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14. ABSTRACT

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A synchronized study has been carried out to investigate the influence of carboxyl functionalized MWCNTs on both quasi static and dynamic mechanical as well as thermal properties of EPON 862 and satin weave carbon/epoxy laminated composites. A combination method of high intensity ultrasonication and magnetic stirring along with a solvent (acetone) was used to incorporate 0.1, 0.2 and 0.3 wt% of CNTs into the epoxy matrix which was then mixed with the hardener using a high speed mechanical stirrer. Uniform dispersion of CNTs in the epoxy matrix was confirmed from scanning electron microscopic (SEM) micrographs and differential scanning calorimetry (DSC). The CNT modified epoxy resin was then used to fabricate satin weave carbon reinforced three phase FRP composites using compression molding at elevated temperature. Matrix digestion test was performed to determine the fiber volume fraction and void fraction. Mechanical and thermal response of epoxy and its laminates were carried out using three-point bend flexure, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and thermo mechanical analysis (TMA). Quasi static compression and low velocity impact tests were performed on the conventional and nanophased CFRP composites using MTS and Dynatup 8210, respectively. Qualitative characterization of tested samples was performed by SEM and digital camera. For two phase CNT/ epoxy composites, 0.1 wt% CNT reinforced epoxy composites performed optimally compared to neat epoxy composite for both cured and (cured+post cured) samples. TGA results revealed that post curing degraded the resin properties and lowers the degradation temperature as also observed from TMA though the CTE was still lower for 0.1 wt% CNT samples. Flexural strength and stiffness, storage and loss modulus as well as glass transition temperature improved moderately for only cured samples but all type of modulus got to be down for post cured samples. For CFRP composites, addition of 0.2 wt% CNT introduced optimum properties in CFRP composite with an increase of 17.58% in flexural strength and 35.27% in flexural modulus compared to control system (without CNTs). In addition, storage modulus, glass transition temperature, thermal stability were all improved in MWCNTs modified carbon/epoxy composites. Also, both tensile strength and Young's modulus increased up to 0.2 wt% loading by maximum of 33% in tensile strength and 28% in Young's modulus. Compressive strength and stiffness both increased for 0.2 wt\% CNT incorporated composite by 52% in compressive strength and 29% in compressive modulus. This improvement in the properties is attributed to the homogeneous load carrying capability of carbon fiber due to the good dispersibility of CNTs and hence, better interfacial characteristics between the epoxy and the CNTs as evident from SEM micrographs. In terms of impact response, CNT modified samples exhibited better performance compared to neat composite impact damage was lower for CNT samples. This improvement in damage tolerance was attributed to enhanced absorption capability and resistance to crack propagation of CNTs.

THESIS APPROVED BY

Major Professor

Dean of College

Dean of Graduate Program

For

NUSRAT JAHAN

INFLUENCE OF ADDITION OF CARBOXYL FUNCTIONALIZED MWCNTs ON PERFORMANCE OF NEAT AND CARBON FIBER REINFORCED EPON 862

Title of Thesis

INFLUENCE OF ADDITION OF CARBOXYL FUNCTIONALIZED MWCNTs ON PERFORMANCE OF NEAT AND CARBON FIBER REINFORCED EPON 862

by

NUSRAT JAHAN

A Thesis Submitted to the Graduate Faculty
of Tuskegee University
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

TUSKEGEE UNIVERSITY
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CHAPTER I

INTRODUCTION

Background

Fiber reinforced polymer composites (FRPC) have been used commercially, especially in the aerospace, automotive and recreational sports industries [1–5]. Generally, multiple fabric layers are arranged in a specific sequence and bonded together by a matrix material (usually brittle) to provide a strong, stiff and light weight composite laminate whose mechanical properties are optimized for a specific loading configuration. While in plane properties of the composite laminate are better served for optimum mechanical solution, often the out-of-plane mechanical, thermal or electrical properties are much lower. There exist many limiting factors, including a susceptibility to out-of-plane damage as well as delamination which hinders the potential use of FRPCs. For typical FRPCs, the reinforcing fiber generally consists of a carbon or glass fiber with various configurations while the polymer matrix is a brittle epoxy or polyester resin. The brittle nature of the epoxy resin often leads to matrix cracking. At the same time, weak fiber/matrix interface can end up with a catastrophic interfacial failure and delamination. Finally, insulating (both thermal and electrical) nature of epoxy produces a large discrepancy between the in-plane and out-of-plane conductivities.

Researchers as well as industries are trying to develop multifunctional materials or materials that possess both optimized mechanical and electrical properties or mechanical and thermal properties to use the same bulk material for multiple uses. While conventional CFRP composites are getting developed as potential multifunctional materials, their poor out of plane properties leave much to be desired. Improvement in the transverse mechanical properties of FRPCs such as enhanced fiber/matrix interfacial strength as well as improved matrix toughness would reduce the chance of out-of-plane damage as well as improve the overall efficiency of the composites [6].

For years, extensive research has been conducted to modify the polymer matrix with the addition of nanoparticles such as clays, carbon nano fibers, silicon carbide and many more to improve out of plane properties as well as reduce cost of fiber reinforced composite. Extensive research has been reported on composites modified with these nanoparticles. In 1991 a new class of nanomaterials, multi-walled carbon nanotubes (MWCNTs) was first discovered by Iijima [7]. Thereafter, two other forms of CNTs were discovered, double-walled carbon nanotubes (DWCNT) [8] in 1993 and single-walled carbon nanotubes (SWCNT) in 1993 [9]. With their tiny size and outstanding mechanical, thermal and electrical properties, carbon nanotubes (CNT) are unique materials and have come to the forefront of today’s materials research. Their outstanding strength to weight, stiffness to weight and strain to failure properties make them ideal reinforcements, while their characteristics electrical properties make them ideal candidates for use as sensors and actuators [10, 11]. Several works on development of multifunctional fiber reinforced composites have been reported with CNT modified resin matrix. Gojny et al. [12] have demonstrated this by measuring mechanical, electrical and thermal properties including interlaminar shear strength as well as transverse thermal and electrical conductivities of glass fiber reinforced epoxy composite with the addition of carbon nanotubes.

Motivation

Motivation for this research is the significant potential of functionalized multi-walled carbon nanotube (MWCNT) for creating so called ’multifunctional materials’ like composites. Such materials can exhibit several properties that are usually not found together in a single material. Inclusion of very small quantities of carbon nanotubes can render epoxy resin multifunctional, without diminishing the otherwise desirable properties of the epoxy matrix, however many challenges exist. Of primary concern in this work is the fact that carboxylic acid functionalized multi-walled carbon nanotubes are highly aggregating due to the tendency of formation of weak hydrogen bond among -COOH groups and thus difficult to disperse and stabilize in a polymer matrix. Achieving the desired properties in a bulk composite strongly depends on the successful dispersion of nanotubes within the matrix. Data will be presented to show that these factors depend strongly on the methodology used for mixing nanotubes in the resin and also offer some solutions for achieving greater control over dispersion and the resulting properties.

Approach

An attempt has been made to produce multifunctional carbon fiber reinforced composites through modification of the epoxy resin matrix by COOH-functionalized multi-walled carbon nanotubes (MWCNT-COOH).

Due to the cost associated with the incorporation of CNTs within traditional FRPCs, it is desirable to handle the composite in such a way that the most beneficial attributes of CNTs are employed while minimizing the amount of materials used. To achieve this, novel methods of CNT dispersion within the bulk composite are needed which allow easy processability as well as direct control on CNT dispersion. In this research, a combination method of sonication and mechanical stirring along with a solvent was used to disperse the nanotubes in epoxy matrix and compression hot press to manufacture laminated composites. Various weight percentages of CNTs were added in the epoxy matrix. Sonication creates acoustic cavitations which can effectively mix the nanotubes with the resin without destructing the chiral properties of nanotubes. High speed magnetic stirring just after sonication was performed to confirm the breakup of the nanotube agglomerates and subsequently heat was applied to ensure complete removal of solvent (acetone). After dispersing CNTs, part B (hardener) of epoxy resin was mixed with part A by a high speed mechanical stirrer at a stoichiometric ratio of 100:26.4 followed by vacuum degassing to remove entrapped air bubbles. To prepare neat epoxy samples, this prepared resin was poured in a casting mold of desired shape and put in an oven at high temperature for curing. DSC (dynamic scan) was performed to observe the cure behavior of neat and CNT infused epoxy samples. Flexure, DMA, TMA and TGA was performed subsequently to evaluate their performance. To fabricate fiber reinforced samples, hand layup and compression hot press was used to give the final shape of the product by applying both temperature and pressure. MWCNT modified epoxy resin was applied on carbon fabric and impregnated with modified resin by hand layup method followed by stacking and finally putting in compression in hot press at desired time, temperature and force. The benefit of using this method is that the applied pressure is well enough to squeeze out excess resin and also the air bubbles. Prepared laminate was placed in an oven for post curing and cut in desired shape for various testing. Flexure, tension, compression, DMA, TMA along with low velocity impact test was performed to characterize mechanical and thermal properties of various CNT infused samples.

Layout of Thesis

Chapter I provides a general background on carbon nanotubes, their effect on laminated composites, application, motivation and approach of current research, last but not least layout of the thesis. **Chapter II** describes details about the fabrication and multifunctional properties of nanoreinforced epoxy and its laminated composites. In **Chapter III**, materials used for this research and manufacturing detail are presented. Experimental characterization methods and test details are discussed in C**hapter IV**.

Discussions on the cure behavior of epoxy composites by adding CNTs at various percentages are presented in **Chapter V. Chapter VI** discusses the effects of MWCNTs on the mechanical and thermo-mechanical properties of epoxy nanocomposites. Also, thermal stability of composites is addressed by TGA. Multifunctional properties including both mechanical and thermal properties are addressed in **Chapter VII**.

Depending on the service conditions, carbon fiber reinforced epoxy laminates with nanophased matrix are subjected to various types of mechanical and thermo-mechanical loading. Sometimes, many of these structures are prone to dynamic loadings which induce considerable damage to the composite structures. In many cases, level of impact at which visible damage is formed is much higher than the level at which substantial loss of the residual properties occurs. Sometimes, even when there is no visible impact damage on the surface, matrix cracking, interlaminar failure may occur which considerably reduces the load carrying capacity of composites. Therefore, low velocity impact properties of the nanophased carbon fiber reinforced composites were investigated and are presented in **Chapter VIII**. In **Chapter IX**, major conclusions obtained from this study and scope of future works is discussed. **References** are given at the end of the thesis.

CHAPTER II

LITERATURE REVIEW

Introduction

Typically, Fiber reinforced composite materials consist of fibers of high strength and modulus embedded in or bonded to a matrix with distinct interfaces between them. Both fibers and matrix keep their corresponding physical and chemical identities, yet produce a combination of properties that cannot be accomplished by either of the constituents separately. In general, fibers are the primary load carrying members, while the surrounding matrix keeps them in place and acts as a load transfer medium between them. Fiber reinforced composite most commonly termed as laminate, consist of stacking a number of fiber layers and matrix and solidifying them into a desired thickness. A wide variety of mechanical and thermal properties can be found by controlling the stacking sequence as well as the orientation of fibers. Other types of composites that have emerged with full potential in advanced application are nanocomposites. They are getting a high degree of attention from academia as well as a large number of industries, including aerospace, automobile and biomedical industries. The effective diameter of the reinforcement in nanocomposite is of the order of 10^{-9}m where as effective diameter of the reinforcements used in tradition fiber reinforced composites are of the order of 10^{-6}.

Matrix Materials

One of the major constituents in a fiber reinforced composite is the matrix. Various matrix materials have been used either commercially or in research. Among them, thermoset polymers such as epoxies, polyesters and vinyl esters are most commonly used as matrix materials. In thermoset polymers, molecules are chemically bonded together by crosslinks, forming a rigid, three-dimensional network structure. Epoxy is a two part thermoset polymer. The first part is a polymer of low molecular weight with epoxy groups at both ends. Figure 1 represents the most common type of diglycidal ether of bisphenol A (DGEBA) based epoxy resin prepared from the reaction between bisphenol A (DGEBA) and epichlorohydrin.

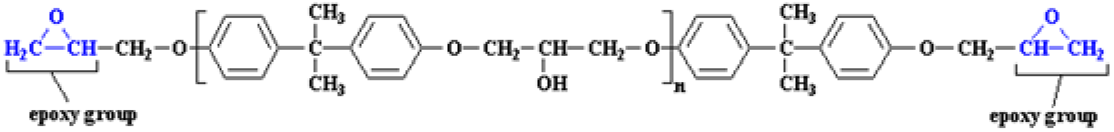


Fig. 1. Diglycidal ether of bisphenol A (DGEBA) based epoxy resin ([33])

Epoxy resins are easily identifiable by their amber or brown color. They are have very low viscosity and are easily processable. This type of resin is easily cured within the temperature of 5°C to 150°C depending on the choice of curing agent and number of epoxide groups. The two ring groups staying at the center of epoxy molecule are more capable of absorbing both mechanical and thermal loads compared to the linear groups and

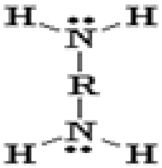


Fig. 2. Diamine ([33])

thus, offer very high toughness, stiffness and heat resistant properties. The curing (polymerization and cross-linking) reaction for transforming this liquid resin to the solid form starts by adding a small amount of a reactive curing agent or hardener, which is usually a diamine (Fig. 2). As the reaction continues diepoxy and diamine reacts with each other (Fig. 3) and slowly forms a three dimensional network structure (Fig. 4).

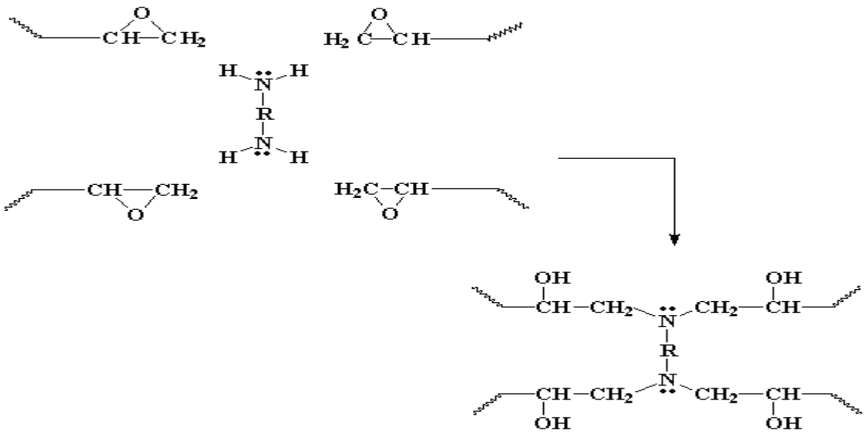


Fig. 3. Reaction of diepoxy and diamine (http://pslc.ws/macrog/epoxy.htm)

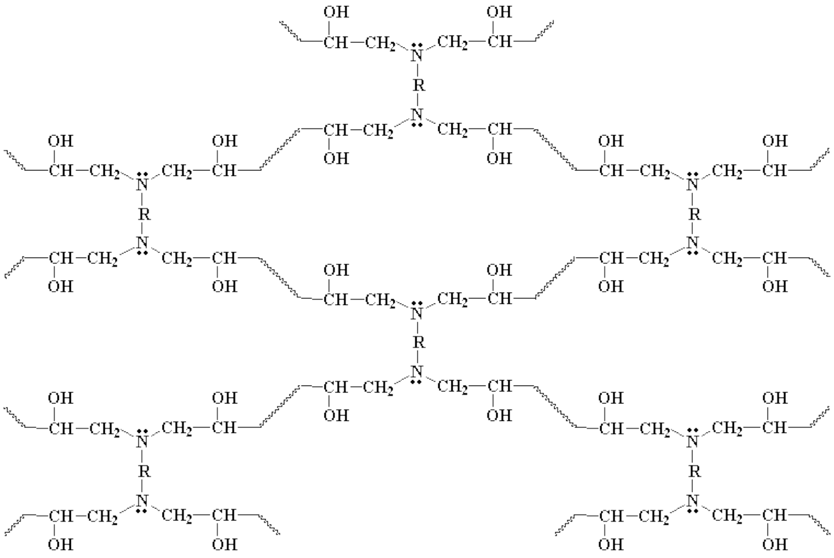


Fig. 4. Network structure of epoxy (http://pslc.ws/macrog/epoxy.htm)

Both the curing time and temperature required to complete the polymerization reaction depends on the type and amount of curing agent. For some curing agents, curing reaction initiates and continues at room temperature; but others may require elevated temperatures for completion of reaction [13]. Epoxy resins find wide variety of application in electronics, aeronautics and astronautics, automotive, packaging and strapping industries.

Structure and Functionalization of Carbon Nanotubes

Carbon nanotubes (CNTs) are basically cylindrical carbon macromolecules formed by rolling graphene sheet in a seamless cylinder or built from sp^2 hybridized carbon units wrapped in a honeycomb structure. CNTs in the form a cylinder have partial sp^3 character that steps up with decreasing the radius of curvature of the cylinder. The end of the cylinder may or may not be capped with hemisphere. CNTs are having well defined atomic structure which attributes to their outstanding thermal, mechanical and electrical properties. Nanotubes consist of a single layer of rolled graphene are called single-wall carbon nanotubes (SWCNTs), whereas those having concentric multiple layers of graphene bonded together by weak van der waals force are called multi-wall carbon nanotube (MWCNTs). Typically SWCNTs are having diameter of about 1nm and lengths of about few micrometers and MWCNTs are having much higher diameter of ten to hundred nanometer with a length of few micron and the sheets are separated by a distance of 0.34 nm [14–16]. Double-wall carbon nanotubes (DWCNTs), a special case of MWCNT consist of two concentric graphene cylinders. In many cases, DWCNTs show similar properties of SWCNTs like size of tube bundle, aspect ratio, electrical and tensile properties [17].

Rolling up of graphene sheets into cylindrical tubes can be done following a couple of ways. Depending on how the graphene sheets are rolled, they can have an armchair, zigzag or chiral shapes as shown in Figure 5. These shapes can be defined by their unit cells which are determined by the chiral vector, C_h and chiral angle, θ. Chiral vector is given by the equation: $C_h = na_1 + ma_2$ where n and m integers indicating number of repeating units; a_1 and a_2 are unit vectors in the two dimensional lattice. The other important parameter is chiral angle, the angle between C_h, and a_1. Basically θ determines the amount of twist (in Fig. 5) [14–16].

When chiral angle approaches to 30° and n=m in the above mentioned equation, orientations of carbon atoms around nanotube circumference are specified as armchair, Again, when the n=m=0 and the chiral angle is equal to 0°, nanotube is called as zigzag. Finally, when chiral angles are in between 0° and 30° it is referred as chiral nanotube. The chirality of nanotubes has significant influence on its transport properties, specifically electronic properties. It has been seen that graphite behaves like a semi-metal but carbon nanotubes which are made from graphite can either be metallic or semiconductor, based on the chirality. For a given (n, m) nanotube, this metallic behavior happens only when (2n+m) is a multiple of 3 resulting in a band gap of 0 eV. Otherwise, it is semiconductor.

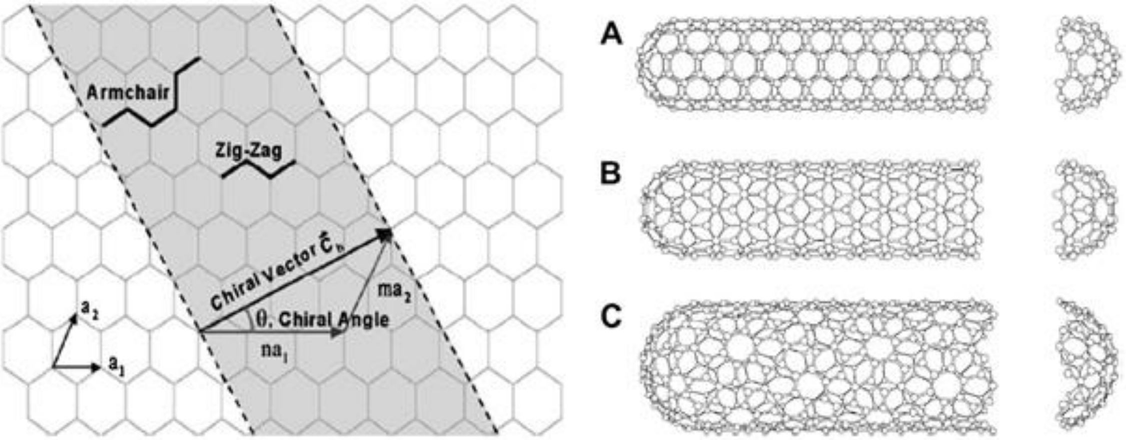


Fig. 5. Schematic representation of formation of CNT with different chiralties (A: arm chair; B: zigzag; C: chiral) [1]

MWCNTs consist of multiple layer of rolled graphene and each graphene layer can reflect different chiral properties. So it is hard to predict overall properties of MWCNTs than that of SWCNTs [1].

CNTs have attractive material properties due to their symmetric structure, topology and highly anisotropic nature as compared to planar graphite where the graphene sheets do not posses any symmetry or anisotropy. Although there is no consensus on the exact properties of CNTs, theoretical and experimental results have indicated Young’s modulus as high as 1.2 TPa (15 to 20 times higher than steel), tensile strength of 50 to 200 GPa [1], electrical conductivity as high as copper and thermal conductivity similar to diamond but more than five times higher than that of copper. CNTs with their surprisingly high aspect ratio can profoundly affect the mechanical as well as thermal properties of the host material like polymer at a very low concentration which makes them a wise choice as reinforcement in polymeric resin [18]. These potentials of CNTs motivated the researchers to experimentally investigate nanotube based composite. Although there has been a pretty good number of work published on CNT based polymer composites, expected improvements in the mechanical as well as thermal properties has not yet been achieved fully. The issues behind this are the tendency of nanotubes to form agglomerates due to their high specific surface area resulting in an electrostatic attraction between them which ends with a non-homogeneous dispersion of CNTs within the matrix, also the smooth nonreacting [1, 19, 20] surface of CNTs leading to no chemical interaction with the polymer molecule and slipping of CNTs in the bundle as well as the lack of interfacial bonding thereby limiting load transfer from matrix to nanotubes [20–22]. To overcome these issues and to utilize full potential of CNTs functionalization seems to be the most efficient way [15, 23, 24].

During mechanical loading, pristine nanotubes are pulled out from polymer matrix instead of being fractured. Thus, their contribution as reinforcement is limited, thereby absorbing significant energy leading to improved properties. Only when the reinforced nanotubes are strongly bonded to the matrix, the load can be transferred effectively from matrix to nanotubes and upon loading the nanotubes will fracture instead of being pulled out. This phenomenon can be accomplished efficaciously by functionalization of nanotubes. Functionalization involves the covalent (oxidation sidewall defect) or non-covalent (wrapping or adsorption) attachment of various functional groups to either nanotube end cap or sidewalls. The functional groups can be covalently bonded to the nanotube using oxidation, fluorination, or other chemical reaction. The covalent functionalization is generally considered to provide better load transfer between nanotubes and surrounding polymer matrix, hence improved mechanical properties. On the other hand, non-covalent functionalization may be chosen if electronic characteristics of carbon nanotubes need to remain unchanged [13]. Both covalent and non-covalent bonds facilitate chemical interaction between the functional group and the polymer matrix. Thus, they become a constitutional part of crosslinked polymer structure [20, 25].

The covalent functionalization can be accomplished in two different ways: i) direct attachment of functional groups to nanotubes, and ii) two-step functionalization process in which nanotubes are chemically treated first to attach simple chemical groups i.e. -COOH or -OH at their end or at the defect sides. Then these chemical groups are substituted with more active groups. Silane coupling agents can also be used for functionalization of carbon nanotubes.

A variety of chemical and electrochemical functionalization processes have been developed [26]. Among numerous available methods, open-end functionalization [15] is mostly reported for functionalization of CNTs. This method is of an oxidative route i.e. refluxing in nitric acid or a mixture of HNO_3 and H_2SO_4 which shorten the length of nanotubes consisting of carboxylic acid end group or hydroxyl group. This refluxing treatment tends to cut nanotube length thus reducing tubes aspect ratio. Other milder treatment has also been reported: Ozone treatment [13]. Ozonized surface is treated with various reagents such as hydrogen peroxide to create the acidic group attachments. A mixture of thionyl chloride ($SOCl_2$) and dimethyl formamide or an amine is then applied on carbon nanotubes which create amide functionality on the surface of nanotubes that are more reactive than acidic groups.

Carbon Nanotube/Polymer Nanocomposites

In recent years, carbon nanotube modified polymer composites have raised increasing interest due to their excellent multifunctional properties. All types of carbon nanotubes (SWCNT, DWCNT and MWCNT) have been used as effective fillers even at very low concentration. Therefore, CNT based composites get to be widely investigated using different polymer matrix material [27]. But effective exploitation of these properties of CNTs in order to enhance the composite performance is generally controlled by types of CNTs, surface modification, degree of dispersion, impregnation with matrix and also on the interfacial adhesion [28, 29].

