

Mechanical strength of epoxy/organoclay/carbon fiber hybrid composites

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Abstract: The influence of organoclay (bentonite BS) modified with quaternary ammonium (QAS) and phosphonium salts (QPS) on the mechanical properties of epoxy/organoclay/carbon fiber hybrid composites was investigated. The longitudinal flexural strength of the composites containing 1 wt % BSQAS and BSQPS increased by 4 and 10 %, respectively, compared to the reference sample (epoxy resin/carbon fiber). Moreover, there was also a significant improvement, up to 13 %, of Young's modulus and transverse elastic modulus for the composites with modified bentonites. On the basis of the atomic force microscopy cross-section analysis (AFM), it was found that the composites with matrix containing the modified bentonites were characterized with larger interfacial surface, about 50 %, than that of unmodified matrix (epoxy resin/carbon fiber).

Keywords: epoxy/carbon fiber nanocomposites, bentonite, mechanical properties, electron microscopy.

Wytrzymałość mechaniczna hybrydowych kompozytów polimerowych

Streszczenie: Zbadano wpływ dodatku glinokrzemianu (bentonit BS) modyfikowanego czwartorzędowymi solami amoniowymi (QAS) lub fosfoniowymi (QPS) do nienasyconej żywicy epoksydowej (EP6) na właściwości mechaniczne hybrydowych kompozytów wzmocnionych włóknem węglowym (żywica epoksydowa/glinka/włókno węglowe). Stwierdzono, że dodatek 1 % mas. BSQAS lub BSQPS do osnowy żywicy EP6 powoduje zwiększenie wytrzymałości na zginanie w kierunku równoległym do ułożenia włókien węglowych o, odpowiednio, 4 i 10 % w porównaniu z wytrzymałością kompozytów na osnowie niemodyfikowanej (żywica epoksydowa/włókno węglowe). Dzięki modyfikacji uzyskano również wyraźną poprawę (powyżej 13 %) modułu Younga oraz modułu elastyczności. Na podstawie badań z zastosowaniem mikroskopii sił atomowych (AFM) stwierdzono, że kompozyty na osnowie żywicy epoksydowej zawierającej modyfikowane glinokrzemiany charakteryzują się większą (o ok. 50 %) powierzchnią międzyfazową na granicy włókno węglowe-polimer niż kompozyty na osnowie żywicy bez udziału glinki (żywica epoksydowa/włókno węglowe).

Słowa kluczowe: nanokompozyty epoksydowo-węglowe, bentonit, właściwości mechaniczne, mikroskopia elektronowa.

Carbon fiber-reinforced polymers (CFRP) are recognized among the most advanced and attractive structural materials in aerospace, marine, defense and other industries, since they exhibit high strength-weight and modulus-weight ratios. Among polymer matrices commonly used in fiber-reinforced composites are thermosetting resins such as epoxy (EP) and vinyl ester (VE) or unsaturated polyester resins (UP), which are cheaper and have lower viscosity than epoxy, nonetheless are characterized by worse mechanical strength, chemical and thermal stability and much higher processing shrinkage [1]. However, cured epoxy resins are fairly brittle and show low toughness. Over the past decade, a significant amo-

unt of work has focused on improving the properties of epoxies with the use of nanoclays. Nanoparticles such as organoclay, due to their high aspect ratio and unique intercalation/exfoliation characteristics, are commonly used for improving, *e.g.*, mechanical and thermal properties [2–6], or for reducing moisture and gas permeation [7–9]. Some studies have shown potential improvement in the properties of fiber-reinforced composites, in which organoclay was incorporated. The failure mechanism of fiber-reinforced composites depends on the direction of force. During flexural test, delamination is a major damage mechanism, while fiber breakage determines the ultimate tensile strength. The incorporation of nanosized second phase has been widely believed to significantly improve polymer mechanical properties by effective load transfer at the fiber-matrix interface. The bonding between matrix and fiber depends on the chemical and molecular structure of the fiber and the matrix, as well

