 21 °C ± 2 °C;
- humidity: 33% ± 2%;
- curing time: 7 days.

The conditioning of the specimens prepared under the above conditions was set to 14 days. Fig. 3 shows the shape and dimensions of the specimens. 10 specimens were made per each of 20 obtained adhesive compositions, producing in total 200 specimens of adhesive compositions in the cured state.

After conditioning (14 days), the specimens of the adhesive compositions were subjected to TGA, FTIR-ATR analyses and strength testing.

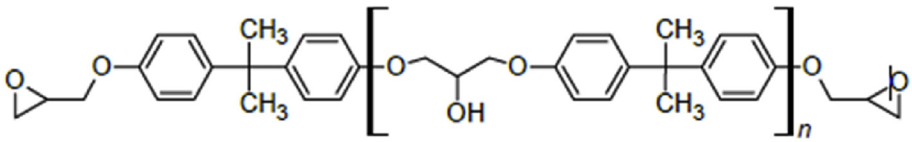

Fig. 1. Structure of Epidian 5 epoxy resin [36].

2.3. Thermogravimetric analysis (TGA)

Thermal stability of the adhesive compositions was measured by thermogravimetric analysis (TGA) using the STA 449 Jupiter F1 thermobalance with an S TG – DSC thermocouple, manufactured by Netzsch, Germany. A linear temperature increase of 10 °C/min was applied. The measurements were conducted in a temperature range from 35 °C to 1000 °C. The protective temperature was set to 1010 °C. The measurements were made in an 'air' atmosphere (8 ml O_2 and 32 ml N_2). The total gas flow was 40 ml/min. The analysis was performed with a reference line (two empty crucibles were measured). Next, the weighed amounts (approx. 10 mg) of the adhesive compositions were put in a crucible made of aluminium oxide (Al_2O_3). Two crucibles: one with a specimen and the other without a specimen (reference), were put in a furnace and heated. The decrease in mass of the specimens after their degradation was measured using the thermobalance. Variations in heat capacity were measured, too.

2.4. FTIR-ATR spectroscopy

The formation of a high molecular weight polymer structure during curing resin consists of two processes - linear chain growth and the joining of linear elements (with branches) into a three-dimensional network structure. The proportion of both reactions can be estimated from the degree of conversion (cure) and degree of crosslinking.

The degree of conversion determines the percentage conversion of reactive resin (or curing agent) groups. It is a total measure of the progress of both reactions - linear growth and crosslinking. One of the methods of physical quantification of the degree of conversion during curing of epoxy resins is Fourier-transform infrared spectroscopy (FTIR spectrometry). The advantage of this method is the ability to investigate the entire curing process and the ability to simultaneously observe changes for several characteristic groups or bonds that disappear or form during curing, allowing for a better understanding of the mechanism of reaction.

ATR is one accessory of FTIR spectrophotometer to measure surface properties of solid or thin film samples rather than their bulk properties. FTIR-ATR spectroscopy was employed to identify functional groups in the tested adhesive compositions. The specimens were placed on a diamond crystal with a source of infrared radiation underneath, its wave number ranging from 600 cm^{-1} to 4000 cm^{-1}. The wavenumber resolution was 4 cm^{-1}, and the number of scans was set to 16. The measurements were made using a FTIR Tensor 27 spectrometer provided with a diamond ATR crystal plate manufactured by Bruker, Germany.

Table 3
Typical amounts of curing agent per 100 g of epoxy resin [38].

Type of curing agent	Typical amounts of curing agent per **100 g** of epoxy resin (g)	
	Epidian 5	Epidian 6
PAC	60–100	
PF	50–60	

Table 4
Tested ratios of resin to curing agent.

Curing agent	Epoxy resin	
	Epidian 5	Epidian 6
PAC	100:60 (6)	100:60 (11)
	100:70 (7)	100:70 (12)
	100:80 (8)	100:80 (13)
	100:90 (9)	100:90 (14)
	100:100 (10)	100:100 (15)
PF	100:50 (16)	100:50 (1)
	100:52 (17)	100:52 (2)
	100:54 (18)	100:54 (3)
	100:56 (19)	100:56 (4)
	100:60 (20)	100:60 (5)

Note: numbers in brackets denote specimens of the tested adhesive compositions.

2.5. Strength testing

After the specified curing time and conditioning, the produced adhesive compounds in the cured state were subjected to strength testing. The tests were performed in compliance with the PN EN ISO 527-1 standard [40], using the Zwick/Roell Z150 testing machine (manufactured by Zwick, Germany) with the traverse movement of strength machine set to 2 mm/min. The tests were conducted at the temperature of 22 °C ± 1 °C and the relative air humidity of 30 ± 2%.

3. Results and discussion

3.1. TG results

Figs. 4–7 show a selection of TGA/DTG/DSC curves obtained for the following adhesive compositions: Epidian 5/PAC/100:60 (6), Epidian 5/PF/100:50 (16), Epidian 6/PAC/100:60 (11) and Epidian 6/PF/100:50 (1).

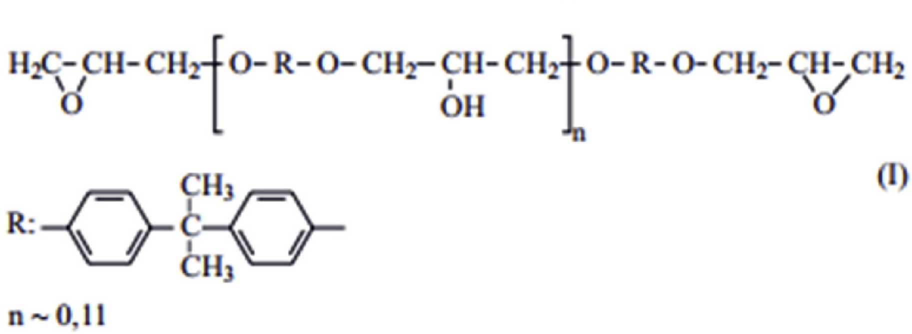

Fig. 2. Structure of Epidian 6 epoxy resin [37].

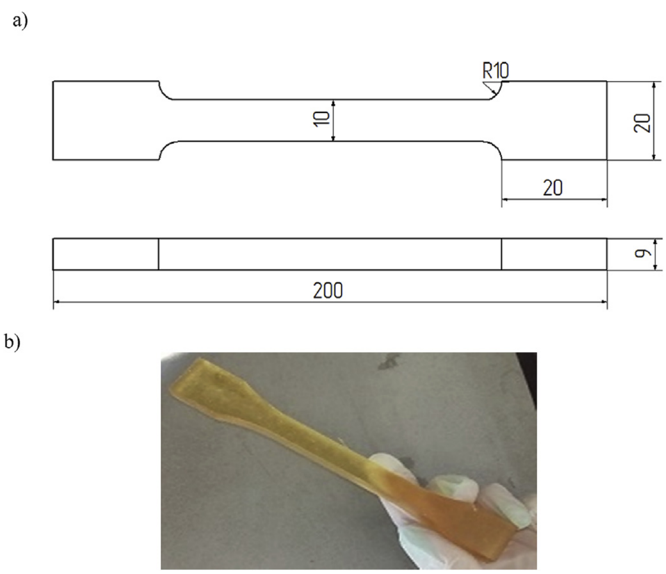

Fig. 3. Specimens of adhesive compositions used in the strength tests: (a) schematization in mm, (b) view of produced specimens.

