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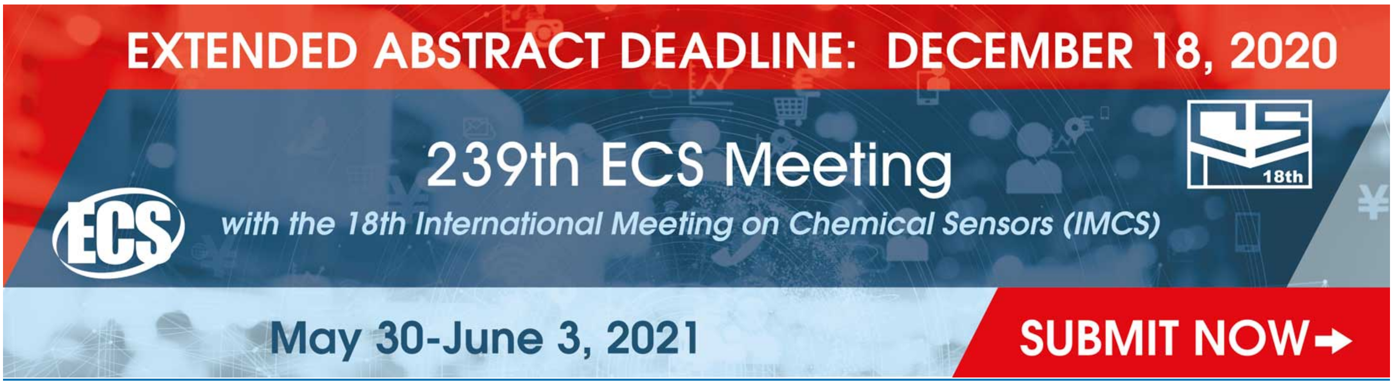

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The effects of interface and matrix reinforcements on fracture toughness of E-Glass/epoxy laminate

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Abstract

In this study, the effects of low amount (0.1 wt%) multi-walled carbon nanotube (MWCNTs) distributed homogenously in epoxy via cationic surfactant (cetyl pyridiniumchloride-CPC), polyacrylonitrile nanofiber (in the range of 240–570 nm diameter) mats between each lamina, main fiber-matrix interface improvement using γ-Glycidoxypropyltrimethoxysilane and intermediate combinations were investigated on the fracture toughness of E-Glass/epoxy laminate. Considering the data obtained from three-point bending test samples with a single edge crack, it was found that the ultimate bending strength, modulus and fracture toughness of the silane-treated samples increased by 25.6%, 4.9 and 16.6% respectively, with respect to the reference sample. When MWCNTs was added to the silane treated sample, it was observed that it did not enhance the fracture toughness and decreased the strength and modulus slightly (1%) with the effect of CPC. The effect of 128 μm thick nanofiber mats on the silane-treated sample did not occur as expected and was found to cause delamination by working as a separate layer between the laminae.

1. Introduction

The bisphenol-A diglycidyl ether (DGEBA) type epoxy was mostly used in the studies to increase the toughness of nanocomposites. This is due to that synthesis of epoxy monomer from bisphenol-A and epichlorohydrin gives the highest three-dimensional cross-link structure [1]. But, the high cross-link structure of the epoxy as a matrix and the relatively weak bonds at the fiber-matrix interface restrict the applications of the polymeric composite laminates. Since the cross-link structure is important for the material to be used in industrial applications, it is imperative to use some reinforcing elements in the matrix to increase fracture toughness [2–5].

Many researchers have investigated the use of rubber particles to increase the fracture toughness of the epoxy matrix. In the examinations, they found that the use of low modulus rubber increases the fracture toughness and flexibility of the matrix while at the same time reducing the stiffness of the material [6, 7]. However, it has been found that by using the liquid rubber such as hydroxyl terminated polybutadiene (HTPB) in epoxy matrix, the stiffness of the material can be enhanced as well [8].

Carbon nanotubes (CNTs) have been the most widely studied nano-scale component. These reinforcing elements provides improvements in electrical conductivity, thermal and mechanical properties (elasticity modulus and strength) of the nanocomposite if provided a homogeneous distribution in the matrix [9]. In addition, the end points of each tube constitute stress concentration points, which is a common problem of staple reinforcement elements.

If single-walled carbon nanotubes (SWCNTs) is added to epoxy at a rate of 0.1 wt% without functionalization, the modulus, ultimate tensile strength and fracture toughness of the material increased by 3%, 3% and 10.7% respectively. But at 0.3% rate, the fracture toughness began to weaken again [10]. This is due to the fact that the specific surface area of the SWCNTs is large and facilitates stress transfer with the matrix. But, this feature also causes agglomeration and leads to a decrease in fracture toughness after a certain rate. In the same study, it was also studied with 0.1 wt% multi-walled carbon nanotubes (MWCNTs) and a slightly reduction in ultimate tensile strength, 7% increase in modulus and 21.6% increase in fracture toughness were observed. However, when this ratio was increased to 0.3%, the modulus began to decrease, ultimate tensile strength and fracture toughness remained almost the same as in the 0.1 wt% rate. This is due to the fact that MWCNTs are better in terms of dispersion than other CNT kinds, but worsen in terms of agglomeration and the load-transfer feature with the increase in the rate.

Many researches are conducted to improve the mechanical properties of the epoxy matrix using different nanoparticles with the addition of MWCNTs. In a study, although silica nanoparticles are used more than MWCNTs in the matrix, it was found that silica nanoparticles do not cause agglomeration, but even at low rate as 0.06%, MWCNTs creates small dispersion problem [11]. This reveals that even in MWCNTs, which is the least prone to agglomeration due to its structure, it is difficult to provide a homogeneous mixture. This situation is due to the presence of van der Waals forces between nanotubes.

