Effects of MWCNTs/ g-C_3N_4 on Mechanical and Thermal properties of Epoxy Hybrid Nanocomposites

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ABSTRACT

This experimental study is devoted to the analysis of Multiwall Carbon Nanotubes (MWCNTs) and graphitic carbon nitride (g-C_3N_4) nanofiller reinforced epoxy hybrid nanocomposites using casting technique. Different weight fraction of nanofiller such as 0.5, 1, 3, and 5% were developed. Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) were used to confirm the morphological behaviors of developed hybrid nanocomposites and the agglomeration free uniform dispersion of nanofillers in epoxy matrix. The effects of reinforcements on the tensile, flexural, and water absorption properties of epoxy hybrid nanocomposites were also investigated. The results were tabulated and recorded. It was observed that the increase in reinforcement is found to be increased the behaviors of epoxy hybrid nanocomposites.

Keywords: Composites; Multiwall Carbon Nanotubes; Graphitic Carbon Nitride; Mechanical Property; Thermal Stability.

INTRODUCTION

The nanocomposite is more important than the normal composites whichever, the addition of small amount of nanofillers to improve the thermal, mechanical, optical, magnetic and electrical properties. Epoxy resin is an important and most commonly used as thermosetting polymers in the production of various applications. It is widely used as adhesives, coatings, encapsulation, printed electronic circuit board materials and hardware components. But, it's specific usage as matrix materials rather than polyester and other polymers are due to its inherent properties such as high stiffness, ultimate tensile strength, and excellent non reactant chemical resistance. For the improvement of fundamental properties and the presence of multifunctional behaviours of matrixes like electrical, optical, magnetic properties and flame retardancy using various of nanosized fillers which includes iron and iron oxides, carbon nanofibers, carbon nanotubes, graphene, silica, alumina, polyaniline, nanoclay and zinc oxide for the development of an advanced polymer nanocomposites. Polymer nanocomposites have attracted greatest attention in industries because of their significant enhancement behaviour when compared to pristine polymer or micro and macro level composites. Polymer nanocomposites are generally used in the combination of matrix material and filler material that have one dimension within 100 nm (Shan Liu et al., 2014; Konstantinos et al., 2012).

Among all other fillers, the carbon based nanofillers are more promising due to their distinctive properties. However, carbon nanotubes (CNTs) is mostly used in several applications among the carbon based nanofillers such as high performance structural nanocomposite materials, electromagnetic shielding, hydrogen storage, energy conversion devices and semiconductors (Sushant Sharma et al., 2018). The recent years have witnessed CNTs based nanomaterials analysis to produce unique properties such as light weight, large surface area, excellent thermal, mechanical and electrical

properties. This set of excellent properties of CNTs, make it a perfect reinforcement for polymer, ceramics, and metals for functional and structural applications (Starkova et al., 2013; Shrikant et al.,2017 ; Tasis et al.,2006).In addition the carbon based polymer nanocomposites have attracted a significant interest in biomedical applications based research. During the fabrication process, the reinforced CNT nanocomposites facing agglomeration and poor adhesion nature in matrix due to their high vandar wall force on the surface. To overcome these issues, the process of recusing by ball milling, roll milling, twin screw extrusion, solvent casting, ultra-sonication and functionalization of CNTs were attempted in the earlier research (Ali Naem et al., 2014; Noa Lachman et al.,2010 ; Erik Thostenson et al ., 2002). However, the effectiveness of all the process remains deficient to eradicate the clusters of CNTs to get uniform dispersion of fillers in the matrix. In this study, subsequent process was made for homogeneous dispersion of CNT with inorganic nanofillers on polymer matrix. It is evident that a better mechanical, thermal, electrical and optical properties were observed in nanocomposites based appliances (Hasan Ulus et al., 2014; Weikang Li et al., 2014 ; Arun Kumar et al., 2018)

