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Dynamic Characteristics of Functionalized Carbon Nanotube Reinforced Epoxy Composites: An Experimental Approach

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ABSTRACT
The effects of amine functionalization of carbon nanotubes (CNTs) and CNTs weight percent (wt. %), on the first bending natural frequencies and damping properties of CNT/epoxy composites are investigated in this paper. CNTs and amine functionalized CNTs (AFCNTs), with two different weight percentages, are used to manufacture the beam shaped specimens. Epoxy, CNT/epoxy (0.25 and 0.5 wt. % of CNTs) and AFCNT/epoxy (0.25 and 0.5 wt. % of AFCNTs) were fabricated. Experimental vibrational test is utilized in order to study the free vibration behavior of specimens under clamped-free boundary conditions. Natural frequencies and damping ratios are extracted from the experimental time response graphs. Results indicated that adding AFCNTs (0.5 wt. %) into the matrix material has the most effect on the natural frequency of the beam. In this case, the damping ratio has the lowest value. Moreover, scanning electron microscopy (SEM) images of the fracture surface of the specimens are prepared. The images illustrate that amine functionalization of CNTs leads to better dispersion of CNTs into the epoxy matrix. Further, it can be observed that enhancement in the value of damping ratio is more dominant than enhancement in stiffness value by dispersing AFCNTs into the epoxy resin.

Keywords: Amine functionalization; Nanocomposite; Vibrational properties; Scanning electron microscopy.

1 INTRODUCTION

SINCE their discovery in 1991 by Iijima [1], many interesting properties of CNTs have been reported by several researchers. Carbon nanotubes, with superior mechanical, electrical and thermal properties, have received

