On the nature of interface of carbon nanotube coated carbon fibers with different polymers

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Abstract. Experimental investigations are carried out to analyse the wetting behaviour of carbon nanotube (CNT) coated carbon fiber to determine their suitability to process carbon nanotube coated carbon fiber/polymer multiscale composites for structural applications. To overcome the problem of agglomeration, CNTs are grown directly on the surface of carbon fibers as well as fabric using thermal chemical vapour deposition (CVD) technique. The term multiscale is used because different reinforcement mechanisms operate at the scale of long fibers and CNTs which are of few micrometers in length. The load carrying capacity of these multiscale composites critically depends on the efficiency and extent of load transfer from low strength matrix to high strength fiber which in turn depends on the interfacial strength between CNT coated carbon fiber and polymer matrix. A systematic analysis of wetting behaviour of CNT coated carbon fiber with epoxy and polyester matrix is carried out in this study. It is shown that CNT coated carbon fibers as well as fabric show better wettability with epoxy matrix as compared to polyester matrix. This results in stronger interface of CNT coated carbon fiber with epoxy as compared to polyester in multiscale composite system. A similar observation is made in nanoindentation testing of single fiber multiscale composites processed with epoxy and polyester matrix. In addition, it is observed that wettability, interfacial strength and average properties of CNT coated carbon fiber/polymer composites are a function of CNT density on the surface of carbon fibers.

1. Introduction
Advances in aviation and automobile industry, military and sports equipment demands better carbon fiber reinforced polymer (CFRP) composites with improved strength to weight ratio. To serve this purpose, nano-materials such as carbon nanotubes (CNTs) have proven to be an unmatched candidate [1]. Tensile modulus of the order of 1 TPa, tensile strength of 100-600 GPa and low density of 1.3 g/cm^3 along with high thermal and electrical conductivity [2] are some of the excellent properties of carbon nanotubes (CNTs) that may be harnessed into CFRP composites to improve their average properties. However, agglomeration of CNTs in polymer matrix [3] poses a difficult challenge for their use in polymer composites. To address this issue, CNTs are grown directly on the surface of carbon fibers [4] rather than being mixed with polymer resin. CNT coated carbon fiber/polymer multiscale composites show improvement in interfacial shear strength [5], enhanced fracture toughness [6] and tensile strength [7]. However, the observed improvement in overall properties of the composite is not as much as expected. One of the possible reasons could be the lower load/stress

transfer due to weaker adhesion at CNT coated carbon fiber-polymer interface. Since, the quality of fiber-polymer interface and the extent of adhesion critically depends on the wetting of fiber surface by polymer resin [8]; an attempt is made in this work to characterize the effect of CNTs on the wetting behaviour of CNT coated carbon fiber with different polymer resins. Interfacial strength and average properties are studied by nanoindentation and uniaxial tensile testing of single carbon fiber/polymer multiscale composites processed with epoxy and polyester matrix. It is shown that epoxy matrix is better suited as compared to polyester matrix to process CNT coated carbon fiber/polymer multiscale composites.

2. Experimental

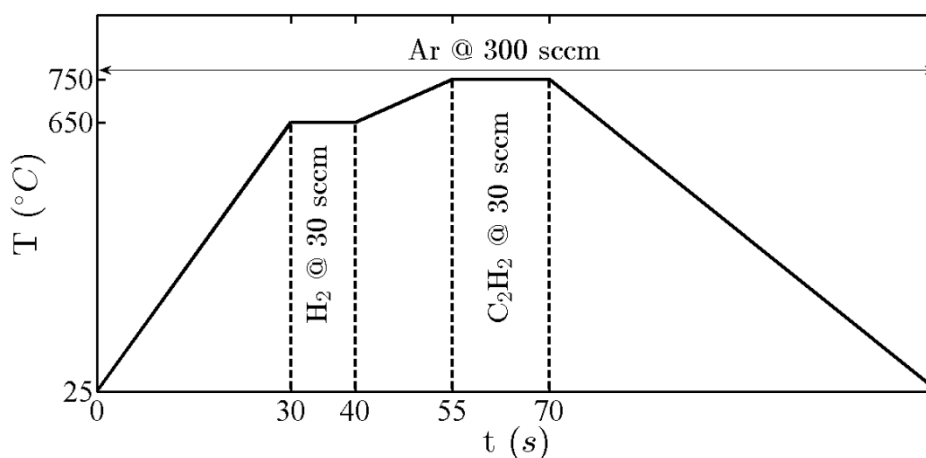### 2.1. Raw materials and catalyst coating