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as the morphological and atomic arrangement. Thus, the interfacial adhesion is specific to each polymer and fiber. Moreover, the fiber-matrix adhesion can be attributed to various mechanisms such as adsorption and wetting, as well as the electrical and chemical bonding [10]. Fiber-matrix bonding could be improved by filling the matrix with nanoparticles such as carbon nanotubes (CNT), silica and organoclay [11–17]. Khan *et al.* [18] have investigated the influence of octadecylamine modified montmorillonite on fracture resistance and mechanical properties of nanocomposites and the corresponding carbon fiber/epoxy hybrid composites. The flexural strength and modulus of the nanocomposites were increased by 13 % and 21 %, respectively, with 3 wt % clay content, whereas the improvements in the flexural strength and modulus of carbon fiber-reinforced composites were less prominent, *i.e.*, 9 % and 7 %, respectively. Siddiqui *et al.* [19] have also applied octadecylammonium modified montmorillonite to carbon/epoxy/clay composites. The organoclay content was varied between 0, 3, 5 and 7 % of the epoxy resin weight. The mixture of resin and clay was subjected to sonication using an ultrasonicator at an ultrahigh frequency for 12 h at 75 °C. They observed that the flexural modulus slightly increased whereas the flexural strength marginally decreased with higher clay content. On the other hand, Xu and Hoa [20] showed that a small amount of nanoclay (2 phr) added into the epoxy of carbon/epoxy composites could enhance the flexural strength and mode I interlaminar fracture toughness by 38 % and 53 %, respectively. A similar tendency was also achieved in the mechanical properties of woven carbon fabric-reinforced laminates as a result of adding 0.6 vol % silanized clay [21]. The flexural modulus, tensile modulus and mode I interlaminar fracture toughness increased by 24 %, 16 % and 14 %, respectively. The SEM microphotographs (scanning electron microscopy) of the CFRP composite containing nanoclay presented a rougher matrix surface than those with neat epoxy, which could be responsible for the improved mechanical properties. The delaminations and alignment of nanoclay along the fiber axis were additional failure mechanisms in the CFRP hybrid composites.

Therefore, the behavior of nanofillers and fillers in fiber-reinforced composites is an interesting area of research. In our previous study we observed an enhancement of mechanical and thermal properties in unidirectional epoxy/clay/glass fabric composites [22]. The objective of the present study was to investigate the influence of clay content on the mechanical and thermal properties of unidirectional carbon fabric-reinforced epoxy composites.

EXPERIMENTAL PART

Materials

The resin matrix used in this study consisted of diglycidyl ether of bisphenol A epoxy resin Epidian® 6 (EP6) and triethylenetetramine (Z1) used as the curing agent,

both commercial grade products of Ciech-Sarzyna Plant, Poland. The resin : hardener ratio was 100 : 13 by weight as per the manufacturer's recommendations.

To make the epoxy/organoclay nanocomposite, the resin was mixed with bentonite (BS) "Specjal" (Zębiec SA Plants, Poland) modified with a butyltriphenylphosphonium chloride (BSQPS, $d_{hkl} = 21.5 \text{ \AA}$) or benzyl C12–C14-alkyldimethylammonium chloride (BSQAS, $d_{hkl} = 29.6 \text{ \AA}$) [22]. The procedure of modifying smectic clays with quaternary ammonium or phosphonium salts had been previously patented [23, 24] and described in detail in our previous papers [22, 25]. Unidirectional carbon fabric 200 g/m² (TC) purchased from Havel Composites was used as the main reinforcement. All the materials were commercial grade and used without further purification or modification.

Preparation of epoxy/organoclay compositions and epoxy/organoclay/carbon fiber compositions laminates

The organoclay was dispersed in the epoxy matrix (EP6) using four step homogenization procedure [25]. The hardener (Z1) was then added to the mixture. The epoxy compositions containing 0, 1 and 3 wt % organoclay were used for the preparation of four-ply epoxy/clay/carbon fiber composites using hand lay-up technique [26]. The fiber-weight ratio was kept at 40 % in total resin with carbon fiber content. 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 samples were cut from the laminates in the parallel [0] and transverse [90] directions with respect to the direction of fibers, with an oscillating cutting disk. The samples were used to measure the mechanical properties.

Methods of testing

– Plate specimens (200 x 20 x 1.5 mm) were employed to perform tensile tests according to ISO 527-1:1998 using Instron 5967 machine. All specimens were tested at a speed of 2 mm/min in the longitudinal direction with respect to the direction of the carbon fiber.