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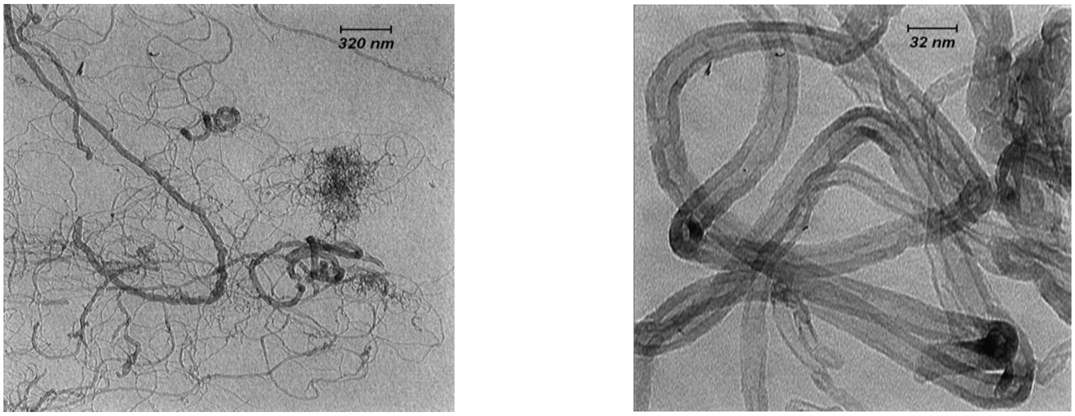
intensive attention in recent years [2]. CNTs can be dispersed into the polymer matrix to form a nanocomposite with enhanced properties. Since CNTs tend to agglomerate, because of the van der Waals forces, dispersion of CNTs into the matrix is the most challenging step to make a CNT reinforced polymer composite material. CNT functionalization is a chemical method that leads to exfoliation of CNTs bundles, and enhances interfacial compatibility between the CNTs and polymer matrix. In this method, a chemical group such as hydroxyl (–OH), carboxyl (–COOH), or amine (–NH2) is attached to the CNT, and reacted with the epoxy or curing agent or both during the curing process. Mechanical properties of nanocomposites, including the functionalized nano-scale reinforcement, have been investigated in a few reported research studies. Farrash et al. dispersed AFCNTs with different weight percentages into the epoxy matrix and studied the effect of CNTs functionalization on the thermo-mechanical properties of nanocomposites [3]. Sharma and Shukla utilized AFCNTs to fabricate fiber reinforced polymer composites. The results showed that the presence of functionalized CNTs (1.0 wt. %) in the resin increases Young's modulus, inter-laminar shear strength, and flexural modulus [4]. Ma et al. observed that AFCNTs result in improved flexural and thermo-mechanical properties of CNT/epoxy nanocomposite [5]. Bank-Sills et al. enhanced the mechanical properties of poly methyl methacrylate (PMMA) matrix by different weight fractions of CNTs functionalized by two methods [6]. Cha et al. used melamine functionalized CNTs to improve the dispersibility of CNTs into the epoxy matrix. They performed tensile tests and single edge notch bending tests at various weight fractions of functionalized CNTs. Moreover, they observed that melamine functionalized graphene Nano platelets have noticeable effect on the Young's modulus, ultimate tensile strength and fracture toughness of epoxy nanocomposites [7, 8]. Fang et al. utilized functionalized graphene oxide to improve flame resistance and thermo-mechanical properties of epoxy resin nanocomposites [9]. Pokharel et al. studied the effects of functional groups on the graphene sheet for improving the thermo-mechanical properties of polyurethane nanocomposites [10]. Marin presented a generalized solution in elasticity of micro polar bodies with voids, and existence and uniqueness of solutions for the mixed initial-boundary value problems in thermoelasticity of dipolar bodies [11, 12]. Furthermore, several researchers have focused on the dynamic properties of polymer matrix composites with nano reinforcements. Farrash et al. manufactured unidirectional hybrid composites, using carbon and glass fibers, and investigated the effect of interfacial adhesion between CNT reinforced epoxy and different types of fibers [13]. Alva and Raja studied stiffness and damping properties of a laminated composite reinforced with nano alumina and multi-walled CNTs (MWCNTs) [14]. Rajoria and Jalili analyzed the stiffness and damping properties of CNT/epoxy composites. They stated that MWCNTs are better reinforcement than single-walled carbon nanotubes [15]. Her and Yeh demonstrated the influence of MWCNTs on the Young's modulus, natural frequency and damping ratio of CNT/epoxy composites [2]. Using free vibrational tests, Her and Lai investigated the effect of carboxyl functionalization of MWCNTs and interfacial bonding between the nanotubes and epoxy resin, on the natural frequency and damping ratio of MWCNT/epoxy nanocomposites [16]. Alva and Raja concentrated on the effect of CNT aspect ratio and specific surface area on the natural frequencies and damping ratios of CNT/epoxy nanocomposites [17]. Jangam et al. aligned MWCNTs in polymer matrix and studied the damping behavior of the nanocomposites [18]. Marine presented contributions on uniqueness in thermos-elastodynamics on bodies with voids [19].

To the best knowledge of the authors, little research has been focused on the effect of AFCNTs dispersion into the epoxy resin, on natural frequencies and damping properties of CNT reinforced polymer composites. In the current work, the role of amine functionalization of CNTs and CNTs weight percentages, on the stiffness and damping properties of CNT/ epoxy composites is examined using vibrational tests. Plain CNTs and AFCNTs with two different weight percentages (0.25 wt. % and 0.5 wt. %) used to fabricate CNT/epoxy composite beams. Free vibration time responses of the beam specimens were analyzed under clamped-free boundary conditions, and first bending natural frequencies and damping ratios of the specimens were characterized.

2 EXPERIMENTS

2.1 Materials

Epolam 2040-resin and Epolam 2047 hardener (Axson technologies, French) are used. Also MWCNTs and amine functionalized MWCNTs (with purity$\succ$95% and medium outer diameter of 20-30 *nm*) manufactured by Carbon Structure Company are utilized. Fig. 1 shows the TEM (transmission electron microscope) images of CNTs. Fig. 2 illustrates the Fourier transform infrared (FTIR) spectroscopy of the AFCNTs. Based on the figure, the peak at 3448.38 cm^{-1} corresponds to the amine stretch vibrational mode.