Several studies have been conducted in recent years to incorporate CNTs in polymer composite. Gojny et al. [28] investigated the effect of functionalization of MWCNTs on the thermo-mechanical properties of MWCNT/epoxy nanocomposite using both pristine and amino-functionalized MWCNTs ranging 0.05-0.75 wt%. Sonication was the primary mixing method in this case. Transmission Electron Microscopy (TEM) revealed homogeneous dispersion in case of functionalized MWCNT but small agglomerates were found for pristine MWCNT reinforced nanocomposites. They reported an almost unaltered storage modulus in the glassy region but an increased value with increasing CNT loading in the rubbery region and the region near T_g. While the loss modulus increased for 0.05 wt% CNT loading, a continuous decrease in peak height with higher CNT loading was observed. The glass transition temperature also increased with increasing CNT loading because the large interfacial interaction resulted in restricted movement of epoxy matrix around nanotubes which lead to higher thermal stability. In all cases, best results were achieved for functionalized MWCNTs due to their better dispersion and higher interfacial interaction. Alexandre et al. [30] studied the influence of MWCNT addition in MWCNT/ epoxy nanocomposite using both pristine MWCNT and debundled-MWCNT (MWCNT-D). MWCNTs were dispersed in matrix resin by a combination of mechanical stirring and sonication method but MWCNT-Ds were mixed with an additional solvent (acetone) mixing step followed by mechanical stirring and Sonication. Optical micrograph revealed much more homogeneous dispersion in case of solvent mixing than without solvent. Scanning Electron Micrograph (SEM) also revealed efficiency of solvent dispersion. Thermal stability measured from TGA showed no change as a function of CNT concentration for MWCNT/epoxy composites whereas thermal stability decreased with

CNT loading for MWCNT-D/epoxy composites. The glass transition temperature (T_g) obtained from both DSC and TMA remained almost same irrespective of CNT loading. They concluded that though the dispersion was improved due to solvent addition thermal expansion co-efficient before and after T_g remains unaltered for both MWCNT/epoxy and MWCNT-D epoxy composites. They found defective structure of MWCNTs during manufacturing by CVD and residual bundle of CNTs to be responsible for this behavior. Moniruzzaman et al. [31] characterized the properties of SWCNT/epon 862 composites based on the concentration of SWCNT (0.01-0.05 wt%). They found combination of Sonication, heat treatment and high shear mixing along with solvent (Dimethylformamide (DMF)) as the best dispersion methods for SWCNTs in the resin. The heat treatment facilitates formation of covalent bond between the epoxy resin and SWCNT. After curing this covalent bond aids in load transferring from the matrix to CNTs. The formation of this bond was confirmed by FTIR. Optical micrograph showed an even distribution of CNTs in the matrix which was further confirmed by Scanning electron micrograph. TGA results at 150°C (isothermal at air) showed no significant decomposition of the composites. Glass transition temperature measured from the DSC also showed almost a constant value of 129°C for all the systems. They reported improved flexural properties that are 8% by flexural strength and 15% by flexural modulus for 0.05 wt% loading. Zhou et al. [32] found combination of Sonication and high speed shear mixing as the best dispersion method for MWCNTs (0.1-0.4 wt%) in Epon 862 resin with improved mechanical and thermo-mechanical properties. They reported around 28% improvement in flexural strength and 12 % in flexural modulus for 0.3 wt% CNT loading over the reference (0 wt. % CNT) system. They found a dramatic improvement (93%) in storage modulus and glass transition temperature (17°C) for 0.4 wt% loading of CNTs but reduction in loss modulus due to CNT addition. The decomposition temperature obtained from the thermogravimetric analysis remained unchanged with CNT loading. Theodore et al. [33] studied the effect of various functionalized MWCNTs (MWCNT-F, MWCNT-COOH) on the properties of MWCNT/Epon 862 nanocomposites. They found combination of Sonication and mechanical stirring as an effective method for dispersing nanotubes in epoxy matrix. The addition of MWCNTs improved flexural properties of composite samples but effect of functionalization was not prominent. Flexural strength improved by 27% for both unmodified and carboxyl functionalized MWCNTs reinforced composites and 13% for MWCNT-F reinforced composites. Carboxyl functionalized MWCNTs can directly react with epoxide groups which give them better properties than fluorine functionalized MWCNT where secondary interaction occurs between the nanotubes and epoxy matrix. They reported significant improvement in storage modulus and glass transition temperature for functionalized MWCNTs-epoxy composite as compared to unmodified MWCNTs-epoxy composites. Hasan et al. [34] examined the effect of MWCNTs/CNF reinforced in an epoxy matrix and cured in a high (28 T) magnetic field. Sonication was found to be most potential method for the dispersion of MWCNTs/CNFs in the epoxy matrix. Enhancement in mechanical properties such as 126% in compressive strength and 166% in compressive modulus was phenomenal with CNT addition. Glass transition temperature and thermal decomposition temperature also improved significantly by 30° and 23° respectively due to the addition of CNTs. They reported that anisotropy imparted by the magnetic field was modest and remarkable improvement in composite properties was due to magnetic flocculation. Mechanical properties were highest in the direction parallel to magnetic field. Abdalla et al. [35] confirmed these observation by reinforcing fluorine functionalized MWCNTs in an epoxy matrix and curing under medium strength magnetic field (9.4 T). They also reported an improved thermal stability by thermomechanical analysis (TMA) when CNTs were aligned parallel to the applied field direction. Okoro et al. [36] studied effects of XD-grade CNTs on the mechanical properties of Epon 862/W nanocomposite. Dual phase (Sonication and calendaring mixing) dispersion technique was successfully employed to disperse the CNTs. They reported improved flexural properties due to the addition of CNTs in the resin matrix but storage modulus remained unchanged in the glassy region. A slight increase in storage modulus was found near the glass transition region. Glass transition temperature remained unchanged upon addition of CNTs because CNTs have minimal effect on restricting polymer chain movement at higher temperature. Siengchin et al. [27] compared the effect of carboxyl functionalized SWCNT and MWCNT on the viscosity and thermo-mechanical properties of Epon 828 polymeric nanocomposite. High shear mixing and ultrasonication was chosen as the prime mixing method. They observed that viscosity of the polymer nanocomposite increases with increasing CNT loading which is in line with the recently reported results. Addition of SWCNTs led to lower viscosity than that of MWCNT composites. The storage modulus improved up to 0.2 wt% loading of both MWCNT and SWCNT and glass transition temperature shifts to a higher temperature with increasing filler content. Better properties were achieved by using MWCNTs as compared to SWCNTs due to their lower tendency for re-agglomeration tendency, hence better interfacial interaction, and higher load transfer capability. Guadagno et al. [37] investigated the effect of increasing concentration of chemically functionalized MWCNTs on the mechanical properties of epoxy nanocomposites. They confirmed a uniform distribution of both modified and unmodified MWCNTs in the epoxy matrix. They reported an improvement in storage modulus of about 20% by the addition of 1 wt% carbon nanotubes but more interestingly addition of functionalized carbon nanotubes did not show an increase in elastic modulus as well as glass transition temperature due to formation of a second phase by homo polymerization because of the presence of carboxyl groups. Hosur et al. [71] studied on finding an optimum technique to disperse vapor grown carbon nanofiber in epoxy resin and evaluated their effect on performance of SC-15 epoxy resin. They found solvent and higher processing temperature useful in getting CNF incorporated nanocomposites.

Qui et al. [38] observed the effect of graphene oxide (GO) on the cure behavior and thermal stability of epoxy resin. They found that GO can act as a catalyst lowering the activation energy due to their presence and catalytic effect increased with increasing GO percentage but the addition of GO decreased the thermal stability. On the other hand, Yang et al. [39] studied the influence of MWCNTs on cure reaction DGEBA/EMI-2,4 system and found that CNTs imposed a retarding effect on the cure reaction of epoxy system. They concluded the cure reaction to be diffusion controlled at higher degree of conversion. Tao et al. [40] founds CNTs decreased the overall degree of cure though initiates the cure reaction at lower temperature. They also observed that CNTs promote both thermal degradation and glass transition at lower temperature compared to neat epoxy.

Multiscale Composites (Fiber/Polymer/Carbon Nanotubes)

From the last few decades fiber reinforced polymer composites have been studied extensively due to their high stiffness and strength with relatively low density.

This combination of properties makes them ideal candidates for many applications in aerospace, automotive and energy sector. However, potential use of these composites is sometimes hindered by their poor out of plane properties especially delamination resistance [2, 3]. Factors contributing to poor delamination resistance are weak fiber/matrix interfaces and the brittle nature of polymer matrix. To overcome these issues, different nanoscale reinforcing elements have been employed which were able to modify the fiber surface or toughen the matrix. Carbon nanotubes (CNTs) possessing outstanding thermal, mechanical and electrical properties, are considered as ideal reinforcements for fiber reinforced polymer matrix composites for various structural and functional applications [2, 5, 41]. But the transfer of individual properties of CNTs in the weaker polymer matrix and subsequently in laminated composite with superior mechanical, thermal and electrical properties is still a challenge. Several studies have been conducted in recent years showing a positive effect of CNTs on the performance of different types of thermoset polymer including epoxy resin.

Godara et al. [29] investigated the effect of different types of CNTs (functionalized and non-functionalized) of 0.5 wt% loading on mechanical properties of CNT/ Carbon fiber/epoxy laminated composite which is manufactured by autoclave molding process. For better understanding, MWCNT, thin-MWCNT, DWCNT and MWCNT with a compatibilizer were incorporated in resin system. Rheological study showed that, viscosity decreased continuously up to 50°C in a similar manner for all CNTs which are an indication of similar state of dispersion. This trend of decreasing viscosity continued until 120°C, followed by an increase with temperature for all the system except MWCNT/epoxy. In MWCNT/epoxy system, increasing the temperature beyond 50°C resulted a plateau in the viscosity up to 120°C, and then increased further. This erratic behavior was described by them as the re-agglomeration tendency of CNTs. This statement was further confirmed from the thermal response of all the system by thermo-mechanical analysis (TMA). An increased thermal stability was observed for all the system except MWCNT/epoxy where agglomerated CNTs were not able to block polymer chain motion. The fracture toughness was reported to increase significantly for all the nanophased systems but only the compatibilized system with MWCNT showed an increased interlaminar shear strength (ILSS) and 75% improvement in crack initiation energy over the control system. Naveed et al. [5] compared the effect of pristine and functionalized MWCNTs on the rheology and cure properties of carbon fiber reinforced epoxy resin (EPON 828 and araldite LY556) prepreg composite systems. They reported from the rheological study that viscosity of both epoxy system increases with increasing MWCNT loading but decreases with increasing shear rate because of the breakage of agglomeration and alignment of CNTs under higher shear stress which was further confirmed by optical microscopy. Functionalized CNTs showed lower viscosity than pristine CNTs for a given loading. From the DSC study it was reported that CNTs can act as catalysts at higher loading like 1.0 wt%. They observed an increment of around 10°C in glass transition temperature (T_g) for 0.75 wt% MWCNT infused laminated system over the control system. Lee et al. [42] investigated the effect of three different types of MWCNTs (unmodified, acid-modified and silane-modified) on the mechanical and thermal properties of carbon/epoxy laminated composite manufactured by autoclave molding. The elastic moduli and tensile strength were significantly improved for silane-modified MWCNT system as compared to other two systems. They also reported a significant improvement in storage modulus and glass transition temperature for silane-modified MWCNT system. These observations were further confirmed by Kim et al. [4] upon testing modified carbon nanotube (acid treated and silane-treated) infused carbon fiber/epoxy composite prepared by autoclave molding process. They reported that silane treated CNTs imparted an increment in flexural stress and modulus by 20% and 34% respectively over the control system which is much greater than acid treated composite. They also reported improved wear properties for silane modified system. Whereas Sunkuk et al. [43] reported unaltered tensile properties upon adding 0.5 wt% of both pristine and silane modified MWCNTs in DGEBA epoxy/ carbon fiber composite. But both decomposition and glass transition temperature improved remarkably due to the addition of functionalized MWCNTs. The co-efficient of thermal expansion (CTE) also showed a diminished value. In other words, higher thermal stability was confirmed for the nanophased system as compared to carbon/epoxy composite. These results were supported by FE-SEM analysis of fracture surface of tested samples. Rahman et al. [44] studied effect of amino functionalized MWCNTs on the thermal and mechanical properties of E-glass/epoxy laminated composite which was cured in compression hot press. They reported improvement in flexural properties of 37% in flexural strength, 21% in flexural modulus and 21% in strain to failure for 0.3 wt% loading over the control system. For the same loading of CNTs, viscoelastic properties were also improved. The reported improvement was 41% in storage modulus, 52% in loss modulus and 20°C in glass transition temperature (T_g). Good interfacial interaction and effective load transfer were contributing for such outstanding properties which were further confirmed by Scanning Electron Microscopy (SEM) images. Yip et al. [45] also reported improved mechanical properties upon addition of pristine MWCNT on

E-glass/epoxy laminated composite fabricated by hand lay-up method. They documented improved flexural and interlaminar shear strength due to the addition of 0.75 phr MWCNT. From the Dynamic Mechanical Analysis (DMA) they observed that CNTs significantly increase laminate's useful operating temperature range, its storage modulus, loss modulus but deteriorate the glass transition temperature. They also observed temperature sensitivity of above mentioned properties and found a good correlation among them. Warrier et al. [46] studied effect of 0.5 wt% MWCNT on E-glass/epoxy prepreg composite when CNTs were grown on glass fiber sizing or mixed in the resin by calendaring or both. They reported the successful bundling of glass fibers due to the CNT-modified sizing by Scanning Electron Microscopy (SEM). They concluded on potentiality of CNT-modified sizing over the CNT-modified matrix, or both over the unmodified system by the significant improvement in glass transition temperature and thermal stability (lowest CTE) determined by thermo-mechanical analysis. Fracture toughness was also improved in case of CNT-modified sizing composites because of their potential of effective bundling the glass fibers. Davis et al. [47] investigated effects of fluorinated XD-CNT on tensile strength, stiffness and durability of carbon/epoxy laminated composite both in tension-tension or tension-compression cyclic loading. The laminates were prepared using heated-vacuum assisted resin transfer molding (H-VARTM) while CNT loading was 0.2, 0.3 and 0.5 wt%. They reported improved mechanical properties of tensile strength, stiffness and durability due to the covalent bonding between epoxy resin and reactive sites of CNTs which was concluded from SEM micrograph. While a number of literature study has been included here focusing on the outstanding mechanical and thermal properties of MWCNT modified system. Ashrafi et al. [48] reported improved fracture toughness in SWCNT modified carbon/epoxy system over the MWCNT modified system due to the high aspect ratio, smaller diameter, and higher load transfer capability of SWCNT over MWCNT.

Low Velocity Impact Properties of Laminated Composites

Over the last few decades fiber reinforced polymer (FRP) composites have been extensively used in structural components where they are subjected to quasi static loading on behalf of their excellent specific strength and stiffness. However, in some applications i.e. aerospace, pipelines, military etc. composite structures are prone to strain rate loading during impact or blast event [49, 50]. In such cases, composite component shows poor performance along with brittle fracture behavior in comparison to other ductile materials like a wide range of metals. Impact damage in metal starts on the impacted surface. So they are easily detectable. But in case of composite components, damage usually starts on the unimpacted surface or in the form of an internal delamination. Therefore, fully understanding the possible reasons for such damages and improving the damage resistance of composite parts are very important. When composite components are subjected to impact loading, possible failure modes reported are: matrix cracking, lamina splitting, delamination, debonding, fiber breakage as well as pull out which arises because of their heterogeneous and anisotropic nature [51, 52]. There are few intrinsic and extrinsic parameters that can affect the damage initiation and propagation such as, plate materials and thickness, dimension and configuration, stacking sequence of lamina, fiber volume fraction and impact parameter like mass, impact velocity, impactor type etc.

Woven fabric composites have attracted attention of researchers because of their higher impact resistance, better damage tolerance, high toughness, dimensional stability and ease of manufacturing. Several studies have been reported so far addressing the behavior of woven fabric composite structure with or without nano infusion upon impact loading. Naik et al. [53] studied the effect of fabric geometry on the damage behavior of laminated composite using modified Hertz law and a three dimensional transient finite element analysis method. They observed that during loading multiple contacts occurred between impactor and the plate. They reported much higher compressive normal stress on the upper layer than the tensile normal stress in the bottom layer in both woven fabric (WF) and cross ply (CP) laminates. In case of impact damage, WF laminates are more resistant to damage than the CP laminates as the failure function is reported lower in the former case than the later one. In another study [52], they investigated the effect of plate thickness on the damage behavior of woven carbon/epoxy and woven E-glass/epoxy system. They observed a linear relationship between the peak contact force and plate thickness for both systems, also the first possible mode of failure was delamination initiated on the top surface for all thickness. Soliman et al. [50] investigated low velocity impact response of a system of woven carbon/epoxy by infusing carboxyl functionalized MWCNTs (0.5 wt%, 1 wt% and 1.5 wt%) at 15, 24, 30, 60 and 120 J. They defined the penetration limit from the difference between the incident and residual velocities and reported that below the penetration limit, peak force remained almost same for all nanophased system but penetration energy improved significantly especially 50% for 1.5 wt% MWCNT nanophased systems, whereas above the penetration limit, penetration energy remained almost same irrespective of applied energy. It was also observed that with increasing MWCNT loading damage size decreased to a significant level. Kostopoulos et al. [54] also reported decreased damage area upon adding 0.5 wt% pristine MWCNTs. They investigated a system of quasi-isotropic (0, +45, 90, -45) carbon fabric reinforced epoxy based composites under five different applied energy 2, 8, 12, 16, 20 J. They observed that reinforcing effect of CNTs was remarkable for higher applied energy. At various impact energy levels, significant difference was observed in delamination area or absorbed energy per unit delamination area between control nanophased systems. Hosur et al. [55] investigated the effect of nanoclay on the impact properties of plain weave carbon/epoxy composite laminates at three different energy levels i.e. 10, 20 and 30 J by an instrumented drop-weight system along with nondestructive evaluation system (c-scan). They reported an increased peak load and absorbed energy with increasing impact energy but remained almost unaltered with increasing the nanoclay loading (1-3 wt%). The damage area got reduced for all nanophased system as the laminates were stiffer upon addition of nanoclay which facilitates narrow localized damage area. These observations were further confirmed by Iqbal et al. [56] upon testing carbon fiber (unidirectional) reinforced epoxy composite infused with nanoclay. Whereas Avila et al. [57] reported a irregular behavior of damage area with respect to nanoclay loading as well as impact energy for the system of nanoclay (1wt%, 2wt%, 5 wt%, 10 wt%)/ woven S-2 glass fabric/ epoxy. They observed that only for 5 wt% loading damage areas consistently decreased with impact energy otherwise it did not follow any increasing or decreasing trend with respect to impact energy or nanoclay loading. With the addition of nanoclay, 48% improvement in absorbed energy was reported over neat composite laminate. But the amount of absorbed energy decreased with increasing impact energy.

Conclusion

Numerous studies have been conducted since last few decades showing the positive effect of CNTs on the polymer matrix as well as fiber reinforced composites. But the full potential of CNTs is not yet been materialized because of the issues of agglomeration tendency, unreactive nature of CNTs etc. which yet need to be addressed. For this reason, investigation is going on by several researchers and our present study has been carried out as an attempt to resolve these issues.

CHAPTER III

MATERIALS AND MANUFACTURING TECHNIQUE

Introduction

Different types of characterizations process were carried out to investigate the response of prepared composite samples under different loading conditions, different loading modes as well as different thermal treatments. Flexure and tensile tests were performed to determine the mechanical properties of the laminated composite. To investigate the dynamic behavior, low velocity impact test was performed on the composite samples. Quasi-static compression was also carried out. Thermal characterization was performed by DSC, DMA and TMA to evaluate the effect of CNT on the thermal behavior of Epon 862 resin. Optical microscopy and scanning electron microscopy was done on the failed samples.

Materials Used

Matrix Material

The matrix used in this research is a two part system. Part A is Epon 862 (Diglycidyl Ether of Bisphenol F, Part A), which is a low viscosity liquid epoxy resin manufactured using epichlorohydrin and Bisphenol F, purchased from Miller Stephenson Chemical Company (Danbury, Connecticut). A molecular illustration and properties of

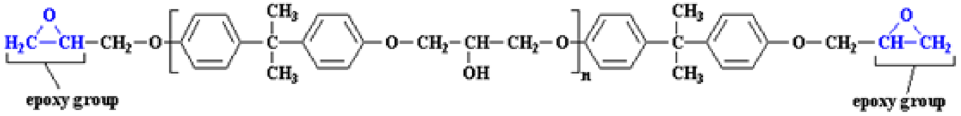


Fig. 6. Molecular Structure of Epon 862 (www.miller-stephenson.com)

Epon 862 are given in Figure 6, and Table 1, respectively. This resin contains no diluents or modifiers. Properties of Epon 862 include low viscosity, low color, and reacts with a full range of epoxy curatives, good mechanical, adhesive, and electrical properties, good chemical resistance, and superior physical properties vs. diluted (6 poise) resins.

Table 1. Properties of Epon 862

Properties	Value
Epoxide Equivalent	165-173 g/eq
Viscosity at 25° C	25-45 poise
Color	200 max. Pt/Co
Density at 25°C	9.8 lbs/gal

Suggested uses for Epon 862 are fiber-reinforced pipes, tanks and composites; construction, electrical and aerospace adhesives. Part B is Epicure W, shown in Figure 7, an aromatic diamine used as curing agent epoxy resins. It is has a high degree of chemical resistance, low viscosity, high distortion temperature. To achieve optimum performance it is required to be normally heat cured.

Fig. 7. Molecular Structure of Epicure W (www.miller-stephenson.com)

Carbon Nanotube

The reinforcing phase in this research is carboxyl functionalized multiwalled carbon nanotubes (MWCNT). Carbon Nanotubes were purchased from Nanocyl

(Belgium). These carbon nanotubes were synthesized by catalytic Chemical Vapor Deposition (CCVD) process. Nanotubes which exit the CCVD reactor are then purified to greater than 95%.This nanotubes were then functionalized with COOH by nanocyl patened process. The MWCNT dimensions are listed in Table 2. Figure 8 refers the SEM micrograph of COOH modified short thin MWCNT.

Table 2. Physical Properties of Carboxyl Functionalized MWCNTs

Properties	Value
Avg. Diameter (nm)	9.5
Avg. Length (μm)	< 1
Purity	> 95%
Metal Oxide	< 5%
Conc. Of Functional group	<4 %

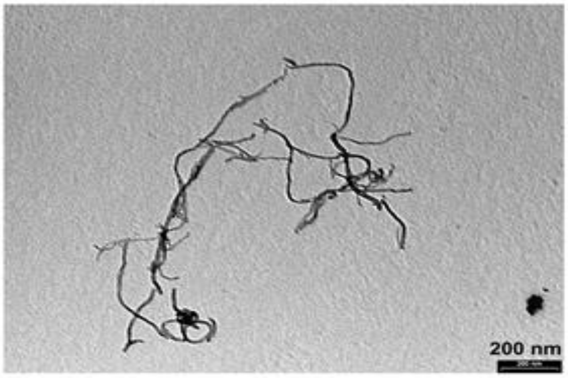


Fig. 8. SEM micrograph of COOH modified short thin MWCNT (http://www.nanocyl.com)

This type of nanotubes is used widely in various applications because of their ease of dispersibility.

Carbon Fiber

In current research 8-harness satin weave carbon fiber with a tow size of 3K was used to fabricate laminates using Compression Hot Press technique and this fabric was obtained from US composites. Typical properties of this carbon fabric are listed in table 4. The interlacing of wrap (0°) and weft (90°) fibers in a regular pattern or weave style produces woven fabrics.

Table 3. Physical Properties of T300 Carbon Fiber

Properties	Value
Fabric type	8 harness satin weave
Weight (oz)	10.9
Thickness (inch)	0.018
Density (g/cm^3)	1.79
Yield (mg/m)	200%
Tensile Strength (MPa)	4410
Tensile Modulus (GPa)	235

The fabric’s integrity is maintained by the mechanical interlocking of the fiber tows. Drape which is the ability of a fabric to conform to a complex surface; surface smoothness and stability of a fabric are controlled primarily by the weave style. In 8 harness satin weave fabric, each warp yarn floats over seven weft yarns and under one. This very dense 3K style weave keeps resin weight low but require attention for proper resin saturation. This type of carbon fabric is of medium duty and used for fast buildup and superior strength.

Fabrication Method

In this study, control, 0.1, 0.2 and 0.3 wt% CNT modified epoxy samples as well as their carbon fiber reinforced epoxy laminates were fabricated by a combination method of sonication and magnetic stirring using a solvent (acetone) and hot press.

Matrix Modification

First, pre-calculated amount of MWCNTs (0.1, 0.2 or 0.3 wt%) were physically mixed with 30 mL acetone in a beaker. Probe sonication was used to disperse the MWCNTs in acetone for 30 min. During the sonication process, beaker was placed in a cooling bath to resist heating up the beaker. At the same time, pre-calculated amount of epoxy (part A) was heated at 70°C to reduce the viscosity of resin to ensure proper wetting of both nano and micro filler. After sonication, MWCNT/acetone mixture was added to heated resin, manually mixed, and sonicated further for 1 hr. Upon completion of sonication process, MWCNT/acetone/epoxy mixture were then mixed with curing agent and placed on a hot plate set to a temperature of 70°C. A magnetic bar was placed in the beaker and set to rotate at a speed of 1000 rpm for 3 hr. The stoichiometric ratio of epoxy (Epon 862) and EpiCure W was 100: 26.4, as suggested by the manufacturer. The mixture was then placed in a vacuum oven at 60°C for 2 hrs to ensure complete removal of both the entrapped bubbles and acetone.

Epoxy Sample Preparation

The modified resin was poured into preheated mold and kept in an oven for 4 hours at 121°C. The samples were then cooled slowly in the furnace atmosphere. After that, samples were taken out from mold and put in over for another 2 hours at 177°C for post curing.