Graphitic Carbon nitride (g-C_3N_4) ceramic fillers are graphene like structure, high stiffness, high refractory index, good chemical and thermal stability, good corrosion resistance, capable to absorb UV light and the most important behaviour of carbon nitride is high photocatalytic activity (Shuanglong Ma et al., 2016 ; Wenjie Shan et al.,2016). In addition to this kind of ceramic nanofillers enhance the properties of polymer is not only on the intrinsic properties but also creates the synergistic effects. The presence of g-C_3N_4 nanofillers on the surface of MWCNTs increases the homogeneous dispersion of MWCNTs in epoxy matrix without compromising fundamental behavior of MWCNTs. The combined reinforcement of MWCNTs and g-C_3N_4 nanofillers to the epoxy matrix play a major role in the development of epoxy hybrid nanocomposites. In this work, the MWCNTs/g-C_3N_4 reinforced epoxy hybrid nanocomposites were prepared and mechanical, thermal properties were studied. The homogenous dispersion of MWCNTs in epoxy matrix was achieved by addition of g-C_3N_4 inorganic nanofiller. The results were confirmed using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

EXPERIMENTAL WORK

Materials

The raw materials used in the fabrication namely,Diglycidyl ether of bisphenol-A (DGEBA) based epoxy resin; LY 556 epoxy equivalent of 185 g/eq and viscosity of 10,000 cP) and the hardener, 4, 4´-diaminodiphenylmethane (DDM) and the MWCNTs having diameter of 10-20 nm, surface area of 200 m^2/g, length >10μ, purity > 98%. The above materials were procured from M/s Sisco Research Laboratories Ltd, India.

Synthesis of MWCNTs/ G-C_3n_4 Hybrid Nanofiller

The hybrid nanofiller of MWCNT/ g-C_3N_4 were prepared as follows. First in 160 mL of acetonitrile solution, melamine (6 mmol) and cyanuric acid (6 mmol) were added as precursors, and then a certain volume of MWCNTs was added. The reaction solution obtained was ultrasonicated for 30 min and then mixed for another 12 h. Then the uniformly distributed mixture was moved to a flask of Teflon. After the temperature had been held at 180 °C for 12 h, the precipitate was isolated and dried overnight, It was then calcinated in a porcelain crucible (5 °C min−1) for 2 h at 520 ° C. The solids obtained after grinding are g-C3N4/MWCNTs hybrid nanofiller.

Fabrication of MWCNTs/ G-C_3n_4 Reinforced Epoxy Hybrid Nanocomposites

The epoxy resin was used as matrix material with a DDM hardener and reinforcing material as MWCNTs/g-C_3N_4 in order to form as epoxy polymer hybrid nanocomposite material. As shown in Figure 1, the fabrication process of MWCNTs/ g-C_3N_4 reinforced epoxy nanocomposites are illustrated. The required quantity epoxy resin was taken in a beaker and maintained with 80°C for 10 minutes, afterwards the prepared MWCNTs/g-C_3N_4 nanofillers was added into the epoxy resin and thoroughly mixed by vigorous magnetic stirrer, followed by the uniform dispersion of hybrid MWCNTs/g-C_3N_4 nanofillers using sonication process. The required quantity of DDM hardener was homogeneously added in MWCNTs/g-C_3N_4 /epoxy mixture using mechanical stirring. Afterwards, it was degassed for 20 minute to remove air particles formed during mixing.

Then, the mould release agent was applied on the mould for the easy removal of specimen once the fabrication was completed. Finally, the MWCNTs/g-C_3N_4 /epoxy mixture was poured into the mould uniformly, then mould was maintained at the room temperature for 24 hours for curing process. Then, it was kept in electric curing oven at the

temperature of 100ºC for 3 hour, followed by post curing at 140ºC for 4 hour. Then, the mould was taken out from the oven and allowed it for cooling purpose. The specimens were removed from the mould by tightening screws provided in the mould. As shown in Figure 2 (a-b), the prepared specimen of neat epoxy and MWCNT/g-C_3N_4 hybrid epoxy nanocomposites is discussed in detail.