One of the techniques used to ensure homogeneous distribution of MWCNTs is sonication. Although positive results have been obtained with this technique, it has been concluded that increasing the duration of the process decreases the fracture features of the material [12]. It is, however, obvious that the low use of carbon nanotubes improves the fracture properties of the epoxy matrix. In a study, when MWCNTs were added 0.1 wt% to the epoxy matrix of the 3-point bending sample, it was found that the Mode-I fracture toughness increased by 30% compared to pure epoxy, but the properties began to decrease after 0.5% [13].

The main fibers determine the strength of the composite material [14]. Carbon nanotubes and other reinforcements are meant to make the function of matrix longer under load. Nanofibers are also used for this purpose. However, unlike nanoparticles, their filament state ensures that stress concentration points do not occur. As nanomat layers, which are generally obtained from the thermoplastic materials by the electro-spinning method, have arbitrary fiber directions, which in turn increases the toughness of the matrix independently of any direction. The other advantages of nanofibers, which become almost perfect at the molecular level with their high aspect ratio, are much less harmful to human health than carbon nanotubes and do not form agglomeration.

Interleaving the nanofiber mats between two laminae has been a method followed against the delamination problem of the material [15, 16]. Nanofibers can be placed as stand alone form or directly deposited during electro-spinning process on the main fiber fabric. It has been stated that the latter provides direct mechanical contact and some increase in tensile strength can be achieved [14, 17].

The thickness of the nanofiber mats interleaved is undoubtedly effective on the mechanical properties of the material. In a study, it was stated that the thickness values of 70 μm and 128.1 μm were optimal thicknesses against Mode I and II loads, respectively [18]. Generally, thin nanofiber mats appear to provide more stable crack propagation in the bending sample. However, it seems that the effect of nanofibers is mostly under shear stress [14]. The bridging effect of nanofibers against the crack propagation also has an effect on increasing the fracture toughness of the nanocomposite material [19].

The formation of strong bond between the main fiber and the matrix is an input and complementary element for the nano-reinforced matrix. Also, the stated advantages of nanofibers remain limited to the region between the two laminae of the composite. This necessitates the use of coupling agents to strengthen the matrix-main fiber adhesion and to enhance the tensile strength [20]. If the reactivity of these agents, which serve as a bridge between the matrix and the fiber, is high for both surface types, the fiber-matrix stress transfer of the material under load will be much higher.

Silane also draws a barrier to moisture attack at the interface regions of the composite material [21]. Moisture decreases the mineral structure of the fiber by reaching the interface and consequently decreases the mechanical performance of the material. Therefore, silane also offers an advantage in terms of corrosion.

It was stated that in the composite materials which the fibers are treated with silane is similar to brittle fracture, whereas in untreated samples a broom-like fracture surface occurs due to adhesion of the fibers [22, 23].

In a study, it was concluded that the coupling agents increase the transverse strength and crack initiation load of the material as it creates a strong covalent bond between the matrix and the fiber, but the toughness value of the composite with the untreated fiber is higher due to the fiber bridging [24].

When the literature is examined, it is seen that the interface and matrix reinforcement need to be evaluated in a whole. It was also desired to see whether the thickness limitation of the nanofiber mats for Mode I fracture toughness varies if the main fiber-matrix interface is strengthened. For this purpose, interface reinforcement was made with γ-Glycidoxypropyltrimethoxysilane in E-Glass/epoxy laminate in this study. The nano-particle and nanofiber effects on the pure and functionalized laminates were compared separately by using 0.1 wt% MWCNTs distributed with cationic surfactant and stand alone 128 μm electrospun polyacrylonitrile (PAN) nanofiber mats.

Table 1. The components and their suppliers used in this study.

Material	Supplier	Material	Supplier
Bisphenol-A type epoxy resin and amine hardener (Epikote MGS LR160 and H160)	Hexion	E-Glass non-crimp fabric, 300 g m^{-2}, thickness = 0.229 mm	Metyx Composite
MWCNT, KNTI13/10–30 nm, purity 90%, surface area >200 m^2 g^{-1}	Grafen Chemical Industry	Polyacrylonitrile (PAN) (M_w = 110 kDa)	Aksa Akrilik
Dimethylformamide (DMF, 99.8%)	Sigma Aldrich	Coupling agent (OFS-6040)	Biesterfeld
Cationic surfactant (Cetyl Pridiniumchloride)	Sigma Aldrich		

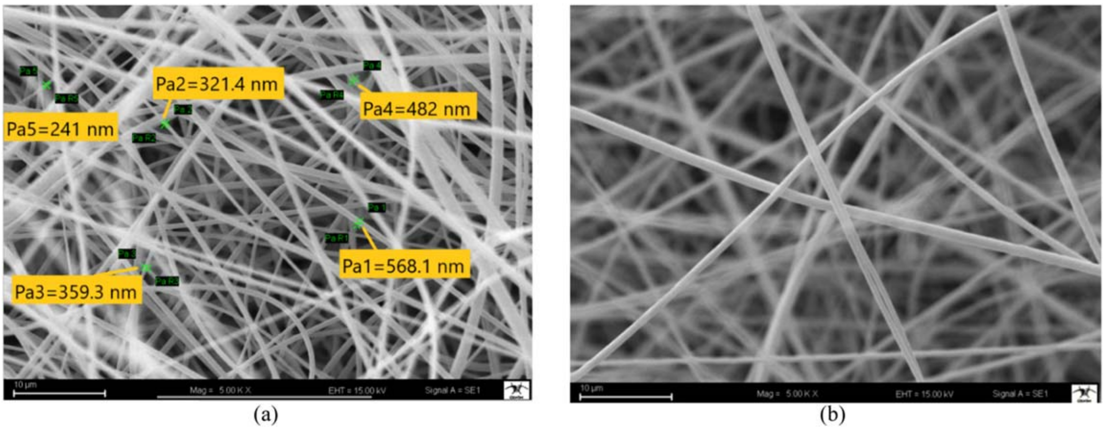


Figure 1. The PAN nanomats (a) thickness distribution (b) surface situation.