Laminate Fabrication

The CFRP composite was prepared by employing both hand lay-up and compression hot press technique. Eleven layers of carbon fabrics were properly stacked maintaining their parallel orientation. Each of the layers was infiltrated uniformly with MWCNT modified epoxy resin using a roller pin. The stacked plies were then placed in hot press and set to a curing temperature of 121°C for 4 hrs. After completion of curing process, laminate was allowed to cool slowly at room temperature. Finally, the cured laminate was taken out from hot press and placed in an oven at 177°C for 2 hr for post curing. The final thickness of the laminate was measured to be around 3.2 mm. Schematic presentation of fabrication process is shown in Figure 9:

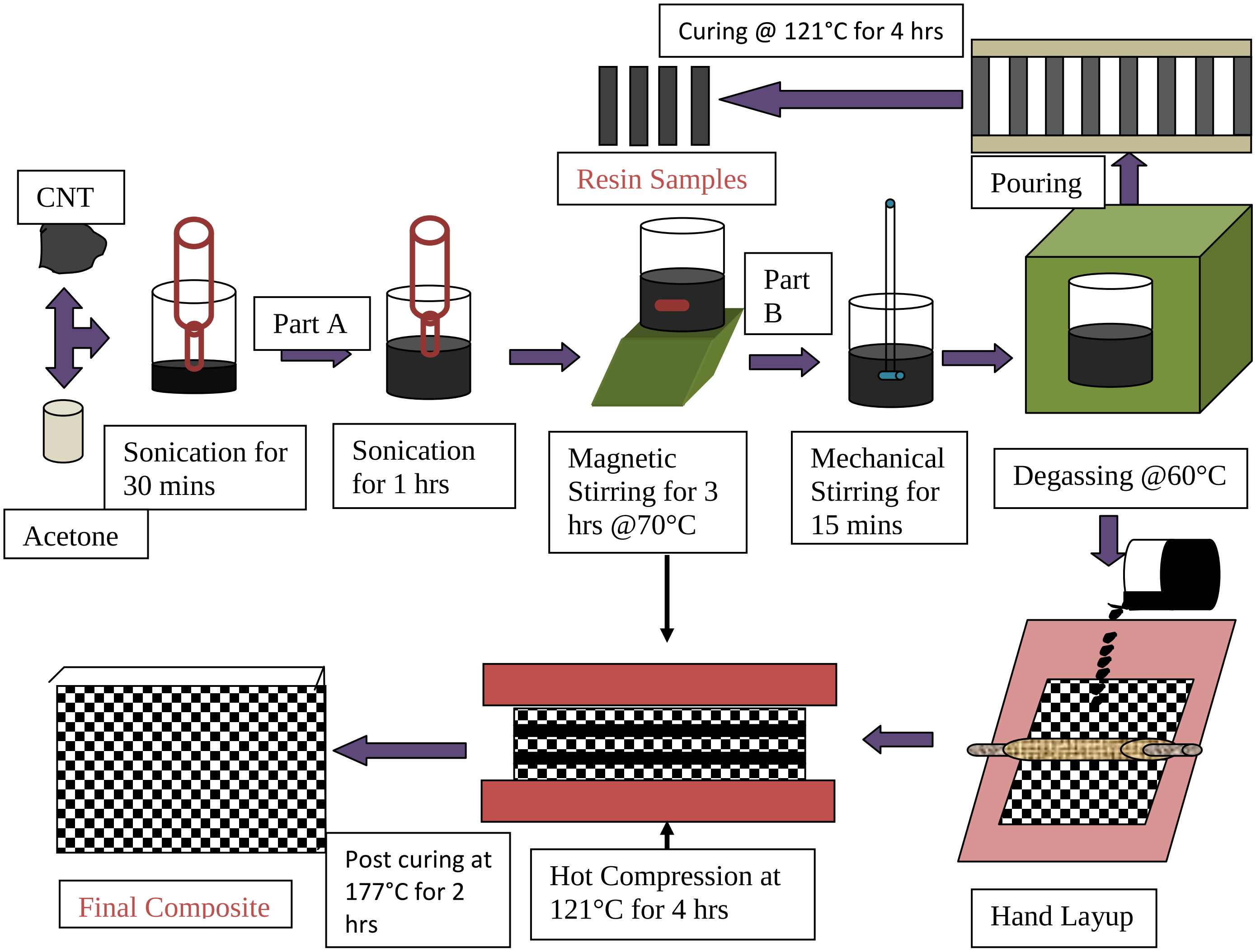


Fig. 9. Schematic presentation of the fabrication of three phase composites

CHAPTER IV

EXPERIMENTAL CHARACTERIZATION TECHNIQUE

The neat and nanophased samples were investigated by various test procedures. SEM was performed to qualitatively characterize failed samples for both epoxy and its laminated samples. DSC dynamic scan was taken into consideration to observe cure kinetics of neat and nanophased samples. Flexural, tensile and quasi-static compression test was performed to determine mechanical performance of samples under various loading conditions. DMA and TMA were performed to obtain viscoelastic properties and to measure thermal stability of both epoxy and their laminated samples. TGA was performed to get the decomposition characteristics of epoxy samples. Low velocity Impact (LVI) testing was done to evaluate the dynamic properties of laminated samples and Ultrasonic C-scan technique helped in evaluating the damage size of tested samples.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is an advanced technique to measure the heat flow through a sample as the sample is heated at a controlled rate or in isothermal condition. The amount of heat flow is dependent on sample morphology. DSC test was carried out using a TA instrument Q 1000 in dynamic mode using four different heating rates: 2, 5, 10, 15°C/min. For dynamic scan, 10mg of uncured sample was heated from 30◦ C to 400°C for each specific heating rate. All DSC tests were run using aluminum sample pans and 50 mL/min of N_2 purge. Upward peaks were considered exothermic for all DSC thermograms.

Matrix Digestion Test

Matrix digestion test was performed according to ASTM D 3171-99 to estimate the fiber volume fraction and void content of carbon/epoxy and carbon/MWCNT/epoxy laminated composites. Samples were cut from three different locations of the laminates and the sample edges were passed through polishing to have smooth surfaces. First, samples were weighed and dimensions were measured accurately. Each sample was then placed in a bath of 80% concentrated nitric acid maintained at 70°C for about 5 hrs. After 5 hrs, matrix resin was digested completely by nitric acid, only carbon fibers were left. The fibers were then taken out from nitric acid and washed with distilled water and acetone repeatedly. Fibers were then dried in an oven maintained at 100°C for about an hour. After that, fiber weight was measured. Following equations were used to calculate the fiber, matrix and void volume fraction in the laminated composite:

Fiber vol. fraction, V_f ——

Matrix vol. fraction, $V_m =$ ——

Void vol. fraction, $V_o = 100 - (V_f + V_m)$

Where,

W = Weight of fiber after drying,

w= Weight of initial composite specimen,

F = Fiber density,

C = Composite density

M= Matrix density, and

V= Volume of composite

Flexural Test

Flexural test was performed under three-point bend configuration on the Zwick Roell Z 2.5 testing unit according to ASTM D 790- 02 [59] to estimate both the flexural strength and flexural modulus of various composite samples. The machine was run under displacement control mode at a cross head speed of 1.2 mm/min. All samples were tested at room temperature. Sample size was 52×12.25×3.2 mm to maintain span to thickness ratio of 16:1. Load-deflection data was collected for each sample. Thus, using the homogeneous beam theory, flexural strength was calculated using three-point bend configuration according to the following equation:

Flexural strength =

Flexural Modulus was calculated from the following equation:

Flexural modulus =

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical Analysis was performed to study the viscoelastic behavior of composite specimen using TA instrument Q 800 operating in dual cantilever mode according to ASTM D 4065-01 [60]. Width of the specimen was 12 mm and span length to thickness ratio was 10. The specimens were cut of nominal dimensions 60 × 12 × 3mm.

Heating rate was 5°C/min ranging from 30° to 200°C along with an oscillation frequency of 1 Hz as well as amplitude of 15μm. Minimum of five samples were tested for each batch. From the test data, storage modulus and tanδ were measured for all samples.

Thermo-Mechanical Analysis (TMA)

Thermo mechanical analysis was performed to measure the co-efficient of thermal expansion (CTE) using TA instrument Q 400 system operating in expansion mode according to ASTM D 696-08. Heating rate was 5°C/min ranging from 30° to 250°C and test was run in nitrogen gas atmosphere. Five samples of each type were tested. The coefficient of thermal expansion (CTE) in the temperature range of 30° to 90°C was measured from the slope of dimension change versus temperature curve.

Thermo-Gravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) was conducted by a TA instrument Q 500 fitted with nitrogen purge gas in order to obtain the information on the stability of the neat and nanophased composites. The samples were cut into pieces of weight with 10 to 15 mg. Samples were put in a platinum sample pan and heated from 30°C to 800°C at a ramp of 10°C/min. Characteristics parameters were determined using TA universal analysis-2000 data acquisition system.

Quasi Static Compression Test

In order to investigate the response of composite specimen under compression loading, samples were tested in the in-plane direction using servo-hydraulically controlled Material Testing System (MTS) machine according to ASTM D 695-10. The test was carried out in displacement control mode and crosshead speed was 1.27 mm/min. The nominal size of the samples was 13.2 × 12.8 × 4.9mm (length, width, thickness). In order to ensure evenly distributed compressive loading, each specimen was polished so that the opposite faces were parallel to each other. The Load-deflection data recorded by the data acquisition system was converted to the stress-strain curve after dividing load by cross-sectional area and deflection by specimen height.

Tension Test

Tensile test was carried out to observe the response of composite samples under tensile loading using servo-hydraulically controlled Material Testing System (MTS) machine according to ASTM D638-03 [61]. The test was carried out in displacement control mode and crosshead speed was set to 1 mm/min. All the samples were tabbed in aluminum grip in a 100 kN load cell. The gage length was 25 mm with a thickness of 3.2 mm and width of 5 mm. The Load-deflection data recorded by the data acquisition system was converted to the stress-strain curve after dividing load by cross-sectional area and deflection by gage length.

Scanning Electron Microscopy

Morphological properties of composite samples were determined by scanning electron Microscope (SEM). SEM also facilitates to determine failure modes. Failed samples were cut through the cross section of failed region. SEM analysis was carried out using Zeiss EVO 50. Samples were positioned on a sample holder with a silver paint and coated with gold to prevent charge accumulation during electron irradiation. A 20 KV accelerating voltage was applied to achieve desired magnification.

Low Velocity Impact (LVI) Test

Low velocity impact tests were conducted according to ASTM D5628-07 using a drop tower (DYNATUP Model 8210) manufactured by GRC instruments. Impulse data acquisition system (version 3) was equipped with the system. Test was conducted by placing the sample in a clamped edge fixture placed at the bottom of the drop tower with a circular support span of diameter 75mm. 6.62 kg hemispherical impactor with a diameter of 20 mm was equipped with the drop tower. After each impact event, visible damage was examined on the composite panel and following the way three different impact energy was defined for this study; 20, 30 and 40J. Required impact energy was delivered by adjusting initial impactor height. To calculate the required impactor height from which it should be dropped, following equation was used:

$$E=mgh$$

Where, E is desired impact energy, m is weight of impactor which equals to 6.62 Kg, g is acceleration due to gravity, equals to 9.81 ms^{-2} , h is the required height from the tip of the impactor to the top surface of sample held between the pneumatic clamp. Using the above equation, height required for each different impact energy level was calculated.

To keep track of the transient response of specimens, impactor end was fitted with an instrumented tup of 15.56 kN. The tower was also equipped with rebound brakes to prevent multiple impacts on the sample. The dimension of the composite sample was 100 ×

100 × 3.2 mm. During loading, load, deflection, velocity, energy as a function of time was recorded.

Ultrasonic C-scan

Nondestructive evaluation of impact damage was carried out using an ultrasonic C-scan. Ultrasonic pulse receiver unit along with FlexSCAN-CT M was supplied by Okos Solutions Inc. 1 MHz 50 mm focus transducer fitted with a 19 mm piezoelectric element was used in scanning the samples in pulse-echo immersion mode. During scanning, impacted surface of a sample was placed facing the transducer to get a projected image. From the image, damage area was calculated using ImageJ software.

The overall performance of samples under impact was evaluated by both data acquired from non-destructive techniques and data gathered during impact test.

CHAPTER V

CURE BEHAVIOR OF EPOXY COMPOSITE BY DSC DYNAMIC SCAN

The study of the cure reactions of polymer composites as a function of the processing conditions is extremely critical for the analysis and design of processing operations. In addition, the performances of CNT/polymer composites are closely related to their microstructures. The research of cure behaviors is beneficial to understand the relationship between the microscopic structures and the macroscopic performances of CNT/polymer systems. Therefore, the study of the cure behaviors contributes to process development and an improvement of the quality of final products correlated with the structures of polymer network. Numerous studies have been conducted on dynamic scanning with the differential scanning calorimeter (DSC). Some studies show that the addition of CNTs can act as a catalyst whereas some studies reveals the retarding effect of CNTs on cure reaction.

The dynamic DSC thermograms for pure epoxy and MWCNT modified epoxy nanocomposites at three different heating rates is shown in Figure 10. As can be seen from the Figure, addition of CNTs in epoxy lowers the exothermic peak height when compared to that of neat epoxy which indicates decreased degree of curing of MWCNT/epoxy nanocomposites possibly due to the physical hindrance of nanotubes to the polymer chain mobility. The effect of CNT concentration on epoxy can be verified by checking the total heat of reaction (ΔH), onset temperature (T_i) and peak temperature (T_p). All these data have been summarized in Table 4. It can be seen from the Table 4, heat of reaction decreases with increasing heating rate for every system. Also, CNT concentration leads to a reduction in total heat of reaction up to 0.2 wt% loading beyond which ΔH goes up. As per earlier discussion, well dispersed CNTs can act as physical hindrance to the mobility of polymeric chain and lower mobility of polymeric molecule may result in the reduction of the total heat of reaction. On the other hand, aggregated CNTs are much less efficient in hindering polymer chain movement and have hardly any effect on the value of total heat of reaction [62].

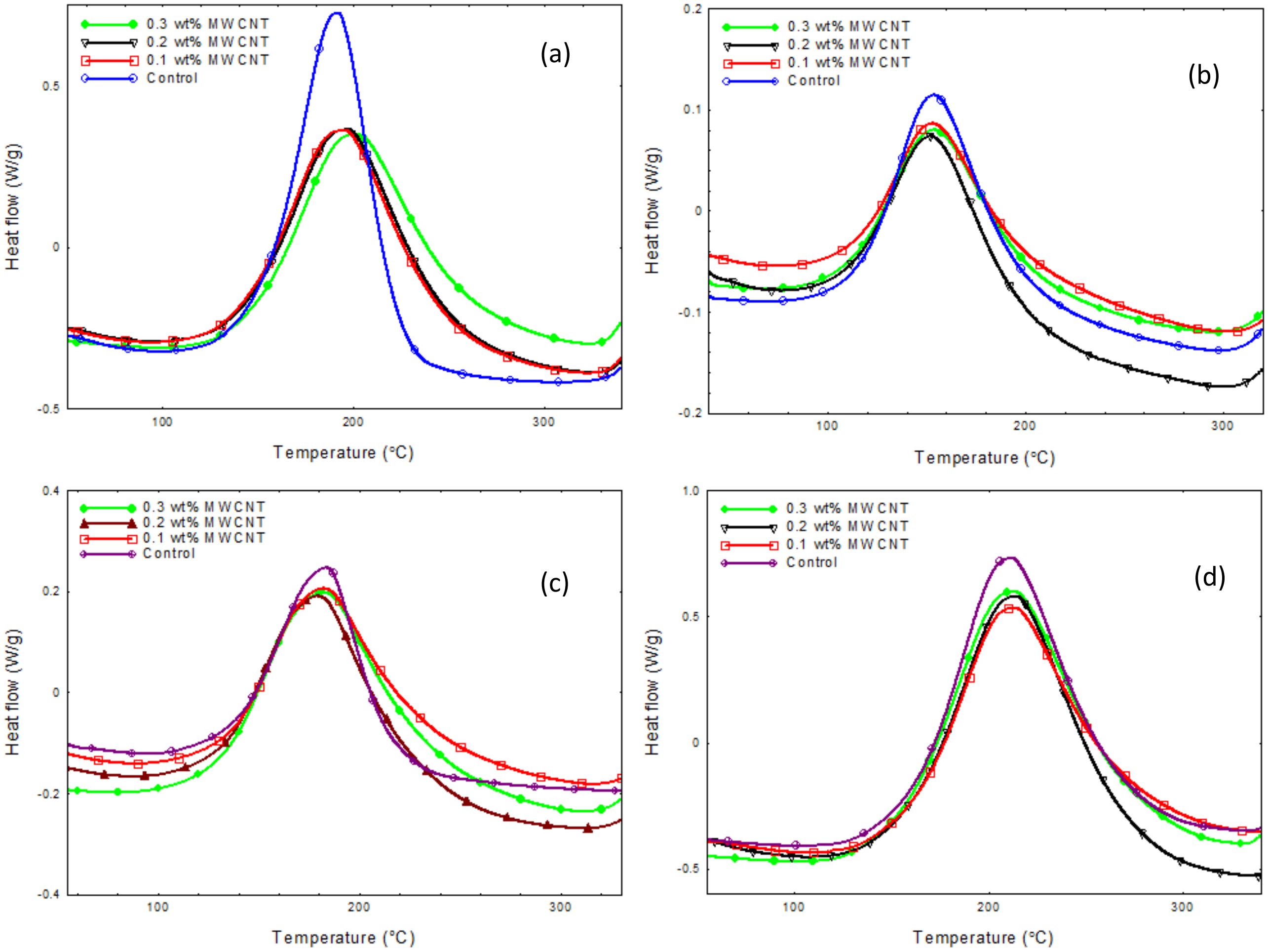


Fig. 10. Dynamic DSC thermograms of different system at various heating rate (a) 2 deg/min (b) 5 deg/min (c) 10 deg/min and (d) 15 deg/min

Table 4. Characteristics Parameter obtained from DSC Thermograms

Sample ID	Heating rate(deg/min)	ΔH	T_i	T_p
Neat	2	421.2	118.3	157.05
	5	376.6	134.47	182.05
	10	323.5	148.54	199.9
	15	321.4	158.86	208.51
0.1 wt% CNT	2	387.3	109.26	153.26
	5	341.4	126.57	178.0
	10	321.5	139.91	196.19
	15	316.3	148.74	207.43
0.2 wt% CNT	2	359.2	116.23	157.96
	5	323.3	133.78	182.99
	10	302.3	148.64	202.01
	15	288.7	157.78	209.8
0.3 wt% CNT	2	367.6	112.6	157.47
	5	383.3	128.85	182.45
	10	304.2	144.65	202.01
	15	328.9	153.86	20.81

Therefore, decrease in ΔH value due to addition of up to 0.2 wt% CNT can be attributed to the hindrance of polymer chain mobility due to well dispersed CNTs whereas increase of ΔH due to further addition of CNTs can be attributed to presence of aggregated CNTs inefficiently participated in hindering polymer chain movement. The onset temperature for curing is lowest for 0.1 wt% CNT loaded samples followed by 0.3 and 0.2 wt% CNT incorporated samples indicating that addition of CNTs facilitates the curing initially by lowering the onset temperature where 0.1 wt% CNT demonstrates the most noticeable effect on onset temperature while the other two loading of CNT showed similar but more modest effect on T_i. Similar results have been observed by Tao et al. [40] for short SWCNT/ HiPco- SWCNT/ XD-CNT infused DGEBF/DETDA system.

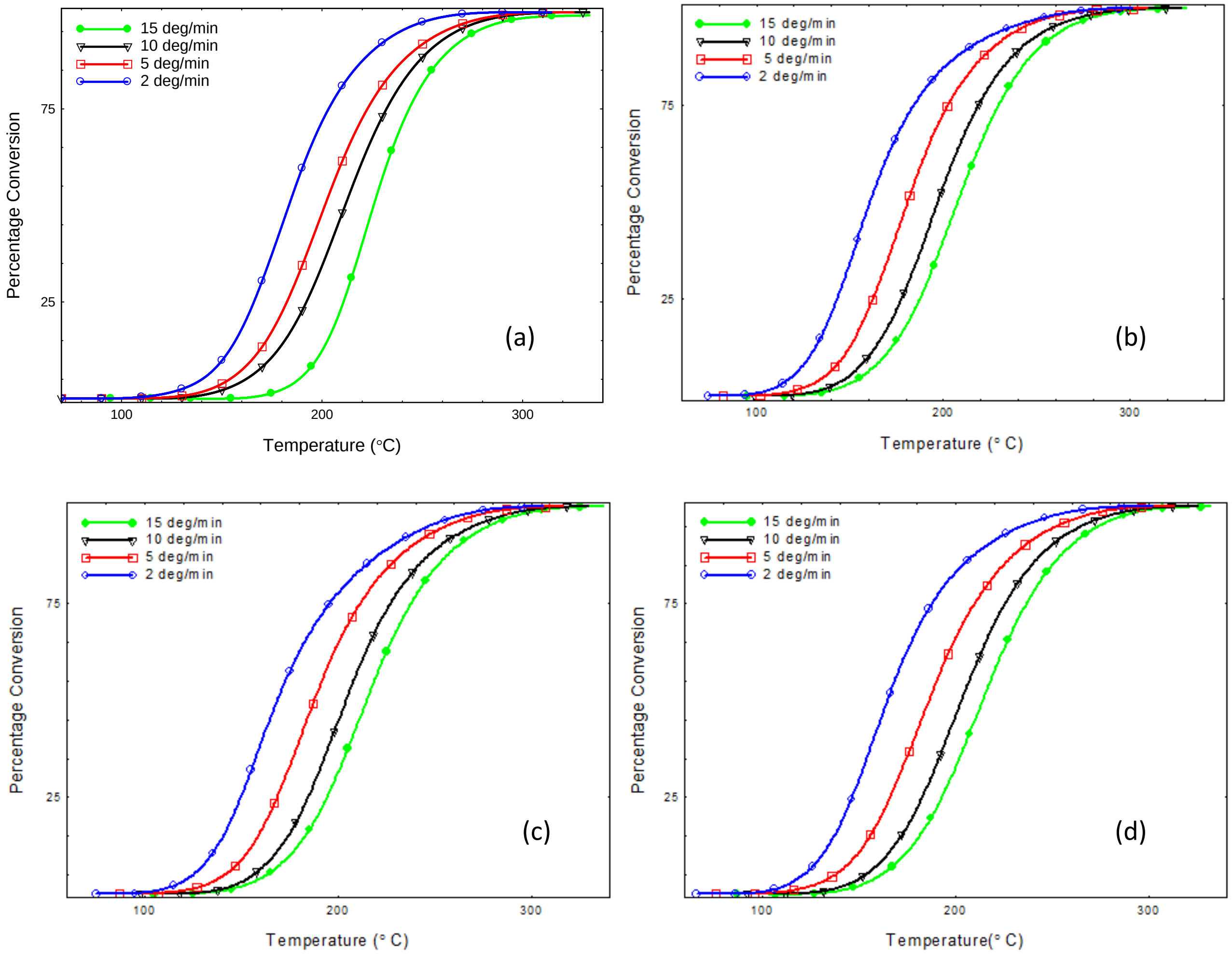


Fig. 11. Degree of conversion as a function of temperature for various CNT added composites (a) Neat (b) 0.1 wt% (c) 0.2 wt% and (d) 0.3 wt%

The peak temperature (T_p) increases with increasing heating rate. Small amount of CNTs (0.1 wt%) causes slight decrease of peak temperature compared to neat epoxy because of their catalytic action but higher loading of CNTs (0.2 and 0.3 wt%) results greater peak temperature as shown in Table 4 which demonstrates the retardation effect of MWCNTs due to their steric hindrance [63].

Figure 11 represents the degree of conversion (α) as a function of temperature for neat epoxy and various MWCNT/epoxy nanocomposites at four different heating rates. As can be seen from the Figure, all the curves are in the sigmoidal form and only shift a distance along the temperature axis which indicates the autocatalytic nature of cure reaction of all the studied system which is in well agreement with earlier studies [40, 64]. That is, incorporation of MWCNTs and their carboxyl groups on their surfaces does not change the cure reaction mechanism of DGEBF/DETDA system. Also, degree of conversion increases with decreasing heating rate for all the neat and naophased composites.

Degree of conversion curve as a function of temperature of various studied system at four different heating rates has been shown in Figure 12. It is observed that for different heating rate, low loading of CNTs like 0.1 wt% act like a catalyst by converting more epoxies into cured matrix whereas for higher percentage of CNT loading, epoxy showed lower degree of conversion compared to neat epoxy system which means that MWCNTs have significant retarding effect on curing characteristics of epoxy. This retarding behavior of CNTs might be attributed to the increasing surface area and tendency to form agglomerates at higher loading. Close look to Figure 12 reveals the cure inhibition effect due to the increasing concentration of MWCNTs from 0.2-0.3 wt% MWCNT loading. For the development of laminated composites, cure retardation effect caused by the addition of

MWCNTs could have some negative effect on the properties since it requires longer post curing time.

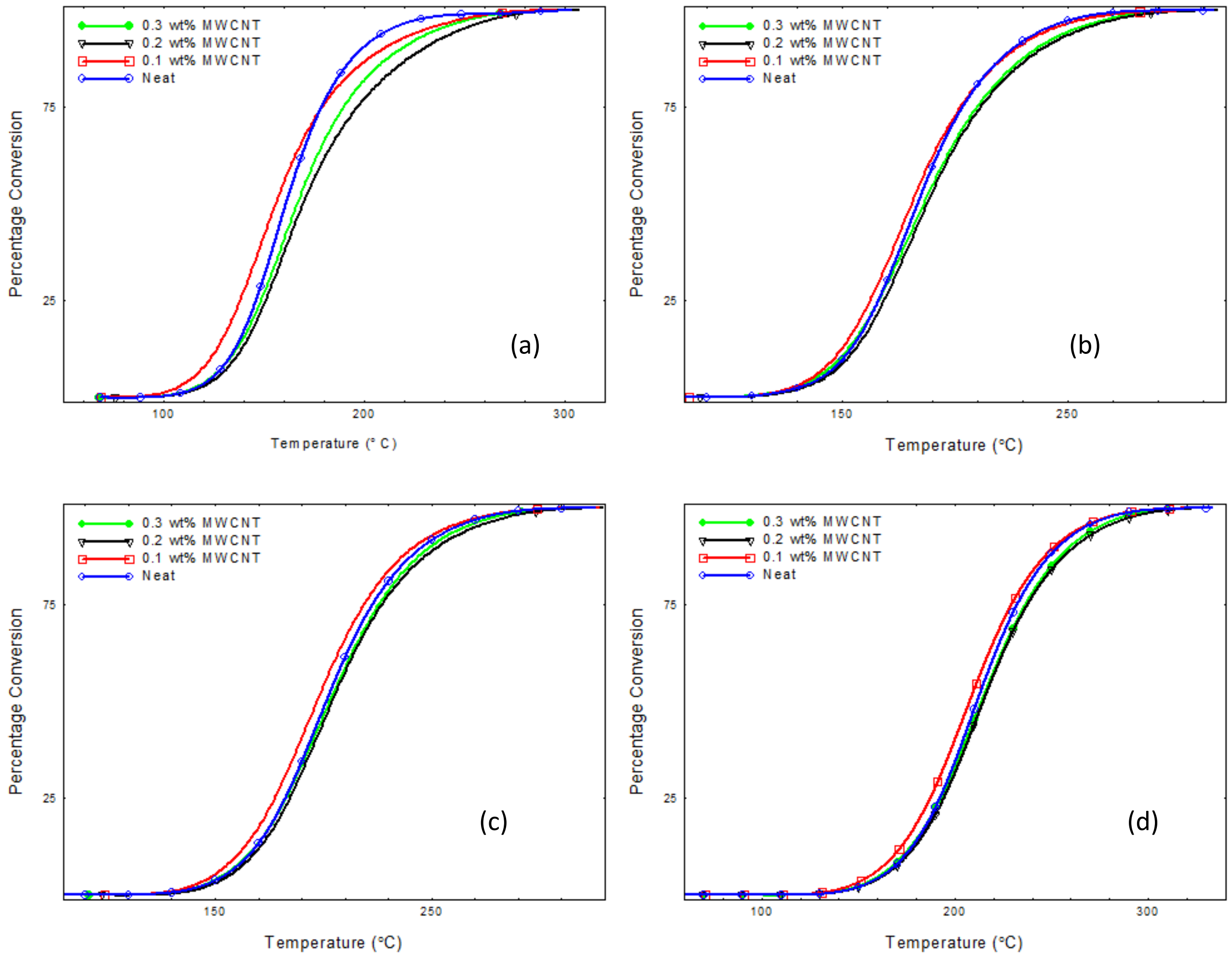


Fig. 12. Degree of conversion as a function of temperature for various composites at different heating rate (deg/min) (a) 2 (b) 5 (c) 10 and (d) 15

The activation energy of a cure reaction represents the potential barrier of the cure reaction. For better understanding of cure behavior of DGEBF/MWCNT/DETDA systems, study on activation energy is contributory. During a cure reaction, reaction rate (dα/dt) as a function of time (t) was calculated from the heat flow in DSC dynamic scan by using equation (1):

$$d\alpha/dt = dH/dt/ = k(T)f(\alpha) \text{.......................}(1)$$

Where, T is the temperature, f (α) is the reaction model and k (T) is the rate constant which follows Arrhenius equation as in equation (2):

$$K\ (T) = A \exp\ (-E_a / RT) \text{.............................}(2)$$

Where A is the pre exponential factor, Ea is the activation energy and R is the gas constant.