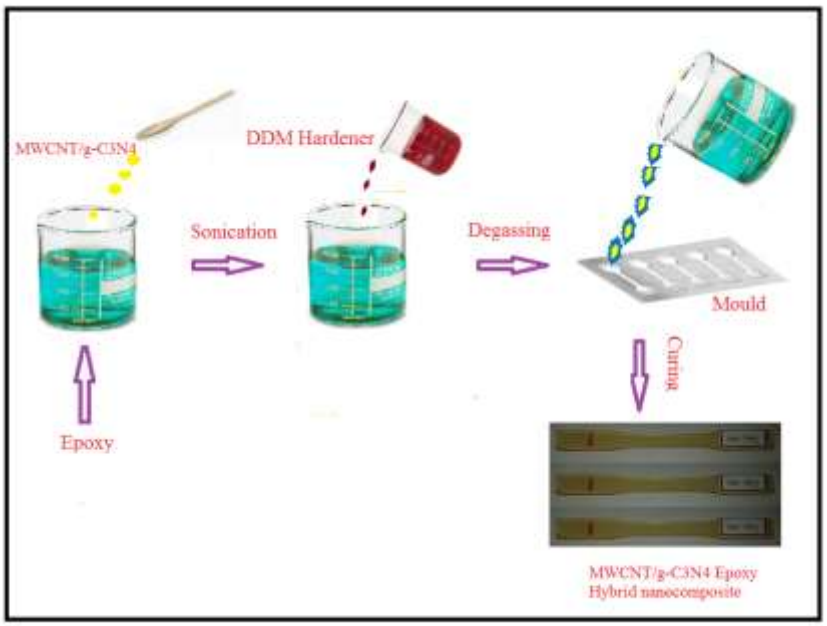

Figure 1. Fabrication of MWCNT/ g-C_3N_4/epoxy hybrid nanocomposite

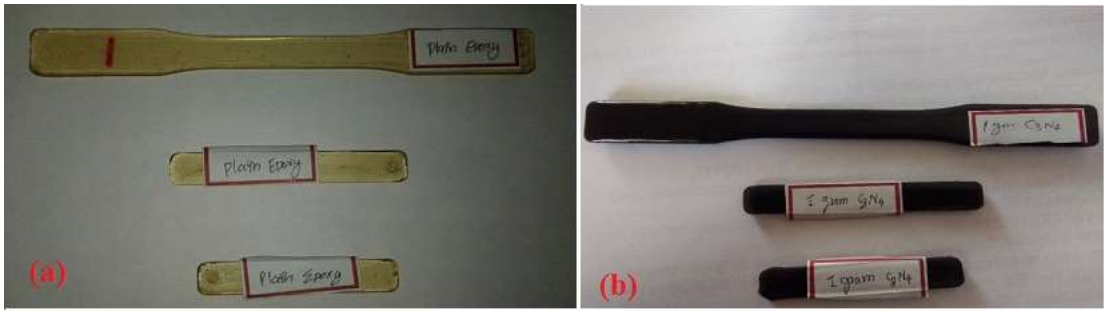

Figure 2. Prepared specimen (a) Neat epoxy, (b) MWCNT/g- C3N4 epoxy hybrid nanocomposite

Characterization of MWCNTs/G- C_3n_4 Epoxy Hybrid Nanocomposite

Thermo gravimetric Analysis (TGA) test was conducted in Pyris 6 TGA thermo gravimetric analyzer with 0.5µg weight resolution and temperature resolution 0.2^0C temperature resolution. The temperature range was set between 100-700^0C at a heating rate of 10^0C per minute. The mass of 10 mg of each sample initially was loaded on the aluminum crucible under nitrogen gas environment and continuously monitored the mass loss with respect to the change in temperature and time. The SEM and TEM were used to identify the dispersion of MWCNT/g- C_3N_4 in epoxy matrix. The Computerized Universal Testing Machine (UTM) was used to examine the tensile behaviour of composite material with the results of ultimate tensile strength and Young's modulus. The ASTM D 638 standard was followed for the preparation of tensile test specimens with the dimensions of 165×19×3 mm. The three point bending technique was used to analyse the flexural behaviour of composite materials with help of modified universal testing machine. The ASTM D 790 standard was followed for the preparation of flexural test specimen with dimensions of 50.8× 12.7× 3mm. In each case, 4 numbers of specimen were used and an average value was tabulated. The water absorption test was conducted for

calculating the maximum water absorption rate of composites. Specimens were prepared with dimensions of 10x 10 x 3mm and maintained at the room temperature for 48 hour and then maximum water absorption rate was calculated as given below:

$$\text{Maximum water absorption rate} = ((m_2-m_1)/m_1) \times 100 \quad (1)$$

Where, m_1 – mass of the reference sample m_2 –mass of wet sample.

