INVESTIGAȚII ALE PROPRIETĂȚILOR MECANICE ALE COMPOZITELOR EPOXY CU FIBRE DE CARBON, CARE ÎNCORPOREAZĂ NANO ARGILE ȘI NANO TUBURI DE CARBON CU PEREȚI MULTIPLI

INVESTIGATION OF MECHANICAL PROPERTIES OF CARBON FIBRE/EPOXY COMPOSITES INCORPORATING NANOCLAY AND MULTI WALLED CARBON NANOTUBE

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This study was conducted for the purpose of examining the mechanical relations of the multi-walled carbon nanotube (MWCNT) and the nanoclay (NC) with each other on the carbon fiber composite materials. Samples were prepared by reinforcing the MWCNT and the NC into the epoxy matrix at various rates to have them absorbed into the carbon fiber laminates via the vacuum infusion method. Carbon nanotube (CNT) was added into all the epoxy samples at a rate of 0.3 wt% of the epoxy weight, while the nanoclay was added at rates of 1 wt%, 3 wt% and 5 wt% of the epoxy weight. Additionally, the only CNT-reinforced samples (also, not reinforced with NC) were also readied in order to observe the difference. Tensile tests and three point bending tests were conducted to determine the mechanical properties. The NC and the CNT were observed to adhere to the carbon fiber filaments in the scanning electron microscope (SEM), and NC-based bridge cracks were noted.

Keywords*: Multi Walled Carbon Nanotube, Nanoclay, Tensile Test, Three Point Bending Test*

1. Introduction

Composite materials are important in the space, aviation and defense fields, as these sectors need lightness and strength rather than cost-effectiveness. For example, a manufactured plane can gain lightness when composite materials are added into it, this lowers the fuel cost and increases the distance gained during flight. As the first planes were being manufactured, one thing was noticed: the strength/weight ratio (specific strength) is a must as a criterium for the choice of material [1]. Today, new multi-functional composite materials with nano-components are being developed and tested in order to meet new design criteria, and produce pieces of equipment that are long-lasting and have high-safety factors. Examination and research of the laminated composite plates manufactured with the addition of CNT and highly-durable materials such as carbon fiber made the headlines of many papers.

Due to the high mechanic properties shown by the carbon nanotubes, the nano-structures gained prominence in the science world and researches. Because the CNT's are costly in their manufacture, their production methods improve more day-by-day to serialize their production and reduce the costs. Additionally, in the sectors of advanced material technologies; required criteria and high performance are essential factors, whereas the costs are trivial [2].

Nanoclays can make the materials that they are used in gain properties based on that specific material. To wit; strength, heat resistance, fire retardancy, friction resistance, ultraviolet protective effect etc.

Carbon fiber reinforced polymer (CFRP) composites are used widely in military planes [3,4]. For example, CFRP composites are used in the manufacture of A400M, F-22, F-35, Eurofighter [5], Eurocopter Tiger [6]. Fiber composite materials generally make up 40% of the structural mass and 70% of the surface area [7]. Other usage areas of CFRP composites are the pieces that require high heat resistance such motor bearings, mounts, air ducts etc [8]. The electrochemical properties of the nanotube and nanoclay, determining the electrical resistance and prospective studies have been made to improve the electrical and thermal properties [9-12].

N. A. Siddiqui, M. Sham, B. Z. Tang et al. (2009) covered the surfaces of glass fibers with CNT-reinforced epoxy, thereby they managed to improve the mechanical properties of the material by filling its capillary, brittle fractures. By using the 0.3% CNT-added epoxy matrix on the fiber surfaces, they were able to determine an increase in the tensile strength in the tests that they conducted at various fiber lengths, as the stress is distributed among the fibers much better [13].

K. L. Kepple, G. P. Sanborn, P. A. Lacasse et al. (2008) worked on the fracture toughness of

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the CNT-added carbon fibers. In the tests that they conducted with CFRP matrix composites in accordance with the ASTM D 5528 standards, they detected an increase in the fracture toughness by 50%, and another increase approx. by 5% in the three point bending tests related to the bending strength [14].

S. K. Singh, S. Singh, S. Sharma and V. Sharma (2014) added NC into the epoxy in rates of 1 wt%, 3 wt%, 5 wt%, which yielded a 10:4 hardening ratio in wt, 30% glass fiber and epoxy resin; they then manufactured composite laminates with the hand layup method and conducted tests on these samples. In the wake of the tests they conducted, it was concluded that the 3% reinforced samples gave the best results, in that their bending strength increased by 57% and their tensile strength increased by 8% [15].

