

An investigation of fracture toughness and dynamic mechanical analysis of polymer nano-composites

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Abstract

The study deals with development of a new composite material with an objective to increase the mechanical and thermal properties. The proposed work involves the preparation of novel polymer based composite material reinforced with cenosphere and multi walled carbon nanotubes (MWCNTs) and to investigate fracture toughness and dynamic mechanical properties. MWCNTs have high tensile strength which contributes to increase in strength of composite as well as the load transfer capability. The 20 weight % of cenosphere and upto 0.5wt% of MWCNTs are used for the study. Dynamic mechanical analysis and fracture toughness tests of the composite were carried out. It was found that fracture toughness of the sample with 0.2 wt% MWCNT increased by 12% than the epoxy cenosphere composite. The results obtained by experimental test are compared with the simulation results. Thermal properties obtained by DMA have shown better thermal stability. The SEM analysis was carried out to study the interfacial bonding between the fiber-matrix and also to substantiate the fracture toughness result.

Keywords: MWCNT, Cenosphere, Dynamic Mechanical Analysis, Fracture toughness

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1. Introduction

Polymer composites have found great importance in this emerging world due to their high strength to weight ratio. According to Lee *et al.* (1967) epoxy resin has vast applications, although it has some drawbacks such as brittleness, low strength, stiffness, low resistance to the fatigue crack propagation and poor fracture toughness. It needs some reinforcement so that the properties are enhanced. Allaoui *et al.* (2002) note that the addition of rigid particles like carbon nanotubes shows some improvements in the properties of the epoxy by increase in modulus and strength. Research suggests that MWCNTs due to their high aspect ratio and unique properties such as high strength, stiffness, thermal and electrical conductivity will help in forming a better composite.

Some studies have showed that the fracture toughness of epoxy resin could be improved by the addition of the fly ash particles as fillers. Hussain *et al.* (2016) has carried out a research work which shows the enhancement in the mechanical properties by the addition of MWCNTs in epoxy resin. Jalageri *et al.* (2015) has showed in the work that the addition of cenosphere particles along with MWCNTs showed a significant change in the mechanical properties like tensile strength, flexural strength and the impact strength. Padal *et al.* (2014) states that addition of the nanoparticles in the epoxy showed better mechanical and thermal properties like storage modulus, glass transition temperature, compared to the plain epoxy. Divya *et al.* (2015) showed that the mechanical & thermal properties showed synergism when both cenospheres and MWCNT were added and hence led to their improvement. In an investigation done by Arijit *et al.* (2011) the damping properties of cenosphere filled polypropylene composites enhanced and is particularly observed in 10 wt% cenosphere. In the composites relative to the soft PP-phase, 30% increase in the storage modulus was observed. Although a nominal decrease in tensile strength was observed, the tensile modulus increased up to 43%. Alumina and silica are the main constituents of fly ash that improve the composite properties. Cenospheres are found to some extent in the form of hollow spherical particles in fly ash which help to maintain low density values for the composites as suggested by M R Doddamani *et al.* (2011). Geethamma *et al.* (2005) carried out dynamic mechanical analysis which concludes that the poor interfacial bonding of the reinforcing particles with the base material was related to the dissipation of more energy and vice versa. Different experimental

tests like thermal analysis technique, dynamic mechanical analysis (DMA) and fracture tests have been carried out to study the effect of carbon nanotubes dispersion on the mechanical properties of the epoxy-cenosphere composite.

2. Experimental Details

2.1. Materials

2.1.1. Epoxy Resin

They are a class of reactive pre-polymers and polymers that contain two or more epoxy groups. It has high mechanical properties due to low shrinkage and relatively unstressed structures. It also assists in the formation of strong unstrained adhesive bonds. The cured epoxy usually has a good thermal and dimensional stability. They absorb low moisture because of the moisture barriers. They also have good insulating properties viz., dielectric strength and tracking resistance. They also possess good electrical properties for various range of temperatures. It is used in the composites in various applications like construction, electronics, packaging and as a protective coating in aerospace applications. Epoxy L12 resin was used in the study with hardener K6.

2.1.2. Cenosphere

Cenospheres are exclusive free flowing powders of tiny spheres collected from coal ash. Their amount is based on the carbon and iron content present in the fly ash. Due to higher particle strength, ultra-low density, impermeability they are used for various applications. Cenosphere of 75 to 150 Microns size was supplied from Sarlachim Ahmedabad. It is used as the primary reinforcement material in the composite.