– The static bending tests in the transverse [90] and longitudinal [0] direction of carbon fiber were performed according to EN ISO 14125, using the same tensile machine equipped with a three point flexure fixture. The vertical displacement speed of the rig during the test was 1 mm/min. The specimens were 100 mm long, 15 mm wide, 3 mm thick and the span was 80 mm.

– Short beam shear test was applied to the laminates to determine the interlaminar shear strength (*ILSS*), in accordance with PN EN 2563 using the MTS-Q test 10 kN machine. The testing was done on short beams of 25 x 15 x 3 mm at a cross-head speed of 1 mm/min. The *ILSS* was determined using equation (1):

$$ILSS = \frac{3P}{4bh} \quad (1)$$

where: P – the peak load (N), b, h – the width and thickness of the specimens (mm), respectively.

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

– The limiting oxygen index (LOI) for the samples (100 x 10 x 3 mm) was determined according to the standard EN ISO 4589-3 at room temperature using Fire Testing Technology Ltd instrument (United Kingdom).

– The brittle fracture morphology of the laminates was analyzed using scanning electron microscopy (Phenom ProX desktop SEM, Netherlands). The fractured specimens were obtained after cooling in dry ice and impact-break.

– The interfacial surface between carbon fiber and epoxy matrix was examined using an atomic force microscope (AFM) by means of the Quantitative Nanomechanical Property Mapping (QNM) technique.

– The influence of the modified bentonite on the interphase was determined based on the local changes of the Young's modulus. The tests were performed using a Nanoscope V microscope (Bruker Nano Surfaces Division, USA) with a RTESPA probe with spring constant $k = 80$ N/m. The scanning speed was 1 Hz, and the resolution 512 lines.

RESULTS AND DISCUSSION

Limiting oxygen index

As it is shown in Fig. 1, the addition of modified bentonites improves limiting oxygen index of prepared laminates. Furthermore, it was found that the LOI of the composites slightly increase with organoclay loading. The highest improvement in LOI was recorded for laminates with matrix containing 3 wt % BSQPS. The oxygen index increased by 4.8 % O_2 , compared to the reference sample, while the LOI of EP6+3%BSQAS/carbon fiber composite

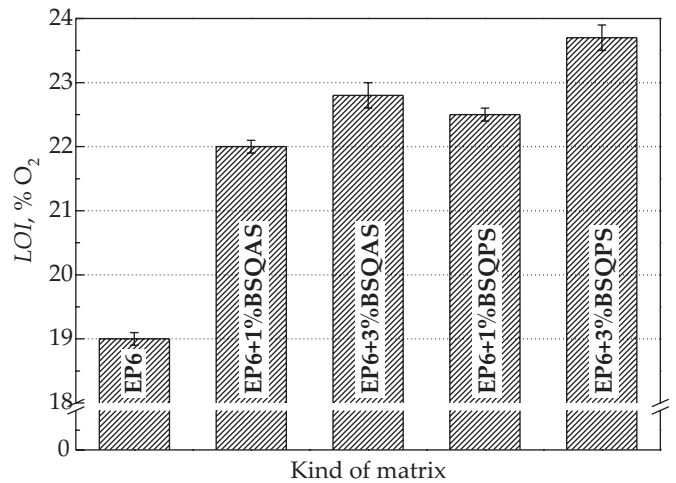


Fig. 1. Limiting oxygen index (LOI) of investigated composites

increased by 3.5 % O_2 . The improvement of fire resistance for the composites with modified bentonites is attributed to increased barrier properties as a result of creating a maze or tortuous path that retards the progress of oxygen and flammable gases as well as combustible products of polymer degradation through the material [27]. Moreover, the modified organoclays promote the formation of tight char with improved thermal resistance caused by silicon accumulation. As a result, it decreases the heat release rate from the surface [28].

