VIBRATION DAMPING BEHAVIOR OF EPOXY MATRIX COMPOSITES REINFORCED WITH CARBON FIBERS AND CARBON NANOTUBES

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VIBRATION DAMPING BEHAVIOR OF EPOXY MATRIX COMPOSITES REINFORCED WITH CARBON FIBERS AND CARBON NANOTUBES

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ABSTRACT

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The main objective of this study was to investigate contribution of the non-functionalized multi-walled carbon nanotubes (CNT) on the vibration damping behavior of first neat epoxy resin and then unidirectional and bidirectional continuous carbon fiber (CF) reinforced epoxy matrix composites. Epoxy/CNT nano-composites were produced by ultrasonic solution mixing method, while the continuous CF reinforced composite laminates were obtained via resin-infusion technique. Vibration analysis data of the specimens were evaluated by half-power bandwidth method, while the mechanical properties of the specimens were determined with three-point bending flexural tests, including morphological analyses under scanning electron microscopy.

It was generally concluded that when even only 0.1 wt% CNT were incorporated into neat epoxy resin, they have contributed not only to the mechanical properties (Flexural Strength and Modulus), but also to the vibration behavior (Damping Ratio) of the epoxy. When 0.1 or 0.5 wt% CNT were incorporated into continuous CF reinforced epoxy matrix composites, their contribution in terms of Damping Ratio of the composites were significant.

Keywords: carbon nanotubes, continuous carbon fibers, epoxy, damping ratio

ÖZ

KARBON ELYAF VE KARBON NANOTÜP TAKVİYELİ EPOKSİ MATRİS KOMPOZİTLERİN TİTREŞİM SÖNÜMLEME DAVRANIŞLARI

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Bu çalışmanın temel amacı, yüzeylerine işlevsellik işlemleri yapılmamış çok duvarlı karbon nanotüplerin (CNT) ilk önce saf epoksi reçinesinin ve daha sonra tek yönlü ve çift yönlü sürekli karbon elyaf (CF) takviyeli epoksi matris kompozitlerinin titreşim sönümleme davranışlarına katkısını araştırmaktır. Epoksi/CNT nano-kompozitler ultrasonik çözelti karıştırma yöntemiyle üretilirken sürekli CF takviyeli kompozit laminatlar reçine infüzyon tekniği ile elde edilmiştir. Numunelerin titreşim analizi verileri yarı-güç bant-genişliği yöntemiyle değerlendirilirken, numunelerin mekanik özellikleri üç-nokta eğme testleriyle belirlenmiştir, morfolojik inceleme ise taramalı elektron mikroskobu altında yapılmıştır.

Genel olarak, saf epoksi reçinesi içerisine ağırlıkça yalnızca %0.1 CNT dahil edildiğinde bile, sadece mekanik özelliklere (Eğme Dayanımı ve Modülü) değil, aynı zamanda epoksinin titreşim davranışına (Sönümleme Oranı) da katkıda bulundukları sonucuna varılmıştır. Ağırlıkça %0.1 veya %0.5 CNT sürekli CF takviyeli epoksi matris kompozitlere dahil edildiğinde ise, mekanik özelliklere ek bir katkıları olmamakla birlikte, kompozitlerin Sönümleme Oranı değerlerinde önemli katkıları olmuştur.

Anahtar Kelimeler: karbon nanotüpler, sürekli karbon elyafları, sönümleme oranı

To my dear precious family

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NOMENCLATURE

σ_{Flex}	:	flexural strength
E_{Flex}	:	flexural modulus
f_n	:	natural frequency
E_{Dyn}	:	dynamic modulus
ζ	:	damping ratio
E	:	epoxy
CF	:	carbon fiber
CNT	:	carbon nanotube
SWCNT	:	single walled carbon nanotube
MWCNT	:	multi walled carbon nanotube
SEM	:	scanning electron microscopy
TEM	:	transmitted electron microscopy
DMA	:	dynamic mechanical analysis
UD	:	unidirectional
DGEBA	:	Diglycidly Ether of Bisphenol A
PTFE	:	Polytetrafluoroethylene

CHAPTER 1

INTRODUCTION

1.1. Vibration and Damping

Vibration is a reaction motion of any object or particle to keep their equilibrium at stable condition when disturbed by an external stimulus. Vibration takes place in many aspects of our daily life. For example, sound is heard by the vibration of the air particles. The air particles in equilibrium condition start to vibrate and transport the energy created by the source to the adjacent particle. With the transportation of the energy, particles turn to their stable state. At the end, the air particles vibrate our eardrum and hearing occurs (Figure 1.1) [1].

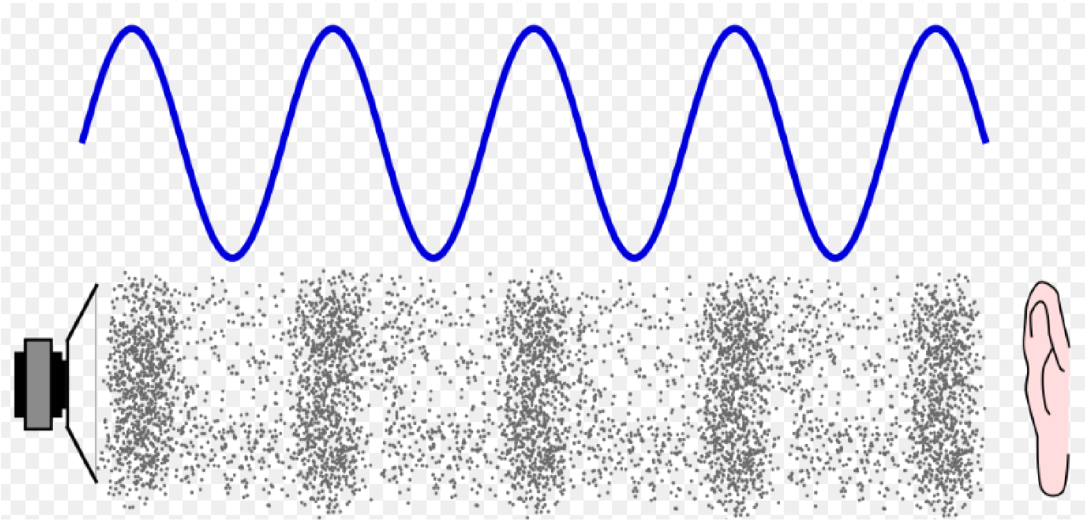


Figure 1.1 Vibration of air particles from source to ear [1]

The same phenomena takes place in the sounds of drums (Figure 1.2). The skin of the drums are so stretched that the air particles around are compressed. When the drumstick forces the skin, the stability of the air particles are disturbed leading to vibration of the air particles to reach their stable state [2].

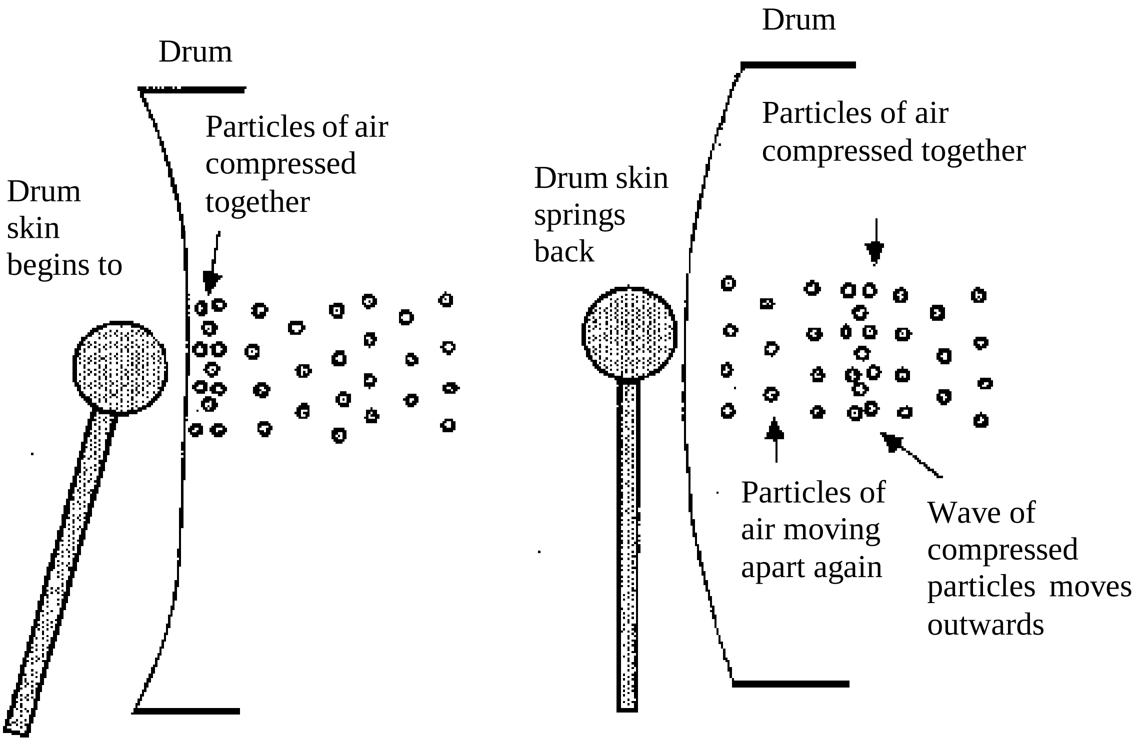


Figure 1.2 Sound vibrations travelling through the air [2]

It is also stated by Eichhorn et al. [3] that application of vibration to the patients during plastic surgery decreases their pains. Vibration phenomenon also used for the simulation of earthquakes for geological investigations, drilling of geotechnical wells and harvesting of fruit bearing trees [4].

Although vibration might have certain beneficial aspects, it could also lead to harmful situations in certain engineering applications. Before discussing that topic, two important parameter i.e. the "frequency" and "amplitude" of the vibration should be defined. Frequency is basically speed of the vibration and amplitude is the size of the vibration as shown in Figure 1.3.

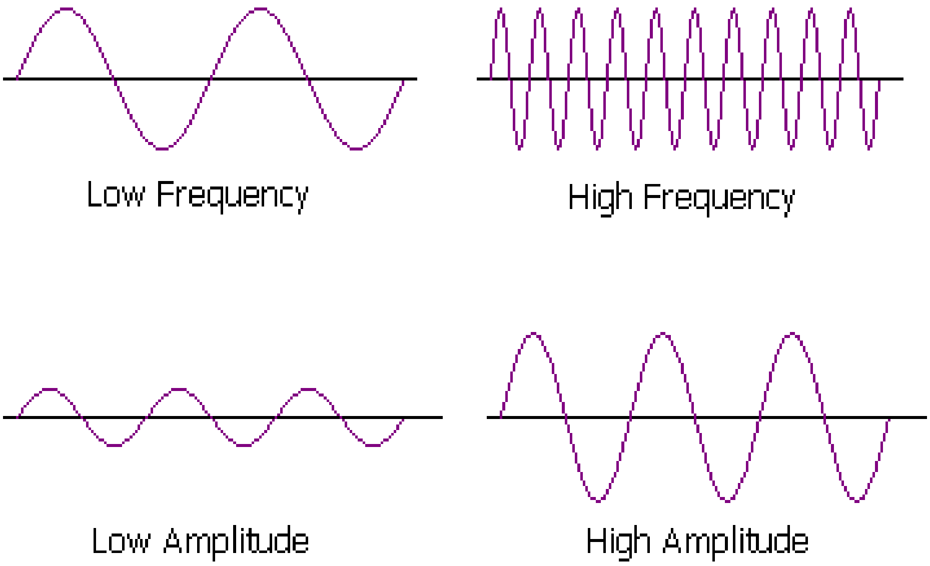


Figure 1.3 Schematic diagram showing low and high values of the frequency and amplitude of the vibration

In nature, everything vibrates when it is disturbed by a kind of force. They tend to vibrate at a particular frequency or a set of frequencies. The frequency at which an object tends to vibrate in the absence of any driving force is defined as “natural frequency” of that object. It is an inherent material property depending on the mass and stiffness. If one external source creates a frequency equal to the natural frequency of the object; then, this object starts to vibrate. This phenomena is called “resonance”. In resonance, the amplitude of the vibration is at the highest value. Therefore, from the point of engineering, the amplitude of the vibration becomes very critical issue. Because, higher amplitudes cause higher displacements of the object which might be harmful for the integrity of the object. The most well-known example for that situation is the Tacoma Bridge disaster happened in 1940 (Figure 1.4). After a short period from its completion, the bridge was collapsed due to high levels of vibration amplitude during a very windy day. Because; the wind resonated with the natural frequency of the structure, causing a steady increase in amplitude until the bridge was collapsed [5].

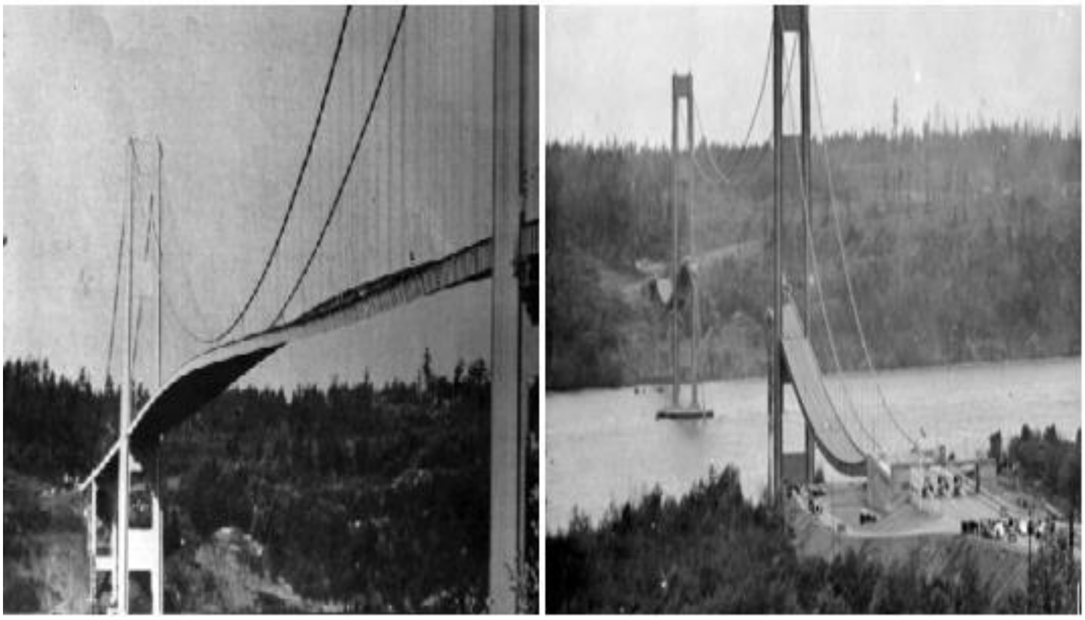


Figure 1.4 Tacoma Bridge failure [5]

In order to prevent that type of detrimental vibrational energy of the wind to the suspension bridges, two approaches could be used. One of them is altering the bridge design which will also change the natural frequency of the bridge. Of course, the natural frequency of the bridge should not be close to the frequency of the regional winds. Another approach to improve vibration damping behavior of the bridge could be internally (by using certain materials) or externally (by using dampers).

1.2. Testing for Vibration Damping Properties

"Vibration damping", simply named as "damping", is the restraining of vibratory motion by dissipation of energy via friction and other resistances. Therefore, during damping analyses, there are two important stages: "excitation of the vibration" to the specimen and "measurement of the response" of the specimen. As discussed in the literature [6, 7] and the standardization by American Society for Testing and Materials (ASTM) with the standard title "Standard Test Method for Measuring Vibration-

Damping Properties of Materials (ASTM E756-05)" [8]; these two stages can be performed by using various techniques and apparatus.

In the literature for composite materials, vibration excitation stage was mostly applied via an "exciter transducer" which is called as "free vibration", or via an external force (e.g. by hitting with a hammer) which is called as "forced vibration". In this thesis, vibration excitation was supplied with a hammer, i.e. forced vibration. For the vibration response measurement stage, again mostly one of the two techniques was used; i.e. "contact measurements" for example via a "response transducer" or "non-contact measurement" for example via a "laser doppler". In this thesis, vibration response measurement was achieved by using a laser doppler set-up, i.e. non-contact measurement.

As the specimen geometry, either "plate" or "beam" specimens with certain dimension ranges and boundary conditions such as "clamped-free", "clamped-clamped", "free-free" etc. could be used. In this thesis, bar shaped beam specimens with clamped-free boundary condition and Mode-I type displacement was used.

In the literature, damping data are evaluated either in the "frequency" domain, named as "half-power bandwidth" method; or in the "time" domain, named as "logarithmic decrement" method. In this thesis, half-power bandwidth method was used. In this method, after obtaining the Amplitude vs Frequency curves (Figure 1.5), "Natural Frequency, f_n" of the specimen could be easily determined as the frequency value corresponding to the amplitude peak. Thus, f_n is also named as "Resonant Frequency".

