CARBON FABRIC REINFORCED HYBRID EPOXY COMPOSITES

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S u m m a r y

The effect of the amount of nanofiller and commercial flame retardant into the epoxy matrix on the mechanical properties of laminates reinforced carbon fabric was described. The total content of the fillers did not exceed 23 wt.%. The local strain and stress distribution on the surface of composites using the Aramis system during the static tension tests was examined. Studies of structure of cross-linked epoxy compositions were also performed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The presented results indicate that the nanofillers and commercial flame retardants acting synergistically.

Keywords: hybrid composites, mechanical properties, Aramis, carbon fiber

Hybrydowe kompozyty epoksydowe wzmocnione włóknem węglowym

S t r e s z c z e n i e

W pracy opisano wpływ dodatku nanonapełniaczy i handlowych środków zmniejszających palność na właściwości mechaniczne kompozytów epoksydowych wzmacnianych tkaniną węglową. Zawartość dodatków w osnowie epoksydowej <23%. Prowadzono analizę lokalnego stanu odkształcenia i naprężenia na powierzchni kompozytów z użyciem systemu Aramis podczas próby statycznej rozciągania. Wykonano badania mikrostruktury usieciowanych kompozycji epoksydowych za pomocą skaningowego mikroskopu elektronowego (SEM) i mikroskopu sił atomowych (AFM). Analiza uzyskanych wyników wskazuje, że wprowadzenie nanonapełniaczy i handlowych uniepalniaczy powoduje uzyskanie synergicznego efektu ich działania.

Słowa kluczowe: hybrydowe kompozyty, właściwości mechaniczne, Aramis, włókno węglowe

1. Introduction

One of the most modern and dynamically developing kind of engineering materials are composites. A type of composite depend on the kind of matrix (polymer, metal, ceramic) and dispersed phase (particle, fiber, structural). Among the composites with polymer matrix, the fiber reinforced composites have been widely used in the construction industry, and their applications are increasing.

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Carbon fiber reinforced composites due to their high strength, high stiffness and lower density than these one of traditional plastics and design flexibility have become attractive structural materials in aerospace industry, marine, armor, automobile, railways, sport goods etc. Epoxy resin is the most commonly used polymer matrix with reinforcing fibers for advanced composites applications. The epoxy, when polymerized, is an amorphous and highly cross-linked material. This cross-linked microstructure results in many useful properties such as a high modulus and failure strength, low creep, etc. However, it leads also to an undesirable property whereby the polymer is relatively brittle and has a poor resistance to crack initiation and growth which may affect the overall fatigue and fracture performance of FRP composites. Moreover, epoxy resins perform very poor fire resistance, since most of them burn easily and violently, so the addition of a flame retardant is essential. Unfortunately, the addition of flame retardant led to reduce of mechanical properties [1, 2]. Moreover, the main damage of laminates is delamination, which causes a reduction of stiffness. FRP are characterized by anisotropy of properties (Fig. 1).
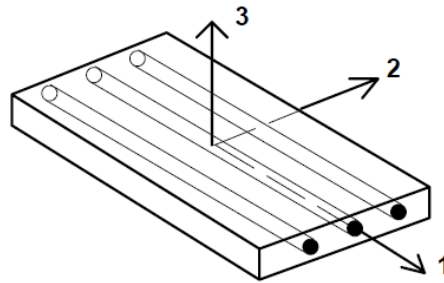

Fig. 1. Axis coordinates for one ply of unidirectional fabric
reinforced composite, based on [3]

Elastic modulus of composite in parallel direction to fibers $E_{c\parallel}$ can be described by the formula:

$$E_{C\parallel} = E_f V_f + E_m V_m \tag{1}$$

For transverse direction $E_{c\perp}$ it can be presented as:

$$E_{C\perp} = \frac{E_m \cdot E_f}{E_f \cdot V_m + E_m \cdot V_f} \tag{2}$$

where: E_m, E_f – elastic modulus of respectively: polymer matrix and fiber
V_m, V_f – volume fraction of respectively: polymer matrix and fiber

Transverse Young's modulus and other mechanical properties is affected significantly by morphology of polymer matrix and interfacial bonding [4]. The interfacial adhesion between the fiber and the matrix also influence on the longitudinal mechanical properties, because the matrix serves to transfer load between the reinforcing fibers and provide a good interlaminar shear strength [5].