Longitudinal tensile strength and longitudinal flexural strength [0]

Addition of modified bentonites led to a decrease in the tensile strength (σ_{T0}) in the direction parallel to carbon fibers in the reinforced composites (Table 1). The composites prepared with EP6 matrix containing 1 wt % modified bentonites had slightly lower tensile strength within the range of measurement error, while the tensile strength significantly decreased, by 23 and 25 %, for the composites containing 3 wt % BSQAS and 3 wt % BSQPS, respectively, compared to the composites with unmodified EP6 matrix. In the case of Young's modulus (E_{T0}), the different results were obtained. For the composites prepared with the matrices containing 1 wt % of BSQAS and BSQPS Young's modulus was higher by 10 and 11 %, re-

Table 1. Longitudinal tensile (T0-index) and flexural (F0-index) properties of prepared composites

Matrix	σ_{T0} MPa	E_{T0} GPa	ε_{T0} %	σ_{F0} MPa	E_{F0} GPa	ε_{F0} %
EP6	519.7 ± 5.3	36.33 ± 0.11	1.47 ± 0.05	590.0 ± 25.3	28.82 ± 0.92	2.14 ± 0.12
EP6+1%BSQAS	490.1 ± 12.8	39.91 ± 1.42	1.25 ± 0.14	615.4 ± 29.4	28.39 ± 1.55	2.55 ± 0.14
EP6+3%BSQAS	400.5 ± 27.4	37.45 ± 1.09	1.10 ± 0.15	566.6 ± 21.4	27.71 ± 2.12	2.22 ± 0.13
EP6+1%BSQPS	486.7 ± 31.7	40.25 ± 1.28	1.23 ± 0.18	652.6 ± 28.0	28.71 ± 1.13	2.53 ± 0.08
EP6+3%BSQPS	388.5 ± 27.1	36.39 ± 1.15	1.10 ± 0.06	594.7 ± 25.0	25.66 ± 1.01	2.51 ± 0.06

± number – standard deviation, σ_{T0} – tensile strength, E_{T0} – Young's modulus, ε_{T0} – strain at maximum tensile strength, σ_{F0} – flexural strength, E_{F0} – flexural modulus, ε_{F0} – strain at maximum flexural strength.

spectively, in comparison to the unmodified one. This enhancement could be attributed to the improvement of matrix stiffness but the brittle behavior of the matrix should be responsible for the decrease in tensile strength. Moreover, Young's modulus of EP6+3%BSQAS/carbon fiber composite slightly increased, by 3.5 %, while no changes for EP6+3%BSQPS/carbon fiber composite compared to the reference sample (EP6/carbon fiber) were observed.

Contrary, the composites prepared with matrices containing 1 wt % of BSQAS and BSQPS had higher longitudinal flexural strength (σ_{F0}), by 4 and 10 %, respectively, than that of composite with unmodified matrix (Table 1). Moreover, among the composites with the modified matrices, EP6+1%BSQPS/carbon fiber composite was characterized by the similar Young's modulus value (E_{F0}) as in the case of the laminates with pristine EP6. However, increasing the content of BSQPS above 3 wt % resulted in a slight decrease of the modulus, by 11 %, compared to the reference sample (EP6/carbon fiber). The obtained results confirm that using 1 wt % modified bentonite gives better composite properties and that the longitudinal flexural strength is determined by the fiber properties.

Transverse flexural strength [90]

In contrast to the study in the direction parallel to the direction of carbon fibers, which was mainly determined by the delamination mechanism of failure, the transverse flexural strength mainly depends on the morphology of the epoxy matrix as well as its adhesion forces to the carbon fiber. It was found that the transverse flexural strength (σ_{F90}) of the laminates prepared using the modified matrix did not change significantly compared to the σ_{F90} of EP6/carbon fiber composites (Table 2). However, the composites with the modified matrices were characterized with higher elastic modulus (E_{F90}) 9–13 %, compared to the E_{F90} of unmodified compositions. In the case of the transverse tensile modulus, an improvement could be attributed to the stiffened behavior of the matrix modified by organoclay and to the improved interfacial adhesion [29]. In order to understand the tensile and flexural mo-

Table 2. Transverse flexural properties of prepared composites

Matrix	σ_{F90} , MPa	E_{F90} , GPa	ϵ_{F90} , %
EP6	50.99 ± 0.93	3.58 ± 0.07	1.52 ± 0.15
EP6+1%BSQAS	50.32 ± 2.53	4.05 ± 0.18	1.28 ± 0.05
EP6+3%BSQAS	51.68 ± 2.77	3.96 ± 0.09	1.43 ± 0.08
EP6+1%BSQPS	49.97 ± 2.10	3.89 ± 0.10	1.34 ± 0.13
EP6+3%BSQPS	50.38 ± 1.98	3.98 ± 0.20	1.37 ± 0.11

± number – standard deviation, σ_{F90} – transverse flexural strength, E_{F90} – transverse flexural modulus, ϵ_{F90} – strain at maximum flexural strength.

dulus enhancing mechanism, the failure surfaces of the samples were examined using scanning electron and atomic force microscopy.