Hindoostan Technical Fabrics, India, supplied the unidirectional carbon fiber (CF) fabric that is preheated at about 550°C for 30 minutes to remove any polymer sizing applied to it. These sizing free (will be referred as unsized from here onwards) CFs are then coated with nickel catalyst using dip coating technique [4] (refer table 1). The catalyst solution is prepared by dissolving nickel sulphate, sodium hypophosphite, sodium succinate and succinic acid in distilled water. Variation in number of nucleation sites on the surface of carbon fiber is achieved by dipping CFs in the catalyst solution for different time varying from 3 to 10 minutes. Catalyst coated carbon fibers are then heated in an oven at 120°C for 20 minutes to remove any moisture content. While, 1wt% of accelerator and hardener is used to cure the polyester resin, the cross linking in epoxy resin is facilitated by mixing 60wt% of hardener in uncured epoxy.

Table 1. Composition of the acidic dip coating solution [4].

Nickel sulphate [$NiSO_4.6H_2O$] (g/l)	Sodiumhypophosphite [$NaH_2PO_2.H_2O$] (g/l)	Sodium succinate [$Na_2C_4H_4O_4.6H_2O$] (g/l)	Succinic acid [$C_4H_6O_4$] (g/l)	Coating temperature (°C)
30	15	15	0.36	75

2.2. CNT synthesis on catalyst coated carbon fibers

Growth of CNTs on the surface of catalyst coated CFs is facilitated inside a CVD reactor at an initial vacuum of the order of 10^{-2} Torr using CNT growth protocol shown in figure 1. Argon (Ar) helps in achieving an inert atmosphere and acts as a carrier of hydrogen (H_2) and acetylene (C_2H_2) gases. H_2 is used for dissociating the NiP film deposited on CF surface into Ni or NiP particles which act as CNT growth sites. C_2H_2 dissociates at 750°C providing carbon for the formation of CNTs at nucleation sites.