2.1.3. MWCNT

MWCNTs are of special interest to the industry in the current world. Their excellent properties of strength to weight ratio make them a good fit for the family of nano-composites. They also exhibit good thermal and electrical conductivity, strength, stiffness and toughness. Such properties of these materials make them an important part of various applications such as electromagnetic shielding, coatings, catalysts, textiles and fibers, fuel cells, aerospace, medical implants and many more. MWCNTs was purchased from Quest International, Bangalore. It is used as the secondary reinforcement material. Benefit of the addition of primary reinforcement cenosphere is to improve mechanical and chemical properties of the composite. Also, it controls the material cost of the resin matrix. Secondary reinforcement MWCNT is added to increase the strength and stiffness of the composite.

2.2. Preparation

The Epoxy L12 Resin was heated for 15-20 min in a beaker to reduce its viscosity. Appropriate amount of cenosphere and MWCNTs as per the calculations, are added to the epoxy in a beaker and stirred well for the homogeneous dispersion of both primary and secondary reinforcement materials in the epoxy for 20-25 min using the magnetic stirrer. The composition in a beaker was kept in the ultra-sonicator for degassing and homogenous dispersion of the nanoparticles in the base material, as mentioned by Shubham *et al.* (2015). The mixture was poured into the mould after the addition of hardener and cured at 30°C for 24 hours. The mixing ratio of Epoxy and K6 Hardener was 10:1. The specimens are designated as ECC0 for epoxy (80%), cenosphere (20%) and MWCNT(0%), ECC1 for epoxy(79.9%), cenosphere (20%) and MWCNT (0.1%) and so on up-to ECC5 with epoxy (79.5%), cenosphere (20%) and MWCNT (0.5%).

2.3. Experimental tests

2.3.1. Dynamic mechanical analysis(DMA)Test

The test is conducted as per ASTM D4065. The specimen size is 55mm×10mm×5mm. Parameters such as frequency, amplitude and temperature range were given as inputs. Testing was carried out at ambient temperature to 150°C, at which the material starts to degrade. Experiments were conducted by applying a small cyclic deformation to a sample over a wide temperature range. The following experimental conditions were used to analyze the composite specimen, Jianing *et al.* (2012). Heating rate - 5° C/min, frequency - 1Hz, maximum load range - up to 5 N, deformation mode -dual cantilever, deformation amplitude - 5 µm and cooling - liquid nitrogen. The influence of weight percent of MWCNT (0.1- 0.5%) of ECC polymer composites has been studied using a dynamic mechanical analysis test. DMA results show the changes in a composite material, i.e. storage modulus, loss modulus and tan delta with respect to temperature and revealed useful information about its thermal transition.

2.3.2. Fracture toughness

An attempt has been made to find the fracture toughness of newly developed nano-composite material using SENB (single edge notch bending) specimen for Mode-I. The specimen of dimensions 100x30x13 mm and a 45°V notch of width 0.3mm and depth 13mm was prepared as shown in Figure 1. The specimen was tested on the computerized universal testing machine at uniform crosshead velocity of 1mm/min. Using load displacement diagram and at the onset of crack propagation the fracture load was obtained. Using Equation (1), mode-I critical fracture was calculated. Four specimens of each composition were tested to obtain the fracture toughness value and average is used as a fracture toughness of material.

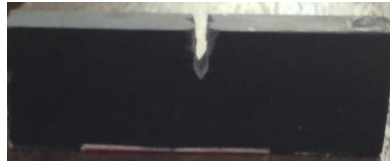


Figure 1: Composite specimen for fracture toughness test

$$K_{IC} = \frac{PS}{BW^{1/2}} f(a/w) \tag{1}$$

3. Results and Discussion

3.1. DMA Test

Glass transition temperature of the epoxy/cenosphere composite with MWCNTs measured by DMA is given in Table 1. Glass transition temperature is often taken at the temperature of the maximum tan delta, Shubham *et al.*(2015) as shown in Figure 2. It was observed that T_g of all the composite with MWCNTs is shifted towards the lower temperature compared to epoxy /cenosphere composite. The amount of energy needed is more with addition of MWCNTs due to high crosslink density. Adding 0.1wt.% MWCNTs does not effect on the T_g much, while adding 0.2wt% MWCNTs led to increase in the T_g . It is due to the reason that presence of properly dispersed MWCNTs that are attached to the matrix molecule chains limit their motion, which ultimately increased T_g .