From equation (1) and equation (2) we get,

$$d\alpha/dt = A \exp(-E_a / RT)f(\alpha)\text{......................}(3)$$

By taking natural logarithm in both side,

$$\ln(d\alpha/dt) = \ln(Af(\alpha)) - E_a / RT\text{……………}.(4)$$

Thus the plot of ln(dα/dt) versus (1/T) at the same α from a series of DSC thermograms at different heating rates would provide a straight line where the slope allows to determine the activation energy, E_a . Figure 13 represents the curves of ln(dα/dt) versus (1/T) for neat epoxy and MWCNT/epoxy nanocomposites at different values of α (α = 0.05, 0.1, 0.15, 0.2,........0.90, 0.95 and 1). Activation energy (E_a) as a function of degree of cure (α) is plotted in Figure 14 for both neat and nanophased epoxy. Slope of the curve in Figure 13 was used for calculating the activation energy using equation (4). As can be seen from the Figure, CNTs can act as a catalyst when added at very low concentration like 0.1

wt% and lowers the activation energy of the system. On the other hand, activation energy is higher for higher percentage of CNTs like 0.2, 0.3 wt% loading, which indicates that higher concentration of carboxyl groups on MWCNT surface hinders the curing process of the epoxy system. In other words, higher CNT loading contributes in increasing the activation energy which indicates that more carboxyl groups on the surface of MWCNTs might hinder COOH- epoxide reaction because of the electrostatic repulsion among the carboxyl groups obstructing the easier reaction path and effectively enhancing the influence of steric hindrance caused by the MWCNTs in the cure reaction [39]. The higher content of carboxyl groups significantly accelerates the interaction between CNTs and epoxy and thus, facilitates the occurrence of diffusion controlled vitrification process.

For all epoxy system, activation energy increases significantly beyond 80% conversion that is, α =0.80 can be considered as the gel point of DGEBF/DETA system as shown by Qui et al. [38] for TGDDM/DDS system.

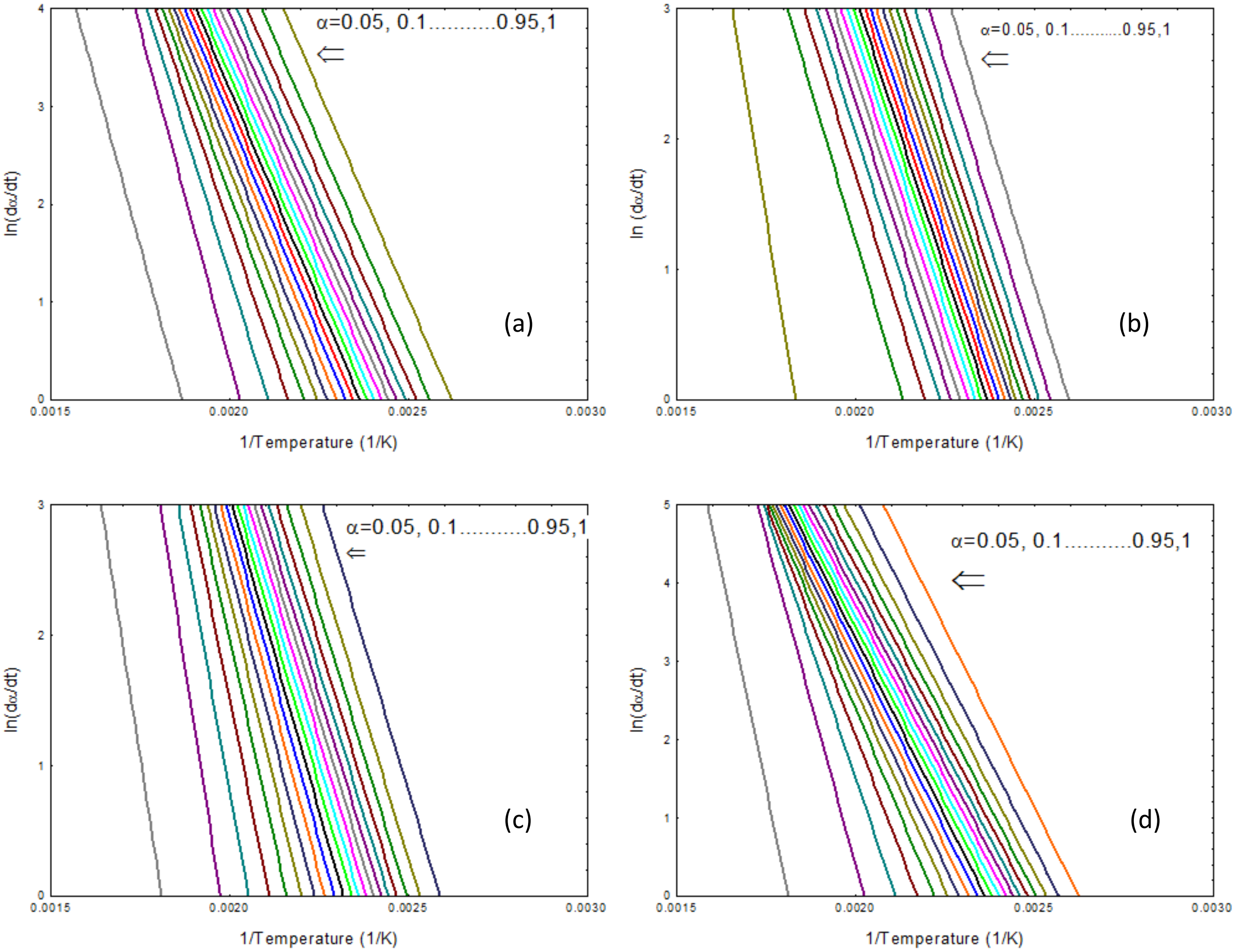


Fig. 13. Plot of ln (dα/dt) versus (1/T) for (a) neat (b) 0.1 wt% (c) 0.2 wt% and (d) 0.3 wt% composites

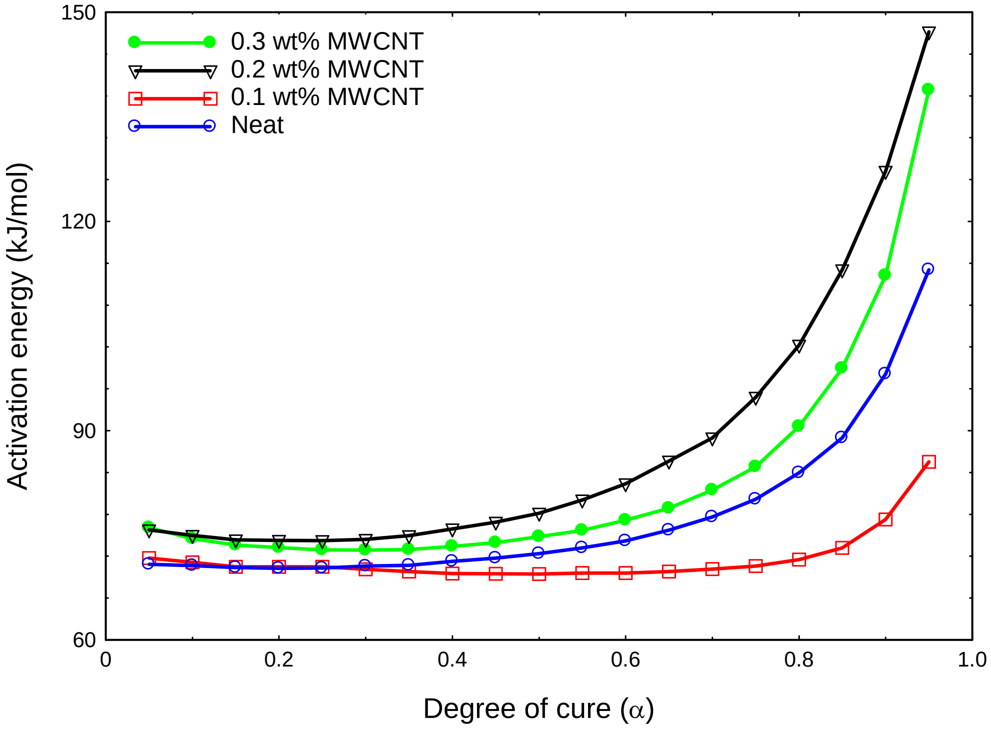


Fig. 14. Activation energy as a function of degree of conversion for various composite systems

In conclusion, it was found from DSC dynamic scan that addition of CNTs initiated the curing reaction at lower temperature but did not change the auto catalytic curing mechanism of the epoxy system as evident by their sigmoidal shaped curve of percentage conversion versus temperature. Also, CNTs significantly reduced the total heat of reaction and overall degree of cure of epoxy system understandably by hindering the molecular movement of polymer chain. Additionally, from the plot of percentage conversion and activation energy, it is clear that very low loading of CNTs (0.1 wt%) can act as a catalyst and thus, facilitates the cure reaction but higher loading of CNTs (0.2 and 0.3 wt%) have retarding effects on the cure reaction, might be due to the higher specific surface area of CNTs causes higher electrostatic repulsion and greater steric hindrance on cure reaction.

So for infusing higher percentage of CNTs in epoxy polymer, post curing is necessary to get higher degree of cure.

CHAPTER VI

STUDIES ON MWCNTS/EPON 862 NAMOCOMPOSITES

MWCNTs have been considered as potential reinforcements in epoxy polymer since their discovery in 1991. Because of their outstanding properties CNTs have found their way in polymer composite imparting excellent enhancements in mechanical and thermal properties. Due to the inherent inactive nature of CNTs to react with epoxy resin, chemical functionalization of CNTs finds its way to increase chemical interaction with polymer matrix. Functionalization alters the CNT morphology and provides an abundance of reactive sites, thus increasing the possibility of crosslinking with the polymer matrix. Mechanical and thermal response of various CNT reinforced composites have been discussed in detail in this chapter.

Flexural Properties

Flexural tests were performed to evaluate the bulk strength and stiffness of neat and nanophased epoxy composites. Typical stress-strain behavior of neat and nanophased composites has been shown in Figure 15. Significant non-linearity was observed in stress-strain curve. Functionalization not only improves the interaction and dispersion of CNTs but also improves the flexural properties of nanocomposites as shown in Figure 15. Due to the higher aspect ratio of MWCNTs, they can effectively prevent crack generation and crack propagation in the matrix and thus contribute in improving the strength and stiffness of nanophased composites.

The direct impact of functionalized nanotubes on the mechanical properties of epoxy composite has been evaluated by the measurements of flexural strength and flexural modulus. The average properties obtained from this test is summarized in Table 5. It can be seen from the table that 0.1 wt% CNT reinforced epoxy samples showed maximum improvement in flexure strength by 14% and flexure modulus by 33 % for 0.1 wt% samples. These improvements in strength and modulus might be attributed to the good dispersibility and CNT/epoxy interfacial interaction due to the presence of small amount of CNTs in the matrix. Both strength and modulus decreased for higher percentage of CNTs

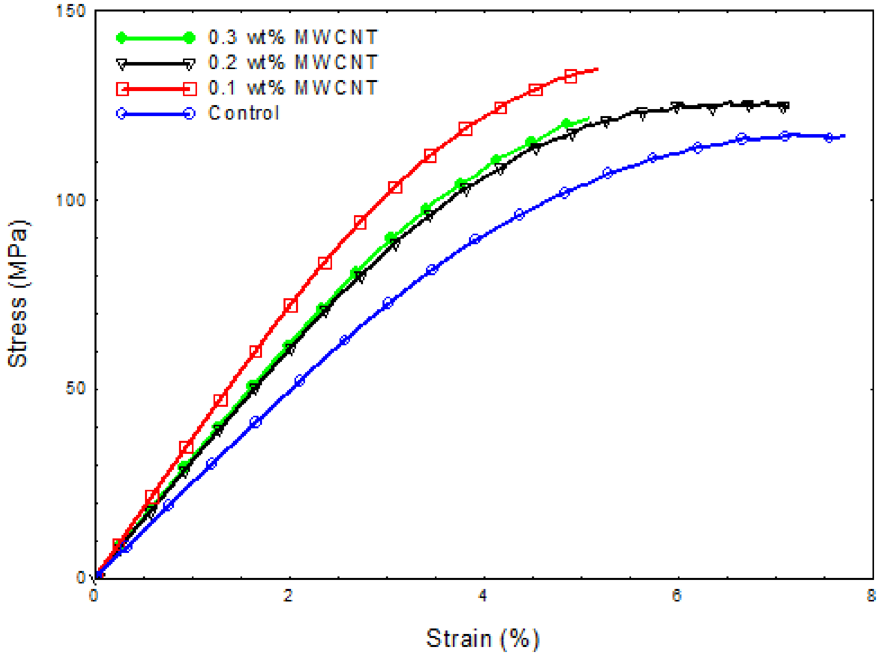


Fig. 15. Typical stress-strain curve obtained from Flexural response of various concentrations of MWCNTs

which might be due to the tendency to form agglomerates at higher loading as can be seen in SEM micrograph.

Figure 16 shows the SEM micrograph of neat and nanophased composites. Nanophased samples showed much rougher surface due to the strong interfacial interaction of CNTs with the polymer matrix compared to neat epoxy samples. Presence of small agglomerates was evident in 0.2 wt% samples and that for 0.3 wt% samples was higher in number and density. On the other hand, much uniform dispersion of CNTs was observed for 0.1 wt% samples.

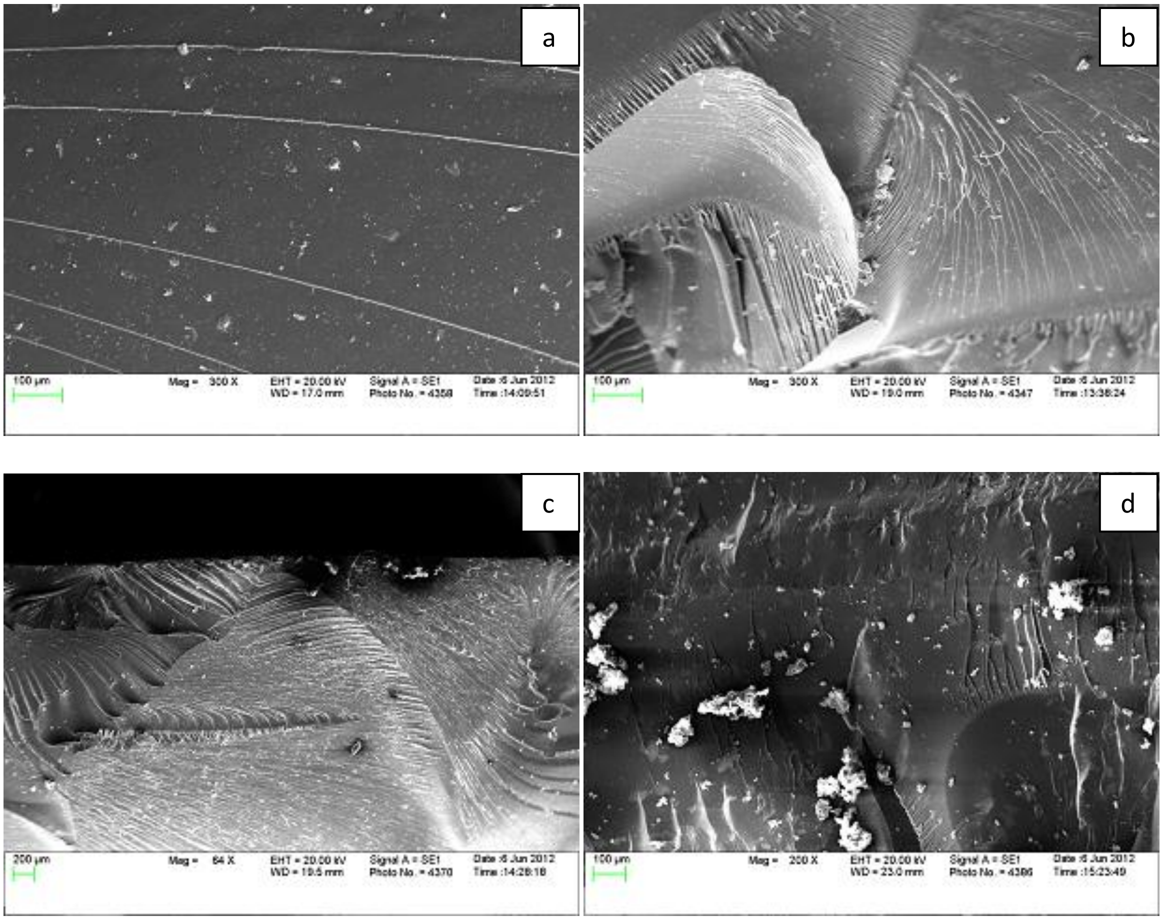


Fig 16. Fracture surface of neat and nanophased samples (a) neat (b) 0.1 wt\% (c) 0.2 wt\% and (d) 0.3 wt\% CNT added samples

Dynamic Mechanical Analysis (DMA)

A dynamic mechanical analysis was performed to obtain the temperature dependent properties of composite samples, such as the storage modulus, loss modulus and tanδ. These dynamic properties determine the amount of energy stored in the composites as elastic energy and the amount of energy dissipated during mechanical strain, which are highly influenced by the existence of the fillers: their geometrical characteristics, volume fractions, dispersion in the matrix and adhesion between filler and the matrix [25]. Variations of storage modulus as a function of temperature for several composites have been plotted in Figure 17. As can be seen from the plot, addition of very small amount of CNTs can significantly improve the storage modulus compared to the pure epoxy polymer. Storage modulus increased for 0.1 wt% CNTs and then decreases gradually for higher percentage of CNTs. More specifically, maximum of 15% improvement in storage modulus was observed for 0.1 wt% CNT reinforced sample. Improvement in storage modulus can be attributed to the better dispersion and interfacial interaction of CNTs with epoxy matrix. Enhanced interfacial interaction reduced the mobility of local polymers around the CNTs and thus increasing the thermal stability at elevated temperature. These behaviors are also pronounced in rubbery region where storage modulus was also much higher for CNT infused samples. On the other hand, increased percentage of CNTs creates greater chances of forming agglomerates and lowers the properties of composites. Due to the van der waals force and coulomb attraction among CNTs, they have a strong tendency to agglomerates and also re-agglomerates at the earlier stage of curing at high temperature where the resin viscosity goes down enough to cause re-agglomeration of dispersed CNTs .These agglomerated CNTs can act as stress raiser and detrimental to composite properties. Table 5 summarized the data collected from the dynamic mechanical analysis including storage modulus, loss modulus and glass transition temperature for all composites samples.

Table 5. Mechanical and Thermal Properties of MWCNT/Epoxy Composites Samples

	Sample Specification			
Property	Control	0.1wt% MWCNT	0.2wt% MWCNT	0.3wt% MWCNT
Flexural strength(MPa)	117.98±1.03	133.53±2.5	125.63±3.3	118.2±3.9
Difference with control (%)	-	+13.18	+6.48	+1.86
Flexural Modulus (GPa)	2.7±0.3	3.6±0.1	3.16±0.3	3.39±0.4
Difference with control (%)	-	+33.33	+17.04	+25.55
Storage modulus$_{35}$ (MPa)	2500.5±83	2869.33±35	2628.5±85	2320±79
Difference with control (%)	-	+14.75	+5.11	-7.2
Loss modulus (MPa)	280.6±0.9	320.6±0.3	298±0.7	250.6±1.3
Difference with control (%)	-	+14.24	+6.2	+10.69
Tg (°C)	126.21±0.8	132.41±1.3	131.3±1.8	124.22±0.93
Decomposition Temperature (°C)	413.6±2	414.64±1.17	413.93±1.5	411.1±1.4
CTE ($10^{-6}/°$ C)	73.61±7.6	70±8.5	78.7±7	73.6±7.96
Difference with control (%)	-	-4.9	+6.93	0

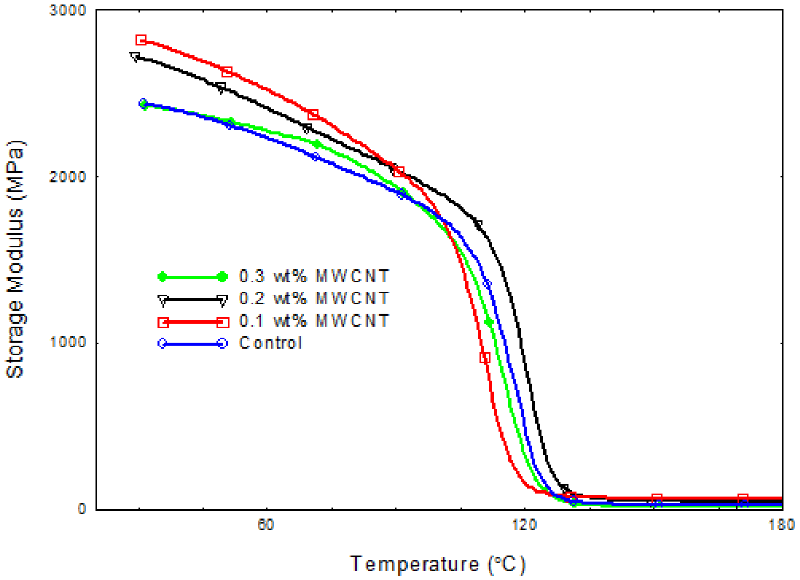


Fig. 17. Variation of storage modulus as a function of temperature various composite samples

Figure 18 shows the variation of loss modulus as a function of temperature for both neat and nanophased systems. As can be seen from Table 5, addition of CNTs enhanced loss modulus, maximum of 15% for 0.1 wt% CNT samples again because of their improved interfacial interaction with the epoxy matrix.

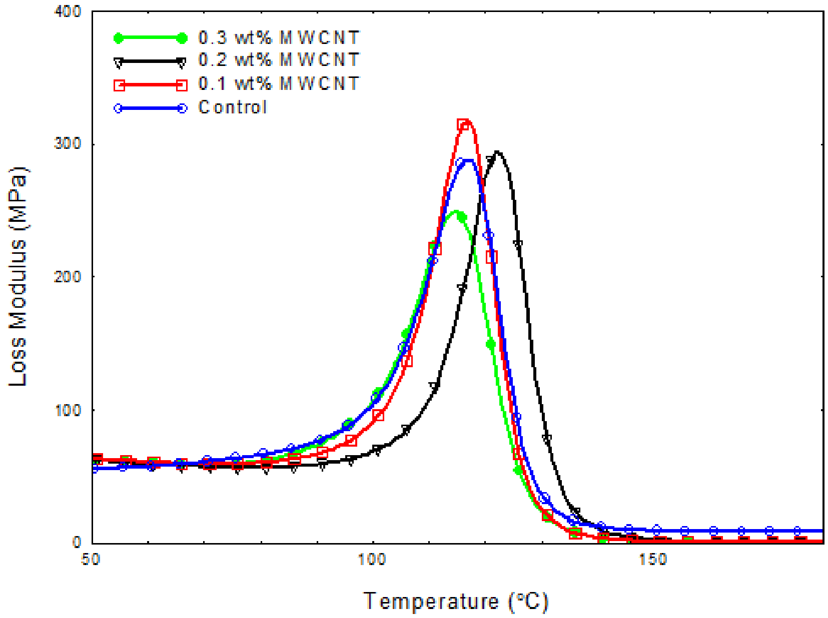


Fig. 18. Variation of loss modulus as a function of temperature various MWCNTs incorporated samples

Glass transition temperature (T_g) is one of the most important properties of nanocomposite measured as the temperature corresponding to the peak of tan δ curve whereas tanδ is calculated by dividing the loss modulus by the corresponding storage modulus. Figure 19 represents the variation of tanδ as a function of temperature for neat and nanophased composites where determination of T_g is based on the onset of sharp drop of tanδ. T_g for neat epoxy was 124°C. Addition of CNTs in epoxy shifted the peak to a higher temperature and maximum of 8°C improved T_g was observed for 0.1 wt% CNT samples as can be seen in Table 5. The presence of CNTs hindered the segmental motion of polymer chains in composites. Peak height of tanδ curves for CNT infused composites was consistently lower than neat epoxy. This phenomenon can be attributed to the fact that functionalized CNTs promoted the cross linking reactions of epoxy (as shown from DSC dynamic scan in previous chapter) and hardener and effectively discouraging the molecular

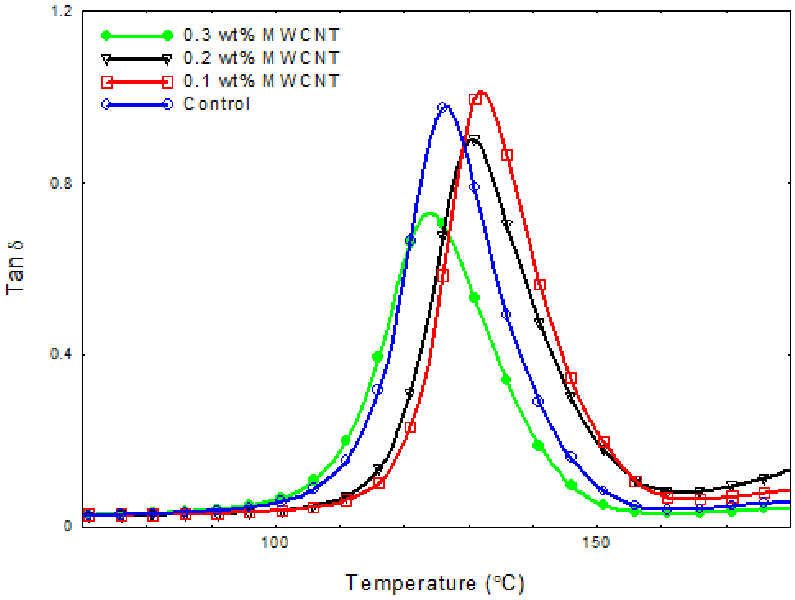


Fig. 19. Variation of tanδ as a function of temperature various concentrations of MWCNTs

movement of polymer chains. Also, the covalent bonds between carboxyl and epoxide groups enhanced the efficiency of load transfer from matrix to fillers, resulting in an increase in loss modulus due to more energy loss and dissipation in composites.

