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Mechanical Properties of Graphene/Epoxy Nanocomposites under Static and Flexural Fatigue Loadings

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ABSTRACT

In the present study, the effect of various weight fractions of graphene nanoplatelet (GPL) on flexural fatigue behavior of epoxy polymer has been investigated at room temperature and generally the temperature was monitored on the surface of specimen during each test. The flexural stiffness of graphene nano-platelet/epoxy nanocomposites at 0.1, 0.25 and 0.5 wt. % as a main effective parameter on flexural bending fatigue was considered. The samples were implemented to different displacement fatigue amplitudes and it led to the known bending strength ratio. Finally, the flexural fatigue responses of graphene nano-platelet/epoxy nanocomposites at mentioned graphene contents were taken into account. The experimental results show that the addition of 0.25 wt. % of graphene nano-platelet on fatigue life was more effective in comparison with 0.1 and 0.5 wt. % epoxy graphene nanocomposites. According to the addition of graphene nano-platelets, a remarkable increase in fatigue life of epoxy was observed. For instance, at the bending strength ratio equal to 43% by adding 0.1, 0.25 and 0.5 wt. % of graphene into epoxy resin, 22.4, 27.4 and 17 times improvement in flexural bending fatigue life of the neat epoxy were observed, respectively.

1. Introduction

Fatigue life is a major concern of designers and actually they deal with predicting it. Normally in fatigue tests, load or displacement can be controlled. For instance, in the displacement-controlled method the specimen is subjected to the known displacement as well as the variable loadings. In this method, the flexural bending fatigue testing machinery based on the cantilever beam theory is used. This test method describes a precedure to determine the reversed or repeated bending fatigue properties of neat polymers or reinforced composites with nanoparticles by fixed cantilever, constant amplitude of displacement testing method. The specimen is held at one end, acting as a cantilever beam and cycled by flexure followed until complete failure. Then the number of cycles to failure is recorded as a measure of the fatigue life. In the literature, the flexural fatigue behavior of composites and nanocomposites has been carried out by many researchers [1-3]. For composites under displacement-controlled condition, Paepegem and Degrieck developed an experimental setup for bending fatigue loading [1] and they adopted a residual stiffness model which describes the fatigue damage behavior of the composite material [2]. Also, Paepegem et al. [3] used a finite element approach for composites fatigue life prediction. For nanocomposites material under the displacement controlled fatigue loading condition, many researchers investigated the fatigue life using this technique [4-9]. Ramkumar and Gnanamoorthy [4] studied on improving the stiffness and flexural

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fatigue life of polymer matrix reinforced nanocomposites with nanoclay. Their study described the effect of nanoclay fillers addition on the flexural fatigue response of Polyamide 6 (PA6). Rajeesh et al. [5] considered the influence of humidity on flexural fatigue behavior of commercial grade polyamide 6 granules and hectorite clay (organically modified with a hydrogenated tallow quaternary amine complex) nanocomposite. Timmaraju et al. [6] investigated the influence of environment on flexural fatigue behavior of polyamide 66/Hectorite nanocomposites in still air and circulated water mist environments. Also, they conducted the effect of initial imbibed moisture content on flexural fatigue behavior of polyamide 66/Hectorite nanocomposites (PA66CN) conducted under the deflection control mode using a custom built, table-top flexural fatigue test rig at a laboratory condition [7]. Shokrieh et al. studied the bending fatigue behavior of epoxy resin reinforced with carbon-nanofiber (CNF) [8] and industrial graphene [9]. They also investigated the bending fatigue behavior of synthesized graphene/CNF hybrid nanocomposites subjected to different displacement amplitudes fatigue loadings [10]. Due to the addition of hybrid nanoparticles, a remarkable improvement in fatigue life of epoxy resin was observed in comparison with the results obtained by adding 0.25 wt. % CNF or graphene into the resin, separately. In the literature, it was also found that the presence of multi-nanoparticles in composites improves the properties of nanocomposites. Some researchers used hybrid fillers in order to obtain a perfect potential of both fillers. For instance, Silica and Carbon nano tube (CNT) nanoparticles were taken into account in the literature [11, 12] to improve the fatigue behavior of reinforced composites. Boeger et al. [11] appointed Silica and MWCNT hybrid nanoparticles to increase the high cycle fatigue life of epoxy laminates and finally reported that the life was increased by several orders of magnitude in number of load cycles. Fritzsche et al. [12] investigated the CNT based elastomer-hybrid-nanocomposites prepared by melt mixing and showed promising results in electrical, mechanical and fracture-mechanical properties. On the other hand, the CNT and graphite nano-platelets (GNPs) to epoxy nanocomposites were shown by Li et al. [13]. It was represented that the flexural mechanical as well as electrical properties of the neat resin were marginally changed by hybridization.

