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EFFECT OF LAYERED SILICATES ON MECHANICAL PROPERTIES OF CARBON FIBER FABRIC EPOXY LAMINATED COMPOSITES

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The paper presents the obtaining, characterization and testing of hybrid composites based on montmorillonite layered silicates filled DGEBA (diglycidyl ether of bisphenol A) epoxy resin based matrix and carbon fiber fabric. The nanocomposite matrix was processed via ultrasonication, and the final nanofilled matrix/carbon fabric laminates were obtained by direct contact and room temperature pressing. The nanocomposite laminates were tested under tensile and 3-point bending, exhibiting overall superior mechanical performance compared to the sample without nanofiller. The results showed that 2% montmorillonite content ensures the highest strength and modulus of carbon fabric based composites.

Keywords: carbon fiber composites, montmorillonite, tensile strength

1. Introduction

In the last decades, the use of composite structures in both aeronautics and automotive applications has increased tremendously. In 1982, 8% of Airbus A130 was composed of composite materials, twenty years later the percent increased up to 25% for Airbus A380 [1], while nowadays composite materials represent 53% of Airbus A350 XWB and 50% of Boeing 787 Dreamliner structure. This high percentage is reported to generate 20 – 25% reduction in fuel consumption [2].

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Today, the most used composites in aeronautics industry are CFRP (carbon fiber reinforced plastics), based on carbon fiber in form of bidirectional weave or unidirectional fibers and epoxy resin. One of the major issues of fiber reinforced composites is the weak interface between the phases that can lead to degradation of the final composite properties and premature failure. Therefore, studies focus on property enhancement through interface improvements, simultaneously with matrix performance improvements. One promising method is represented by inorganic nanoparticles embedment into the organic matrix of the fiber based composites. Nanometric fillers such as layered silicates, carbon nanotubes, nanofibers or metallic nanoparticles [3, 4] exhibit high specific areas, ensuring extensive interface with the matrix, that leads to large contact areas, the nanofiller/matrix interaction supporting a better reinforcing of the fibers. Experimental studies regarding layered silicate/epoxy/carbon fiber composites present different results in terms of mechanical properties, as a function of nanofiller content in the matrix. There are studies showing that organo-montmorillonite addition in epoxy matrix of carbon fiber satin fabric led to increase of compressive strength and modulus for 1-3% nanofiller content [5]. Montmorillonite/epoxy/carbon fiber fabric composites processed in autoclave showed flexural properties improvements for 2% nanofiller, followed by a decrease when using 4% content [6]. 3% montmorillonite in epoxy matrix of Kevlar fabric composites led to higher tensile and flexural stiffness, but lower strength [7]. The absence of intercalated/exfoliated structure of the montmorillonite/epoxy nanocomposite and poor dispersion led to mechanical properties decrease of both epoxy matrix and its glass fiber based composites. A 10% increase of flexural modulus was noticed at lower contents, followed by a decrease at higher contents, while strength was unaffected [8].

The paper presents a study concerning organo-montmorillonite addition effect on epoxy carbon fiber twill fabric based composites. The aim of the study was the evaluation of mechanical properties of nanofilled matrix composites reinforced with 11 carbon fiber fabric layers, as a function of nanofiller content, as well as an optimization of the most efficient nanofiller percent. The hybrid composites were characterized using physicochemical and morphological analysis and they were subjected to tensile and 3-point bending tests, exhibiting overall superior mechanical performance compared to the control sample.

2. Materials and Methods

2.1. Materials

The matrix was epoxy system, purchased from Policolor, Romania, based on diglycidyl ether of bisphenol A (DGEBA) resin (Ropoxid P401-Policolor), with 1400-2500 mPa·s dynamic viscosity and 222-250 g/eq epoxy equivalent, and triethylentetramine (I3361-Policolor) as curing agent. The layered silicate was Cloisite30B (Southern Clay Products), a montmorillonite with methyl, tallow, bis-2-hydroxyethyl quaternary ammonium salt intercalating agent. The carbon fiber was twill weave fabric with 193 g/m^2 areal weight and 3K warp (3000 filaments) produced by Chemie Craft, France, purchased from Polydis, Romania.