Interlaminar shear strength (ILSS)

The results presented in Fig. 2 indicate that the interlaminar shear strength of composites slightly decreased with an increase in organophilized layered aluminosilicates loading. Also, the composites containing 1 wt % of

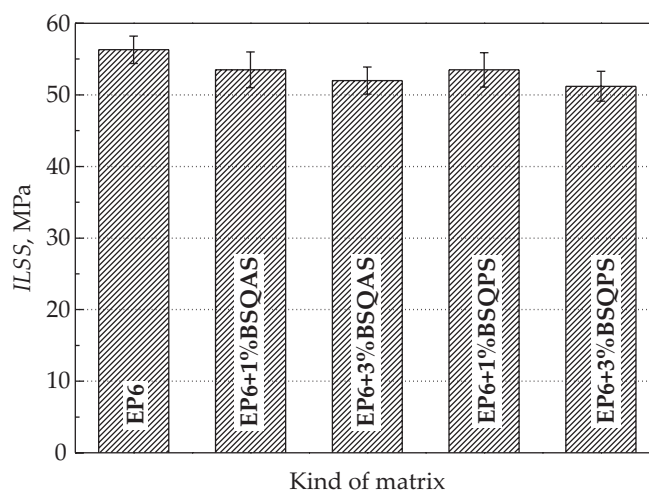


Fig. 2. Interlaminar shear strength (ILSS) of investigated composites

the modified bentonites had slightly lower ILSS, by ~ 4 %, in the range of measurement error. On the other hand, the ILSS of the laminates prepared from the compositions containing 3 wt % BSQAS and 3 wt % BSQPS decreased by 7 and 9 %, respectively, compared to the ILSS of laminates made from unmodified epoxy resin. Moreover, other studies suggested the orientation effect of organoclay platelets along the carbon fiber and the crack propagation direction. This alignment may be detrimental as it does not provide any mechanism to stop or retard the propagating crack and therefore may be the reason behind the reduction in the interlaminar shear strength [17, 30]. Given that the main damage of laminates during ILSS tests is delamination as well, the improvement of longitudinal flexural strength is attributed to different sample geometries and loading modes in these tests.

Transverse Charpy impact strength [90]

As shown in Fig. 3, the filling of epoxy matrix with 1 wt % organoclay slightly improved transverse impact strength of carbon fabric-reinforced laminates. The impact strength of the composites containing 1 wt % BSQAS and 1 wt % BSQPS increased by 6 %, compared to the reference sample. Greater improvements in the examined property, by about 11 %, were obtained for the laminates with 3 wt % modified bentonites. These findings confirm that the presence of modified bentonite in the ma-

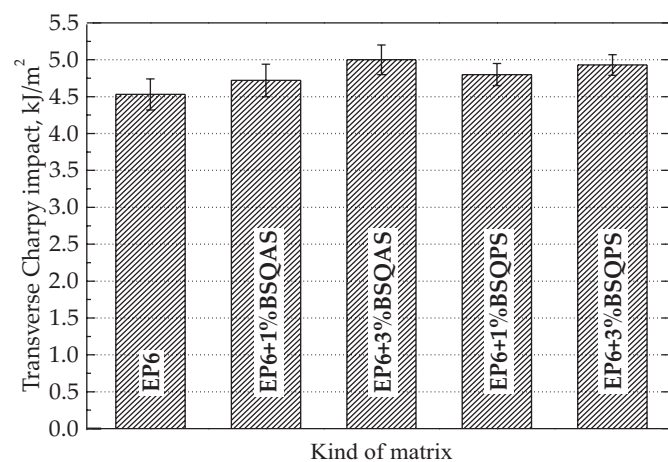


Fig. 3. Transverse Charpy impact strength of investigated composites

trix can improve interfacial interactions between carbon fibers and epoxy matrix. However, the improvement of transverse Charpy impact as well as transverse flexural strength of unidirectional carbon fabric-reinforced composites is still lower, compared to epoxy nanocomposites without carbon fiber. As it is well known, organoclay

changes the morphology of epoxy as well as other polymer nanocomposites, as a result of which significant improvements in mechanical properties of nanocomposites are observed [31–33].