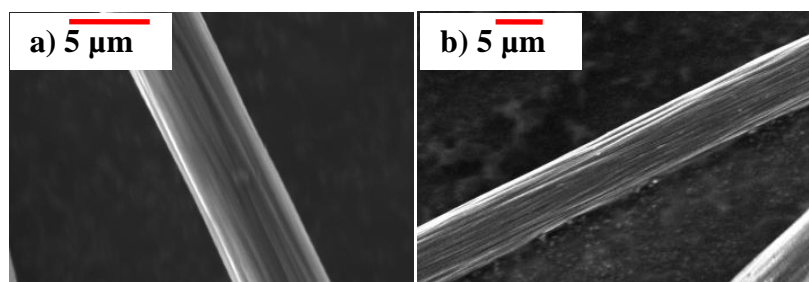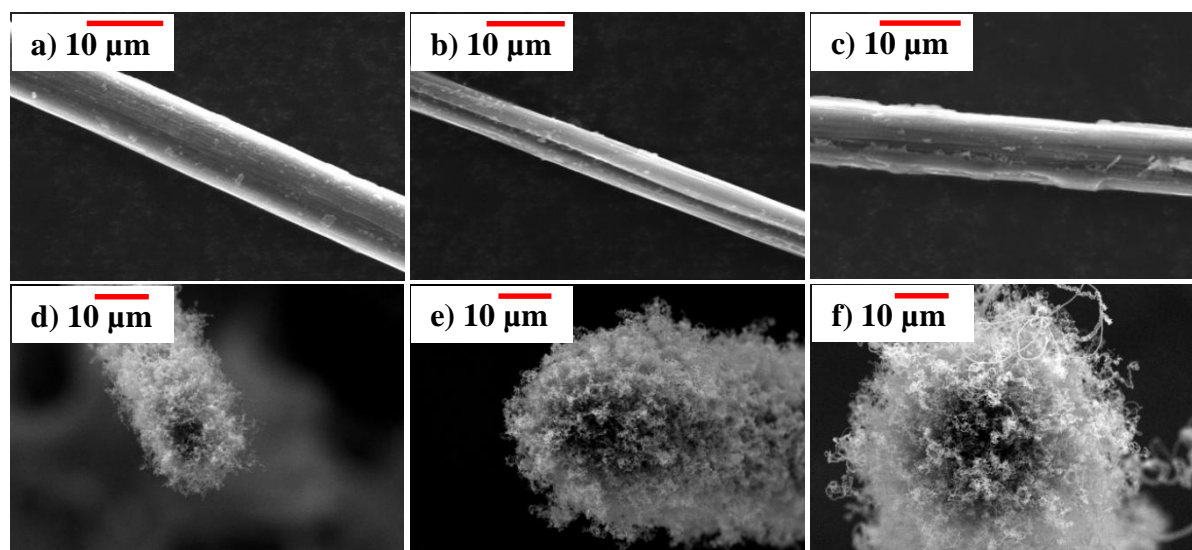**Figure 1.** CNT growth protocol used in chemical vapour deposition (CVD) reactor.

3. Results and discussion

3.1. Effect of catalyst coating time on the growth of CNTs

Scanning electron microscopy (SEM, JEOL 6610 LV, Japan) of CF with and without sizing layer (figure 2) reveals their average size of 7-10 μm. Figure 3(a-c) shows the SEM micrographs of catalyst coated CFs with different coating times displaying an increase in thickness of catalyst film on fiber surface with increasing coating time. This leads to a higher number of nucleation sites for CNTs on reducing the catalytic layer during CNT growth process. Energy dispersive spectroscopy (EDS) of catalyst coated carbon fibers predicts a rise in the amount of Ni from 0.3wt % to 1.25wt% as catalyst coating time is increased from 3 mins to 10 mins. Increase in the number of growth sites leads to denser CNTs on the surface of catalyst coated carbon fiber as observed in SEM micrographs shown in figure 3(d-f).

Figure 2. SEM micrograph of (a) as received and (b) unsized (sizing free) carbon fibers.
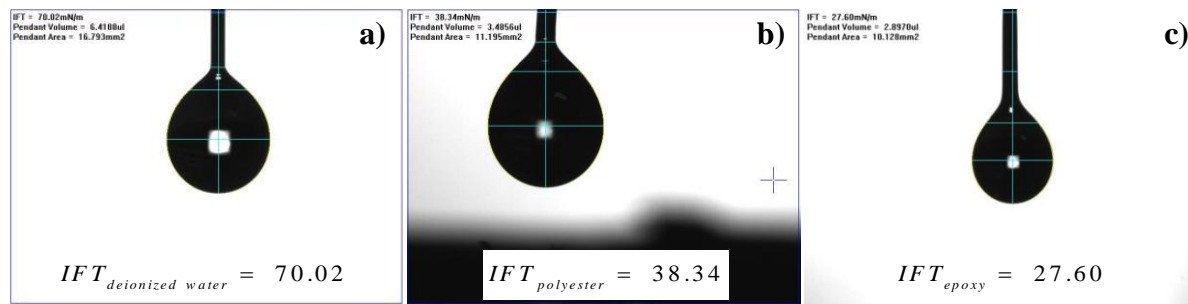

Figure 3. SEM micrograph of catalyst coated carbon fibers with dip coating time of (a) 3 mins (b) 5 mins and (c) 10 mins. Corresponding CNT coated carbon fibers are shown in micrographs 3(d-f).