2.2. Nanocomposite laminates obtaining

The nanocomposite mixture was obtained by adding 1, 2 and 4 wt% Cloisite30B to the DGEBA resin, homogenization by ultrasonication using a probe for 15 min and using a sonication bath for 30 min at 60°C. The curing agent was added in a weight percent relative to DGEBA. 11 plies of carbon fiber fabric were impregnated with the mixture, using a roll to uniformly distribute the nanomodified matrix on the fabric surface. Each sample was pressed for 24 h at room temperature, using 3 kg/cm^2 pressure, in hydraulic CARVER press. The pressure value was established by trial program, and it was chosen high enough to obtain a compact laminated structure and low enough to avoid excessive drain of the impregnation mixture between the fabric plies before resin curing during pressing. Laminates with 2 mm thickness were obtained, and afterwards cut into specimens with specific geometry for tensile and flexural tests.

2.3. Nanocomposite laminates characterization and testing

The nanomodified matrix in the laminates was analysed using FTIR spectrometry (iN10 MX Mid Infrared FT-IR Microscope) and X-ray diffraction (Panalytical X'Pert PRO MPD diffractometer). The nanofilled laminates were mechanically tested by flexural (3-point bending) and tensile tests (INSTRON 5982), the fracture cross section was analyzed by scanning electronic microscopy (QUANTA INSPECT F microscope with 1.2 nm resolution) and the fracture mechanisms in mechanical testing were established using optical microscopy (Meiji 8520 microscope), at 40x magnification.

3. Results and discussion

3.1. Density and fiber content calculation

The hybrid laminates density values were calculated using the constituents' percentages and characteristics. The percentage that each constituent occupies in the laminated structure can be calculated using the characteristics of each constituent as well as final laminate weight and thickness [9].

The fiber volumetric content (the ratio between fiber volume in a definite volume of composite and the volume) was determined taking into consideration the average thickness of the sample:

$$V_f = \frac{n \cdot m_{0f}}{e \cdot \rho_f} \tag{1}$$

m_{0f} - fabric areal weight (kg/m^2), n- number of carbon fabric plies in the laminate, e- thickness of the final laminate.

The nanomodified matrix density was calculated for each montmorillonite content, using the equation:

$$\rho_{NC} = \frac{1+x}{\frac{1}{\rho_{pol}} + \frac{x}{\rho_{nanofiller}}} \quad (2)$$

x- montmorillonite weight content relative to the matrix, ρ_{pol}- cured epoxy density (g/cm^3), $\rho_{nanofiller}$- Cloisite30B montmorillonite density (g/cm^3).

The composite density can be calculated using the equation:

$$\rho = \rho_f V_f + \rho_m V_m. \quad (3)$$

ρ_f- fiber density, ρ_m- matrix density, V_f- fiber volumetric content, V_m- matrix volumetric content; $V_m = 1 - V_f$.

The relationship between volumetric and weight content of the constituents is defined by the following equations:

$$V_f = \frac{\frac{M_f}{\rho_f}}{\frac{M_f}{\rho_f} + \frac{M_m}{\rho_m}}; \; M_f = \frac{V_f \cdot \rho_f}{V_f \cdot \rho_f + V_m \cdot \rho_m}. \quad (4)$$

M_f- fiber weight content (ratio between fiber weight in a definite volume of composite and composite total weight); M_m- matrix weight content; $M_m = 1 - M_f$.

The average values obtained for each laminate are presented in Table 1:

Table 1

Hybrid nanofilled laminates characteristics

Sample	Thickness (cm)	Fiber volumetric content (%)	Fiber weight content (%)	Density (g/cm^3)
Epoxy/11FC	0.2	59	70	1.49
Epoxy+1%Cloisite30B/11FC	0.2	58	69	1.49
Epoxy+2%Cloisite30B/11FC	0.2	60	69	1.5
Epoxy+4%Cloisite30B/11FC	0.2	59	68	1.5

The average fiber/matrix volumetric ratio is 60/40, while weight ratio is 70/30, fitting in the optimum ratio values range for epoxy/carbon fiber composites [10], so that optimum fiber-matrix mechanical load transfer is achieved. Too high fiber contents lead to delamination and layers debonding, due to poor impregnation, while too low fiber contents lead to laminate premature failure due to matrix failure. The calculated density is insignificantly modified when adding higher nanofiller contents, the laminates average density being 1.495 g/cm^3, which is appropriate for lightweight materials.