Based on the ASTM E756-05 standard, it is stated in the literature [9] that, by using this f_n value and the geometric parameters and the boundary conditions; "Dynamic Modulus, E_{Dyn}" also named as "Dynamic Stiffness" of the specimen can be calculated by using the following Equation 1;

$$f_n = \frac{1}{2\pi} \times (\frac{\lambda_1}{l})^2 \times \sqrt{\frac{E_{Dyn} I}{\rho t b}} \quad (1)$$

Where:

f_n = Natural Frequency of the specimen (Hz)

E_{Dyn} = Dynamic Modulus of the specimen (GPa)

t = Thickness of specimen in vibration direction (m)

l= Length of the specimen (m)

b= Width of the specimen (m)

I = Moment of inertia of the specimen (m^4)

λ_1 = 1st eigenvalue of the specimen for the clamped-free condition (taken as 1.88) [10]

ρ = Density of the specimen (kg/m^3)

Then, in order to determine the most important vibration damping property, i.e. "Damping Ratio, ζ"; first "half-power bandwidth" range $\Delta f_n = f_2 - f_1$ should be determined, which is the frequency range corresponding to the $1/\sqrt{2}$ of the maximum amplitude, as illustrated in Figure 1.5. After that, Damping Ratio ζ could be calculated from the Equation 2 as;

$$\zeta = \frac{\Delta f_n}{2 f_n} \quad (2)$$

In the literature, another vibration damping property cited is "Loss Factor, η" which is also related to the Damping Ratio ζ as indicated in Equation 3;

$$\eta = \frac{\Delta f_n}{f_n} = 2\zeta \quad (3)$$

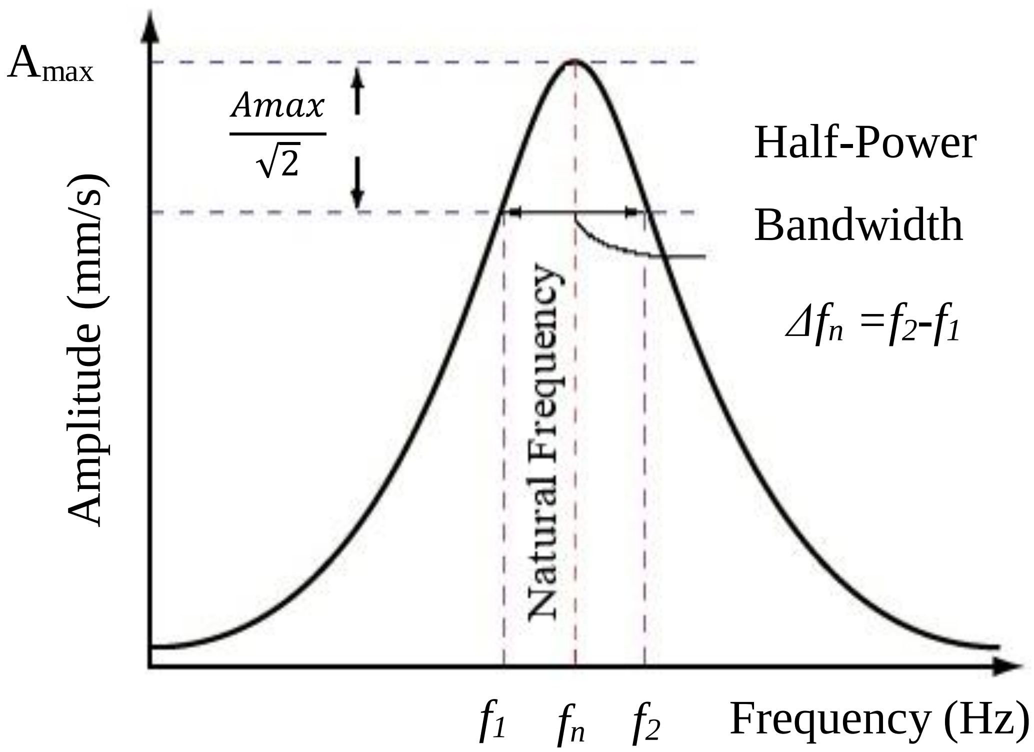


Figure 1.5 Amplitude vs frequency damping curve showing parameters used in the half-power bandwidth method

In the literature, apart from the half-power bandwidth method, “logarithmic decrement method” is also used in order to determine Damping Ratio of the specimens especially after “free” vibration tests [11]. In this method, first, displacement vs time curves are obtained (Figure 1.6). Then, the decrease in displacement from one cycle to the next was analyzed to determine the Damping Ratio by calculating the following Equations 4 and 5 together:

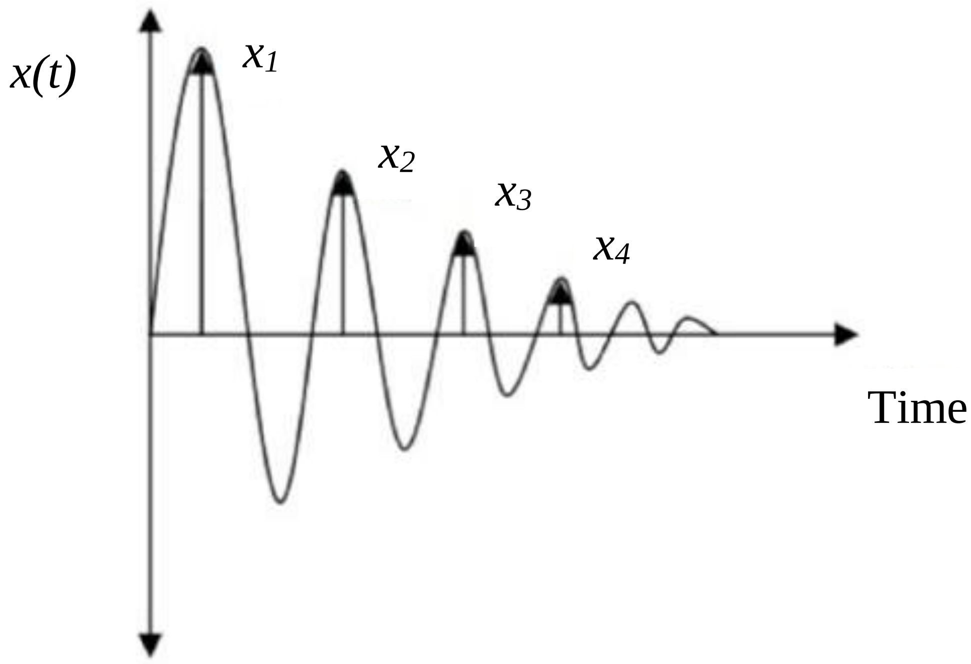


Figure 1.6 Displacement vs time curve used in the logarithmic decrement method [11]

$$\zeta = \frac{1}{\sqrt{1+(\frac{2\pi}{\delta})^2}} \quad (4)$$

$$\delta = \frac{1}{j} ln \frac{x_i}{x_{i+j}} \quad (5)$$

Where:

δ = Logarithmic decrement coefficient

x_i = i_{th} amplitude of the peak (mm)

x_{i+j} = j_{th} amplitude after the I_{th} cycle (mm)

1.3. Vibration Damping Behavior of Materials

Vibrations are unwanted for many structures ranging from large ones like helicopters to small ones like electronic devices because of the need for their structural integrity, stability, durability, adequate performance, and noise reduction.

Vibration damping properties of the materials depend on their elastic strain energy dissipation abilities under vibrational disturbance, which is called as damping capacity of the materials. In most engineering applications, to decrease the effect of mechanical vibrations, either external ways, like air damping or vibration absorbers, or internal ways, that is, materials having high damping capacity are preferred. High damping materials reduce the need for additional damping control devices and thus weight reduction can be achieved for these structures. The microstructure of the materials substantially has an impact on their damping capacity. Defects such as dislocations, phase boundaries, grain boundaries and various interfaces also contribute to damping, since defects may move slightly and surfaces may slip slightly with respect to one another during vibration, thereby dissipating energy. Thus, the microstructure greatly affects the damping capacity of a material.

For the structures requiring high levels of mechanical strength and modulus, metallic materials are good candidates for vibration damping such as shape-memory alloys (by phase transformation from austenite to martensite or vice versa), ferromagnetic alloys (by movement of the magnetic domain in boundaries during vibration) and other alloys (by microstructural design). Alloys for vibration damping include those based on iron (e.g., cast iron, steel, Fe-Ni-Mn, Fe-Al-Si, Fe-Al, Fe-Cr, Fe-Cr-V, Fe-Mn and Fe-Mn-Co), aluminum (e.g., Al-Ge, Al-Co, Al-Zn, Al-Cu, Al-Si, alloys 6061, 2017, 7022 and 6082), zinc (e.g., Zn-Al), lead, tin (e.g., Sn-In), titanium (e.g., Ti-Al-V, Ti-Al-Sn-Zr-Mo and Ti-Al-Nb-VMo), nickel (e.g., superalloys, Ni3Al and NiAl), zirconium (e.g., Zr-Ti-Al-Cu-Ni), copper (e.g., Cu-Al-Zn-Cd) and magnesium (e.g., Mg-Ca) [12].

If the applied loads are not so high, i.e. if mechanical strength and modulus requirements are not so high, the polymer materials could be best alternative for vibration damping requirements. Because, compared to metals their viscoelasticity is much higher while their stiffness is much lower. In this class, elastomers have the highest damping capacity, thermoplastics being the second subclass, and the thermosets being the worst subclass. Apart from the rubbers, other examples used for vibration damping include polytetrafluoroethylene (PTFE), polyurethane, a polypropylene/butyl rubber blend, a polyvinylchloride/chlorinated polyethylene/epoxidized natural rubber blend, a polyimide/polyimide blend, a polysulfone/polysulfone blend, and a nylon-6/polypropylene blend [12].

In general, elastomers and other amorphous thermoplastics with a glass transition temperature below room temperature are attractive for damping. Polymer blends are also attractive, due to the interface between the blend phases providing frictional damping mechanisms. For the continuous fiber reinforced polymer matrix composites, the situation is problematic. Because, these continuous fiber reinforced polymer composites have very high levels of elastic modulus which decreases the efficiency of the interfacial friction damping mechanisms between the matrix and continuous fibers.

Ceramic materials, due to their extremely high levels of stiffness and brittleness, their damping capacity is extremely poor. The most widely used structural ceramic in civil engineering is concrete, which is actually a cement-matrix composite material. Therefore, the addition of silica fume (a fine particulate) as a filler in the cement results in a large amount of interface and hence a significant increase in the damping capacity. The addition of rubber particles also enhances damping, due to the viscoelastic nature of elastomers [12].

It can be generally concluded that, vibration damping enhancement mainly involves microstructural design in metallic materials, while it involves interface design in polymer blends, polymer composites including ceramic and metal matrix composites.

1.4. Literature Survey on the Vibration Damping Behavior of Epoxy Matrix Composites

Since there exists significant structural instability and noise problems in the engineering components under vibration; determination of the damping properties of structural materials become very crucial. Due to their low density and high specific strength and specific modulus properties, there is a growing interest in the damping behavior of polymer matrix composites reinforced with fibers and/or micro, nano-particles as discussed, modelled and reviewed in the literature [19-29]. On the other hand, in the literature, there are still limited number of studies conducted for the epoxy matrix composites reinforced with carbon fibers (CFs) and/or carbon nanotubes (CNTs); which are summarized in the following three subsections.

1.4.1. Studies for Epoxy/CF Composites

In the study conducted by Bozkurt and Gökdemir [30], effects of using Basalt Fiber layers in between the Epoxy/CF composite laminates was investigated. Composite laminates were produced by using vacuum-assisted resin transfer molding (VARTM) process, while vibration damping was analyzed by using half-power bandwidth method. They indicated that although use of Basalt Fiber layers decreased the tensile strength and tensile modulus of the composite laminates, there were significant improvements in the Damping Ratio of the structure. They revealed that increasing Basalt Fiber layers increased the Damping Ratio of the Epoxy/CF composite laminates up to 61%. They pointed out that Basalt Fibers have much lower stiffness compared to Carbon Fibers, leading to higher levels of damping. It is known that damping and stiffness are antagonist properties and an increase in one is often accompanied by a decrease in another.

Kishi *et.al* [31] studied the effects of both fiber orientations (0˚, 90˚ and 45˚) and also use of different thermoplastic elastomer polymer films in between the Epoxy/CF composite laminates. They compared the damping behavior of the Epoxy/CF laminates with and without thermoplastic-elastomer film layers in terms of Loss Factor. They simply revealed that composite laminates having lower stiffness (e.g. 90˚ and ±45˚ CF oriented ones) and with additional thermoplastic-elastomer film layers (having inherent viscoelasticity) resulted in higher Loss Factor values.

Another study for the carbon fiber (CF) reinforced composites were conducted by Bhudolia *et.al.* [32]. In this study, vibration damping properties of the Epoxy/CF composites were compared according to two different aspects. First, they investigated effects of matrix resin by comparing a well-known thermoset epoxy with a thermoplastic methylmethacrylate (MMA) liquid resin. The second investigation was effects of carbon fiber ply thickness by comparing thin (100 g/m^2) and thick (200 g/m^2) plies. Composite specimens having 60 vol% CF plies were produced by vacuum assisted resin infusion (VARI) technique; while damping properties were measured by using both logarithmic decay vibration analysis and dynamic mechanical analysis (DMA). They indicated that the Damping Ratio of the thin CF ply composite was 12% higher compared to the thick CF ply composite mainly due to the increased stiffness and more number of interfaces. Moreover, MMA matrix composite had 27% more damping compared to the epoxy matrix; due to higher level of inherent damping capability of thermoplastics compared to thermosets.

1.4.2. Studies for Epoxy/CNT Composites

Rafiee *et al.* [33] studied effects of the surface modification of carbon nanotubes (CNTs) on the vibration damping behavior of epoxy nanocomposites. For this purpose, they used pristine (unmodified) and amine functionalized CNTs with the amounts of 0.02, 0.04, 0.06, 0.12, 0.25 and 0.37 wt% by solution mixing with the epoxy matrix. Vibration damping properties of the nanocomposites were determined by applying half-power bandwidth method. They indicated that Damping Ratio of the neat epoxy specimen was increased as much as 46% when 0.37 wt% unmodified CNT was loaded. On the other hand, no improvements were observed for the nanocomposites having surface modified CNTs.

Similarly, in the study of Borbon *et al.* [34], effects of surface functionalization of CNTs on the damping properties of epoxy matrix composites were also investigated. They applied the neat epoxy and 5 wt% pristine and functionalized CNT filled epoxies first on one side of an aluminum beam (simple beam) and also two sides of the aluminum beam (sandwich beam). They used both bandwidth and logarithmic decrement method to determine the damping ratios of the beams. Compared to the beams with neat epoxy; they revealed that use of unmodified CNT resulted in increased damping ratios as much as 35% in the sandwich beams and 73% in simple beams. No improvements were obtained for the beams having nanocomposite layers with functionalized CNTs. The responsible mechanism explained by the authors was the ‘‘stick–slip’’ mechanism, which occurs efficiently when the adhesion between the nanotube and the epoxy matrix was poor. Because, the nanotubes elongated with the epoxy matrix and remain bonded until a critical value, but once the external load exceeded this critical value, the epoxy matrix started flowing over the nanotube surfaces in the slipping phase.

In the work of Alva and Raja [35], it was indicated that the aspect ratio of CNTs could be also important for the effectiveness of the “stick-slip” mechanism. For that purpose, they mixed the epoxy matrix with 0.75 wt% CNT having both low (~50) and high (>10000) aspect ratios. They showed that the damping ratio evaluated by the logarithmic decrement method was much larger for the specimen having the high aspect ratio CNTs. For instance, compared to the neat epoxy specimen, the Damping Ratio of the specimen having high aspect ratio CNTs was 78% higher, while this increase was only 50% for the specimen with low aspect ratio CNTs. They discussed that CNTs having high aspect ratio, i.e. high specific surface area would contribute to the “stick-slip” mechanism more effectively. Because amount of interfacial slippage between the epoxy matrix and CNTs, i.e. the interfacial frictional energy dissipation would be higher, leading to on a macroscopic scale as damping.

Rajoria and Jalili [36] furthermore pointed out that morphology of CNTs could be also effective on the vibration damping behavior of epoxy nano composites. For this purpose, they mixed epoxy resin with 2.5, 5 and 7.5 wt% multi-walled and single-walled CNTs. Their free and forced vibration tests using half-power bandwidth method indicated that use of multi-walled CNTs resulted in much higher values of Damping Ratio. Because, they indicated that multi-walled CNTs distributed in the matrix more uniformly than the single-walled CNTs, leading to higher efficiency in “stick-slip” mechanism.

1.4.3. Studies for Epoxy/CF/CNT Composites

Apart from the works of Han *et al.* [37] and Hsieh *et al.* [38], Khan *et al*. [39] studied possibility of the additional contribution of CNTs on the vibration damping characteristics of carbon fiber (CF) reinforced epoxy composites with and without 0.5 and 1 wt% CNTs by using both bandwidth and logarithmic decrement methods via free and forced vibration. Epoxy/CF composites were formed by hand layup technique using 9 layers of unidirectional [0˚] prepregs. They revealed that, in general, use of CNTs improved Damping Ratios of the both neat epoxy specimen and Epoxy/CF composites with certain amounts; which was especially attributed to the sliding at the matrix-CNT interface.