2. The experimental details

The component names and their suppliers used in this study were given in table 1.

2.1. The nanofiber mat production

The 13 wt% of PAN granules was dissolved in dimethylformamide (DMF) by employing magnetic stirrer for 6 h at room temperature. The obtained solutions were filled in the 10 c.c. syringes. The electrospinning process parameters were set to distance of 15 cm, 18 kV and 0.3 g h^{-1} leading to a uniform nanofibers without any beads. The diameters of the electrospun nanofibers are in the range of 240–570 nm (figure 1). It has been determined that the density of the produced mats is in the range of 17–20.8 g m^{-2}.

The tensile tests of nanofiber mats were carried out according to ASTM D-638 standard from 3 strips of 128 μm thickness and 22.2 mm wide nanofiber mat using Zwick/Roell D-89079 Ulm. The tensile strength and elasticity modulus were found as 3.49 MPa and 36.6 MPa, respectively (figure 2).

2.2. The production of the laminates containing nanofiber mats

The viscosity, epoxy equivalence and epoxy value ranges of the epoxy resin (DGEBA) used in the production is 700–900 mPa, 166–182 g/equivalent, 0.55–0.60 equivalent/100 g, respectively. The viscosity and amine quantity of the hardener is in the range of 10–50 mPa, 50–650 mg KOH/g, respectively.

The mechanical values given by the manufacturer for the neat resin show that the tensile strength, the flexural strength and the elasticity modulus are in the ranges of 70–80 MPa, 110–140 MPa, 3.2–3.5 GPa, respectively.

The bi-directional [0/90] non-crimp glass fiber fabric weighing 300 g m^{-2} has a 12 μ fiber diameter and offers an advantage in terms of the absence of resin dense areas at the weft-warp transition points due to the fabric structure.

The two-stage production process is preferred for the production including nanofiber layers. In the first stage, the glass fiber plies of 140 × 240 mm were cut with attention to the angle of fibre. The bisphenol-A type epoxy resin of 150 g and amine hardener were mixed at the rate of 100:25 by weight recommended by the manufacturer and poured into a container. The glass fiber layers were immersed in the epoxy pool and each ply was placed on the peeling fabric of the infusion process such that a nanofiber layer was placed on each glass fiber layer. Eight glass fiber laminae and seven nanofiber layers were provided in each sample (figure 3). The nanofiber mats were kept open for at least 24 h at an ambient temperature between the electro-spinning process and the

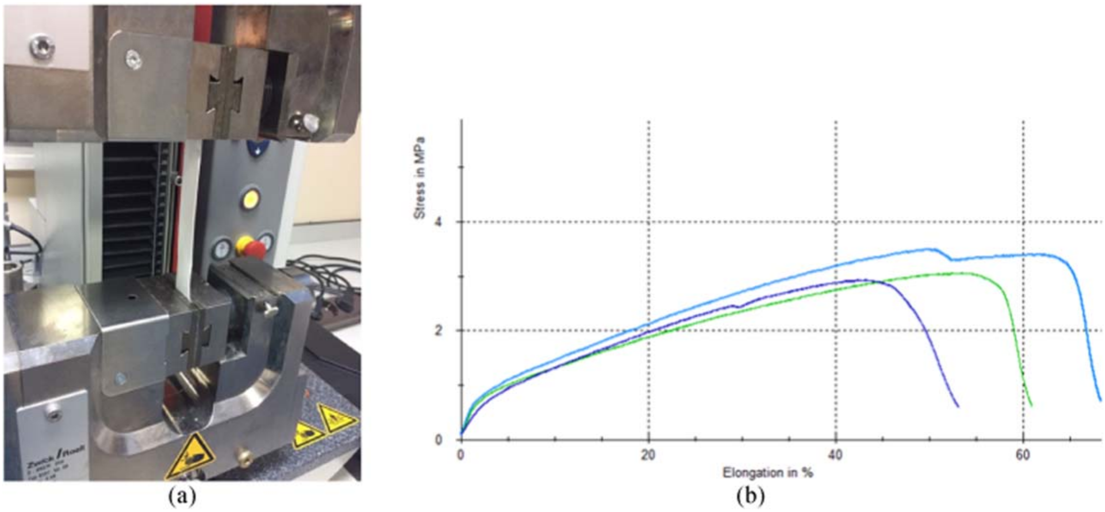


Figure 2. (a) Nanofiber mat strip tensile test (b) Stress-elongation (σ-E) curve of the nanofiber mat.