3.2. FTIR spectroscopy

FTIR spectroscopy analyses were performed to evaluate the chemical interactions in montmorillonite filled/cured DGEBA matrix. Fig. 1 presents the spectra of epoxy control sample (cured DGEBA) and 1, 2, 4% Cloisite30B based samples. All spectra present the characteristic peaks of the cured DGEBA: N-H stretching (3480-3200 cm^{-1}), C-H stretching (2965-2930, 2864 cm^{-1}), C=C and C-C stretching from aromatic ring (1600, 1509 cm^{-1}), C-H bending (1457 cm^{-1}), C-O stretching (1374 cm^{-1}), C-H in plane bending (1288, 1238, 1180, 1119, 1030 cm^{-1}), C-H out of plane bending (944, 825, 742 cm^{-1}) [11, 12].

For Cloisite 30B based samples the band intensity increase in the region 1000-1100 cm^{-1} is due to Si-O from montmorillonite out-of-plane stretching vibrations, the intensity increasing with montmorillonite content increase. At 2850- 2960 cm^{-1} the peaks intensity increase is owned to the bending vibration of CH_3 from quaternary ammonium salt intercalating agent.

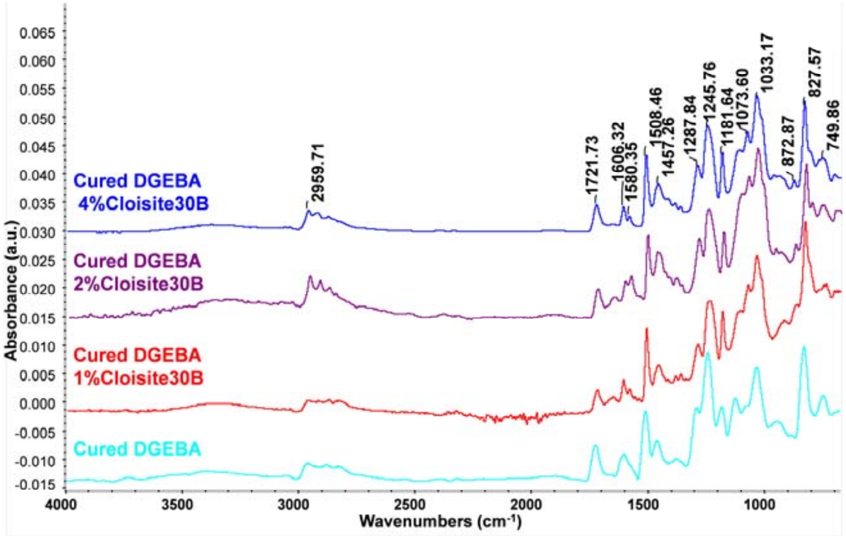

Fig. 1. FT-IR spectra of cured DGEBA, DGEBA+1%Cloisite30B, DGEBA+2%Cloisite30B, DGEBA+4%Cloisite30B

3.3. XRD analysis

X-ray diffraction analysis offer information on the nanofilled matrix structure, through the evaluation of the distance between the layers of the silicate gallery, to assess if the interaction between polymer chains and montmorillonite layers formed an intercalated or exfoliated nanocomposite or if the structure remained at microcomposite level [13, 14]. XRD was performed on nanofilled matrix flat samples processed in the same conditions as the laminated composites, because the matrix is mainly arranged in layers between the carbon fabrics and there is no supplementary interaction with carbon fiber in the 1-10° range of 2θ.

