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# Engineering Science and Technology, an International Journal

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## Evaluation of the effect of MWCNT amount and dispersion on bending fatigue properties of non-crimp CFRP composites

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### ARTICLE INFO

#### Article history:

Received 26 May 2021

Revised 20 October 2021

Accepted 26 November 2021

Available online 23 December 2021

#### Keywords:

Non-crimp fabric

Carbon fiber-reinforced polymer composite

MWCNT

Fatigue property

Fatigue fracture

### ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) have many unique features that improve composite material properties, including a large surface area, thermal and chemical stability, and thermal and electrical conductivity. Our study aimed to examine the influence of MWCNT weight percentage on the fatigue characteristics of a polymer matrix composite strengthened with carbon fiber in fabric form. This study aimed to explore the additional properties and functions of these MWCNTs. For the experiments, MWCNTs were prepared by mixing them in solution with epoxy in three different weight percentages (0.5 %, 1.0%, and 1.5%) using a surfactant, and at 0.5 wt% without a surfactant. The prepared solutions were injected into four-axis non-crimp carbon fiber fabric plates via the vacuum mixture method and then cured for 48 h to produce nanocomposite plates. Using five types of composites, fatigue tests were carried out at six different amplitudes and a fixed frequency. Fatigue test specimens were subjected to detailed SEM analysis of their fatigue fracture surfaces. The investigational results revealed that the 0.5 wt% MWCNT epoxy solution had been homogeneously dispersed and exhibited the highest absorbance spectrum. The 0.5 wt% MWCNT specimen achieved the highest value in the fatigue life experiments. In addition, electron microscopy studies of the fracture surfaces of the test specimens determined that individual COOH-MWCNTs interrelated with the fibers and formed a bridge between fiber and matrix, whereas agglomerations caused weak bonding between the reinforcement fibers and matrix, making the material more brittle.

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### 1. Introduction

In recent years, carbon fiber-reinforced polymer (CFRP) composites, especially due to their light weight and high strength, have been applied in many sectors, including the aviation, automotive, and maritime industries [1]. Research on CFRPs is effectively expanding with increasingly more emphasis on developing and improving the qualities of the composites [2]. Formability for high curvature is important in many applications such as those in the aerospace and automotive industries. Non-crimp fabrics (NCFs) can be laid into curved molds without fiber crimp and folding affecting mechanical performance [3]. Non-crimp fabric CFRPs consist of layers of unidirectional (UD) fibers sewn together. Excess resin in the seam areas can cause a stress concentration leading to fatigue damage. The stitches also provide a slight in-plane waviness in the fiber bundles that may affect the fatigue properties of

the composite [4]. Additionally, microstructural defects including fiber fracture, matrix cracking, separation, and delamination have been reported in previous studies to cause fatigue behavior in composite materials [5,6]. These researchers found that fatigue was one of the most important sources of catastrophic damage to structural materials [5,6]. These defects may result from the properties of the composites and the test conditions. In light of previous studies, first, it was determined that the fatigue performance of composites is a complex issue [7]. Secondly, it was predicted that fatigue performance could be improved by adding CNTs or MWCNTs to matrix structures as an important way to overcome these problems or reduce their negative effects.

In recent decades, researchers have studied the CNT and MWCNT reinforcement of polymers as another composite matrix. Among these, Azimpour-Shishevan et al. tried different weight percentages (0.1 and 0.5 wt%) of MWCNT and graphene nano platelets (GNPs) to investigate the effect of nanoparticles on the mechanical and thermal properties of CFRP composites. They reported that the addition of 0.5% MWCNT demonstrated the highest tensile strength [8]. In another study, Kumar et al. reported that they

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Peer review under responsibility of Karabuk University.

had investigated epoxy nanocomposites containing 0.25, 0.5, 0.75, and 1.0 wt% MWCNTs and by applying a variety of methods achieved homogeneous dispersion of the carbon nanotubes in the polymer matrix. They found that whereas the tensile strength had increased with the addition of 0.25–0.75 wt% MWCNT, the addition of 1.0 wt% MWCNT had reduced the strength [9]. Ayatollahi et al. also reported that by adding 0.1, 0.5 and 1.0 wt% of MWCNTs to epoxy resin, tensile strength had increased in specimens containing additions of 0.1 and 0.5 wt%. They concluded that agglomeration had occurred with the addition of 1.0 wt% MWCNT [10]. Another study found that addition of up to 0.5 wt% MWCNT increased tensile strength, although tensile strength declined with the addition of 0.9 wt% MWCNT [11]. Vallons et al. examined the fatigue life of carbon-epoxy non-crimp fabric composite specimens according to fiber directions (cross direction-CD and machine direction-MD) of  $\pm 45^\circ$ . As a result they determined that the fatigue performance in the MD and CD of the composites was higher at the applied load level [12].

As seen in the studies cited above, the nanotube reinforcement rates were quite low. However, despite their amount being nano or micro, one of the most important problems for particle-reinforced composites is that these particles form agglomerations in the matrix-resin during production, i.e., they cannot be dispersed homogeneously [13–15]. Therefore, researchers have worked to solve this and other problems associated with the properties of these composites.

Shekar et al. [15], used a sonication strategy to achieve steady dispersion of MWCNTs into the polymer composition. Gojny et al. [16] implemented a calendaring system for predictable dispersing of double-wall carbon nanotubes throughout the resin. The expansion of the unassertive weight was contrasted with a comparable proportion of carbon black-filled tar epoxy. Test outcomes showed that by supporting pliability, the nanotube-filled epoxy resin had improved the unbending nature, break sturdiness, and modulus of flexibility. Karapappas et al. [17] attempted to analyze mechanical and fracture behavior of carbon nanotube built-up composites, using nano filler levels of 0.1, 0.5, and 1.0 wt% for optimal compatibility with the epoxy matrix. Considering the test selectivity, basic improvements in fracture energy (by about 60%) and in fracture toughness were obtained with 1.0 wt% carbon nanotube addition into the carbon fiber polymers. Examinations revealed that further development of nano filler substances could improve the strength and glass transition temperature.