Morphology of epoxy/organoclay/carbon fiber composites

SEM microphotographs of brittle surfaces of composites, as shown in Fig. 4, indicate that the filling of epoxy matrix with modified bentonites significantly changes the fracture surface morphology of the hybrid composites. The fracture surface of the composites with unmodified epoxy matrix is smooth. Furthermore, the striations and flow were observed, which indicates that the failure is brittle in nature (Fig. 4a). This suggests that the resistance for crack propagation is lower, which results in a decreased strength. In spite of this the brittle fracture of the composites with modified bentonites show a much rougher fracture surface (Fig. 4b). Just like the extent of morphology could be improved, the interfacial adhesion between carbon fiber and epoxy matrix has also increased the tortuous path of propagating the crack [34]. In

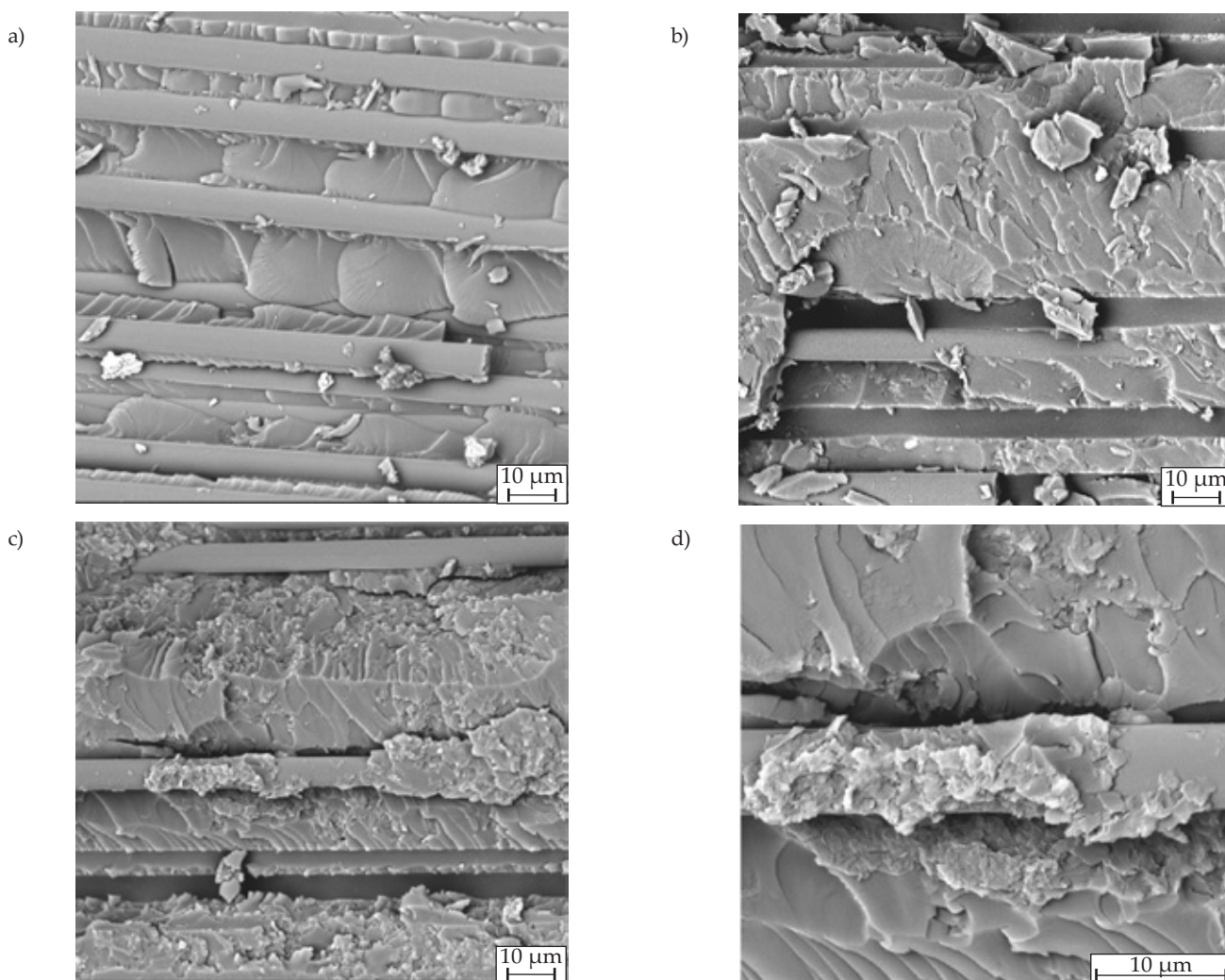


Fig. 4. SEM microphotographs of brittle fractures of hybrid composites with matrices: a) EP6, b) EP6+1%BSQAS, c) EP6+3%BSQAS, d) EP6+3%BSQAS with higher magnification