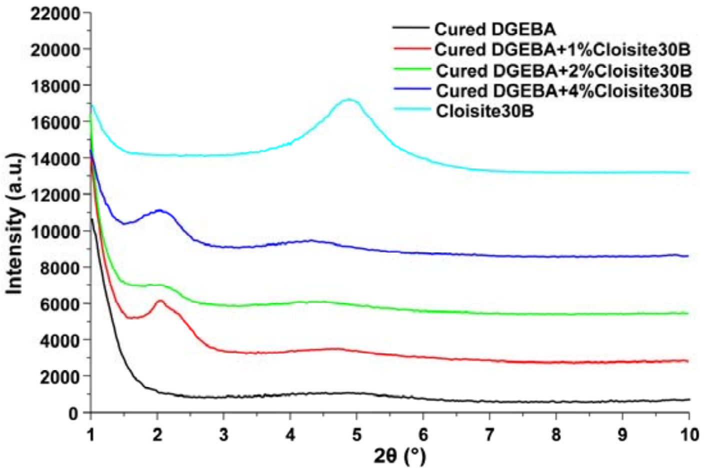

Fig. 2. X-ray diffraction spectra of the cured DGEBA, DGEBA+1%Cloisite30B, DGEBA+2%Cloisite30B, DGEBA+4%Cloisite30B and Cloisite30B

XRD spectra illustrate the characteristic peaks of Cloisite30B, cured DGEBA (epoxy) and nanofilled cured DGEBA. Cloisite30B distinctive peak appears at 4.9° value of 2θ, the distance between silicate layers being 18 Å. All nanofilled samples present a shift of this peak towards lower values, at approximately 2°. The distance between the layers increases up to approximately 43 Å for all nanofilled samples (42.63, 43.25, 42.3 Å for 1, 2 and 4% content), with the highest value for 2% Cloisite30B. Therefore, the polymer macromolecules diffused into the silicate gallery, increasing the distance between the montmorillonite layers and suggesting a high probability for the nanofilled matrix to have an intercalated/exfoliated structure. The complete disappearance of the peak would have supported the idea of exfoliated structure formation, in which the layered gallery is destroyed and the polymer chains are uniformly exfoliated between the silicate planes, however it is difficult to evaluate the intercalation/exfoliation degree by XRD only (since, if the nanocomposite presents a highly ordered structure, it can also lead to the peak disappearance).

3.4. Tensile testing of the nanofilled laminates

Tensile tests focused on the modification of tensile strength and Young's modulus of elasticity, in order to compare the nanofilled laminates with the control sample. The tests were performed on dumbbell specimens using 5 mm/min tensile rate [15]. Table 2 presents the properties average values and standard deviation (Std Dev) values obtained for each sample.

Table 2

Average values of tensile test results for the nanofilled laminates

Sample	Load at break (N)	Tensile strength (MPa) ± Std Dev	Young's Modulus (GPa) ± Std Dev	Tensile strain (%)
Epoxy/11FC	8433.5	408.8± 22.6	54.3 ± 0.07	0.9
Epoxy+1%Cloisite30B/11FC	7806	410.4 ± 28.3	48.4 ± 4.53	1.04
Epoxy+2%Cloisite30B/11FC	13092	635.8 ± 39.1	69.4 ± 2.62	1.06
Epoxy+4%Cloisite30B/11FC	10962	529.7 ± 17.56	63.6 ± 5.01	1.05

The average values of the tensile strength and stiffness of the nanofilled laminated composites show the positive effect of organo-montmorillonite addition. The materials having 2% Cloisite30B in the polymeric matrix presented the highest performance in tension, showing an increase of approximately 55% for tensile strength and 30% of Young's modulus compared to the control sample. 4% Cloisite30B based samples showed 30% tensile strength and 20% modulus improvements. The 1% Cloisite30B samples did not present significant changes in terms of tensile strength compared to the control sample, while Young's modulus presented a decreased value. In order to explain this exception, the fracture surface was examined by optical microscopy.

3.6. Tensile testing fractography

Tensile results were explained with the aid of optical microscopy analysys of the fractured area after tensile testing, the fractography supporting the numerical values obtained during mechanical testing. All nanocomposite laminates presented fracture mechanisms reported by literature [16, 17].