(a) (b)

Fig.1
TEM images of MWCNTs (a) Scale bar 320 *nm* (b) Scale bar 32 *nm*.

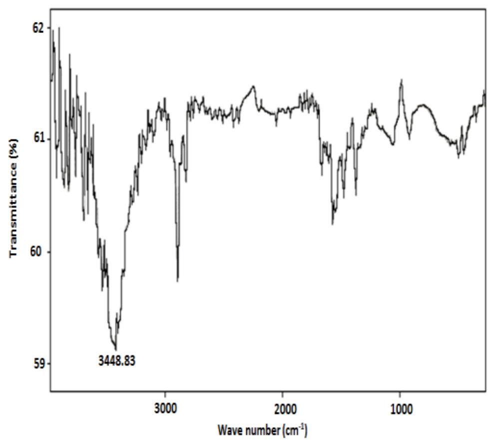


Fig.2
FTIR spectra of the amine functionalized MWCNTs.

2.2 Fabrication process

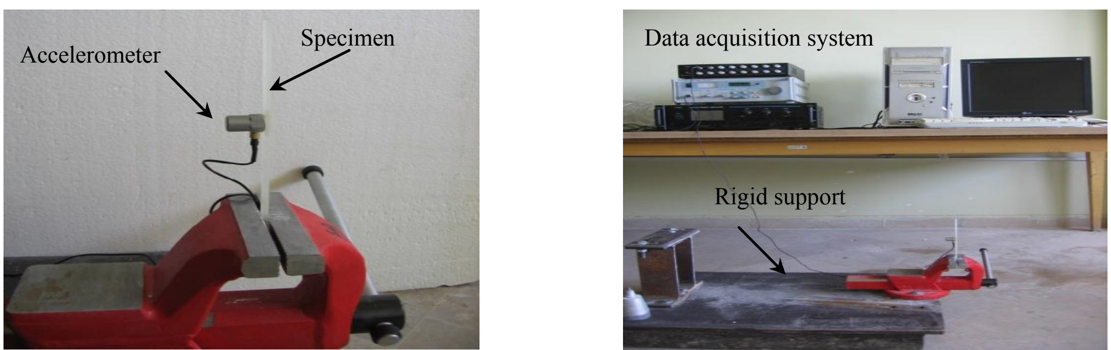
Five beam shaped specimens for experimental free vibrational tests were fabricated. Beam specimens included neat epoxy, epoxy reinforced with plain CNTs (0.25 and 0.5 wt. % of CNTs) and epoxy reinforced with AFCNTs (0.25 and 0.5 wt. % of AFCNTs). To uniformly disperse the CNTs into the epoxy resin, Elma ultrasonic bath (S40 *H*, 340 *W*, 37 *KHz*) was employed for 2 hours. Next, the hardener was added and completely mixed with the CNT/epoxy mixture. Then, the mixture degassed in a desiccator chamber under vacuum for 30 minutes (Fig. 3). The bubble free CNT/epoxy mixture molded and cured for 24 *h* at room temperature. Finally the specimens post cured for 16 *h* at $70^{\circ}C$. Fig. 4 shows the manufactured neat epoxy and CNT/epoxy test specimens. The length, width and depth of each beam are 200 *mm*, 15 *mm* and 3 *mm*, respectively.

Fig.3
Degassing of CNT/epoxy mixture under vacuum condition.

Fig.4
Beam specimens, left to right: neat epoxy, CNT/epoxy (0.25 wt. % of CNTs), CNT/epoxy (0.5 wt. % of CNTs), AFCNT/epoxy (0.25 wt. % of AFCNTs) and AFCNT/epoxy (0.5 wt. % of AFCNTs).

