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Effect of carbon nanotubes on the interlaminar and fracture properties of carbon fiber/epoxy composites

Harpreet Singh Bedi* & Prabhat Kumar Agnihotri

Mechanics of Advanced Materials Laboratory, Department of Mechanical Engineering,
Indian Institute of Technology Ropar, Punjab 141 001, India

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The average properties of carbon fiber reinforced plastics (CFRPs) depend on the extent of interaction between the fiber and matrix. Any means, therefore, to modify either of the two constituents of CFRPs is the key to design the composite. Carbon nanotubes (CNTs) are often used to tailor the interface/interphase in conventional CFRPs either by mixing the nanotubes in matrix or by growing them on the surface of fiber. However, the incorporation of nanotubes, by either means, may affect the mechanical performance of the matrix and that of the composite as a whole. Experiments are carried out to assess the effect of CNT dispersion on the rate sensitivity of matrix, and the effect of CNT grafting on the average mechanical properties of laminated composites. For better dispersion and interfacial interaction of nanotubes with matrix, molecular level designing of nanotubes is carried out by way of functionalization. It is found that the ultimate strength of epoxy composites increases with applied loading rate, and that neat epoxy is more rate sensitive than CNT based epoxy nanocomposites. Significant enhancements are also observed in the interlaminar and fracture properties of CFRPs after the incorporation of grafted nanotubes in the composite.

Keywords: CFRP, CNT, Rate sensitivity, ILSS, Fracture toughness

1 Introduction

There is a growing interest to develop multifunctional polymer composites by suitably tailoring their properties to meet the material requirements for advanced applications[1]. Widespread use of carbon fiber reinforced plastics (CFRPs) in modern day engineering is possible due to the ability of these materials to be customized as per requirement and better in-plane properties[2]. While, the in-plane properties of laminated CFRPs are fiber dominated, the off-axis and out-of-plane properties are majorly dominated by the matrix[3]. The presence of a weak matrix interlayer between the laminas may lead to delamination or interlaminar shear failure, separating the laminas from each other. Further, it is of utmost importance for composites used in structural applications to be able to withstand complex and varying loading environments. These issues can be overcome if somehow the neighboring laminas can grasp each other under the varying vary conditions and by strengthening the matrixpresent in-between the laminas. This can be achieved with the help of carbon nanotubes (CNTs) because of their very high specific surface area, low density and extraordinary mechanical properties[4].

Generally, there are two ways to introduce CNTs in composites[5]. The primary method of mixing CNTs in matrix[6], increases the resin viscosity, hinders matrix impregnation into the fabric, and is prone to poor and inhomogeneous dispersion of CNTs[7,8]. This results in the formation of CNT agglomerates that can act as stress concentration sites and lead to premature failure of the composite. Hence, CNTs are frequently subjected to purification and functionalization processes to ensure their better dispersion in polymer matrix[9]. To overcome these issues, CNTs are often synthesized directly on the surface of fiber reinforcement through chemical vapor deposition (CVD) process[10-12]. The incorporation of CNTs significantly changes the interfacial chemistry and microstructure in hybrid and multiscale composites as compared to conventional CFRPs. While the interface in conventional CFRPs is marked by a sharp change in properties from fiber to that of matrix, the transition is more gradual and occurs in an interphase region of finite thickness in CNT reinforced CFRPs[13]. Moreover, by combining these two approaches, there is a third possibility to realize a hybrid-multi scale composite having partly dispersed and partly concentrated interphase region.

However, before realizing such hybrid-multiscale composites in real world applications, it is imperative

*Corresponding author (E-mail:harpreet.bedi@iitrpr.ac.in)

to evaluate the effect of both the CNT incorporation strategies on the mechanical response of the matrix as well as that of the laminate. Accordingly, a systematic study is carried out to evaluate the rate sensitivity of epoxy modified with different variants of nanotubes, namely as-grown, oxidized and functionalized CNTs. Further, the effect of CNT grafting on the average mechanical response of CFRP laminates is investigated in terms of interlaminar shear strength and mode-II fracture toughness.

