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INFLUENCE OF SURFACE MODIFIED MWCNT ON MECHANICAL AND THERMAL PROPERTIES OF CARBON FIBER/EPOXY RESIN HYBRID NANOCOMPOSITE

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In this present study surface modified Multi walled Carbon nanotube reinforced epoxy resin along with carbon fibre was fabricated and studied. The principal aim of this work is to reduce cluster formation by surface modification of carbon nano tubes. Surface modification was carried out by 3-aminopropyletrimethoxysilane with aqueous solution method. Surface modified carbon nano tubes were mixed into epoxy matrix by sonication process with 24KHz. Carbon fibre fabric was laid along with epoxy matrix in suitable wtume ratio 40% and composites were prepared by compression moulding technique. Different weight percentages of 0.3%, 0.6%, 0.9%, 1.2% and 1.5%of MWCNT were reinforced with epoxy matrix to evaluate the significant need of filler addition on matrix. Samples were cured by room temperature for 24 Hrs.The tensile, flexural, impact, hardness and inter laminar shear strength tests shows the surface modified MWCNT/Carbon fibre reinforced epoxy composites gives better results than unmodified MWCNT/carbon fibre reinforced epoxy resin composites. The TGA results shows modified MWCNT/carbon fibre epoxy resin composite gives maximum delay in degradation.Scanning electron microscope images revealed that the dispersion of surface modified MWCNT on epoxy matrix was better at high frequecny sonication than unmodified MWCNT/epoxy system.

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1.Introduction

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindricalnanostructure [1]. Nanotubes have been constructed with length-to-diameter ratio of significantly larger than any other material. These cylindrical carbonmolecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of material science and technology [1]. In particular, owing to their extraordinary thermal,mechanical and electrical properties, carbon nanotubes have finer applications as additives to various structural materials[2]. Carbon fibers possess very high specific properties, in particular stiffness and strength which make attractive as the reinforcing elements in the composite materials. To take full advantage of these properties, it is necessary to combine them with a matrix material like polymer, those bonds well with the fiber surface [3]. Epoxy has always been the preferred choice as the matrix for carbon fiber due to its excellent properties and its suitability for various processing techniques [3].Traditional fiber reinforced composites have shown great promise as high strength structural materials due to their high stiffness to weight ratio and their ease of processing [3]. Fiber reinforced composites have found extensive use in aerospace, automotive, construction and recreational equipment industrial sectors but their previously stated limitations have prohibited them from reaching full potential [4]. Research in polymer-based nano composites have shown explosive growth and many recent

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publications have been focused on fiber reinforced composites that have thermoset polymer matrices. In recent years, micro and nano scaled particles have been considered as filler materials for epoxy to produce high performance composites with enhanced properties [4,6]. Nanotube-reinforced epoxy systems hold the promise of delivering superior composite materials with high strength, light weight and multi functional features and have attracted great attention [4, 7]. Keith etal [5] showed that the flexural strength and modulus increased (16–20%) and (23–26%), respectively for the 0.1 wt% and 1 wt% Multiscale fiber reinforced composites(M-FRCs) when compared to the neat FRCs. ILSS properties increased (6% and 25%) for the 0.1 wt% and 1 wt% M-FRCs, respectively when compared to neat FRCs [5].The focus of present study is to determine the effect of adding carbon nanotubes on the mechanical properties of carbon fiber/epoxy composite. The filler material (MWCNT) at different weight proportions (0.3%, 0.6%, 0.9%, 1.2% and1.5%) is loaded in to epoxy matrix and different polymer matrix composite have been prepared. The fabrication process has two steps namely sonication process and compression molding process. The nanotubes of required proportions are made to disperse in epoxy resin by sonication process which leads to a well dispersed MWCNT/epoxy matrix. Unidirectional prepregs of carbon fibers were taken and bonded with MWCNT dispersed epoxy resin using compression molding process which leads to a finished fabricated laminate. In this studytensile, flexural and inter laminar shear strength (ILSS) tests were conducted to evaluate the mechanical performance of the resulting composites. Thermogravimetric analysis could be employed to learn the effect of MWCNT addition on epoxy matrix. The different composition of nanotubes yielded different effective properties to the resulting composites. The results obtained then are compared and interpreted for various proportions of carbon nanotube addition.