RESULTS AND DISCUSSION

Mechanical Properties of MWCNTS/G-C_3N_4 Epoxy Hybrid Nanocomposite

As shown in Figure 3 and 4, the ultimate tensile strength and flexural strength epoxy nanocomposites increases with addition of MWCNTs/g-C_3N_4 hybrid nanofiller at low loading from 0.5wt% to 3wt% of nanoparticle dispersion because of its homogeneous and cluster free dispersion of nanoparticles in epoxy matrix. Afterwards, the ultimate tensile strength and flexural strength decreases with further addition of nanofillers by 5wt% and more. It was observed that the 3wt% of MWCNTs/g-C_3N_4 nanofillers reinforced epoxy nanocomposites produces maximum tensile strength when compared to the neat epoxy. It shows that the tensile behavior of neat epoxy is brittle in nature in case of failure but significant variation was noticed in the MWCNTs/g-C_3N_4 hybrid nanofiller reinforced epoxy nanocomposites. While higher loading of MWCNTs/g-C_3N_4 hybrid nanofillers as 5wt% and more, it was observed that a decrease in the tensile strength and flexural strength as well as toughness is due to their cluster formation which leads to poor dispersion of nanoparticles in epoxy matrix and poor interfacial interaction between the epoxy matrix and filler materials. The maximum water absorption of neat epoxy and epoxy nanocomposites incorporating with different weight percentage of MWCNTs/g-C_3N_4 as shown in Figure 5. It shows that an addition of nanofiller into the epoxy matrix gradually reduces the water absorption of epoxy nanocomposites. This phenomenon is due to excellent barrier properties and high aspect ratio of MWCNTs/g-C3N4 hybrid nanofillers. Moreover, an excellent properties of nanofillers provides a tortuous pathway for water molecules by diffusing into epoxy nanocomposites.