A survey in the available literature reveals that the addition of nanoparticles can improve the fatigue behavior of composites. However, there is a lack of research on the fatigue behavior of epoxy resin filled with various weight fractions of graphene nano platelets.

Table 1. Properties of ML-526 epoxy resin

Physical Properties		Mechanical Properties	
Viscosity at 25 °C (Centipoise)	Glass transition temperature (°C)	Tensile Modulus *(GPa)*	Tensile Strength *(MPa)*
1190	72	2.6	60

In this research, the static and flexural fatigue behavior of graphene/epoxy nanocomposites at different weight fractions under displacement controlled flexural loading is investigated.

Falkner and Skan considered two-dimensional wedge flows. They developed a similarity solution method in which the partial differential boundary-layer equation was reduced to a nonlinear third-order ordinary differential equation which does not have an exact solution ;besides, the numerical solution for this equation is time consuming and difficult.

2. Materials Specification

2.1. Epoxy Resin

In the present research, ML-526 (Bisphenol-A) epoxy resin was selected because of its low viscosity and extensive industrial applications to fabricate the specimens in Iran. The low viscosity of the matrix makes the dispersion of additives easier. Physical and mechanical properties of ML-526 epoxy resin are shown in Table 1. The curing agent was HA-11 (Polyamine). The ML-526 resin and the HA-11 polyamine hardener were supplied by Mokarrar Company, Iran.

2.2. Graphene Nano-Platelets

In this research, GPLs were supplied from Chemical Engineering School, Shandong University, China. The GPL powders have an average thickness of approximately 3-5 nanometers and a typical surface weight of 500 m2/g obtained from Brunauer-Emmett-Teller (BET) test of nano graphene powders. The diameter range is 40-120 nm and the average particle diameters are around 80 nm. The physical properties of GPLs are shown in Table 2. The Raman spectra of the synthesized graphene nano sheets powder, D, G and 2D bands are demonstrated in Fig. 1.

Table 2. GPL nano particles specifications

Nano particle	Diameter (*nm*)	Thickness (*nm*)	Specific Surface area (m^2/g)
GPL	40-120	3-5	500

3. Specimen Preparation

The polymer nanocomposites reinforced with 0.1, 0.25 and 0.5 wt. % graphene were prepared as described below. The mixture containing of GPL content was sonicated for 30 min.

The mixture containing of GPL content was sonicated for 30 min. It is worth mentioning that during the sonication, the mixture container was kept by the aid of ice-bath to prevent the overheating of the suspension to keep the temperature around 40 °C. After sonication, the hardener at a ratio of 15:100 was added to the mixture and stirred gently for 5 min. Then, it was vacuumed at 1 mbar for 10 min to remove any trapped air. Six samples were prepared and cured at room temperature for 48 h and followed by 2 h at 80 °C and 1 h at 110 °C for post curing.