Glass transition temperature of polymer composite is directly related to the cross linking density of the corresponding system. Cross linking density can be calculated from the rubbery modulus using the following equation: λ = G/RT

Where, λ = Cross linking density, G= Rubbery modulus, R= Universal gas constant, T= Temperature (175°C).

Variation of cross linking density with the concentration of CNTs is shown in Figure 20. As can be seen from the Figure, cross link density was maximum for 0.1 wt%

CNT added samples, hence T_g is much higher than the other. This increased crosslinking density contributed in increasing the T_g significantly for post cured samples.

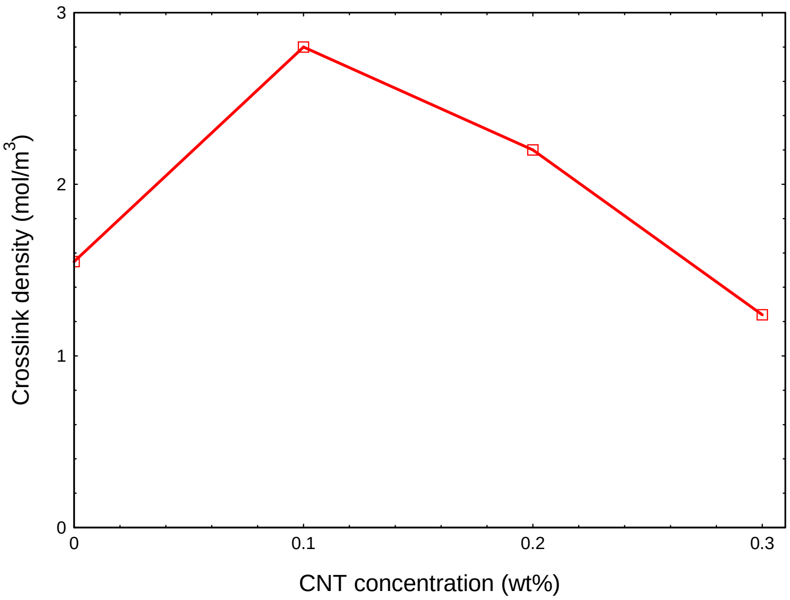


Fig. 20. Variation of crosslink density as a function of CNT percentage various composite samples

These results confirmed the improved interfacial interactions between the functionalized CNTs and epoxy matrix.

Thermogravimetric Analysis (TGA)

TGA was performed to investigate the thermal decomposition characteristics of epoxy nanocomposites. Figure 21 shows the variation of decomposition temperature (T_d) as a function of CNT percentage. The temperature corresponding to the peak of derivative weight curve was pointed as the true decomposition temperature of composite samples. Decomposition temperature increased slightly upon addition of CNTs, in other words

CNTs can improve the thermal stability of nanocomposites. More specifically, maximum of 8°C improvement in T_d was observed for 0.1 wt% CNT incorporation. Usually the interface of CNT and polymer matrix is affected by the temperature. CNTs prevent the segmental motion of polymer chain and increase the thermal stability of nanocomposites. Further addition of CNTs (0.2 or 0.3 wt%) pushed down the Td close to neat samples. This might be due to the tendency of formation agglomerates at higher percentage of CNTs. Agglomerates have hardly any effect on obstructing the movement of polymer chain and hence, on thermal stability. Variation of decomposition temperature with CNT percentage has been summarized in Table 5.

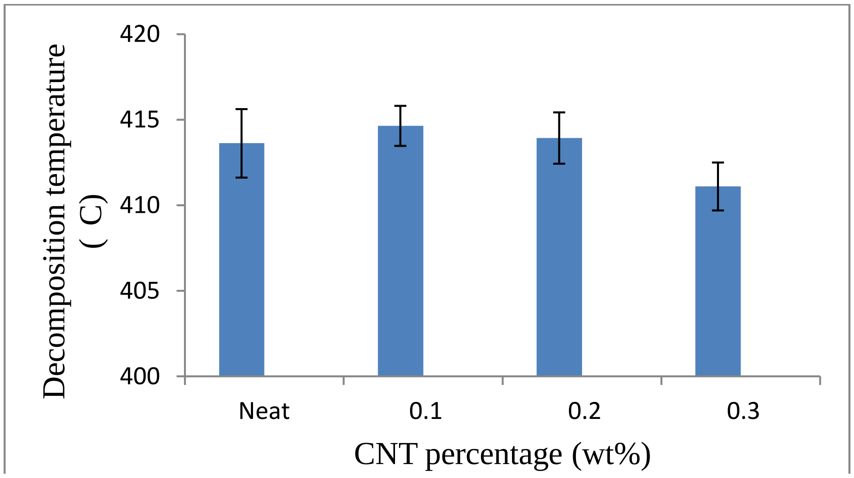


Fig. 21. Variation of decomposition temperature as a function of CNT

Based on the mechanical performance, TGA and DMA analyses, TMA was performed on neat and nanophased epoxy samples to investigate thermal response as well as thermal stability based on coefficient of thermal expansion (CTE). Typical curve of dimension change as a function of temperature is shown in Figure 22 composite samples. The coefficient of thermal expansion of the composites was measured from the dimensional change. Since the dimension change was measured in thickness direction of the sample, the slope of these curves represents the CTE in that particular direction. The linear thermal expansion was investigated in the region before the glass transition temperature (T<Tg) that is glassy region. As can be seen from the Figure, dimension of

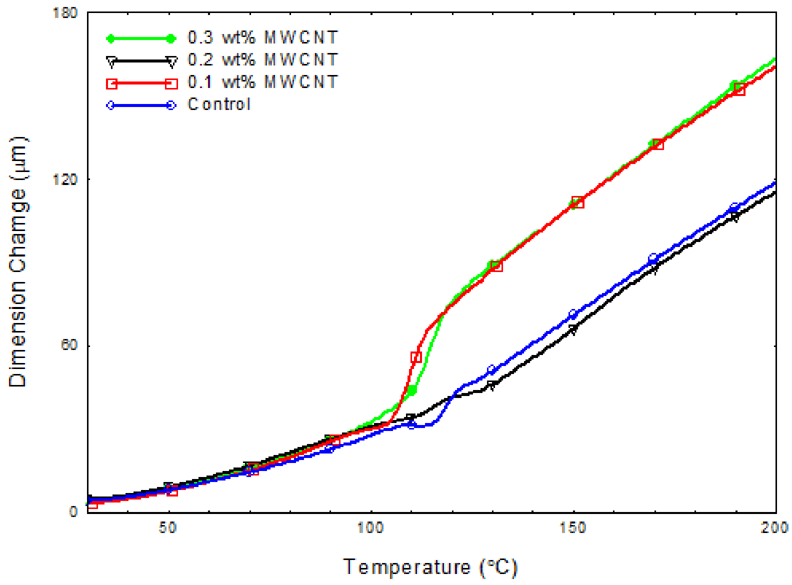


Fig. 22. Variation of dimension change as a function of temperature for various concentrations of MWCNTs infused composites

Samples changed gradually with temperature. Addition of CNTs had only a slight effect on thermal stability. Maximum of 5% reduction in co-efficient of thermal stability was observed for 0.1 wt% CNT added samples. In other cases of CNT incorporation thermal stability didn’t change much. Even this smaller decrease in CTE as well as improvement in thermal stability is attributed to the higher crosslink density due to the addition of CNTs. The crosslinked CNTs hindered the movement of adjacent polymer chain and resulted in decreased dimension change and increased thermal stability with temperature.

Overall, well dispersed CNTs are able to significantly affect the properties of epoxy matrix because of their excellent load transfer capability and higher aspect ratio. Functional groups on the surface not only help in dispersing CNTs in the matrix but also create a scope of huge interfacial interaction with the matrix which attributes the enhanced properties of nanocomposites.

CHAPTER VII

STUDIES ON CARBON FIBER REINFORCED EPON862/MWCNTS COMPOSITES

Effect of very low concentration (0.1, 0.2 and 0.3 wt%) of carboxyl functionalized MWCNTs on flexural and thermal properties of multiscale carbon/MWCNT/epoxy composites were investigated. CNTs act as bridging elements for epoxy resin and carbon fiber due to the presence of functionalized groups on the surface. Mechanical and thermal properties improved significantly due to the presence of CNTs.

Matrix Digestion Test

Fiber volume fraction (V_f) and void fraction (V_o) calculated from matrix digestion test of CFRP composite with and without nanotubes are summarized in Table 6. As can be seen from the table, with the addition of increasing concentration of MWCNTs, fiber volume fraction decreased but the void fraction increased due to the increased viscosity. The overall fiber volume fraction was in the range of 63-66.5% and void fraction was in the range of 4.2-6.5%. Calculated fiber volume fraction is higher than the theoretical calculation which is around 50% [13]. This might be due to highly dense weave pattern of carbon fabric which does not facilitate easy infiltration of resin into them. Moreover, the pressure applied during hot press also played an important role in determining the fiber volume fraction. Sundarisman investigated effect of compressive pressure applied during composite fabrication along with the fiber volume fraction on the mechanical properties of carbon/epoxy laminated composite [65]. He showed that, higher compressive pressure reduces void content in laminate with flexural properties being optimized at around 63% fiber volume, which is approximately the same obtained in our current study.

Table 6. Mechanical and Thermal Properties of Carbon/MWCNT/Epoxy Composites

	Sample Specification			
Property	Control	0.1wt% MWCNT	0.2wt% MWCNT	0.3wt% MWCNT
Fiber volume fraction (v_f)(%)	66.33±1.41	65.11±2.03	65.26±1.92	64.19±2.32
Void fraction (v_o)(%)	4.24±0.33	4.55±0.49	5.27±0.29	6.50±0.41
Flexural strength (MPa)	681.39±36	740.31±25	801.18±27	766.77±32
Difference with control (%)	-	+8.65	+17.58	+12.53
Flexural Modulus (GPa)	47.24±3.97	54.44±1.5	63.90±4	62.67±2
Difference with Control (%)	-	+15.24	+35.27	+32.66
Tensile Strength(MPa)	714.12±22.5	815.67±18.5	907.48±34.06	872.49±33.4
Difference with Control (%)	-	+14.22	+27.07	+22.14
Young's Modulus (GPa)	31.14±2.6	32.13±0.83	37.02±1.8	35.68±1.94
Difference with Control (%)	-	+3.18	+18.88	+14.58
Compressive Strength(MPa)	220.63±10.6	325.35±23.18	344.07±17.96	333.1±18.27
Difference with Control (%)	-	+43.8	+52	+47.35
Compressive Modulus (GPa)	72.92±3.07	88.01±3.68	93.55±3.21	91.25±4.97
Difference with Control (%)	-	+20.55	+28.29	+25.1
Storage Modulus$_{35}$ (MPa) Difference with Control (%)	18572.67±57 7+10.88	20592.76±306 +28.97	23953.29±662 +23.40	22919.06± 798
T_g (°C)	131.07±0.64	145.11±0.59	148.56.77	155.09.93
Difference with Control (%)	-	+10.71	13.34	+18.33
CTE (10^{-6}/°C)	27.80±2	26.55±0.9	23.70±1.4	25.13±1.96
Difference with Control (%)	-	-4.51	-14.74	-9.60

Flexure Properties

Flexural tests of composite samples were performed to evaluate bulk strength and stiffness of carbon/MWCNT/epoxy laminated composite. Figure 23 (a) shows typical stress-strain curves of tested composite samples. As can be seen from the Figure, specimen showed linear flexural behavior until stress reached its peak value beyond which there was a gradual decrease until failure which is an indication of load transfer from the failed area towards the unaffected zone.

Summary of the flexure test results is also shown in Table 6. Both flexural strength and modulus are compared between nanophased and control system, where flexural strength of each composite type was determined as the peak stress of corresponding stress-strain curve and flexural modulus was calculated using the slope of the linear portion of the corresponding stress-strain curve and geometric features like span, width and thickness of sample [Figure7.1 (a)]. Figure 23 (b) shows comparison of both flexural strength and moduli of different composite system. As can be shown from Table 6, flexural strength improves moderately but the flexural modulus enhances significantly due to addition of nanotubes. Addition of 0.2 wt% CNT in carbon/epoxy composite increases flexural strength by 17.58 % and flexural modulus by 35.27%. For multiscale carbon/MWCNT/epoxy composites, it was postulated that matrix dominated properties will be significantly affected by the nanoscale reinforcement. Increase in flexural properties is attributed to reinforcement effect of carbon nanotubes in z direction, as the flexural properties are matrix dominated. Better dispersion of CNTs and enhanced interfacial interaction between CNTs and the matrix enable effective load transfer from the matrix to the carbon fiber, leading to better flexural strength and flexural modulus of carbon/MWCNTs/epoxy composites up to 0.2 wt% loading [4, 66–69].

A slight drop in flexural strength and flexural modulus was observed for 0.3 wt% loading of CNTs. This drop in strength and modulus might be attributed to the tendency of MWCNTs to form agglomerates. At higher loading, CNTs got closer to each other in the matrix; hence strong attractive force acting among themselves might have lead them to form agglomerates. These agglomerates can act as stress risers and also increase the free volume (by creating voids) [66] in the matrix.

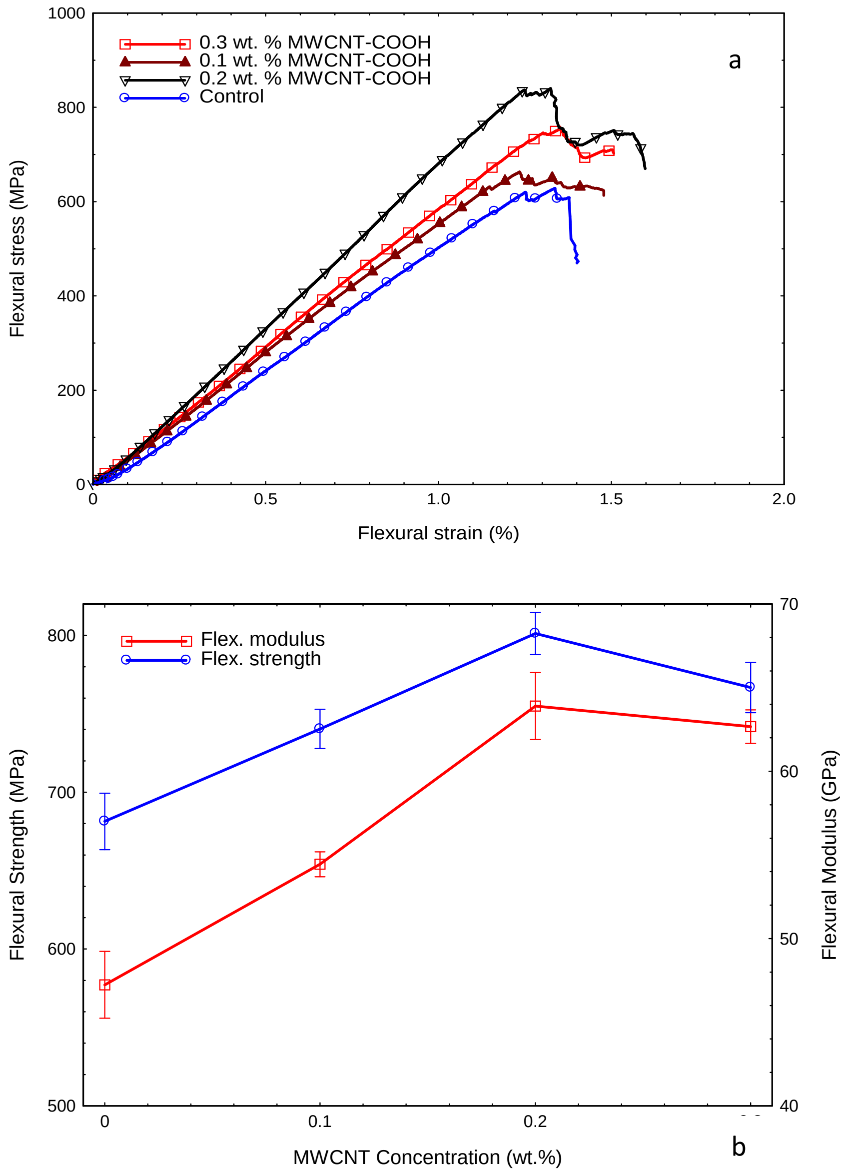


Fig. 23. (a) Typical stress-strain curve obtained from Flexural response of different composites (b) variation in flexural properties with the concentration of MWCNTs

This phenomenon may contribute to matrix failure and hence, lower mechanical properties. At the same time, higher concentration of nanotubes in the resin may increase the resin viscosity significantly and prohibit proper wetting of carbon fiber with the resin, as it became difficult for the viscous resin to conform with fiber preform and infiltrate the inter-filament spaces which in turn, resulted in poor interfacial bonding between the carbon fiber and the matrix [3, 69-71]. Slipping between the shells of MWCNTs due to the weak van der Waal's force existing between individual graphene shells [66], mismatch between the material properties of neighboring plies with different orientation due to applied compressive force [65, 72] along with the tendency of forming agglomerates and voids have all been reported to cause reduced mechanical properties of multiscale composites.

The fracture morphology of the control, 0.2 and 0.3 wt% MWCNTs infused CFRP composite samples are presented in Figure 24. Figure 24(a) and 24(b) represent single fiber of carbon/epoxy and multiscale carbon/ 0.2 wt% CNT/ epoxy composites respectively. As can be seen from the Figure, carbon fiber of 0.2 wt% CNT sample was associated with considerable amount of resin as compared to control sample which is a good indication of better interfacial interaction between the matrix and the fiber through MWCNTs. Figure 24(c) and 24(d) represent the fracture surface of control sample. Figure 24 (c) represents the region where a bunch of fibers have been pulled out and Figure 24 (d) represents fiber pull out and fiber-matrix debonding phenomenon due to the weaker interfacial interaction between carbon fiber and the matrix. The fracture morphology of 0.2 wt% and 0.3 wt% nanotubes infused samples are presented in Figure 24 (e) and 24 (f) respectively. For 0.2 wt% samples, the carbon fibers were held together in a bundle by epoxy resin. The phenomenon of fiber pull out and extensive fiber-matrix debonding that was seen in control sample [Figure 24 (d)], reduced significantly in case of 0.2 wt% sample. This might be attributed to the good dispersion and better interfacial

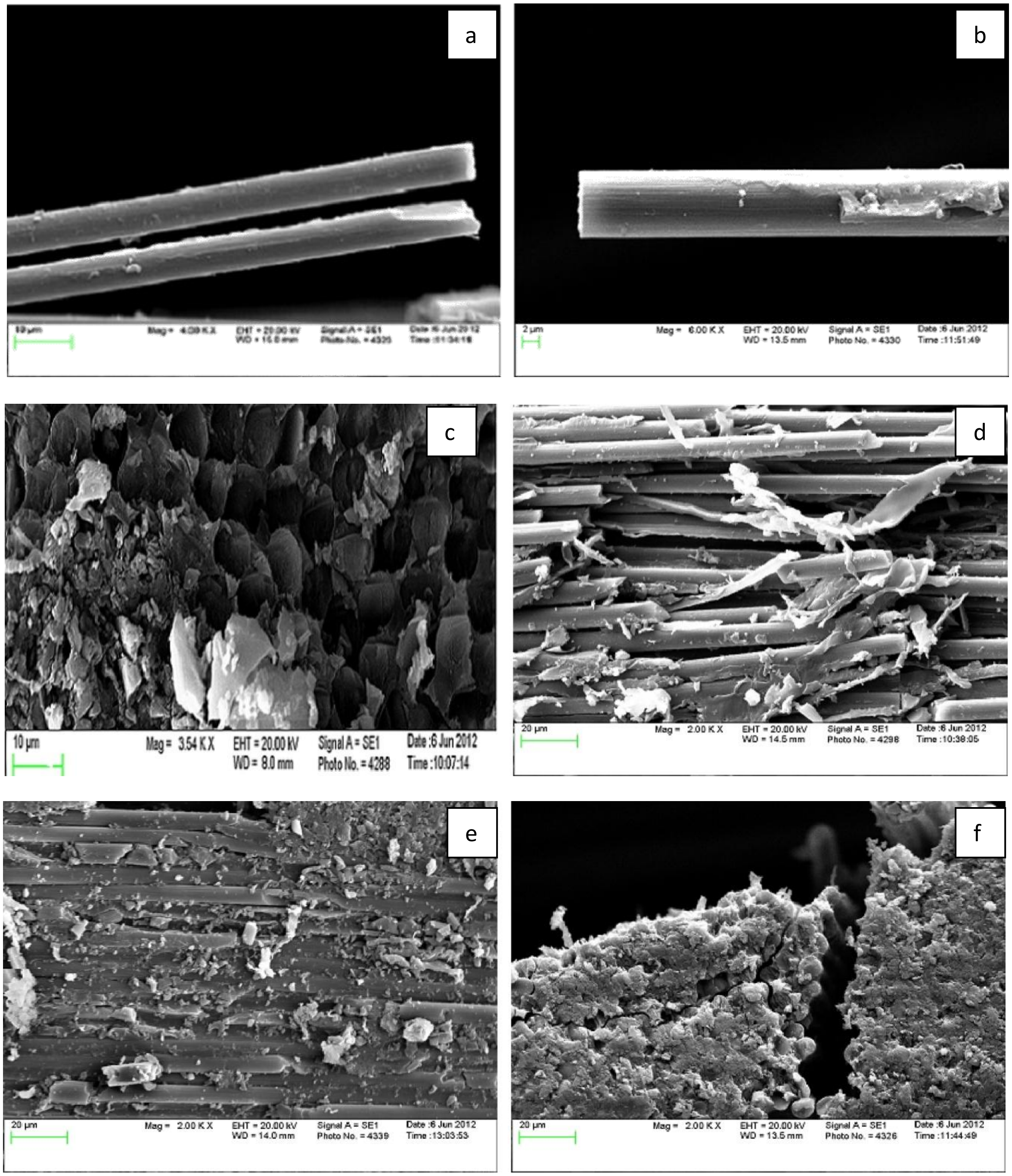


Figure 24. SEM micrographs obtained from fracture surface of fractured samples: (a), (c) and (d) carbon /epoxy composite; (b) and (e) carbon/0.2 wt% MWCNT/epoxy composite; (f) carbon/0.3 wt% MWCNT/epoxy composite

bonding between carbon fiber and matrix through the functionalized MWCNTs. When an external load was applied, the load transferred to the carbon fiber was reduced because part of the load may have been carried by the well dispersed and well adhered nanotubes. Ultimately, fibers pull out or fiber-matrix debonding was significantly reduced. In composites with 0.3 wt% CNT as shown in Figure 24(f), fibers were well bonded with the epoxy matrix but the phenomenon of matrix cracking was evident. This might be due to the presence of small agglomeration and voids (as already calculated from matrix digestion test) in the epoxy matrix resulting in weak bonding between the matrix and the fiber phase and ultimately matrix cracking.

Tension Test

The static tensile properties of the laminated composites were also measured and the typical room temperature tensile Stress-Strain curves are shown in Figure 25 (a). As shown in Figure, tensile stress increases almost linearly with strain for all composites. To be specific, CNT addition in CFRP composite demonstrated brittle tensile behavior, irrespective of CNT concentration. The reduction in fracture strain due to the addition of CNTs is attributed to the impediment of molecular movement and formation of strong cross-link network due to the better dispersion and strong interfacial interaction between CNTs and the epoxy matrix [42]. On the other hand, tensile strength and Young's modulus were found to improve significantly with CNT concentration which is in good agreement with results of Rana et al. [73] found for carbon/epoxy/f-XD-CNT composite. An improvement of 33 % in tensile strength and 28 % in Young's modulus was observed for 0.2 wt% CNT loading. Tensile strength of each composite was measured as the peak stress in the corresponding stress-strain curve and Young's modulus was calculated from the slope of initial portion of corresponding stress-strain curve. Variation of tensile properties (tensile strength and elastic modulus) with respect to the percentage of CNTs is shown in Figure 25 (b).