2 Materials and Methods

2.1 CNT synthesis

The as-received carbon fibers (Hindoostan Technical Fabrics, India) were unsized by heating at 450°C for 20 min, then coated with nickel catalyst solution. Nickel coated fibers were then put inside a CVD chamber and subjected to a combination of argon, hydrogen and acetylene gases to grow CNTs on fiber surface[14]. Since, homogeneous dispersion is the key to attain positive interfacial modifications[9], CNTs grown on alumina plate inside CVD are purified and functionalized with carboxylic acid group[15].

2.2 Tensile testing

With respect to viscosity considerations of CNT modified matrix,[16]0.05wt% of each variant of nanotubes were dispersed in epoxy matrix by probe-sonication[15] to prepare three types of epoxy matrices. Dogbone samples were then prepared by mixing the epoxy resin and polyamine hardener in 1:2 ratio. The rate sensitivity of different variants of epoxy was then studied by performing the tensile tests on dogbone samples at cross-head speeds of 0.5 mm/min and 5 mm/min on a universal testing machine (Shimadzu Corp., Japan).

2.3 Short beam shear and mode-II fracture testing

CFRP laminates were prepared by hand lay-up technique. ISO-14130 and ASTM D7905 were followed to evaluate the interlaminar shear strength (ILSS) and mode-II fracture toughness (G_{IIc}), respectively. To this end, a total of six and 16 laminas were used, respectively, to prepare unidirectional CFRP laminates for the short beam shear and mode-II testing procedures. Both the tests were performed at a cross-head speed of 0.5 mm/min on a universal testing machine (Tinius Olsen, United Kingdom). It is to be noted that in order to investigate the effect of CNT grafting on the average laminate properties, only the middle two laminas of the respective laminates were modified with grafted nanotubes.

3 Results and Discussion

3.1 Sensitivity of CNT modified epoxy

Figure 1a illustrates the representative load vs displacement curves for neat epoxy and epoxy nanocomposites subjected to tensile loading. With increase in cross-head speed, the ultimate strength of neat epoxy as well as CNT modified epoxy nanocomposites increases (Figs 1(a,b)). Though the relative increase in strength was higher in neat epoxy rather than epoxy nanocomposites, indicating that neat epoxy was more sensitive to cross-head speeds than epoxy nanocomposites[17-18]. CNT based nanocomposites show a self-stiffening behavior under dynamic loading[19]. It was suggested that the plastic deformation of a material alters the microstructure and hence strengthens the bulk properties. Also with increasing crosshead speed, the ductile to brittle transition of polymers leads to a rise in composite strength[20-21]. This increase was due to the fact that, relative to fibers, the ductile polymer undergoes increased yielding and strain hardening owing to a change in microstructure of plastically deforming matrix under high strain loading[20]. Further, the largest relative increase was in the ultimate strength of neat epoxy composites, the extent of increase in strength is diminished for epoxy nanocomposites (Fig. 1b). This is because dispersed nanotubes toughen the matrix, reducing the overall ductility of the nanocomposite. In other words, molecular mobility of the polymer chains is reduced at higher cross-head speeds, which results in a more brittle material. That is why the relative increase in failure strength of epoxy nanocomposites with cross-head speed was more or less

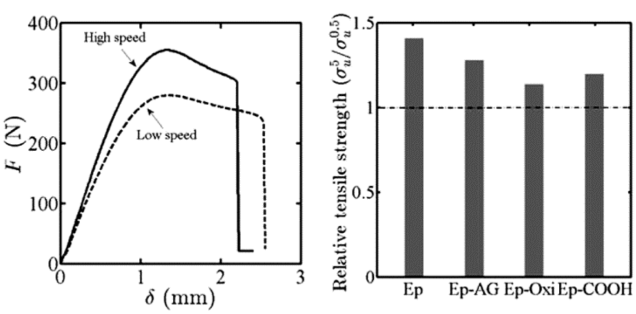

Fig. 1 — (a) Typical load-displacement curve for epoxy composites showing the increase in failure load with cross-head speed and (b) Relative tensile strength of neat epoxy composite (Ep) and epoxy nanocomposites prepared with as-grown CNTs (Ep-AG), oxidized CNTs (Ep-Oxi) and functionalized CNTs (Ep-COOH) tested at 5 mm/min and 0.5 mm/min of cross-head speed.

the same (Fig. 1b). Previously, it has been established that there was negligible effect on the tensile strength of carbon fiber coated with nickel catalyst as well as with CVD grown nanotubes[14]. Even if there are any effects of catalytic deposition (specifically of iron particles[22] and high temperatures during thermal CVD on fiber properties, such local variations in fiber properties were averaged out over the large volume of material used in laminated composites[14]. Hence, it can be said that it is the matrix that plays a greater role in the failure process of CFRPs.