A detailed TGA analysis was performed on the specimens with the lowest, medium and highest contents of a given curing agent in a given resin. The results of individual specimens were produced in the form of thermograms. Table 5 lists the temperature at the initial mass decrement caused by heating (5% mass decrement, IDT; this parameter describes thermal stability of the tested materials) and the maximum temperature when the degradation rate (T_{max}) is the highest.

When the temperature drops below 150 °C, a small exothermic peak can be observed in the DSC curves of all tested specimens with the exception of Specimens 10 and 15. This may result from inadequate cross-linking. Specimens 10 (Epidian 5/PAC/100:100) and 15 (Epidian 6/PAC/100:100) contain the highest curing agent content recommended for the investigated resins and curing agents based on the stoichiometric ratio of curing agent to resin. This may prove that the use of smaller curing agent contents does not lead to decreasing the thermal and mechanical properties of a given adhesive composition.

With an increase in the temperature, the DSC curves reveal both exothermic and endothermic signals due to the oxidizing degradation of the specimens, which is confirmed by the mass decrement visible in the TGA/DTG curves. In addition, the results demonstrate that the thermal degradation of all tested adhesive compositions occurs in at least three stages, which is proved by the presence of three peaks in the DTG curves. The first stage of degradation can be observed up to the temperature of approx. 380 °C, with T_{max1} ranging 354°C-360 °C and mass decrement range of 35%–44%. The second stage of degradation occurs in the temperature range 380°C-490 °C with T_{max2} between 394 °C and 442 °C and a mass decrement of approx. 33%–47%. The third stage of degradation takes place when the temperature is above 490 °C with T_{max3} ranging approx. 545°C-564 °C and mass decrement below 26%. Moreover, it can be noted that all tested specimens undergo total degradation in oxidizing atmosphere when heated to the temperature exceeding 750 °C (gas decomposition products occur).

Thermal stability is described by initial decrement temperature (IDT). As mentioned earlier, the higher this temperature is, the higher the thermal stability of the specimen can be observed. Based on the results listed in Table 5, among the four tested groups of adhesive compositions (Table 4) it was possible to determine the compositions with the highest thermal stability (5% mass decrement). These compositions are given in Table 6.

Two adhesive compositions: Epidian 6 with PAC curing agent and Epidian 5 with PF curing agent, show a decrease in their thermal stability with increasing the curing agent contents. The composition of Epidian 6 and PF curing agent in 100:54 ratio (3) has the highest thermal stability, whereas the lowest thermal stability is exhibited by Epidian 6 and PAC curing agent in 100:100 ratio (15).

3.2. FTIR-ATR spectrum

Based on the FTIR-ATR spectrum, functional groups occurring in the tested adhesive compositions were determined. Fig. 8 shows a FTIR spectrum obtained for Specimen 1.

The band with low absorbance visible in a range of

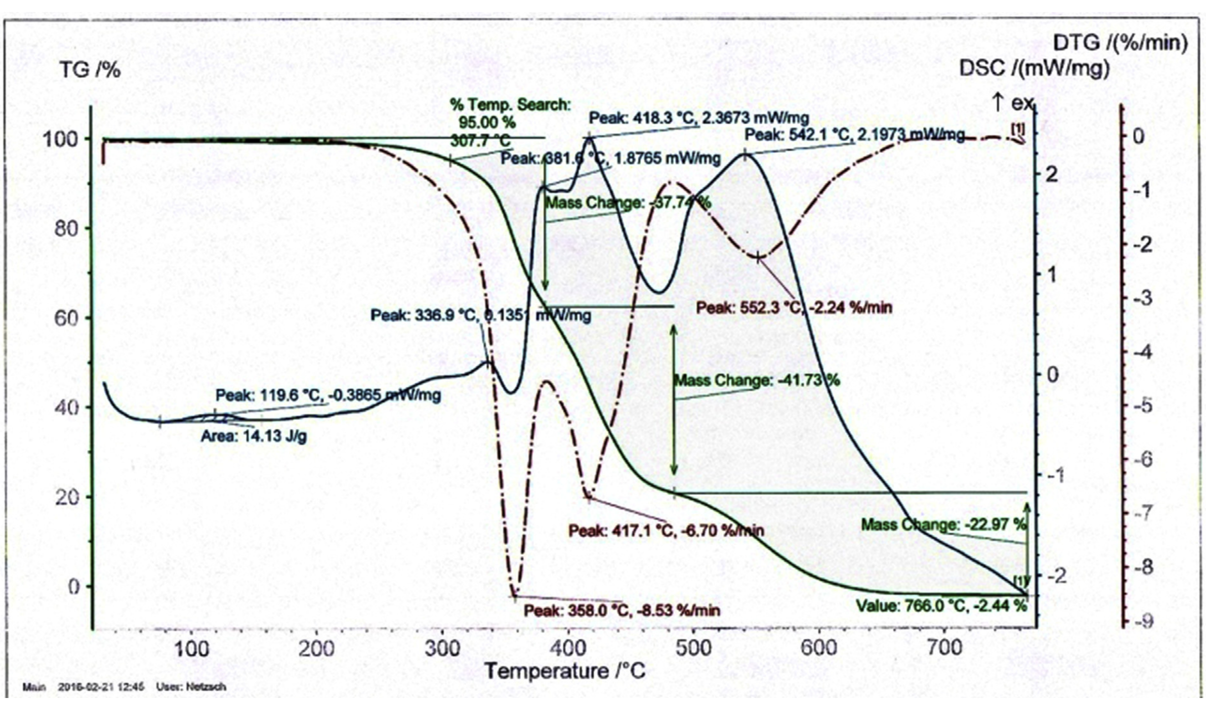

Fig. 4. TGA/DTG/DSC curve of Epidian 5/PAC/100:60 (6).

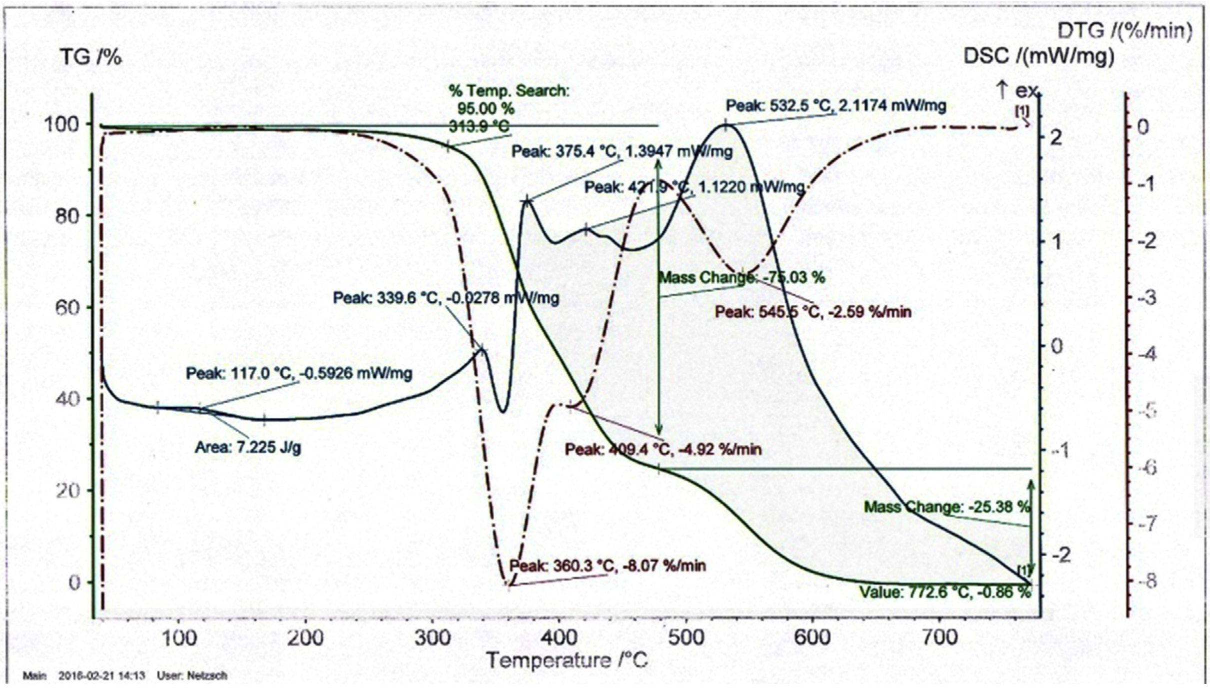

Fig. 5. TGA/DTG/DSC curve of Epidian 5/PF/100:50 (16).

