

Influence of natural fillers on the thermal and mechanical properties of epoxy resin composites

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Abstract: The influence of a natural filler (lignin, chitosan, starch) used in the amount of 1, 5 and 10 wt% on thermal and mechanical properties of composites based on epoxy resin (Epidian[®]5) was investigated. Cross-linking of the resin with polyamine (IDA) was confirmed by the ATR/FT-IR method. The differential scanning calorimetry (DSC) was used to evaluate the thermal properties. Tensile and flexural mechanical properties as well as Shore hardness were also determined.

Keywords: epoxy resin, crosslinked composites, biopolymers, thermal properties, mechanical properties.

Wpływ napełniaczy naturalnych na właściwości termiczne i mechaniczne kompozytów na bazie żywicy epoksydowej

Streszczenie: W pracy zbadano wpływ napełniacza naturalnego (lignina, chitozan, skrobia) stosowanego w ilości 1, 5 i 10% mas. na właściwości termiczne i mechaniczne kompozytów otrzymanych na bazie żywicy epoksydowej (Epidian[®]5). Sieciowanie żywicy poliaminą (IDA) potwierdzono metodą ATR/FT-IR. Do oceny właściwości termicznych zastosowano różnicową kalorymetrię skaningową (DSC). Oznaczono również właściwości mechaniczne przy rozciąganiu i zginaniu oraz twardość metodą Shore'a.

Słowa kluczowe: żywica epoksydowa, usieciowane kompozyty, biopolimery, właściwości termiczne, właściwości mechaniczne.

Biopolymers are an inexhaustible, naturally available group of natural polymers produced by the cells of living organisms. Sugars, amino acids and nucleotides are referred to as monomeric units of biopolymers [1]. Based on the monomers and the structure they form, three main classes of biopolymers can be distinguished. Polynucleotides are composed of 13 or more nucleotide monomers where RNA and DNA are the examples. Polypeptides and proteins are amino acid polymers such as collagen and fibrin. Polysaccharides can be linear or branched and are polymeric carbohydrates, among others, starch and cellulose [2].

For many years the world has been struggling with the huge amount of plastics that need to be disposed of. This is partly due to the growing use of plastics in the economy and everyday life, combined with bad consumer habits and

insufficient waste management infrastructure. The result is an increasing strain on the environment. Therefore, expectations concerning plastic quality, processing and removal methods are growing. Thus, the plastics industry is urgently faced with the task of implementing technologies to reduce plastic waste and enable greater recycling and recovery [3–6]. The application of natural biopolymers could be the solution to many of the problems facing the plastics industry. Due to the long and troublesome decomposition of conventional plastics, it is very important to create materials containing natural biopolymers. Their biodegradability reduces the decomposition time significantly and thus facilitates their disposal [7–14].

The best-known biocomposites that offer the greatest benefits include lignin, chitosan and starch. Lignin is an amorphous compound that consists of p-hydroxycinnamic alcohols, coniferyl and sinapyl alcohols. The aromatic units bind through the ether and carbon-carbon bonds [15–16]. Lignin has binding properties that allow wood to maintain a compact structure. Due to its lignin content wood is resistant to compression, wood is stiff, and prevents decay processes. The lignin structure contains aliphatic and aromatic groups -OH, which makes it possible to use it to create polymeric materials with specific characteristics while not affecting the environment

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negatively [17]. It is used in felsen-formaldehyde resins, polypropylenes, and polyurethanes. The researchers have also suggested its use in numerous biomaterials [18].

Starch is a polymeric carbohydrate composed of glucose units linked by the glycosidic bonds. It is produced by many plants as it enables energy storage. This is a white, tasteless and odourless powder. It is insoluble in cold water and alcohol. Its structure includes linear and helical amyloses as well as branched amylopectin [19]. Starch is used in industry to produce sugars by malting and is also used to produce ethanol by fermentation. It is transformed to form polysaccharides for processed foods. It is used as a thickening, adhesive and stiffening agent. It is a binder for the paper industry [20].

Chitosan is a polysaccharide found in abundance in nature. It has a lot of functional characteristics due to its chemical properties. Chitosan is a deacetylated derivative of chitin. It is composed of linked *N*-acetyl-2-amino-2-deoxy-D-glucose residues. Unlike chitin chitosan is soluble in the aqueous acidic medium [21]. Chitin can be found in the exoskeleton of crustaceans, algae, and the cell wall of fungi. Chitosan is found in some fungi such as Mucoraceae [22]. It is characterized by the anti-inflammatory, antimicrobial, and antifungal properties, thus it is of great interest in biological and technological sciences [23].