Mahato et al. [18] considered the impact of MWCNT weight percentage rate (0.1, 0.3, and 0.5 wt%) on the structure of glass fiber-reinforced polymer composites in order to select the most flexible composite depending on diverse crosshead speeds (1, 10, 100 mm/min). The outcome showed that the flexibility had been consistently improved with 0.1–0.3 wt% for each crosshead speed, but with further additions of 0.3–0.5 wt% there was a minor decrease in elastic properties when compared with the control specimens. Wang et al. [19] performed impact tests on GFRP sheets using epoxy modified with different (0.1, 0.3, and 0.5) wt.% of MWCNT with the aim of improving the damage resistance properties under low velocity drop weight impact loads. The impact behaviors were enhanced by the MWCNTs added to the epoxy structure. Damage prevention mechanisms (i.e., fracture, debonding, shrinkage, etc.) and the damage factor were also significantly improved with the pre-stretched glass fabrics compared to non-stretched fabrics. The extended fatigue life of carbon nanotube-reinforced composites under dynamic loads and their successful application in critical areas such as wind turbine blades and aircraft parts provided an understanding of the success and the capabilities of CNTs in primary applications [20]. Zhang et al. [20] noted a crucial decrease in the amount of weakening and crack propagation of the epoxy structure with the development of 0.5 wt% CNTs. They reported

that bridging of the crack was accomplished by a pull-out of the nanotubes connected with the crack line interface. A similar study on the effect of CNTs found that the fatigue crack development rate can be effectively diminished by (i) reducing the diameter of the CNTs, (ii) expanding the length of the CNTs, and (iii) enhancing the dispersion of the nanotubes. Thus, a 20-fold decrease was determined in the fatigue crack proliferation rate [21]. Other studies [5,6,22,23] have also investigated the fatigue strength of nanocomposite materials using different types of fiber reinforcement fabric and manufacturing methods. The organization of this study differs from the existing studies in the material and method used, as stated below. The nanocomposite materials fabricated in this study have not been previously studied in the literature to date. This study examined fatigue strength at machining direction using quadriaxial ( $-45^\circ/90^\circ/+45^\circ/0^\circ$ ) NCF-CFRPs modified by COOH-MWCNTs (0.5, 1.0, and 1.5 wt%) via the vacuum infusion technique. In order to examine the influence of COOH-MWCNTs on nanocomposite fatigue strength, we produced five different nanocomposites in terms of MWCNT content: D28 (neat), D29 (0.5 wt%), D30 (1.0 wt%), D31 (1.5 wt%), and D32 (0.5 wt% and surfactant-free). The percentages were determined according to previously conducted studies stated in the literature.

## 2. Experimental Procedure

### 2.1. Material

In this study, epoxy resin and hardener (EPOSIS 120), ( $-COOH$ ) MWCNTs, polyethylene glycol *tert*-octylphenyl ether (Triton X-100), ethanol, and NCF-CFRP were procured to produce the composites. For the composite fabrication, the resin/hardener proportion was chosen as 100:60. All components were used as received from the manufacturer. The MWCNTs were in dimensions of 10–20 nm in external diameter, 5–10  $\mu\text{m}$  long, and having a purity of higher than 96%. The polyethylene glycol *tert*-octylphenyl ether (Triton X-100) nonionic surfactant was suitable for epoxy composites. The MWCNTs were finished with ethanol. The orientation of the four-axis NCF-CFRP was  $-45^\circ$ ,  $90^\circ$ ,  $+45^\circ$ , and  $0^\circ$ , as depicted in Fig. 1 [24].

In this investigation, diverse weight percentage rates of MWCNTs (0.5, 1.0, and 1.5 wt%) were utilized to create MWCNT NCF-CFRP epoxy composites. Triton X-100 was added as a surfactant to achieve higher homogeneity of the epoxy and MWCNT mixture. The molecular weight of Triton-X averages 650 g/mole and the critical micelle concentration (CMC) value of Triton-X is 0.2 mM at  $25^\circ$  [25–27]. To study the effect of MWCNTs on mechanical properties of the NCF-CFRP composites, five types of specimens were prepared: neat, in three different weight percentages (0.5%, 1.0%, and 1.5%) using a surfactant, and at 0.5% without a surfactant. [24]

The base materials for this study were 300\*300-mm MWCNT composites produced in two consecutive phases. The first step was the preparation of the mixture according to the weight percentage formulation (0.5, 1.0, and 1.5 wt%) of MWCNT in epoxy resin, with addition of the Triton-X weight of 0.13 mg/mL to the solution volume ratio, and then all these added to 200 mL ethanol. This solution was mixed in a beaker and then poured into a recycling tank and sonicated in the flow cell at 80% amplitude using a 19-mm diameter sonotrode for 1 h. Immediately afterwards, 300 g epoxy resin was added to the mixture and sonicated for 10 h more at a fixed 80% sonication level. An ultrasonic processor (UIP200hdT, Hielscher) was used to disperse the MWCNTs. The temperature of the solution was kept at a constant 30–35  $^\circ\text{C}$  to prevent the MWCNTs from deteriorating at high temperatures. Fig. 2

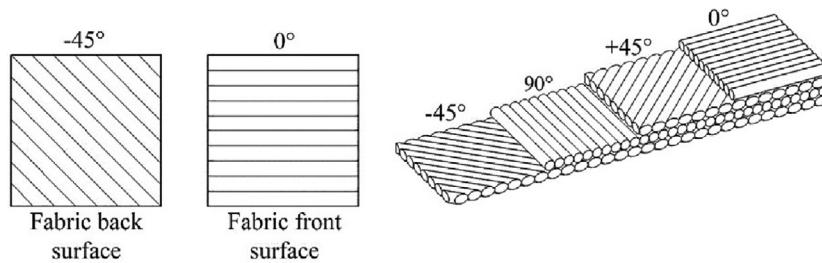


Fig. 1. Fiber orientations of four-axis non-crimp fabric CFRP [24].