One of the ways to enhance the interfacial interactions and mechanical properties of FRPs is to improve the properties of the epoxy matrix by incorporating nanofillers into the resin. Inorganic nanoparticles have gained use as potential reinforcing materials because of their low cost and ease of fabrication [6, 7]. Many researchers attempted to enhance properties of epoxy resin by the addition of nanoclays [8-11]. Small accounts of nanoparticles (≤ 5 wt.%) and uniform dispersion in polymer matrix, causes that the interface in the nanocomposites is repeatedly increased (up to 1000 times), as compared with a conventional composites. It is due to the formation of weak, hydrogen-like bonds, dipole-dipole and van der Waals interactions between polymer chains and a plates of nanoclay. However, the mechanical properties of polymer nanocomposites are much lower than these required to engineering structural materials, such as advanced composites reinforced with continuous fibers [12]. In the case of fiber reinforced composites, delamination is a major failure mechanism that is different from the dominant failure mode in a unreinforced resin system [13-15]. Thus, fracture properties in the unreinforced resin may not necessarily reflect in the interlaminar fracture behavior of the composite. there are still diverse reports on the optimum levels of nanoclay loading into the polymer matrix and the resulting increase in the properties of hybrid fiber/organoclay nanocomposites. Khan et al. [16] showed that by dispersing 3 wt.% organoclay Nanomer I.30P, carbon/epoxy-nanocomposites exhibited an improvement of 12, 9, 21 and 7% in tensile strength, flexural strength and modulus, respectively. A similar tendency on the mechanical properties of the unidirectional carbon fabric reinforced laminates was also achieved by addition of 2 wt.% nanocaly K-10 [17]. Chowdhury et al. [18] fabricated carbon fiber reinforced composites with a matrix of nanoclay Nanomer I.30E/epoxy system. They observed that addition of 2 wt.% nanoclay increased the flexural strength and modulus of 25 and 14%, respectively. Meanwhile, Izod impact strength decreased with increased clay content (1-7 wt.%) [19].

Therefore the behavior of nanofillers and fillers reinforced fiber composites is an interesting area of study. Our previous work on modified bentonite nanocomposites with a synthetic resin matrix [20, 21] and its influence on the mechanical and thermal properties of glass fiber reinforced composites was determined. The objective of this research was to study the effect of use of nanoclay and commercial flame retardant dispersion into epoxy matrix on the mechanical properties of epoxy/carbon hybrid composites. The carbon fabric laminates with V-0 classification in UL94 epoxy matrix with flame retardant and/or nanoclay to investigate a synergistic effect was fabricated.

2. Experimental section

2.1. Materials

The epoxy resin and the curing agent used in this work were Epidian® 6 (EP6) containing mostly diglycidyl ether of bisphenol A and triethylenetetramine (Z1) respectively, both commercial grade products of Ciech-Sarzyna Plant, Poland. The organoclay – bentonite "Specjal" (Zebiec SA Plants, Poland) modified with a butyltriphenylphosphonium chloride used as the nanofiller (BSQPS). The modification procedure of smectic clays with quaternary ammonium or phosphonium salts has been previously patented [22, 23] and described in detail in our previous papers [20, 21]. Commercial flame retardants: amonium polyphosphate (APP), (Tecnosintesi S.p.A., Italy) and dipentaerythritol (DPER), (Sigma-Aldrich). Unidirectional carbon fabric 200 g/m2 (TC) purchased from Havel Composites. All the materials were commercial grade and used without further purification or modification.

2.2. Preparation of epoxy composition

Epoxy resin compositions were prepared with 3 wt.% of modified bentonite and/or commercial flame retardants so that total amount of filler did not exceed 23 wt.%. Preparation of the compositions started with introducing modified bentonite to the resin and homogenizing the mixture. Then, the remaining flame retardants were introduced and homogenized with the epoxy composition. After introducing of each component, the four-stage homogenization procedure was applied [21]. In the choice of type and amount of fillers, suggestions of producers were taken into account. The prepared compositions are listed in Table 1.

Table 1. Epoxy compositions with nanofiller and commercial flame retardant

Epoxy composition	Components of epoxy compositions, %		
	BSQPS	APP	DPER
K0	3	0	0
K2	3	15	5
K14	0	17	6

2.3. Preparation of cured epoxy compositions

Composites based on the resin matrix Epidian 6 were cured using Z-1 (13 wt.%), according to the resin manufacturer's instructions. The composites were then vented in a laboratory vacuum chamber Vakuum UHG 400 (Schuechl, Bawaria, Germany) and cast in silicone molds prepared in accordance with ISO 527-1:1998. The cast parts were cured at room temperature for 24 h and then post-cured at 100 °C for 6 h. After two days, the morphology and structural properties were analyzed.

2.4. Preparation of carbon fiber/epoxy compositions laminates

The epoxy composition based on EP6, containing mixtures of flame retardants as shown in Table 1, were used to prepare four-layer laminates with unidirectional carbon fabric (200 g/m^2) acting as reinforcement. Hand lay-up method was used. Successive sheets of fabric were placed on a Teflon film and impregnated with epoxy composition containing amine curing agent using a grooved roller. The top layer, after removing the excess of resin, was covered with another Teflon film before the sample was placed between two steel plates of dimensions 200×300 mm as a mold. The plates were pressed to exert a pressure of about 10 MPa. The laminates were left to cure at room temperature overnight and then post-cured in an oven with hot air circulation at 100°C for 6 hours. The resulting laminates contained ca. 40% of carbon fabric by weight. The samples were cut from the laminates in the parallel *[0]* and transvers *[90]* directions to the direction of fibers with an oscillating cutting disk. The samples were used to measure the mechanical properties.