In this paper the effect of natural fillers such as lignin, chitosan and starch on the thermal and mechanical properties of rigid, cross-linked biocomposites based on Epidian 5 epoxy resin was investigated.

EXPERIMENTAL PART

Materials

Epoxy resin: Epidian[®]5 (density at 25°C: approx. 1.17 g/cm³, viscosity at 25°C: 20,000–30,000 mPas, epoxy number: 0.48–0.51 mol/100 g) was used as a monomer,

IDA polyamine was used as a crosslinking reagent. These reagents were purchased from Ciech Sarzyna S.A. (Nowa Sarzyna, Poland). The naturally occurring biopolymers: lignin and chitosan (Sigma Aldrich, Steinheim am Albuch, Germany) and starch (CHEMPUR, Piekary Śląskie, Poland) were used as fillers.

Methods

ATR/FT-IR (Attenuated Total Reflectance Infrared Spectroscopy) analysis was performed to confirm the chemical structure of the obtained composites. The spectra were recorded from 4000 to 600 cm⁻¹. 32 scans every 4 cm⁻¹ were performed using the powdered composite samples. A Bruker FT-IR TENSOR 27 spectrophotometer (Bruker GmbH, Mannheim, Germany) was used.

The thermal stability of TG/DTG samples was tested on a Netzsch STA 449 F1 Jupiter thermal analyzer (Netzsch, Sebl, Germany). The following parameters were used: temperature range: 0–600°C, heating rate 10°C/min, carrier gas flow rate (helium) 20 cm³/min. The sample mass was about 10 mg. The measurements were made in the Al₂O₃ crucibles and an empty crucible was used as a reference sample. The differential scanning calorimetry analysis was performed using the DSC Netzsch 204 calorimeter (Netzsch, Günzburg, Germany). The samples of approximately 10 mg were placed in aluminum crucibles. The empty crucible was used as the reference sample. The dynamic scans were made with a heating rate of 10°C/min, in the temperature range of 25 to 500°C.

The single-axis tensile tests were carried out using a Zwick/Roel Z010 testing machine according to EN-ISO 527, with the crosshead speed of 50 mm/min at 23°C. The specimens of 4 × 10 × 80 mm in size were used.

In order to examine the flexural properties, the test including the three-point bending (EN-ISO 170, ASTM D-790) standards was carried out. All tests were carried