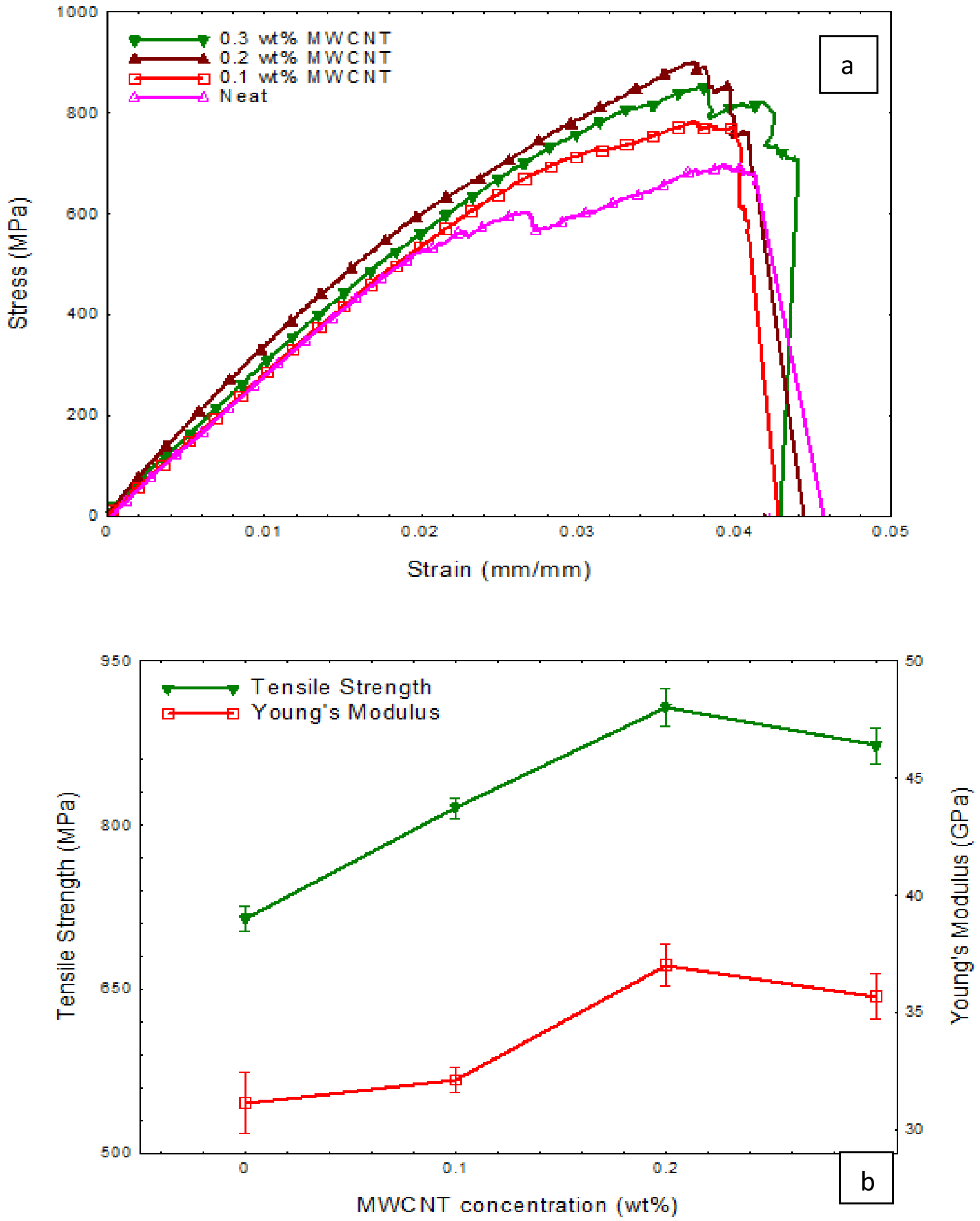


Fig. 25. (a) Typical stress-strain curve obtained from tensile test (b) variation in tensile strength and Young's modulus with the percentage of MWCNTs

Further increase in CNT percentage to 0.3 wt% lead to slightly decreased tensile properties, which may be due to the tendency to form agglomerates of CNTs when they get closer to each other. Agglomerates ultimately result in weaker interfacial interaction between the carbon fiber and epoxy matrix. Variation of tensile properties with CNT percentage is summarized in Table 6.

Consistency of experimental data can further be evaluated by calculating coefficient of variation (COV) based on average tensile strength of each batch of samples. COV for neat sample is around 3.17 %. On the other hand, not only the tensile strength increased for 0.1 and 0.2 wt% CNT but also COV reduced remarkably (2.78 and 2.87% respectively) for both composites. This observation indicates that this composite has more consistent tensile properties than conventional CFRP composite. Also, for 0.3 wt% samples though the tensile strength was higher than neat samples, COV was much higher (3.87%) than neat which indicates the inconsistency in experimental data might be due to the agglomerations formed randomly all over the matrix.

Figure 26 represents the fracture morphology of conventional CFRP and various CNT reinforced three phase composite obtained from tensile test. Figure 26 (a) shows the fracture surface of neat composite where clear debonding at fiber/matrix interface is visible due to the weaker interfacial interaction of fiber and matrix. Smooth fiber surface with no matrix was observed. Addition of CNTs can contribute in improving fiber/matrix interfacial interaction which can be seen by the strong adherence of carbon fibers to the matrix in Figure 26 (b) than pure carbon/epoxy composites. Presence of random agglomerates at higher loading (0.3 wt%) causes weaker inter face in some places but stronger interface between carbon fiber and epoxy matrix in other places introduced ’pull out’ phenomenon of fiber as indicated in Figure 26 (c). Presence of agglomerates causes poor fiber wetting at that place and eventually results in premature failure. Overall, optimum amount of CNTs is capable of enhancing fiber matrix interfacial strength and the mechanical toughness of the matrix due to carbon-MWCNT-epoxy interfacial covalent bonding [47, 74].

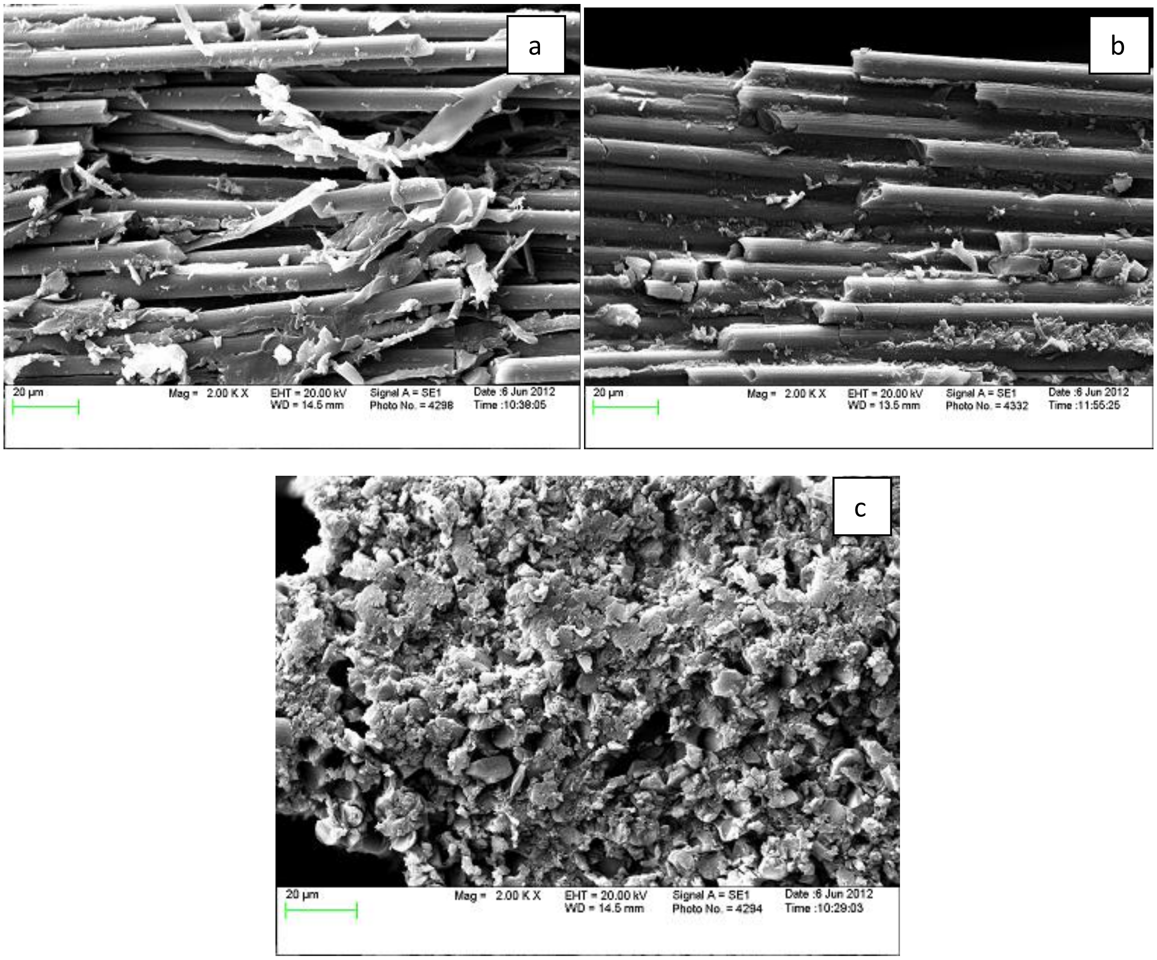


Fig. 26. Fracture surface of failed samples obtained from tension test (a) neat (b) 0.2 wt% CNT and, (c) 0.3 wt% CNT added samples

Tensile properties are basically fiber dominated and it has been shown in earlier study [42] that it changes moderately with the change in fiber volume fraction. In this study it has been shown in Table 6 that there exists a very small difference among the fiber volume fraction of various laminated composite. Therefore, it is believed that the difference in tensile properties is solely attributed to the CNT concentration of CFRP composite.

Quasi Static Compression Test

Quasi-static compression test was performed on neat and 0.1-0.3 wt% CNT incorporated composite samples to measure compressive strength and stiffness. Typical stress strain curve obtained from quasi static compression test is shown in Figure 27(a). Compressive strength and modulus improved significantly due to the addition of CNTs. Both the compressive strength and modulus improved by 52% and 29% respectively for 0.2 wt% CNT added composite compared to conventional CFRP composite. The remarkable improvement in compression properties is attributed to the enhanced matrix properties and better interfacial interaction between carbon fiber and epoxy matrix which originated from the increased residual stresses or interface pressure of epoxy at carbon fiber surface due to the presence of CNTs as reported by Rana et al. [73] in case of CNF incorporated carbon/epoxy composite. Further improvement in compression strength was not possible by adding 0.3 wt% CNTs in CFRP composite which might be due to the fact that the selected dispersion method was unable to effectively disperse 0.3 wt% CNTs in the matrix. Heterogeneous dispersion resulted in agglomerates deteriorated the mechanical properties of three phase composite. Compressive properties are summarized in Table 6.

A close look to the stress-strain curve (Figure 27(a)) reveals that the failure was sudden rather than progressive. This sudden drop indicates an increasing deformation in mid plane where ultimate failure happened [75]. Also, if we observe the slopes of the stress strain curves, slope of curves increases due to the addition of CNTs in CFRP composite. This observation indicates that addition of CNTs in carbon/epoxy composite makes it stiffer than the neat. This is due to the fact that interaction of CNTs with the

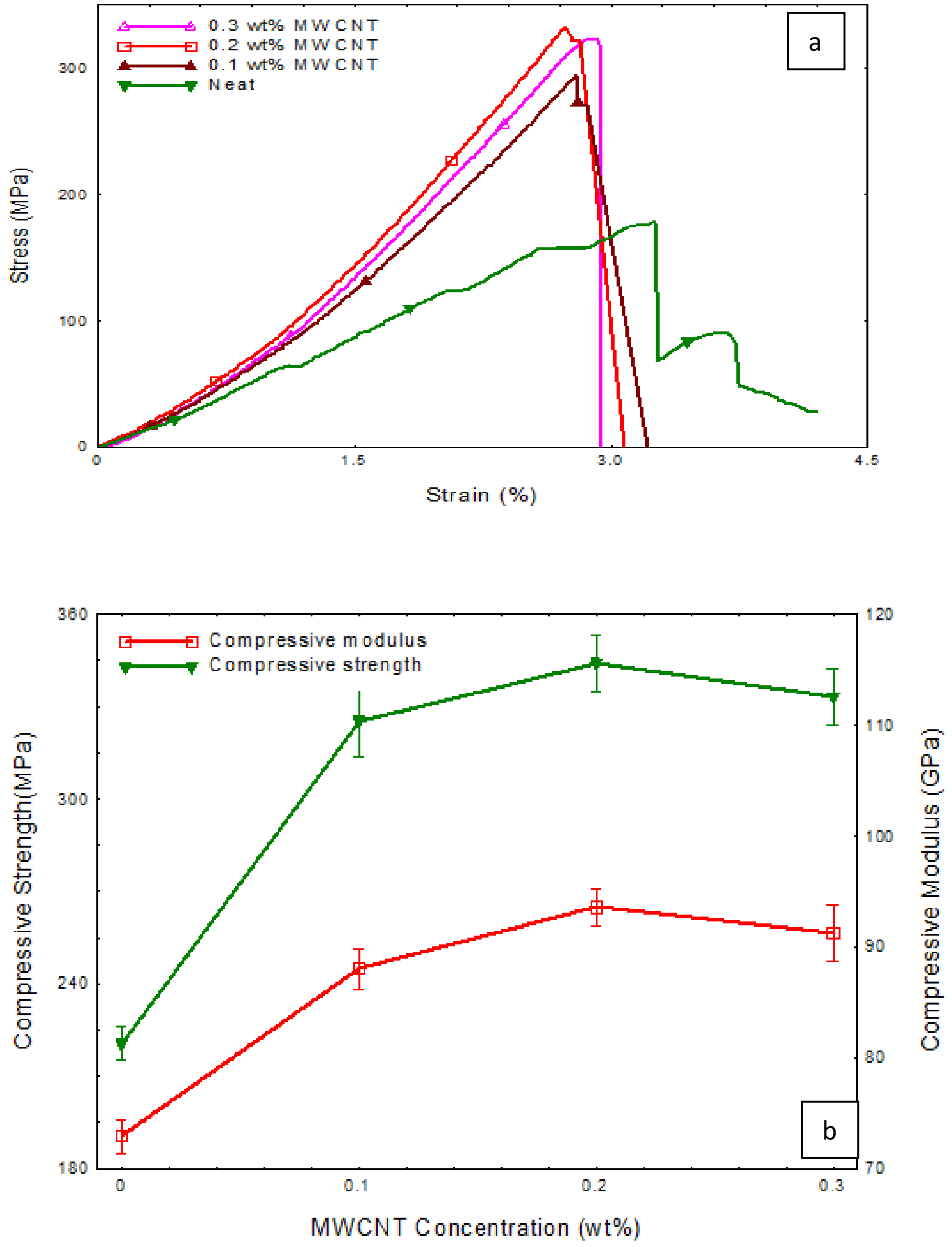


Fig. 27. (a) Typical stress-strain curve obtained from quasi static compression test (b) variation in compression strength and stiffness with the concentration of MWCNTs

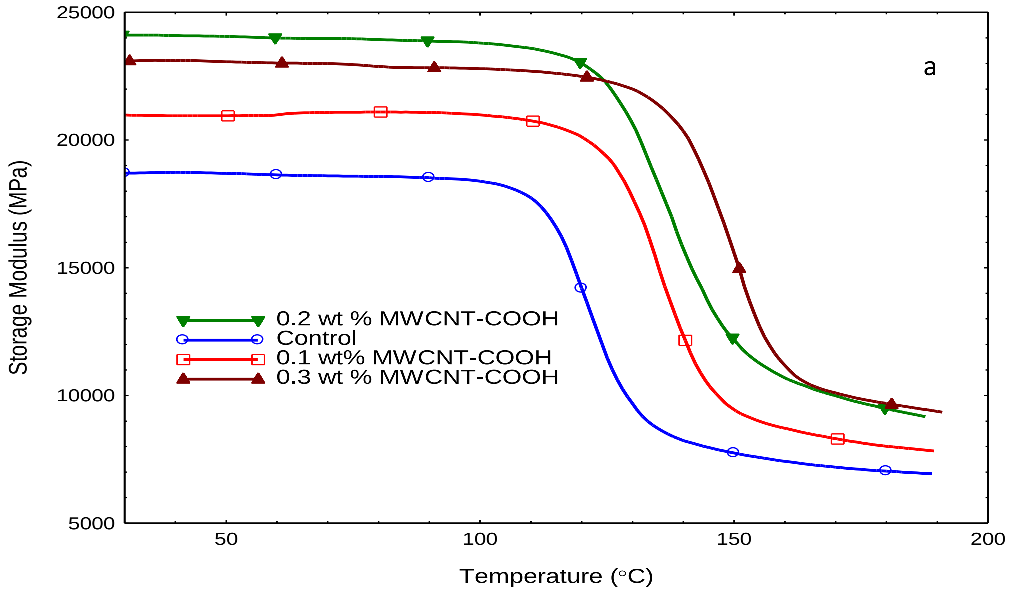
matrix contributed to change the compliance of matrix and fiber/matrix interface from ductile to brittle matrix/CNT dominated behavior as observed by Rodriguez et al. [75] for CNF reinforced CFRP composite. The covalent bonding between the epoxide groups of the epoxy resin and carboxyl group on CNTs surface restricts the mobility of polymeric chain and ultimately improves the composite properties. Mechanical interlocking of CNTs with the matrix is also expected to happen for CNT containing composites due to the presence of large carboxyl acid groups on CNT surface.

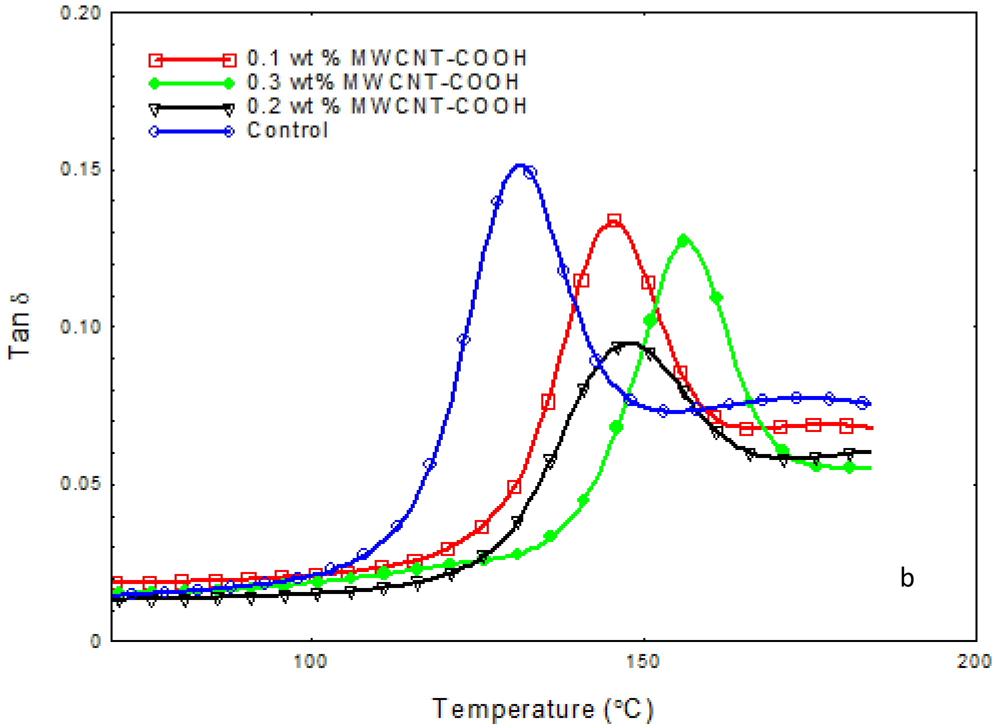
Premature failure due to micro buckling and end crushing has made the compression testing as one of the difficult types of testing for composite laminates. Misalignment of fibers [76] and development of kink band due to yielding of samples [77] have also been reported responsible for premature failure of composite. CNTs can act as a barrier to kink formation and also its spread resulting in improved compressive properties. Variation of compressive strength and modulus with CNT concentration are represented in Figure 27 (b).

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed to obtain temperature dependent properties of laminated composites, such as storage modulus and tan δ. These dynamic properties represent stored elastic energy and the energy dissipated during mechanical strain both of which are highly affected by fillers characteristics i.e. geometry, weight fractions, dispersion state in matrix as well as adhesion between the reinforcements (both microscale and nanoscale) and matrix [25,78]. Figure 28(a) shows the temperature dependence storage modulus in a range of 35-200°C. Storage modulus for different laminates at 35°C has been presented in Table 6. As far as storage modulus is concerned, significant improvement was found with the addition of CNT concentration. In particular, addition of 0.2 wt% of carbon nanotubes showed improved storage modulus up to 28.97% at the temperature of 35°C, possibly due to enhanced interaction of well dispersed nanotubes with the matrix. These dispersed nanotubes can restrict the mobility of molecular chain around the nanofiller causing the storage modulus to increase. However, a slight drop in storage modulus was observed for 0.3 wt% CNT loading, understandably due to the presence of small agglomerates, which is illustrated in the SEM micrograph [Figure 24 (f)]. Also, the gaps within the carbon fiber tows are in the order of few micrometers, lower than the length of MWCNTs. Therefore, it is difficult for the nanotubes to penetrate the fiber tows, especially at higher concentrations due to agglomerations on fiber surface. Such agglomeration result in weaker interfacial adhesion between matrix and carbon fiber. Hence, a property mismatch results between fibers at the subsurface and fibers that are deep into tows which eventually causes lowering of storage modulus [3] .

A sharp drop in storage modulus was observed above 100°C due to the easier movement of the polymer chain. The region with such a behavior is roughly termed as glass transition temperature, T_g of the composite. The region before T_g is the operating region and beyond T_g is termed as rubbery plateau. A significant improvement in rubbery plateau modulus was observed for the carbon/MWCNT/epoxy composite. The average rubbery plateau modulus at 175°C is measured as 7100, 8100, 9500 and 10000 MPa for control, 0.1, 0.2 and 0.3 wt% nanotubes infused composites respectively. Factors that may affect the enhanced rubbery plateau modulus are reinforcing effect by the nanotubes, increased crosslink density and restricted mobility from enhanced polymer-nanotube interaction. The rubbery behavior of composite is of significant importance in industrial application because it gives the information on composite performance at higher





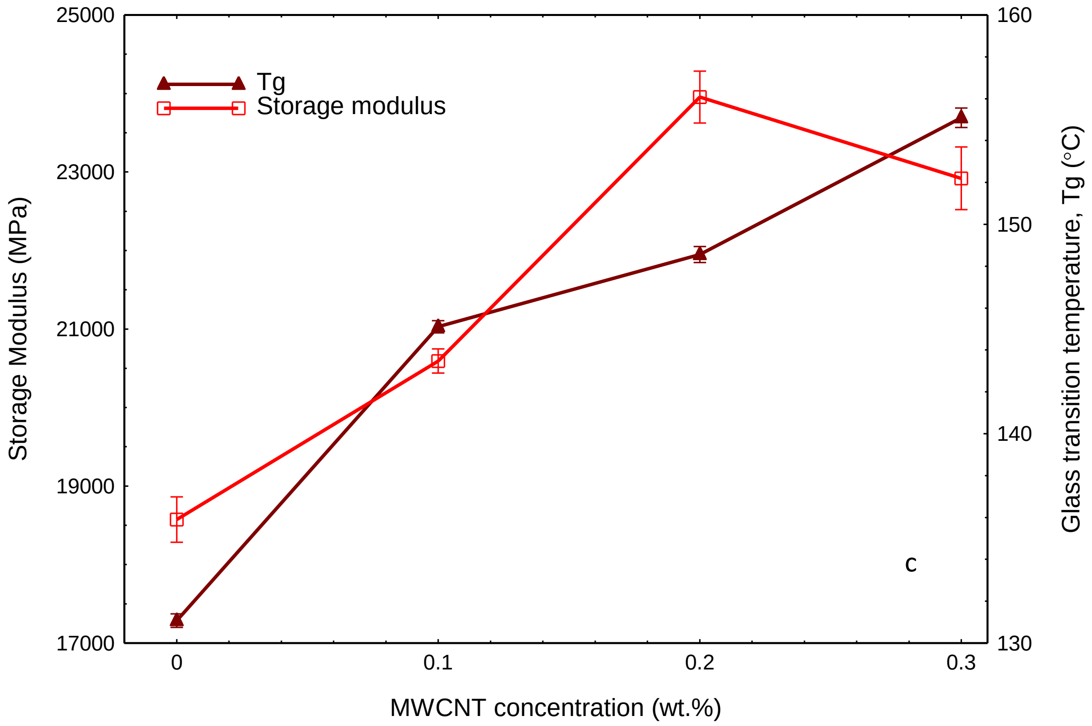


Figure 28. Evolution of (a) storage modulus (b) tanδ as a function of temperature of carbon/MWCNT/epoxy composites (c) variation of storage modulus and T_g as a function of MWCNT concentration.

temperature. Improvement in rubbery modulus indicates an enhancement of T_g through increased crosslink density of the polymer [79]. Hence, maximum rubbery modulus obtained from 0.3 wt% MWCNT reinforced composite is assumed to have maximum crosslink density, thus maximizing T_g.

The effect of nanotube concentration on damping properties of laminated composite is shown by tanδ vs temperature relationship in Figure 28(b). Glass transition Temperature (T_g) is the temperature at which tanδ is maximum. T_g shows a significant improvement even with small addition of CNTs. T_g of control (without CNTs) system is about 131°C while it was 145 , 148 and 155°C for 0.1, 0.2 and 0.3 wt. % MWCNT reinforced composites, respectively (Table 6). The rise in T_g in the polymeric system is predominantly affected by dispersion of CNTs, degree of crosslinking and interfacial interaction [79, 80]. In our study, it is most likely that the dispersed nanotubes restricted the molecular motion and also reduced the free volume. As a result, a positive shift of T_g was observed. Variation of T_g as a function of MWCNT loading is presented graphically in Figure 28(c) where 0.3 wt% sample shows the maximum. According to Lee et al. [42], the agglomerates make it easier for the polymer chain to flow around and lower the T_g. It was found that, even if there is a chance of agglomeration in 0.3 wt% samples (according to earlier section), T_g increases due to the increase of crosslink density. This is probably due to agglomerates acting like large particles as if higher amount of MWCNTs were present. These agglomerates cause localized trapping of matrix resin in the voids between nanotubes. Hence, the composite behaves as if it had lower volume fraction of resin compared to well dispersed composites; as reported by Song et al. [66]. As a result, crosslink density per local resin might go up due to localized entrapment of resin in agglomerates, for which the entrapped resin can no longer take part in crosslink formation with CNTs. Consequently, T_g goes up despite the presence of agglomerates. However, such improvement in crosslink density is less likely to affect the room temperature properties of the composite [78].

The height and width of the tanδ peaks give additional information about the relaxation behavior as well as the mechanical properties of samples. Average peak height of tanδ curves is measured as 0.152, 0.129, 0.095 and 0.124 for control, 0.1, 0.2 and 0.3 wt% samples respectively. Tanδ peak height decreases up to 0.2 wt% and then increases for 0.3 wt% nanotubes. The lower peak height indicates enhanced interfacial adhesion among fiber-matrix-MWCNT and reduced mechanical loss due to lower friction among molecular chains [3, 79]. Increase of tanδ peak for 0.3 wt% sample indicates somewhat lower interfacial adhesion between nanofiller and matrix as well as higher molecular mobility from the presence of agglomerates. In addition, significant widening of the tanδ peaks of composite sample by addition of MWCNTs can be interpreted by enhanced filler-matrix interaction, resulting in broader distribution of relaxation time. Nanotubes can disturb relaxation of neighboring polymer chain whereas those situated far from nanotubes remain unaffected. Such variation in the nanotube concentration affects the formation of crosslinking and the relaxation behavior [3, 79, 81].