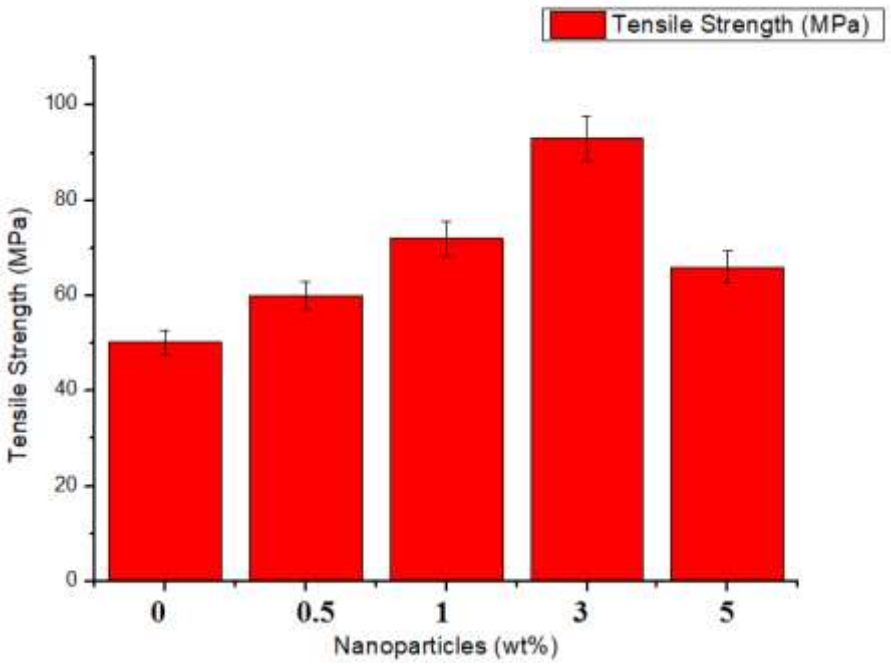

Figure 3. Tensile Strength of MWCNTs/g-C_3N_4 epoxy hybrid nanocomposite

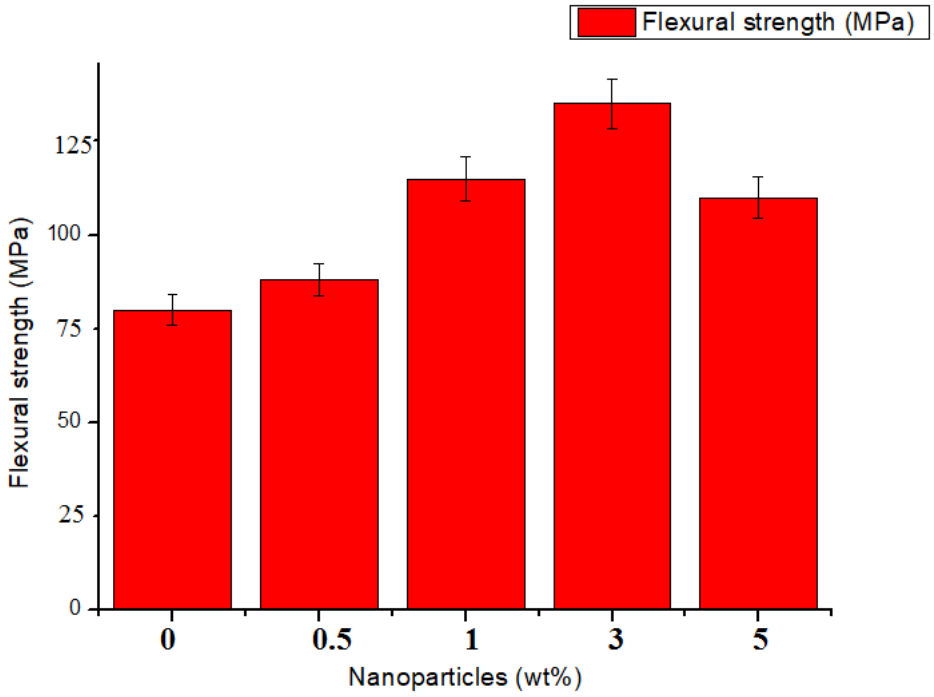

Figure 4. Flexural Strength of MWCNTs/g- C_3N_4epoxy hybrid nanocomposite.

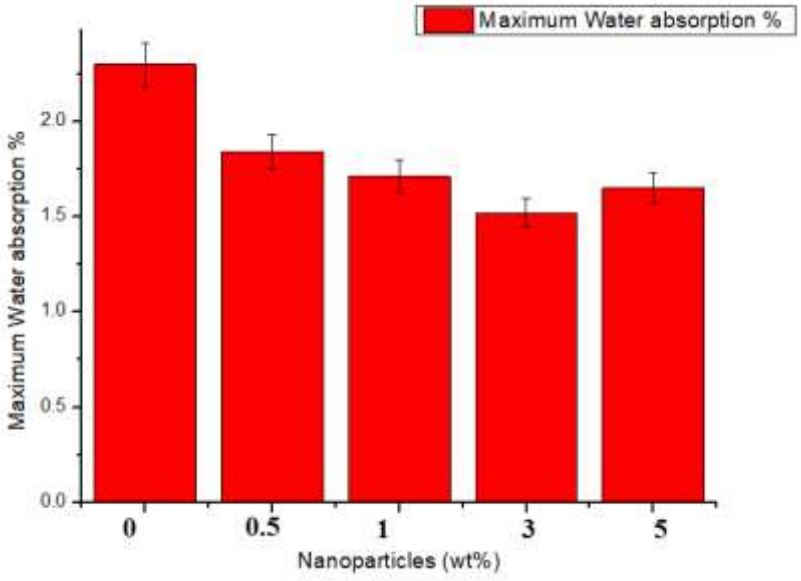

Figure 5. Water absorption rates of MWCNTs/g-C_3N_4 epoxy hybrid nanocomposite.

Thermal Properties MWCNTs/g-C3N4 Epoxy Hybrid Nanocomposite

One of the most important thermal properties of encapsulation materials is thermal stability. As shown in Figure 6, the effect of MWCNTs/g-C_3N_4 hybrids on the thermal stability of MWCNTs/g-C_3N_4 hybrid nanofiller reinforced epoxy nanocomposites is discussed in detail. For understanding the thermal effects of nanocomposites, the pristine epoxy and nanocomposites with weight fraction of 0.5,1,3 and 5 of MWCNTs/g-C_3N_4 hybrids were selected for Thermo Gravimetric Analysis (TGA). It was observed that the incorporation of MWCNTs/g-C_3N_4 hybrid nanofiller in epoxy matrix

significantly improves the thermal stability of epoxy nanocomposites. The two definite degradation temperature were selected to analyze the weight loss percentage with an increase in temperature, ie after 5% of weight loss of the sample (T_{d5}) and after 10% of weight loss of the sample (T_{d10}).