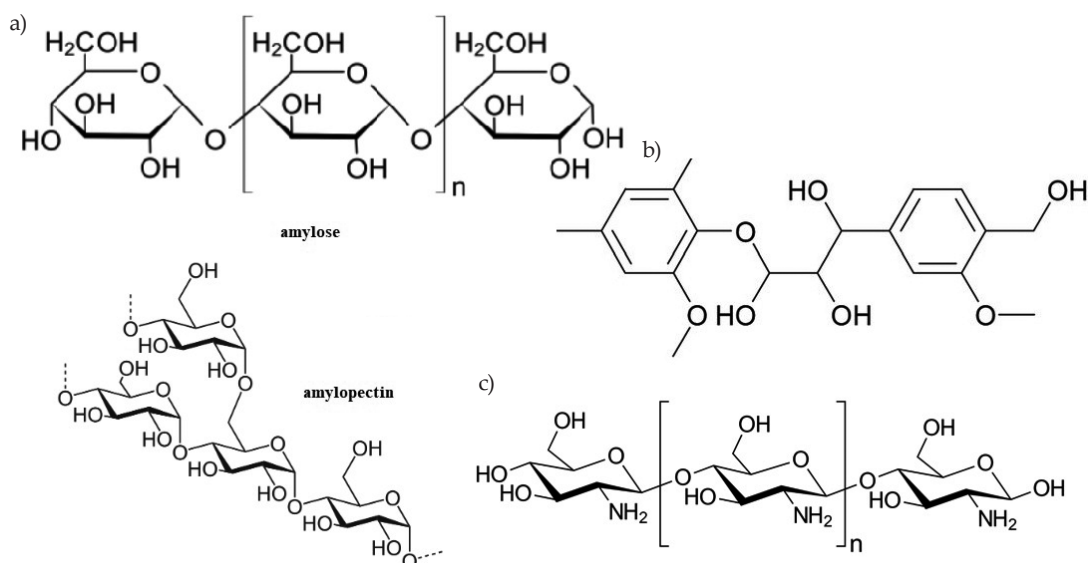


Fig. 1. Chemical structure: a) starch, b) lignin, c) chitosan

Table 1. Composition of tested composites

Sample	Epidian [®] 5, wt%	IDA, wt%	Filler content, wt%
EP5+IDA+1%CH	66,7	33,3	1
EP5+IDA+5%CH	66,7	33,3	5
EP5+IDA+10%CH	66,7	33,3	10
EP5+IDA+1%L	66,7	33,3	1
EP5+IDA+5%L	66,7	33,3	5
EP5+IDA+10%L	66,7	33,3	10 </td
EP5+IDA+1%S	66,7	33,3	1
EP5+IDA+5%S	66,7	33,3	5
EP5+IDA+10%S	66,7	33,3	10

out using the Zwick/Roell Z010 universal tensile-testing machine (Ulm, Germany).

The hardness was measured by the Shore method according to ISO 868 using the electronic hardness testing apparatus model: Art. 13 Affri (Induno Olona, Italy), with the D scale head at 23°C. The NIKON Eclipse LV100ND microscope (Tokyo, Japan) was used to observe the depressions created by the hardness test.

Preparation of composites

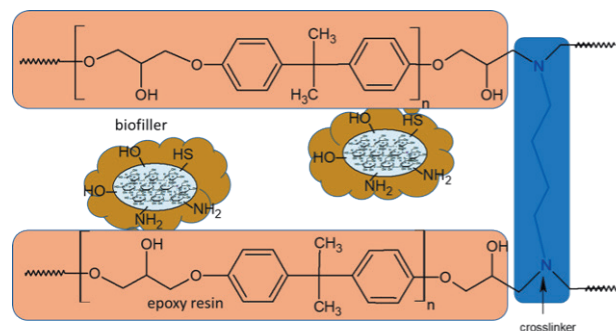
Six crosslinked materials containing 5 and 10 wt% filler were synthesized. The epidian[®]5 epoxy resin (EP5) was used as the main monomer and the commercial IDA mixture was used as the crosslinking agent. Chitosan (CH), starch (S) and lignin (L) were used as fillers. The structural formulae of the biopolymers are shown in Figure 1.

In each system the epoxy resin mass and IDA hardener ratio was 2:1 by weight. Epidian[®]5 was placed in a glass beaker, the appropriate amount of hardener was added, and everything was mixed thoroughly. The specified amounts of filler were then added and mixed again. The ingredients were transferred into the glass moulds (10 × 10 × 0.4cm) and left to cure. The predicted structure of the obtained material is shown in Figure 2. Lignin and starch in their structures have -OH groups which can combine with the hydroxyl groups from the epoxy resin through the hydrogen bonds. Chitosan has the -NH₂ groups in its structure which may also be responsible for the polymer additional crosslinking. Table 1 presents the quantities of the reagents.

Chemical structure

The chemical structure of the obtained materials was confirmed using the ATR/FT-IR analysis. The spectra were made for all obtained composites. Figure 3 shows the spectra of the samples, Table 2 presents the wavelength values for each band.

In the range of 3358–3366 cm⁻¹, broad bands originating from the stretching vibrations of the -OH groups can be observed. This is due to the presence of the -OH groups

**Fig. 2.** The simplified scheme of the obtained composite

in the structure of all the fillers. In addition, the epoxy ring opens after the curing process which also results in the -OH groups formation. The bands from the methylene and methyl groups are observed in the range of 2960–2961 cm⁻¹, 2925 cm⁻¹ and 2870 cm⁻¹. There are sym-

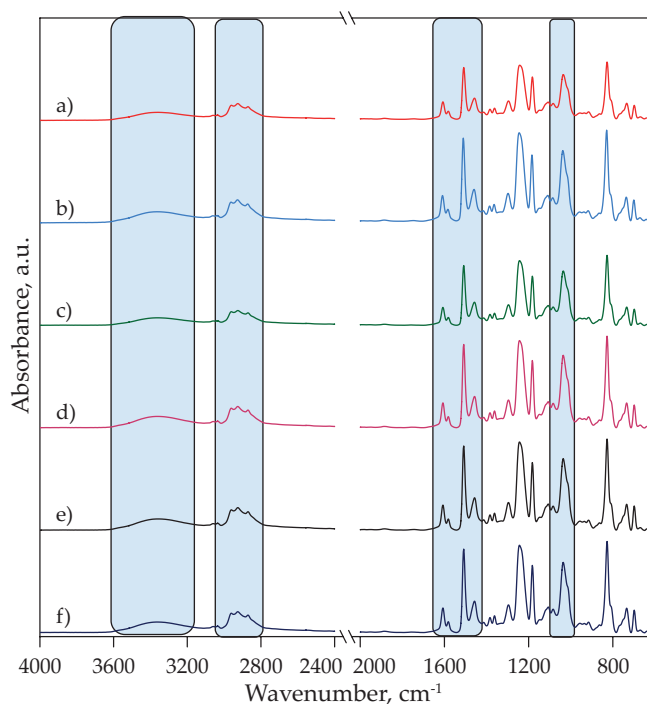
**Fig. 3.** ATR/FT-IR spectra of the composites: a) EP5+IDA+10%CH, b) EP5+IDA+10%L, c) EP5+IDA+10%S, d) EP5+IDA+5%L, e) EP5+IDA+5%S, f) EP5+IDA+5%CH