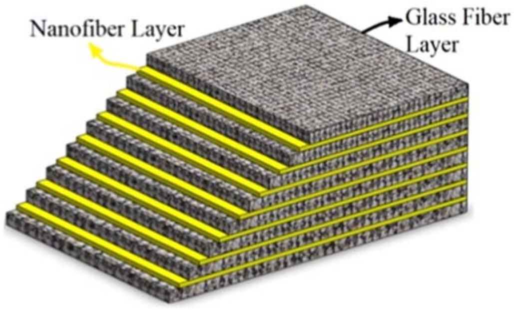


Figure 3. Schematic view of stacking sequence of nanofiber reinforced composite plate.

vacuum infusion process, and the probability of having dimethylformamide on the fiber surface was kept to a minimum.

It was also determined that the thickness of samples containing seven layers of nanofiber is 3.6 mm and this figure is approximately 1.2 mm more than the reference E-glass/epoxy plates.

2.3. The production of the laminates containing carbon nanotubes

In the samples containing 0.1 wt% carbon nanotubes (MWCNTs), cetyl pridiniumchloride (CPC) from the cationic surfactant family was used to ensure homogeneous distribution of MWCNTs in the matrix.

Cetyl pyridiniumchloride, which has the $C_{21}H_{38}C1N$ molecular formulation, consists of a hydrophobic long (alkyl) tail and hydrophilic polar head. While the tail part is attached to the CNT surface, the hydrophilic head creates thrust to the hydrophilic heads bounded to other CNTs. Thus, the van der Waals forces of the CNTs are prevented [25].

For the production of the laminates containing carbon nanotubes, 0.21 g of CPC and 0.25 g of MWCNTs were placed in a 250 c.c. beherglass containing 50 g of ethyl alcohol, and the mixture was left to stir in the ultrasonic bath at 25 °C for 1 h. Then, 150 g of epoxy resin was added to this solution and the mixture was continued in the bath for 30 min. Afterwards, the solvent was completely evaporated by placing it in a magnetic stirrer for 6 h at 50 °C and made ready for the vacuum infusion process.

2.4. The glass fiber surface preparation with coupling agent

For the silane (γ-Glycidoxypropyltrimethoxysilane) reaction to take place, the pH of the pure water is adjusted to 4.5 using acetic acid. The coupling agent was added to the acidic water as a dilute solution (0.3% silane concentration) and mixed for 15 min before hydrolysis, according to the manufacturer's recommendation. After this mixture, the process of immersing the glass fiber layers cut in size according to the sample into this solution and waiting for the reaction for 1 h is included. After the glass fiber layers were kept in this solution pool

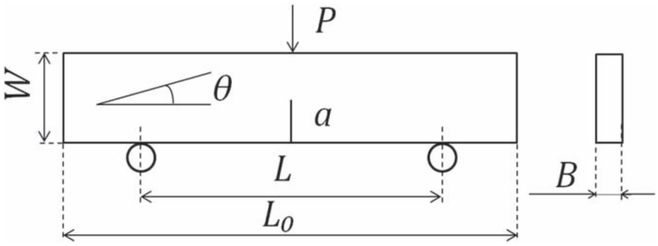


Figure 4. The schematic view of 3PSENB specimen.

Table 2. Abbreviations and definitions of the produced samples.

Sample abbreviations	Definition of E-Glass/epoxy laminates
R	Virgin
$R + NF$	Nanofiber reinforced
$R + CNT$	MWCNTs reinforced
$R(F)$	Silane-treated
$R(F) + NF$	Nanofiber reinforced silane-treated
$R(F) + CNT$	MWCNTs reinforced silane-treated

at rest, the glass fiber layers were removed from the solution and placed in the oven at 105 °C for 30 min for drying. It is kept in a closed container until it is used in production in order not to absorb the moisture of the medium.

2.5. The preparation of three-point bending test samples

The average fiber volume of E-glass/epoxy $[0/90]_{4s}$ laminates produced as a reference is 38.6%, and the main fiber and nanofiber volume ratios in the nanofiber reinforced samples are approximately 33% and 3.7%, respectively.

Three-point bending test method with single edge crack (3PSENB) was used to determine the fracture toughness of the samples (figure 4). The test method is not only important for giving the mechanical values of the material, but also for the adhesion of the layers forming the material under load. Total (L_0) and span length (L) of the samples were prepared as 100 mm and 64 mm, respectively. Span to width ratio (L/W) of 4.9 was chosen for the nanofiber-free samples and 4.2 for the nanofiber reinforced samples due to thickness difference. The crack length to width ratio (a/W) range of 0.4–0.61 was investigated in considering the effect of crack size and the resistance to crack growth and the magnitude of crack extension. The cracks were made by a 0.13 mm diamond-wire tool.

The samples were placed on the bend fixture with two 12.7 mm diameter parallel rollers, while the third roller was pressed directly into the area where the crack was located. Bending (four and five-specimens in each set) properties of the composite specimens were investigated in accordance with ASTM D790-03 standard. The crosshead speed of the testing instrument was selected to be 2 mm min^{-1}. The deflections of SENB samples were measured from the cross-head displacement. The Point Stress Criterion [26] and the Failure Theory [27] were also used in fracture strengths and toughness calculations. Table 2 shows the abbreviations of the sample types.

3. Results and discussion

The 3-point bending test is important for both providing information about the tensile characteristics of the sample and for the adhesion between the laminae.

The average ultimate tensile strength, elasticity modulus and Poisson's ratio of the E-Glass/epoxy laminate used in the 3-point bending tests are 281 MPa, 24.5 GPa and 0.27, respectively.

In figure 5, the load-deflection plots of the virgin, the MWCNTs and nanofiber reinforced samples were given. It is observed that when the virgin and MWCNTs reinforced samples reaches the maximum load, the load decreases suddenly, whereas the nanofiber reinforced sample shows a gradual decrease. This indicates that the nanofiber-saturated matrix increases the crack path as much as possible.