4. Calculation of Flexural Stress

In this study, high cycle fatigue properties of nanocomposites are measured by a modified cantilever beam bending test. A typical fatigue life test specimen for the cantilever beam bending test is shown in Fig. 2. The presented specimen is designed based on B593-96 ASTM Standard [14] and the method presented by Ramkumar and Gnanamoorthy [4]. The wide end of the specimen is clamped to a bed plate, while the narrow end is cyclically deflected (See, Fig. 2(a)).To catch reliable results of the flexural fatigue strength, the gage area of the specimen is designed based on stress concentration concept (Fig. 2(b)).

To obtain reliable results, the surface area available for crack initiation must not be too small.
If the cross section of a beam is symmetrical with respect to its neutral plane, then the maximum tension or compression stress at a given cross section for small displacements within elastic deformation behavior is calculated according to the following equation.

$$\sigma_{\max} = \frac{M \times H}{2 \times I} \quad (1)$$

where, $\sigma_{\max}$ is the maximum stress, M is the local bending moment, H is the thickness of the beam, I is the second moment of area of the cross section.

According to Fig. 3, the specimen is a wedge-shaped beam and the cross section is not uniformed and defined by means of a parameter called "local B". Therefore, the magnitude of the second moment of area of the cross section depends on the position along the x-axis.

$$B(x) = \frac{B_0}{L_0} \times (L_0 - x) \quad (2)$$

$$I(x) = \frac{B_0 (L_0 - x) H^3}{12 L_0} \quad (3)$$

where, L_0 is its overall length and B_0 is the width at the base of the wedge-shaped beam. The curve of the neutral plane in a bent beam is described by the differential equation of the deflection curve. Finally by integrating the following equation, the maximum stress in the critical cross section is obtained as follows [15]

$$\sigma_{\max} = -\frac{z_0 \times E \times H}{L_0{}^2} \quad (4)$$

where, $z_0$is the displacement at point x = z_0 and E is the Young's modulus. The relation between the displacement z_0 at the tip and the maximum stress σ_{max} for small deformation is linear.

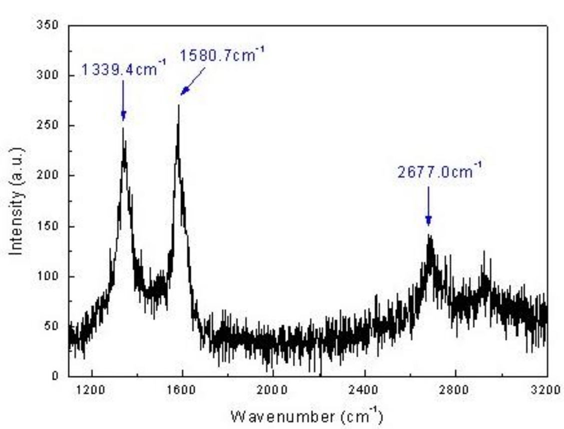

Figure 1. Raman spectra of synthesized graphene platelets (GPL), D, G and 2D bands

5. Test Instruments

5.1. Static Testing Instruments

The Santam universal testing machine STM-150 was utilized to perform bending tests in accordance with the ASTM D790 standard [16]. The cross-head speed for bending tests was 16 mm/min.

To analyze hybrid nanoparticles, gold sputtered samples were used. Field-Emission Scanning Electron Microscopy (FESEM) photographs were taken by using a Zeiss-Germany Sigma and Hitachi-Japan S-4160 Microscopes with gold sputtered samples.

5.2. Experimental Setup for Flexural Bending Fatigue

The pure epoxy and reinforced polymer specimens are mounted into a fixed cantilever, constant deflection type fatigue testing machine. The machine called BFM-110, shown in Fig. 4, is designed and manufactured based on a developed version of a