Table 2. Wavelength values with the attributed intramolecular vibrations

Symbol of vibration	Composite					
	EP5+HDA+5%L	EP5+HDA+5%S	EP5+IDA+5%CH	EP5+IDA+10%L	EP5+IDA+10%S	EP5+IDA+10%CH
	Wave number, cm ⁻¹					
$\nu_{\text{-OH}}$	3361	3364	3360	3362	3366	3358
$\nu\text{-CH}_2\text{-CH}_2\text{-}$	2960	2961	2961	2960	2960	2960
	2925	2925	2925	2925	2925	2925
	2870	2870	2870	2870	2870	2870
$\nu\text{-Ar}$	1607	1607	1607	1607	1607	1607
	1508	1508	1508	1508	1508	1508
$\delta\text{-CH}_2\text{-CH}_2\text{-}$	1456	1457	1456	1457	1459	1457
$\nu_{\text{C=O arom.}}$	1295	1295	1295	1295	1295	1295
ν_{CCO}	1243	1243	1243	1243	1243	1242
$\nu_{\text{C=O alk.}}$	1035	1035	1035	1035	1035	1035
$\gamma_{\text{Ar, Ar-H}}$	827	827	827	827	827	827
$\gamma_{\text{N-H}}$	734	734	734	734	734	734

metric and asymmetric vibrations of both groups. The doublets being 1607 cm⁻¹ and 1508 cm⁻¹ are symmetric and asymmetric stretching vibrations from the aromatic ring. At 828 cm⁻¹ the deformation vibrations of Ar and Ar-H can be seen. At 1243 cm⁻¹ wavelength there are found the bands from the stretching vibrations of oxygen atoms which are combined with the aromatic carbon atoms. The wavelength of 1035 cm⁻¹ corresponds to the stretching vibrations of the hydroxyl groups located close to the primary carbon atoms. The deformation vibrations of methyl and methylene group can be seen in the range

of 1456–1459 cm⁻¹. The presence of amino groups is confirmed by the band at 734 cm⁻¹.

Thermal properties

In the next step the thermal behavior of the obtained composites and the fillers was investigated. The DSC curves are shown in Figure 4 (a–c).

The glass transition temperatures (T_g) were recorded for lignin, starch, and starch-containing composites, which are in the range of 53–60°C. The endothermic peaks in