2.3 Test procedure

Experimental vibrational test was utilized to investigate the response of each beam specimen under clamped-free boundary conditions. An accelerometer (YMC 122A100, sensitivity 100 *mV/g*) was stuck at the middle part of the beam specimen, and the specimen subjected to a small displacement at the free end (Fig. 5(a)). Using a data acquisition system (YMC 9062), the time response of each specimen was plotted in YMC software. To avoid the effect of noises, the vice bench was fasten on a rigid support. Data acquisition system and rigid support are demonstrated in Fig. 5(b).



(a) (b)

Fig.5
(a) Clamped-free epoxy beam specimen with accelerometer, (b) Data acquisition system and rigid support.

Based on the theory of vibration, the equation of the envelope curve (*f*) of the time response for a single degree of freedom system with damping is [20]:

$$f\left(t\right)=Ae^{-\zeta\omega_n t} \tag{1}$$

where ζ and ω_n are damping ratio and natural frequency, respectively. A is a constant, and t is time. ω_n is the frequency at which a system tends to oscillate in the absence of any driving or damping force. When damping is considered, the system oscillates at the frequency of damped vibration (ω_d), that is [20]:

$$\omega_d=\omega_n\sqrt{1-\zeta^2} \tag{2}$$

It can be seen that the frequency of damped vibration is always less than the undamped natural frequency. Having determined the time response of the system, fast Fourier transform (FFT) [21] is used to acquire the frequency response of the system. Using the time and frequency responses, the equation of the envelope curve and the frequency of the damped vibration are determined, respectively. Simultaneous solution of Eqs. (1) and (2) yields ζ and ω_n .

3 RESULTS AND DISCUSSION

3.1 Natural frequencies and damping ratios

The experimental test procedure was examined for all beam specimens. The time and frequency responses of the neat epoxy beam specimen are illustrated in Figs. 6 and 7, respectively. First bending natural frequency and damping ratio are extracted from these graphs according to the method mentioned in section 2.3. To validate the results, Young's modulus and density of neat epoxy were obtained from experiment. To determine the Young's modulus, five dog bone shape specimens were fabricated according to ASTM D638. According to this standard, the crosshead speed was set to 5 $mm.min^{-1}$ at room temperature. The tensile testing machine (Zwick Z250) employed to perform the tensile tests. The average Young's modulus was 2.8 *GPa*. Also to determine the epoxy density, the weight and volume of the epoxy beam specimen were measured precisely. The density of neat epoxy was obtained 1.15 $gr.cm^{-3}$. Also the Poisson's ratio of neat epoxy was considered 0.36 [22]. Utilizing the measured material properties, the neat epoxy beam was modeled in the Abaqus software and the first bending natural frequency of the clamped-free beam was determined. Since the accelerometer weight was not negligible, it was modeled as a 20 *gr* concentrated mass. The finite element model and the results are shown in Fig. 8 and Table 1., respectively. According to the table, finite element method (FEM) result is in good agreement with that obtained from the experiment.

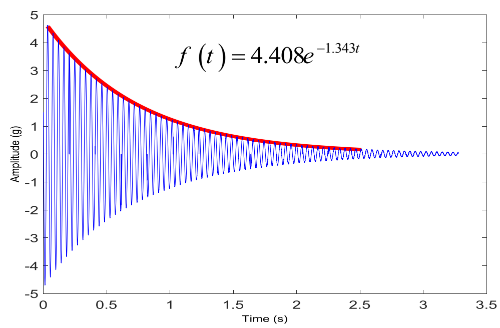


Fig.6
Time response of free vibrations of clamped-free epoxy beam.

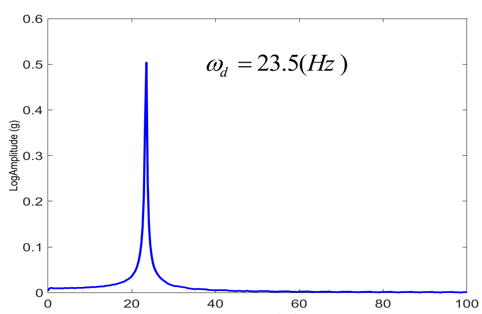


Fig.7
Frequency response of free vibrations of clamped-free epoxy beam.