Coefficient of Thermal Expansion (CTE)

Coefficient of Thermal Expansion (CTE) is an important thermo physical property of polymeric material for engineering applications. A low CTE value is most desirable to ensure good dimensional stability. Most of the polymeric materials have high CTE value which limits their application. But incorporation of a lower CTE filler material in the polymeric matrix can significantly reduce the overall CTE of carbon/epoxy composites. Multi-walled carbon nanotubes have very low CTE [82], hence it is anticipated that their presence in matrix will significantly influence the CTE of composite material. MWCNTs are expected to be dominant in determining the shrinkage or expansion of the composites in the transverse direction as measured in current study for matrix dominated properties where fiber phase has little or no effect on it. Figure 29(a) presents the change in sample dimension in transverse direction as a function of temperature. Figure 29(b) compares the CTE value of control, 0.1, 0.2 and 0.3 wt% MWCNT reinforced laminated composite in the temperature range of 30-

90°C, well below the glass transition temperature. The effect of MWCNTs on the transverse thermal expansion behavior of composites has been summarized in Table 6.

The average coefficient of thermal expansion of carbon/ epoxy composite was measured as 27.8 ppm/°C. The addition of 0.2 wt% nanotubes reduced this value by

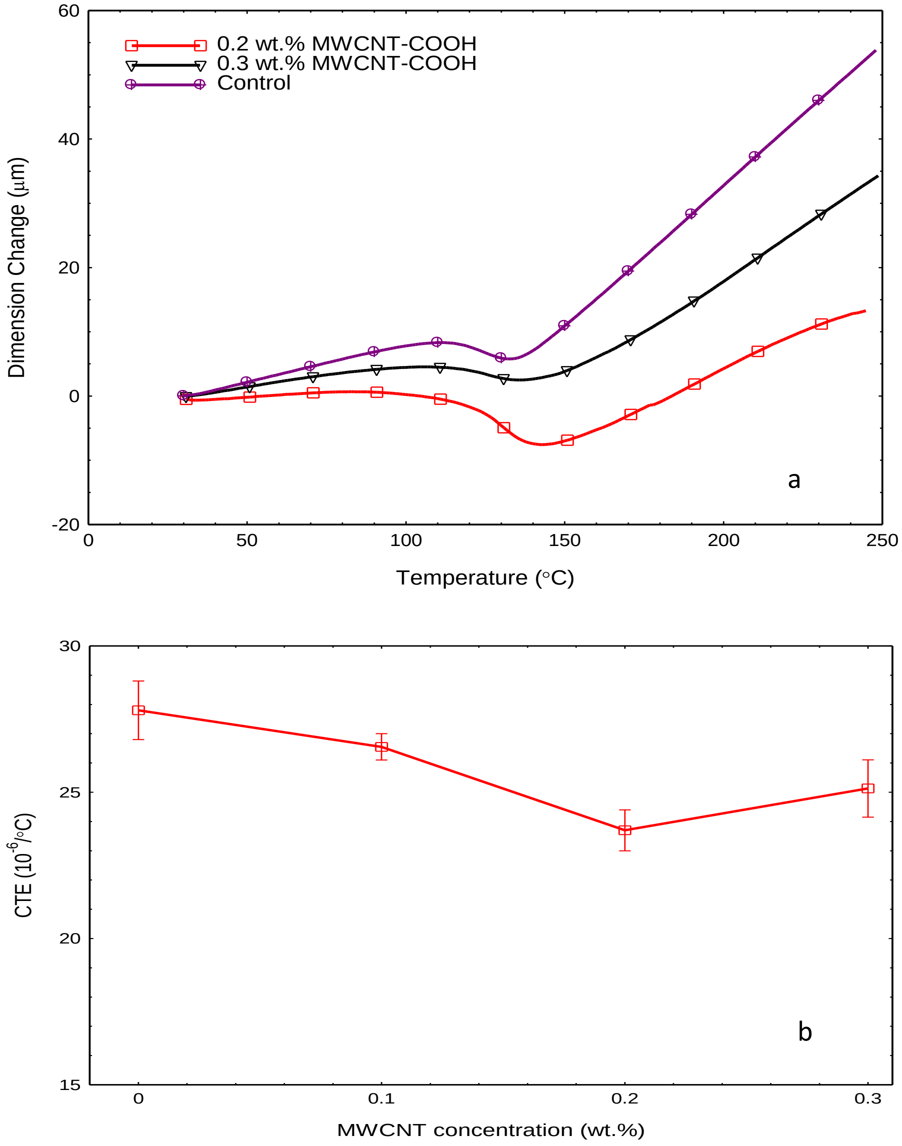


Figure 29. (a) Graphical presentation of dimension change versus temperature (b) variation in CTE with the concentration of MWCNTs

14.74 % to 23.70 ppm/°C as compared with the carbon/epoxy sample. Such a significant reduction in CTE can be attributed to the potential matrix modification like increased rigidity by the addition of CNTs. Well dispersed CNTs can effectively reduce the free volume in the polymer and prohibit its thermally induced movement resulting in a reduced CTE value. Moreover, well dispersed CNTs can align the polymer chain along their axial direction, thus can easily get associated with the polymer molecule. Since MWCNTs have almost zero CTE, addition of MWCNTs with polymer chain may end up with an overall reduction in CTE of composite [29]. Further addition of CNTs (0.3 wt %) resulted in slight increase in CTE as compared to 0.2 wt% samples but still low in comparison with control system. This higher value of CTE can be demonstrated by the aggregates formed at higher loading as mentioned in earlier sections. The aggregates offered fewer obstacles to the polymer chain movement and thus, aid in increasing the value of CTE. Chang [41] also investigated the CTE of carbon/MWCNT/epoxy composite and concluded that the addition of CNTs up to a certain concentration can lower the CTE to some degree due to their uniform dispersion. Beyond this concentration, CTE started increasing probably due to the tendency of the aggregates formation of MWCNTs and the material becoming less thermally stable.

Finally, Mechanical properties were much higher for carbon/MWCNT/epoxy composites than that of carbon/epoxy composite. Specifically, addition of 0.2 wt% CNTs came out with an optimum condition compared to control system (without CNTs). In addition, along with storage modulus and glass transition temperature, thermal stability derived from coefficient of linear thermal expansion were all improved in MWCNTs modified carbon/epoxy composites. This improvement in the properties is attributed to the homogeneous load carrying capability of carbon fiber due to the good dispersibility of CNTs and hence, better interfacial characteristics between the epoxy and the CNTs as evident from the SEM micrographs.

CHAPTER VIII

LOW VELOCITY IMPACT PROPERTIES

Drop-weight test of neat and CNT modified composite specimens with an average thickness of 3.2 mm was performed at three different impact energy: 21.5, 30 and 40J. Various parameters have been proposed in literatures [50, 83–85] to evaluate the impact performances of control and CNT reinforced laminated composite. These parameters include force at first material damage, peak force, absorbed energy, delaminated area (measured by C-scan), damage degree (ratio of dissipated to impact energy), specific delamination energy (SDE) and few more. Among different parameters we focused our study on characteristics like peak forces, absorbed energy and delamination area.

Peak Force

The peak force is defined by the maximum load that material can withstand without failure. It is measured from the maximum point in load vs. time plot. Figure 30 represents the Load vs. time response of neat and various CNT modified CFRP composites at three different energy levels. Table1 gives the summarized data obtained from the impact test. Figure 30(a) shows low velocity impact response of neat and CNT modified samples at 21.5 J impact energy where maximum of 11% improvement in peak load is observed for 0.3 wt% CNT composite. On the other hand, maximum of 6% and 8% improvement is found for 0.3 wt% nanotube loadings at 30J and 40J impact energy, shown respectively [Figure 30(b) and 8.1(c)]. Thus, no significant improvement was observed in peak loads by adding various concentrations of CNTs due to fiber controlled load capacity of the composites, which closely resembles various earlier studies [50, 86].

Figure 31 shows load vs. time and energy vs. time response of neat and various concentration of CNT doped samples at different impact energy. In most cases, load vs.

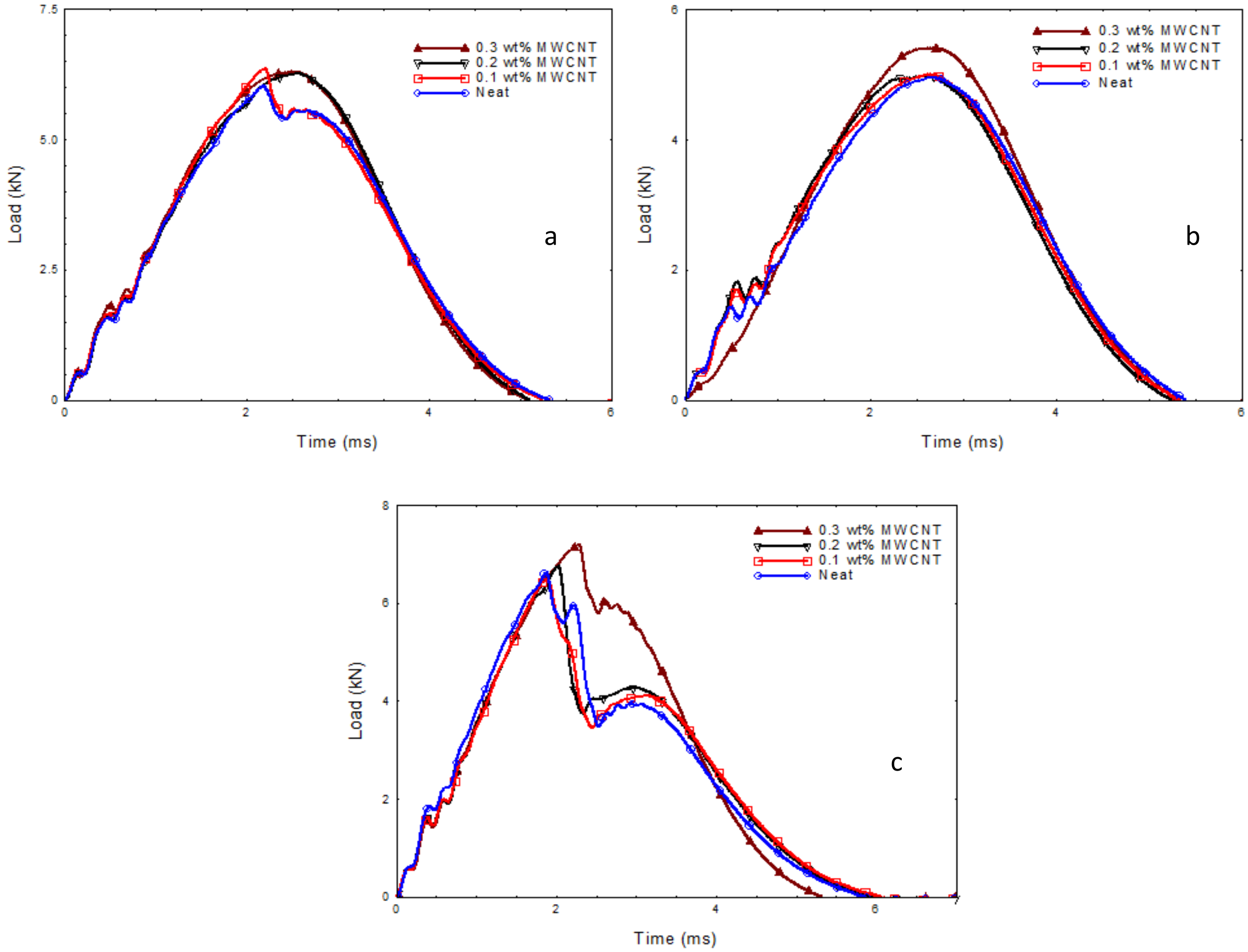


Figure 30. Load-time response of various composite samples at different energy levels for (a) 21.5 J, (b) 30 J and (c) 40 J

to that point and unloading path also follows a smooth way. While in other cases, sudden drop in load is observed which is due to the unstable propagation of delamination. The initial knee found in the curves is supposedly due to the inertia effect of impactor and specimen. As soon as, the inertia matches with each other, a smooth rise in load is observed [55, 87]. Contact stiffness, measured from slope of load vs. time curve increases with increasing impact energy but does not show notable change with changing CNT loading for particular impact energy. In general, peak load increases with increasing impact energy. Also, general pattern of the curves of these composite systems [Figure 31 does not exhibit any remarkable difference. Only longer contact durations between the impactor and specimens were observed among different impact energy level in a particular system as expected [84, 86] but no major difference was observed among different systems. As can be seen from Figure 31, time delay increases with increasing impact energy indicates more amount of damaged fibers.

Table 7. Impact Response of Neat and Various MWCNT Modified Carbon/Epoxy Composites

Property	Neat	0.1 wt% MWCNT	0.2 wt% MWCNT	0.3 wt% MWCNT
21.5 J				
Peak load (kN)	4.97	5.06	5.12	5.53
Damage area (cm^2)	48.71	27.13	33.84	37.89
30 J				
Peak Load (kN)	6.00	6.36	6.27	6.17
Damage area (cm^2)	64.52	44.62	37.70	43.26
40 J				
Peak Load (kN)	6.81	6.61	6.77	7.17
Damage area (cm^2)	84.17	62.98	71.83	66.67

Finally, low velocity impact response can be characterized by categorizing these impact energies in three different zones: Rebound (21.5J), On-set of perforation (30J) and Partial perforation (40J).

From Figure 31 it can be seen that, in all cases at 21.5 J impact energy, absorbed energy in specimens was slightly lower than the corresponding impact energies. The excessive impact energy is termed as elastic strain energy and is the driving force for impactor and specimen to rebound. When the impact energy is increased further such that dissipated energy in the specimen is almost equal to the corresponding impact energy, the situation is termed as ‘on-set of perforation’. Figure 31 clearly shows that ‘on-set of perforation’ takes place at 30 J. In this case, impactor sticks on the specimen and almost no rebound is observed. Energy in the specimen increases continuously until end of the impact event where absorbed energy is almost equal to the impact energy.

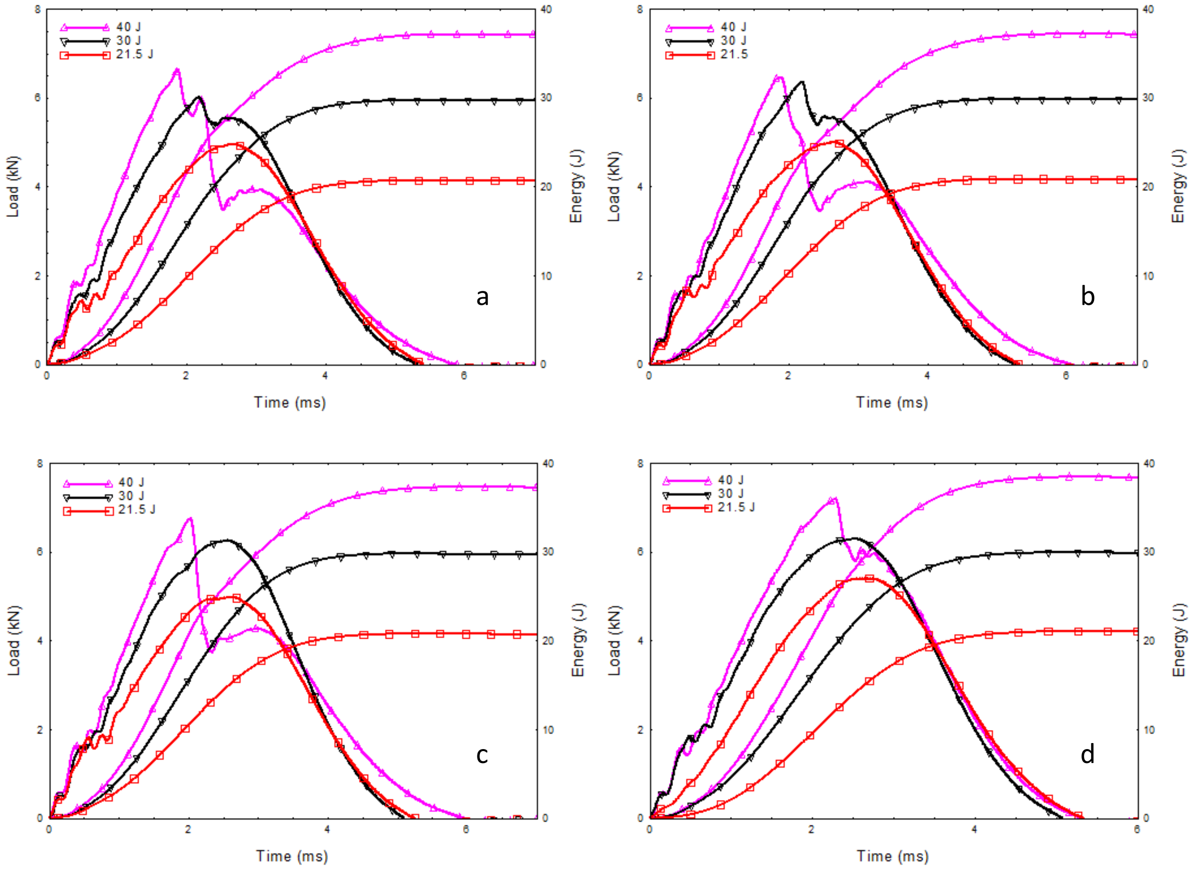


Figure 31. Load-time-energy histories of various composite samples at different energy levels for (a) Neat, (b) 0.1(c) 0.2 and (d) 0.3 wt\% MWCNT

Further increase of impact energy beyond on-set of perforation energy causes partial penetration of laminated composite and this situation is termed as perforation. As can be seen from Figure 31, 40 J energy level is termed as partial perforation energy level except for 0.3wt% sample where no sign of perforation was observed. In this case, the load reaches to its maximum, then decreases down to a lower level and finally falls to ground. In this case, absorbed energy is much lower than the initial impact energy [2].

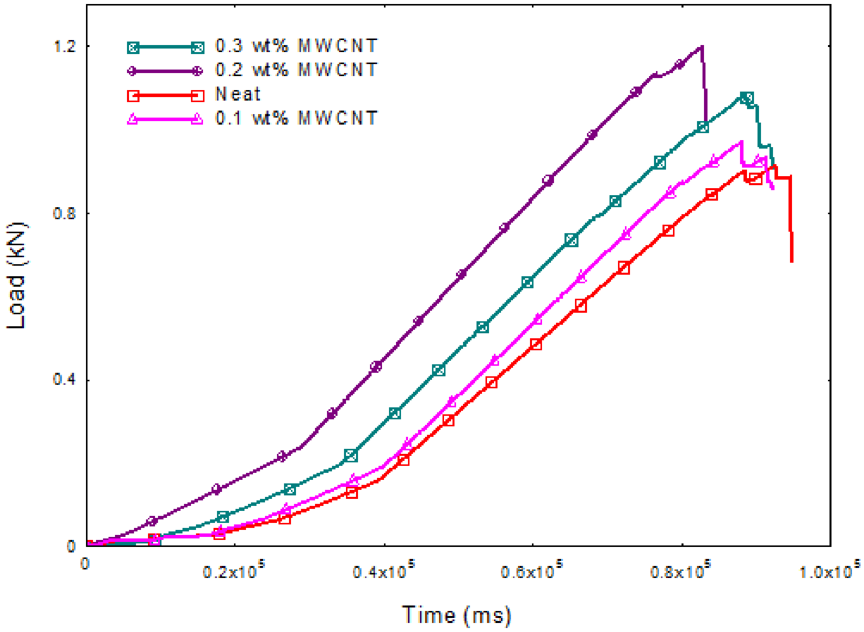


Figure 32. Three-point bend quasi static response of various composite samples

Comparison of results obtained from three point bending and dynamic drop weight test can provide important information on how loading rate can affect the material properties. Figure 32 shows the load-time response of various composite specimens in quasi-static three point bending flexural test. By comparing Figure 32 and Figure 31, it is clear that load bearing capacity in dynamic loading is up to 4 times higher than that in case of static loading for both neat and CNT modified composites.This result is in agreement with that obtained by Evci and Gulgec [88].

Absorbed Energy

The impact energy is defined by the amount of energy introduced on the specimen by the impactor. The absorbed energy is the total amount of energy dissipated by composite specimen during an impact event by the formation of damage inside it. Absorbed energy was calculated as the integral area between loading and unloading phase of the load vs. displacement curves. As the composite laminates are brittle in nature and responds elastically until the load reaches to its maximum, if impact energy is higher than the energy absorbed by the material till maximum load, additional energy is absorbed by the material in damage creation with a small amount of energy lost in friction between the material and the impactor [55]. Therefore, total absorbed energy can be divided in two parts: (1) energy absorbed at peak load signifies the part of absorbed energy until load reaches the maximum without failure, and (2) part of total energy absorbed in damage creation or delamination energy.

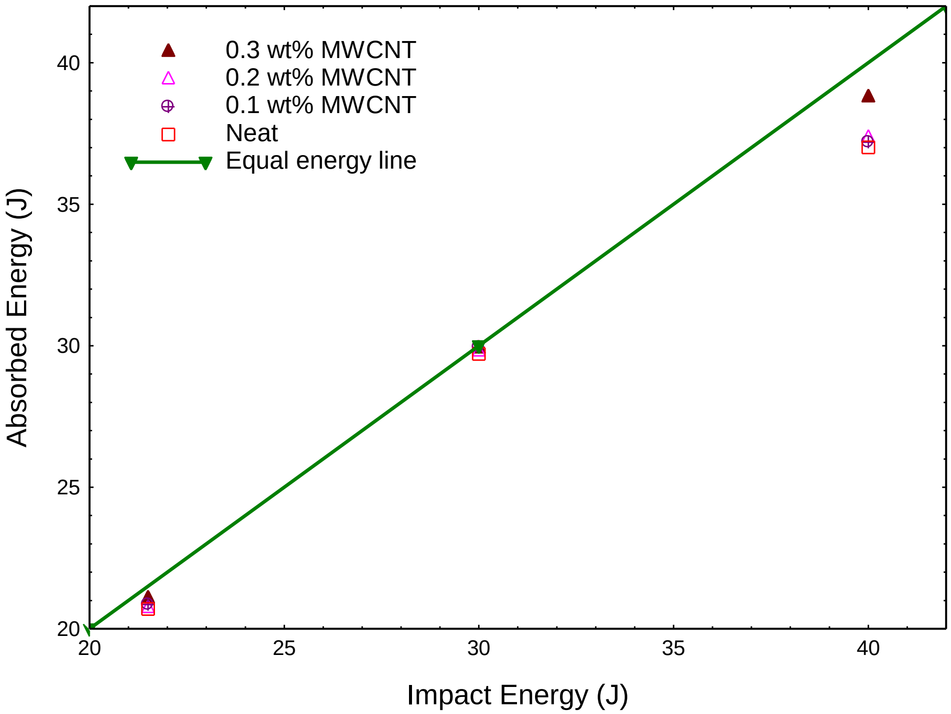
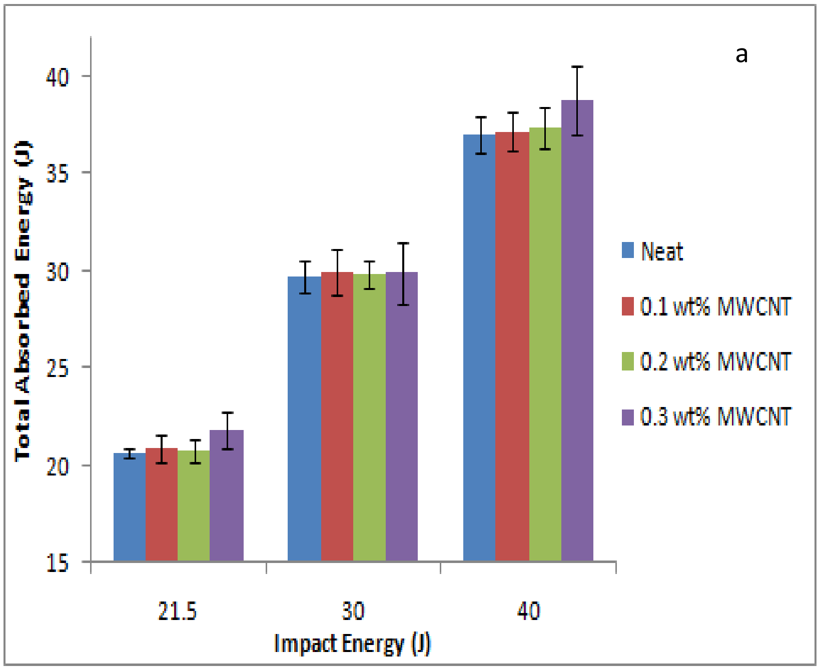
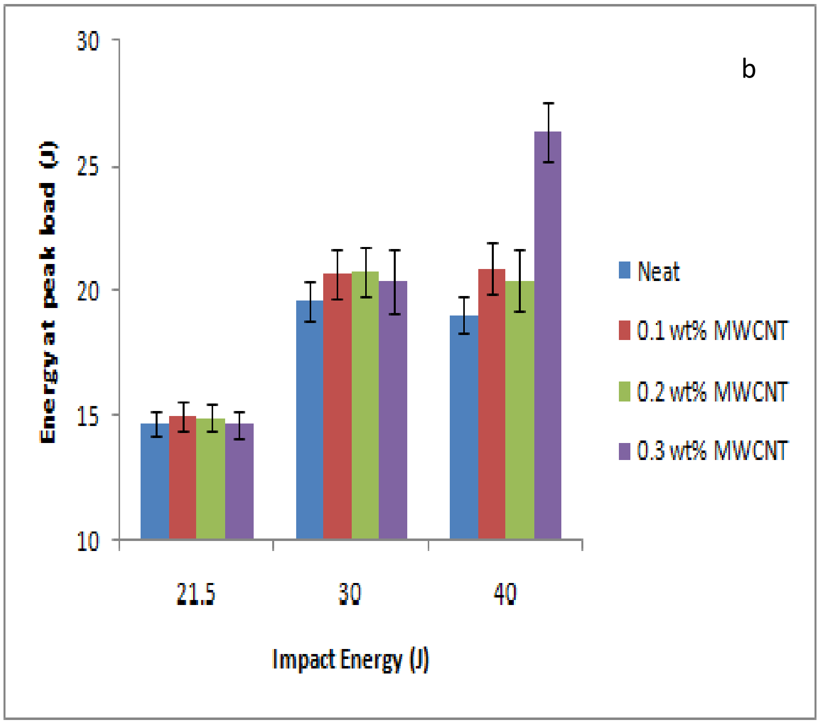


Figure 33. Energy profile diagram

Details of the characteristics energies measured from low velocity impact data are presented in Table 7. Energy profile diagram [83, 86] of composite specimens is plotted as absorbed energies vs. impact energy. This diagram has been established as a very





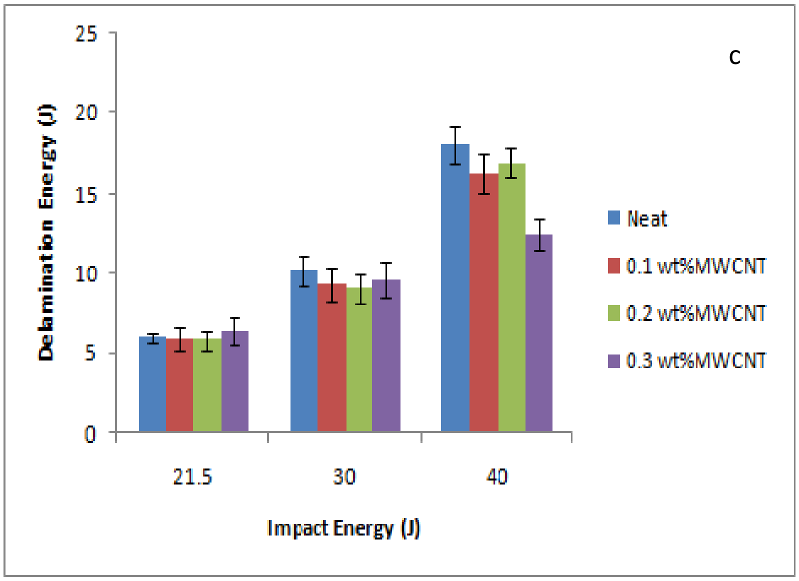


Figure 34. Comparison of absorbed energy among neat and various MWCNT doped samples (a) Total energy (b) Energy at Peak load and (c) Delamination energy

effective tool in understanding low velocity impact response of composite materials. Energy profile diagram of both neat and nanophased composites have been presented in Figure 33. In this diagram, equal energy line indicates that absorbed energy is equal to impact energy. When compared among neat CFRP and CNT modified composites, data points of 0.3 wt % CNT reinforced composite is slightly closer to equal energy line which means that a slight improvement in total absorbed energy is evident for CNT reinforced composite, especially at higher loading of CNT and higher impact energy compared to neat composite due to higher energy absorbency by the larger amount of nanotubes. At the same time, graphical representation of total energy, energy at peak load and delamination energy vs. impact energy in Figure 34 shows that more energy was absorbed by larger amount of CNTs, prominent at highest impact energy [Figure 34(a)]. Also, peak load energy is greater for CNT doped composites, especially for 0.3 wt % CNT samples [Figure 34(b)] while delamination energy drops for CNT reinforced composites [Figure 34(c)]. The effect of CNT reinforcement in epoxy composite is distinct with increasing CNT loading as well as increasing impact energy. In more detail, at lower impact energy (21.5J) it can be shown that no major difference is observed in energy absorption capability. However, upon increasing the impact energy up to 40J, CNT modified composite resulted in higher absorption performance. At this point, we can demonstrate that CNT reinforced CFRP composites tend to present better impact behavior compared with neat composite in terms of damage reduction.