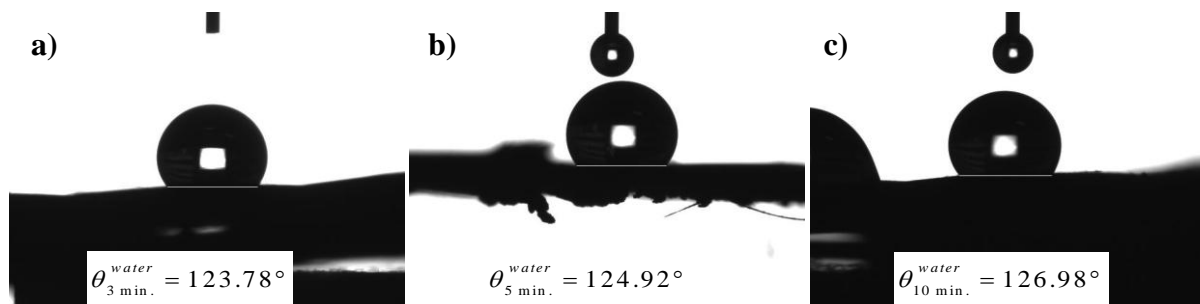*3.2. Effect of CNT density on the wettability of CNT coated carbon fiber*

Effect of CNT growth on the wetting behaviour of CNT coated carbon fiber fabric as well as single carbon fiber with deionized water, polyester and epoxy is investigated by performing contact angle measurements using First Ten Angstroms (FTA) contact angle setup, Virginia, USA.

First, interfacial tension (IFT) of deionized water is measured to check the accuracy of FTA system and is found to be in good agreement with the value reported in literature (see figure 4a). Next, IFT of epoxy and polyester is also determined which will later be used in the calculation of work of adhesion (Wa).
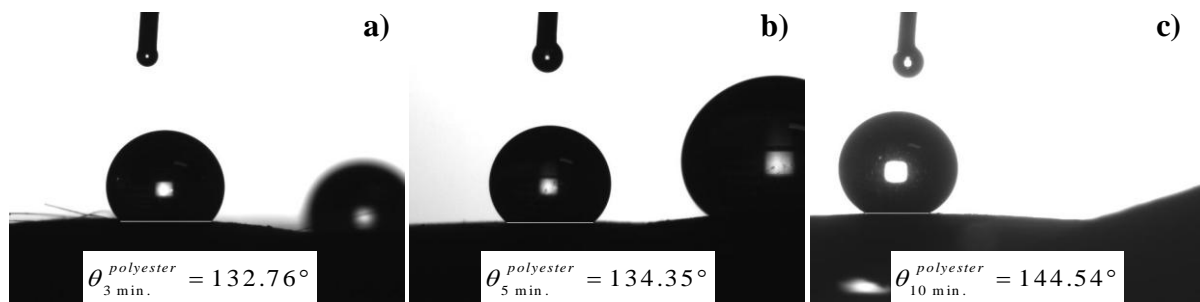
Figure 4. Interfacial tension (IFT) of various liquids in mN/m.

3.2.1 Wettability analysis of CNT coated carbon fiber fabric with deionized water. Liquid droplets are placed on CF-fabric and average contact angle (θ) is measured using freely available imageJ software (http://imagej.nih.gov/ij/download.html). θ for deionized water droplets on various CNT coated CF-fabric is found to be $\geq 123.78°$ (see figure 5), showing hydrophobic nature of deionized water with CNT coated CF-fabric. Moreover, hydrophobicity strengthens with increase in CNT density on the fabric surface (see figure 5(a to c)). This behavior is not surprising as the increase in catalyst coating time increases the CNT density on the fiber surface which in turn increases the surface roughness factor *r* of carbon fibers. According to Wenzel's equation [9], increase in *r* magnifies the inherent wetting property (hydrophobicity in this case) of a rough surface.