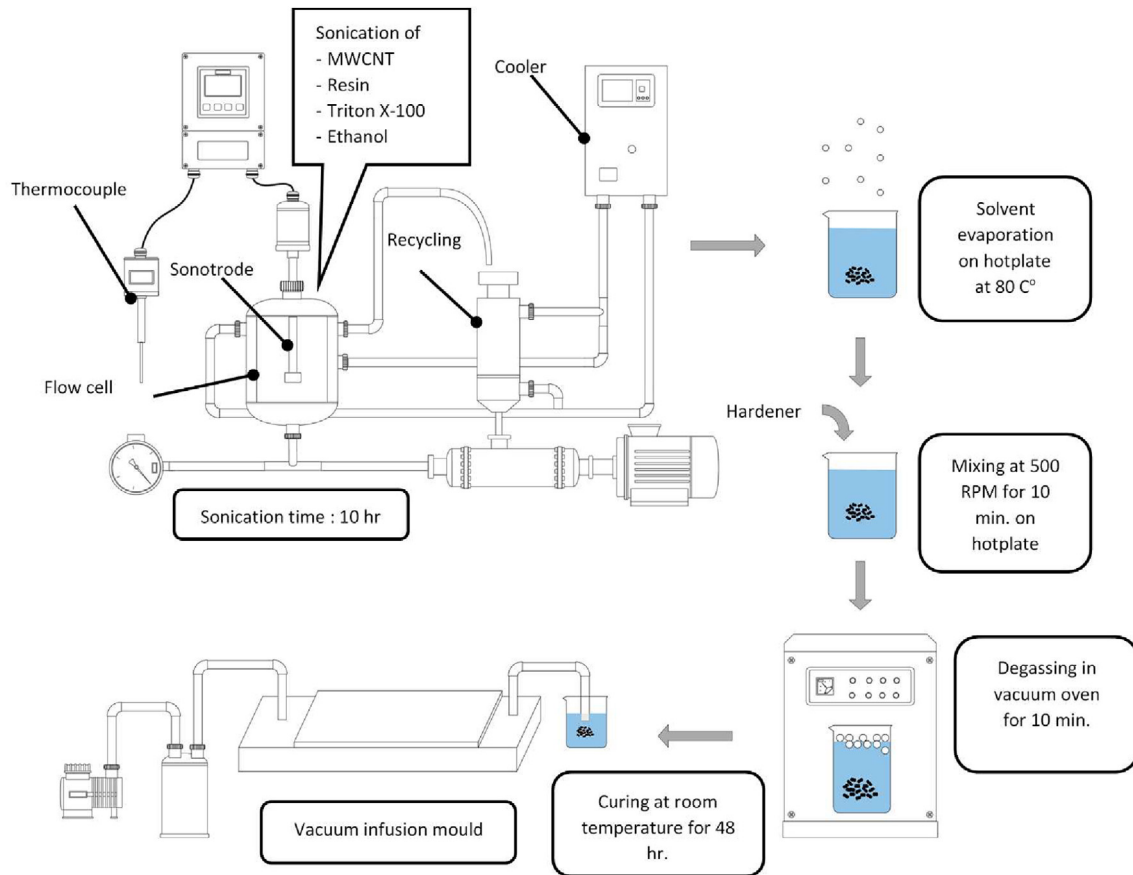


Fig. 2. Manufacturing setup of MWCNT-reinforced carbon nanocomposites [24].

shows the production system of the MWCNT NCF-CFRP composites [24].

To measure the homogeneity and dispersion of the MWCNTs within the composite material, UV-Vis spectroscopy was used in the wavelength range of 0–1000 nm [24,28]

### 2.2. Bending fatigue test

To investigate the fatigue property of the developed composite material, we used a bending fatigue testing machine, with test specimens prepared according to ASTM D3039 standard, as shown in Fig. 3. All fatigue tests were conducted at room temperature

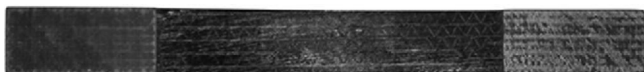


Fig. 3. Specimen prepared according to ASTM D3039 standard for plane bending fatigue test.

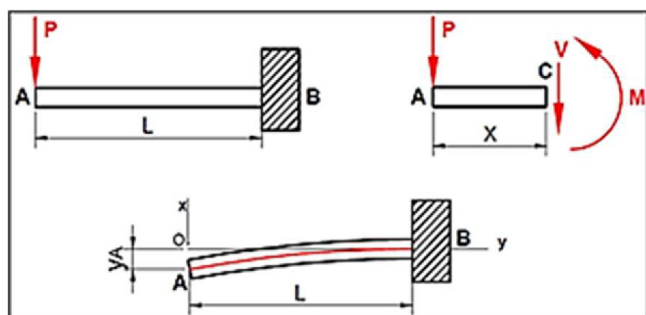
using a TURKYUS fatigue testing machine. Fatigue tests were load-controlled, and the stress ratio, defined as the ratio of the minimum to maximum stress, was set as 0.1 and the loading frequency as 10 Hz [29-32]. The test specimens were divided into five groups. The details of the specimens are shown in Table 1.

A schematic showing the working principle of the fatigue testing machine used in this study is given in Fig. 4. Plane bending fatigue tests were performed at different displacement amplitude strain values (11, 12, 13, 14, 15, and 16 mm) and a constant frequency value (10 Hz). Experimentally obtained load (Newton)-time (s) values were converted to stress-cycle values by performing calculations according to the maximum strain energy hypothesis. An example of the force-versus-time graphs obtained from the plane-bending fatigue test is given in Fig. 5. Here, fatigue test results are expressed as Wohler S-N (fatigue stress/number of cycles) graphics.

The fractured surfaces of the NCF-CFRP composite specimens obtained after the bending fatigue test were coated with gold for

**Table 1**  
Details and composition of the prepared fatigue test specimens.

Specimen Number	Material Code	Reinforcement	Matrix	MWCNT (wt.%)	Surfactant
Known	D28	quadriaxial (-45/90/+45/0) Non Crimp Carbon Fiber	Epoxy resin	0	-
2	D29	quadriaxial (-45/90/+45/0) Non Crimp Carbon Fiber	Epoxy resin	0.5	Triton X-100
3	D30	quadriaxial (-45/90/+45/0) Non Crimp Carbon Fiber	Epoxy resin	1.0	Triton X-100
4	D31	quadriaxial (-45/90 + 45/0) Non Crimp Carbon Fiber	Epoxy resin	1.5	Triton X-100
5	D32	quadriaxial (-45/90/+45/0) Non Crimp Carbon Fiber	Epoxy resin	0.5	-

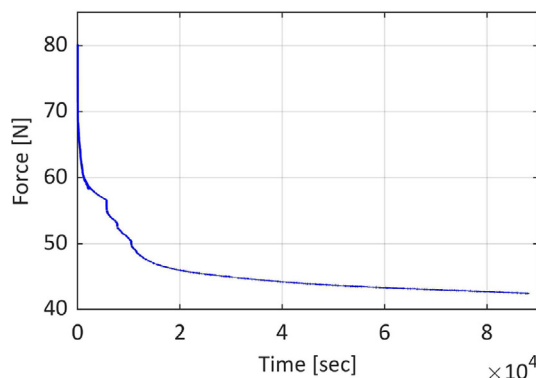


**Fig. 4.** Working principle of the plane bending fatigue testing machine.

electrical conductivity and then observed under scanning electron microscopy (SEM) to analyze the fracture behavior of the material.