Damage Evaluation

C-scan imaging is performed to evaluate the impact induced damage in composite samples. To quantify, damage area was measured using image processing software ImageJ. C-scan images are shown in Figure 35-37 at impact energy of 21.5, 30 and 40J.

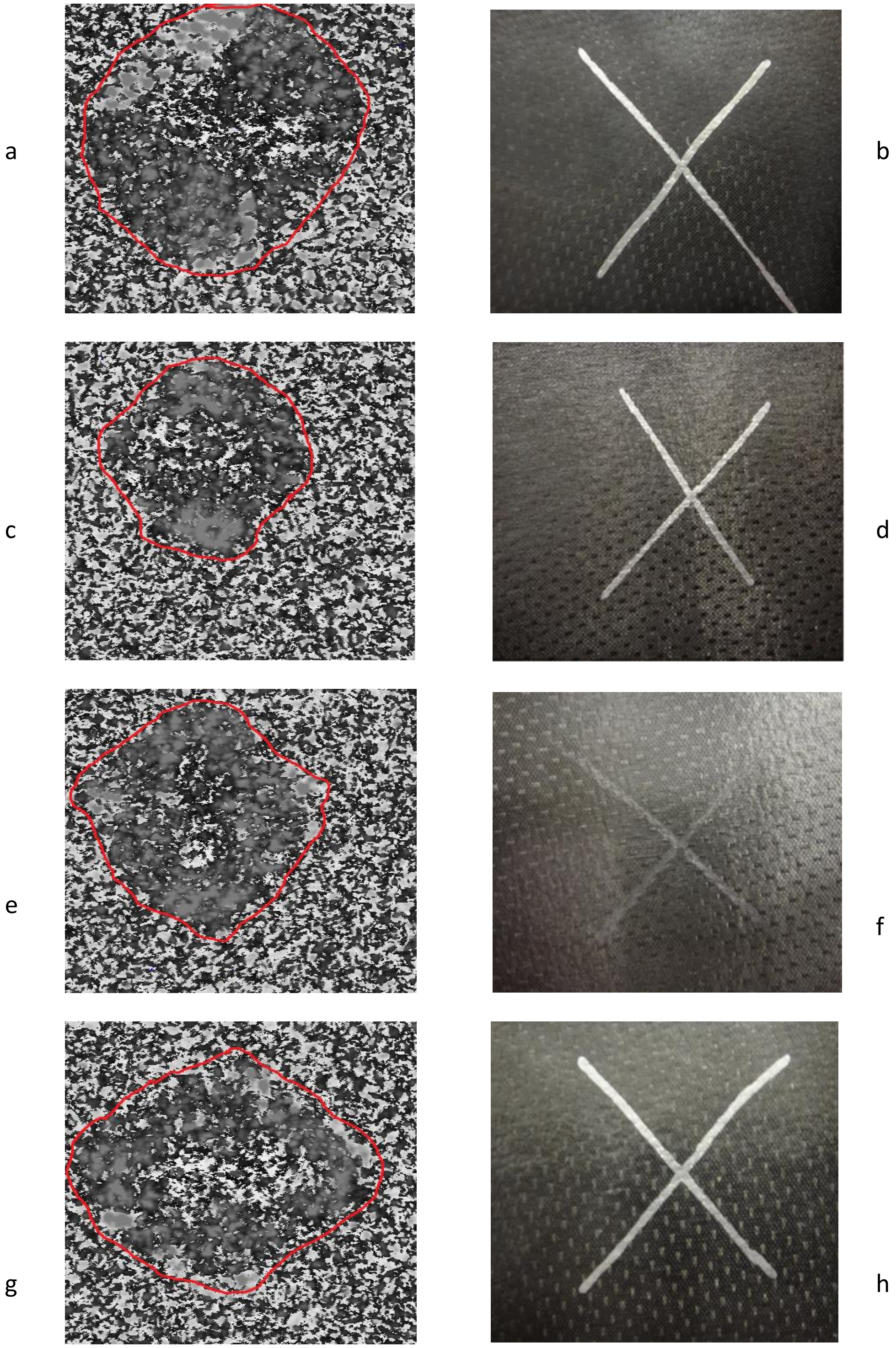


Figure 35. C-scan and back surface images of various composite samples at 21.5 J: (a-b) neat, (c-d) 0.1 (e-f) 0.2 and (g-h) 0.3 wt\% MWCNT. First column- C-scan images and second column-back surface images

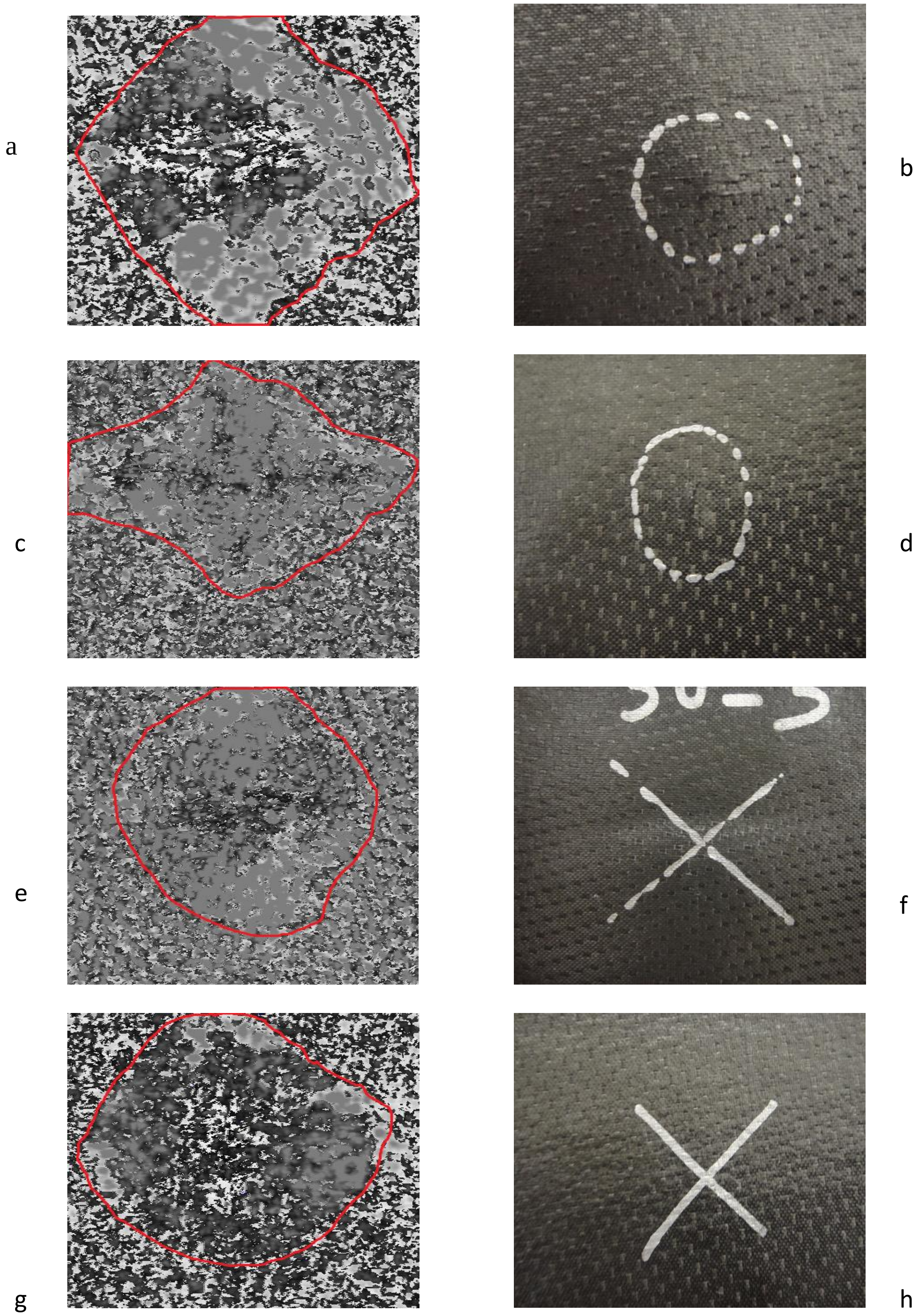


Figure 36. C-scan and back-surface images of various composite samples at 30 J: (a-b) neat, (c-d) 0.1 (e-f) 0.2 and (g-h) 0.3 wt\% MWCNT. First column- C-scan images and second column-back surface images.

Figure 35 represents C-scan and back surface images of both CNT modified and un-modified samples at 21.5 J impact energy. This is the characteristics case of rebound. No discernible damage was observed on back surface in any sample but c-scan image revealed presence of notable damage. Moreover, the damage is spread out rather being localized. In this case, around 54% reduction in damage area is observed in case of 0.1 wt% CNT sample.

Both C-scan and back surface images of neat, 0.1, 0.2 and 0.3 wt% CNT modified composite at 30J are presented in Figure 36. Visible damage, mainly fiber splitting is present on back surface in both neat and 0.2 wt% samples. C-scan image reveals the actual extent of damage inside the sample. In this case also CNT reinforced sample shows much lower damage area than neat sample. Maximum of 54% reduction in damage area is achieved for 0.2 wt% CNT samples. This represents the case of ’on-set of perforation’.

Figure 37 shows C-scan and back surface images various composite samples at 40 J impact energy. Perforation of samples is observed. On the back surface images, significant damage is observed for all samples except 0.3 wt% composite where insignificant amount of fiber splitting is visible. CNT doped 0.1 wt% samples shows maximum of 25% reduction in damage area compared to neat samples. This is the characteristics case of partial perforation.

In comparison, though overall damage area increases increasing impact energy for a specific composite. According to Azouaoui et al. [89] delamination crack preferentially propagates through the resin rich area which is relatively less resistant than the fiber pathway. Therefore, the matrix modified with the CNTs might effectively arrest or blunt the crack tip due to the presence of dispersed CNTs. Thus, various amount of CNT

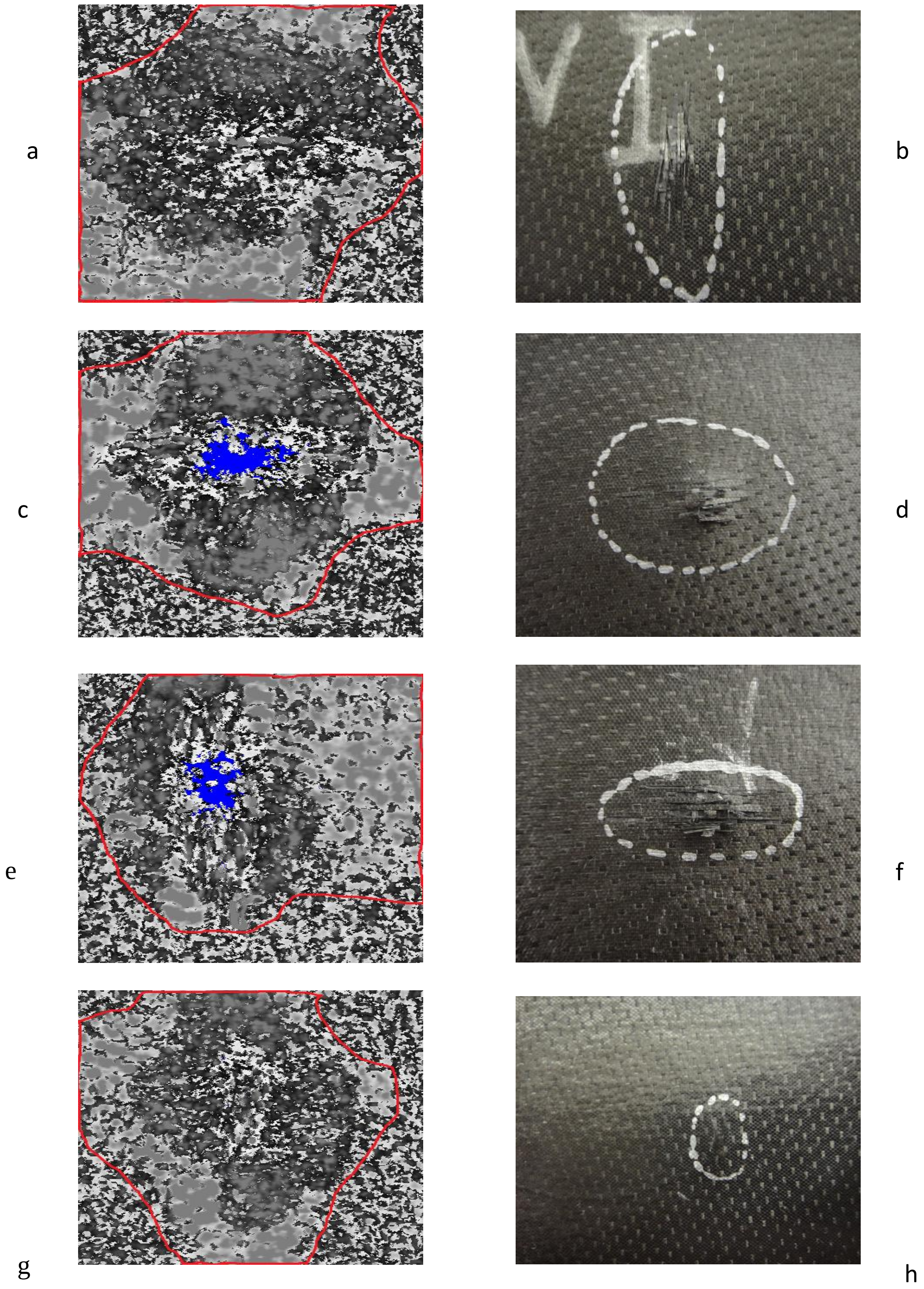


Figure 37. C-scan and back surface images of various composite samples at 40 J: (a -b) neat, (c-d) 0.1 (e-f) 0.2 and (g-h) 0.3 wt\% MWCNT. First column- C-scan images and second column-back surface images.

modified composite performs better compared to neat composite in terms of damage reduction. With higher loading of CNTs, relative reduction of damage is loss but was close to the neat composite might be due to the higher chance of forming agglomeration [55]. These agglomerates can act like stress raiser and show poor performance in arresting the crack propagation, thus resulting in relatively larger damage formation. It has been reported that delamination is main damage mode in low velocity impact test and also delamination energy is directly related to the damage size. As can be seen from Table 7, delamination energy is sometimes higher for CNT doped samples than neat composites but delamination area is lower for that nanophased sample than the neat sample. This might be due to the presence of additional delamination mechanism in nanophased sample which absorbs more energy but creates less damage as reported by Kostopulous et al. [86]. They showed that due to the reinforcement of CNTs in the direction of maximum interlaminar shear (45°), more energy is absorbed by the CNTs than the overall composite samples thus resulting in smaller damage area than that is approximated from delamination energy. In case of 0.3 wt% MWCNT samples, at 40 J impact energy delamination energy does not reflect the exact damage area which looks remarkably higher compared to the energy spent here. This might be due to the fact that higher loading of CNTs demonstrates higher chance of agglomerate formation which ultimately results in significant delamination but without spending significant amount of energy [55].

In order to further interpret the experimental data, specific delamination energy (SDE) was calculated which corresponds to the energy required to develop a unit delamination area as imaged by C-scan. SDE is considered an effective measure of energy needed for the development of equivalent damage within composite structure, especially in aerospace. It is already reported that total absorbed energy especially the delamination energy is directly related to the amount of damage introduced via through-thickness matrix cracks, fiber breakage or pull out, fiber-matrix debonding within plies etc. As SDE correlates the dissipation energy to the effective damage area, therefore it is believed that it will also be able to identify or estimate the presence of additional energy dissipation mechanisms.

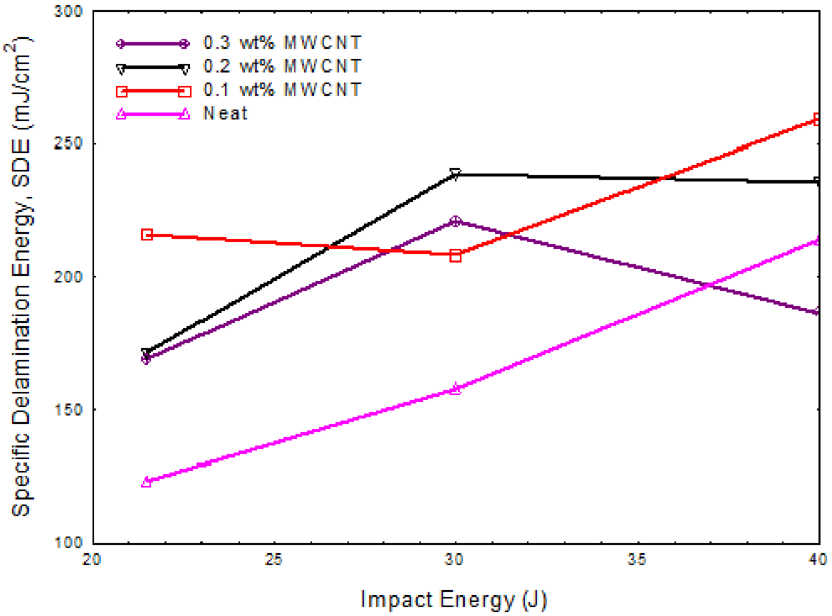


Figure 38. Specific delamination energy vs. impact energy

Though in earlier studies [86] SDE has been calculated with respect to total absorbed energy, in this study, SDE with respect to delamination energy has been Figured out on the basis that damage formation is solely contributed by delamination energy not by total absorbed energy. SDE of both neat and CNT doped samples is presented graphically in Figure 38. It can be seen from the Figure, SDE increases with increasing impact energy for neat but up to the point of on-set of perforation (30J) for 0.2 and 0.3 wt% CNT samples. But, in case of partial perforation at 40 J, SDE decreases gradually but yet higher than neat sample at this high impact energy zone. From the result it can be shown that addition of nanotubes into the matrix creates additional energy absorption mechanisms as shown in earlier studies [86, 90, 91].

Breakage or pull-out of CNT absorbs larger amount of energy and presence of these energy absorption mechanisms is verified by Kostopoulos et al. [86]. Larger interface area of CNTs has been reported to facilitate more energy absorption than neat samples. Additionally, it has been demonstrated [91,92] that CNTs can prevent further development of delamination by arresting crack propagation path or by toughening the matrix. It is assumed that CNTs aided in reducing delamination in earlier stage by arresting or blunting the crack tip resulting in a smaller delamination area. Overall, CNT reinforced CFRP composite shows a higher SDE value, indicating an enhanced toughness compared to neat composite.

CHAPTER IX

CONCLUSION AND SCOPE OF FUTURE WORK

Conclusion

Carbon fiber reinforced polymer composite has been used as an effective structural material for numerous applications. Due to property variation of constituent materials as well as their physical arrangement in fiber reinforced composite, the out-of-plane properties are much weaker compared to in-plane properties. As an effort to improve the out-of-plane properties in addition to in-plane properties, carboxyl functionalized multi-walled carbon nanotubes were used in this study to fabricate carbon/epoxy multi-functional composites using various percentage of CNTs. CNT percentage was increased gradually up to 0.3 wt% and compared with conventional CFRP composite. From this study it is demonstrated that CNTs can be successfully used to modify the conventional epoxy nanocomposites and their fiber reinforced composites.

To meet up the challenge to uniformly disperse the CNTs in the matrix, a combination method of sonication and magnetic stirring was used along with a solvent. DSC dynamic study of neat epoxy and MWCNT/epoxy nanocomposites revealed that up to 0.2 wt% addition of CNT in epoxy had a retarding effect on the cure reaction though addition of 0.3 wt% CNT catalyzed the reaction to some extent. Due to the retarding effect of CNTs, additional post curing for both epoxy nanocomposites and their fiber reinforced laminated composites was required. Also, from the data calculated for total heat of reaction, presence of agglomerates was predicted in 0.3 wt% CNT reinforced composites.

Matrix digestion test gives the fiber volume fraction around 63 to 65 % which is much higher than the theoretical requirement but with a reasonable limit of void content. The very dense texture of T300 carbon fiber restricted the flow of resin within the fiber and thus resulted in such higher percentage of fiber fraction. Flexural properties (flexural strength and flexural modulus) were improved due to the addition of MWCNTs and found to be maximum for 0.2 wt% MWCNTs. As with flexural properties, viscoelastic properties (storage modulus, glass transition temperature) were also superior for 0.2 wt% MWCNT reinforced composite. Coefficient of thermal expansion was found to be significantly lower indicating an increased thermal stability of MWCNT reinforced composites. Enhanced flexural, viscoelastic and thermal properties were attributed to better dispersion and improved interfacial interaction between the epoxy and MWCNTs in carbon/MWCNT/epoxy composite as postulated from SEM micrographs.

In agreement with other properties, tensile and compressive properties of CNT modified carbon/epoxy composites improved significantly up to 0.2 wt% MWCNT. Addition of 0.2 wt% CNT improved the fiber dominated tensile properties maximum by 33% in tensile strength and 28% in Young's modulus followed by 0.3 wt% CNT added composite and finally 0.1 wt% composite samples when compared with conventional CFRP composite. Also, quasi static compressive properties improved significantly due to the addition of 0.2 wt% MWCNT in carbon/epoxy laminated composites. 52% improvement in compressive strength and 29% in compressive modulus was observed for 0.2 wt% CNT added composites. The improved tensile and quasi static compressive properties of 0.2 wt% CNT added carbon/epoxy composites were attributed to the better dispersibility and excellent load carrying capability of multi-layered CNTs.

In agreement with earlier studies, though no significant improvement in peak load and absorbed energy was observed when directly comparing the neat and the CNT modified samples for impact test, delamination area and specific delamination area (delamination area per unit delamination energy) improved remarkably for CNT modified samples. Within the scope of our present study, higher loading of CNTs seem to perform better under impact test but damage tolerance and damage resistance was higher for low loading of CNTs which demands further investigation on a wide range of CNT loading to optimize both the impact and damage properties of CNT reinforced composites.

Scope of Future Work

Present study reveals that the higher percentage of CNT loading did not offer promising results in most cases. The secret of success might be in mixing the CNTs with the epoxy resin. All the mixing parameters like mixing time, volume of mixure, amplitude of oscillation mixing temperature etc. set for ultrasonication can be varied to explore the strength of sonication in mixing higher loading of CNTs. Subsequently, another mixing method like mechanical stirring, three roll mixing etc. could be found to substitute sonication. For the sake of fully understanding the curing behavior of neat epoxy and MWCNT/epoxy composites, DSC isothermal scan should be run along the dynamic scan. Since the long term durability of these composites is an important concern from the view point of end users, before recommending this type of composite for end application, the issue of long term environmental condition like humidity on the composite system must be addressed. Since composites are subjected to dynamic loading when used as structural components, their dynamic properties like high strain rate, fatigue and high velocity impact (ballastic) properties could be determined before using them in end applications.

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