3600–3200 cm^{-1} corresponds to tensile vibration in the −OH group. Two bands: 2960-2850 cm^{-1} (high intensity) and 2885-2860 cm^{-1} (medium intensity), as well as the medium intensity bands in the ranges 1390-1370 cm^{-1} and 1470-1430 cm^{-1} correspond to tensile and deformation vibrations C−H in the $-CH_3$ and $-CH_2$ groups. The medium intensity band (1650-1560 cm^{-1}) points to the presence of deformation vibration N−H in the $-NH_2$ group. The 900-800 cm^{-1} bands indicate the presence of deformation vibration in the aromatic group (CAr–H). Figs. 9–12 present a FTIR spectrum obtained for specimens of the highest contents of curing agent, i.e. for 5, 10, 15 and 20 adhesive compositions speciemens.

The absorption signal visible in the range of 3120–3560 cm^{-1} with a maximum of approx. 3300 cm^{-1} corresponds to the tensile vibrations of the groups −OH and the tensile vibrations of N−H. In the range of 1606–1645 cm^{-1}, signals from N−H deformation are observed, the peak intensity of about 1295 cm^{-1} peak is the result of C−N stretching, while the absorption signals of low intensity below 800 cm^{-1} are related with deformation vibrations not in the N−H plane. The signal at 3060 cm^{-1} corresponds to the CAr−H stretching vibrations, the two bands at maximum 1509 cm^{-1} and 1582 cm^{-1} indicate the presence of C = C vibration on the aromatic ring, while the absorption signals at maxima 806, 827 and 874 cm^{-1} are the result of deformation

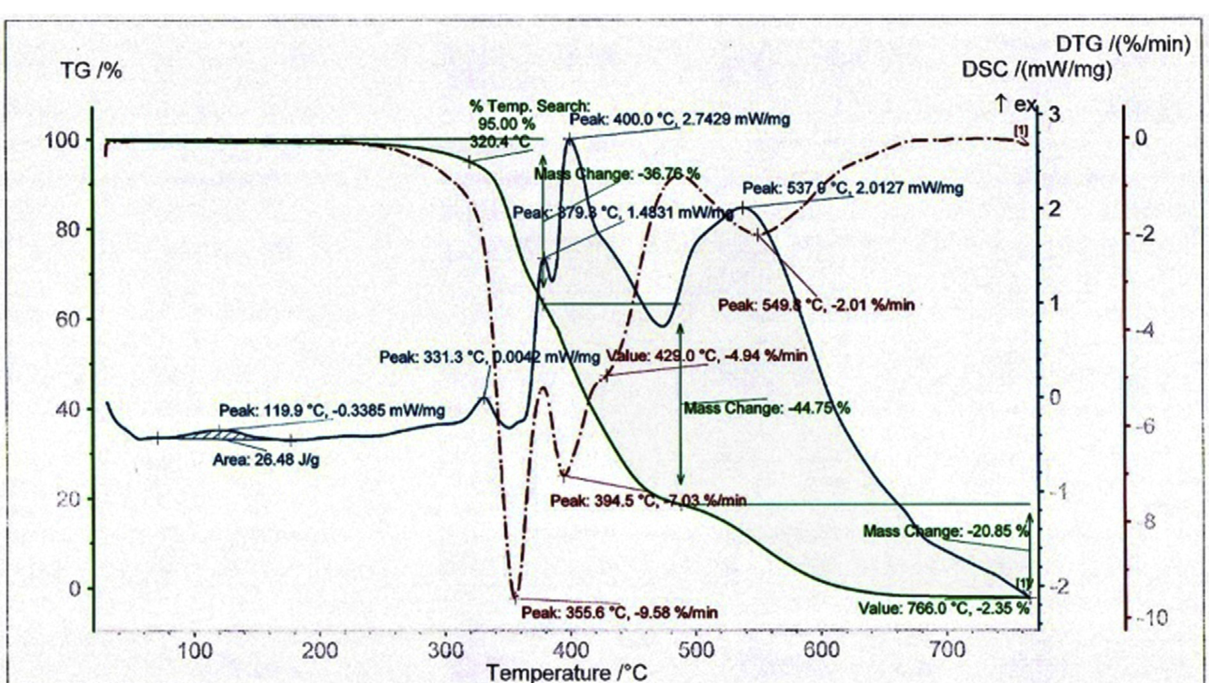

Fig. 6. TGA/DTG/DSC curve of Epidian 6/PAC/100:60 (11).

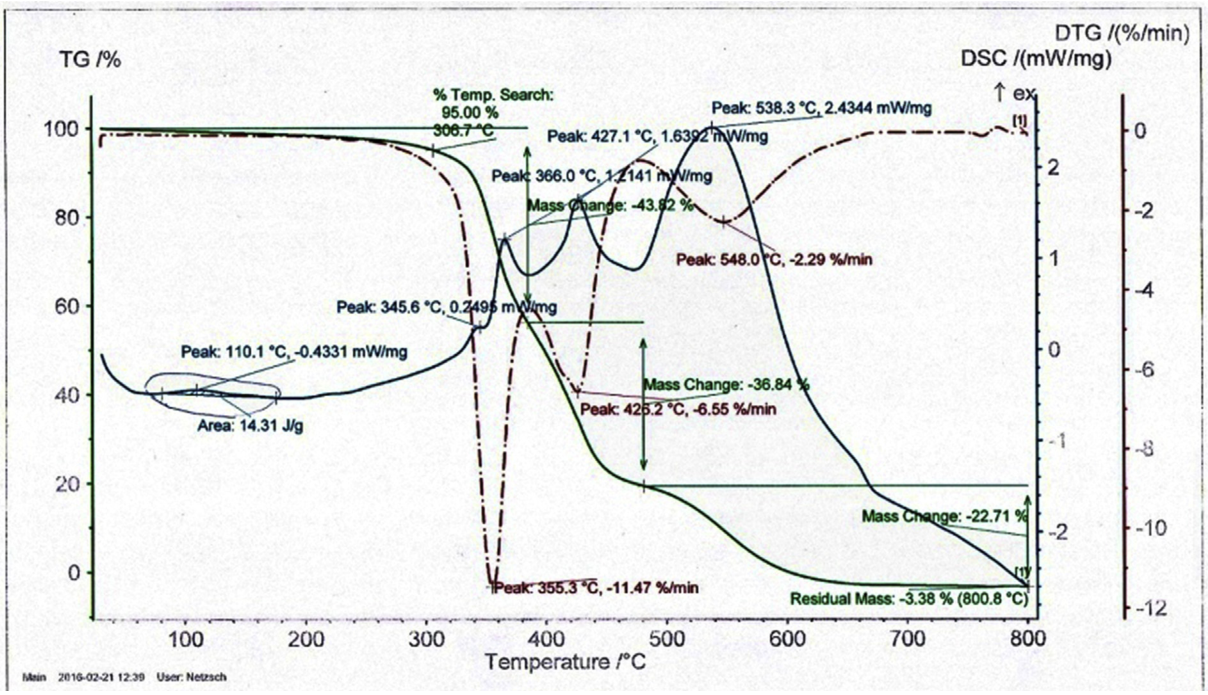

Fig. 7. TGA/DTG/DSC curve of Epidian 6/PF/100:50 (1).