Table 1: Glass transition temperature for different samples

Composite specimen	Glass transition temperature(T_g)°C
ECC0	84.00
ECC1	88.67
ECC2	91.33
ECC3	83.37
ECC4	87.03
ECC5	79.08

Addition of 0.3wt%,0.4wt% and 0.5wt% caused a drop in the T_g value. It is because of the agglomeration of MWCNTs and also proves that after 0.2wt% MWCNTs will not diperse uniformly in base material. Due to this agglomeration there will be large number of voids between the molecules of the base material which leads to an increase in segmental motions in the base material network, therefore there is a decrease in the value of T_g , Putz (2008).

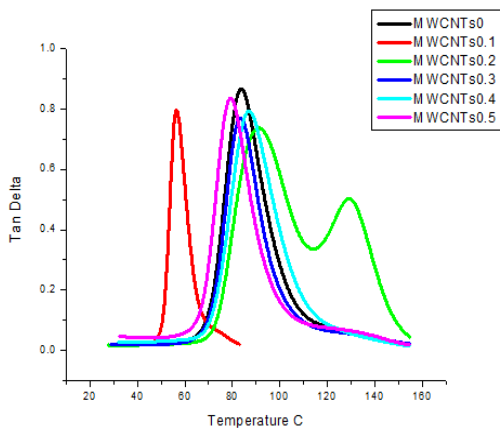


Figure 2: Tan Delta vs Temperature

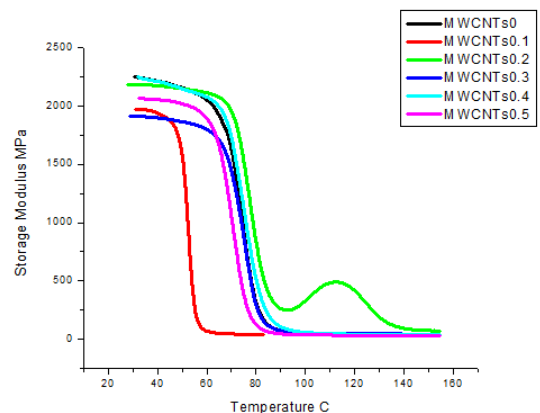


Figure 3: Storage modulus vs Temperature

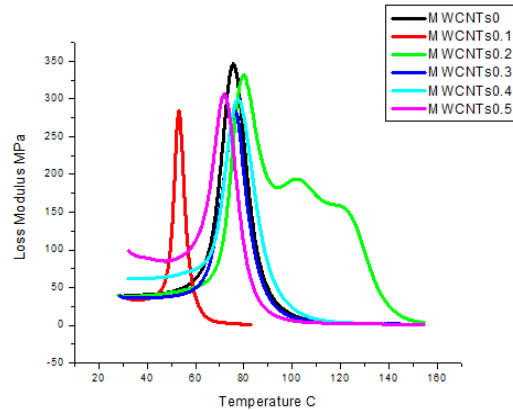


Figure 4: Loss modulus vs Temperature

The storage modulus of the composites for the different composition is shown in the Figure 3. It is observed that the storage modulus of the composition with 0.2wt% MWCNT shows the highest value when compared to the other samples of different compositions. The storage modulus at the temperature of 100°C above the glass transition of all the samples, Jianing *et al.* (2012) was 328.3 MPa and for the sample of ECC0 is 49.95 MPa. The value of storage modulus is enhanced by 84% when compared to the sample with ECC0. The modulus is increased due to high modulus of MWCNTs at 0.2 wt% which is properly dispersed in the epoxy-cenosphere composite. Similar work was carried out by the Shubam *et al.* (2015) which had revealed the same results that the addition of the MWCNTs increased the modulus when compared to that of plain polymer epoxy. The work carried out by Song *et al.* (2012) showed the same results that the addition of MWCNTs to the epoxy has improved the storage modulus and concluded that MWCNTs can increase the cross link density of the composite. Loss modulus of the samples with the different composition is shown in the Figure 4. It is observed that the increase in temperature leads to increase in the loss modulus for the 0.2wt% MWCNTs sample when compared to the plain epoxy-cenosphere and at 0.3 wt% of MWCNTs there is slight increase in the loss modulus .