**3. Results and discussion**

According to the UV – Vis spectroscopy examination of the distribution performance of the CNTs in the solution as a whole, the highest value in the spectrum was observed as around 330 nm. The absorbance values of the D29, D30, D31, and D32 specimens were 1.52, 0.96, 1.24, and 0.89, respectively [24]. The 0.5 wt% MWCNT epoxy solution showed a higher absorption at 330 nm than the others. The results indicated that the number of individual

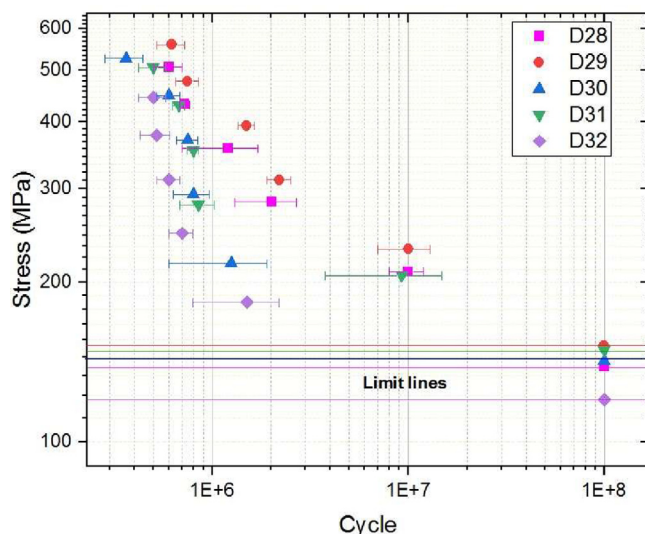


**Fig. 5.** Plane bending test result specimen.

nanotubes in the solution was greater. The MWCNT particles inherently tended to agglomerate with the strength of the Van der Waals’ bond. [33]. The steric driving force of the surfactant is important in dissolving CNT agglomerates [27]. The surfactant ratio was ineffective when the amount of nanotubes was increased [25]. The ratios of 1.0 and 1.5 wt% MWCNT epoxy showed a sudden drop from the peak in these tests. This was interpreted and accepted as indicating a higher rate of agglomeration [34].

**3.1. Bending fatigue**

The experimental plane bending fatigue behavior of all specimens as stress-versus-cycle (S/N) in a Wohler diagram is presented in Fig. 6. The highest fatigue life value was obtained in specimen D29 (0.5 wt% MWCNT), followed by D28 (neat CFRP), D31 (1.5 wt



**Fig. 6.** Stress-cycle (S/N) curves of composite specimens containing neat CFRP with different % MWCNT.

% MWCNT), D30 (1.0 wt% MWCNT), and D32 (0.5 wt% MWCNT without surfactant), respectively. The fatigue life of all specimens increased with decreasing fatigue loading, as presented in the S/N diagram. Across the entire range of applied stresses, the 0.5 wt % MWCNT-modified CFRP showed an increase in the number of cycles to failure [35].

As seen before, D29 (0.5 wt% MWCNT) had the highest absorption level, which indicated that it contained more individual nanotubes than the others. Therefore, these experimental quantitative findings could be understood as the result of higher homogeneous distribution. Moreover, homogeneous distribution of MWCNT increased the strength, with strong interface bonding between the MWCNT and the epoxy [36,37]. Consequently, this morphological circumstance could indicate that the initiation and propagation of cracks in the epoxy resin had been obstructed, and that the fracture energy needed for cracking had been improved, enhancing the fatigue strength [34]. In other word, the reason for the increment in fatigue strength values for the specimen having 0.5 wt% MWCNT was the formation of covalent bonds between the epoxy matrix due to the enhanced Van Der Waals forces and the better distribution of nanotubes in the epoxy [34,38].

However, UV - Vis spectroscopy results of the nanocomposite specimens containing 1.0 and 1.5 wt% by weight of MWCNT showed low values, which can be interpreted as indicating increased agglomeration in these specimens. These results also show that the number of single nanotubes had decreased, which meant that the amount of absorption and homogeneity and the small transportation barriers against deformation had been reduced. As a result, the increase in agglomeration decreased the fatigue strength of the materials. These effects of small or large particles are known in the plastic deformation theory. Even if it is in the same amount, the homogeneous distribution of the small secondary particles in the matrix is much more effective than non-dispersion of the particles and agglomeration because the homogeneous distribution of the fine particles creates a barrier in too many areas for the mechanical effect to successfully achieve deformation. In this way, the strength increases. According to the literature and UV-absorption test results, the reduction in fatigue strength for higher percentages of MWCNT can be explained by the increase in agglomeration, i.e., poorer dispersion/individual distribution of MWCNTs in the NCF-CFRP matrix and hence, low homogeneity. Some researchers even interpret the decrease in strength at higher MWCNT amounts as agglomeration defect behavior of the MWCNTs due to local MWCNT differences and the impairing of the charge transfer to the epoxy matrix [35,38-40].