Similarly, Farrash *et al*. [40] also studied effects of CNT (0.25 wt%) on the damping behavior of Epoxy/CF composites having 4 layers of unidirectional [0˚] prepregs. Their vibration tests via logarithmic decrement method revealed that use of CNTs increased Damping Ratio of the Epoxy/CF composite as much as 46%, again due to the additional "stick-slip" mechanism.

Kim *et al.* [41] also investigated contribution of adding 3, 5 and 7 wt% CNTs this time to the woven carbon fiber reinforced epoxy matrix composites. These hybrid composites were produced by using a "resin film infusion" technique. Although use of CNTs decreased the Tensile Strength values of the Epoxy/woven-CF composites, vibration tests via half power bandwidth method indicated that significant improvements in the Damping Ratios could be obtained. For instance, Damping Ratio of the Epoxy/woven-CF composite increased as 12.3 % when 7 wt% CNT was incorporated.

1.5. Aim of this Thesis

It is well-known that many metallic components of the engineering structures have been replaced with their Carbon Fiber Reinforced Epoxy Matrix Composite counterparts due to their very high values of "Specific Strength" and "Specific Modulus". On the other hand, many parts of these engineering structures, such as helicopters, are working under severe levels of vibration; which could lead to significant problems in their structural integrity. Even, catastrophic failures might happen. In this respect, determination of the vibration damping characteristics of these composite materials become very crucial.

Unfortunately, the literature survey summarized in the previous sections revealed that there are still very limited number of vibration damping studies conducted for the epoxy matrix composites reinforced with carbon fibers (CFs) and carbon nanotubes (CNTs). Therefore, the main objective of this study is to contribute to the related literature, first investigating the effects of CNT content to neat epoxy and then to the epoxy matrix composites reinforced with uniaxial and biaxial CF forms.

CHAPTER 2

EXPERIMENTAL WORK

2.1. Materials Used

2.1.1. Epoxy Matrix

Today, the most widely used thermosetting matrix material for the fiber reinforced composite structures in the aerospace, automotive, marine and military applications is the epoxy resin systems composed of an epoxide prepolymer and usually an amine type cross-linking agent (i.e. hardener). In this respect, the most frequent epoxy resin component preferred in industry is the Diglycidly Ether of Bisphenol A (DGEBA), as shown in Figure 2.1.

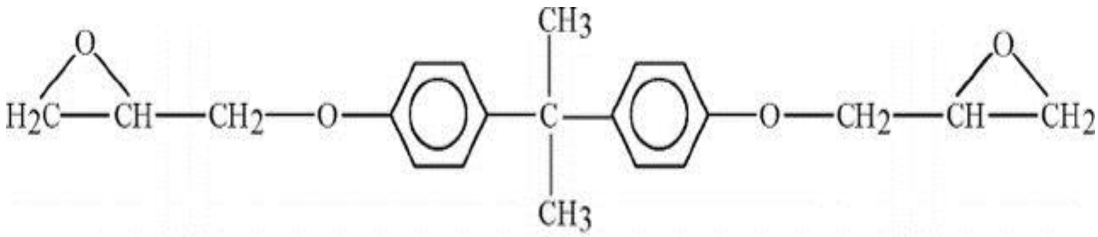


Figure 2.1 Chemical structure of the DGEBA type epoxy resin

Therefore, the commercial DGEBA type epoxy resin and the amine type hardener system chosen in this thesis were a product of Huntsman Inc. trade named as Araldite LY5052 and Aradur 5052, respectively. That matrix resin system is suitable for many composite manufacturing techniques including Hand Layup, Resin Transfer Molding, Vacuum Infusion, Filament Winding, etc. In this study, the parts by weight ratio used for the epoxy resin and hardener was 100:38, while the curing cycle preferred was 8 hours at 80˚C.

2.1.2. Carbon Fibers (CF)

Just like epoxy matrix system, today the most widely used fiber reinforcement type in many structural applications is carbon fibers (CF); due to their four times lower density, five times higher strength and two times higher modulus compared to steel. Carbon fibers have hexagonal layered graphite structure all oriented with the fiber axes having diameters less than 10 microns.

In this thesis, unidirectional (UD) carbon fiber forms shown in Figure 2.2 are used. These commercial UD forms were produced by using the yarns of Toray Inc. trade named as Torayca T700SC-12000. According to their data sheet, these CF yarns have tensile strength of 4900 MPa, elastic modulus of 230 GPa, filament diameter of 7 μm, and density of 1.8 g/cm^3 with a tex number of 800 g/km.

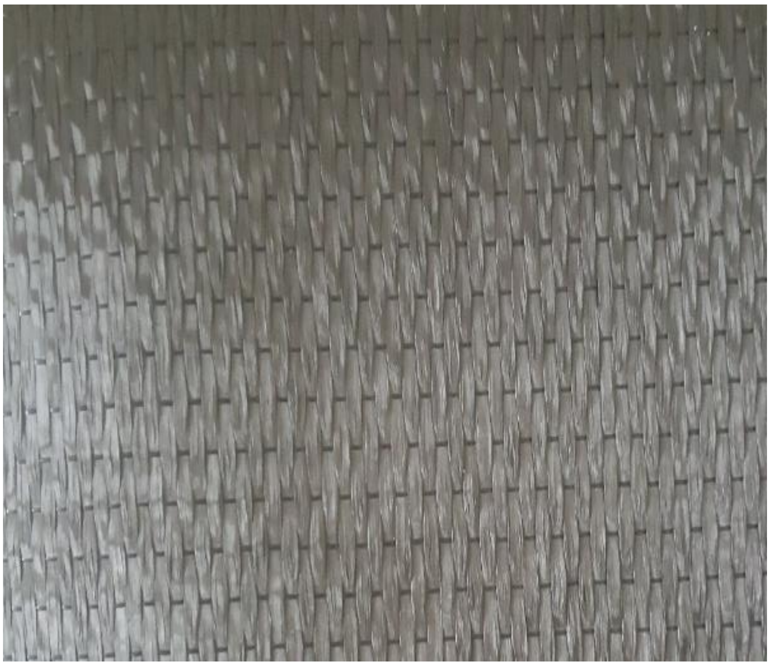


Figure 2.1 UD form of the carbon fibers used in this study

2.1.3. Carbon Nanotubes (CNT)

Recently, due to their excellent mechanical and other properties with very high levels of aspect ratio and surface area to volume ratio, use of nano-reinforcements in the polymer matrices is becoming one of the most attractive study topic both in the academia and composite industry. In this respect, use of carbon nanotubes (CNT) is one of the most frequent case due to their for instance 400 times higher tensile strength and 6 times lower density compared to steel. The tubular structure of CNTs is formed basically by rolling of the one or more hexagonal graphene layers (named as single-walled and multi-walled) having nano-scale diameters and micro-scale lengths.

In this study, a commercially available multi-walled CNT produced by Nanocyl Inc., trade named as Nanocyl-7000, synthesized via catalytic carbon vapor deposition (CCVD) process was used. According to its datasheet, their average diameter and length are 9.5 nm and 1.5 μm, respectively; with a purity of 90%, and surface area range of 250-300 m^2/g. Transmission electron microscopy (TEM) image of the nanotubes taken by the producer was shown in Figure 2.3.

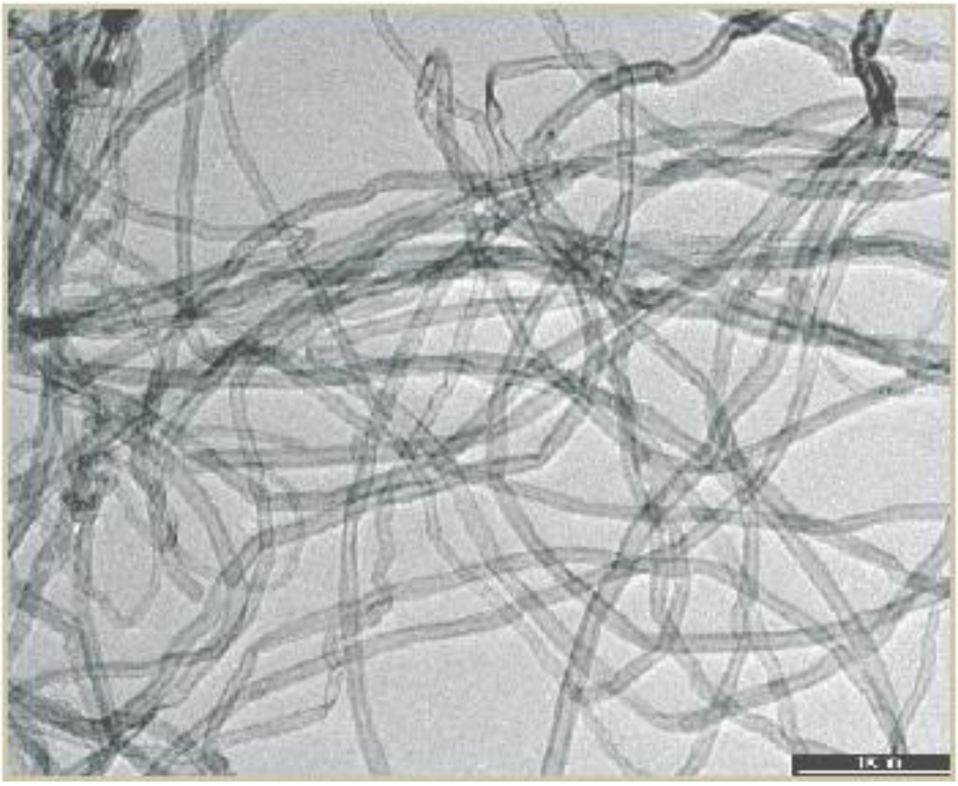


Figure 2.2 TEM image of the multi-walled CNTs used in this study (Nanocyl Inc., the bar in the image is 100 nm)

2.2.Production of the Composite Plates and Specimens

In this study, in order to compare their flexural mechanical properties and vibration damping behavior, specimens were produced in four different groups; the first one being a reference, i.e. neat epoxy specimen, the second and the third ones being epoxy matrix composites having only CNTs and unidirectional and bidirectional CFs; and the fourth group having both CNTs and CFs. The difference in the production of these four groups were as follows:

2.2.1. Neat Epoxy Specimens

As the base reference material, neat epoxy specimens having no reinforcements were produced by mixing the DGEBA type epoxy resin and amine type hardener mixture with the ratio of 100:38 parts by weight, manually. In order to obtain bar-shaped specimens, required for the mechanical and vibration tests, the mixture was poured into a PTFE mold having bar-shaped cavities of 200x20x3 mm as shown in Figure 2.4. Of course, before pouring, mold cavities were carefully cleaned (by acetone) and a mold release agent (Polivaks Max 9) was applied. Curing of the specimens (in the mold) were achieved in a conventional oven at 80˚C for 8 hours.

Figure 2.3 Bar-shaped mold cavities used for the production of Neat Epoxy and Epoxy with CNT composite specimens

2.2.2. Composite Specimens with CNTs

In order to compare effects of using different amounts (i.e. 0.1, 0.3 and 0.5 wt%) of CNTs on the properties of epoxy matrix, almost the same production technique explained above (for the neat epoxy) was used. The only difference was the mixing stage of CNTs with the matrix resin system. In this stage the "Solution Mixing" technique (as defined in the nanocomposites literature) was used. That is, the required amounts of CNTs were first mixed with the hardener and then epoxy resin. In order to increase efficiency (i.e. homogeneous distribution of CNTs), mixing was done via an ultrasonic homogenizer (Comecta CY-500) with a power of 500 W (Figure 2.5). During all sonication processes the parameters used were 50% amplitude, 20 s on / 2 s off and 40˚C max temperature. In order to prevent temperature rise, the mixture was hold in an ice bath during mixing. First, hardener/CNT mixture was sonicated for 30 minutes and then the epoxy resin was added into the mixture and sonicated together for another 20 minutes.

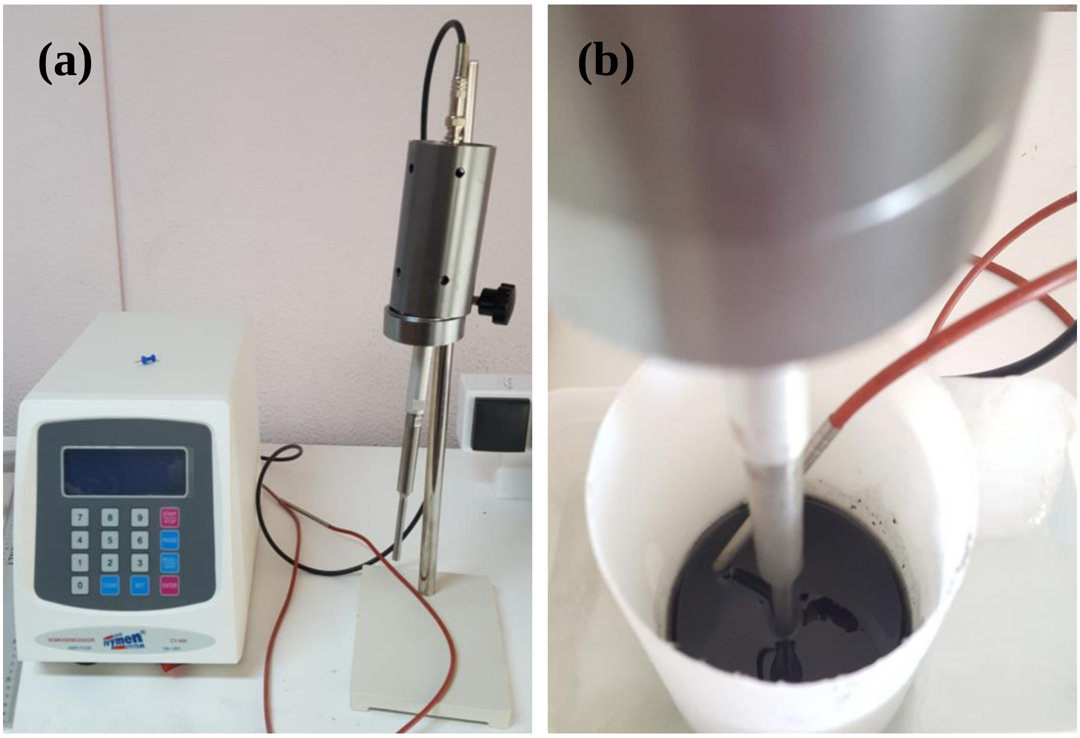


Figure 2.4 (a) General and (b) Closer views of the Solution Mixing set-up via Ultrasonic Homogenizer used for the Epoxy/CNT composite specimens

2.2.3. Composite Plates with Unidirectional and Bidirectional CFs

In this group, bar shaped specimens were cut from the composite plates produced via a laboratory scale "Resin Infusion" set-up (Figure 2.6) onto an aluminum flat tool of 400x400 mm. The procedure was as follows; after cleaning the aluminum tool with acetone and applying release agent together with one layer of "peel ply" (for easy removal of the composite plate); 8 layers of fiber forms were layed-up both uniaxially and biaxially. On top of them, again two layers of "peel ply" and one layer of "infusion mesh" were placed for the efficient impregnation of the fiber layers by the matrix resin mixture. After connecting the resin infusion "inlets" and "outlets", and covering all the layers with the "vacuum bag", and sealing all the edges with a temperature resistant tape; vacuum action was supplied by using a 370 W power vacuum pump (Value-VE245). When the resin infusion was over, to prevent air leakage, both inlet and outlet tubes were clamped carefully. Finally, all the layers together with the base aluminum tool were placed into a conventional oven for the same curing procedure explained before. It was also determined that use of 8 layers of fiber forms resulted in approximately 60 wt% CFs in the composite specimens.