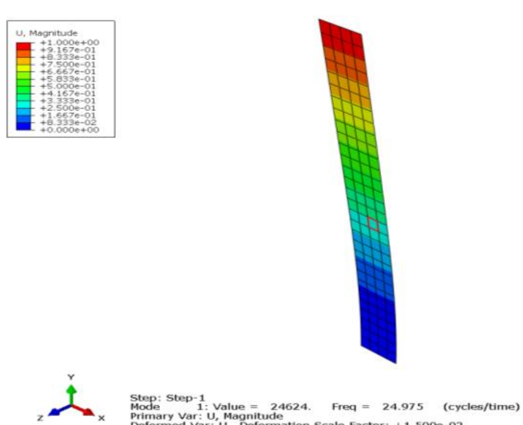


Fig.8
First bending natural frequency of clamped-free epoxy beam in finite element software.

Table 1
First bending natural frequencies obtained from FEM and experiment vibrational test.

FEM	Experiment	Error (%)
24.98 (*Hz*)	23.50 (*Hz*)	6 %

Experimental natural frequencies and damping ratios for all specimens are listed in Table 2. Moreover, an identification code was set for each specimen that is mentioned in this table. As the results show, the natural frequency of EP specimen is reported 23.50 *Hz*. To compare the results, all natural frequencies and damping ratios are normalized with respect to those parameters of EP specimen. Figs. 9 and 10 illustrate the normalized natural frequencies and damping ratios, respectively. Fig. 9 demonstrates that adding 0.25 wt. % of MWCNTs into the epoxy resin causes 2% increase in the natural frequency value of the EP+0.25%CNTs with respect to that of the EP. In addition, when the wt. % of dispersed MWCNTs reaches to 0.5 wt. %, this parameter decreases approximately by 9% in comparison with that of the EP. This reduction states that plain CNTs cannot be dispersed into the epoxy matrix well. The value of natural frequency of EP+0.25%AFCNTs is a little more than that of EP and the most increase of the natural frequency is related to the EP+0.5%AFCNTs. It indicates that amine functionalization of CNTs leads to better dispersion of CNTs into the matrix material, and adding 0.5 wt. % of AFCNTs has the most effect on the improvement of the stiffness of the nanocomposite. Moreover, Fig. 10 shows 3% increase in the value of the damping ratio of EP+0.25%CNTs with respect to that of EP. These values are 4% and 7% for EP+0.5%CNTs and EP+0.25%AFCNTs, respectively. It seems that slippage mechanism between CNTs and matrix material develops energy dissipation and results in an increase of damping ratio. On the other hand, for EP+0.5%AFCNTs, 6% reduction in the value of damping ratio is observed with respect to that of EP. This decrease shows that in this specimen, there are strong bonds between AFCNTs and epoxy resin that prevents sliding between CNTs and matrix material and between matrix material layers. It can be observed that enhancement in the value of damping ratio is more dominant than enhancement in stiffness value by dispersing AFCNTs into the epoxy resin.

Table 2
First bending natural frequencies and damping ratios of the beam shaped specimens.

Specimen	Code	Frequency (*Hz*)	Damping ratio
Epoxy	Ep	23.50	0.0089
CNT/epoxy (0.25 wt. % of CNTs)	EP+0.25%CNTs	24.07	0.0092
CNT/epoxy (0.5 wt. % of CNTs)	EP+0.5%CNTs	21.36	0.0093
AFCNT/epoxy (0.25 wt. % of AFCNTs)	EP+0.25%AFCNTs	23.72	0.0095
AFCNT/epoxy (0.5 wt. % of AFCNTs)	EP+0.5%AFCNTs	24.42	0.0084