Table 5
Selection of thermogravimetric analysis results.

Adhesive composition	IDT [˚C]	Tmax1 [˚C]	Tmax2 [˚C]	Tmax3 [˚C]
1	306.7	355.3	426.2	548.0
3	329.1	355.5	420.7	553.0
5	314.7	354.2	428.8	547.4
6	307.7	358.0	417.1	552.3
8	306.6	358.4	423.3	547.9
10	309.0	355.6	442.0	564.2
11	320.4	355.6	394.5	549.8
13	308.3	356.3	421.7	557.7
15	294.9	356.0	434.9	551.5
16	313.9	360.3	409.4	545.5
18	303.4	355.2	417.0	550.6
20	298.4	356.2	417.9	551.7

Table 6
Adhesive compositions with the highest thermal stability.

Adhesive composition	Epoxy resin	Curing agent	Ratios of resin to curing agent
3	Epidian 6	PF	100 : 54
10	Epidian 5	PAC	100: 100
11	Epidian 6	PAC	100 : 60
16	Epidian 5	PF	100 : 50

vibrations not in the CAr–H plane. In the range of 2853–2955 cm^{-1}, the presence of C—H stretching in the groups —CH3 and —CH2 is observed, whereas in the range of 1362–1378 cm^{-1} and in the 1457 cm^{-1} there are visible C—H deformation vibrations. The absorption signal at a maximum of approximately 1740 cm-1 corresponds to the vibration of the carbonyl groups (C = O) embedded in the curing agent structure. The range of 918–1247 cm^{-1} is characteristic for the vibrations of stretching ether groups (C—O—C). A very low intensity band at 918 cm^{-1} is responsible for the presence of C—O—C stretching vibrations in the epoxy ring, which may indicate incomplete reactivity epoxy resin with the polyamine amine curing agent. Absorption bands with a maximum of 1182 cm^{-1} and 1247 cm^{-1} indicate the presence of C—O—C stretching characteristics of aromatic ethers (epoxy resin). In turn, the bands with a maximum of 1034, 1086 and 1120 cm^{-1} are the result of the vibrations of the newly formed etheric bonds (C—O—C) in the epoxy resin and curing agent reaction.

The examination of the infrared spectrum led to the determination of the following functional groups: hydroxyl (—OH), methyl (—CH_3), methylene (—CH_2), amine (—NH_2 or —NHR) and aromatic. For adhesive compositions of the highest contents of curing agent it can be observed a small signal from the epoxy resin groups which indicating that these groups were not fully reacted in the curing reaction with the polyaminoamide curing agent.

3.3. Strength test results

The following were measured in uniaxial tensile tests of the investigated adhesive compositions in the cured state:

- F_{max} – maximum load,
- E_t – tensile elastic modulus,
- σ_M – tensile strength,
- ε_M – elongation at maximum load.

Tables 7–10 list the average tensile strength of the tested adhesive compositions obtained from 10 measurements per each batch (20 batches in total).

The highest values of maximum load and tensile strength are observed for the Specimen 3 (resin to curing agent ratio: 100:54), these values being 2758.98 N and 23.43 MPa, respectively. In contrast, Specimen 1, with the lowest content of the curing agent, exhibits the lowest strength properties. The elongation at maximum load is 1.88% for the specimen with the highest curing agent content and 5.36% for Specimen 4 (resin to curing agent ratio: 100:56).

Epidian 5 and PAC (6–10) (Table 8)

Specimens 6, 7 and 8 with lower curing agent contents have higher strength and strain at maximum load than the adhesive compositions with the resin to curing agent ratios of 100:90 (9) and 100:100 (10). For

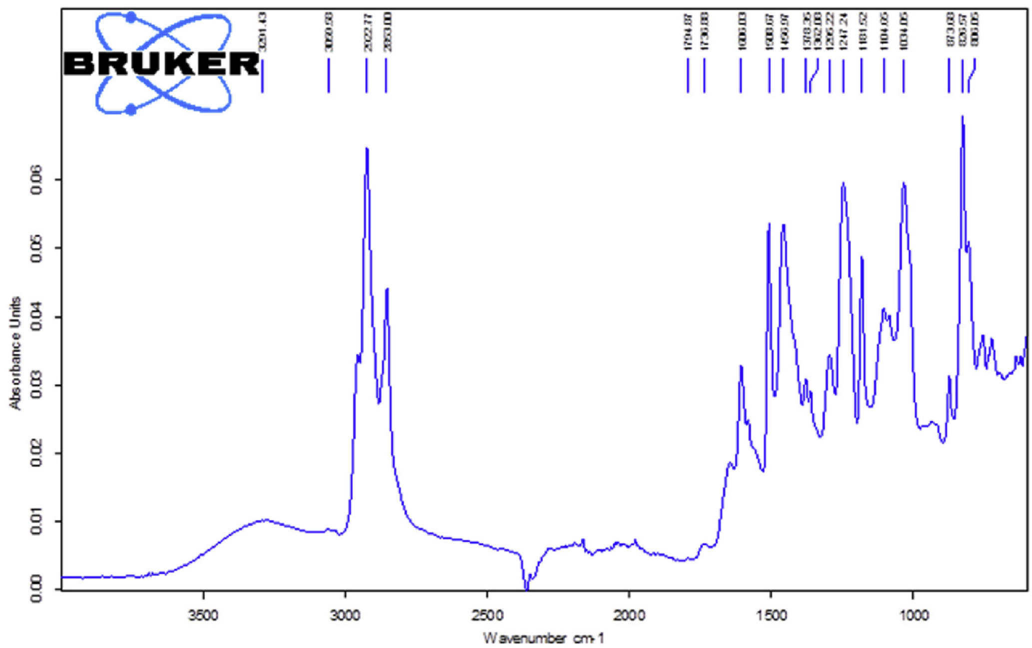

Fig. 8. FTIR spectrum of Specimen 1 (Epidian 6/PF/100:50).

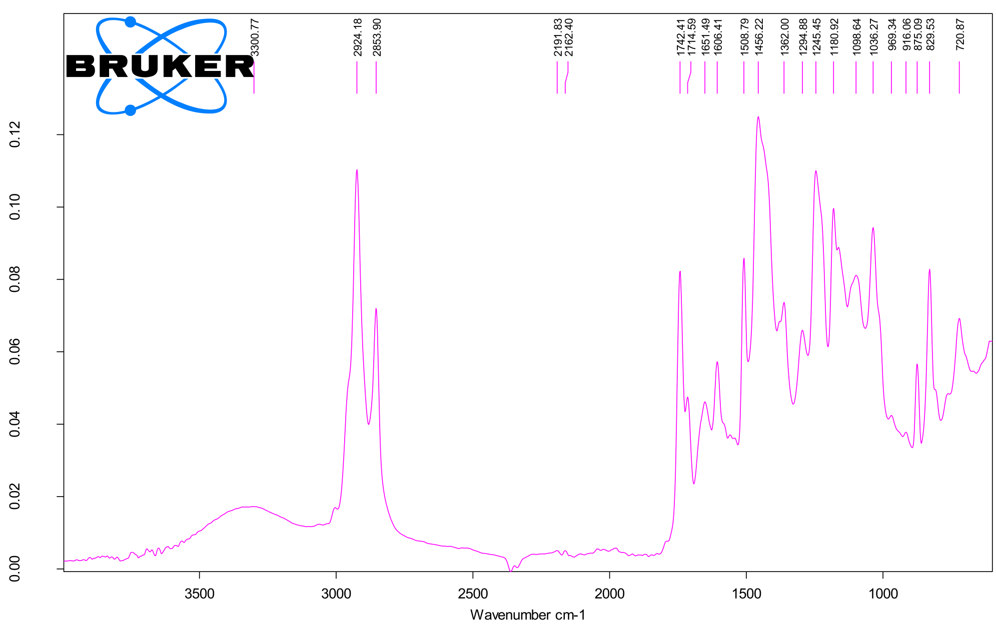

Fig. 9. FTIR spectrum of Specimen 10 (Epidian 5/PAC/100:100).