Figure 5. Average contact angle *(θ)* of deionized water droplets on CNT coated carbon fiber-fabric dip coated in Ni catalyst solution f*o*r different time durations.
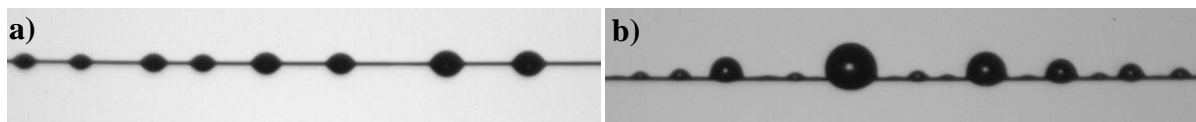
3.2.2. Wettability analysis of CNT coated carbon fiber fabric with polyester. Average contact angle θ for polyester droplet on various CNT coated CF-fabric is found to be $\geq 132.76°$ (see figure 6), showing poor wetting of CNT coated CF-fabric with polyester resin. Moreover, θ increases with increasing CNT density on the fiber surface (see figure 6(a to c)) further deteriorating the capacity of polyester to wet the fabric, in accordance with Wenzel's equation.

Figure 6. Average contact angle (θ) of polyester droplets on CNT coated carbon fiber-fabric dip coated in catalyst solution for different time durations.

For epoxy droplets θ cannot be measured effectively due to their instant spreading on all types of CNT coated carbon fiber fabric samples. This shows good wetting of CNT coated carbon fibers with epoxy matrix. To quantify the wetting behavior of epoxy resin, shapes of polymer droplets on single carbon fiber filaments are studied in the next section.

3.2.3. Wettability analysis of CNT coated single carbon fibers. To get further insight, the wetting behavior of carbon fibers is characterized by examining the shape of polymer droplets on CNT coated single carbon fiber (SCF) filaments, as shown in figure 7. While epoxy forms axially symmetric barrel type droplets (see figure 7a) indicating good wettability, clam type non-axisymmetric droplets of polyester suggest poor wetting [9] of CNT coated SCF (see figure 7b). This further indicates that probability of having stronger interface is higher with epoxy resin as compared to polyester resin in CNT coated carbon fiber/polymer multiscale composites.
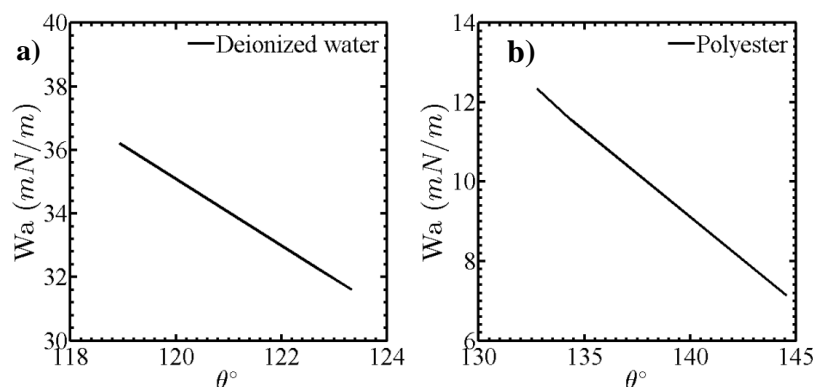

Figure 7. Optical micrographs of (a) barrel type epoxy droplets and (b) clam type polyester droplets on CNT coated single carbon fibers.