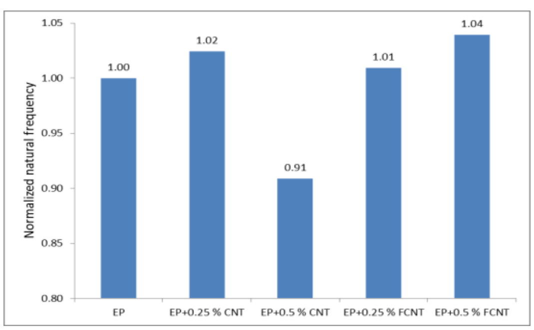


Fig.9
Normalized first bending natural frequencies of beam specimens.

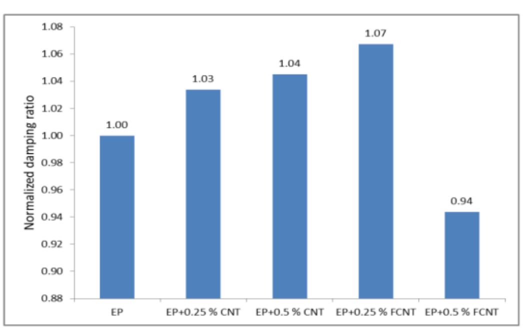


Fig.10
Normalized damping ratios of beam specimens.

3.2 SEM images

The SEM images of the fracture surface of the tensile test specimens are illustrated in Fig. 11. SEM images are taken from different regions of the fracture surface areas. Figs. 11a-c show CNT agglomerations in almost all regions of the fracture surface of EP+0.5%CNTs. These agglomerations lead to the reduction of Young's modulus and natural frequency of this specimen with respect to those of neat epoxy specimen. Figs. 11d, e display homogenous dispersion of AFCNTs in more regions of epoxy matrix of the EP+0.5%AFCNTs. However, as it can be seen in Fig. 11f, accumulation of AFCNTs is observed in some zones of the fracture surface of this specimen.