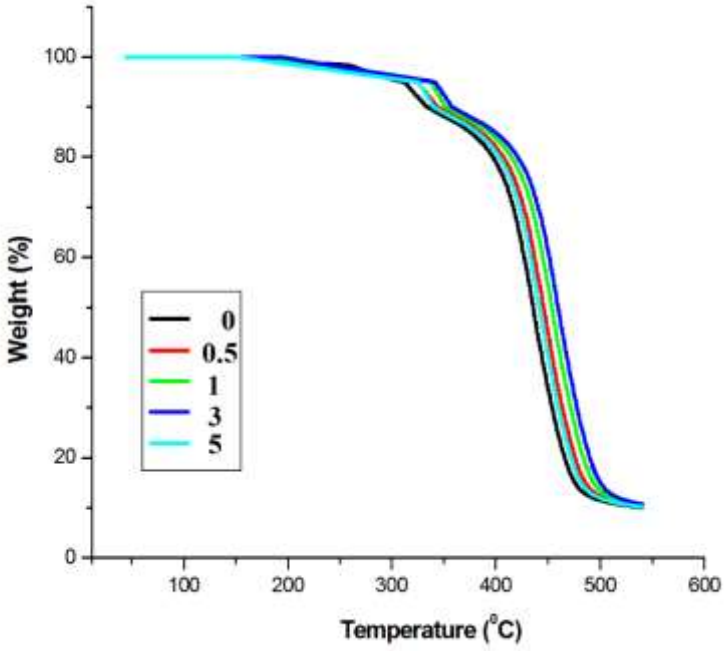

Figure 6. TGA curves of MWCNTs/g-C3N4 epoxy hybrid nanocomposite.

As shown in Table 1, the experimental results of TGA is illustrated. The thermal degradation after 5% of weight loss completed at 312^0 C for pristine epoxy, while the same degradation takes place at 325^0 C, 338^0 C and 342^0 C for the weight fraction of 0.5,1 and 3 of MWCNTs/g-C_3N_4 filled epoxy nanocomposites respectively. The thermal degradation after 10% of weight loss completed at 334^0C for pristine epoxy, while the same degradation takes place at 344^0 C, 352^0 C and 358^0 C for the weight fraction of 0.5,1 and 3 of MWCNTs/g-C_3N_4 hybrid epoxy nanocomposites respectively.

Table 1. Experimental Data of TGA.

Weight loss %	Degradation Temperature (^{0}C)				
	Neat epoxy	05.%MWCNTs/g-C_3N_4	1% MWCNTs/g-C_3N_4	3% MWCNTs/g-C_3N_4	5% MWCNTs/g-C_3N_4
5	312	325	338	342	326
10	334	344	352	358	340

Morphological Analysis of MWCNTS/g-C_3N_4 Epoxy Hybrid Nanocomposite

As shown in Figure 7 (a-d), the SEM images of tensile fracture surface of neat epoxy and MWCNTs/g-C_3N_4 epoxy nanocomposites are discussed in detail. It is observed that the smooth and clearly indicated brittle failure of neat epoxy were developed without any resistance for crack introduction and transmission. However, the addition of MWCNTs/g-C_3N_4 hybrid nanofillers in epoxy matrix significantly improves the roughness of fracture surface with more

number of fracture branches of MWCNTs/g-C_3N_4 epoxy nanocomposites. It was clearly observed that the homogeneous dispersion of MWCNTs/g-C_3N_4 in epoxy matrix as shown in Figure 7 (b & c). But, in the case of 5 % weight fraction of nanofillers addition was noticed in some clusters of MWCNTs in epoxy matrix as shown in Figure 7 (d). Normally, a high fracture energy is dissipated for more roughness.