3.2.4. Work of adhesion (Wa). Effect of CNT density and hence surface roughness of carbon fiber on wettability is quantified by calculating *Wa* of the polymer using Young-Dupre equation (1) [10].

$$W_a = \gamma_{LA}(1 + \cos\theta) \tag{1}$$

Where, γ_{LA} is the surface energy of the liquid-air interface as determined from IFT value. On various CNT coated CF-fabrics, *Wa* of deionized water and polyester is found to be decreasing with increasing θ (figure 8). This implies that less amount of work is required to separate the liquid-solid phases from one another. Hence, the contact strength between the two phases gets diminished with the increase in density of CNTs on fiber surface which supports our earlier findings, that polyester has poor capacity to wet carbon fibers and wettability degrades with increasing CNT density.
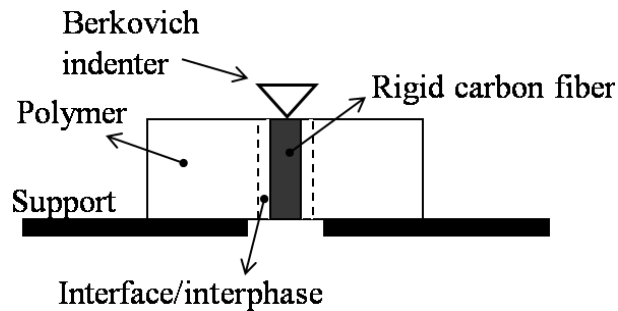

Figure 8. Work of adhesion (*Wa*) of (a) deionized water and (b) polyester with static contact angle θ.

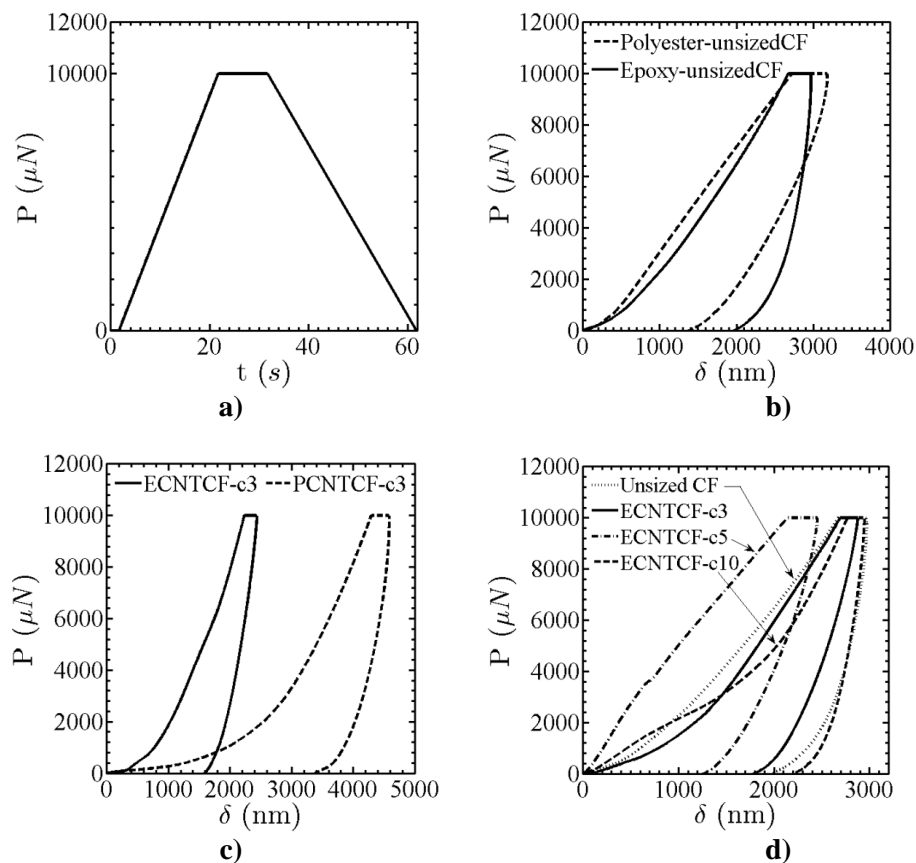*3.3. Effect of CNT density on interfacial stiffness.*
Nanoindentation testing on various samples is performed to qualitatively investigate the effect of CNT coating on interfacial stiffness in single carbon fiber composites processed with epoxy and polyester matrix using TI 950 TriboIndenter, Hysitron. To this end, single carbon fibers (SCF) are embedded vertically into epoxy and polyester resins mixed with corresponding hardeners and allowed to cure at room temperature. Circular discs of epoxy and polyester SCF composites, with an approximate diameter of