3.2. Fracture toughness

Fracture toughness value of the epoxy /cenosphere composite with MWCNTs is obtained by experiment and is shown in Figure 5. From the Figure, it can be seen that there is increase in fracture toughness by 12% and 2% at 0.2% and 0.3wt% of MWCNTs respectively when compared to ECC0. It is also observed that there is a decrease of fracture toughness at 0.1% and also for the 0.4% and 0.5% samples. Increase in the value of fracture toughness at 0.2 % and 0.3% MWCNTs is due to proper dispersion of MWCNTs, as surface area of the MWCNTs is more, Domun *et al.* (2015) and also may be due to even distribution of load. However, beyond 0.3 wt% of MWCNTs there is no proper dispersion of the MWCNTs in the epoxy/cenosphere composite, as there is agglomeration of MWCNTs which results in ease of crack propagation through the specimen. It also results in the stress concentration in the agglomeration which may enhance the propagation of the crack in the specimen. The other reason for the agglomeration of MWCNTs is due to the high viscosity of the epoxy which limits the movement of MWCNTs as stated by Domun *et al.* (2015). Similar work carried out by Natarajan *et al.* (2014) on the epoxy glass fiber has shown the good result when compared to the plain epoxy composite. Research carried by Parween *et al.* (2013) on the sugar palm reinforced epoxy composite has shown that the addition of sugar palm has increased the fracture toughness value $1.25 \text{ MPa}\sqrt{\text{m}}$, which is in good agreement with the present work. The maximum value of fracture toughness was found at 0.2% MWCNT and is $6.15 \text{ MPa}\sqrt{\text{m}}$.

Analysis of the SENB specimen for the fracture toughness is also carried out using ABAQUS software. Due to symmetry of the specimen, half symmetry of the specimen is used for the analysis. The loads applied on the specimen were same as obtained in experiment. In the vicinity of the crack front fine mesh is used and appropriate boundary conditions were applied to meet the experimental requirements and are shown in Figure 5. Fracture toughness of the composite specimen was obtained from the simulation, compared with experimental results and are presented in the Figure 6.

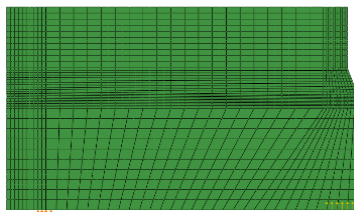


Figure 5: Model of composite specimen with meshing and boundary conditions

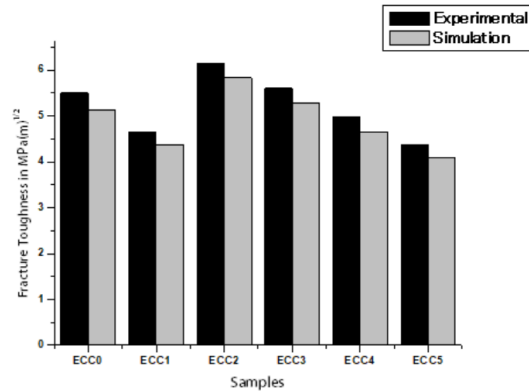


Figure 6: Results of fracture toughness

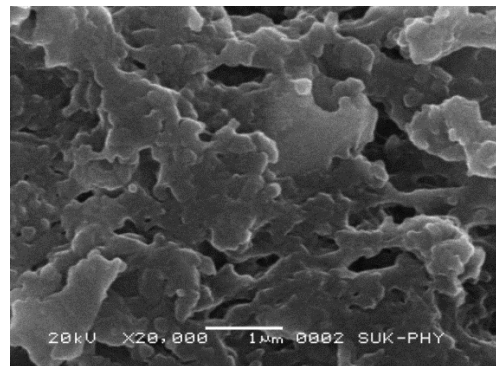
From the results obtained, error is within 10% indicates that both experimental and simulation results are in good agreement with respect to percentage error.

3.3. SEM Analysis of composite specimens

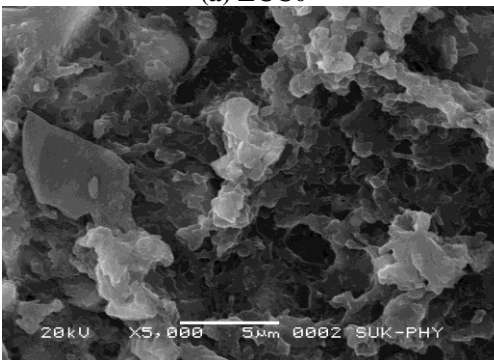
The surface morphology of epoxy-cenosphere-MWCNT composites are studied using Scanning electron microscope. SEM analysis helps in analysing the mode of dispersion of reinforcement material in the base matrix. Basically cenosphere and the MWCNTs are carbon particles, when the light is made to fall on the carbon particles it will reflect, which will indicate their presence in the base matrix. SEM image of each sample is shown in the Figure 7(a-f). It can be observed that in the sample with 0.2 and 0.3 wt% of MWCNTs, there is a better dispersion of nano fibers and beyond 0.3wt%, results in agglomeration of MWCNTs.