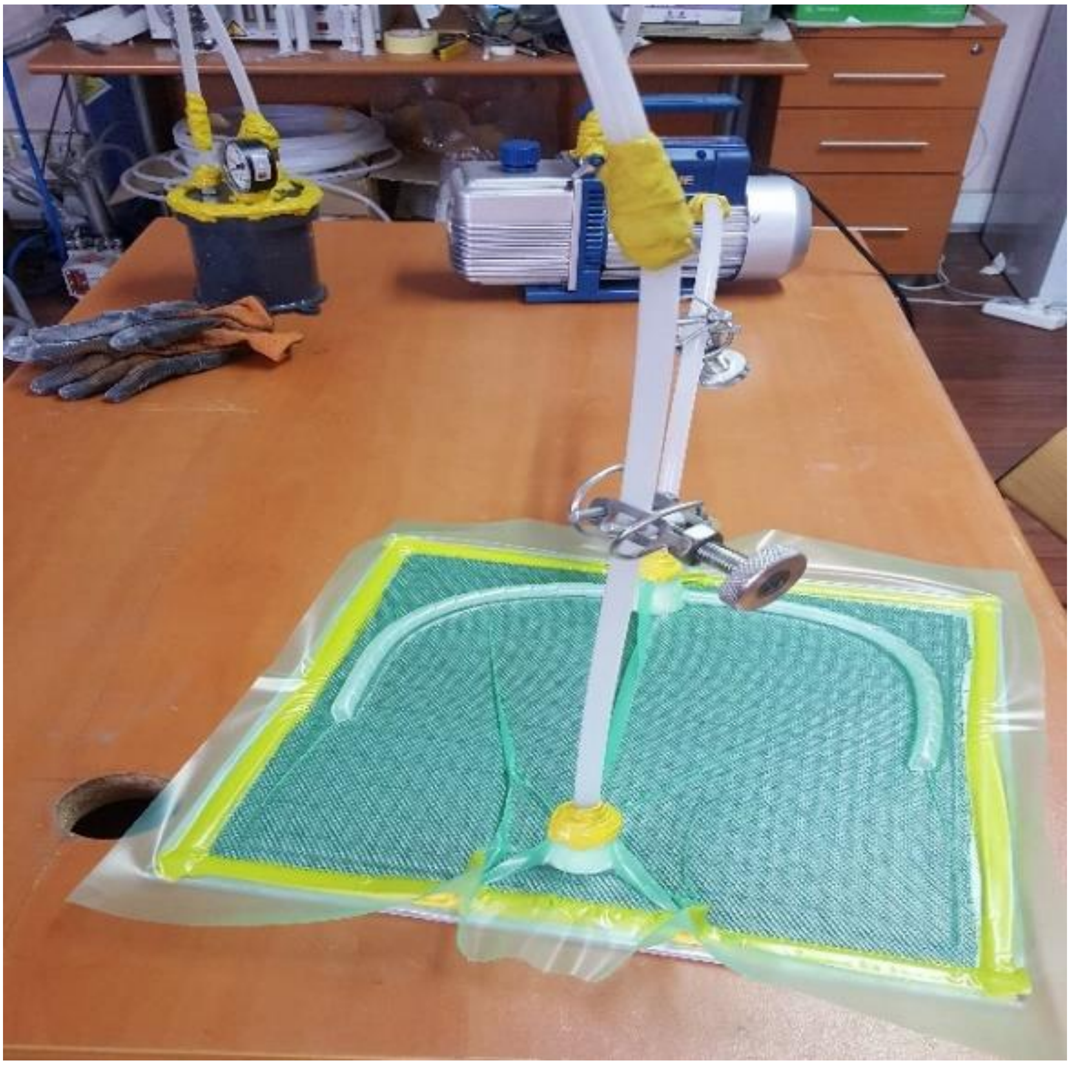


Figure 2.5 Laboratory scale Resin Infusion set-up used for the production of CF reinforced composite plates with and without CNTs

2.2.4. Composite Plates with CNTs and CFs

In this group, the composite plates were produced with the same "Resin Infusion" process mentioned above. The only difference was, before resin infusion, the matrix resin mixture was first mixed with the required amounts of CNTs via an ultrasonic solution mixing method as described in Section 2.2.2 in detail.

2.2.5. Specimen Cutting from Composite Plates

Bar shaped specimen geometry required for the flexural tests and vibration analysis were obtained by cutting of the composite plates (having CFs with and without CNTs) via a table saw (Dewalt DW744XP) carefully for maximum precision and minimum structural damage at the edges.

In order to compare effects of uniaxial (both 0˚ and 90˚) and biaxial (0˚/90˚) alignment of the CFs on the properties, three different specimen cutting configurations were used;

(I) Specimens having 8 layers of CFs all aligned parallel (0˚) to the bar specimen length, defined as "longitudinal unidirectional" specimen and designated with $[0]_8$

(II) Specimens having 8 layers of CFs all aligned perpendicular (90˚) to the bar specimen length, defined as “transverse unidirectional” specimen and designated with $[90]_8$

(III) Specimens having sequentially aligned 4 parallel (0˚) and 4 perpendicular (90˚) CF layers, defined as “cross-plied bidirectional” specimen and designated with $[0/90]_4$

These specimen cutting configurations are illustrated in Figure 2.7; while designations and definitions of all specimens used in this study are tabulated in Table 2.1.

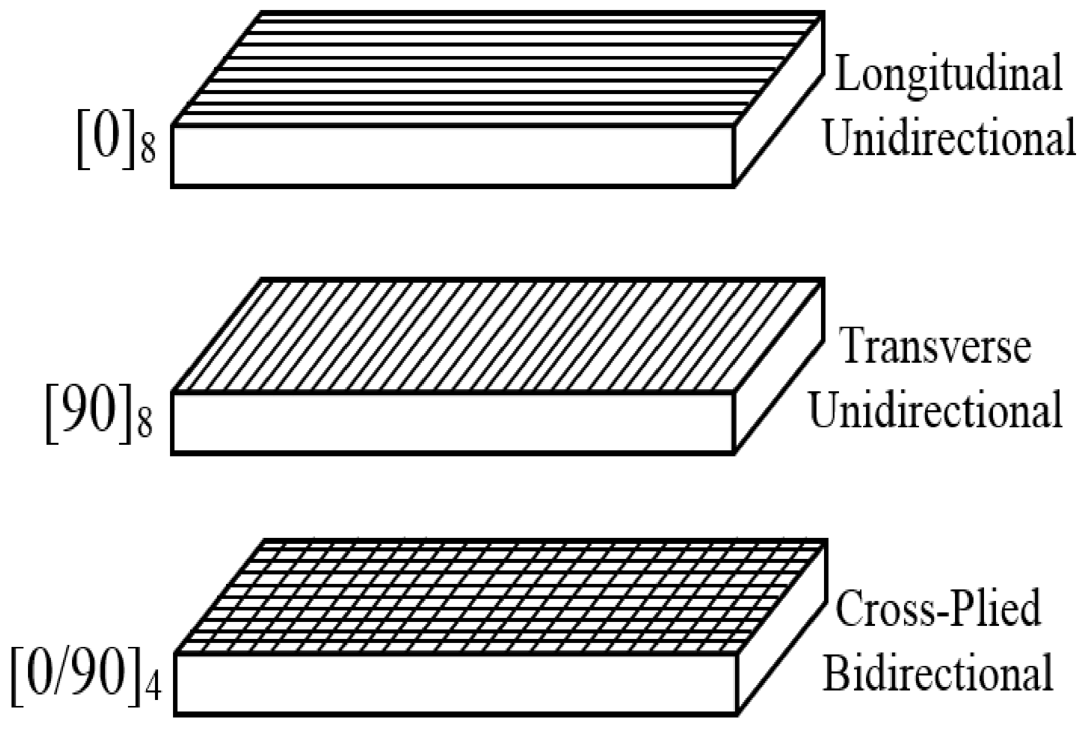


Figure 2.6 Three different cutting configuration used for the bar shaped specimens for testing

Table 2.1 Designations and definitions of the specimens produced

Designations	Definitions
E	Neat Epoxy
E/CNT 0.1	Epoxy with 0.1 wt% CNT
E/CNT 0.3	Epoxy with 0.3 wt% CNT
E/CNT 0.5	Epoxy with 0.5 wt% CNT
E/CF $[0]_8$	Epoxy with 8 layers of 0˚ unidirectional CF
E/CF $[90]_8$	Epoxy with 8 layers of 90˚ unidirectional CF
E/CF $[0/90]_4$	Epoxy with 4 successive layers of 0˚ and 90˚ bidirectional CF
E/CF $[0]_8$/CNT 0.1	Epoxy with 8 layers of 0˚ unidirectional CF and 0.1 wt% CNT
E/CF $[0]_8$/CNT 0.5	Epoxy with 8 layers of 0˚ unidirectional CF and 0.5 wt% CNT
E/CF $[90]_8$/CNT 0.1	Epoxy with 8 layers of 90˚ unidirectional CF and 0.1 wt% CNT
E/CF $[90]_8$/CNT 0.5	Epoxy with 8 layers of 90˚ unidirectional CF and 0.5 wt% CNT
E/CF $[0/90]_4$/CNT 0.1	Epoxy with 4 successive layers of 0˚ and 90˚ bidirectional CF and 0.1 wt% CNT
E/CF $[0/90]_4$/CNT 0.5	Epoxy with 4 successive layers of 0˚ and 90˚ bidirectional CF and 0.5 wt% CNT

2.3.Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) (Hitachi SU5000 FE) was especially used to observe the distribution morphology of CNTs in the matrix. For this purpose, fracture surfaces of the three point bending type flexural test specimens were first sputtered (Leica ACE 200) with 5 nm gold .Secondary electron detector was used together with 5 kV accelerated voltage and 2 mm spot size in order to prevent specimen surface damage.

2.4.Flexural Tests

Before vibration damping analysis, in order to determine the most important two mechanical properties (i.e. strength and elastic modulus) under static loading condition, 3-point bending type flexural tests were conducted for each specimen under a 10 kN universal testing system (Besmak BMT-E) (Figure 2.8). For the neat epoxy and E/CNT composites, tests were carried out according to the ISO 178 standard for the bar shaped specimen size of 100x20x3 mm. For the E/CF and E/CF/CNT composites, tests were carried out according to the ISO 14125 standard for the bar shaped 125x25x2.5 mm specimens (cut from the plates). For each specimen configuration, at least three specimens were tested; and the values of the "Flexural Strength, σ_{Flex}" and "Flexural Modulus, E_{Flex}" were determined as the average values with standard deviations.

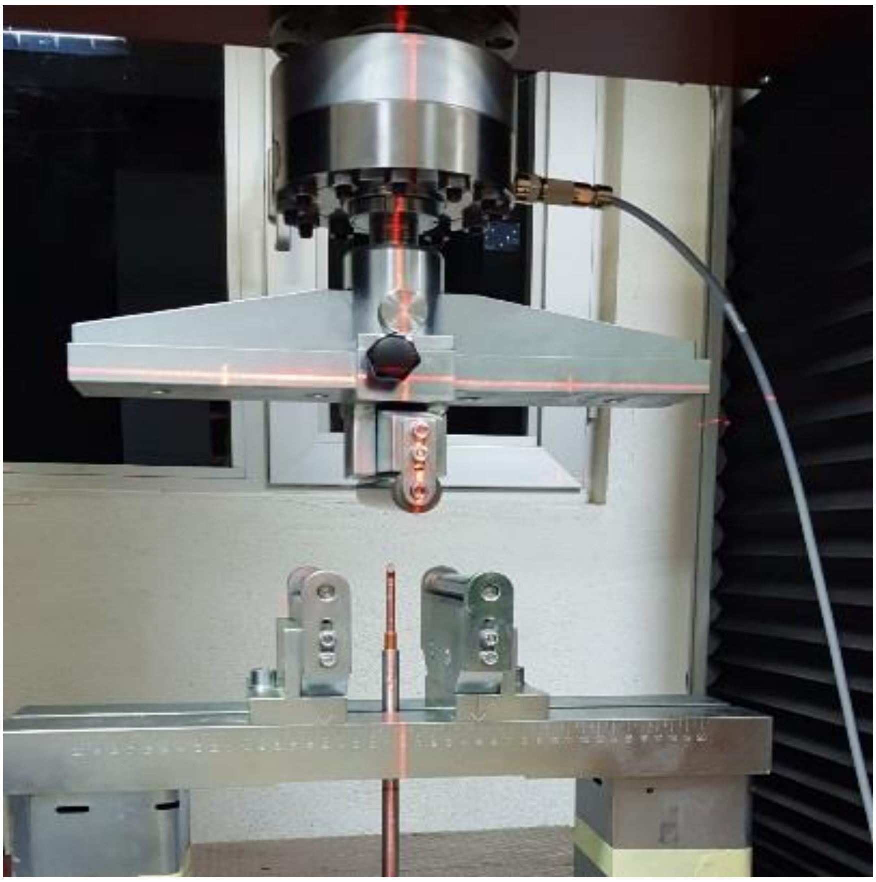


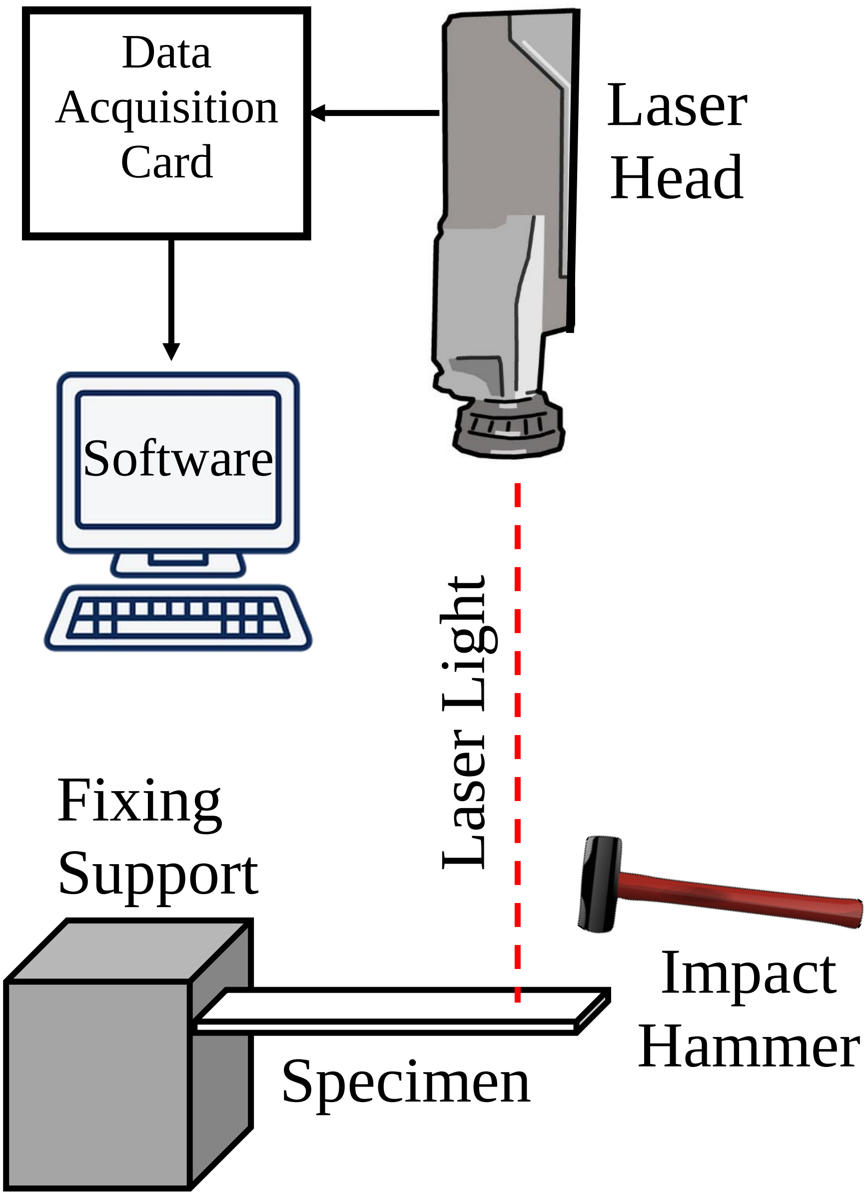
Figure 2.7 Universal testing system used for the 3-point bending type flexural tests

2.5.Vibration Damping Analysis

The setup used in this study to compare the effects of using CF and CNT reinforcements on the vibration damping behavior of epoxy matrix composites is shown in Figure 2.9. In this system, the vibration to the free-end of the fixed bar specimen, having dimensions of 200x20x2.5 mm, was excited by an impact hammer; which is simply defined as “forced vibration test”. Mode I type vibration response of the specimen was recorded with a noncontact mechanism by using a laser system (Optomet Laser Doppler) within the frequency range of 0-500 Hz. The vibration data (amplitude versus frequency) were evaluated in order to determine three important damping parameters; i.e. “Natural Frequency, f_n”, “Dynamic Modulus, E_{Dyn}”, and “Damping Ratio, ζ” in accordance to the “Half-Power Bandwidth” method described in the ASTM E756 standard. The determination method and the equations used for these properties are discussed in Section 1.2 in detail. The average values of these damping properties (f_n, E_{Dyn}, ζ) together with the standard deviations were determined by using the data of at least three vibration tests conducted for each specimen group.

(a)

Figure 2.8 (a) General view and (b) Illustration of the vibration damping test set-up used in this study



(b)

Figure 2.9 (continued)

CHAPTER 3

RESULT AND DISCUSSION

In this chapter, first of all, distribution morphology of carbon nanotubes (CNT) in epoxy (E) matrix was discussed via SEM analysis. Then, flexural three point bending test results were evaluated to determine the mechanical properties of all specimens. Finally, effects of CNTs and uniaxially and biaxially oriented carbon fibers (CF) on the vibration damping behavior of the epoxy matrix composites were discussed by using the "half-power bandwidth" method.

3.1. Distribution of CNTs in Epoxy Matrix

It is known that uniform and homogeneous dispersion of CNTs in the matrix is extremely important for the improvement of all properties of composite materials. For this purpose, SEM analysis was conducted on the fracture surfaces of the flexural 3-point bending specimens.

It was generally observed that, as shown in Figure 3.1, when the CNT content was minimum, i.e. 0.1 wt%, there was no uniformity and distribution problem in the epoxy matrix leading to highest increases in the mechanical properties (flexural strength and modulus) as will be discussed in the next section. When the CNT content was increased to 0.3 and 0.5 wt%, the degree of uniformity and homogeneity started to decrease with the consequent decline in the flexural strength and modulus values. The main reason for this situation should be due to the higher level of difficulty during solution mixing stage of the epoxy resin system with the non-functionalized CNTs used in this study leading to "bundling". This type of agglomeration with the increased amount of CNTs could be also partly due to the higher level of Coulombic attractions between them. Similar observations were also discussed in the literature [42, 43].

Therefore, in this study, epoxy matrix composites having more than 0.5 wt% CNT were not produced.