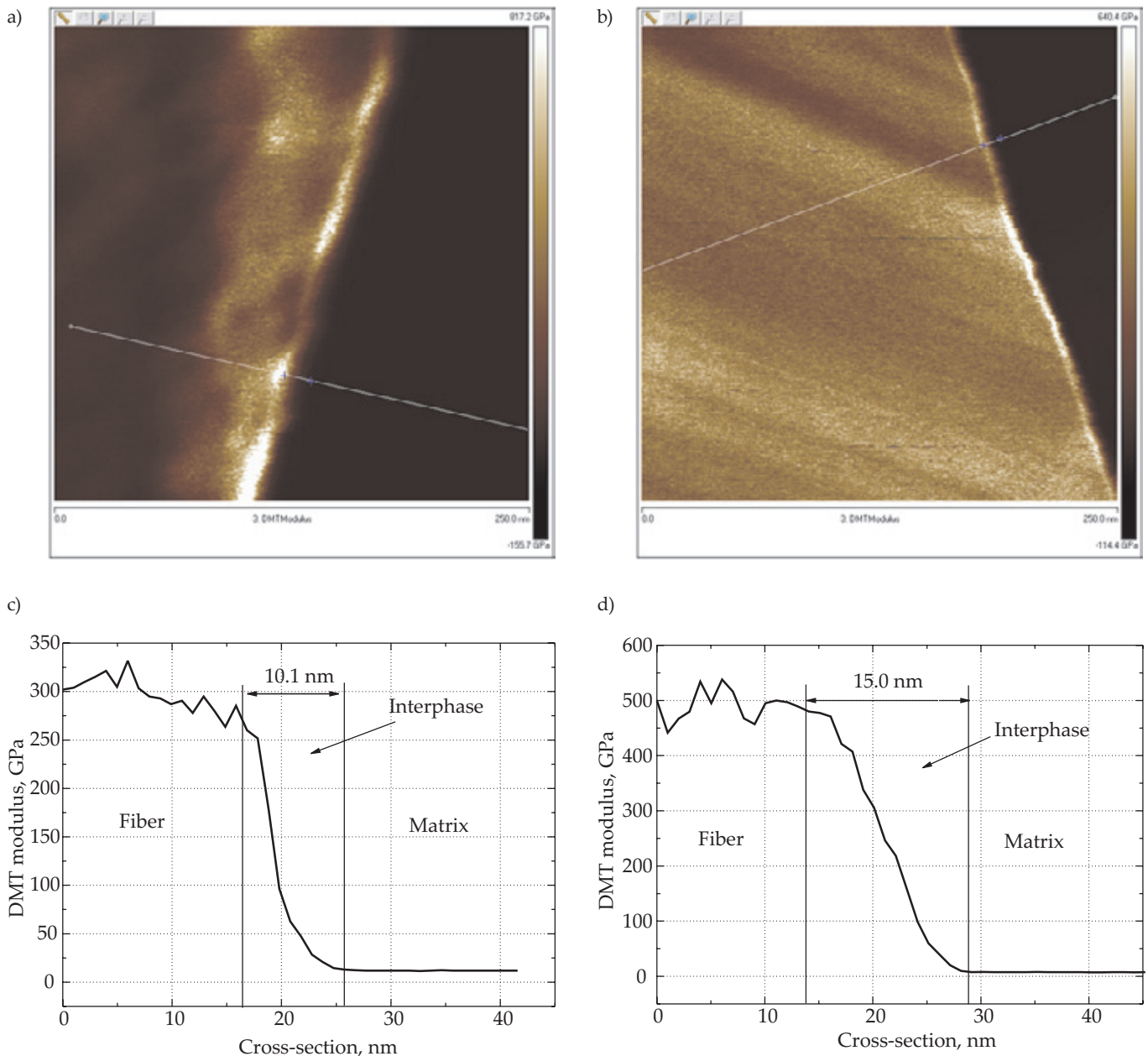


Fig. 5. AFM microphotographs of interfacial surface made using QNM technique and section analysis of the interphase of composites with matrices: a, c) EP6, b, d) EP6+1%BSQAS

the case of composites with 3 wt % organoclay the roughness increased, but small agglomerations were observed (Fig. 4c). These agglomerations may have acted as flaws and crack initiation sites, which resulted in poorer mechanical properties. Moreover, the presence of agglomerates of modifiers resulted in a difficult transfer of loads as well as deformations of the matrix on the fiber which led to a reduction in the ultimate tensile strength and flexural strength, especially in the direction parallel to the direction of the fibers. Nevertheless, images of surface fractures acquired from the EP6+3%BSQAS/carbon fiber composites indicate good adhesion between epoxy matrix and carbon fiber (Fig. 4d). These results confirm that the addition of 3 wt % bentonite improves interfacial adhesion which may be a beneficial effect for the transverse mechanical properties.

AFM analysis of composites interphase area

As defined in [35], the interphase begins at some point on the surface of fiber, wherein the local fiber properties, *e.g.*, modulus, start to change by interacting with the matrix and it extends up to the place where the Young's modulus approaches the value typical of the matrix. The interphase possesses neither the properties of the reinforcing phase nor those of the matrix. Focusing on local mechanical stiffness, the respective size of the interphase may be defined by the width of the cross-section region of interfacial surface [36]. The size of the interphase can range from nanometers to micrometers [37].

The DMT modulus (based on Derjaguin-Muller-Toporov model) images obtained from the cross-section of the carbon fabric-reinforced composites with two matrices