2.Experimental Investigations

2.1 Materials

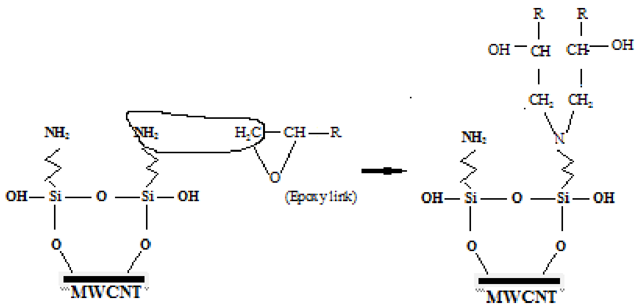
The Multi walled carbon nanotubes used in this study were supplied by Quantum materials corporation, Bangalore, India. The MWCNTs were made by variable catalytic chemical vapour deposition process. The average outer and inner diameters of nanotubes were 12 nm and 8 nm respectively. The length of the nanotube was between 4 and 5 microns and their specific surface area between 250 m^2/g and 290 m^2/g. The epoxy resin used was LY556 and the hardener used was HY951. Unidirectional carbon fiber of 400GSM was used as reinforcement.

2.2 Surface modification of MWCNT

The surface modification oxide particles were prepared by aqueous solution method [8]. The MWCNT were briefly dipped in the ethanol – water solution. Required amount of silane coupling agent generally 2 % concentrations was added drop by drop to get homogeneous mixture. The MWCNT were dipped in the ethanol - silane solution for 10 min. The precipitated MWCNT were separated from aqueous solution. The precipitated MWCNT were washed briefly with ethanol to remove excess silane and dried with 110℃ for 10 min in furnace to remove moisture and forms Si-O-Si structures [9, 10].

2.2 Fabrication of Composite Laminates

A fixed quantity of epoxy resin and different weight percentage of surface modified MWCNT was mixed with epoxy resin at 80 º C to avoid initial filler clustering on matrix. The resulting solution then stirred ultrasonically (24KHz) until a homogeneous mixture was formed. Scheme 1 shows the reaction between surface modified MWCNT to epoxy. The resulted viscous solution was then poured into the mould which consists of 40wt% of carbon unidirectionalwoven mat. The pressure of 30 bar and temperature of 310ºC was maintained throughout the process. The samples were cured on the mould for 3 hrs and post cured at room temperature for 24Hrs.



Scheme 1 Reaction between surface modified MWCNT to epoxy resin

2.3. Specimen preparation

The prepared Carbon fiber – MWCNT reinforced epoxy composite sheets were taken out from mould and then dried in room temperature for 1 hour. Specimens of suitable dimensions according to ASTM standards were cut by abrasive water jet machining (Maxiem water jets 1515, KENT, USA) with garnet size of 80 Mesh; abrasive flow rate of 0.40 Kg/min, maximum pressure of 525 Mpa and nozzle diameter of 1.1mm was maintained.

3. General Characterization

3.1 Mechanical characterization

Thetensile and flexural behavior of hybrid composite were tested based on ASTM-D638, D3039 and ASTM-D790 respectively with a universal testing machine having 40 ton of loading capacity and digital encoder attached at a cross head speed of 5mm/min (FIE. India). The Impact behavior of composite was tested based on ASTM-D256 with an impact machine with maximum load capacity of 40 joules (Krystal equipment Ltd. India). The hardness of composites was tested using Durometer (shore-D) as per ASTM-D 2240. Five identical specimens were tested for each material designation.

3.2 Thermal analysis

The thermal behavior of composite was analyzed with a thermo gravimetric analyzer (NETZSCH STA Jupitar 409 PL Luxx, Germany) under N_2 atmosphere. Samples were scanned from 0-600 ^{o}C at heating rate of 10^{o}C/min and sample crucible material was Al_2O_3. The thermo gravimetric analysis was performed to study the mass loss of polymer composite with rise in temperature.

3.3 Scanning electron microscopy

Fractured surface of composites were analyzed to understand the dispersion of MWCNT on epoxy matrix using scanning electron microscope (HITACHI S-3400 JAPAN). The fractured surface of the samples was coated with gold before scanning.

4. Results & Discussion

4.1 Mechanical properties

The tensile, flexural, interlaminar shear strength and hardness values of carbon fibre/MWCNT reinforced epoxy resin hybrid composite have been displayed in Table 1. It is noted that when 40wt% of carbon fibre reinforced into epoxy resin all the mechanical properties has been improved. This is because of inherent high load bearing capacity of carbon fibre. The increased tensile and flexural strength of 40wt% carbon fibre reinforced epoxy composite is 83% and 68%. Whereas addition of 0.3, 0.6 and 0.9wt% of unmodified MWCNT into carbon fibre/epoxy increased tensile and flexural strength of 3.0%, 7.8%, 10.5% and 2%, 8.7% & 11%

respectively . This is because of load sharing capacity of fibre and MWCNT [11]. It is noted that tensile and flexural strength of 1.2 and 1.5wt% of reinforced un-modified MWCNT decreased because of cluster formation[12]. The Izod impact values of composite shows continual increment with filler addition. The addition of 0.3, 0.6 and 0.9 wt% of unmodified MWCNT into carbon fibre/epoxy system gives 12.5%, 16.1%, 20.1%, 21.3% and 21.8% of improvement. Similarly the hardness of unmodified MWCNT reinforced