2.5. Characterization of carbon fibre/epoxy compositions laminates

Plate specimens (200x20x1,5 mm) were employed for tension test. Instron 5967 machine was used to perform tensile tests according to ISO 527-1:1998. All specimens were tested at a speed of 2 mm/min in the direction longitudinal to the direction of fiber. Three-axis strain and stress distribution on the surface of sample were determined using Aramis system (GOM, Germany) equipped with two cameras.

The bending tests in the transverse *[90]* and longitudinal *[0]* direction of fiber were performed according to EN ISO 14125, using the same tensile machine equipped with a three point bending rig. The vertical displacement speed of the rig during the test was 1 mm/min.

Charpy impact resistance in the transverse *[90]* direction of fiber was determined according to DIN EN ISO 179-1 using Ceast 9050 Impact Pendulum (Italy), using a hammer impact energy of 1 J. Unnotched bars: 100 mm long, 10 mm width and 3 mm height were used.

Instrumented Izod impact strength in the direction longitudinal *[0]* to the direction of fiber, for notched specimens (80x10x3 mm) was measured according PN-EN ISO 180:2004, using a hammer impact energy of 5,5 J (Ceast, Italy).

The brittle fracture morphology of the cured compositions was analyzed using scanning electron microscopy (SEM 234a, JEOL Ltd., Tokyo, Japan). Fractured profiles were obtained after cooling in dry ice and impact-break.

Surface morphology of the samples was performed using an atomic force microscope (AFM) by the QNM technique. On the basis of local changes of the Young's modulus of the sample surface, rigid areas correspond to the presence of fillers, and areas with less rigidity associated with the polymer matrix, were observed. This enabled estimation of the degree of homogenization of the filler on the surface of the polymer matrix, and of the size of its particles. The tests were

performed using a Nanoscope V microscope (Bruker Nano Surfaces Division, USA) with an RTESPA scanning needle, with a resonance frequency of 270 kHz. The scanning speed was 1 kHz, and the resolution 256 lines.

3. Results and discussion

3.1. Longitudinal tensile strength *[0]*

Young's modulus, elongation at break and Poisson coefficient, using curves generated during tests were determined (Fig. 2). The pictures recorded during tensile test to determine a local strain and stress before break were used.
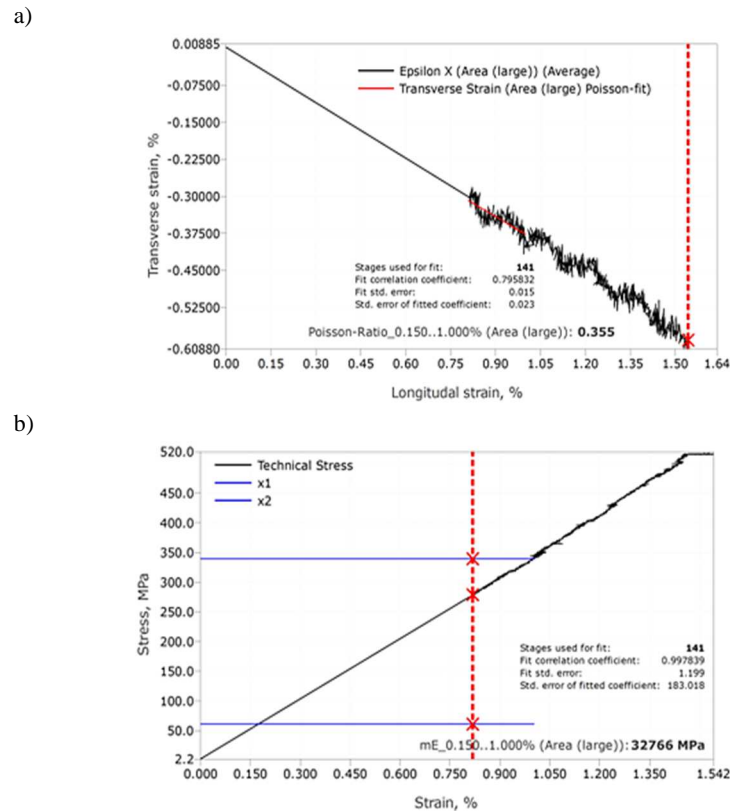
a)

b)