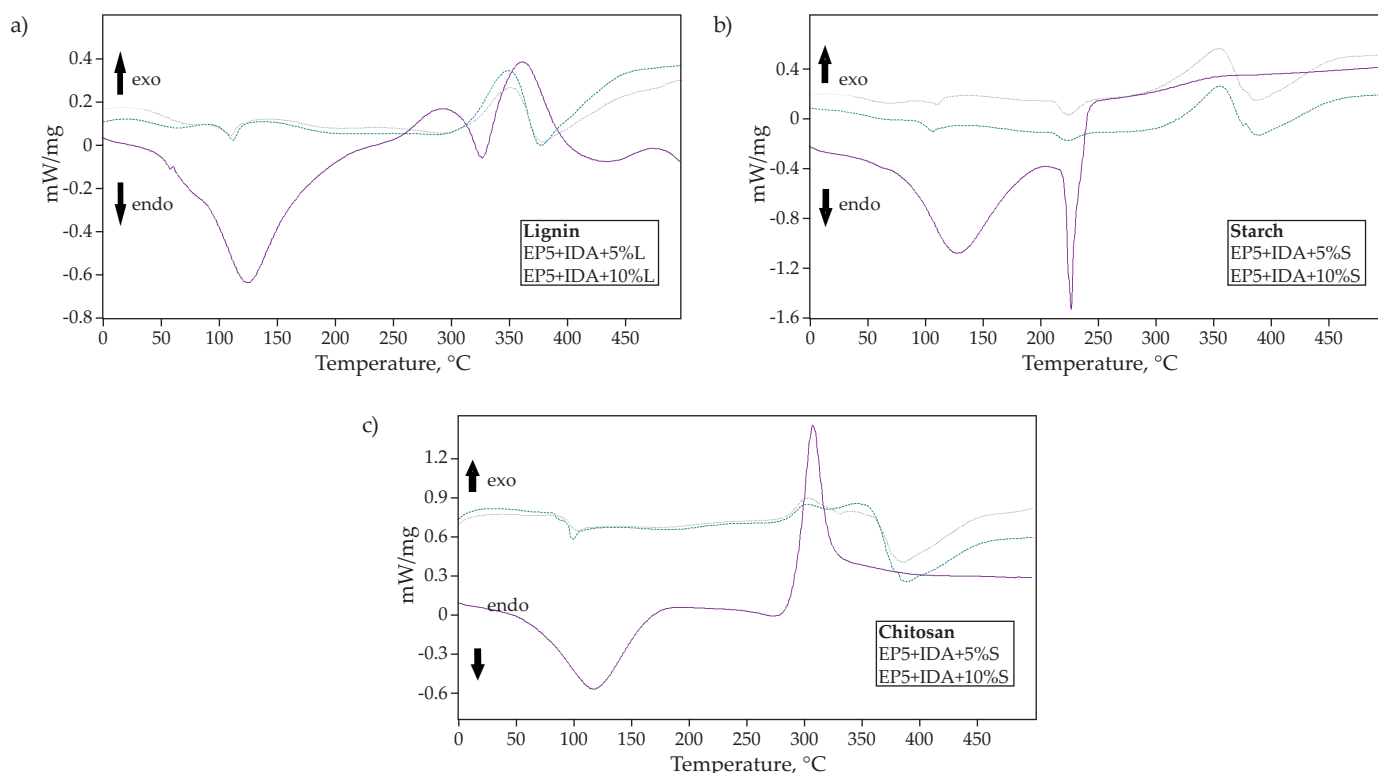


Fig. 4. DSC curves of the composites with: a) lignin, b) starch, and c) chitosan

Table 3. DSC data of the composites

Composite	T_g , °C	$T_{1'}$, °C	$T_{2'}$, °C	$T_{3'}$, °C (EXO)	$T_{4'}$, °C
EP5+IDA+5%L	–	112	287	350	377
EP5+IDA+5%S	58	107	224	356	386
EP5+IDA+5%CH	–	98	295	303	389
EP5+IDA+10%L	–	111	291	351	378
EP5+IDA+10%S	60	111	224	354	388
EP5+IDA+10%CH	–	104	287	303	386
LIGNIN	58	125	326	361	432
STARCH	53	128	227	–	–
CHITOSAN	–	117	294	308	–

the temperature range 98–128°C correspond to the initial distribution of the fillers. For the lignin composites small endothermic peaks can be seen at 287 and 291°C, for lignin there are peaks at 326 and 432°C which correspond to the decomposition of the filler.

The exothermic peaks in the temperature range 350–361°C correspond to the recrosslinking of the epoxy resin. Decomposition of the epoxy resin is evident at 377–378°C. For chitosan and the composites with chitosan, small endothermic peaks can be observed at 287–295°C, corresponding to the decomposition of the filler (Table 3).

The exothermic peaks in the range 303–308°C can indicate the crosslinking of epoxy groups (as well as $-NH_2$ groups responsible for crosslinking in the chitosan structure). At 286–289°C the endothermic peaks originating from the epoxy resin decomposition are visible for the composites with chitosan. In the spectrum of starch and composites with the starch addition there are additionally visible peaks in the range 224–227°C correspond-

ing to the filler disintegration. The exothermic peaks at 354–356°C correspond to the crosslinking of epoxy resin, the resin decomposition is visible at 386–389°C.

The thermal resistance of the composites as well as their degradation behaviour were investigated using the thermogravimetric analysis (TGA). The TG and DTG curves are shown in Figure 5. The weight loss coefficient ITD, which corresponds to a mass loss of 2%, $T_{50\%}$, which is the temperature at 50% mass loss, and the maximum decomposition temperatures T_1 and T_{max} and their corresponding percentage mass loss were determined. The residual masses (RM) were also determined. The data collected for the three samples are summarized in Table 4.