It is also observed that the stiffness slope (k) of the virgin and nanofiber reinforced samples have a linear characteristic up to the maximum load, while the elasticity (strain) in the MWCNTs reinforced sample is

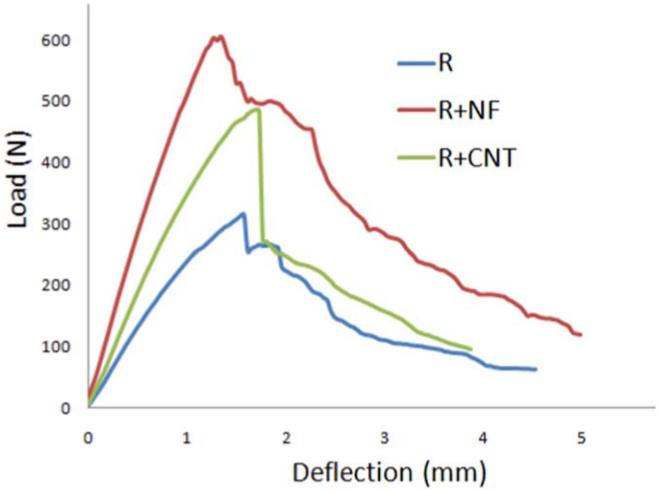


Figure 5. Load-deflection graphs of virgin (*R*), nanofiber reinforced ($R + NF$) and MWCNTs reinforced ($R + CNT$) laminates.

increased and its slope is of a slight curve characteristic. It may be thought that this situation may be encountered in the nanofiber reinforced sample. However, there is an increased rigidity of the matrix saturated with nanofibre. Also, the cationic surfactants used for homogeneous distribution of CNTs are known to increase the elasticity and viscosity of the epoxy [28].

The SEM image taken from the fracture surface of the virgin sample (R) shows the broom-like appearance of 0^0 glass fibers and that there is no delamination problem (figure 6(a)). However, in nanofiber saturated samples, it is seen that the matrix region between each glass fiber lamina expands due to the nanofiber mat thickness, and the matrix saturated with the nanofiber acts as a separate layer, causing delamination (figure 6(b)).

The glass fabric used in the samples has a non-crimp structure. It is seen that delamination occurs less at the points adjacent to the glass fibers of 0^0 that extend along the sample length and undergo tension and compression stress under the bending moment. Since there is a slightly narrower area between the two glass fibers in this region, there is a mechanical contact between the nanofiber mat and the glass fibers (figure 6(c)). This shows that the use of nanofiber in the form of deposited rather than stand alone will be more effective in terms of delamination.

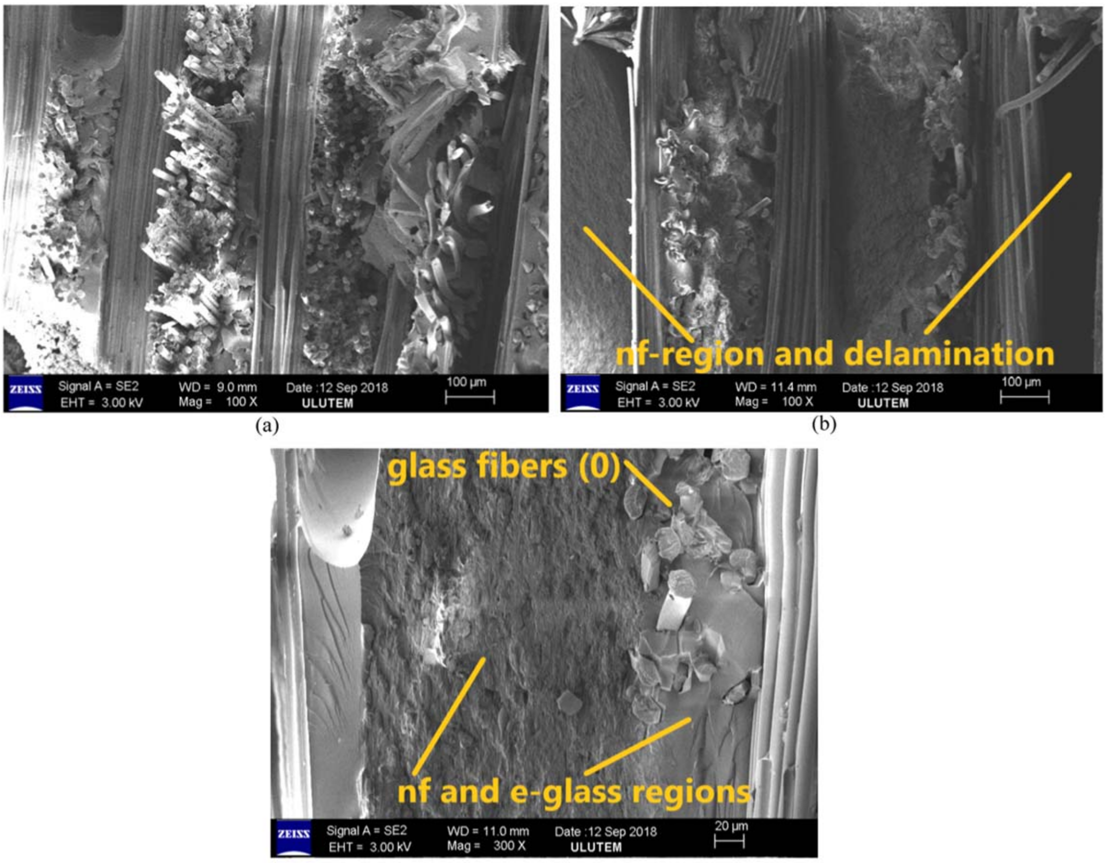
The load-deflection graph characteristics of silane-treated samples are generally similar to those of untreated samples (figure 7). However, the graph of the nanofiber-reinforced sample shows that a sudden drop after the maximum load (figure 7(b)).