Fig. 2. Estimation of Poisson coefficient and Young's modulus by Aramis system

The results showed that the addition of used additives to the epoxy matrix influenced on increasing of the tensile strength of carbon fibre composites. However, replacement of a part of commercial flame retardants with 3 wt.% of bentonite acting synergistically and improves tensile strength of the carbon

fibre/K2 composites as compared to that without modified bentonite (K14). As a results of this the tensile stress of carbon fibre/K2 and carbon fibre/K14 composites was lover by 8 and 14% compared to the reference sample, respectively. A similar effect in Young's modulus was observed. Still, Young's modulus for the composite with K14 matrix was the least, about 2 GPa, than the unmodified one. Whereas, for laminates with K0 matrix the value of Young modulus was the same like for laminates with plain EP6 (Table 2).
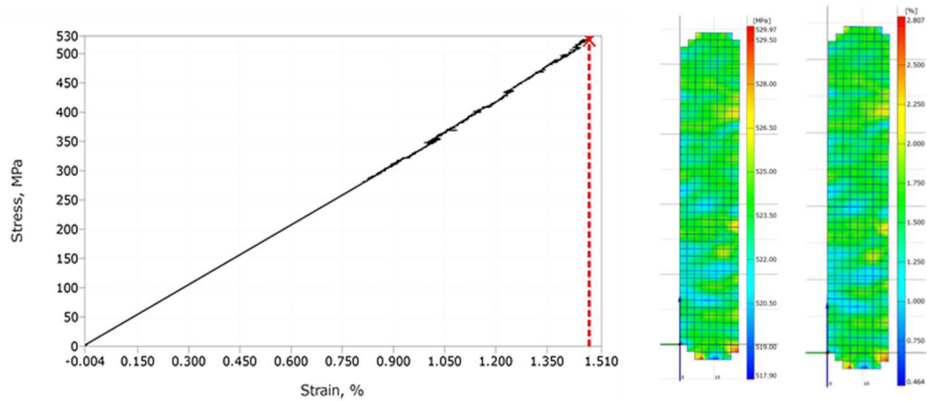

Fig. 3. Stress-strain relationship and stress and strain distribution at maximum tensile force for carbon fiber reinforced laminate with matrix EP6 ($\sigma = 521,0$ MPa, $\varepsilon = 1,45\%$)
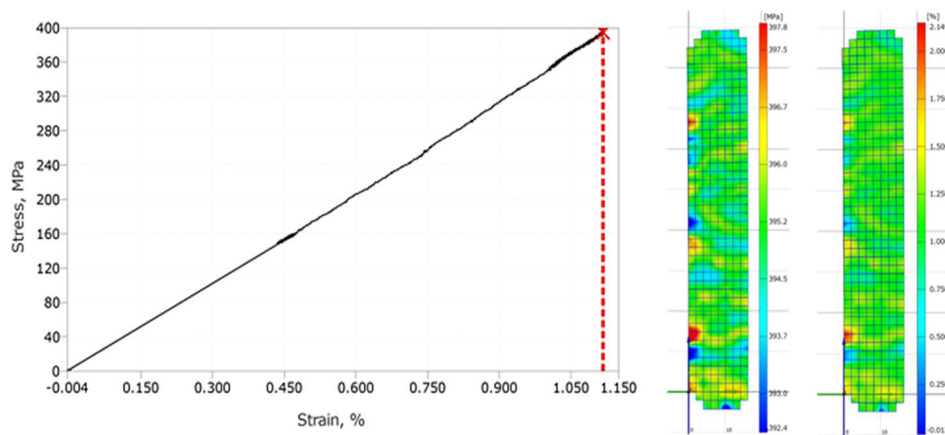

Fig. 4. Stress-strain relationship and stress and strain distribution at maximum tensile force for carbon fiber reinforced laminate with matrix K0 ($\sigma = 392,3$ MPa, $\varepsilon = 1,11\%$)
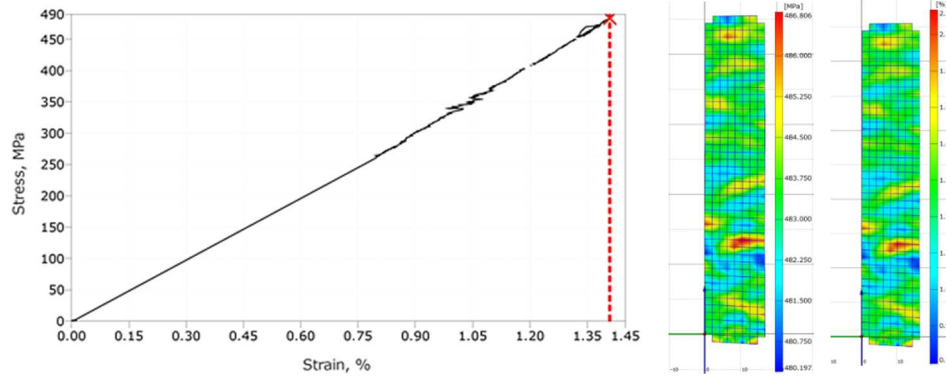
Fig. 5. Stress-strain relationship and stress and strain distribution at maximum tensile force for carbon fiber reinforced laminate with matrix K2 ($\sigma = 482,3$ MPa, $\varepsilon = 1,39\%$)
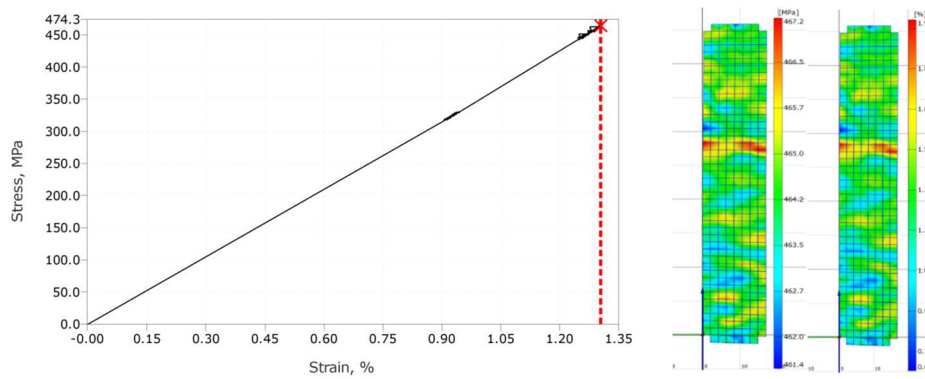