3.2 Shear strength and fracture toughness of CNT grafted CFRP

The effect of CNT grafting on the interlaminar shear strength (ILSS) and the mode-II fracture toughness (G_{IIc}) of CFRP laminates is discussed next. Figure 2(a & c) compares the average load-displacement curves for base laminate and CNT modified laminate. The failure load increases significantly after the incorporation of grafted nanotubes in the laminate. While, the ILSS improves by 102% (Fig. 2b), the fracture toughness of CNT modified laminate is 53% (Fig. 2d) higher compared to the base laminate[23]. One of the possible reasons behind such enhancement is the strengthening of matrix by the grafted CNTs present on fiber surface, as schematically depicted in Fig. 3. This is similar to the reinforcing of matrix by fibers in the direction parallel to fiber length.

Another mechanism that plays an important role here is the mechanical interlocking between the nanotubes present in adjacent laminas (see Fig. 3). Such a behavior is analogous to the clinging phenomenon shown by hooks-and-loops (Fig. 4) or popularly known under the trade name of Velcro®. The working of these materials is based on the interplay of roughness and fuzziness. The presence of a large number of hooks on one and the entangled texture on the other surface allows these materials to mechanically interlock with each other (Fig. 4b). In a similar manner, the grafted nanotubes on neighboring laminas interlock with each other, thereby improving the ILSS.