Table 1. Mechanical properties of MWCNT reinforced carbon fibre/epoxy composite Material

Epoxywt%/fibre wt%/U.M MWCNT/ S.M MWCNTwt%	Tensile strength (MPa)	Flexural strength (MPa)	Izod Impact (Joules)	I.L shear strength (MPa)	Hardness (Shore-D)
100/00/0.00/0.00	75	110	0.63	-	85
100/40/0.00/0.00	322	345	20.62	28	85
100/40/0.3/0.00	330	352	23.52	28	89
100/40/0.6/0.00	349	378	24.60	27	93
100/40/0.9/0.00	360	388	25.80	26	94
100/40/1.2/0.00	351	369	26.21	26	95
100/40/1.5/0.00	344	362	26.37	25	97
100/40/0.00/0.3	344	365	23.78	28	89
100/40/0.00/0.6	360	384	24.80	28	94
100/40/0.00/0.9	374	395	26.30	27	95
100/40/0.00/1.2	359	377	26.81	27	96
100/40/0.00/1.5	357	379	27.12	26	98

U.M- Unmodified; S.M- Surface modified

Composite gives improvement of 4.5%, 8.6%, 9.2%, 9.8% and 10.2% respectively. This is because of hard and rigid MWCNT fillers on epoxy matrix [13].

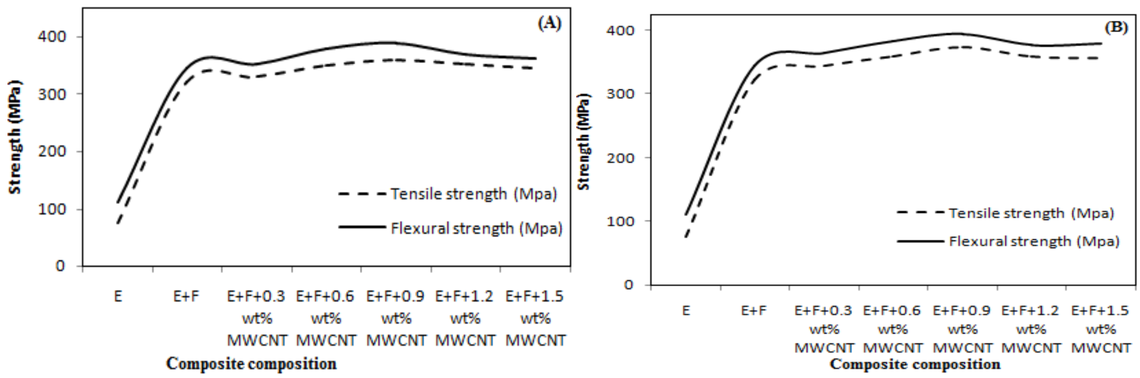


Fig. 1 a) shows tensile and flexural properties unmodified MWCNT reinforced epoxy composite. b) Shows tensile and flexural properties unmodified MWCNT reinforced epoxy composite

From figure 1(b) it is observed that when composites filled with modified MWCNT gives forward trend in tensile and flexural properties than unmodified MWCNT/carbon fibre reinforced epoxy composite. The tensile and flexural strength was increased 6.3%, 10.5%, 14%, 10.3% & 9.8%and 5.4%, 10.1%, 12.6%, 8.4% and 8.9% respectively. This is because of evenly distributed surface modified MWCNT observed the load from matrix due to reaction (scheme 1) hence stress concentrations is lower on matrix. This phenomenon may improve the mechanical properties of surface modified MWCNT/ carbon fibre reinforced epoxy composite. The impact values were increased for modified MWCNT reinforced composites (13%, 17%, 21.5%, 23.5%and 24.5%). The improved hardness values of 4.5%, 9.5%, 10.6%, 12.3% and 14% was observed for modified MWCNT reinforced epoxy composite. It is noted that the Interlaminar shear strength was reduced for all composite designation. This is because of reinforced MWCNT particles affects the laminar adhesion hence delamination took place easily [14].