The thermal decomposition of the analyzed samples occurred in 3 main stages. The first peak in the temperature range 41–47°C and the loss mass of 0.23–0.29% are related to the volatilization of adsorbed small amounts of water or insignificant amounts of monomers. The second peak in the range of 140–150°C can correspond

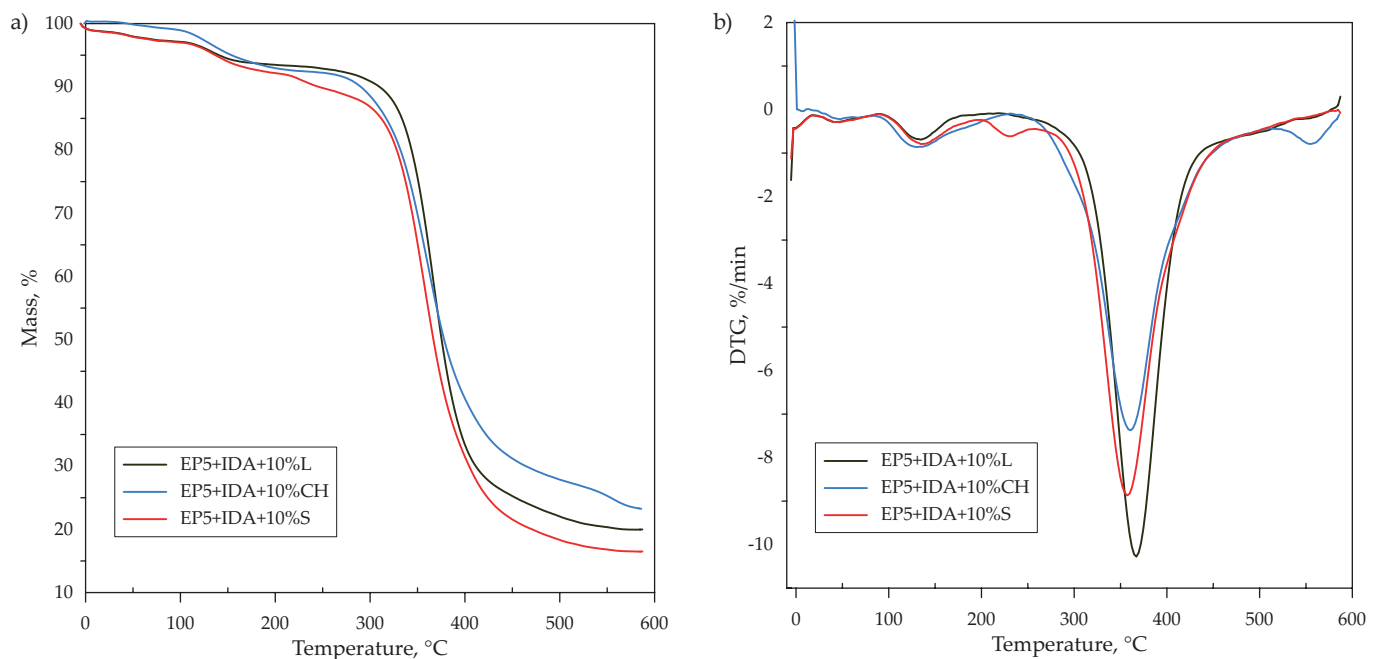
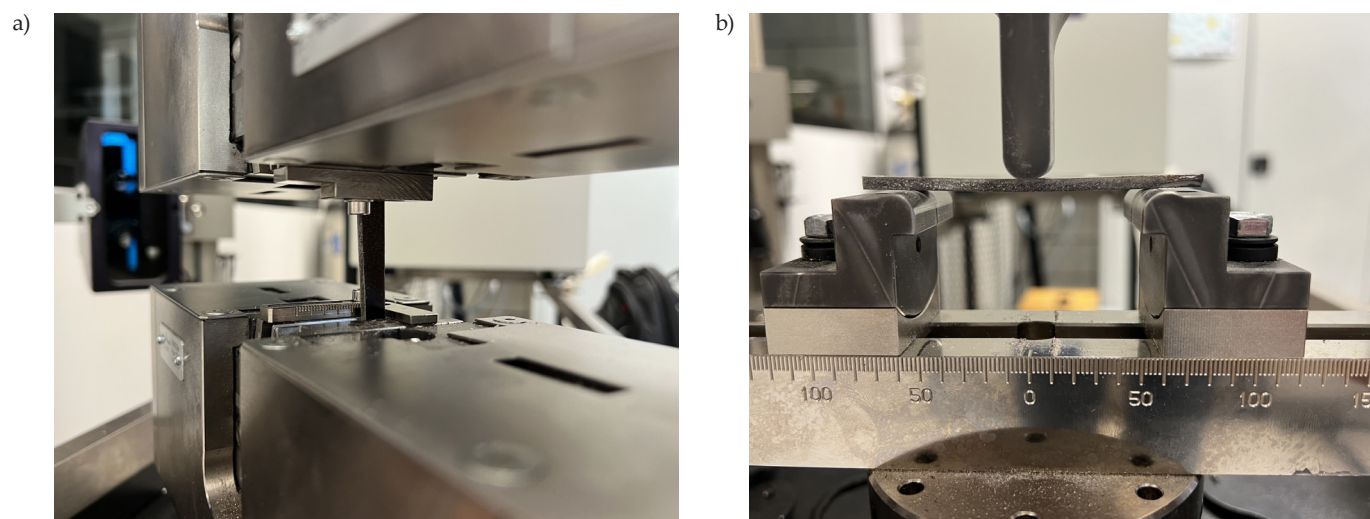