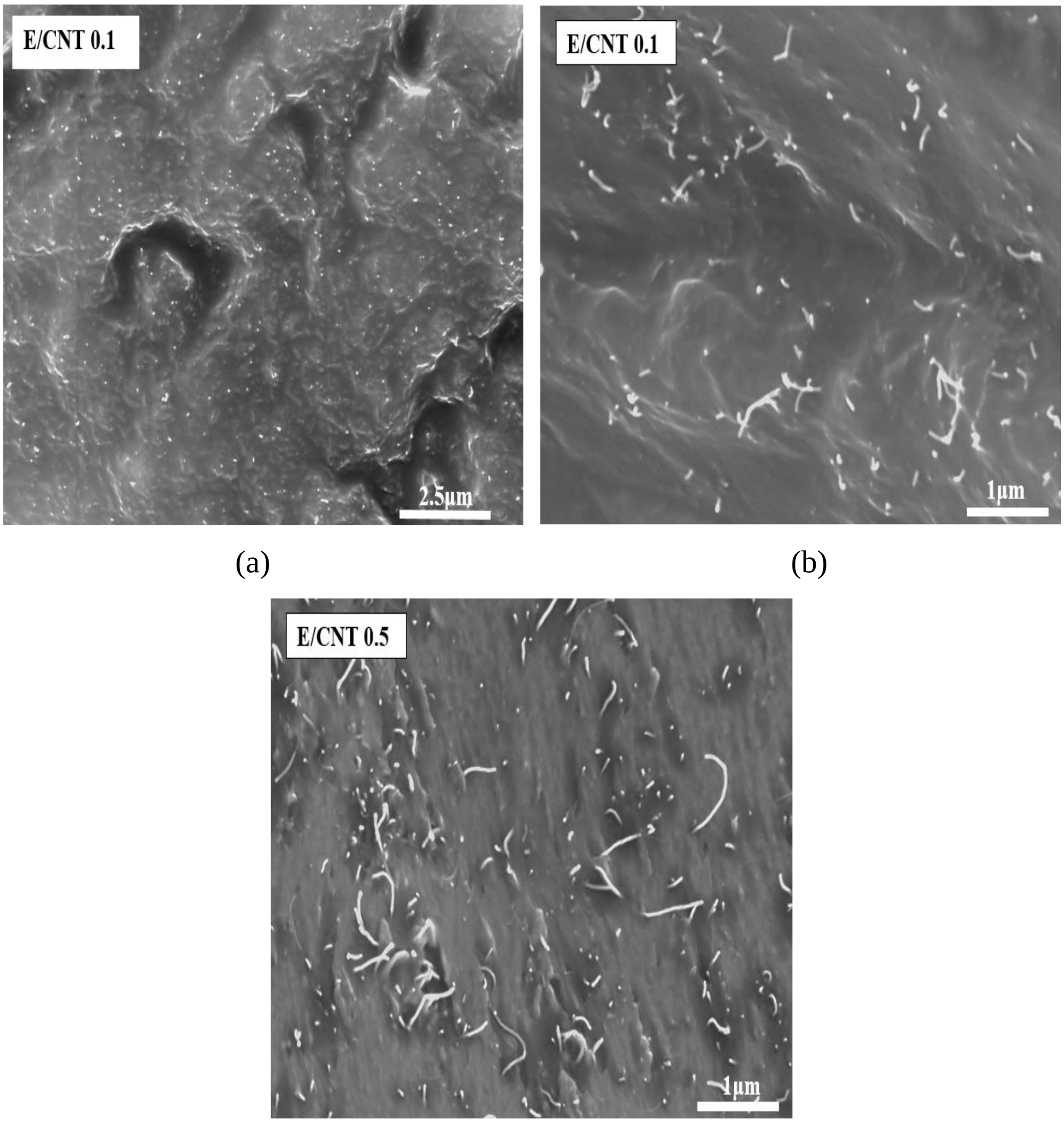
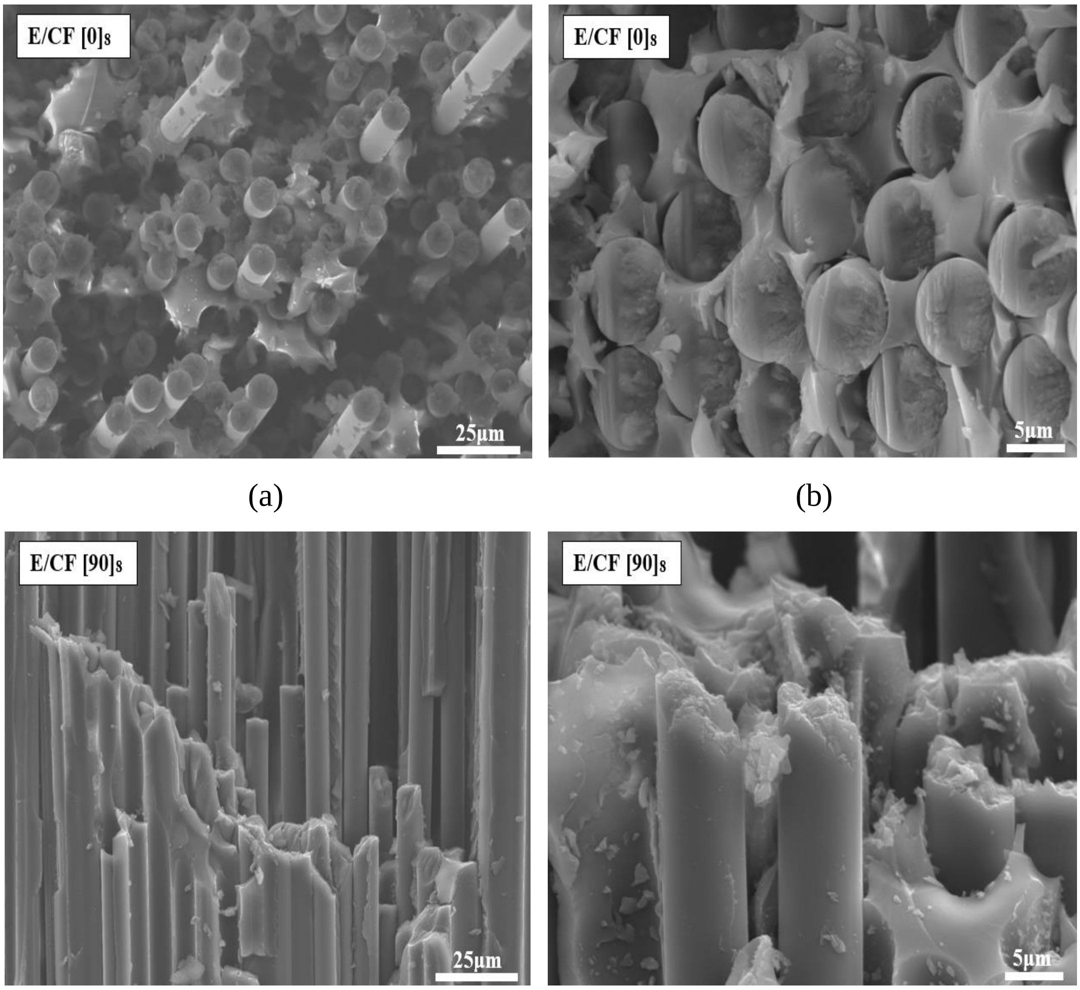


Figure 3.1 SEM images showing (a and b) uniform distribution of 0.1 wt% CNT and (c) bundling of 0.5 wt% CNT in epoxy matrix

In this study, since unidirectional CF forms were layed-up during the production of the composite plates either uniaxially (both 0˚ and 90˚) or biaxially (0˚/90˚), there was no problem of fiber uniformity as seen in the fracture surface morphology (Figure 3.2) taken during the SEM analysis of the specimens having CFs. For the specimens having both CNTs and CFs, unfortunately; SEM studies were problematic. Because, since the fracture surface of these specimens were dominated by continuous CF forms, it was not possible to search and recognize the distribution of CNTs in the very little area of the epoxy matrix left between the CFs.



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

Figure 3.2 SEM images showing (a, c) general and (b, d) closer view fracture surface morphology of the epoxy matrix composites with longitudinal (0˚) and transverse (90˚) CF forms

3.2. Effects of CNTs and CFs on the Flexural Mechanical Properties

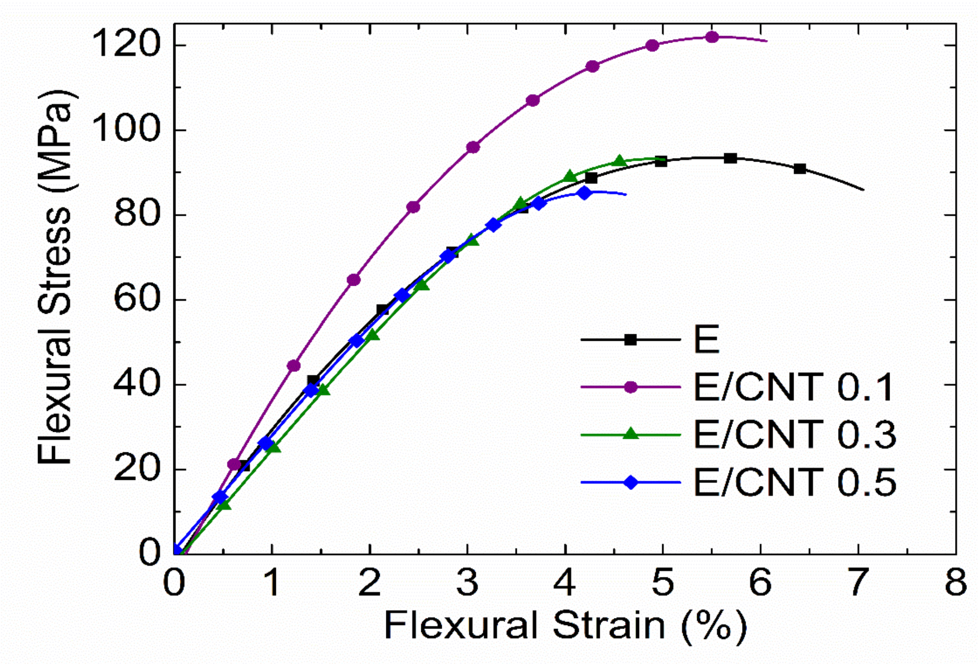
In order to determine effects of using CNTs and CFs on the mechanical properties of epoxy matrix composites; three-point bending type flexural tests were conducted. After obtaining flexural stress and flexural strain curves of each specimen group (as shown in Figure 3.3), then two important mechanical properties, i.e. "Flexural Strength, σ_{Flex}" and "Flexural Modulus, E_{Flex}" were determined. The increasing or decreasing trends of these properties for each group were evaluated in Figure 3.4. It should be noted that, in Figures 3.3 and 3.4, curves and bars were grouped into certain sections in order to emphasize effects of using (i) only CNTs, (ii) only CFs, and (iii) CNTs and CFs together. Finally, all the strength and modulus data with their average values and standard deviations were tabulated in Table 3.1. In this table, "%Δ" values, i.e. %increases or % decreases in the σ_{Flex} and E_{Flex} of the composites, determined with respect to the neat epoxy matrix, were also given.

It is very well known that when a polymer matrix was incorporated with a reinforcement material, its strength and modulus normally increase due to the two basic mechanisms; the first one being "load transfer from the weak matrix to the very strong reinforcement" and the latter one being "decrease in the macromolecular chain sliding mobility of the matrix by the reinforcement barriers". If the reinforcements are in the nano-scale, even with very little amount, these two strengthening and stiffening mechanisms would be effective due to the higher aspect ratio and higher surface area to volume ratio of the nanoparticles, such as carbon nanotubes.

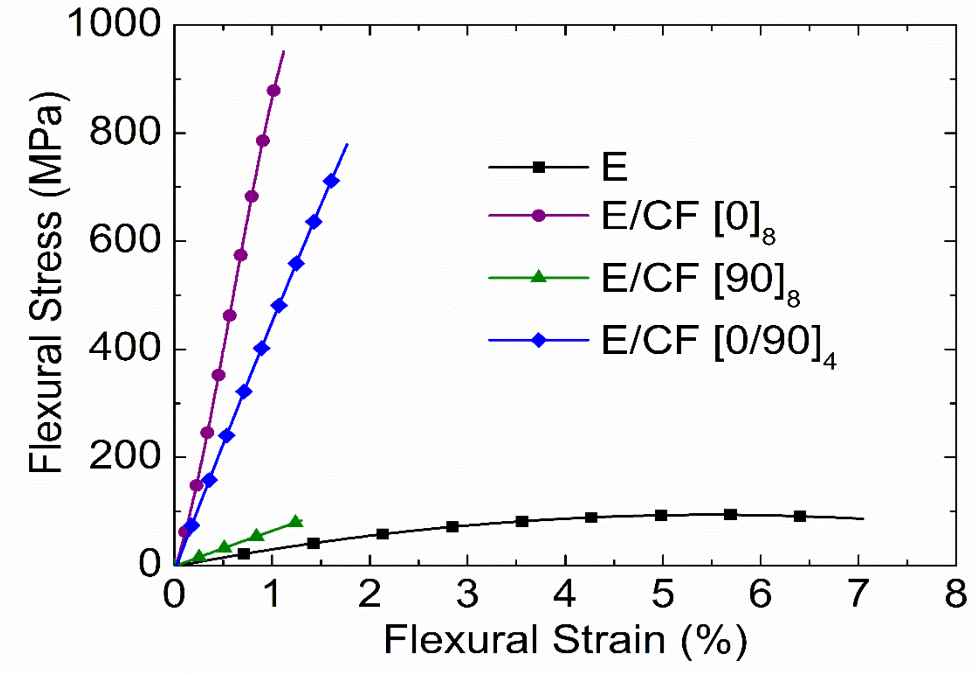
Therefore, Figures 3.3(a), 3.4 and Table 3.1 show that use of only 0.1 wt% CNT increased the flexural strength and modulus values of epoxy matrix as much as 36% and 28%, respectively. On the other hand, because of the decreased efficiency of the strengthening and stiffening mechanisms, increasing CNT content to 0.3 and 0.5 wt% resulted in gradual decreases in these mechanical properties; basically due to the non-functionalized CNT surfaces leading to uniform distribution problems in the epoxy resin mixture with their rather "bundled" morphology.

If the reinforcements are in the micro- and macro-scale, such as fibers, then usually much higher amounts are required for the significant improvements in the strength and modulus values of polymer matrices. For instance, in many engineering structures manufactured with continuous glass, aramid or carbon fiber reinforced epoxy matrix, various fiber forms being not less than 60 vol% were preferred. However, apart from the high fiber content, another very significant parameter in these composite structures is the type of the alignment of these continuous fiber forms with the loading direction. If the continuous fibers are aligned parallel to the loading direction, i.e. “longitudinal loading”, then the strengthening and stiffening mechanisms mentioned above will be very effective. On the other hand, if the continuous fibers are aligned perpendicular to the loading direction, i.e. “transverse loading”, then the separation at the interface between the matrix and fibers would be very easy, leading to absence of the strengthening and stiffening mechanisms.

Under three-point bending type flexural loading, it is known that throughout the cross-section of the beams; there would be tensile, compressive and shear components of the flexural stress. If continuous fibers are all aligned parallel to the length of the beams, i.e. “longitudinal uniaxial” case, then all the components (tensile, compressive, shear) of the applied flexural stress would be carried by the fibers very effectively. Therefore, Figures 3.3(b), 3.4 and Table 3.1 show that, compared to the neat epoxy matrix specimen, flexural strength of the E/CF $[0]_8$ specimen increased more than 9 times; moreover, the increase in flexural modulus was much enormous being more than 34 times.