4.2 Thermal Properties

The degradation stability of composites was measured with thermo gravimetric analysis. The table 2 shows surface modified MWCNT reinforced carbon fibre/epoxy composite gives maximum stability against applied temperature. This delay in degradation occurs because of heat absorbance property of MWCNT nano particles [8, 15 and 16]. The improvement on initial degradation stability when modified MWCNT reinforced carbon epoxy hybrid system is 6%, 7.5%, 10%, 11.2%, 15% and 16.5% respectively. This is because of when heat is increased by external source the nano tubes absorbed due to this more heat energy was needed to activate secondary molecules which are in epoxy matrix [17, 18 and 19].

Table 2. Thermal properties of MWCNT reinforced carbon fibre/epoxy composite Material

Epoxy wt%/fibre wt%/U.M MWCNT/ S.M MWCNT wt%	Initial degradation (º C)	Middle degradation (º C)	Final degradation (º C)
100/00/0.00/0.00	323	378	560
100/40/0.00/0.00	343	386	566
100/40/0.00/0.3	349	395	578
100/40/0.00/0.6	358	398	581
100/40/0.00/0.9	364	405	588
100/40/0.00/1.2	379	415	591
100/40/0.00/1.5	387	418	595

U.M- Unmodified; S.M- Surface modified

4.3 Microstructure analysis

The fig. 2 shows scanning electron microscope images of MWCNT reinforced epoxy composites. The figure 2(a) shows fractograph of pure epoxy resin. Fig. 2(b) shows carbon fibres on epoxy matrix. Figure 2(c) shows the SEM image of unmodified 1.5wt% MWCNT- epoxy composite. The white spots on image show formation of cluster on matrix. These agglomerations results in the poor dispersion of MWCNTs in the epoxy matrix due to this reduction of mechanical properties were observed. Whereas figure 2(d) shows well dispersed MWCNT on epoxy matrix. These well dispersed MWCNT on epoxy observe the applied load and transfer from matrix to fibres. This phenomenon may render superior strength to the composites. Figure 2(c and d) shows fibre on epoxy matrix.

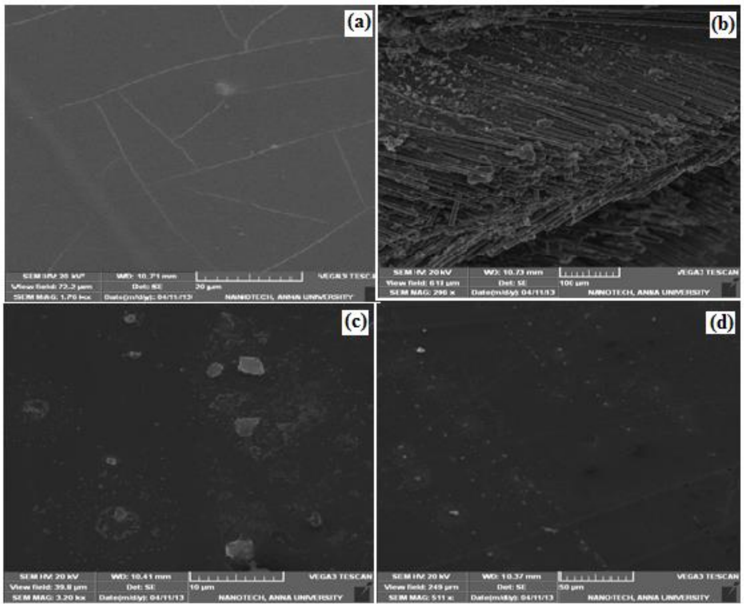


Fig. 2(a) Pure epoxy, 2(b) carbon fibre on epoxy matrix, 2(c) agglomerated un-modified carbon nanotubes on epoxy matrix and 2(d) well dispersed modified carbon nanotubes on epoxy matrix.

4. Conclusions

In this present study, the carbon fiber epoxy composite with different proportions of Multi walled carbon nanotubes were fabricated by using compression molding process. Composite laminates with neat epoxy and nano-phased epoxy (0.3wt%, 0.6wt%. 0.9wt%, 1.2wt% and 1.5wt%) were manufactured and characterized. The tensile andflexural strength of unmodified MWCNT reinforced epoxy composites gives poor results than composites loaded with modified MWCNT.

The surface modified MWCNT gives significant improvement on impact and hardness properties of epoxy hybrid composite. The Inter laminar shear strength test shows decrement in strength for both modified and un-modified MWCNT-epoxy composite. The thermo gravimetric analysis shows that surface modified MWCNT epoxy composites gives better degradation stability than pure and carbon fibre loaded epoxy composites.

The morphology results of composites revealed that un-modified MWCNT were formed cluster on epoxy matrix. Surface modified MWCNT dispersed on matrix evenly due to surface reaction. Thus the surface modification process is essential for polymer composites when they contain fillers.

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