Fig. 6. Stress-strain relationship and stress and strain distribution at maximum tensile force for carbon fiber reinforced laminate with matrix K14 ($\sigma = 463,43$ MPa, $\varepsilon = 1,30\%$)

Stress-strain relationship and stress and strain distribution at maximum tensile force for carbon fiber reinforced laminate are showed in Fig. 3-6. The graphs of the stress and strain distribution indicate that the highest stress and strain on the surface were for laminates with unmodified matrix which characterized the highest ultimate tensile strength (Fig. 3). Furthermore, the stress and strain were higher by 9 MPa and 1,4%, compared to ultimate tensile strength ($\sigma = 521,0$ MPa) and strain at break ($\varepsilon = 1,45\%$), respectively. These results confirm the ability to transfer of the major load and deformations between the matrix and the fiber. On the other hand, for laminates prepared with modified matrices, the maximum of local stress and strain were higher by about 3 MPa and 0,7%, compared to the ultimate tensile strength and strain, respectively (Fig. 4-6, Table 2). This may be due to the presence of agglomerates of modifiers, resulting the difficult transfer of loads and deformations of the matrix on the fiber which affect reduction of

ultimate tensile strength. The obtained results was were confirmed by curves of deformations recorded during the test (Figure 7). The samples with unmodified EP6 had the deformations in the range 2-4,5%. Meanwhile, for composites with matrices: K0, K2 and K14 the values were in the range: 1,3-2,6; 1,6-3,2 i 1,5-2,6%, respectively.
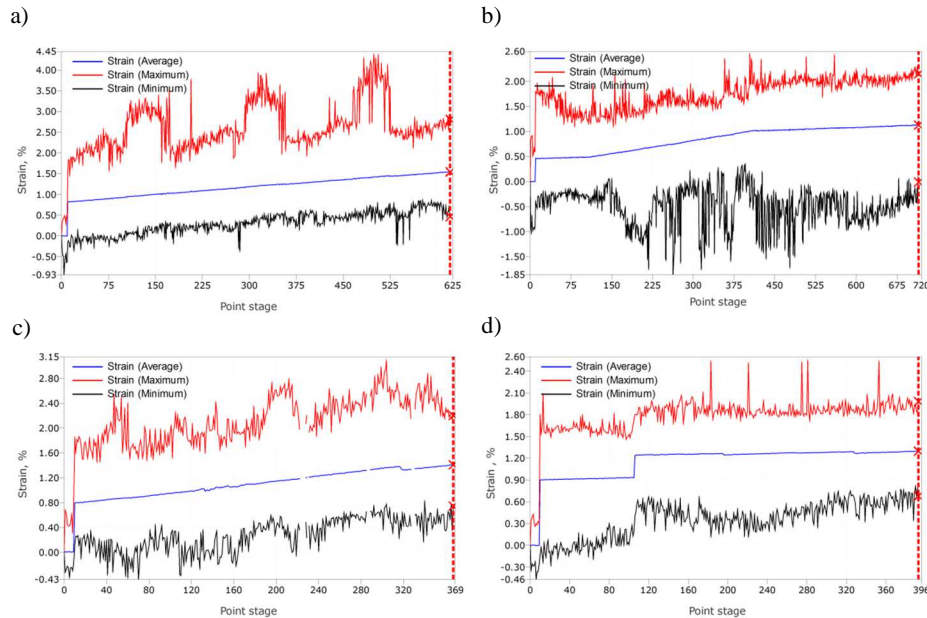

Fig. 7. Strain distribution during tensile test on the samples surface of laminates with matrices: a) EP6, b) K0, c) K2, d) K14