Fig. 5. TGA analysis: a) TG, b) DTG curves of the composites

Table 4. TG and DTG data of the composites

TG/DTG	EP5+IDA+10%L	EP5+IDA+10%S	EP5+IDA+10%CH
T_g , °C	41.0	47.4	47.1
T_1 mass loss, %	0.29	0.29	0.23
ITD, °C	47	47	117
T_{max} , °C	366.8	357.5	360.4
T_{max} mass loss, %	10.28	8.87	7.38
$T_{50\%}$, °C	374.6	365.8	376.8
RM, %	20.01	16.48	23.25

**Fig. 6.** Exemplary photos of the samples during testing: a) tension, b) bending**Table 5.** Tensile and flexural properties of the composites

Property	EP5+IDA+5%L	EP5+IDA+5%S	EP5+IDA+5%CH	EP5+IDA+10%L	EP5+IDA+10%S	EP5+IDA+10%CH
Stress at break, MPa	42	36	33	30	29	35
Elongation at break, %	2.4	2.0	1.8	1.5	1.7	1.8
Young's modulus, MPa	2373	2358	2158	2198	1992	2318
Flexural strength, MPa	63	55	39	44	78	75
Flexural modulus, MPa	3671	3575	3066	3265	3529	3499

Table 6. Hardness of the composites

Hardness	EP5+IDA+5%L	EP5+IDA+5%S	EP5+IDA+5%CH	EP5+IDA+10%L	EP5+IDA+10%S	EP5+IDA+10%CH
Shore hardness (D scale)	81	82	82	81	82	83
Impression diameter, μm	606	612	668	668	602	616
Observations within the imprint area	cracks	cracks	large range of plastic changes	cracks	large range of plastic changes	large range of plastic changes

to the degradation of the aliphatic fragments derived from the natural fillers. The third T_{max} peak in the range 357–366°C corresponds to the main degradation of the samples. The initial decomposition temperature (ITD) of the sample in the range of 250–282°C was also recorded. The largest loss mass corresponding to the residue (RM) was observed for the EP5+IDA+10%CH composite being 23.25%.

Tensile and flexural properties

The yielding point, elongation at break and Young's modulus were determined. During the three-point bending test, with a support spacing of 60 mm and a bending modulus velocity of 2 mm/min, the resistance to fracture was determined by evaluating the flexural strength, and flexural modulus [24–25]. The examples of the specimens