example, when compared to Specimen 9, the tensile strength of Specimen 7 is higher by approx. 60%, its elastic tensile modulus is two times higher, and the strain at maximum load is higher by over 20%.

Epidian 6 and PAC (11–15) (Table 9)

Similarly to the adhesive composition made of Epidian 5 and PAC, higher values of maximum load and tensile strength (even by 40%) and elastic tensile modulus were obtained for the adhesive compositions with low and medium curing agent contents (Specimens 11, 12 and 13). Here, the elongation at maximum load ranges from 2.60% to 6.10%, and is higher than that of Specimens 14 and 15 with high PAC contents. Therefore, it can be claimed that the content of the curing agent has impact on both the strength and elasticity of an adhesive composition.

Epidian 5 and PF (16–20) (Table 10)

As for the adhesive composition made of Epidian 5 and PF, the highest values of maximum load (2368.11 N), tensile strength (16.30 MPa) and elastic tensile modulus (1059.60 MPa) were obtained for Specimen 18 with a mean curing agent content (100:54). The elongation at maximum load varies to a small degree: it is 1.86% for Specimen 17 and 2.68% for Specimen 16.

Examining the results, it can be observed that elongation is smaller in the adhesive compositions made of Epidian 5 and PF (Specimens 6–10).

3.3.1. Effect of resin type on the adhesive joints strength

The results of tensile strength of the tested adhesive compositions versus resin type are given in Figs. 13 and 14.

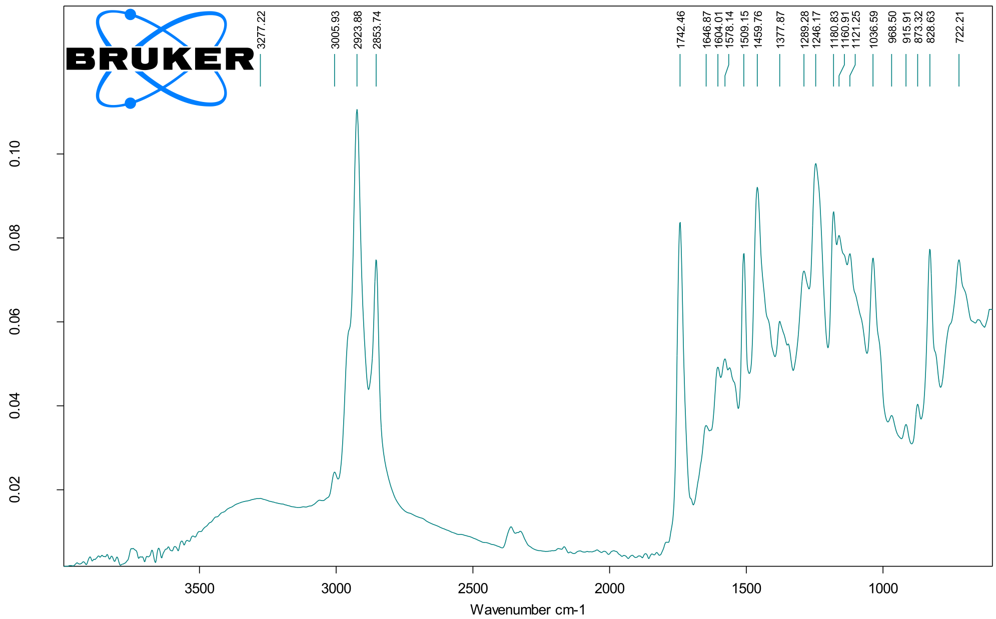

Fig. 10. FTIR spectrum of Specimen 20 (Epidian 5/PF/100:60).

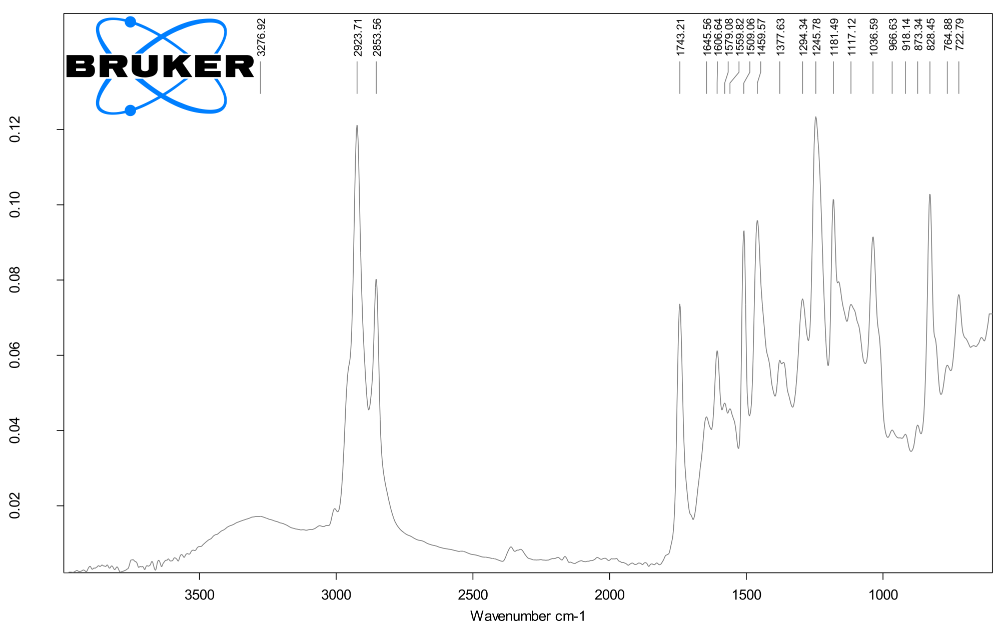

Fig. 11. FTIR spectrum of Specimen 15 (Epidian 6/PAC/100:100).

The results (Fig. 13) demonstrate that adhesive compositions containing Epidian 6 and PF have a higher tensile strength than those made of Epidian 5/PF. In the case of Epidian 6/PF compositions:

- the highest tensile strength (23.43 MPa) is obtained for Specimen 3, i.e., Epidian 6/PF/100:54;
- the lowest tensile strength (15.85 MPa) is obtained for Specimen 1, i.e., Epidian 6/PF/100:50.

In the case of Epidian 5/PF compositions:

- the highest tensile strength (16.30 MPa) is obtained for Specimen 18, i.e., Epidian 5/PAC/100:54;
- the lowest tensile strength (12.47 MPa) is obtained for Specimen 19, i.e., Epidian 5/PAC/100:56.