3.2. Longitudinal flexural strength [0]

From the flexural test it was found, that the flexural strength in the direction parallel to the direction of fibers of composites with matrices containing APP, DPER and/or BSQPS was decreased. The carbon fibre/K2 composites had slightly lower flexural strength in the range of measurement error. However, the reduction of flexural strength by 12% was observed for the laminates prepared using the epoxy matrix containing only the flame retardant. It appears that as the flame retardants were added, the corresponding mechanical properties decreased, while replacement of a part of a commercial flame with 3 wt.% organoclay significantly changes this trend. The same results for the elastic modulus was obtained. The laminates prepared from composition containing APP, DPER and BSQPS had elastic modulus lower only by 6%, while the laminates with compositions K0 and K14 had elastic modulus lower by 11% compared to reference sample (Table 2).

Table 2. Mechanical properties of laminates reinforced with unidirectional carbon fabric with matrix EP6, K0, K2 and K14

Properties	Direction of fibre, deg	Matrix			
		EP6	K0	K2	K14
Ultimate tensile strength, MPa	[0]	519,7±5,3	388,5±27,1	475,8±15,6	456,8±11,7
Young modulus, GPa	[0]	36,33±1,11	36,49±0,91	35,95±0,93	34,49±1,00
Strain at ultimate tensile strength, %	[0]	1,44±0,03	1,10±0,06	1,35±0,05	1,31±0,04
Poisson coefficient	[0]	0,46±0,04	0,45±0,04	0,32±0,01	0,35±0,02
Flexural strength, MPa	[0]	590,03±25,30	594,7±25,0	557,7±15,5	520,72±32,3
	[90]	50,99±0,93	50,38±1,98	50,00±1,32	48,64±1,37
Flexural modulus, GPa	[0]	28,82±0,92	25,66±1,01	27,10±0,67	25,79±0,81
	[90]	3,58±0,07	3,98±0,20	3,86±0,16	3,71±0,23
Strain at ultimate flexural strength, %	[0]	2,14±0,12	2,51±0,06	2,26±0,13	2,32±0,17
	[90]	1,52±0,15	1,37±0,11	1,35±0,05	1,41±0,14
Charpy impact, kJ/m^2	[90]	4,53±0,37	4,93±0,70	3,97±0,41	3,81±0,54
Izod impact, kJ/m^2	[0]	49,42±4,10	32,69±3,38	57,76±5,8	47,11±6,3

± number – standard deviation

3.3. Transverse flexural strength [90]

In contrast to the study in the direction parallel to the direction of fibers, which was mainly determined by the strength of the fiber, the transverse flexural strength mainly depends on the morphology of matrix as well as their adhesion to the fiber. It was found that the transverse flexural strength of laminates prepared using modified matrix has not changed significantly compared to the carbon fibre/EP6 composites (Table. 2). However, the composites with matrices K0, K2 and K14 characterized higher elastic modulus by 11, 8 and 4%, compared to the unmodified sample, respectively.

3.4. Transverse Charpy impact strength [90]

The results presented in Table 2 show that the filling of epoxy matrix with 3 wt.% BSQPS improved the impact strength of composites by 9% compared to carbon fibre/EP6 composites. Much worse impact test results, by about 16%, were obtained for laminates based on epoxy resin containing 17% APP and 5% DPER. However, addition of 3 wt.% BSQPS improved the corresponding properties only by 3% compared to carbon fibre/K14 composites. However the impact strength of carbon fibre/K2 laminates was lower by 13% than the value of reference sample (Table 2).

3.5. Longitudinal Izod impact strength [0]

The data presented in Table 2 show that the addition of modified bentonite to epoxy resin significantly decreased the Izod impact strength of composites.
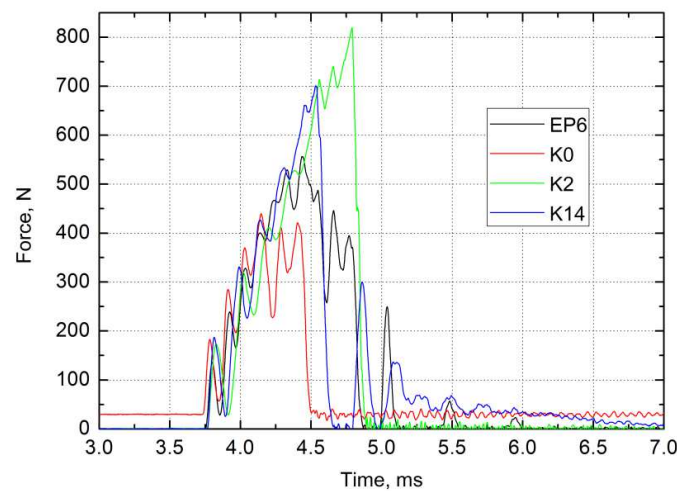

Fig. 8. Force curves as a function of time during impact fracture of laminates
with matrix EP6 and EP6 containing APP, DPER and BSQPS