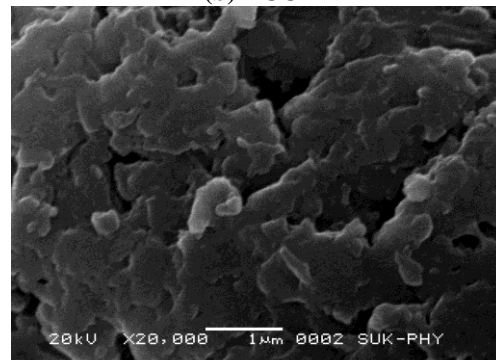
(a) ECC0



(b) ECC1



(c) ECC2



(d) ECC3

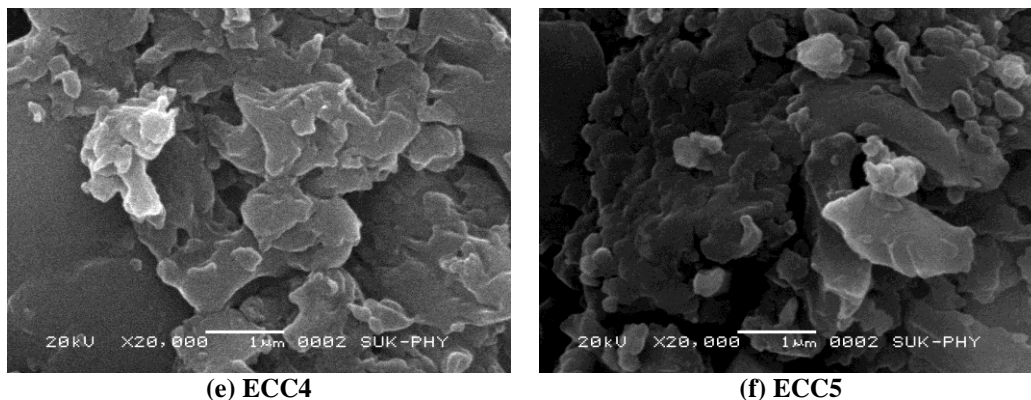


Figure 7(a-f): SEM image of the fracture surface of the samples

4. Conclusion

In the present work, dynamic mechanical analysis and using SENB geometry fracture toughness was investigated. From the DMA test, it has been observed that owing to the MWCNTs functionality, a strong interfacial bond and good dispersion reduced the mobility of the epoxy/cenosphere composite molecules around the MWCNTs and thus increased the thermal stability of the composites. Inclusions of MWCNTs as secondary reinforcement material into the epoxy and cenosphere composite has improved the fracture toughness of ECC2 and ECC3 composites as there is a proper dispersion of MWCNTs. Further, owing to better dispersion and more surface area of MWCNTs, these composites carry more load. Beyond 0.3 wt% of MWCNTs fracture toughness was decreased as there is no proper dispersion of the MWCNTs in the composite and due to agglomeration of MWCNTs which results in ease of crack propagation through the specimen. It may also result in the stress concentration in the agglomeration region. The fracture toughness is increased by 12% in case of 0.2% MWCNTs which shows the improvement of mechanical properties with the addition of MWCNTs. From the DMA test, it was observed that T_g of all the composite with MWCNTs is shifted towards the lower temperature compared to epoxy /cenosphere composite. The amount of energy needed is more with addition of MWCNTs due to high crosslink density. Adding 0.1 and 0.2, wt% of MWCNTs led to increase in the T_g . Also, the storage modulus for the specimen with 0.2 wt% MWCNT shows the highest value when compared to the other specimens. Further, these studies could be extended by carrying out surface modification to the MWCNTs that enhances the mechanical properties of nano-composites. Also, studies could be extended by carrying out post curing of the composite as it plays an important role in obtaining optimum mechanical and thermal properties of polymer based composites. Generally, glass transition temperature (T_g) increases with increasing post curing temperature.

Nomenclature

MWCNT- Multi walled carbon nano tubes
 DMA-Dynamic mechanical analysis
 ECC-epoxy-carbon nanotubes-cenosphere
 SENB- Single edge notch bending

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