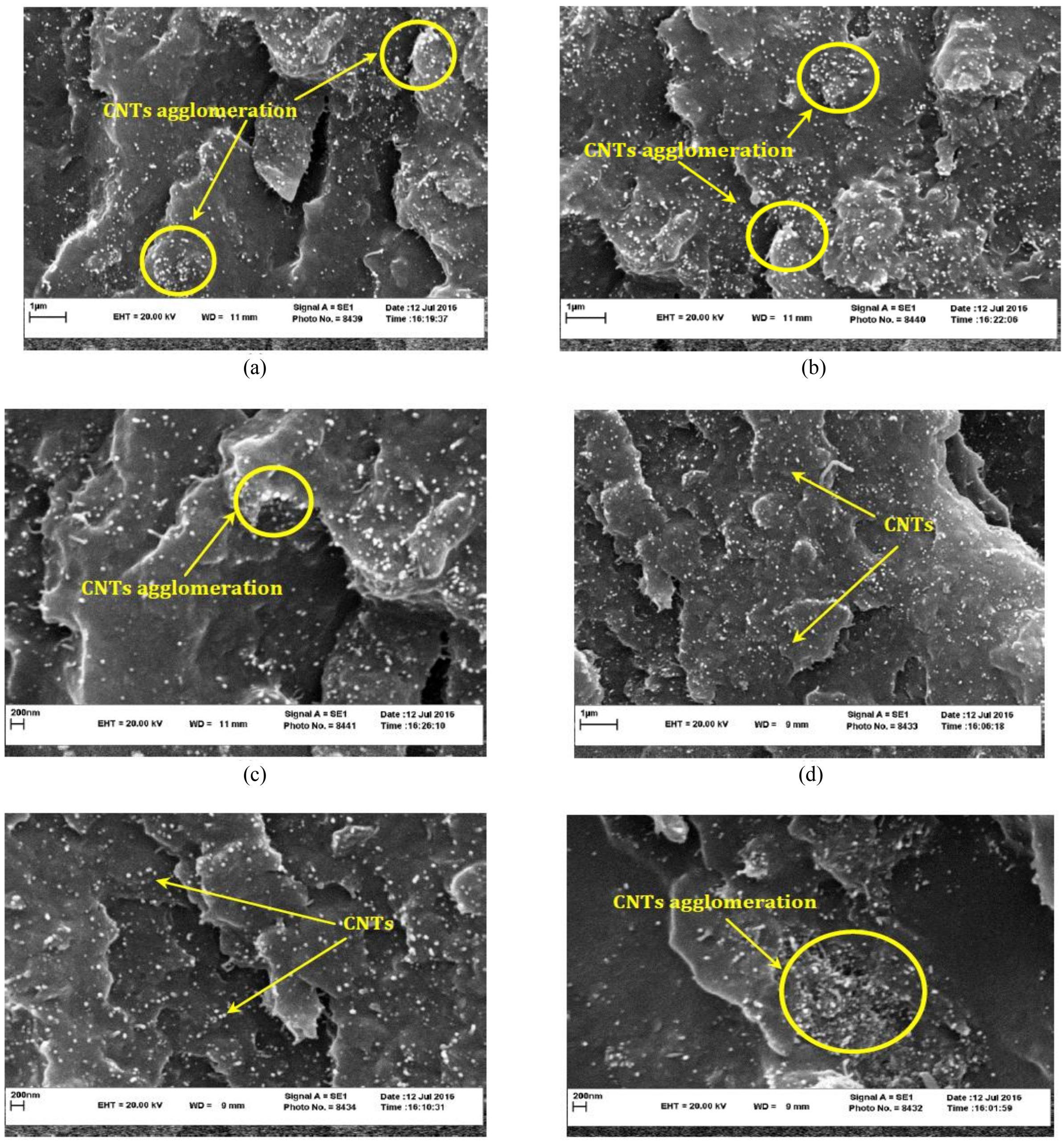


Fig.11
(a), (b) and (c) SEM images of the fracture surface of the EP+0.5%CNTs, CNTs agglomeration can be observed in all images, (d),(e) and (f) SEM images of the fracture surface of the EP+0.5%AFCNTs, good dispersion of CNTs are seen in (d) and (e) images; however, image (f) shows that there are some CNTs agglomeration regions in this specimen.

4 CONCLUSION

In this research, epoxy, CNT/epoxy (0.25 and 0.5 wt. % of CNTs) and AFCNT/epoxy (0.25 and 0.5 wt. % of AFCNTs) beam shaped specimens were fabricated. Further, natural frequencies and damping ratios of these samples are obtained using experimental vibrational tests. It is concluded that amine functionalization of CNTs leads to better dispersion of CNTs into the matrix material which develops the enhanced natural frequency and Young's modulus of the nanocomposite. Based on the experiment results, the most value of natural frequency and the lowest value of damping ratio were seen in EP+0.5%AFCNTs specimen. Further, SEM images demonstrated homogenous dispersion of AFCNTs into the matrix material for this specimen. Homogenous scattering of AFCNTs into the epoxy resin results in an increase of the number of bonds between CNTs and epoxy matrix, which reduces the slippage mechanism between AFCNTs and epoxy resin, and decreases the damping ratio of the nanocomposite beam shaped specimen.

REFERENCES

[1] Iijima S., 1991, Helical microtubules of graphitic carbon, *Nature* **354**(6348): 56-58.

[2] Her S.C., Yeh S.W., 2012, Fabrication and characterization of the composites reinforced with multi-walled carbon nanotubes, *Journal of Nanosci and Nanotechnol* **12**(10): 8110-8115.

[3] Farrash S.M.H., Shariati M., Rezaeepazhand J., 2018, Experimantal study on the effect of amine functionalized carbon nanotubes on the thermomechanical properties of CNT/Epoxy nanocomposites, *Mechanics* of *Advanced Composite Structures* **5**(1): 41-48.