A higher fatigue strength value was obtained in specimens containing 0.5 wt% MWCNT because of the delay in crack formation and propagation. When a nanocomposite is exposed to a load, it forms micro cracks and as the load continues to move, the micro cracks expand in the polymer matrix. A CNT with high strength prevents crack propagation. When micro cracks encounter CNTs, the cracks are deviated [41]

This indicates that the presence of MWCNTs in the matrix contributes to the generation of energy absorption in the bending fatigue test [42,43]. The lower fatigue strength values in specimens containing 1.0 wt% and 1.5 wt% MWCNT indicate that agglomeration had reduced the interface adhesion strength between the carbon fiber and epoxy resin matrix, thereby lowering the resistance of the CFRP to fatigue crack propagation [44]. Under fatigue loading conditions, the agglomeration of MWCNTs in the matrix can cause poor interfacial bonding between the reinforcers (macro and nano) and the matrix material, and the magnitude of load transfer from the matrix zone to the MWCNTs can have a significant negative effect on the fracture [34]. Agglomeration in the resin matrix leads to stress concentration, resulting in a decrease in strength [40].

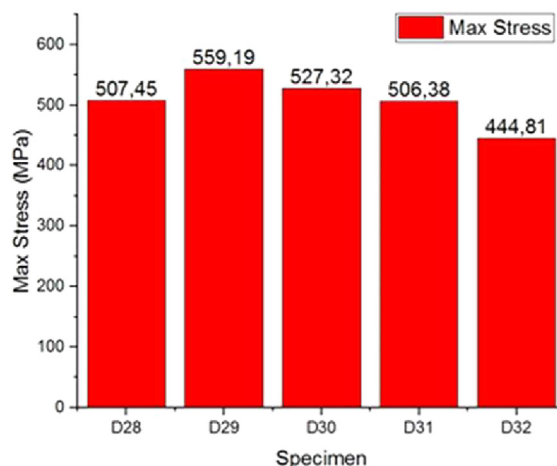


Fig. 7. Maximum stress results of NCF CFRP composites.

The results of the maximum stress obtained from the data in Fig. 6 are shown in Fig. 7. The maximum stress values of the MWCNT NCF-CFRP laminated specimens ranked from highest to lowest were: D29 (0.5 wt% MWCNT), D30 (1.0 wt%), D28 (Neat CFRP), D31 (1.5 wt% MWCNT), and D32 (0.5 wt% MWCNT without surfactant). Fig. 8 shows results of the fatigue limit stress obtained from the data in Fig. 6. The fatigue limit for the MWCNT NCF CFRP composites increased in the following ascending order: D29 (0.5 wt% MWCNT), D31 (1.5 wt% MWCNT), D30 (1.0 wt% MWCNT), D28 (Neat CFRP), and D32 (0.5 wt% MWCNT without surfactant). However, the results of Fig. 7 (max. stress) and Fig. 8 (fatigue limit) differed somewhat from those of Fig. 6. The fatigue limit of the composites was influenced by the compressive stress and heat generated during fatigue testing [22]. Although high stress leads to formation of larger cracks in smaller numbers, low stresses generate large numbers of smaller cracks [45]. Smaller cracks require a great number of fatigue cycles to spread and connect, whereas fewer cycles are sufficient for great cracks to cause major damage and eventual failure [34].

### 3.2. Fatigue fracture surface morphology

Figs. 9–12 present SEM macro and microstructure photographs of the fatigue fracture surfaces of the MWCNT-NCF CFRP epoxy specimens. The SEM macro images in Figs. 9 and 10 shows the morphology of the fractured or broken surfaces. As the strain amplitude

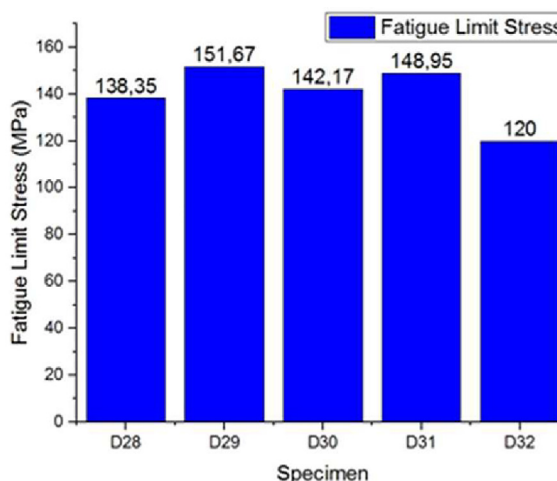


Fig. 8. Fatigue limit results of NCF CFRP composites.