When the SEM images of fracture surface of nano-free but silane-treated sample *R*(*F*) is analyzed, it is seen that brittle fracture occurs across the fibers on the fracture surface and some fibers are pulled out from the matrix collectively (figure 8(a)). In the nanofiber reinforced sample, it is determined that some fibers near the nanofiber rich matrix area where there is no delamination are broken by the plastic deformation, but this does not reflect the general situation (figure 8(b)). This indicates that the coupling agent (silane) cannot prevent brittle fracture and cause delamination between the glass fiber lamina and the nanofibre saturated matrix which acts like a separate layer.

In the SEM image in figure 8(c), it is seen that nanofibers could be pulled off the epoxy matrix in one piece on the fracture surface of the material. This is interesting in terms of both strength and modulus of the nanofibers, because they have lower values than the matrix in this terms. In figure 8(d), the matrix particles on the silane-treated glass fiber surface in $R(F) + CNT$ sample indicate that the interface has a sufficient bonding strength.

It is seen in figure 9 and table 3 that the highest increase in flexural modulus is obtained in *R*(*F*) samples where glass fibers are functionalized with silane. Relative to the reference (*R*) sample, it was determined that the flexural modulus and strength of the silane-treated sample *R*(*F*) increased by 4.9% and 25.6%, respectively. 0.1wt% MWCNTs contribution to the *R*(*F*) sample did not increase the values further. When nanofiber mats are added to the reference (*R*) sample, it is seen that the modulus and strength values decreased by 17.3% and 5.2%, respectively. When nanofiber mats were added to the reference and silane-treated samples, the glass fiber volume ratio decreased from 38.6% to 33%. At 33% volume ratio, the flexural modulus values of the reference sample (R) and the silane-treated sample (R (F)) are 10.85 GPa and 11.38 GPa, respectively. The addition of nanofiber resulted in a 3.3% and 41.6% reduction in flexural modulus, respectively.

Undoubtedly, the inter-region matrix occupied more than necessary volume between two adjacent glass fiber laminae due to the mat thickness may be the most important factor in decreasing these figures. The



(a) (b)

(c)

Figure 6. The SEM Images of (a) virgin (*R*), (b) and (c) nanofiber reinforced laminates (*R* + *NF*).

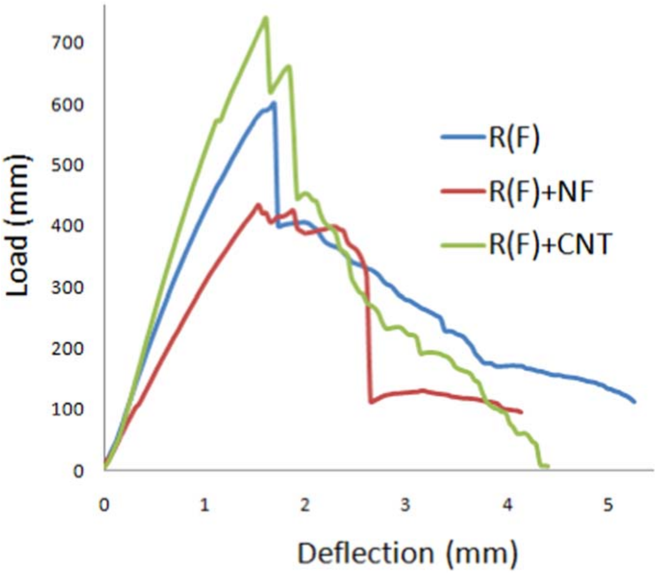
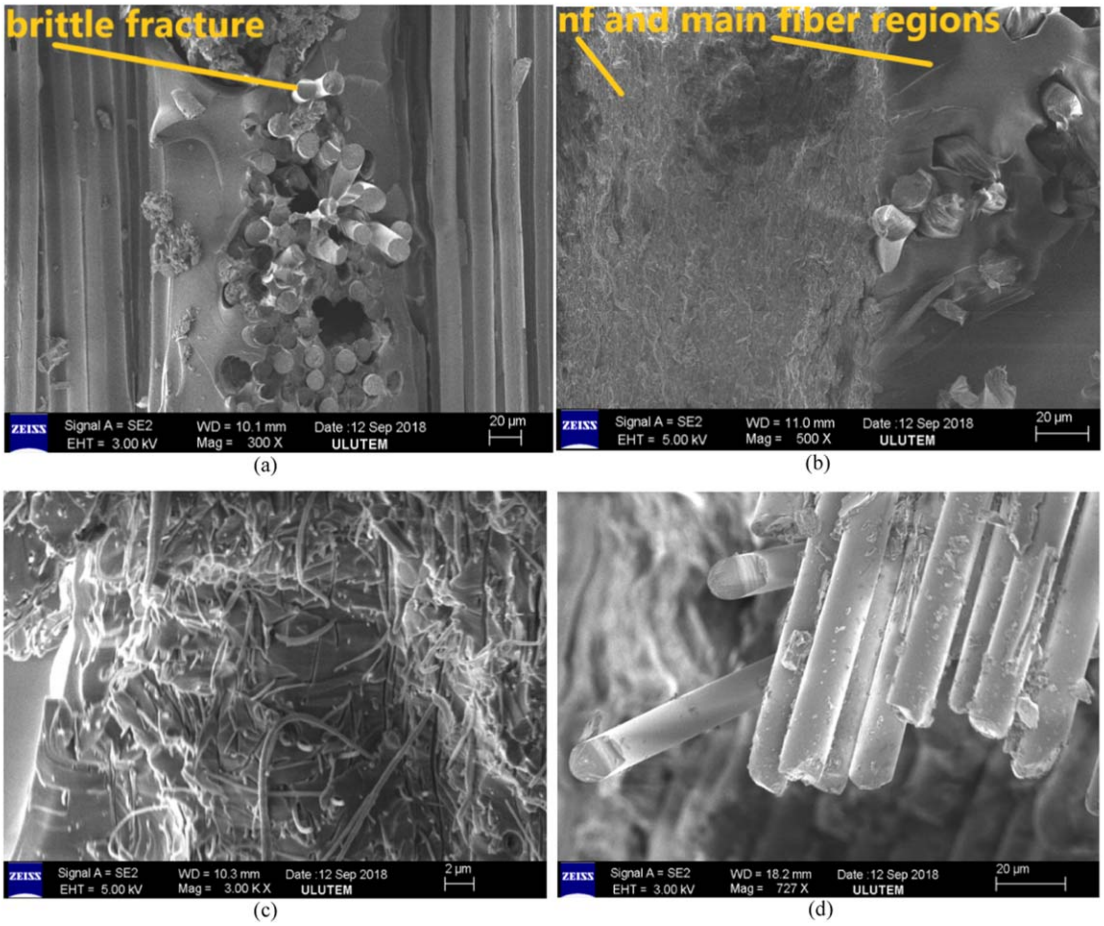