10 mm and 0.5 mm thickness are then post-cured at temperatures of 55°C and 90°C for 4 hours and 2 hours, respectively. These single fiber composites are then indented with Berkovich indenter with a half angle of 65.35° (see figure 9).

Assuming the fibers to be rigid in comparison to matrix and interface/interphase, the displacement of indenter can be thought of primarily due to the displacement of interace/interphase region surrounding the rigid fiber.

Figure 9. Schematic showing nanoindetation testing of single carbon fiber polymer composite.

Figure 10. (a) Rate of loading employed in nanoindentation of single carbon fibers (SCF). (b, c) Contrast in load *P*-displacement *δ* curve between unsized (b) and CNT coated (c) SCF composites made with epoxy (-) and polyester (--) resins. (d) Comparison of *P-δ* curves of multiscale SCF epoxy composites with different CNT density on fiber surface.
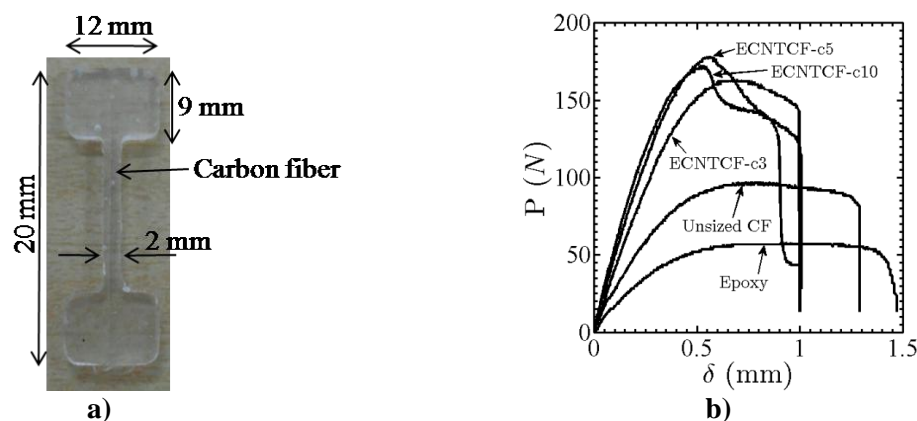
Thus, the load-displacement (P-δ) curves recorded by varying the load on indenter (see figure 10a) will provide a qualitative measure of interfacial stiffness in various SCF composite samples. At first, P-δ curve of unsized carbon fibers embedded in polyester and epoxy matrix is compared in figure 10b. It is to be noted here that multiple samples are tested in each case and a representative curve is shown here for comparison purpose. It has been found (see figure 10b) that displacement at peak load in unsized carbon fiber/epoxy composite is slightly lower as compared to unsized carbon fiber/polyester composite indicating slightly better interface in unsized carbon fiber/epoxy composite.

Similar analysis is carried out for CNT coated carbon fibers corresponding to 3 minute dip coating time and the comparison of P-δ curves has been shown in figure 10c. Here again, the displacement at peak load in CNT coated carbon fibers is significantly higher in polyester matrix as compared to epoxy matrix (see figure 10c). These observations suggest higher interfacial stiffness and hence stronger interphase in composites processed with epoxy matrix than with polyester matrix.

In the next step, the effect of CNT density on the interfacial stiffness is studied by performing indentation experiments on composites processed with CNT coated single carbon fibers having different catalyst coating time in epoxy matrix. Figure 10d compares the P-δ response for this case. It is observed that the load carrying capacity of CNT coated single fiber composites is improved as the dip coating time is increased from 3 to 5 mins but decreases for 10 mins of catalyst coating time (see figure 10d). This suggests that 5 min. coating time provides optimum density of CNTs on fiber surface to improve the interfacial stiffness of CNT coated carbon fiber/epoxy composites.