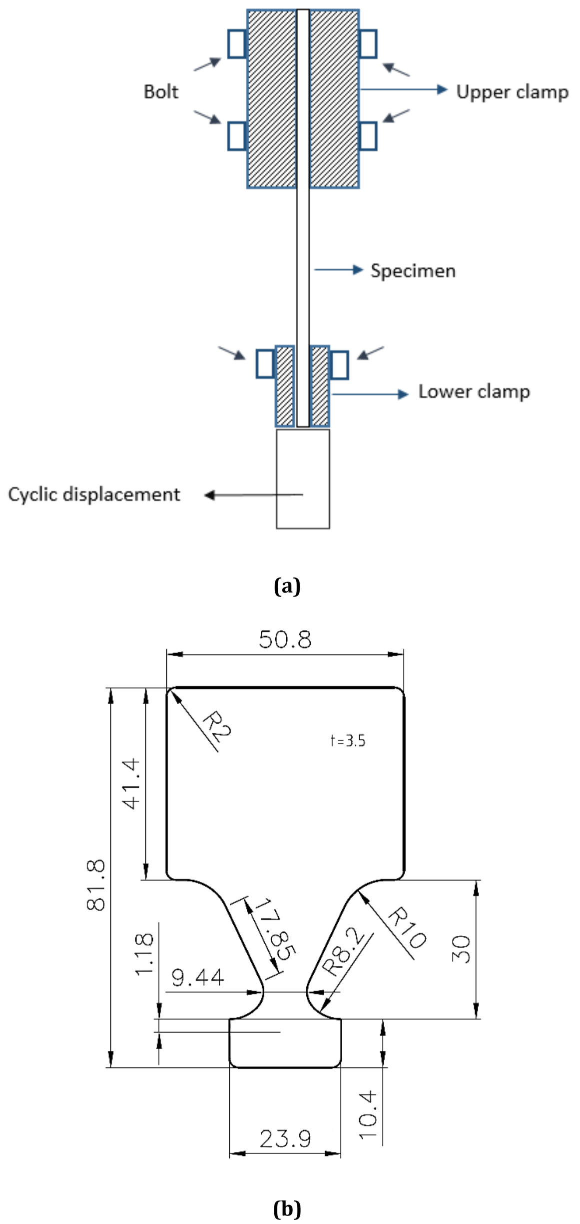

Figure 2. (a) Schematic of specimen clamping procedure (b) Dimensions of the bending fatigue specimen (mm)

testing machine designed by Paepegem and Degrieck [1]. The specimen is held at one end, acting as a cantilever beam and cycled until a complete failure is achieved. The number of cycles to failure is recorded as a measure of the fatigue life during the test. The number of cycles to failure is recorded as a measure of the fatigue life during the test. Generally, the shaft of the motor has a rotational speed of 0-1450 rpm. The power is transmitted via a V-belt to the second shaft, which provides a fatigue testing frequency between 2-20 Hz and gives the possibility to investigate the influence of the frequency in this range of values. The power transmission through a V-belt ensures that the motor and the measuring system are electrically isolated.