The results (Fig. 14) demonstrate that the adhesive compositions made of Epidian 5 and PAC have a higher strength than those made of Epidian 6/PAC. In the variants of Epidian 5/PAC compositions:

- the highest strength (32.46 MPa) is obtained by Specimen 7, i.e., Epidian 5/PAC/100:70,
- the lowest strength (13.93 MPa) is obtained by Specimen 9, i.e., Epidian 5/PAC/100:90.

In the case of Epidian 6/PAC compositions:

- the highest strengths (19.64 MPa and 19.36 MPa) are obtained by Specimen 11, i.e., Epidian 6/PAC/100:60, and Specimen 12, i.e., Epidian 6/PAC/100:70, respectively. As regards the strength of Specimen 13, i.e., Epidian 6/PAC/100:80, it is slightly smaller than that of the above compositions and amounts to 18.88 MPa,

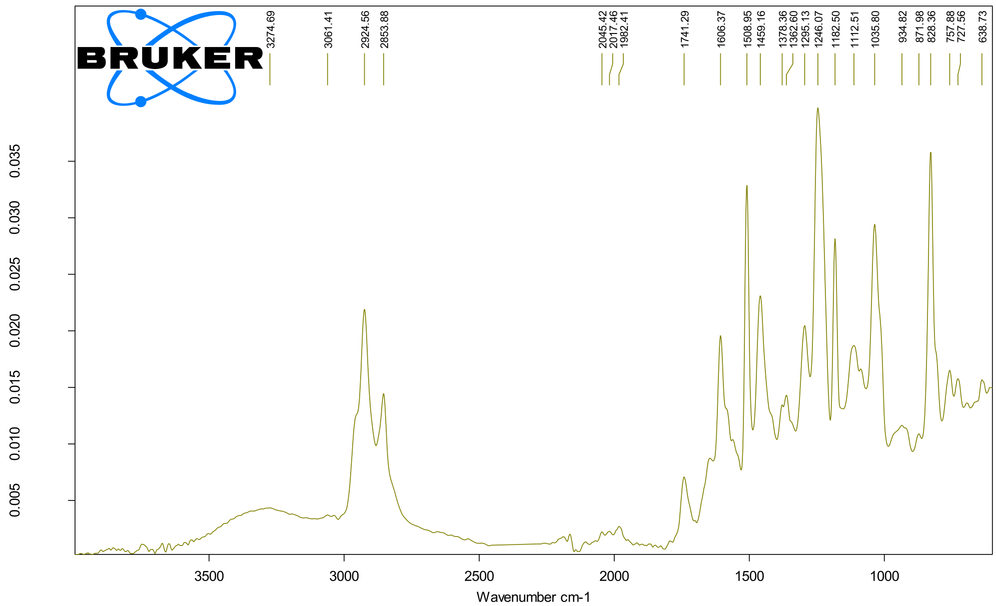

Fig. 12. FTIR spectrum of Specimen 5 (Epidian 6/PF/100:60).

Table 7
Strength results: Epidian 6 with PF.

Adhesive composition	F_{max} [N]	E_t [MPa]	σ_M [MPa]	ε_M [%]
1	1806.55	966.60	15.85	3.38
2	2521.31	1392.00	22.06	3.32
3	2758.98	1105.00	23.43	3.22
4	2121.01	1244.00	17.90	5.36
5	2203.54	1022.80	16.80	1.88

Table 8
Strength results: Epidian 5 with PAC.

Adhesive composition	F_{max} [N]	E_t [MPa]	σ_M [MPa]	ε_M [%]
6	2883.42	947.40	25.14	5.16
7	3657.79	900.00	32.46	4.54
8	3215.09	764.60	26.26	6.88
9	1742.55	451.80	13.93	3.56
10	1969.94	917.75	16.13	2.80

Table 9
Strength results: Epidian 6 with PAC.

Adhesive composition	F_{max} [N]	E_t [MPa]	σ_M [MPa]	ε_M [%]
11	2386.04	1098.20	19.64	2.60
12	242371	906.80	19.36	3.06
13	2407.62	660.00	18.88	6.10
14	1635.76	527.25	11.44	2.38
15	1464.88	742.00	11.75	2.46

Table 10
Strength results: Epidian 5 with PF.
Epidian 6 and PF (1–5) (Table 7)

Adhesive composition	F_{max} [N]	E_t [MPa]	σ_M [MPa]	ε_M [%]
16	1588.99	1064.25	13.95	2.68
17	1462.69	1029.00	13.60	1.86
18	2368.11	1059.60	16.30	2.28
19	1452.09	953.50	12.47	2.13
20	1601.82	912.20	14.78	2.60

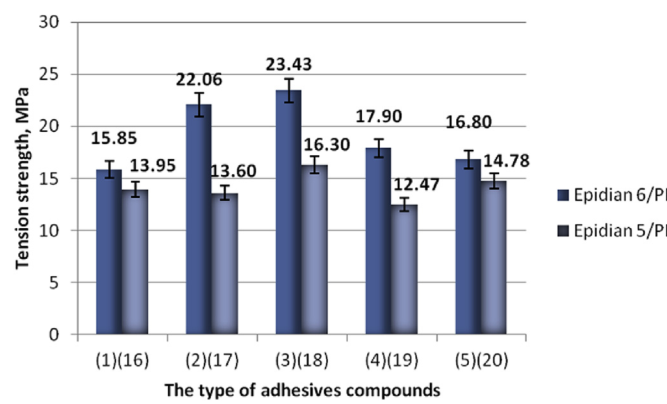

Fig. 13. Epoxy resin type versus tensile strength of adhesive compositions with PF.

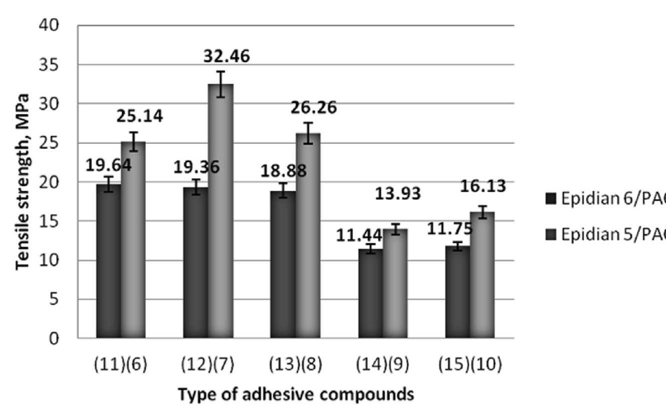

Fig. 14. Epoxy resin type versus tensile strength in adhesive compositions with PAC.

- the lowest strength is exhibited by the compositions with the highest curing agent contents, i.e., Specimen 14 (Epidian 6/PAC/100:90) – 11.44 MPa and Specimen 15 (Epidian 6/PAC/100:100) – 11.75 MPa.

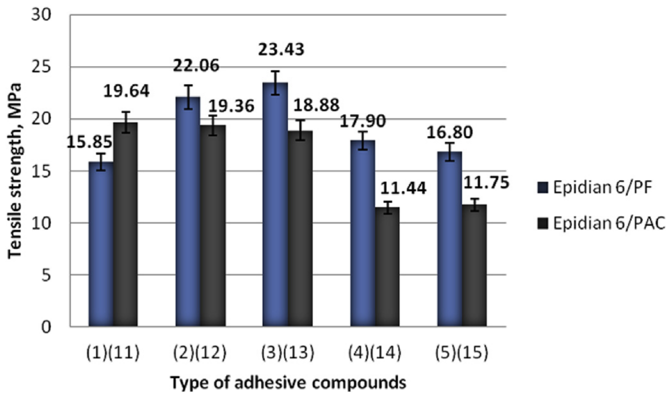

Fig. 15. Curing agent type versus tensile strength of adhesive compositions with Epidian 6.