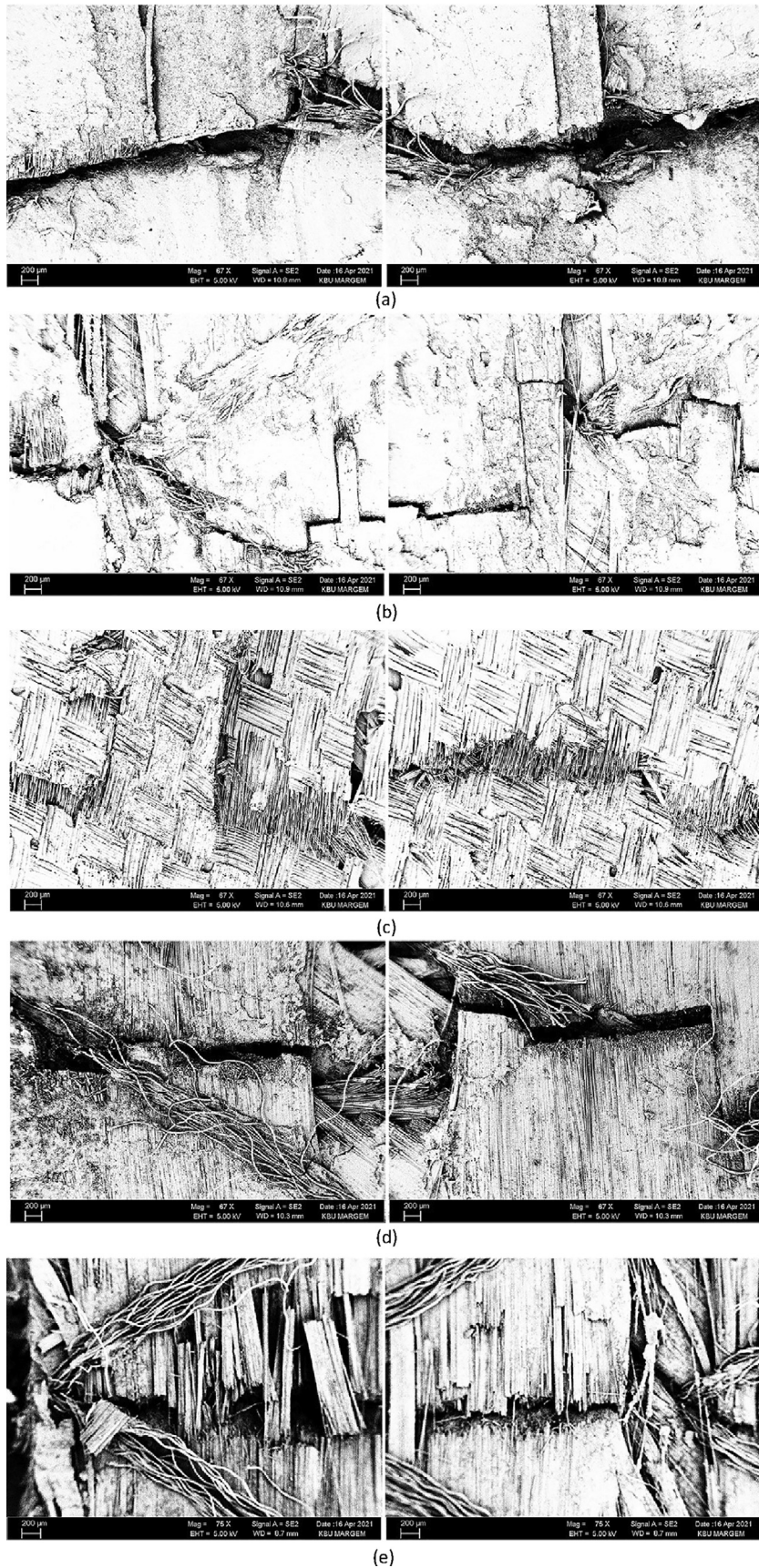


Fig. 9. SEM macrostructure images of the fatigue test specimens at minimum stress amplitude: (a) D28, (b) D29, (c) D30, (d) D31, (e) D32.

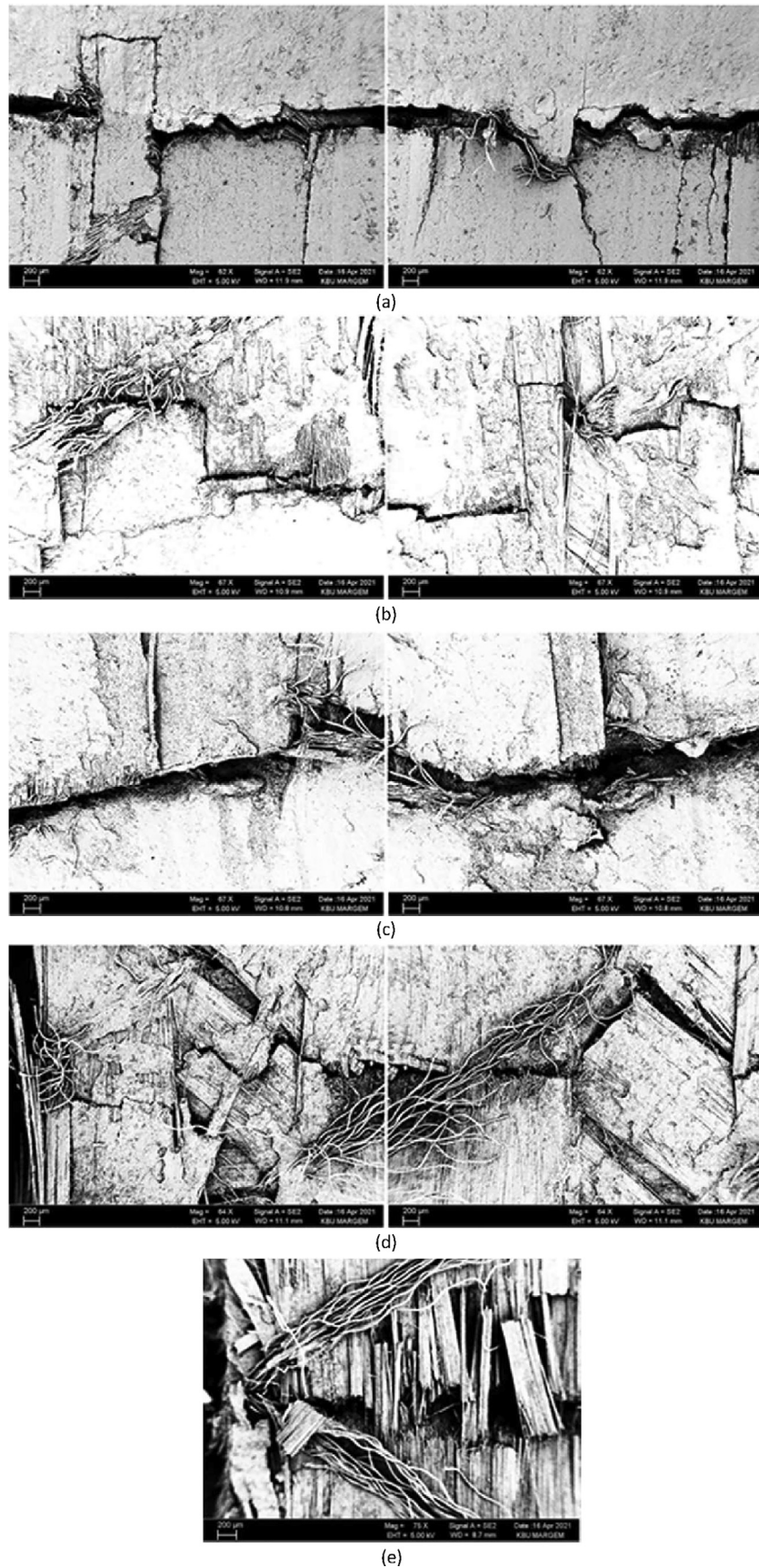


Fig. 10. SEM macrostructure images of the fatigue test specimens at maximum stress amplitude: (a) D28, (b) D29, (c) D30, (d) D31, (e) D32.