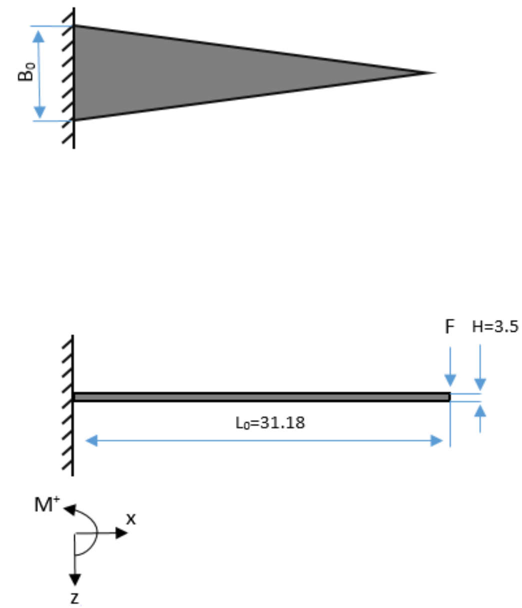

Figure 3. Schematic view of a beam, with coordinates

The amplitude of the imposed displacement is a controllable parameter and the adjustable crank allows choosing between single-sided and fully reversed bending i.e., the deflection can vary from zero to a maximum deflection in one direction, or in two opposite directions, respectively. The maximum deflection is measured by a displacement dial gage at the back of the lower clamp. The number of cycles to failure should be counted directly for each test specimen. A counting signal was generated once per cycle by a PES-R18PO3MD reflector speed sensor which was supplied by IBEST Electric, LTD., China. The counting signal was transferred to the counter fabricated by RASAM Madar electronic Company, Iran. In this setup, there are two parallel stands with counting system implemented separately. To stop the counter of speed sensors, at the bottom of each specimen a thin wire as an electrical contact is used and after failure, the damaged specimen drops down and disconnects the wire and leads to stop the counting system. Therefore, after failure of both specimens, control system acts and turns off the main current of the machine completely.

6. Result and Discussions

6.1. Static Bending Strength

Mechanical properties of polymers are generally supposed to be improved by the addition of graphene. Based on ASTM D790 standard [16], the static tests to acquire flexural strength and stiffness of neat epoxy resin and graphene nanoplatelet/epoxy

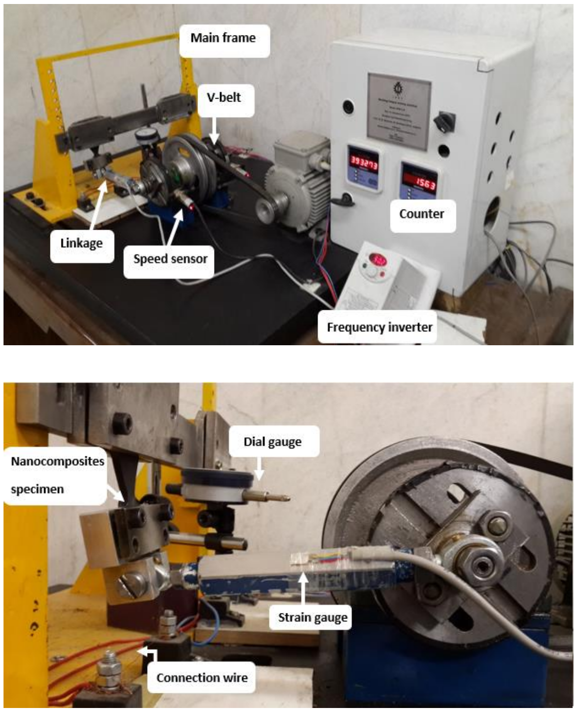

Figure 4. The experimental setup for the displacement controlled flexural bending fatigue loading

nanocomposites at 0.1, 0.25 and 0.5 wt. % were taken into account. The highest magnitude for the flexural modulus was achieved at 0.25 wt. % of GPL by nearly 12% improvement. The flexural stiffness and strength were presented in Fig. 5 and Fig. 6 respectively.

6.2. Cyclic Flexural Fatigue Life

The performance of the neat epoxy resin and graphene/epoxy nanocomposites under fatigue condition was conducted following a comprehensive established method based on ASTM B593-96 standard [14] and the method presented by Ramkumar and Gnanamoorthy [4]. In the experiments, test setup frequency was adjusted on 5 Hz. The effective length of the specimen subjected to the bending is 31.18 mm. The drawing of the specimen is shown in Fig. 2(b). The strength ratio (the bending stress normalized by the bending strength) versus number of cycles to failure is presented in Fig. 7. For example, at an applied bending stress ratio of 43%, the number of cycles to failure of 0.1, 0.25 and 0.5 wt. % of GPL/epoxy nanocomposites is 22.4 , 27.4 and 17 times in comparison with pure epoxy.