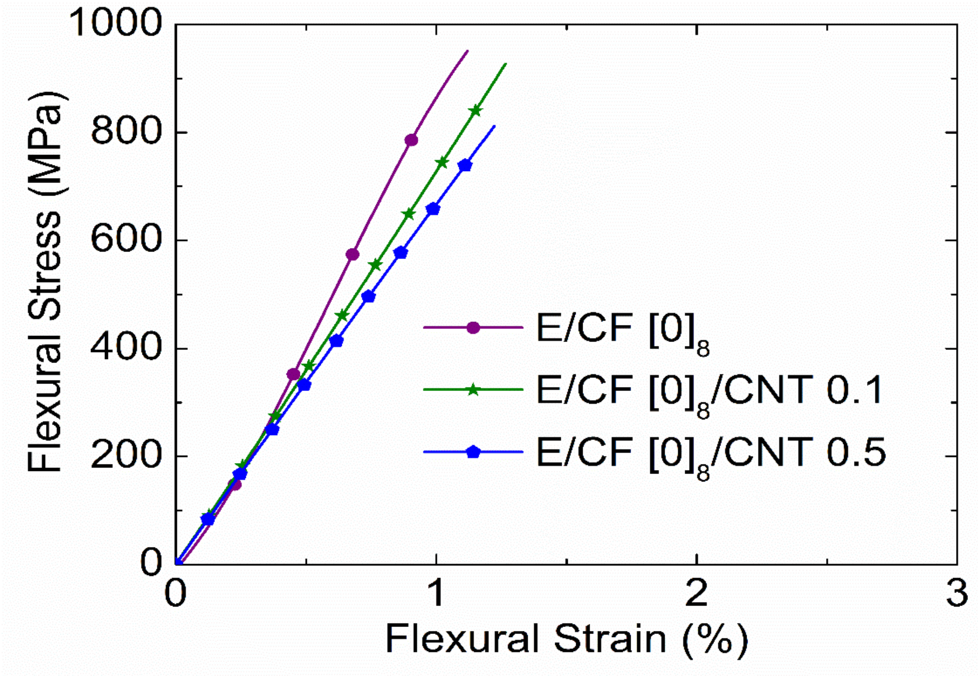


(a)

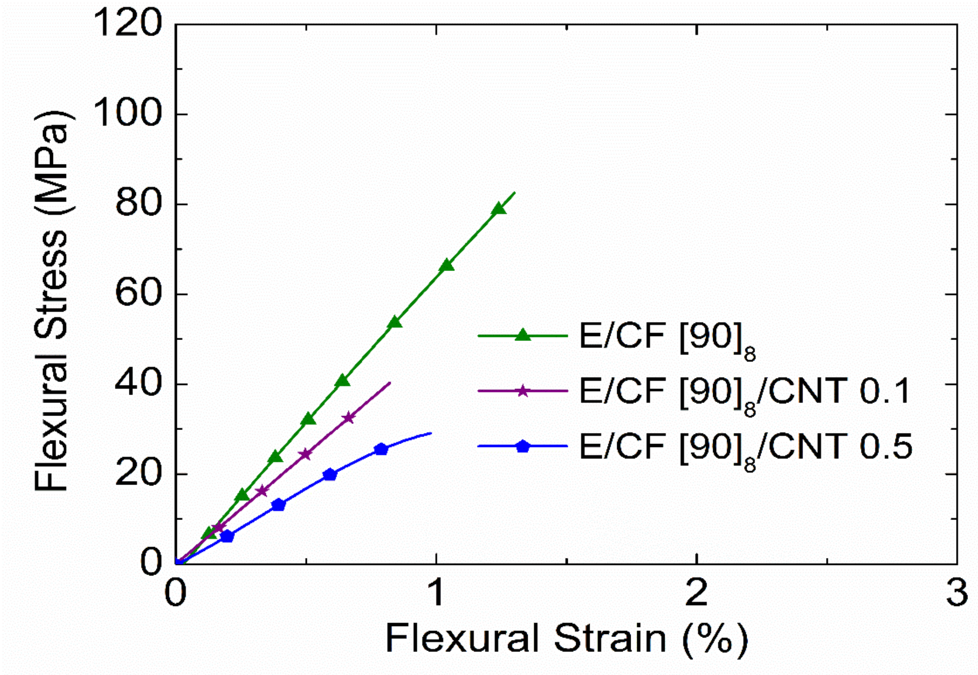


(b)

Figure 3.3 Flexural stress-strain curves of the epoxy matrix and its composites; showing effects of using (a) only CNTs, (b) only CFs, (c) CNTs with longitudinal CFs, (d) CNTs with transverse CFs, and (e) CNTs with bidirectional CFs

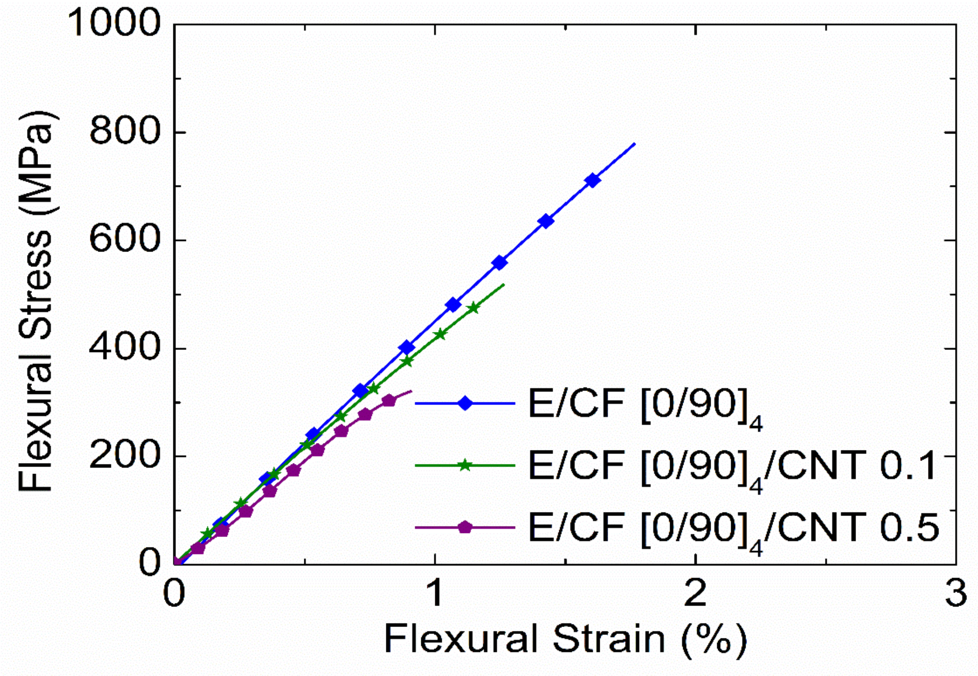


(c)



(d)

Figure 3.3 (continued)



(e)

Figure 3.3 (continued)

Oppositely, for the E/CF $[90]_8$ specimen, in which all the continuous fibers are aligned perpendicular to the length of the beams, i.e. "transverse uniaxial" case; since tensile, compressive and shear components of the applied flexural stress would be carried by the much weaker interfacial phase, no improvement in the flexural strength value was observed. This means that, in the mechanical properties of the E/CF $[0]_8$ and E/CF $[90]_8$ composites, there was enormous level of "anisotropic" behavior.

Therefore, in order to get rid of that kind of very anisotropic behavior observed in the properties of 0˚ and 90˚ uniaxially aligned continuous fiber reinforced composite materials; engineers usually construct their laminate structures with the layers having different orientations, at least along two major axes, which is named as "biaxial" alignment. In this respect, one of the most widely used biaxial case is having both 0˚ and 90˚ aligned fiber layers, also called as "cross-plied" structure. Although their properties would be less than the properties of the longitudinally aligned case, they would still be more than the required levels for many engineering applications. For example, for the E/CF $[0/90]_4$ specimen, it was seen that the increment in the σ_{Flex}

value of epoxy matrix was more than 7 times; while in E_{Flex} value the increase was more than 16 times.

Figures 3.3(c), (d), (e), 3.4 and Table 3.1 also revealed that when CNTs and CFs were used together, even for the case of additional 0.1 wt% CNT, there were no additional contribution of CNTs to the flexural strength and modulus values of the E/CF composites. The most probable reason for this situation could be lower efficiency of the resin flow during resin infusion process. Because, when CNTs were added to the epoxy resin mixture just before the start of resin infusion process, the viscosity of the resin mixture increases which might lead to insufficient impregnation of the CF layers; consequently, resulting in gradual decreases in the mechanical properties of the E/CF composites.

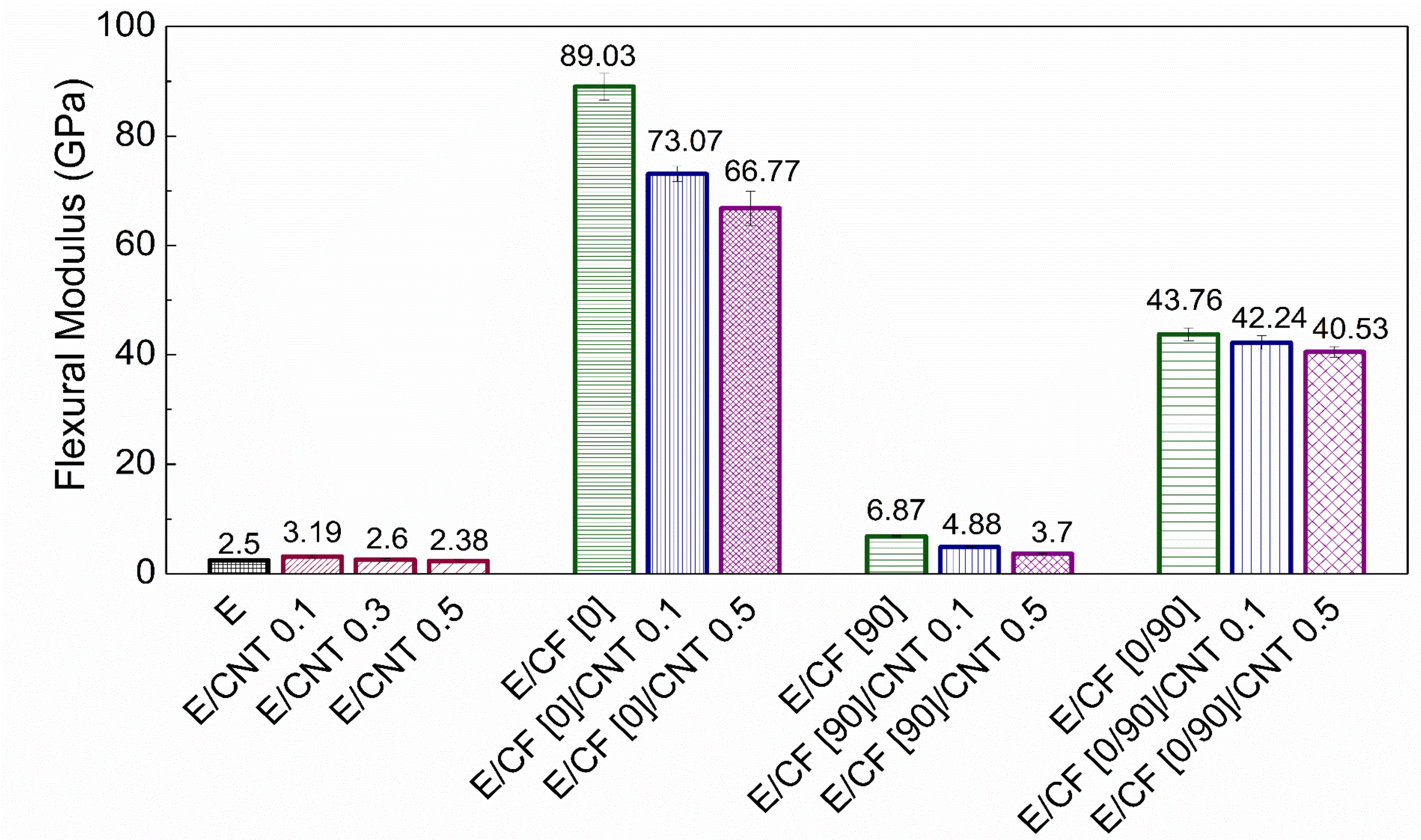
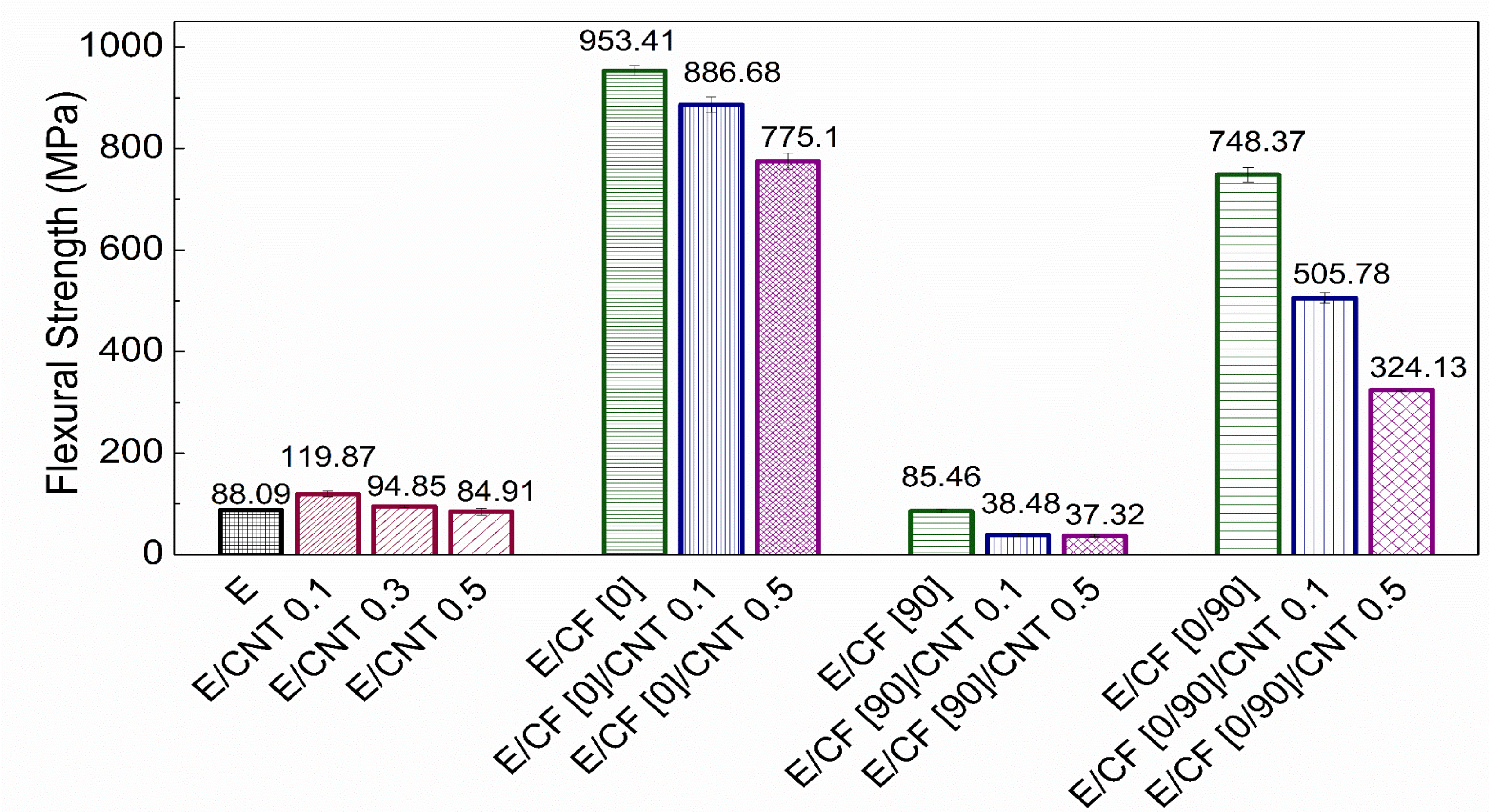


Figure 3.4 Effects of CNTs and CFs on the (a) Flexural Modulus and (b) Flexural Strength of the epoxy matrix composites



(b)

Figure 3.4 (continued)

Table 3.1 Flexural Strength (σ_{Flex}), Flexural Modulus (E_{Flex}) and their %Δ values, i.e. % increases or % decreases, of the composite specimens compared to neat epoxy matrix

Specimens	**σ_{Flex} (MPa)**	**σ_{Flex} (%Δ)**	**E_{Flex} (GPa)**	**E_{Flex} (%Δ)**
E	88.09 ± 2.50	-	2.50 ± 0.15	-
E/CNT 0.1	119.87 ± 5.48	36	3.19 ± 0.24	28
E/CNT 0.3	94.85 ± 2.38	8	2.60 ± 0.20	4
E/CNT 0.5	84.91 ± 6.46	-4	2.38 ± 0.21	-5
E/CF $[0]_8$	953.41 ± 9.31	982	89.03 ± 2.40	3461
E/CF $[90]_8$	85.46 ± 3.50	-3	6.87 ± 0.15	175
E/CF $[0/90]_4$	748.37 ± 14.35	750	43.76 ± 1.17	1650
E/CF $[0]_8$/CNT 0.1	886.68 ± 15.12	907	73.07 ± 1.41	2823
E/CF $[0]_8$/CNT 0.5	775.10 ± 16.11	780	66.77 ± 3.11	2571
E/CF $[90]_8$/CNT 0.1	38.48 ± 3.38	-56	4.88 ± 0.04	95
E/CF $[90]_8$/CNT 0.5	37.32 ± 2.75	-58	3.70 ± 0.08	48
E/CF $[0/90]_4$/CNT 0.1	505.78 ± 10.39	474	42.24 ± 1.25	1589
E/CF $[0/90]_4$/CNT 0.5	324.13 ± 1.55	268	40.53 ± 0.99	1521

3.3. Effects of CNTs and CFs on the Vibration Damping Behavior

As explained in Sections 1.2 and 2.5, vibration damping behavior of all specimen groups were analyzed by using the “half-power bandwidth” method under forced vibration condition with non-contact measurement. After obtaining Amplitude vs Frequency curves of the each specimen group, as indicated in Figure 3.5, then three important damping characteristics, i.e. “Natural Frequency, f_n”, “Dynamic Modulus, E_{Dyn}” and “Damping Ratio, ζ” were determined. The increasing or decreasing trends in these parameters for each specimen group were evaluated in Figure 3.6. It should be pointed out that, in Figures 3.5 and 3.6, curves and bars were grouped into certain sections in order to emphasize effects of using (i) only CNTs, (ii) only CFs, and (iii) CNTs and CFs together. Lastly, all the data (f_n, E_{Dyn}, ζ) with their average values and standard deviations were tabulated in Table 3.2.