L. P. Borrego, J. D. M. Costa, J. A. M. Ferreira, and H. Silva (2014) measured the fatigue strength of the glass fiber composite laminates, which they manufactured via the vacuum infusion method by reinforcing the MWCNT and the nanoclay into the epoxy matrix. Test results concluded that the propagation of capillary fractures was managed to slow down, as the MWCNT and NC acted as a barrier against fatigue fractures [16].

M. M. Rahman, S. Zainuddin, M. V. Hosur et al. (2012) utilized a functionalized MWCNT added epoxy matrix containing glass fiber at rates of 0.1 – 0.2 – 0.3 – 0.4 wt%, and conducted tests to research the material of optimum mechanical and thermo-mechanical characteristics on the composite plates that they produced using hand layup, then hot-press. In the fracture and Dynamic Mechanical Analysis (DMA) tests that they conducted, it was determined that the most appropriate added rate was 0.3 wt%; in addition, 37% - 21% - 21% increases were observed for the yield strength, the elasticity module and the strain, respectively [17].

This study was conducted for the purpose of utilizing the strength increasing properties of NC and CNT on the selected samples, providing appropriate design values and creating a basis for the studies to come to work upon. Tensile test and three point bending tests were conducted to determine the mechanical properties of the layered composite materials. SEM images were examined to identify the metallographic properties of the material manufacture via these tests. Conclusions were drawn regarding to the physical interaction of NC with CNT and the common mechanical properties both contributed to the material.

In the wake of the conducted literature research, it was determined that the 0.3% CNT ratio added into the epoxy via the vacuum infusion method provided the most appropriate digital and mechanical properties. However there is no information in the literature regarding the contribution of NC to the 0.3% CNT containing composites. To this end, CNT was kept stable at 0.3% and the matrix materials containing NC at various rates (1%, 3%, 5%) were prepared, composite plates were manufactured, mechanical properties were then examined.

2. Experimental (Materials and Manufacturing)

During the manufacture phase of the laminated composites produced as MWCNT/NC-added, the following was utilized; Timesnano TNM5 as the CNT, Tenax-E HTA 40 3k as the carbon fiber, Laminating Resin MGS L160 as the resin, Hardener MGS H160 as the hardening agent, EsanNANO 1-140 as the NC.

By taking basis from the previous studies, 4 different samples were prepared. The process took place as follows; the aforementioned MWCNT rate was kept to 0.3 wt%, the aforementioned NC rates were modified to be 1 – 3 – 5%, and in order to be able to draw comparisons, a mere 0.3% CNT reinforcement was used.

The amounts of MWCNT and Nanoclay that were added into the prepared samples are given in Table 1. To make samples easily understandable, carbon nanotube was shown as CNT and nanoclay as NC. The numbers next to them show the weight percents according the resin in the samples. The composite plates were produced from 12 layers carbon fiber.

The mechanical properties of the MWCNT and NC added into the epoxy were initially compared, they were then distributed in nanosize via ultrasonic homogenizers.

Table 1

Prepared samples

	MWCNT (%)	NC (%)
CNT0,3NC0	0.3	
CNT0,3NC1	0.3	1
CNT0,3NC3	0.3	3
CNT0,3NC5	0.3	5

The properties of the Timesnano Co Ltd.'s MWCNT that was used in the study are given in Table 2.

The Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM) images of this MWCNT are given in Figure 1.

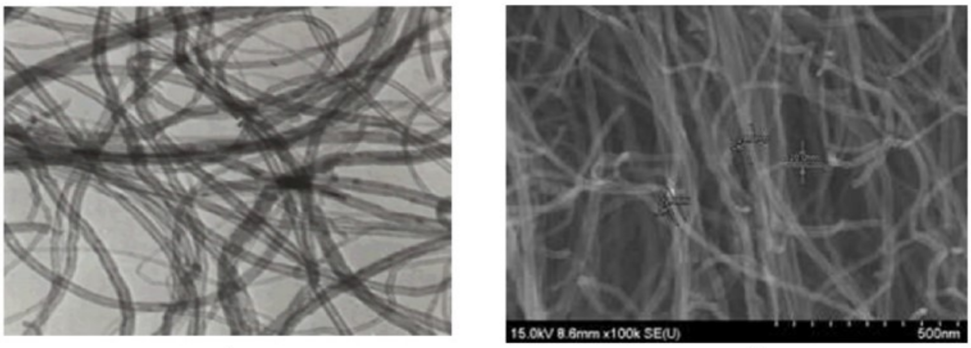
The properties of the carbon fiber, the epoxy, the hardener used in the study are given in Table 3.