The impact strength of carbon fibre/K0 composites decreased by 34% compared to composites prepared with unmodified matrix (Table 2). This is consistent with the force-time curves during impact fracture, which are lower and narrower compared to another laminates. These results indicate that the EP resin becomes more brittle under the influence of the modified bentonite used in the study. Furthermore, the laminates reinforced with carbon fabric are highly rigid compared to composites reinforced with glass fabric, which characterized lower Young modulus [15]. In the case of composites prepared with matrix containing flame retardant, an deterioration was also observed, but not as large as in the case of composites containing BSQPS. The best results were obtained for composites containing both modified bentonite and flame retardant. It should be noted, that replacement of a part of a commercial flame retardant with 3 wt.% organoclay, improved the impact strength by 17% compared to referency sample. The synergistic effect between BSQPS, APP and DPER is confirmed by curves force-time. The peak of maximum force of carbon fibre/K2 composites is the highest and the widest (Fig. 8).

3.6. Morfology of cured epoxy compositions

On the basis of the SEM microphotographs of brittle fractures of composites is observed that the additives were uniformly dispersed in the epoxy resin (Fig. 9). In spite of this the morphology of K14 composites is significantly different compared to composites containing 3 wt.% BSQPS, beside the commercial flame retardant. Fracture surface images observed from the K2 composites indicate that additives are better dispersed in the epoxy matrix as compared to those for K14 composites (Fig. 9a, b). The brittle fracture of K2 composites show a much rougher fracture surface compared to surface of K14 composites. The content of 3 wt.% BSQPS reduced the average particle size and increase the interface between the fillers and the matrix (Fig. 9 c, d). Unfortunetaly, the embedding the particle of flame retardant on the organoclay surface reduces the distance between the plates and forms the small agglomerations. These agglomerations may have begun to act as flaws and crack initiation sites that results in get worse mechanical properties.

The AFM microscope images (Fig. 10) showing the distribution of Young's modulus for the surface of the cured composition K0 containing 3.0% BSQPS (Figure 10b) show a uniform dispersion of nanofiller in the form of bright areas – a high Young's modulus of the polymer matrix can be observed. The average nanofiller particle with modulus above 6 GPa size determined on the basis of the size of these areas is 70.8 nm. Similar areas were not observed for the unfilled EP (Figure 10a). In the case of the composites EP6+17% APP+6% DPER small agglomerates are visible (Fig. 10c), which in the composite K2, containing 15% APP, 5% DPER and 3% BSQPS (Figure 10d) are reduced, thereby lowering the average particle size from 98,6 to 76,3 nm. Differences in the topography of the composites, in terms of the calculated average roughness (Ra), were also

observed. The average roughness increased from 5,68 nm for the unfilled epoxy resin to 9.51 nm for composites K0, to 18,1 and 24,8 nm for composites K14 and K2, respectively. To eliminate noise before determining the roughness, a first-order smoothing function was used. These results confirm that replacement of a part of commercial flame retardants with 3 wt.% of bentonite improves dispersion of additives which may a beneficial effect of the mechanical properties.
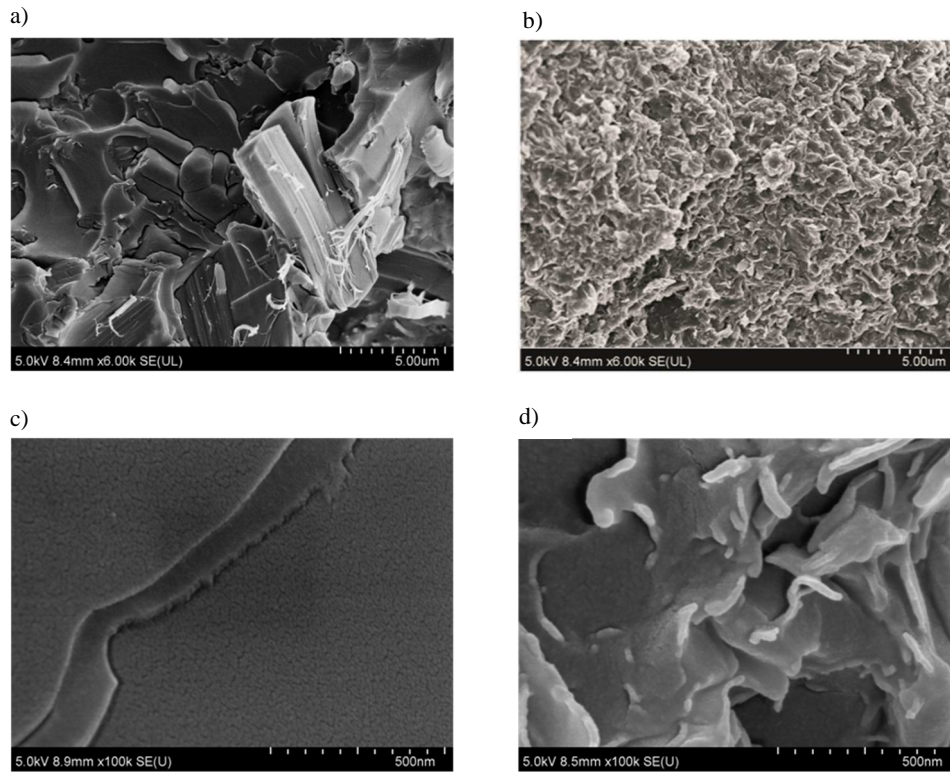
a)

b)

c)

d)