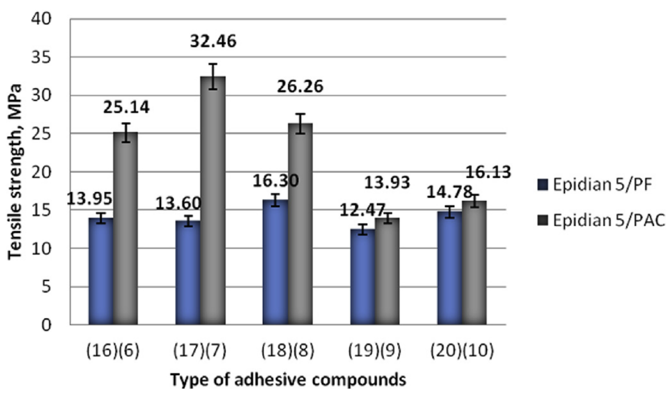

Fig. 16. Curing agent type versus tensile strength of adhesive compositions based on Epidian 5.

3.3.2. Effect of curing agent type on the adhesive joints strength

The results of tensile strength of the tested adhesive compositions versus curing agent type are given in Figs. 15 and 16.

Analysing the results in Fig. 15, it can be observed that with the exception of Specimen 11 (Epidian 6/PAC/100:60) the adhesive compositions containing PF have a higher tensile strength than the compositions with PAC. The difference ranges from 12% to 35%, increasing with an increase in the curing agent content.

The results of Epidian 6/PF compositions reveal that there is a certain optimum resin to curing agent ratio – the highest tensile strengths was obtained for Specimen 3 (Epidian 6/PF/100:54) and Specimen 2 (Epidian 6/PF/100:52), respectively. In contrast, a lower content of this curing agent leads to a decrease in the composition's tensile strength by approx. 32%. A similar observation can be made with respect to higher contents of the curing agent in the adhesive compositions. Compared to the highest obtained value, the tensile strength of Specimen 4 (Epidian 6/PF/100:56) and Specimen 5 (Epidian 6/PF/100:60) decreases by nearly 50%. It can therefore be claimed that among the tested ratios, the combination of 100:54 is the most desired in terms of its effect on tensile strength of adhesive compositions.

Examining the results in Fig. 16, it can be observed that in the group of adhesive compositions based on Epidian 5, the compositions containing PAC have a higher tensile strength than the compositions containing PF. This is particularly evident in the case of adhesive compositions in which the ratio of PAC to Epidian 5 was smaller (100:60, 100:70 and 100:80). Therefore, it can be concluded that a lower PAC content in the adhesive composition based on Epidian 5 has a positive effect on the tensile strength of this composition. In this connection, it must be stressed that epoxy resin and curing agent contents were applied as recommended, based on the stoichiometric ratio of curing agent to resin.

Examining the effect of curing agent type on tensile strength of the adhesive compositions based on Epidian 5, the greatest difference in tensile strength amounting to almost 60% can be observed in Specimen 7 (Epidian 5/PAC/100:70) and Specimen 17 (Epidian 5/PF/100:52). Among the tested adhesive compositions containing PAC, the highest tensile strength (32.46 MPa) was obtained for Specimen 7 (Epidian 5/PAC/100:70), while the lowest tensile strength (lower by approx. 20%) was exhibited by the specimens of two adhesive compositions: Epidian 5/PAC/100:90 (Specimen 9) and Epidian 5/PAC/100:100 (Specimen 10).

Among the group of adhesive compositions containing Epidian 5 and PF, Specimen 18 (Epidian 5/PF/100:54) has the highest tensile strength of 16.30 MPa, while Specimen 19 (Epidian 5/PF/100:56) has the lowest tensile strength of 12.47 MPa. The difference between the highest (16.30 MPa) and the lowest (12.47 MPa) tensile strength of the adhesive compositions containing Epidian 5 and PF is nearly 25%. Examining the results in Fig. 16, it can be observed that the curing agent content has a significantly smaller impact on the tensile strength of the adhesive compositions containing PF than is the case with the adhesive compositions containing PAC.

3.3.3. Failure mode of epoxy compositions samples

An analysis of failure of the tested epoxy compositions was performed taking into account the failure fracture of the epoxy adhesive compositions after tensile strength testing. Some examples of these samples are shown in Fig. 17.

Visual assessment of fracture of the tested epoxy adhesive compositions was carried out in compliance with EN ISO 10365 [41]. According to this standard, failure can be classified into six groups, three of which pertain to substrate failure, while the other three – to the failure of adhesive layer. It should be noted that in all cases of epoxy compositions the samples show the presence of cohesive failure (in the type of brittle fracture), irrespective of the type of epoxy resin and curing agent applied.

3.3.4. Effect of amount of curing agent on the elongation

The results of elongation of adhesive compositions based on Epidian 5 were presented in Fig. 18 and in Fig. 19 the results of elongation of adhesive compositions based on Epidian 6.

Comparing the results in Fig. 18, it can be noticed that:

- the adhesive compositions based on Epidian 5 epoxy resin and contain PAC curing agent for all variants of adhesive compositions have higher elongation than the adhesive compositions based on Epidian 5 epoxy resin and contain PF curing agent. On the basis on this results it can be noticed that adhesive compositions Epidian 5/

Fig. 17. Failure of epoxy adhesive composition - Specimen 7 (Epidian 5/PAC/100:70): a) Specimen 7 after destructive test, b) cohesive failure of two part of Specimen 7.

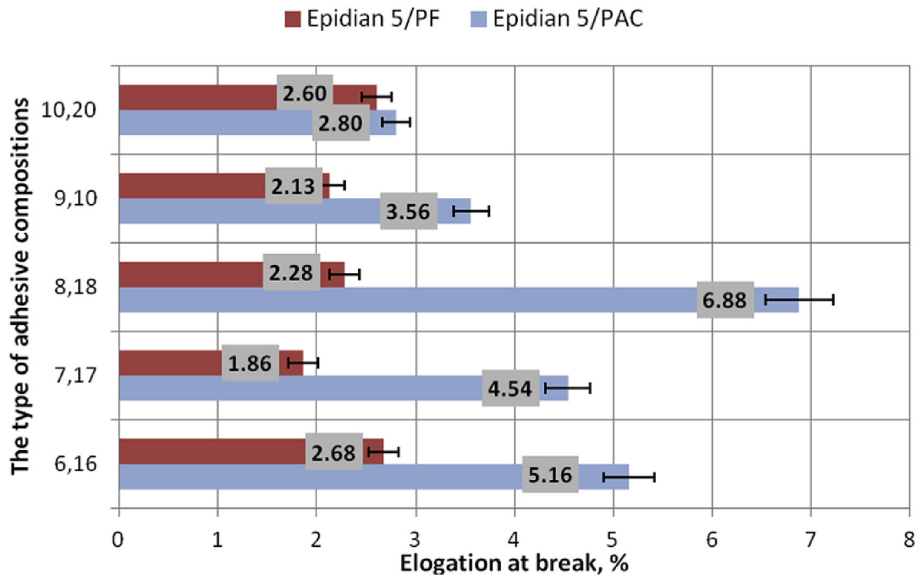

Fig. 18. Elongation of adhesive compositions based on Epidian 5 epoxy resin.

