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Property Enhancement of Epoxy using Multiwalled Carbon Nanotubes

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ABSTRACT

Recently airplanes are manufactured with increased percentage of composite materials. The composites are non-conductive materials. Therefore, increasing the electrical conductivity of the composites is necessary in case of lightning strike. The matrix phase of all the composites used in aircrafts is polymer based, particularly epoxy is used. In this paper epoxy matrix is reinforced with multiwalled carbon nanotubes. The epoxy resin used is Araldite GY257 (based on diglycidyl ether of bisphenol A) which is mixed with hardener Aradur140 (based on polyamidoamine) in the weight ratio of 2:1. Magnetic stirrer method is used to prepare the samples. MWNTs were added into the resin in small amounts to prepare samples containing 0, 0.5, 1 and 2.5 wt% of CNT. Dispersion of multiwalled carbon nanotube in the samples has been examined using characterization techniques SEM and TEM. The electrical conductivity and surface hardness of the samples are found using four probe test and shore D hardness test respectively. Surface hardness of the samples is increased with increase in weight percentage of MWNT in epoxy. Electrical conductivity of the samples also increases with increase in wt% of MWNT. The highest conductance achieved is 0.009 S with 1 wt% of MWNT in epoxy sample.

Keywords - Multiwalled carbon nanotube, Epoxy, Nanocomposite, Electrical conductivity, Surface hardness.

1. INTRODUCTION

One of the important criteria for designing and manufacturing aircraft is to reduce its weight to the minimum level so that the performance of the aircraft could be increased considerably. Aluminium and its alloys play a major role in aircraft structures. It is the metal with low density and high strength to weight ratio. But recently due to the advancements in material science many new materials have been invented. The usage of conventional metals and alloys for aircraft structures has the disadvantage of increasing the self-weight of structural members. In order to rectify this problem composite materials came into play. These materials have exceptional mechanical properties in addition to drastically reduced weight. Some of the composite materials like glass fibre reinforced plastic (GFRP), carbon fibre reinforced polymer (CFRP), aramid fibres like Kevlar etc [1].

The composites offer several features such as light weight due to high specific strength and stiffness, fatigue resistance and corrosion resistance, tailoring the directional strength and stiffness, capability to maintain dimensional and alignment stability in space environment [1]. Despite of all the advantages, the composites suffer very low or no electrical conductivity which is a serious problem while using the material for aircraft structures. Electrical conductivity of aircraft material is of vital importance in the case of lightning strike. A single bolt of lightning contains as much as 1 million volts or 30,000 amps. The amount and type of damage an airplane experiences when struck by lightning vary depending on factors such as the energy level of the strike, the duration of the strike and the attachment and exit locations [2].

As the aluminium has good conductivity for electricity it acts as a faraday shield and protects the interior of aircraft from damage. Lightning attaches to an airplane extremity at one spot and exits from another. The first attachment is to the nacelle, radome, empennage or wing tip [2]. Current travels through the airplane’s conductive exterior skin and structure and exits out another extremity, such as the tail, seeking the opposite polarity or ground [2]. The matrix phase of all the composites used in aircrafts is polymer based, particularly epoxy is used [3]. This epoxy gets evaporated due to the high intensity electric discharge during lightning strike and non-conductive nature of the polymer. Therefore, the composite structure gets damaged. Since repairability of composites is not applicable, the whole damaged structure has to be replaced which is usually a cost inefficient process. In order to improve the conductivity of the epoxy polymer, carbon nanotubes are used as fillers. CNT/epoxy nanocomposite has proved to be promising the increased electrical conductivity and mechanical strength [4][5].