As NC, the montmorillonite-based Eczacıbaşı's EsanNano 1-140 coded clay was used. Montmorillonite is a clay type that is formed with the combination of laminates in very soft

Table 2

MWCNT Properties [18].

Category Number	Purity	Outer Diameter Range	Inner Diameter Range	Length	Production Method
TNM5	> % 95	20 - 30 nm	5 - 10 nm	10 – 30 µm	CVD



a) b)

Fig. 1 - a) TEM image, b) SEM image of MWCNT [15].

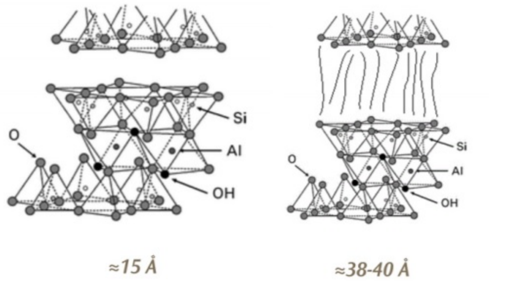
Table 3

Technical Properties of the Used Material [18-20]

	Carbon Fibre	Epoxy	Hardener
Trade Name	Tenax- E HTA 40 3k	Laminating Resin MGS L160	Hardener MGS H160
Number of Filaments (adet)	3000		
Filament Diameter (µm)	7		
Density (g/cm^3)	1.76	1.18 – 1.20	0.96 - 1
Tensile Strength (MPa)	3950	70-80	
Modulus of Elasticity (GPa)	238	3.2 - 3.5	
Elongation at Break (%)	1.7	5 - 6.5	
Viscosity (mPas)		700 - 900	10 - 50
Impact Strength (KJ/m^2)		40 - 50	

crystal forms. This clay has a white and pure structure, and enables improvements in regards to the incombustibility, strength, moisture and gas permeability of the material that it is introduced into. As can be seen from Figure 2, the initial interlaminar distance values of the montmorillonite clay, which is the property of nanoclay, are approx. 15 Å; but when the same nanoclay is organically modified, the obtained value can attain ranges between 38-40 Å. Montmorillonite is purified and organically modified in the manufacture of EsanNANO 1-140. This modification enables the clay to be homogenously distributed in the matrix material [21].

The Chemical Composition of the EsanNANO Clay is given below in Table 4 [22];



a b

Fig. 2 – a) Montmorillonite Base b) Organized Montmorillonite Base

The particle size analysis conducted with the EsanNANO Clay's laser diffractometry is given below in Table 5. [22] ;

Table 4

The Chemical Composition of the EsanNANO Clay

	Al_2O_3	SiO_3	Na_2O	Fe_2O_3	K_2O	CaO	MgO	TiO_2	LOI
%	6 ±1	44±1	0.6 ±0.2	0.4 ±0.2	0.3 ±0.1	0.4 ±0.1	1.4 ±0.2	0.05 ±0.02	45 ±2

Table 5

The grain size analysis of the EsanNANO Clay

Size (µm)	0 – 0.5	0.5 – 1	1 – 2	2 – 2.7	2.7 – 5	5 – 7.5	7.5 – 10	10 – 15
Percentage (%)	2.27	8.66	23.8	15.84	32.25	12.6	3.94	0.64

The processing machine is a special manufacture containing the property of injection double vacuum-assisted resin transfer moulding, whose heat and vacuum values can be adjusted according to the time.

Three point bending and tensile tests were performed with Shimadzu Autograph AGS-X series, MVG 20 kN. Standard TS EN ISO 7500-1 for loads mesured by the load cell from the switch is in Class 1, precision 1%. Elastic displacement (δ) of the central opening of the stepped end sensitivity is 0.1% [23].

3. Test Results

The tensile experiments were carried out with an electromechanical-driven tensile measurement device that has 100 kN capacity. The electronic coulometer sensitivity is 1% in Class 1, and it operates with 1 micron position resolution. The three point bending experiments were conducted with a Shimadzu brand, Autograph AGS-X series, MVG 20 kN loadcell attached measuring device. The loads measured with the loadcell are deemed as Class 1 in the standard TS EN ISO 7500-1, its sensitivity is 1%. The sensitivity belonging to the elastic tensile (δ) of the loading point's center span is 0.1%.