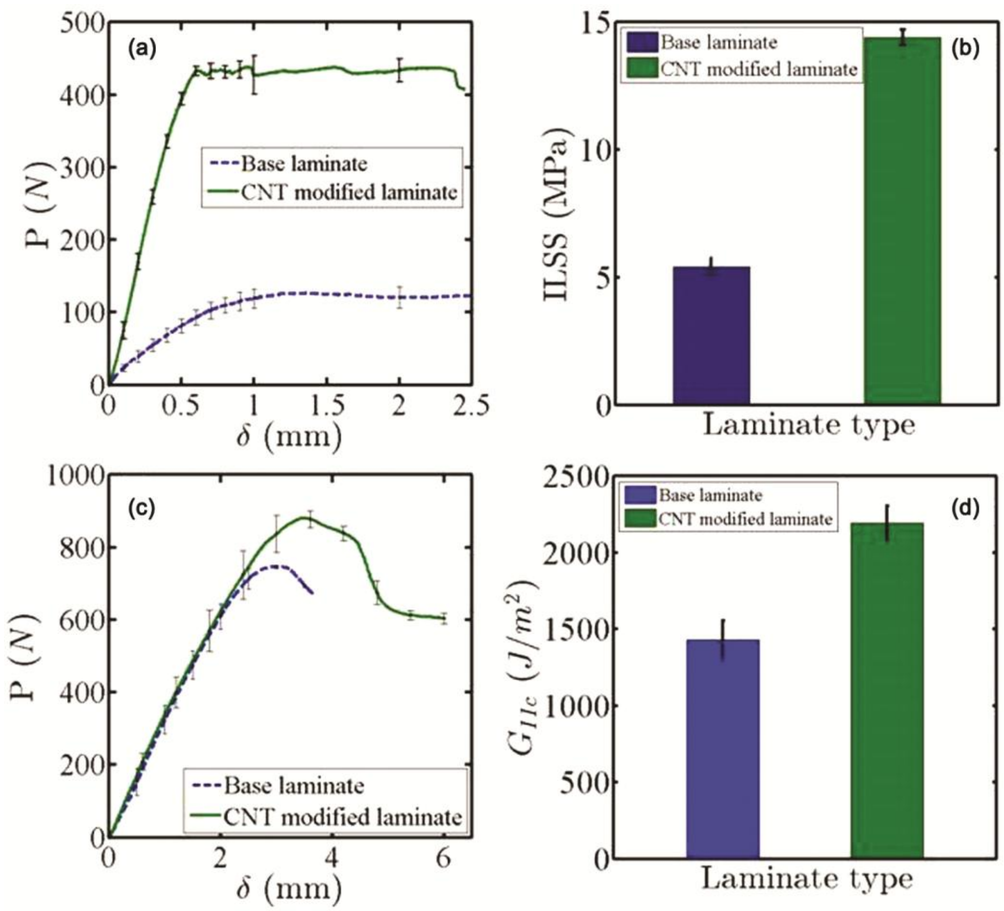

Fig. 2 — Average load (P)-displacement (δ) plots obtained from (a) short beam shear testing and (c) mode-II fracture testing. The results of each test are presented as: (b) average interlaminar shear strength, and (d) average fracture toughness. Error bars in each plot denote the standard deviations in the experimental results[23].

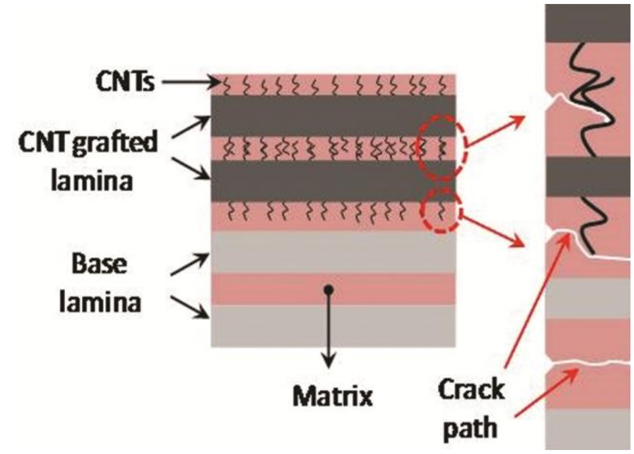

Fig. 3 — Mechanism of CNTs reinforcing the matrix and interlocking with each other. The effect of CNTs on the crack propagation is also demonstrated.

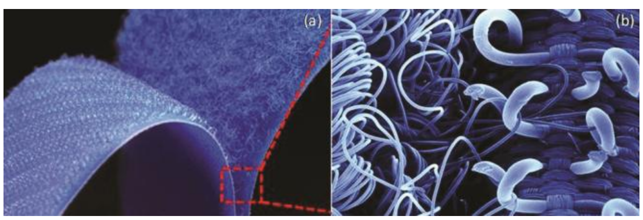

Fig. 4 — Mechanical interlocking in a hook and loop arrangement[24-25].

Moreover, as shown in Fig. 3, the presence of CNTs in a composite arrests a propagating micro-crack. Thus, higher energy was required for a crack to break a hard nanoparticle, raising the fracture toughness of the composite (Fig. 2d). Moreover, the intermingling of nanotubes extends the crack travel path and hence the crack propagation was delayed (Fig. 3), as can be seen from a nearly 23% increase in deformation at failure in Fig. 2c. Hence, more than one failure mechanisms operate when CNTs are introduced in CFRPs, thereby improving the shear and fracture properties of laminated composites. Such a hierarchical structure can prove to be a game changer in structural composites such as airplane wings, rotor blades, actuators, and jet engine components involving complex loading environment.

4 Conclusions

The effect of different CNT incorporation strategies on the mechanical performance of matrix and the laminate as a whole was investigated experimentally. CNTs synthesized using the chemical vapor deposition method are either mixed in matrix or are grown directly on the surface of the fiber. Oxidation and carboxylic functionalization treatments were further given to the CNTs to be mixed in matrix, so as to enhance theirdispersibility and interaction with the matrix. With increase in loading rate, the ultimate strength of neat epoxy and CNT/epoxy nanocomposites increases. However, owing to the stiffening effect of CNTs in matrix, the rate sensitivity of nanocomposites was found to be lower than that of neat epoxy. Not only in dispersed form, but the nanotubes grafted on fiber have the potential to alter the bulk mechanical properties of laminated composites. CNT grafting of the middle two laminas significantly improves the interlaminar strength and the fracture toughness. The findings of the present study throw insights on the usefulness of nanotubes in polymer matrix composites, especially in CFRPs which are widely popular in the structural engineering applications. This opens the path to prepare hybrid and multiscale polymer composites, either individually or simultaneously, so as to process a truly versatile material that may fit in a wide range of loading conditions in structural applications.

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