Fig. 9. SEM microphotographs of brittle fractures: EP with addition of 17% APP and 6% DPER (K14) (a, c) and EP with addition of 15% APP, 5% DPER and 3% BSQPS (K2) (b, d)

4. Conclusions

The effect of bentonite and flame retardant content on the mechanical properties of epoxy composites reinforced with unidirectional carbon fabrics was determined. The tensile test, flexural test, impact strength in the direction parallel and transverse to the direction of fibers were evaluated in order to verify the synergetic action of additives. The local strain and stress on the surface of

composites using the Aramis system during the static tension was examined. Studies of structure of curved epoxy compositions were also analized.
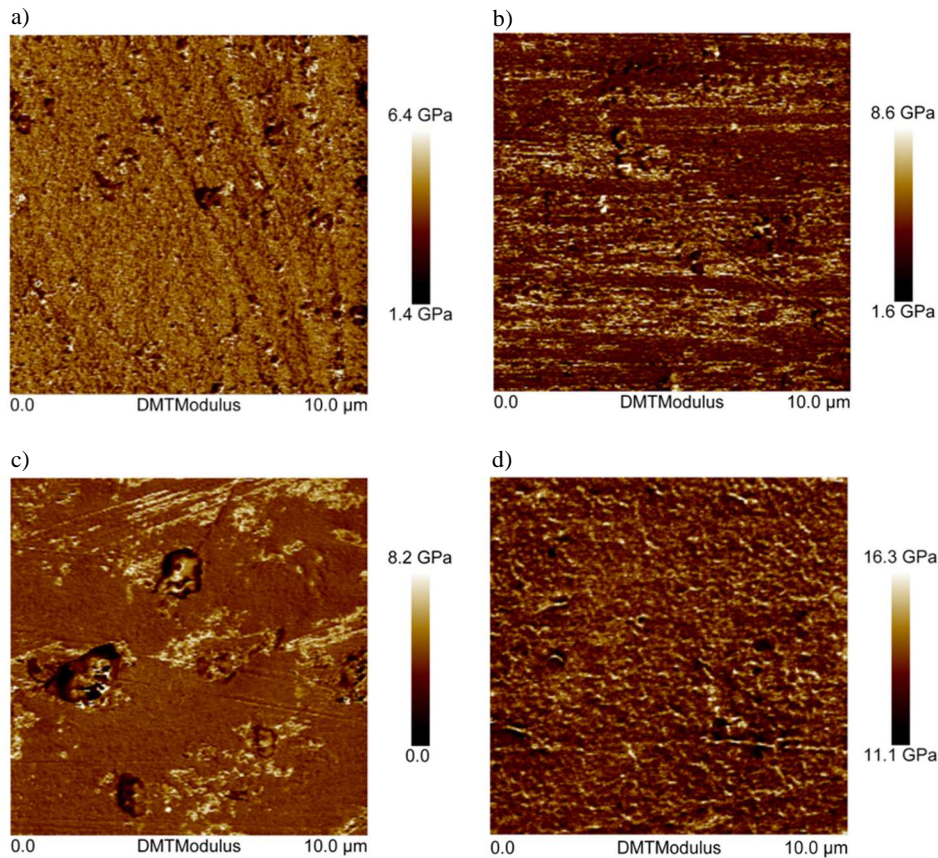

Fig. 10. AMF microphotographs made using QNM technique of surface of unfilled EP6 (a) and composites: EP6 + 3% BSQPS1 (b), EP6+17%APP+6%DPER (c), EP6+15%APP+5%DPER+3%BSQPS (d)

The results indicate that replacement of a part of a commercial flame retardant with 3 wt.% organoclay, improved the mechanical properties. The BSQPS acted synergistically with the commercial flame retardants as fire resistance and in Young's modulus and Izod impact resistance improving. The Aramis graphs of the stress and strain distribution indicate that the highest stress and strain values on the surface were determined for laminates prepared using unmodified matrix which was also characterized by the highest ultimate tensile strength.

The AFM and SEM results showed that the addition of bentonites to epoxy compositions containing flame retardants improved dispersion of them. The brittle

fracture of composites containing APP, DPER and BSQPS was much rougher than this on of composites containing the commercial flame retardant (APP, DPER) only.

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