2. LITERATURE SURVEY

The mechanical strength increased with increased weight percentage of nanotube. The electrical conductivity percolation threshold of 0.5 wt% was observed [4]. Methods of ultrasonication and intensive shear mixing was used for enhancing the distribution of carbon nanotubes in the epoxy matrix. This resulted in conductivity 10^{-2} Sm^{-1} with just 0.1 vol% of filler [6]. The lowest percolation threshold was achieved for electrical conductivity of 0.0025 wt% by preparing aligned CNT/epoxy composite. The CNTs used in this study were synthesized using CVD method [7]. Experiments on both poorly and well dispersed carbon nanotube in epoxy revealed a percolation threshold of 0.5 wt%. The well dispersed CNTs showed higher electrical conductivity and poorly dispersed sample showed enhanced mechanical properties like higher storage modulus and loss modulus. Also, when solvent was not used during the dispersion process agglomerates of carbon nanotubes were formed [8]. Solution casting and ball-milling methods were used to disperse single walled and multi walled carbon nanotubes in epoxy. The MWNTs showed lower electrical percolation threshold than SWNTs. This study also proved ball-milling broke agglomerates of carbon nanotubes but at the same time shortened their length [5]. SWNT/epoxy composite was produced using solution casting and stretching of the sample before complete curing to achieve good dispersion. The sample showed better mechanical and electrical properties along the stretched direction than the perpendicular direction [9].

Carbon nanotube-epoxy composite with desired alignment of CNT was prepared using resin transfer moulding. This method proved to be a promising method to produce samples with large weight loading percentage of 16.5. The mechanical and electrical properties showed drastic improvement along the aligned direction [10]. Aligned MWCNT/epoxy composite was obtained using DC electric fields during curing process. The electrical percolation threshold obtained was 0.0031vol% which was very much less than random orientation of carbon nanotubes [11]. Functionalising of multi walled carbon nanotubes with carboxylic group was done using nitric acid and a mixture of H_2O_2/NH_4OH. The oxidized MWNT/epoxy composite prepared by the latter mixture exhibited higher electrical conductivity [12]. The impact strength, tensile strength, glass transition temperature and electrical conductivity properties of multi walled carbon nanotube enhanced when modified with tannic acid and polyethyleneimine (TA-PEI/MWCNT) [13].

Experiment on pristine, oxidized and fluorinated single and multi-walled carbon nanotubes mixed with epoxy were analysed under different parameters such as stirring rate and degree of pre-curing. The electrical conductivity has increased for pristine and oxidized carbon nanotube composites [14]. MWNT/epoxy composite was prepared by coating the multi walled carbon nanotubes with nickel (Ni-MWNT). An external magnetic field is used to align the CNTs in desired orientation which resulted in increased tensile strength and decreased electrical resistivity than neat epoxy and randomly oriented nanoparticles respectively [15]. Silver nanoparticles were decorated on functionalised carbon nanotubes. The Ag-CNTs exhibited improved electrical conductivity than pristine and functionalised carbon nanotubes [16]. Multiwalled carbon nanotubes modified with carboxyl-terminated butadiene acrylonitrile (CTBN) are used as reinforcement in epoxy matrix. This composite showed vibration damping properties [17]. Multiwalled carbon nanotubes incorporated epoxy resin was produced to measure a threshold for optimal electrical, thermal and mechanical properties. The result arrived at 3 parts per hundred resin per weight MWCNTs [3].

Polysulfone films are loaded with agglomerated and uniformly dispersed multiwalled carbon nanotubes. The conductivity of the films with agglomerated nanotubes was higher than that of the uniformly dispersed ones. The increased conductivity of the agglomerated state is explained by the increased nanotube-to-nanotube contact after the percolating network has formed, which facilitates electron transfer [18]. Conductive composites were fabricated using CNT bundles dispersed in epoxy resins at diverse loadings. Higher conductivity was observed for composites with low CNT loading values due to the existence of a percolative CNT network. Samples with extremely low CNT loading values had no connectivity or close proximity between CNT bundles showed lower conductivity [19]. MWNT was added to a mixture of functionalised liquid rubber (TGMDA-CTBAC) and epoxy which increased the electrical conductivity by 11 orders of magnitude [20]. Surface functionalised multiwalled carbon nanotube with PANI was mixed with epoxy to form nanocomposite. The composite had enhanced thermal stability and electrical conductivity also increased by 5.5 orders of magnitude than neat epoxy [21].

3. METHODOLOGY

3.1. Fabrication

3.1.1. Materials

The epoxy resin used is Araldite GY257 (based on diglycidyl ether of bisphenol A) which is mixed with hardener Aradur140 (based on polyamidoamine) in the weight ratio of 2:1. The epoxy and hardener are mixed using magnetic stirrer. CNTs were added into the resin in small amounts to prepare samples containing 0, 0.5, 1 and 2.5 wt% of CNT.