are shown in Fig. 5a, b. The interphase region shows a transitional modulus which is higher than that of the matrix and lower than that of the fiber. It was found that the modulus of laminates prepared with unmodified matrix sharply changed from the carbon fiber and epoxy matrix region (Fig. 5c, d). In the case of the composites with epoxy matrix containing 1 wt % BSQAS the interfacial region is ~ 50 % larger than this one for unfilled matrix. The larger interphase could be attributed to the improved compatibility between the modified matrix and fiber. This suggestion was confirmed by SEM analysis. Expanded interfacial area can transfer load from the epoxy matrix to the carbon fibers uniformly. However, an interphase with higher modulus than that of surrounding polymer results in greater strength but lower fracture resistance [38, 39].

CONCLUSIONS

Bentonites treated with quaternary phosphonium or ammonium salts were used as modifiers in unidirectional carbon fabric-reinforced epoxy composites. The contents of the modified bentonites varied in the range of 1–3 wt %. The results showed a slight improvement in the mechanical properties. The longitudinal flexural strength of the hybrid composites containing 1 wt % BSQAS and BSQPS increased by 4 and 10 %, respectively, compared to the reference sample. Moreover, there was also a significant improvement, up to 13 %, of Young's modulus and transverse elastic modulus in the hybrid composites with modified bentonites, compared to unmodified composites. Scanning electron microscopy (SEM) and atomic force microscope (AFM) confirmed better compatibility between the epoxy resin compositions and the carbon fiber for modified than that for unmodified matrix. It was found that the composites with epoxy matrix containing the modified bentonites were characterized with larger interfacial surface and a much rougher fracture morphology. Despite this, the deterioration of tensile strength could be attributed to the alignment of nanoclay platelets along the fiber axis which may have acted as crack initiation sites.

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