It is known that, as also presented in Equation 1 (Section 1.2) , Natural Frequency (also named as “Resonant Frequency”) and Dynamic Modulus (that is “Elastic Modulus under Vibration”) parameters are related to each other, and depend on the mass and stiffness of the material. Thus, a decrease in stiffness, i.e. elastic modulus, leads to a decrease in Natural Frequency; or vice versa. Moreover, Figure 3.6 and Table 3.2 indicated that values of the Damping Ratio are inversely related to the values of both Natural Frequency and Dynamic Modulus. Therefore, in the following paragraphs, effects of CNTs and CFs on the vibration damping behavior of the epoxy matrix composites will be discussed, for simplicity, by considering only the values of Damping Ratio of the specimens, which is indeed the most significant vibration damping property of the materials. Thus, in Table 3.2, “percent contribution” of CNTs and CFs to the Damping Ratio of Epoxy Matrix; and “percent contribution” of CNTs to the Damping Ratio of the related E/CF composites were also tabulated.

For the solid materials, apart from their stiffness, vibration damping behavior was especially explained with the phenomenon of “Coulomb Damping” also named as

“Dry-Friction Damping”; in which, damping basically comes from the friction force between two dry surfaces. When one surface slides over the other, the energy is absorbed i.e. damped as frictional force. In the materials, damping would take place via the frictional forces between the phases, grain boundaries, imperfections etc. Therefore, the microstructure of the materials plays a very significant role on their vibration damping behavior.

For the composite materials, in the literature [27, 34-36, 40], that type of vibration damping behavior is basically explained with the “stick-slip” phenomenon; which can be described as surfaces alternating between sticking to each other and sliding over each other, with a corresponding change in the friction force, i.e. damping. According to the “stick-slip mechanism” the vibration energy exposed to the composite materials would be consumed, i.e. damped, by the internal friction taking place between the matrix phase and the reinforcement phases. Of course, increasing the interfacial bond strength between the matrix and reinforcements would decrease the efficiency of that mechanism.

It is known that compared to many metallic and ceramic materials, all subclasses of polymers (even thermosets) have much higher Damping Ratio due to their much lower stiffness. In this study, Damping Ratio of neat epoxy matrix was determined as $240x10^{-4}$. Figure 3.6 and Table 3.2 show that when CNTs were incorporated into the epoxy matrix there was significant contribution to this property. For instance, the increase was 38% when only 0.1 wt% CNT added; while the increases in Damping Ratio were as much as 47% and 82% for the E/CNT 0.3 and E/CNT 0.5 specimens, respectively. That is, increasing the CNT content increased the Damping Ratio of the epoxy matrix. Because, CNTs having extremely high aspect ratios and extremely high surface area/volume ratios resulted in an efficient “stick-slip mechanism” at the Epoxy-CNT interfaces. Moreover, use of non-functionalized CNTs in this study, i.e. rather a weaker interfacial bond strength at the interface, could be an additional contribution to the effectiveness of the stick-slip mechanism. In the specimen having high CNT content (i.e. E/CNT 0.5 specimen), although there were CNT bundling problem (a kind of agglomeration), Damping Ratio continued to rise; which could be due to the stick-slip mechanism this time taking place also at the CNT-CNT interfaces.

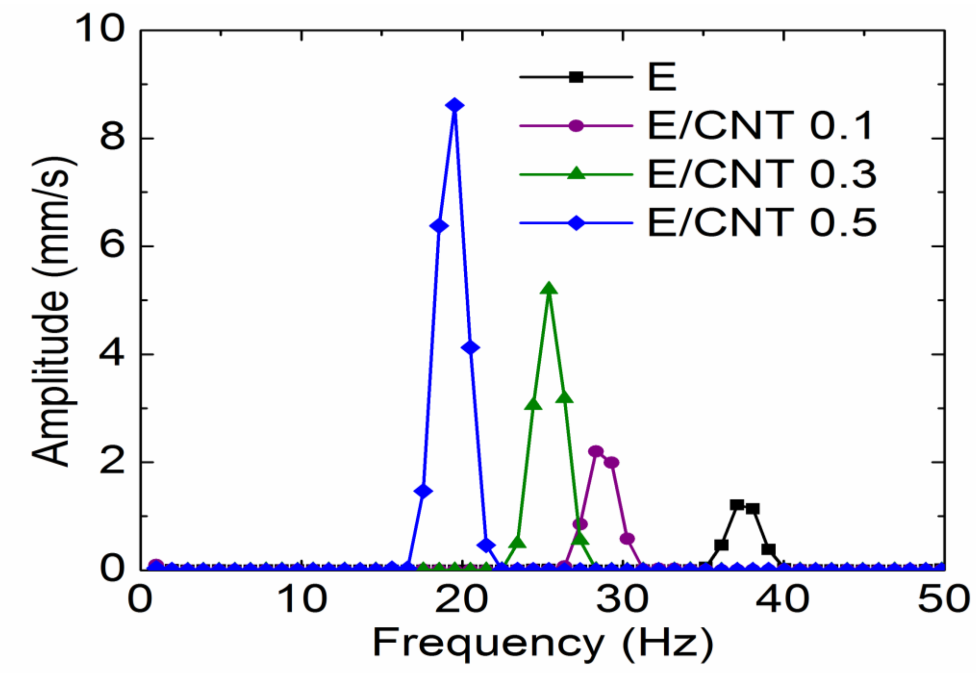
When the epoxy matrix was reinforced with the longitudinal (0˚) unidirectional and cross-plied (0˚ /90˚) bidirectional CFs; Figure 3.6 and Table 3.2 indicate that rather than a positive contribution, there was significant reduction in the Damping Ratio of the Epoxy matrix, the decreases being -70% and -56%, respectively. Because, although stick-slip mechanism of vibration damping operates this time at the interfaces between Epoxy-CFs, but its contribution was not sufficient considering the enormous increases in the stiffness of the composites. For example, Dynamic Modulus of the neat epoxy matrix increased more than 14 times in E/CF $[0]_8$ specimens, while this increase was more than 8 times for E/CF $[0/90]_4$ specimens.

When the epoxy matrix was reinforced with the transverse (90˚) unidirectional CFs, it was seen that, as expected, Dynamic Modulus of the composite was not improved much, it was just above the Dynamic Modulus of neat epoxy matrix. Therefore, due to the no enormous increase in the stiffness of this composite; the level of the stick-slip vibration damping mechanism at the Epoxy-CF interfaces were sufficient to increase the Damping Ratio of the epoxy matrix as 22% in the E/CF $[90]_8$ specimen. This means that, very high levels of "anisotropic" behavior observed in the flexural strength and modulus properties discussed in the previous section was also valid in the vibration damping behavior.

When CNTs and CFs were incorporated into the matrix together, then a synergism in the stick-slip vibration damping mechanism would be expected due to the additional CNT-CF interfaces apart from Epoxy-CNT, Epoxy-CF, CNT-CNT interfaces. For example, Figure 3.6 and Table 3.2 reveal that use of CNTs contributed to the Damping Ratio of the related E/CF composites, significantly. Of course, due to higher amount of interfacial friction, synergism in the "stick-slip" mechanism was more efficient when 0.5 wt% CNT was incorporated compared to 0.1 wt% CNT. For instance, Table 3.2 revealed that contribution of the 0.5 wt% CNT to the Damping Ratio of the E/CF

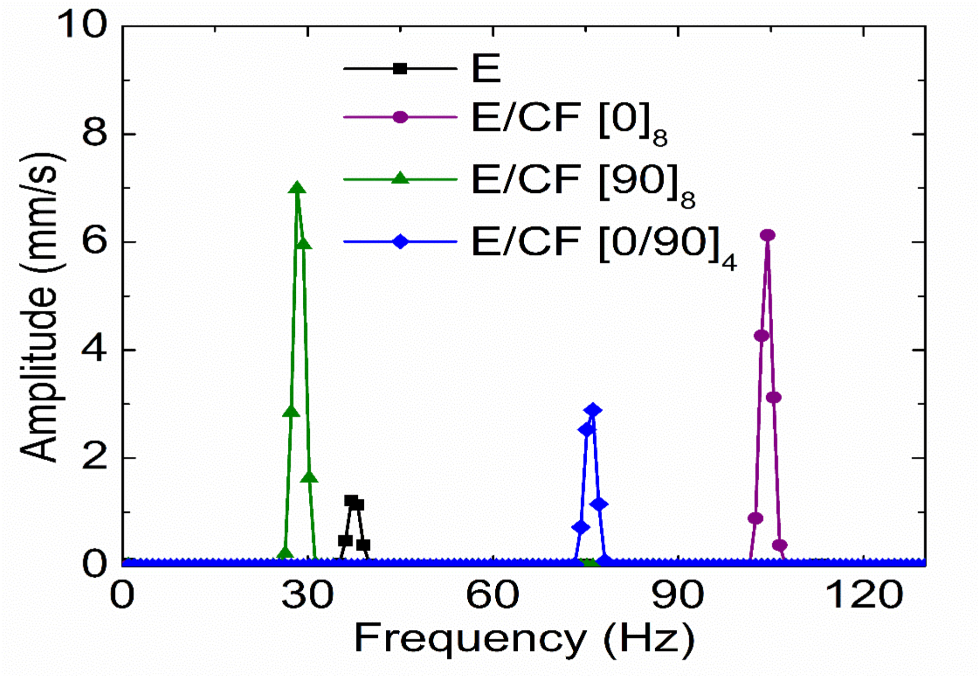
$[0]_8$, E/CF $[90]_8$ and E/CF $[0/90]_4$ composites were as much as 22%, 63% and 34%, respectively.

Therefore, it can be generally concluded that, although additional use of CNTs have no additional contribution to the mechanical properties (Flexural Strength and Flexural Modulus) of the E/CF composites, their contribution in Vibration Damping are significant.

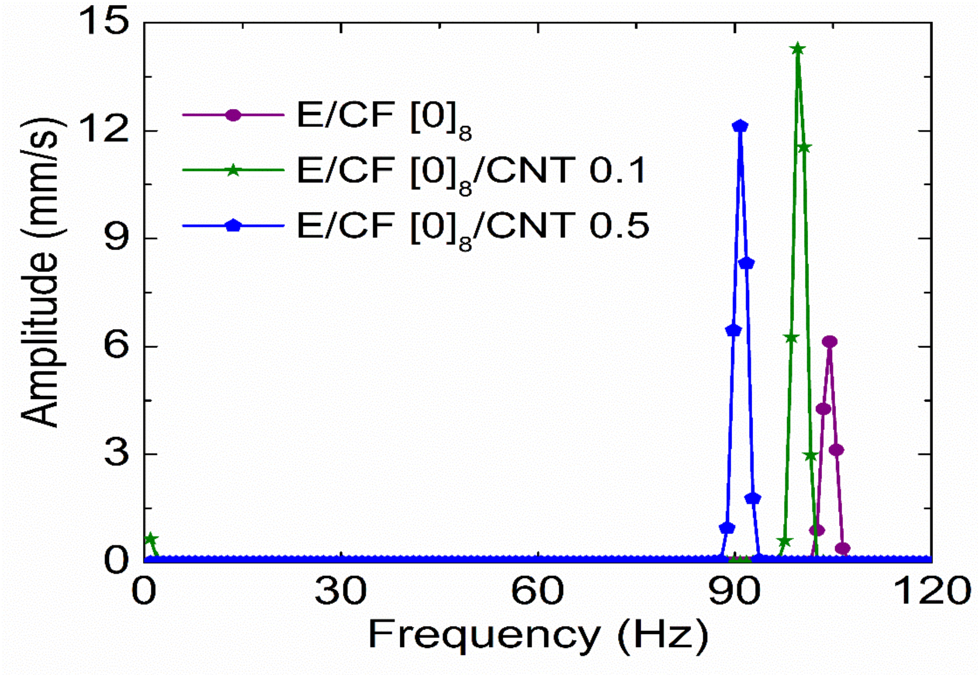


(a)

Figure 3.5 Amplitude vs frequency curves of the epoxy matrix and its composites; showing effects of using (a) only CNTs, (b) only CFs, (c) CNTs with longitudinal CFs, (d) CNTs with transverse CFs, and (e) CNTs with biaxial CFs

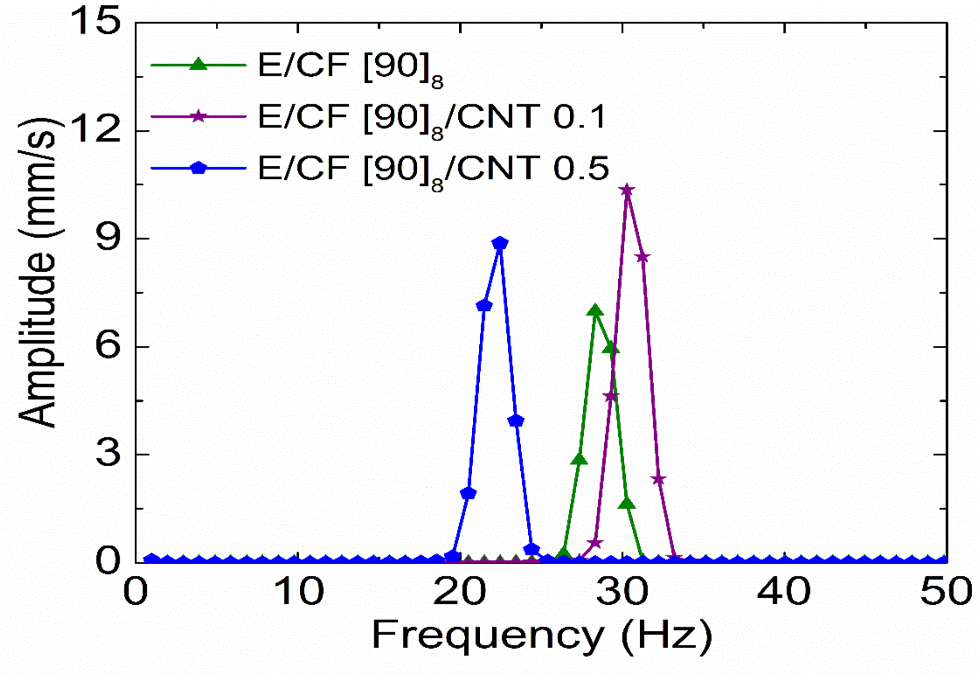


(b)

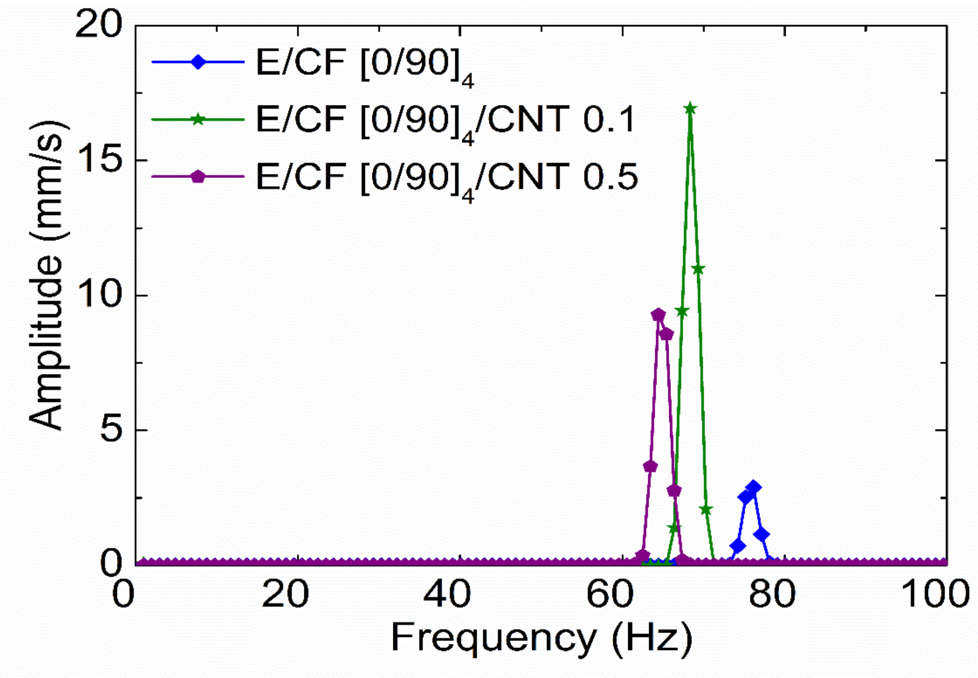


(c)

Figure 3.5 (Continued)



(d)



(e)

Figure 3.5 (Continued)