3.1.2. Moulding

After completion of stirring process the mixture is injected to a Teflon mould lined with silicone rubber using a hand operated plunger [17]. The dimension of the silicone mould is 70 mm× 20 mm×2 mm. The prepared samples are shown in Fig. 1 and Fig. 2.

Fig. 1 Prepared sample of neat epoxy

Fig. 2 Prepared sample of CNT reinforced epoxy

3.2. Characterization

3.2.1. Scanning Electron Microscopy

Inspect F working at 30 kV is used to scan the fractured surface of the samples. Since epoxy is a non-conductive polymer they can't be used as such for SEM. The sample preparation involves covering the stub with carbon tape. The fractured sample is stuck on the carbon tape. Then the sample and the stub are joined using copper tape to form a conductive connection in order to overcome electron accumulation on the surface of the sample. The sample is then sputter coated with a thin layer of gold.

3.2.2. Transmission Electron Microscopy

FEI Tecnai with LaB_6 cathode operating at 200 kV is used to take the microstructure images of the sample. The samples to be tested in TEM are prepared using *Leica Ultramicrotome*. An ultramicrotome has a chuck for holding a specimen block and a stationary knife assembly. Glass knife is used for cutting the specimen. The sample collector is filled with water for easy extraction of micrometre level samples. The sample is then deposited on copper grid and made to dry.

3.3. Testing

3.3.1. Hardness Test

The hardness of materials such as polymers, elastomers and rubbers are tested using *Shore Durometer* [ASTM D2240]. This durometer has various scales for different materials to be tested. These scales are categorised by the type of indenter used. Since epoxy sample being a polymer *Shore D Hardness* scale has been chosen.

3.3.2. Electrical Conductivity Test

The electrical resistivity of the sample is tested by *Four Probe Method*. In this test a constant current is given by the current probes and the voltage difference across the material for the passage of current is measured using voltage probes which is displayed in the form of resistance on the computer screen.