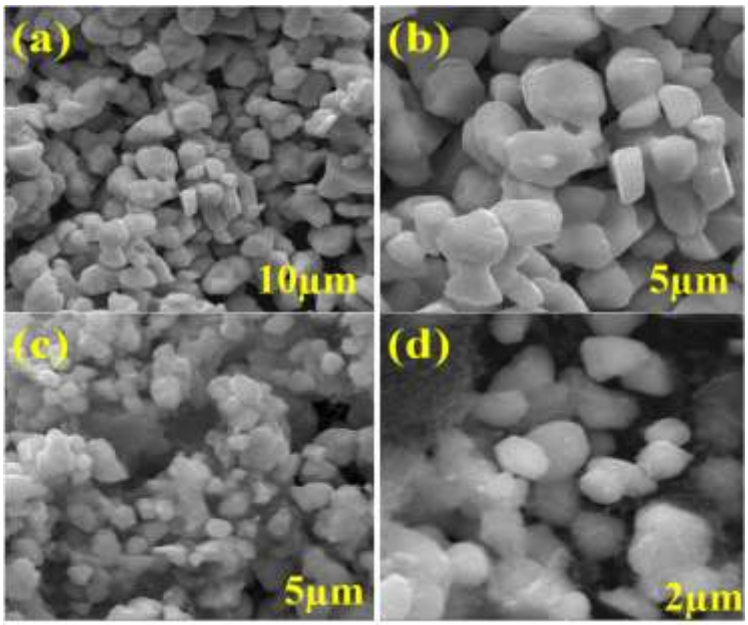

Figure 7. SEM images of MWCNTs/g-C3N4 epoxy hybrid nanocomposite.

It is clearly observed from TEM images as shown in Figure 8 (a-f)) that the g-C_3N_4 nanoparticles are uniformly mixed with the surface of MWCNTs and produces a new class of hybrid nanostructures of MWCNTs and g-C_3N_4. The space between the each MWCNTs occupied by g-C_3N_4 and also restricts the agglomeration of MWCNTs. Due to this phenomenon consistently maintains the mechanical and thermal properties of MWCNTs/g-C_3N_4 hybrid epoxy nanocomposites.

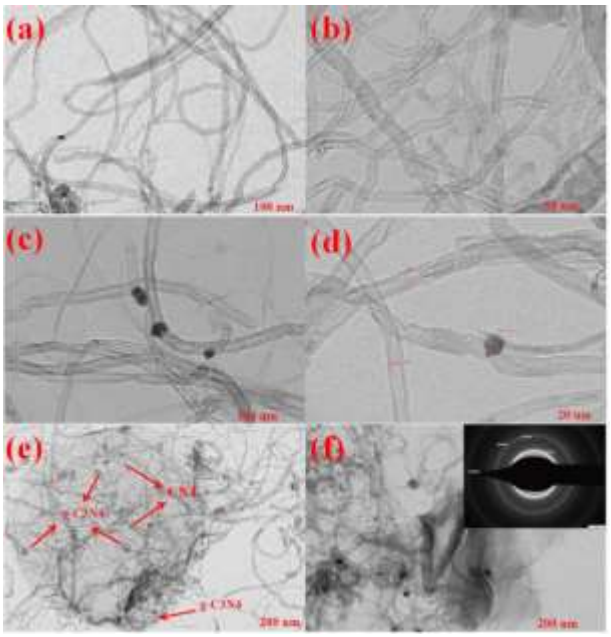

Figure 8. TEM images of MWCNTs/g-C3N4 hybrids

CONCLUSION

The collected data prove that the epoxy polymer nanocomposites incorporating different weight fraction of MWCNT/g-C_3N_4 were effectively prepared. The results reveal that the mechanical and thermal properties of MWCNT/ g-C_3N_4 nanofiller reinforced epoxy hybrid nanocomposites significantly depends on the homogeneous dispersion of MWCNTs in epoxy matrix. SEM and TEM analysis of fractured surface shows that the MWCNT/g- g-C_3N_4 uniformly dispersed in epoxy matrix, and the MWCNT/ g-C_3N_4 epoxy hybrid nanocomposite with 3 weight fraction shows a higher mechanical (Tensile strength as 85.25% and Flexural strength as 68.75%) and thermal (9.61%) properties . The investigator hopes that this study would motivate the industry and academia to pursue further study, keeping MWCNT/ g-C_3N_4 epoxy hybrid nanocomposites in mind.

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