PAC are more flexible than adhesive compositions Epidian 5/PF,

- among the adhesive compositions Epidian 5/PAC, the highest elongation was obtained for Specimens 8 (Epidian 5/PAC/100:80) and the lowest for Specimen 10 (Epidian 5/PAC 100:100 – the highest amount of curing agent), the difference between elongation was 40%,
- among the adhesive compositions Epidian 5/PF, the highest elongation was obtained for Specimens 16 (Epidian 5/PF/100:50 – the lowest amount of curing agent) and also Specimens 20 (Epidian 5/PF/100:60 – the highest amount of curing agent) and the lowest for Specimen 17 (Epidian 5/PF 100:52).

Analysing the results in Fig. 19, it can be observed that:

- the highest elongation (6.10%) was observed for adhesive compositions based on Epidian 6 epoxy resin and contain PAC curing agent for Specimen 13 (Epidian 6/PAC/100:80),
- the highest elongation among adhesive compositions based on Epidian 6 epoxy resin and contain PF curing agent was noticed for Specimen 4 (Epidian 6/PF/100:56),
- in lots of variants of adhesive compositions (based on Epidian 6 epoxy resin) the higher elongation was observed for composition which contain PF curing agent (except the Specimen 15 and Specimen 13).

Examining the effect of curing agent type and the type of epoxy resin on the elongation at break of the adhesive compositions based on Epidian 5, the higher elongation at break can be observed in adhesive compositions containing PAC curing agent. The difference in elongation at break is amounting to even 63% (for Specimen 8 and 18). It can be observed that adhesive compositions based on Epidian 5 containing PAC curing agent are more flexible than adhesive compositions based on Epidian 5 containing PF curing agent. Among the tested adhesive compositions based on Epidian 6 the more flexibility (except two variants) was exhibited by the adhesive compositions contain PF curing agent. But in this variant of adhesive compositions the highest elongation at break (6.10%) was obtained for Specimen 13 (Epidian 6/PAC/100:80).

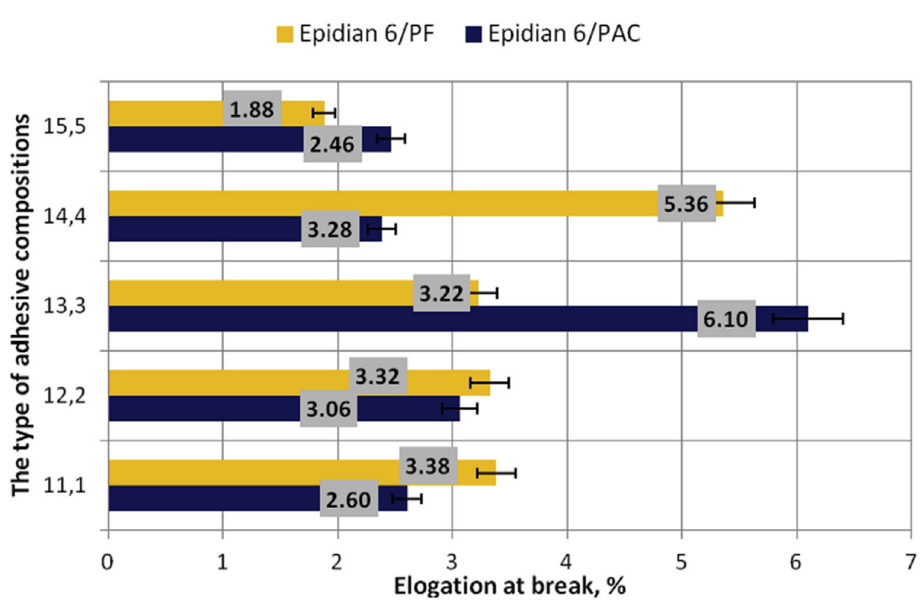

Fig. 19. Elongation at break of adhesive compositions based on Epidian 6 epoxy resin.

4. Conclusions

The experiments were conducted using the recommended stoichiometric ratios of curing agent to epoxy resin, their contents being similar to the contents of epoxy groups (in resin) and functional groups with active hydrogen atom (in curing agent). The experiments were conducted using two types of epoxy resin (Epidian 6 and Epidian 5) and two types of curing agent (PAC and PF). In the case of PF, the combination was 50 g - 60 g curing agent per 100 g epoxy resin, both for Epidian 6 and Epidian 5. As for the PAC content in both types of epoxy resin, the recommended stoichiometric ratio is 60 g - 100 g curing agent per 100 g resin. Taking into account the recommended curing agent/epoxy resin ratios, twenty variants of epoxy adhesive compositions were prepared for the tests.

The experimental results revealed the differences in the properties of the tested epoxy adhesive compositions; moreover, they helped determine the desired ratio of epoxy resin to curing agent. It was found that in most cases the use of a lower curing agent content results in a higher tensile strength of a given adhesive composition. This trend can be observed for both types of curing agent and epoxy resin alike.

The tensile strength results demonstrate that the resin and curing agent types as well as their ratios in adhesive compositions have impact on the tensile strength of the specimens in the cured state. The composition of Epidian 5 and PAC in the ratio of 100:60 (Specimen 6) has the highest tensile strength of 32.46 MPa, while the composition containing Epidian 6 and PAC in the ratio of 100:90 (Specimen 14) has the lowest tensile strength of 11.44 MPa.

Elongation at break results show that the adhesive compositions based on Epidian 5 containing PAC curing agent are more flexible than adhesive compositions based on Epidian 5 containing PF curing agent. Among the tested adhesive compositions based on Epidian 6 in lots of variants the more flexibility was exhibited by the adhesive compositions contain PF curing agent. But the highest elongation at break was observed for adhesive composition containing PAC curing agent - Epidian 6/PAC/100:80 (Specimens 13).

Besides, it can be observed that the curing agent content affects both the tensile strength and elasticity of the adhesive composition.

The thermogravimetric curves, obtained in oxidative atmosphere, reveal that the adhesive composition made of Epidian 6 and PF in the ratio of 100:54 (Specimen 3) has the highest thermal stability, while that made of Epidian 6 and PAC in the ratio of 100:100 (Specimen 15) has the lowest value of $T_{5\%}$ IDT. All specimens undergo three stages of thermal degradation leading to their complete degradation.

The results of the DSC/TGA analysis allow to state that in the case of the analysed adhesive compositions, it is possible to apply a smaller amount of the curing agent in proportion to the resin, without worsening the thermal and mechanical properties of the adhesive composition.

While based on the received FTIR-ATR spectras in the case of the adhesive compositions with the highest contents of curing agent, a small signal from the epoxy resin groups, proves the incomplete reaction of these groups in the curing reaction with the polyaminoamide curing agents. It can be supposed that the properties of these adhesive compositions are worse than adhesive properties with smaller contents of curing agent. These results could elucidate a cause the lower tensile strength of adhesive compositions which contain the highest values if curing agent. It means that it is better to apply the smaller amounts of the curing agent from the recommended amount range, given by the producer, from the stoichiometric ratios range.

Summing up, it can be stated that:

(1) the curing agent content has a significant effect on the properties of adhesive compositions even within the range of stoichiometric ratios. The properties of the adhesive compositions based on the same of epoxy resin containing different curing agent ratios (within the range recommended by the manufacturers and stoichiometric ratios) are different,
(2) use of the smallest and the largest amounts of curing agent (within the range resulted from stoichiometric ratios) contributes to significant differences in properties and the properties is worse than the amount of curing agent from the middle of stoichiometric ratios range,
(3) on the basis on the results it not recommended use the largest amounts of curing agent (within the range calculated from stoichiometric ratios) by reason of obtaining the worse properties of adhesive composition than the smallest. Increasing the amount of curing agents contributes to the greater cost of the adhesive composition itself, which may affect the final costs of the production process, for example adhesive bonding.

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