[4] Sharma K., Shukla M., 2014, Three-phase carbon fiber amine functionalized carbon nanotubes epoxy composite: processing, characterisation, and multiscale modeling, *Nanomater* **2014**: 1-10.

[5] Ma P.C., Mo S.Y., Tang B.Z., Kim J.K., 2010, Dispersion, interfacial interaction and re-agglomeration of functionalized carbon nanotubes in epoxy composites, *Carbon* **48**(6): 1824-1834.

[6] Banks-Sills L., Shiber D.G., Fourman V., Eliasi R., Shlayer A., 2016, Experimental determination of mechanical properties of PMMA reinforced with functionalized CNTs, *Composites Part B* **95**: 335-345.

[7] Cha J., Kim J., Ryu S., Hong S.H., 2019, Comparision to mechanical properties of epoxy nanocomposites reinforced by functionalized carbon nanotubes and graghene nanoplatelets, *Composites Part B* **162**: 283-288.

[8] Cha J., Jun G.H., Park J.K., Kim J.C., Ryu H.J., Hong S.H., 2017, Improvement of modulus, strength and fracture toughness of CNT/Epoxy nanocomposites through the functionalization of carbon nanotubes, *Composites Part B* **129**: 169-179.

[9] Fang F., Ran S., Fang Z., Song P., Wang H., 2019, Improved flame resistance and thermo-mechanical properties of epoxy resin nanocomposites from functionalized graphene oxide via self-assembly in water, *Composites Part B* **165**: 406-416.

[10] Pokharel P., Pant B., Pokhrel K., Pant H.R., Lim J., Lee D.S., Kim H.Y., Choi S., 2015, Effects of functional groups on the graphene sheet for improving the thermomechanical properties of polyurethane nanocomposites, *Composites Part B* **78**: 192-201.

[11] Marin M., 1996, Generalized solutions in elasticity of micropolar bodies with voids, *Revista de la Academia Canaria de Ciencias* **8**(1):101-106.

[12] Marin M., 1999, An evolutionary equation in thermoelasticity of dipolar bodies, *Journal of Mathematical Physics* **40**(3): 1391-1399.

[13] Farrash S.M.H., Shariati M., Rezaeepazhand J., 2017, The effect of carbon nanotube dispersion on the dynamic characteristics of unidirectional hybrid composites: An experimental approach, *Composites Part B* **122**: 1-8.

[14] Alva A., Raja S., 2011, Dynamic characteristics of epoxy hybrid nanocomposites, *Journal of Reinforced Plastics and Composites* **30**(22): 1857-1867.

[15] Rajoria H., Jalili N., 2005, Passive vibration damping enhancement using carbon nanotube-epoxy reinforced composites, *Composites Science and Technology* **65**(14): 2079-2093.

[16] Her S.C., Lai C.Y., 2013, Dynamic behavior of nanocomposites reinforced with multi-walled carbon nanotubes (MWCNTs), *Materials* **6**(6): 2274-2284.

[17] Alva A., Raja S., 2014, Damping characteristics of epoxy-reinforced composite with multiwall carbon nanotubes, *Mechanics* of *Advanced Composite Structures* **21**(3): 197-206.

[18] Jangam S., Raja S., Gowd B.U.M., 2016, Influence of multiwall carbon nanotube alignment on vibration damping of nanocomposites, *Journal of Reinforced Plastics and Composites* **35**(8): 617-627.

[19] Marin M., 1998, Contributions on uniqueness in thermoelastodynamics on bodies with voids, *Ciencias Matemáticas* **16**(2): 101-109.

[20] Rao S.S., 2011, *Mechanical Vibration*, University of Miami, Prentice Hall.

[21] He J., Fu Z.F., 2001, *Modal Analysis*, Oxford, Butterworth-Heinemann.

[22] Heracovich C.T., 1998, *Mechanics of Fibrous Composites*, John Wiley and Sons, New York.