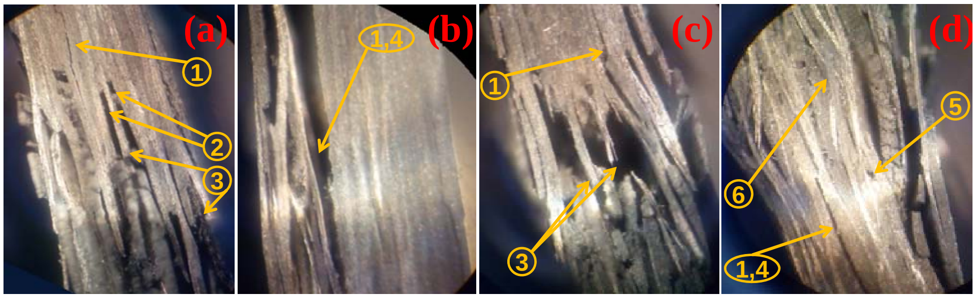

Fig. 3. Fracture area after tensile testing: (a, b) Epoxy+1%Cloisite30B/11FC, (c) Epoxy+2%Cloisite30B/11FC, (d) Epoxy+4%Cloisite30B/11FC with fracture mechanisms: (1) interface debonding/ crack propagation, (2) fiber pull-out, (3) fiber breakage, (4) delamination

1% Cloisite 30B based laminates fracture area shows that failure occurred by fiber breakage, but other dangerous phenomena occurred simultaneously. Fiber breakage generated areas were fibers were pulled out of the matrix, leading to interface debonding and cracks that propagated causing multiple layer delamination that extended over a larger area of the laminate length (**Fig. 3**b). The fiber breakage and pull out is often accompanied by longitudinal delamination, because of stress concentration sites.

2% Cloisite30B based samples images show that the main failure mechanism was by strain, explaining the higher tensile strength and stiffness. The fibers broke in areas with maximum stress, while in adjacent areas there are fibers that were debonded and pulled out of the matrix. Fiber pull out generated some minor interface debonding and subsequent microcrack propagation, that led to ply debond along the crack, while nearby areas remained undamaged.

In the case of 4% Cloisite30B based laminates the stress caused by mechanical loads led to fiber irreversible strain (similar to buckling effect from compression tests). This effect was sustained by matrix micro-cracking phenomenon that was not noticed in 1 and 2% based samples. The microcraks appear transverse to the load direction and they represent points were other effects arise, such as fiber breakage and cracks initiation sites that lead to delamination, finally generating laminated structure failure.

Regarding superior tensile performance of 2 and 4% Cloisite30B based samples compared to the 1% based samples, it is very likely that the isolated interface debonding acted as strain relief points, leading to higher tensile strength and stiffness materials. In the case of 1% Cloisite30B samples, the number of delaminated layers was probably too high for the delamination sites to be able to act as stress relief sources.

3.7. Flexural testing of the nanofilled laminates

3-point bending test was performed on rectangular specimens using 2 mm/min rate and conventional span length (depending on specimen thickness) [18]. The test was conducted until conventional deflection (bending until 1.5 of specimen thickness) and not until break, because mechanical performance of the material is sustainable only until this bending value. The average test results, as well as standard deviation values are presented in Table 3.

Table 3

Average values of 3-point bending test results for the nanofilled laminates

Sample	Maximum load (N)	Flexural strength (MPa) ± Std Dev	Flexural modulus (GPa) ± Std Dev
Epoxy/11FC	559	684 ± 27	50.7 ± 1.46
Epoxy+1%Cloisite30B/11FC	599	701.1 ±15.3	55.7 ±1.56
Epoxy+2%Cloisite30B/11FC	632	775.5 ± 36.5	56.3 ± 4.2
Epoxy+4%Cloisite30B/11FC	629.5	714.3 ± 0.46	52.3 ± 1.15

All nanofilled samples presented superior properties in bending compared to the control sample. The same result was obtained regarding optimum montmorillonite content, 2% Cloisite30B samples showing the highest increments compared to the control sample. Epoxy+2%Cloisite30B/11FC showed 14% higher average strength and 11% higher average modulus. 1 and 4% Cloisite30B contents showed some minor improvements, approximately 5% increase in flexural strength and 3 – 10% higher modulus.