4. RESULT AND DISCUSSION

4.1. Characterization Micrographs

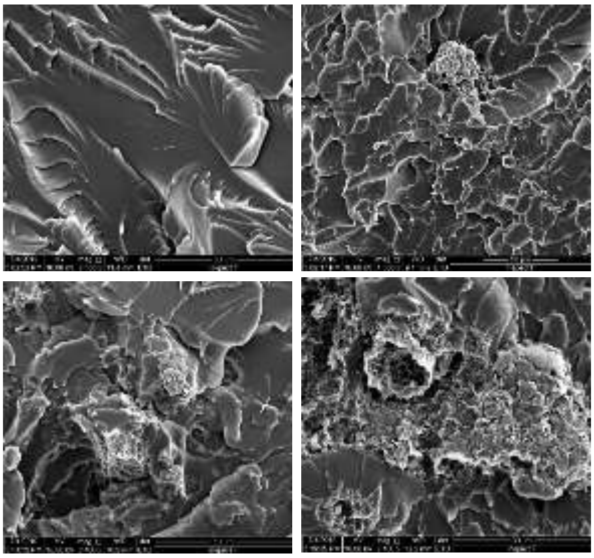

Fig.3 SEM images of sputter coated samples

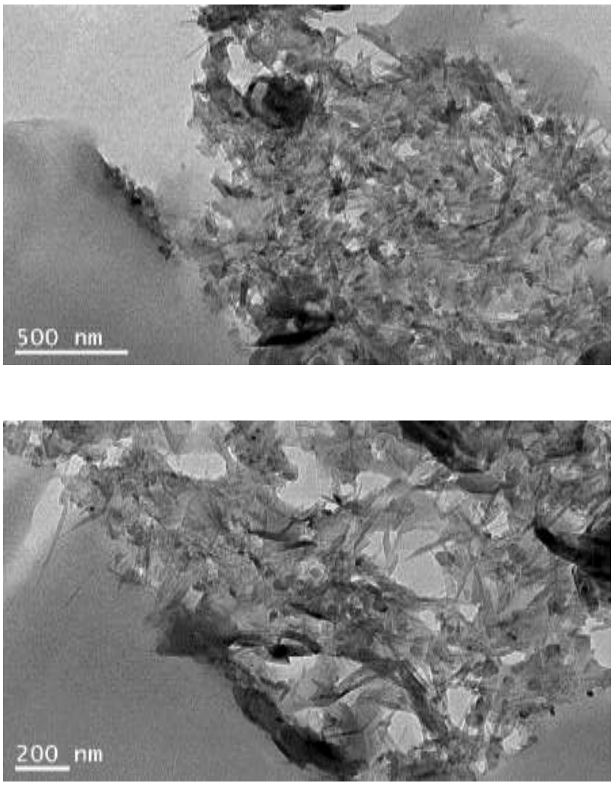

Fig.4: TEM images of microtome cut samples

The micrographs establish that the carbon nanotubes are well dispersed in the epoxy matrix. Physical bonding exists between CNTs and epoxy matrix. A good conductive network is formed between the carbon nanotubes and the matrix which facilitates electron hopping.

4.2. Surface Hardness

For each sample, the readings were taken at 10 different locations and the average of the values were plotted in the form of graph. Fig. 5 proves that the surface hardness of the epoxy increases with increase in weight percentage of multiwalled carbon nanotube content.

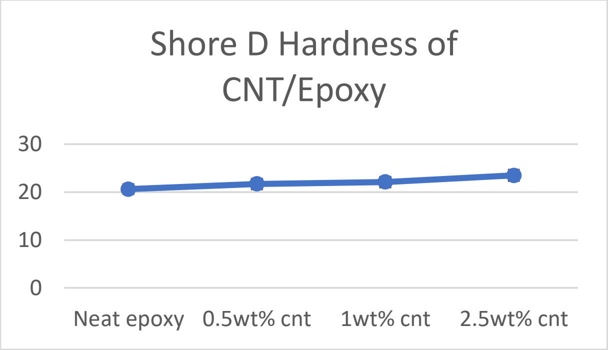

Fig. 5 Surface hardness of samples with different wt% of CNT

4.3. Electrical Conductance

The samples are tested for a constant alternating current of 10 mA which is induced by the crocodile clips attached to the sample. The readings are taken for 500 points between the probes and the average of the values is calculated to find the conductance of the sample. The sample with 0.5 wt% of CNT showed conductance for AC current and 1 wt% CNT sample showed increased conductance than the former sample which proves that the conductivity increases with increasing weight percentage of carbon nanotubes Fig. 6. The decrease in electrical conductivity of 2.5 wt% CNT loaded sample may be due to reduced agglomerates and nanotube contact after the formation of percolation network [18].

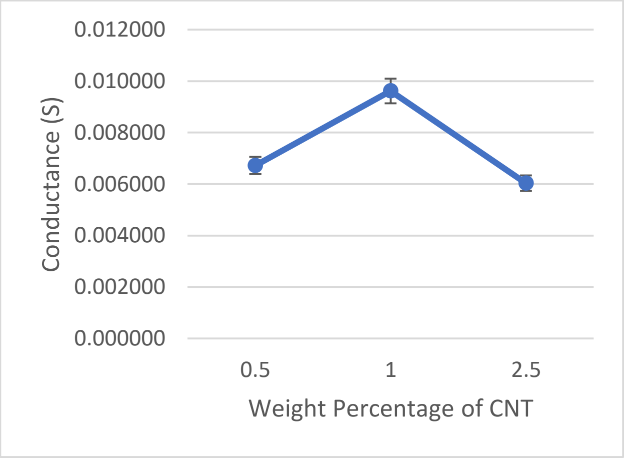

Fig. 6 Conductance of the samples with different wt.% of CNT

5. CONCLUSION

Multiwalled carbon nanotubes reinforced epoxy nanocomposite has been prepared successfully. Characterization of the samples has been carried out which showed dispersion of MWNTs in the epoxy matrix. TEM images has displayed group of CNTs. SEM has revealed CNT bundles scattered throughout the matrix. Addition of carbon nanotubes in epoxy has improved the electrical conductance to 0.009 S. Surface hardness has also been increased considerably with increase in the wt% of CNT.

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