ASTM's D3039/D3039M –standard no. 14 Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials was used in the tensile tests, samples were taken in 25*250 mm in accordance with the measurements that are stated in the Table 2 of the standard. These tests were conducted at a speed of 2 mm/min, as determined by the standard.

D7264/D7264M – standard no. 07 Standard Test Method for Flexural Properties of Polymer Matrix Composite Materials was used in the bending tests. Samples were taken in 13 mm width and in 112 mm thickness (average sample thickness was measured as 2.5 mm) in accordance with the measurements stated in the Figure 5 of the standard; multiplied by 32 plus 40%. These tests were conducted at a compression speed of 1 mm/min, as determined by the standard.

Tensile test results can be seen in Figure 3. and 4. The test results graphic is given in Figure 4 and evaluated in Figure 6., so that the obtained maximum values would be easily understood.

-The maximum stress and strain were measured in the CNTO,3NCO sample.

-The minimum stress and the minimum strain were measured in the CNTO,3NC5 sample

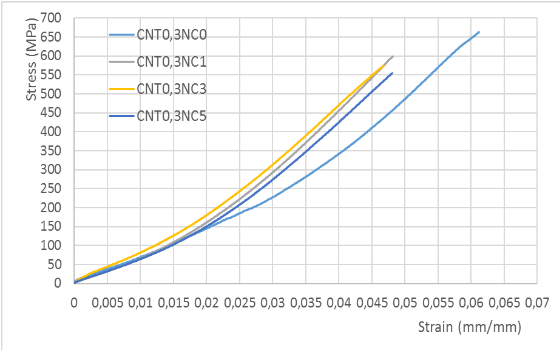


Fig. 3 - Tensile Test Results, Comparative Graphic of the CNT0NC0, CNT0,3NC0, CNT0,3NC1, CNT0,3NC3 and CNT0, 3NC5 Samples' Tensile Test Stress – Strain Values.

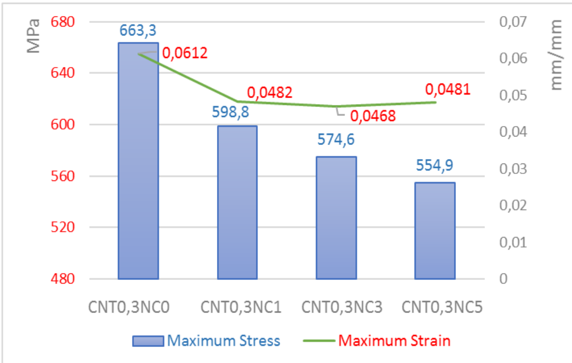


Fig. 4 - Tensile Test Results, Comparative Diagram of the CNT0NC0, CNT0,3NC0, CNT0,3NC1, CNT0,3NC3 and CNT0,3NC5 Samples' Tensile Test Maximum Stress – Maximum Strain Values.

and CNTO,3NC3 sample respectively.

-Based on the details of the tensile stress – strain graphic in Figure 5, the CNTO,3NC3 sample is 10-20 percent higher than the others, when the strain is between 0,015-0,04.

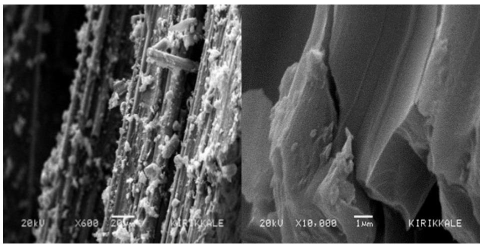


Fig. 5 - SEM images of Nanoclay adhering to the fiber.

The 3% NC and 0.3% CNT reinforced sample was observed to relatively increase the rigidity, as it strained between 0,015-0,04 mm/mm, and displayed the maximum stress.

This effects the MWCNT, carbon fiber and NC in a very apparent fashion. NC, which has been added into the MWCNT reinforced samples, reduces the stress values. This can be linked to the internal voids of the NC, which was added alongside MWCNT, passing through the fracture path with ease.

MWCNT's contribution to the stress and strain is note-worthy, as it causes an important increase. The stress and strain values were pulled down due to the continuously increasing addition of nanoclay to these MWCNT reinforced samples. These results prove that the tensile stress and tensile strain values were affected negatively from the NC that was added alongside MWCNT.