3.8. Flexural testing fractography

Fractography was also performed on flexural tested specimens. The test was conducted until 1.5 of the specimen thickness deflection value, but all specimens presented fracture of at least one outer fabric layer. Flexural testing generates more types of stresses, as the middle point of the inner curve is subjected to compressive stress while the one of the outer curve suffers tensile stress. The fractography shows that most of the tested specimens presented failure of the outer layer due to bending of the composite, but in all samples there were specimens that showed several other fracture mechanisms.

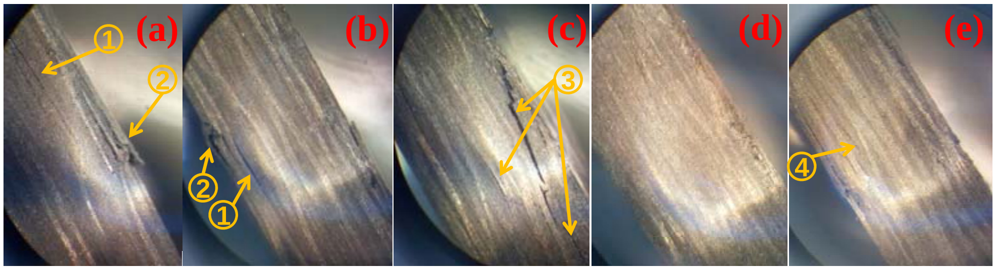

Fig. 4. Fracture area after flexural testing: (a) Epoxy/11FC, (b) Epoxy+1%Cloisite30B/11FC, (c, d) Epoxy+2%Cloisite30B/11FC, (e) Epoxy+4%Cloisite30B/11FC with fracture mechanisms: (1) crack propagation, (2) fiber breakage, (3) interlaminar crack propagation, (4) matrix microcraking

Fig. 4 illustrates specimens of each tested sample. One of the specimens of the sample without nanofiller shows the fracture of 3 outer fabric layers, while in the inner region it can be noticed that the stress induced during bending test led to delamination of two layers (Fig. 4a). In the 1% Cloisite30B based sample (Fig. 4b), both sideways layers failed. Inner curvature layers failed through compressive stresses in the load application point and outer curvature layers failed through tensioning due to specimen bending, leading to layer debonding in the adjacent areas, debonding that would have probably resulted in fiber layer breakage if the load application would have continued. In the case of 4 % Cloisite30B samples, along with outer layers failure, some specimens presented matrix microcracking phenomenon (Fig. 4e), explaining the modulus minor decrease compared to the other nanofilled laminates.

In the case of 2% Cloisite30B laminates, samples that presented the highest average mechanical performance, some specimens presented failure modes that caused more advanced overall damage of the laminates (Fig. 4c). The outer layer fracture generated cracks that propagated between several inner layers of the laminated structure, generating a more pronounced detachment. On the opposite, in this sample there were specimens that presented insignificant damage (Fig. 4d), showing almost unnoticeable fracture of the outside layer due to bending.

3.9. SEM analysis

The fracture cross section was further analyzed using SEM in order to evaluate the nanofilled matrix- fiber interface at higher magnification levels. SEM allows the observation of the nanofilled matrix layer on the surface of the fibers that compose the carbon fabric.