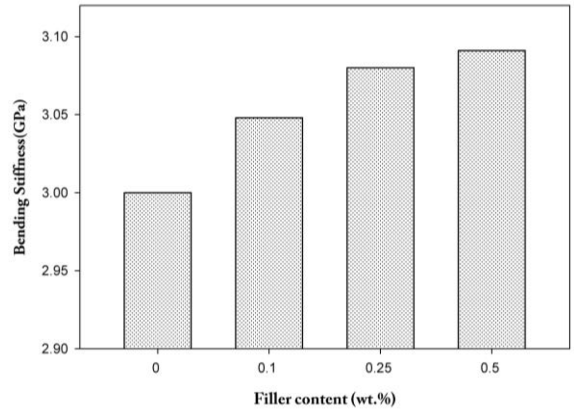

Figure 5. Bending stiffness for neat epoxy resin, 0.1 wt. %, 0.25 wt.% and 0.5 wt. % GPL/epoxy nanocomposites at frequency equal to 5 Hz

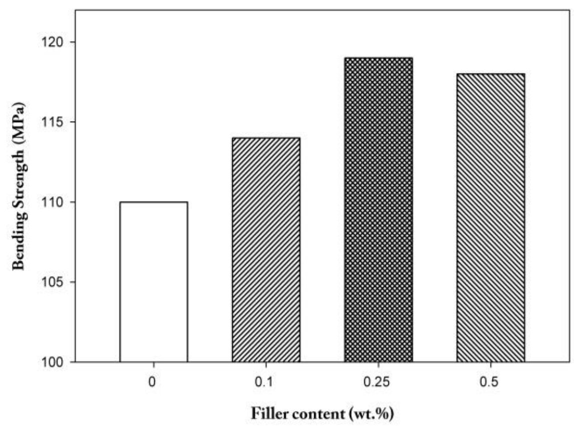

Figure 6. Bending strength for neat epoxy resin, 0.1 wt. %, 0.25 wt.% and 0.5 wt. % GPL/epoxy nanocomposites at frequency equal to 5 Hz

6.3. Monitoring the Temperature During Flexural Fatigue Life

The trend of temperature during fatigue test was demonstrated in Fig. 8. It shows that temperature of the specimen increases in the first early stages until 10000 cycles by 3 °C and after 20000 cycles before final failure slightly changes.

6.4. Dispersion and Morphology Analysis

The fracture surface of specimen of 0.25 wt. % GPL/epoxy nanocomposites was evaluated and presented in Fig. 9. As depicted in FESEM picture of the fractured surface, a uniformed dispersion of graphene nano platelets was observed. The high resolution image of the fracture surface of specimen of 0.5 wt. % GPL/epoxy nanocomposites with insufficient dispersion was evaluated and presented in Fig. 10. As depicted in it, due to the insufficient dispersion of GPL, the stiffness of reinforced

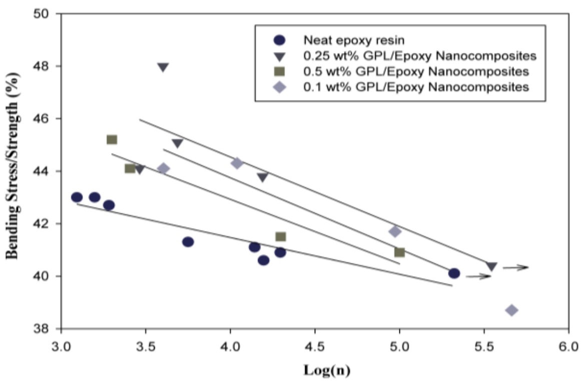

Figure 7. Bending strength ratio vs. number of cycles to failure for neat epoxy resin, 0.25 wt. % and 0.5 wt. % GPL/epoxy nanocomposites at frequency equal to 5 Hz

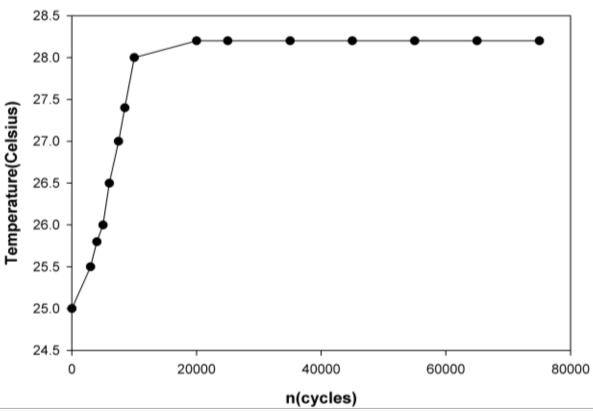

Figure 8. Temperature vs. number of cycles during fatigue test

composites with GPL slightly improved and strength was not influenced like stiffness.