Figure 7. Load-deflection graphs of silane-treated (*R*(*F*)), nanofiber reinforced (*R*(*F*) + *NF*) and MWCNTs reinforced (*R*(*F*) + *CNT*) laminates.

abbreviation *B* in table 3 shows the thickness of the sample and *k* is the slope of the line in the load-deflection graph.

When MWCNTs was added to the reference sample, it reduced the modulus by 13% while increasing the flexural strength by 11.7% (table 3 and figure 10). The cationic surfactant used to ensure the homogeneous



(a) (b) (c) (d)

Figure 8. The SEM Images of (a) silane-treated (*R*(*F*)), (b) and (c) nanofiber reinforced (*R*(*F*) + *NF*), (d) MWCNTs reinforced *R* (*F*) + *CNT* laminates.

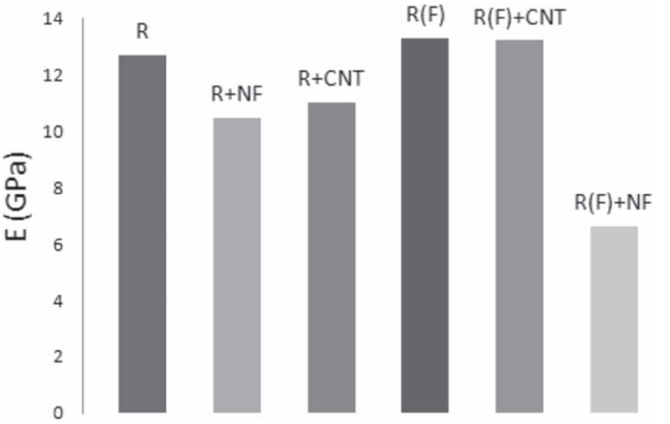


Figure 9. The flexural modulus of the samples.

distribution of carbon nanotubes may increase the viscosity and elasticity of the epoxy, which may have been effective in this result. Note that, when the CNTs are added to the *R*(*F*) sample, the modulus decreases by 0.6%. This indicates that the stiffness increase due to functionalization and 0.1 wt% carbon nanotube additive and the stifness decrease due to cationic surfactant are almost equal.

The fracture toughness values of the samples in the range of $a/W = 0.29–0.33$ are shown in table 4. The *a/W* shows the ratio of crack length to width, σ_{ini} and σ_f indicate, respectively, the initial and final fracture stress of the stable crack progression, K_{ini} and K_{eff}, indicate, respectively, the toughness at the stable crack initiation and the

Table 3. Dimension, stiffness, modulus and ultimate bending strength of the samples.

	B (mm)	W (mm)	k (N mm^{-1})	E_{22} (GPa)	Std. Dev. (GPa)	σ_0 (MPa)	Std. Dev. (MPa)
R	2.6	12.9	416	12.69	3.2	308	9.4
$R + NF$	3.6	15.3	574	10.49	1.7	292	3.4
$R + CNT$	2.7	13.1	379	11.04	1.4	344	12.2
$R(F)$	2.6	12.9	436	13.31	1.5	387	9.6
$R(F) + NF$	3.5	15.0	342	6.64	1.2	244	7.8
$R(F) + CNT$	3.1	14.0	554	13.23	1.4	383	9.1

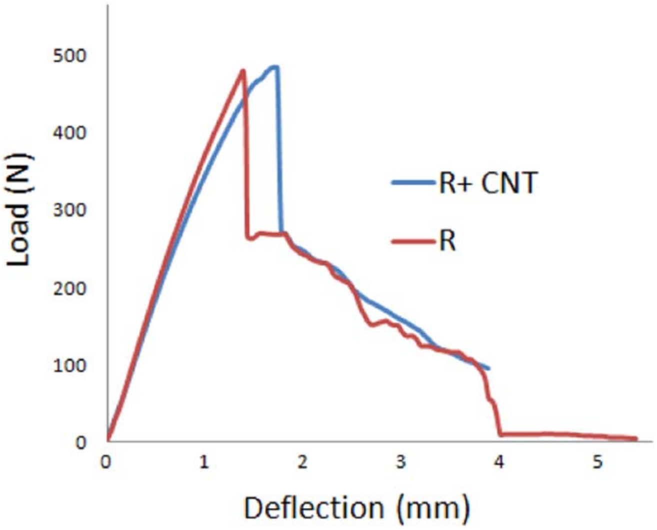


Figure 10. Elasticity effect of cationic surfant on the load-deflection graph.