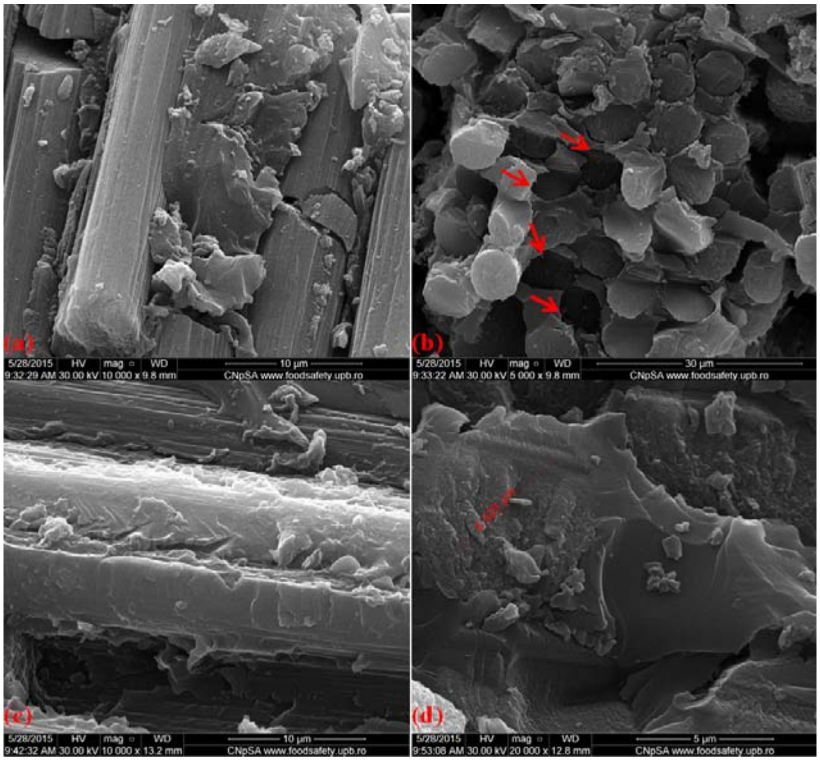

Fig. 5. SEM images of (a, b) Epoxy+1%Cloisite30B/11FC, (c, d) Epoxy+2%Cloisite30B/11FC

Fig. 5 illustrates the cross section of the samples based on 1 and 2% wt. Cloisite30B after tensile testing, representing the minimum and maximum tensile performance. In the case of 2% Cloisite30B based sample, SEM image captured at 10 000X magnification (Fig. 5c) illustrates the presence of nanofilled matrix attached on the fibers surface. Higher magnification level (Fig. 5d) shows a visible area where fiber and polymer broke simultaneously, the polymer remaining attached to the fiber without debonding, even after subjection to tensile stress generated during mechanical testing. This indicates a good interface between fiber and montmorillonite modified matrix.

SEM images of 1% Cloisite30B based samples complement both tensile test results as well as fractography investigations. Fig. 5a illustrates an area where the polymer detached along the fibers surface length following mechanical testing, and at lower magnification level (Fig. 5b) there are various visible points where the fibers were pulled out of the matrix cover (marked by red arrows). These observations are in compliance with the fractography that indicates larger delaminated areas in these composites.

In all cases, the hybrid composite fracture presents a brittle nature, due to both fiber and epoxy matrix brittle character.

4. Conclusions

The mechanical properties of organo-montmorillonite nanofilled epoxy composites reinforced with 11 carbon fiber fabric layers illustrate the positive effect generated by the nanofiller addition. The aim of montmorillonite addition is to improve the properties of the “weak” phase in the composite, represented by the polymer, allowing it to support higher mechanical loads. Stronger and tougher matrix enables the fibers to withstand lower mechanical loading leading to overall composite performance increase. The fracture mechanisms during tensile and bending are complex phenomena due to the hybrid nature of the materials. The results were explained taking into consideration the nanofilled matrix structure, interface between nanofilled matrix and fibers that constitute the fabric as well as fabric-matrix fracture mechanisms. X-ray analysis of the nanofilled matrix indicated that the highest intercalation/exfoliation degree was obtained when using 2% Cloisite30B. The carbon fiber fabric laminates obtained using this nanocomposite content formulation presented the highest mechanical performance both in tensile and flexural tests. SEM images showed that the 2% nanofilled matrix covers the fibers of the fabric, sustaining the good interface between the phases, while fractography shows that the emerging fractures generated stress relief phenomenon, suggesting the effective fiber-matrix mechanical load transfer. All these factors contribute to mechanical performance increase. Therefore, 2% Cloisite30B addition in the epoxy matrix is the optimum content to obtain best mechanical performance of nanofilled carbon fiber composites, leading to lightweight materials that could be used in automotive or aeronautics applications.

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