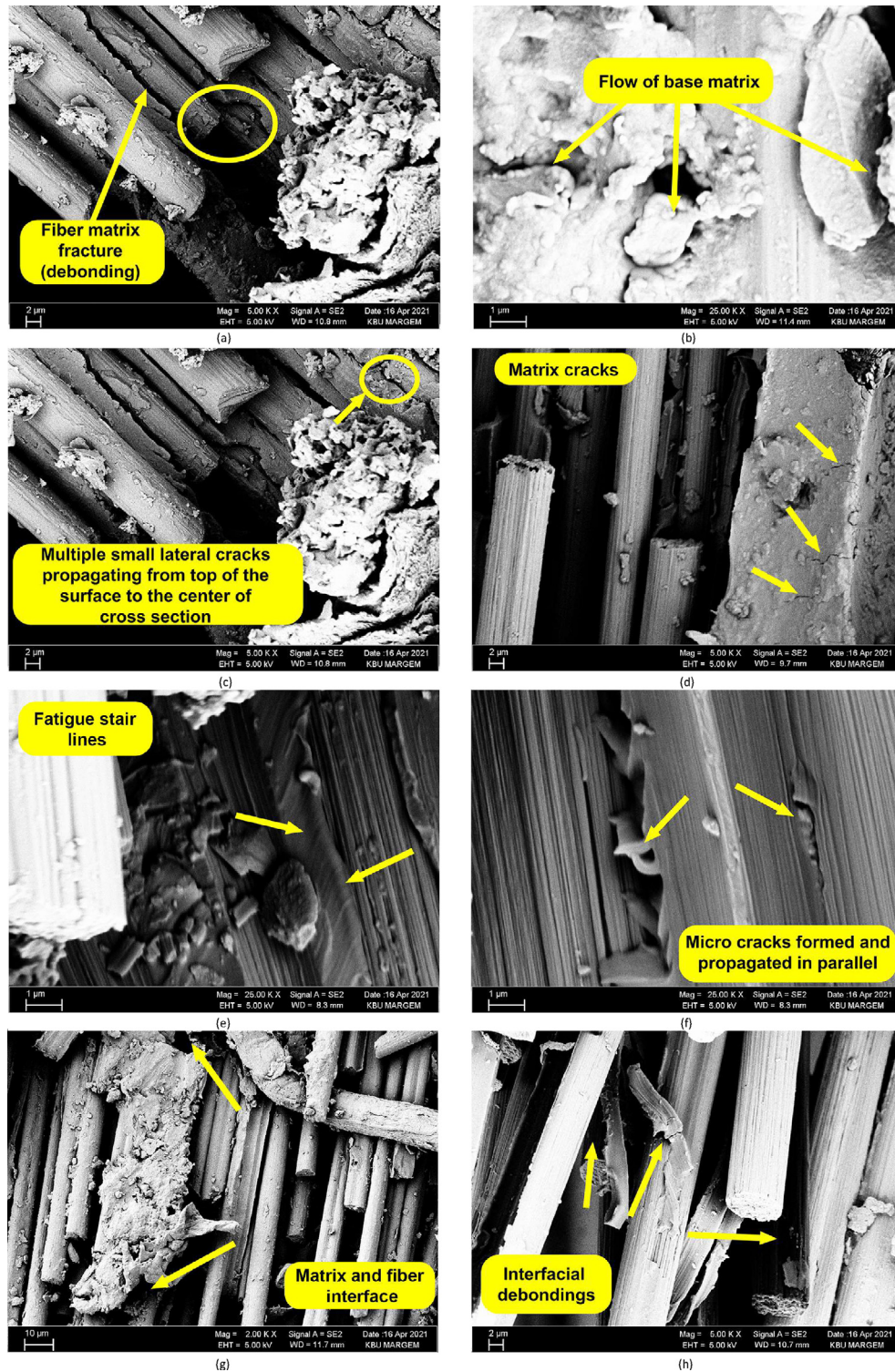


Fig. 11. SEM microstructure images of the fatigue test specimens at minimum stress amplitude.

increased, the severity increased; however, test specimen D29 (0.5 wt% MWCNT) exhibited relatively good resistance to the strain amplitude and displays a small fracture surface. The resin addition of MWCNTs reduced the damage by effectively boosting crack resistance and inhibiting crack propagation [40]. A rougher fracture surface was observed in specimens with increased MWCNT content.

As reported by researchers [46], fatigue failure and also bending fatigue failure can occur in different forms in composite materials, including as broken fibers, fiber–matrix interface failure, delamination, and as cracks present in the matrix. Moreover, the main causes of fracture failure in composite materials due to plane bending fatigue are specified in particular as:

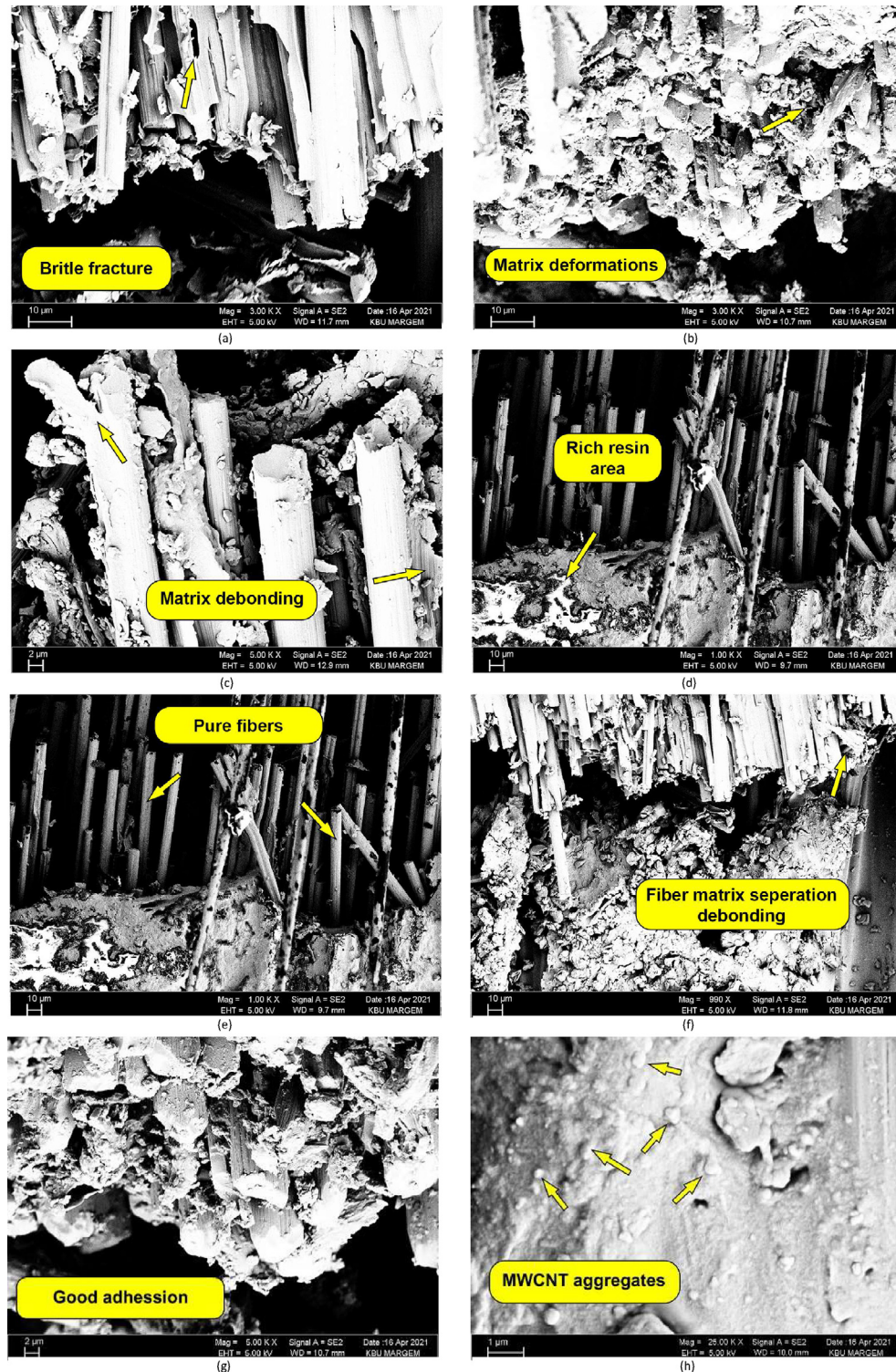


Fig. 12. SEM microstructure images of the fatigue test specimens at maximum stress amplitude.

- A flaw in the base matrix (typical of fatigue)
- Fiber-matrix departure (fiber deboning)
- Separation of the sheets (delamination)

Fig. 11b (D31) shows the structure of the MWCNT-modified matrix. Fig. 11a (D29) and 11 h (D30) show interfacial debonding fatigue damage between the fibers and matrix after the micro cracks inside the specimen had reached saturation. The interfacial debond-

ing amplified and expanded along the interface with continuous fatigue loading. The possibility of fiber breakage became more severe as the stress level increased and multiple lateral cracks arose along the damage line in the specimen (11c-D29, 11d-D32, and 11f-D32). As shown in Fig. 11e (D32), cracks progressed in diverse directions and separated from each other with stair lines. However, as the distortion value decreased with enhanced higher cycles, the stair lines decreased in length and disappeared [47].

Fig. 12a (D32) exhibits the brittle failure characteristics of the composites. Agglomeration led to the induction of micro cracks and intensification of crack propagation in the composite. Moreover, it produced non uniform stress distribution that led to a sudden brittle cracking of the composite and substantial degradation of the mechanical performance and elasticity of the material [48]. In 12b (D29), the interface between fiber and matrix is well bonded so that the applied stress was accordingly transferred throughout the composite, including the matrix and fibers. This was evidence that the enhanced fiber–matrix interface bonding had improved the fatigue properties (12c–D29).

Whereas the amount of epoxy adhering to the surface of the fiber containing 0.5 wt% MWCNT was higher (12g–D29), the surfaces of the 1.0 and 1.5 wt% MWCNT fiber composites (12f–D30) were smooth. Fig. 12e (D32) and 12d (D32) exhibit a clear fiber surface with no matrix residue and a rich matrix area, respectively. Agglomeration of MWCNTs was the cause of the weak interface bond between fiber and matrix, resulting in fiber retraction and delamination (12h–D31).

#### 4. Conclusions

The results obtained were as follows;

- According to the UV–Vis spectroscopy results at 330 nm, the highest amount of individual COOH–MWCNTs was observed in the specimen containing 0.5 wt% MWCNT.
- Although the MWCNTs were functionalized and treated with a surfactant, at high concentrations agglomeration occurred. As a result, the absorbance spectra of the solutions with 1.0% and 1.5% MWCNT were low.
- The highest fatigue life value was obtained in the D29 (0.5 wt% MWCNT) specimen, followed by D28 (neat CFRP), D31 (1.5 wt% MWCNT), D30 (1.0 wt% MWCNT), and D32 (0.5 wt% MWCNT without surfactant), respectively.
- This study demonstrated that with the appropriate ratio of COOH–MWCNT doping, it was possible to produce nanocomposites with lower mass and high equivalent strength, using fewer layers.
- Electron microscopy images taken from the fracture surfaces of the test specimens revealed that individual COOH–MWCNTs interacted with the fibers and formed a bridge between fiber and matrix, whereas agglomerations caused weak bonding between fibers and matrix and caused delamination, making the material more brittle.
- Specimens containing 0.5 wt% MWCNT exhibited a higher fatigue strength value because crack formation and propagation had been obstructed.
- The amount of epoxy adhering to the surface of the fiber containing 0.5 wt% MWCNT was higher, whereas the surfaces of the 1.0 wt% and 1.5 wt% MWCNT fibers were smooth.
- Although the cracked surface of the neat CFRP composite (0 wt% MWCNT) specimen was fragile, the fractured surface of the composite specimen containing 0.5 wt% MWCNT was malleable because of good interfacial bonding.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This study was supported by the Scientific Research Project Coordinator of Karabuk University within the scope of the KBÜBAP–DR project. Some of the experimental studies were supported by the Boğaziçi University Mechanical Engineering Composites Research Laboratory and the Kırklareli University Mechanical Engineering Laboratory. Carbon fabrics and dispersants were supplied by METYX Composites and Balmumcu Kimya. The authors greatly appreciate the sponsorships of the above-mentioned universities and companies for their generous support.

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