Table 4. Fracture strength, toughness and stable crack length of the samples.

	a/W	σ_{ini}	σ_f	K_{ini}	K_{IC}	K_{eff}	a_i	a_c
R	0.31	142 (9.2)	160 (9.0)	567	790	637	4	5.04
$R + NF$	0.32	114 (8.5)	129 (9.4)	498	715	563	5	6.4
$R + CNT$	0.31	140 (14.2)	156 (17.9)	584	846	666	4	5.2
$R(F)$	0.31	165 (13.2)	185 (14.1)	664	921	744	4	5.02
$R(F) + NF$	0.32	93 (9,7)	105 (11.0)	418	599	471	5	6.34
$R(F) + CNT$	0.31	154 (14.2)	173 (15.8)	649	920	738	4	5.17

All dimensions in σ, K and a are MPa, MPa$\sqrt{}$mm and mm, respectively. The standard deviations were given in the parentheses.

effective fracture toughness. On the other hand, a_i and a_c indicate the length of the crack before the stable crack propagation and the total length up to the unstable crack, respectively.

When 0.1 wt% MWCNTs was added to the reference sample, it was determined that the critical fracture toughness K_{IC} increased by 7%, but with the addition of nanofiber layers, decreased by 9.5%. It is important in this study to note that the 0.1 wt% MWCNTs increases the ultimate bending strength and fracture toughness by 11.7% and 7%, respectively, given the 3% and 10.7% increase achieved in the previous study with the more effective SWCNTs [10]. This may be achieved by using cationic surfactant (CPC) to enhance homogeneous distribution of MWCNTs. However, there was also a loss in modulus due to elasticity increasing. In the same study with 0.1 wt% MWCNTs, it is interesting that it was found slightly reduction in ultimate tensile strength and 7% increase in modulus. In this study, the modulus increase rate was found at the same level, however, ultimate bending strength also increased.

If the glass fibers were functionalized, it was observed that the K_{IC} reached 921 MPa$\sqrt{}$mm with an increase of 16.6%. It was determined that the effect of carbon nanotube was not observed on the functionalized sample $R(F)$ and the nanofiber mats reduced the value to 599 MPa$\sqrt{}$mm.

In a study with three-point bending E-Glass/epoxy laminates treated with the same silane group as in this study, if the silane is used at the rates of 0.1%, 0.3% and 0.5%, the bending strengths increase by 39%, 77% and 78%, respectively, and deteriorated after 0.5% silane ratio [29]. However, in this study, the use of 0.3% silane increased the ultimate bending strength by 25.6% compared to the reference sample (*R*). In another study [30] where the same silane was applied to the MWCNTs of neat DGEBA epoxy, it was observed that the modulus and bending strength were improved up to 0.25 wt% compared to the samples containing the same amount but untreated MWCNTs. It is interesting to note that after 0.5 wt% MWCNTs ratio, the values of both samples deteriorated due to epoxy-amine hardener affected by epoxy group on the treated CNTs. The fracture toughness decreased as the untreated MWCNTs rate increased in the samples, but an increase of up to 0.5 wt% was observed in the treated samples.

The critical crack length a_c in table 4 is the end point of stable crack progression, after which unstable progression begins. It is seen that the stable crack length is almost unchanged in the samples where functionalization is performed regarding the reference sample. The 0.1% carbon nanotube additive, on the other hand, appears to increase the stable crack length by approximately 15% in the samples it is added due to the elasticity effect of the cationic surfactant.

4. Conclusion

In this study, a total assessment was made in terms of fracture toughness by considering the carbon nanotube (MWCNTs) and nanofiber supplements in increasing the toughness of the epoxy matrix and by considering the silane coupling agent in the fiber-matrix interface of the E-Glass/epoxy composite laminate. Since the interface reinforcement is not an issue that can compete with increasing the toughness of the matrix, nano-reinforcement is also made in the matrix of the silane-treated sample. At the end of this study, the following conclusions have been reached:

a. The highest flexural modulus, strength and fracture toughness values were determined in $R(F)$ and $R(F) + CNT$ samples whose interface was treated. The cationic surfactant (CPC) was thought to be effective in the reinforcing feature of 0.1 wt% MWCNTs supplement in the $R(F)$ sample and even in lowering the mechanical values by a small amount,

b. If MWCNTs are added homogeneously into the matrix, it can increase flexural strength and fracture toughness of the laminate at even low rates by 3.9% and 7%, respectively. The effect of cationic surfactants is important in ensuring homogeneous distribution,

c. Plastic deformation (ductile) rupture detected in silane-treated glass fibers where the nanofibre-saturated matrix is in mechanical contact with it has been an important indicator of usefulness of the nanofibers. If the thickness of the nanofiber layers is chosen so that the intermediate matrix between two laminae does not act like a separate layer, a much higher yield can be obtained from the main fibers.

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