3.4. Tensile testing of single carbon fiber epoxy composites.
To characterize the effect of CNT density on the average response of single carbon fiber (SCF)/epoxy composites, various samples are tested under uni-axial tensile loading using Tinius Olsen, UTM. Dogbone shaped samples of 1.5 mm thickness are prepared (see figure 11a) by placing SCF at half the mold depth. The fiber is fixed at the ends using an adhesive; epoxy resin/hardener mixture is then poured in the mold and allowed to cure at room temperature. The cured dogbone samples are further post cured at elevated temperature as described in previous section and are tensile tested at a crosshead speed of 0.5 mm/minute. Figure 11b compares the evolution of load P as a function of crosshead displacement δ for different composite samples.

Figure 11. Sample dogbone shaped tensile test specimen (a) and tensile strength of various single carbon fiber dogbone specimens (b).

It is found that ultimate tensile strength of all CNT coated SCF composites is higher than both unsized SCF composites and pure epoxy matrix composite. One of the possible reason for this improvement in tensile strength could be the nucleation effect of CNTs on polymer crystallization [11] leading to microstructural development of polymer nearby CNTs. This results in much better properties of polymer in the interphase around carbon fibers than in the bulk. Moreover, the average response of

CNT coated SCF/epoxy composites show very weak dependence on CNT density on fiber surface and hence catalyst coating time.

4. Conclusions

In this work, a methodology is presented to predict the suitability of a polymer matrix to process CNT coated carbon fiber/polymer multiscale composites. In particular, the effect of CNT density on the wettability, interfacial stiffness and average properties of CNT coated carbon fiber/polymer multiscale composite is investigated. The salient results of the present investigation can be summarized as:

- Clam type droplets, decreasing work of adhesion *Wa* with increasing CNT density (or roughness factor *r*) and hydrophobic nature of polyester shows its poor wetting behavior with CNT coated carbon fibers.
- Axi-symmetric barrel type epoxy droplets on single carbon fibers, instant spreading of epoxy on CNT coated carbon fiber fabric indicates good wettability of CNT coated carbon fiber fabric with epoxy matrix.
- Nanoindentation testing reveals that interfacial stiffness of CNT coated single carbon fiber/epoxy composites is higher as compared to their polyester counterparts. Moreover, the interfacial stiffness is found to be a function of CNT density on the surface of carbon fiber.
- Tensile testing of single carbon fiber epoxy composites indicates an improvement in tensile strength with the use of CNT coated carbon fibers. However, the average tensile response of these composites depends very weakly on CNT density on the fiber surface.

As per the Wenzel's relation [9], increase in roughness of any surface augments its inherent wetting behaviour with a specific liquid. It is observed through SEM analysis (see figure 3) that the growth of CNTs increases the surface roughness of carbon fibers. Hence, consistent with Wenzel's relation, the wettability of carbon fiber fabric as well as single fiber improved with epoxy (see figure 7a) and deteriorated with polyester (see figure 6 and 7b) after growth of CNTs on their surface. The ability or inability of a particular polymer to wet the fiber fabric further gets magnified on increasing the CNT density on the surface of fabric (see figure 6). Moreover, it has been observed that there is an optimum CNT density on the fiber surface to maximize the increase in interfacial stiffness, as observed in [4] as well. The optimum catalyst coating time to achieve this is found to be 5 minutes in the case of CNT coated/epoxy composites studied here. In addition, the average properties as well as interfacial stiffness depends on the type of polymer used to process the multiscale composites (see figure 10 and 11). Hence, the catalyst coating time and the type of polymer matrix needs to be judiciously chosen in order to harness the excellent properties of CNTs in multiscale polymer matrix composites.

Acknowledgments

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