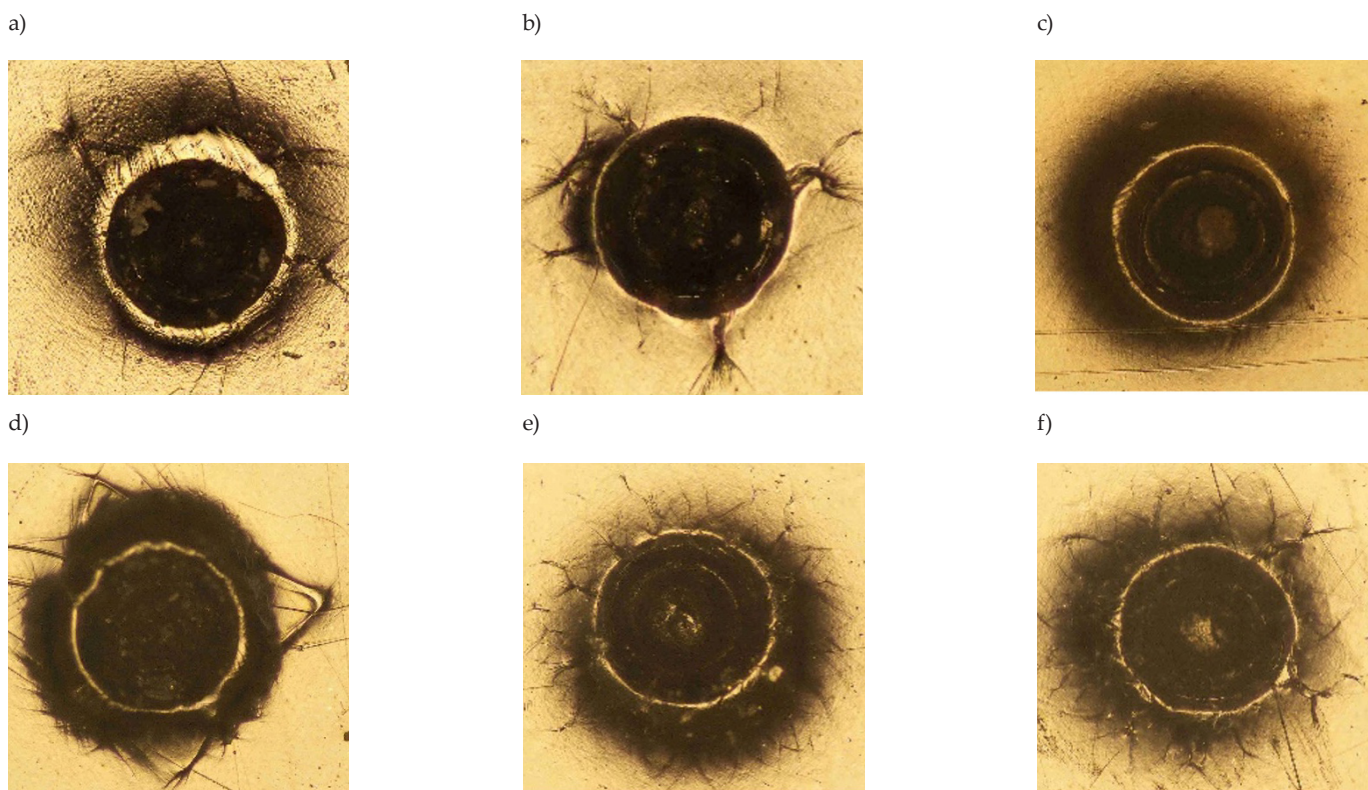


Fig. 7. Images of the composites structure after the hardness test

mounted in lugs during the measurements are shown in Figure 6. The results of the obtained static tensile strength and three-point bending tests are given in Table 5.

Hardness

The results of hardness and selected characteristic values after the indenter removal from the tested sample are presented in Table 6. The images of the structure after the indenter removal are presented in Figure 7.

The images of the composite structure (Figure 7) after the hardness test show that, depending on the amount and type of additive, a large area of plastic changes is formed around the hole when the surface is destroyed. With the additive content of 5%, for the samples with L and S a pronounced cracking of the surface layer occurs, which indicates that the composite is brittle. For the samples with 10% S and CH the cracks are smaller but there is a larger area of plastic change around the hole with smaller cracks.

CONCLUSIONS

The DSC spectra of the composites show the endothermic signals indicating either evaporation of water from the samples (98–128°C) or destruction of the fillers (224–295°C). The exothermic signals can indicate the crosslinking effect of the free epoxy groups. The endothermic signals at 377–432°C are considered to be respon-

sible for the composites degradation. It was observed that the addition of natural filler has a positive effect on the thermal stability of the composites. When the composites were filled with 5 wt% of natural filler, the greatest decrease in the modulus of elasticity was recorded for chitosan as an additive. In the case of the samples with 10 wt% of filler, the largest decrease in the modulus of elasticity was recorded for starch while the 10 wt% addition of chitosan showed a slight increase with respect to the 5 wt% filling from 2158 MPa to 2318 MPa. The three-point bending tests confirmed the correlations obtained for chitosan in the tensile test which showed an increase in the Young's modulus from 3066 MPa to 3499 MPa. Slight differences were observed for the samples with the starch addition, where in the case of 5 wt% versus 10 wt%, the elastic modulus changed by 46 MPa. The composites show similar hardness ranging from 81 to 83°ShD.

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