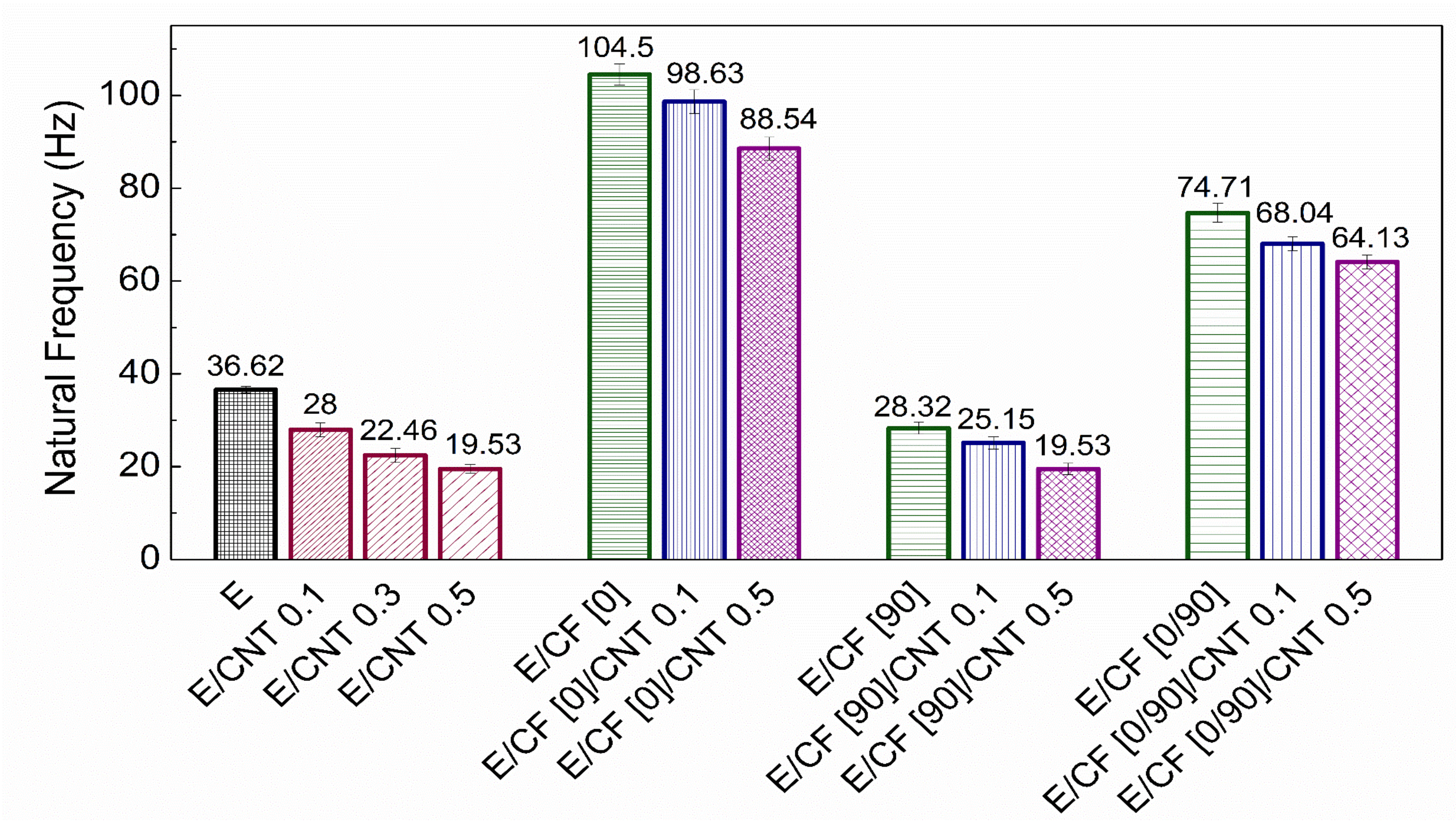
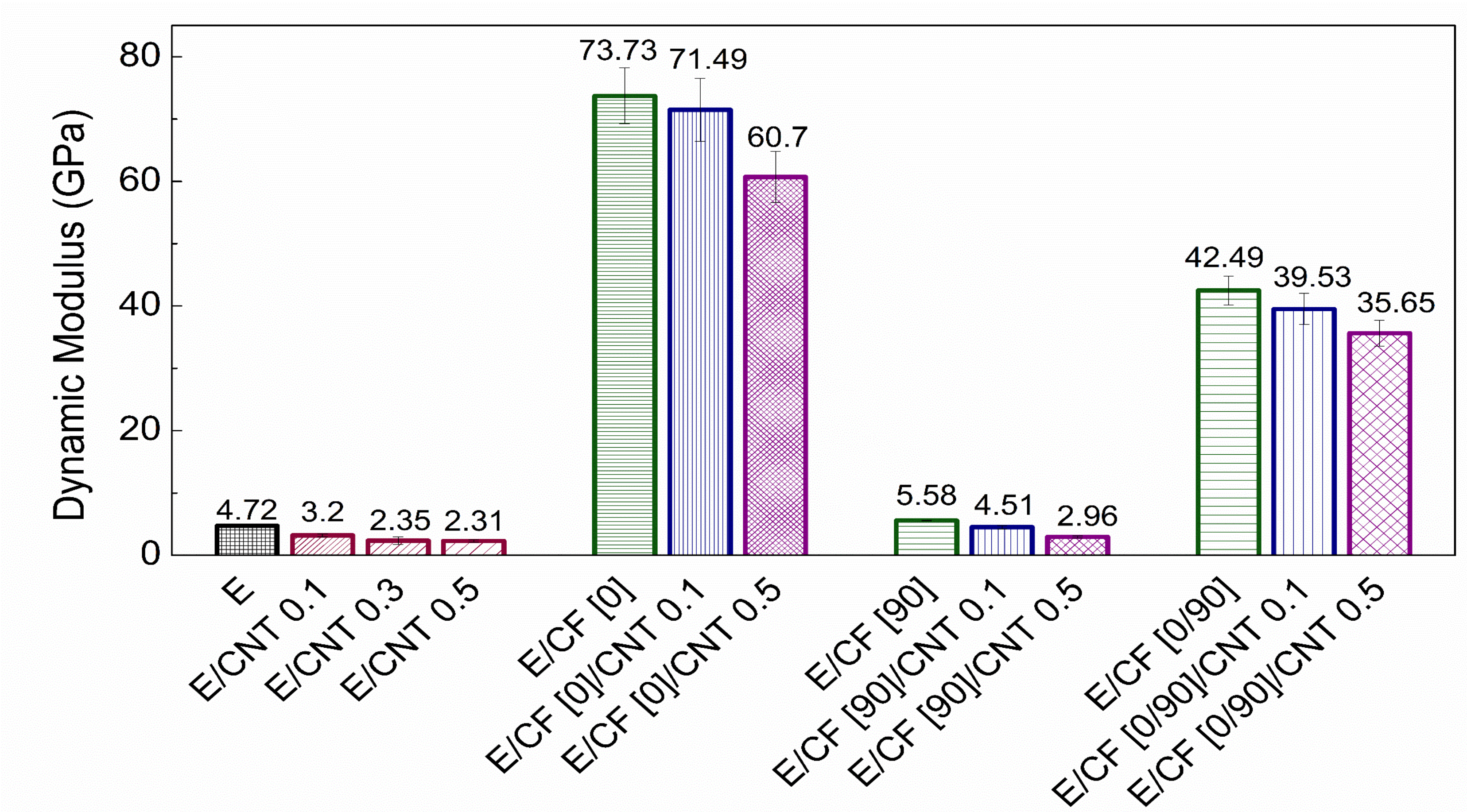
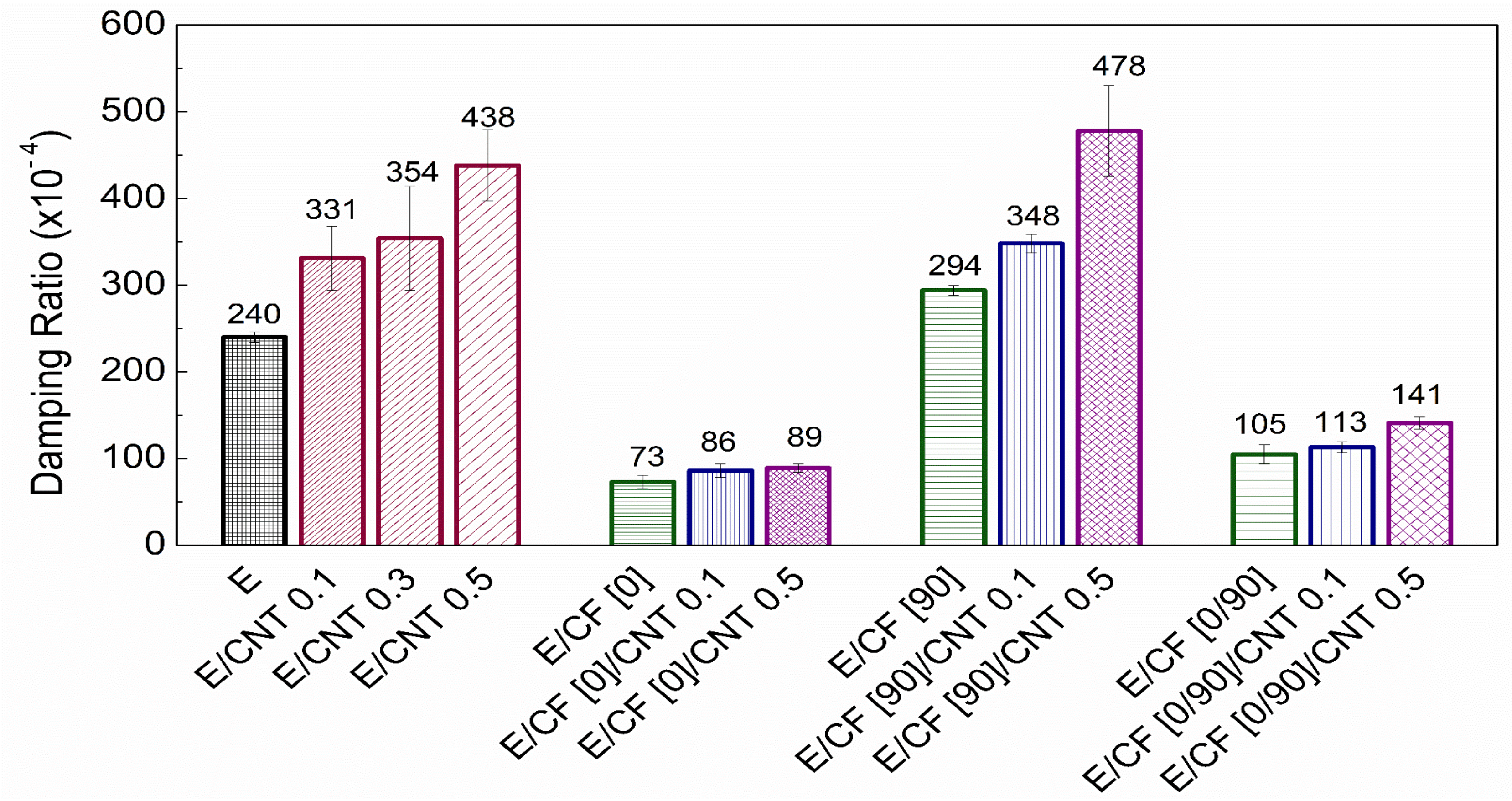


Figure 3.6 Effects of CNTs and CFs on the (a) Natural Frequency, (b) Dynamic Modulus, and (c) Damping Ratio of the epoxy matrix composites



(b)

Figure 3.6 (Continued)



(c)

Figure 3.6 (Continued)

Table 3.2 Natural Frequency (f_n), Dynamic Modulus (E_{Dyn}), and Damping Ratio (ζ) of the specimens; including "percent contribution" of CNTs and CFs to the Damping Ratio of neat Epoxy matrix, and "percent contribution" of CNTs to the Damping Ratio of the related E/CF composites

Specimens	f_n **(Hz)**	E_{Dyn} **(GPa)**	ζ **($x10^{-4}$)**	**% contribution to ζ values of**			
				E	**E/CF [0]$_8$**	**E/CF [90]$_8$**	**E/CF [0/90]$_4$**
E	36.62 ± 0.69	4.72 ± 0.28	240 ± 6	-	-	-	-
E/CNT 0.1	28.00 ± 1.49	3.20 ± 0.22	331 ± 37	38	-	-	-
E/CNT 0.3	22.46 ± 1.54	2.35 ± 0.54	354 ± 60	47	-	-	-
E/CNT 0.5	19.53 ± 0.98	2.31 ± 0.18	438 ± 41	82	-	-	-
E/CF [0]$_8$	104.50 ± 2.30	73.73 ± 4.50	73 ± 8	-70	-	-	-
E/CF [90]$_8$	28.32 ± 1.30	5.58 ± 0.06	294 ±6	22	-	-	-
E/CF [0/90]$_4$	74.71 ± 2.07	42.49 ± 2.30	105 ± 11	-56	-	-	-
E/CF [0]$_8$/CNT 0.1	98.63 ± 2.58	71.49 ± 4.33	86 ± 8	-	18	-	-
E/CF [0]$_8$/CNT 0.5	88.54 ± 2.45	60.70 ± 4.12	89 ± 5	-	22	-	-
E/CF [90]$_8$/CNT 0.1	25.15 ± 1.32	4.50 ± 0.24	348 ± 11	-	-	18	-
E/CF [90]$_8$/CNT 0.5	19.53 ± 1.21	2.96 ± 0.15	478 ± 52	-	-	63	-
E/CF [0/90]$_4$/CNT 0.1	68.04 ± 1.49	39.54 ± 2.14	113 ± 6	-	-	-	8
E/CF [0/90]$_4$/CNT 0.5	64.13 ± 1.49	35.65 ± 1.77	141 ± 7	-	-	-	34

CHAPTER 4

CONCLUSIONS

Main conclusions on the contribution of carbon nanotubes (CNT) alone and together with uniaxially and biaxially oriented carbon fibers (CF) on the flexural mechanical properties and vibration damping behavior of the epoxy (E) matrix composites could be summarized as follows:

(i) Contribution of CNTs and CFs to the Flexural Mechanical Properties

- SEM analysis indicated that when the non-functionalized CNT content was minimum, i.e. 0.1 wt%, there was no distribution problem in the epoxy matrix, while 0.5 wt% CNT content resulted in certain level of “bundling” type agglomeration.

- Therefore, due to the basic strengthening and stiffening mechanisms of “load transfer from the matrix to the reinforcement” and “decrease in the macromolecular mobility of the matrix”; use of only 0.1 wt% CNT increased the flexural strength and modulus values of the epoxy matrix as 36% and 28%, respectively. On the other hand, “bundled” morphology of the 0.5 wt% CNT resulted in gradual decreases in these mechanical properties.

- When the continuous CFs were aligned parallel to the length of the specimens, i.e. “longitudinal uniaxial” case, then all the components of the applied flexural stress were carried very effectively; leading to enormous increases of more than 9 times and 34 times in the values of flexural strength and flexural modulus, respectively.

- Oppositely, when the continuous CFs were aligned perpendicular to the length of the specimens, i.e. “transverse uniaxial” case; then all the components of the applied flexural stress were carried by the much weaker interfacial phase; leading to almost no improvement in the flexural mechanical properties.

- That kind of very anisotropic behavior was prevented when the continuous CFs were aligned both parallel and perpendicular to the length of the specimens, i.e. “cross-plied biaxial” case; leading to significant increases of more than 7 times and 16 times in the values of flexural strength and flexural modulus, respectively.

- When CNTs were incorporated into the epoxy matrix of the continuous CF reinforced composites, there were no additional contribution of CNTs to the flexural strength and modulus values; which could be due to the lower efficiency of the resin infusion process leading to insufficient impregnation of the CF layers with higher viscosity CNT containing resin.

(ii) Contribution of CNTs and CFs to the Vibration Damping Behavior

- Because of their extremely high aspect ratio and surface area/volume ratio, use of CNTs alone resulted in very efficient “stick-slip mechanism” of vibration damping both at the Epoxy-CNT interfaces and CNT-CNT interfaces. For instance, the increase in Damping Ratio of the neat epoxy was 38% when only 0.1 wt% CNT was added, while it was as much as 82% after 0.5 wt% CNT addition.

- Use of both longitudinal unidirectional and cross-plied bidirectional continuous CFs resulted in significant reduction in the Damping Ratio of the Epoxy matrix. Because, although stick-slip mechanism of vibration damping operates this time at the interfaces between Epoxy-CFs, but its contribution was not sufficient considering the enormous increases in the stiffness of the composites.

- Use of transverse unidirectional CFs increased the Damping Ratio of the epoxy matrix as 22%. Because, since the stiffness of this structure was very low; the level of the stick-slip vibration damping mechanism at the Epoxy-CF interfaces were sufficient to increase the value.

- When CNTs were incorporated into the epoxy matrix of the continuous CF reinforced composites, then their Damping Ratio all increased significantly. For instance, contribution of the 0.5 wt% CNT to the Damping Ratio of the longitudinal, transverse, and bidirectional CF composites were as much as 26%, 63% and 34%, respectively. Because, a synergism in the stick-slip mechanism could be expected due to the additional CNT-CF interfaces apart from Epoxy-CNT, Epoxy-CF, CNT-CNT interfaces.

(iii) Overall Conclusion

- When even only 0.1 wt% CNT were incorporated into neat epoxy resin, they have contributed not only to the mechanical properties (Flexural Strength and Modulus), but also to the vibration behavior (Damping Ratio) of the epoxy.

- When 0.1 or 0.5 wt% CNT were incorporated into continuous CF reinforced epoxy matrix composites, although they have no additional contribution to the mechanical properties (Flexural Strength and Modulus), their contribution in terms of vibration behavior (Damping Ratio) of the composites were significant.

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