7. Conclusions

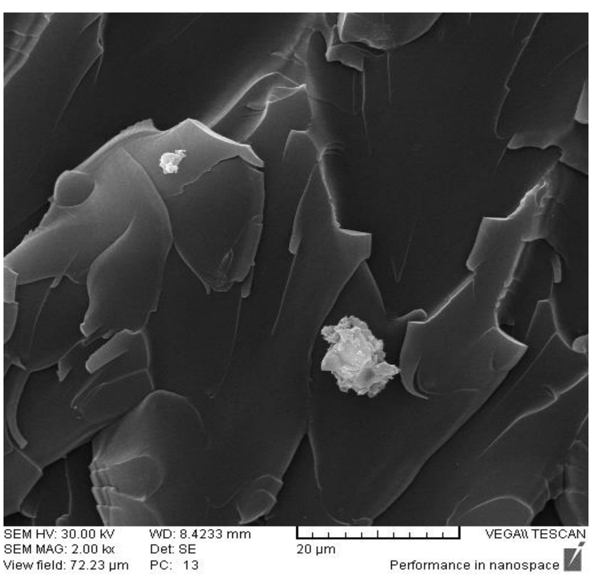

Figure 9. FESEM of the fracture surface with uniform dispersion of 0.25 wt. % GPL/epoxy nanocomposites [9]

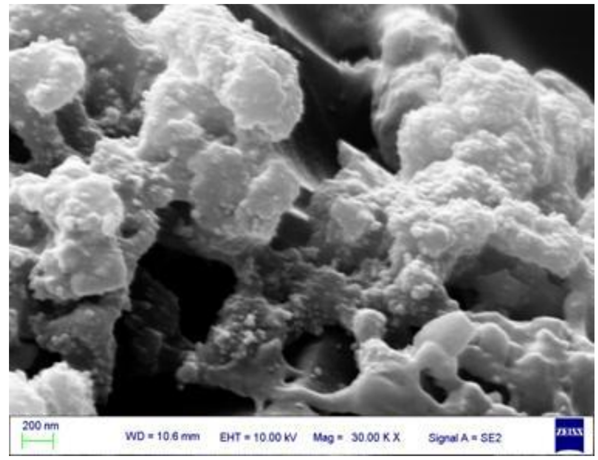

Figure 10. FESEM high-resolution image of fracture surface with insufficient dispersion of 0.5 wt. % GPL/epoxy nanocomposites [17]

In this study, the GPLs were used to improve the flexural bending fatigue life and the performance of neat epoxy resin and GPL/epoxy nanocomposites under displacement-controlled flexural loading conditions at room temperature was compared. The flexural fatigue responses of GPL/epoxy nanocomposites at 0.1, 0.25 and 0.5 wt. % were taken into account. The experimental results show that 0.25 wt. % of graphene nanoplatelet on fatigue life was more effective in comparison with 0.1 and 0.5 wt. % epoxy GPL nanocomposites and found that the performance of the graphene/epoxy nanocomposites is clearly superior in comparison with the neat epoxy. According to the addition of graphene nano platelets, a remarkable increase in fatigue life of epoxy was observed. For instance, at the bending strength ratio equal to 0.43 and adding 0.1, 0.25 and 0.5 wt. % of graphene into epoxy resin, 22.4, 27.4 and 17 times improvement in flexural bending fatigue life of the neat epoxy were observed, respectively.

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