As the NC ratio increases, the yield strength is reduced in the tensile tests. The particles adhering to the fibers in Figure 5 increase the bridge crack ratio in the fractures, this is observable in the SEM samples. The strain is reduced in all the NC-added samples at similar rates, there is more strain in the samples with no added NC.

Three point bending test results can be seen in Figure 6 and 7. The results graphic is given in Figure 6 and evaluated in Figure 7, so that the obtained maximum values would be easily understood.

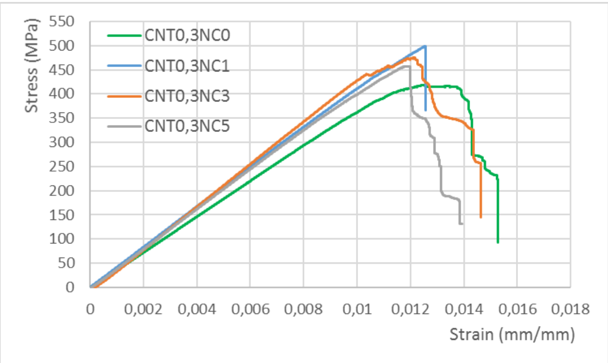


Fig. 6 - Comparative Graphic of the CNT0,3NC0, CNT0,3NC1, CNT0,3NC3 and CNT0,3NC5 Samples' Three Point Bending Test Stress – Strain Values.

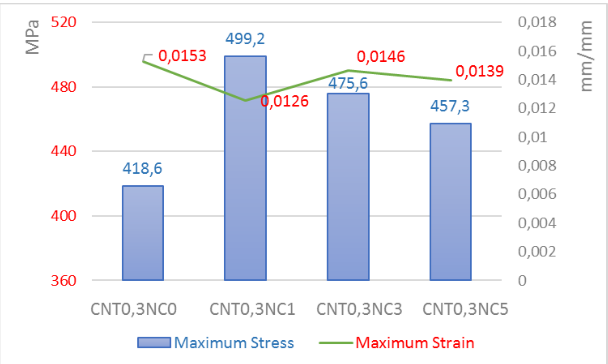


Fig. 7 - Comparative Diagram of the CNT0,3NC0, CNT0,3NC1, CNT0,3NC3 and CNT0,3NC5 Samples' Three Point Bending Test Maximum Stress Maximum Strain Values

-The stress seen in the MWCNT and 1% NC reinforced sample is 19% higher than the sample only with MWCNT reinforced, while the strain value is 18% lower.

- In the portion until 0,01 in strain, the biggest resistance was shown by the sample reinforced with 0.3% CNT and 3 % NC.

Similar to the tensile test; the most rigidity was shown by the CNT0.3NCC3 sample in the portion until 0.004-0.01 mm/mm in strain in the three point bending tests. 3% NC reinforcement gave the best result as opposed to other ratios.

From the three point bending test results, we can see that the stress values decrease, as the ratio of NC increases, which was added alongside MWCNT to the samples CNT0,3NC1, CNT0,3NC3 and CNT0,3NC5. The optimum value in terms of strain was reached by the 3% nanoclay added to the 0.3% MWCNT. The fracture bridges caused by both NC and MWNCT are the reason for why the increasing NC ratio diminishes the strain value and the stress value. The bridge crack can find its path and progress through it with ease, which causes fraction.

The optimum stress was seen in the 1% NC reinforced sample, while the optimum strain was seen in the 3% NC reinforced sample.

4.Conclusion

The NC added to the MWCNT reinforced CFRP samples was observed to reduce the tensile strength and ductility in the rupture point, and the maximum stress values were obtained by the 1% NC reinforcement in the three point bending tests. 19% increase in the bending stress caused by the 1% NC reinforcement is noteworthy.

Until the CNT0.3NC3 sample reached values of 0.04 mm/mm in the tensile test and 0.01 mm/mm in the three point bending test, it displayed higher stress values in comparison with the others, thus proving the increased rigidity.

The decrease in the bending stress occurring as a result of the increase in NC stems from NC connecting to each other easier through the fractures. The bending strain seen in the 1% NC reinforcement is caused by the increase in bending stress. The bending strain is clearly diminished, which means embrittlement occurs.

In the tensile test, there is no compression in any axis unlike the three point bending test. This creates fracture-crack paths in the NC based epoxy, thus causing rupture in the fibers, which leads to the decrease in the rupture stress values.

If high rigidity, little strain, toughness in the material when the said material is in the elastic region are desired, then the 0.3% CNT + 3% NC reinforced sample will give the best results, as was determined by the study.

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