Since the carbon nanotubes (CNTs) have been discovered, there has been a marked increase in the scientific literature dealing with multi-scale composites. The multi-scale hybrid composites with CNTs could endow the composites with some superior mechanical properties, such as improving the tensile performance, modest increasing compressive and flexural properties, and significantly enhancing interlaminar, interfacial and fracture strength. In addition, composites with CNTs can also develop the functional properties. A small quantity of CNTs can significantly increase the electrical properties of composites and lower the coefficient of thermal expansion of composites. The purpose of this work is to review the available literature in mechanical and functional properties of multi-scale hybrid composites manufactured using CNTs. POLYM. COMPOS., 32:159–167, 2011. © 2010 Society of Plastics Engineers

INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima, CNTs have been used extensively by researchers in various fields such as nano-electronic components, catalyst, electrode materials, hydrogen storage materials, and composites [1–9]. And new structural composite concepts harnessing the attractive properties of CNTs are being intensely researched around the world [10–14]. In recent years, CNTs have been the excellent candidates for a new generation of high-strength, high-stiffness materials. And CNTs have been shown to have potential applications in composites due to their remarkable mechanical, thermal, and electrical properties, and because of their high aspect ratios and low densities [15]. Therefore, there have been many attempts to use CNTs in reinforcement of composite materials for overcoming the performance limits of conventional materials. However, most efforts in this area have dealt with CNT/polymer composites, which present tremendous strengthening effect for the composites [16–22]. Later, a number of research groups demonstrated that the tensile, shear, flexural, fracture toughness, and thermal properties of polymer composites could be significantly improved, which contained loading CNTs between 0.1 and 5 wt% [23–28].

Because there is a much strong interfacial interaction, especially in the surface functionalized CNT/polymer composite interphase, some investigations have been done recently on the design and preparation of the CNT/fiber hybrid composites by growing CNTs on fibers [29–32]. The growth of CNTs offers potential for selective reinforcement, improves through-thickness properties of polymer composites or is used to stiffen the fiber/matrix interface [29, 33]. The CNTs in the multi-scale hybrid composites can not only grow directly on the fiber (see Fig. 1) or fabric surface (see Fig. 2), but also be dispersed in matrix. The CNTs in polymers hold a potential to improve the mechanical, thermal and electrical properties in the host materials [19, 35]. It has been demonstrated that adding only 1wt% of CNTs to matrix material, the stiffness of the resulting composite can increase as high as 36–42% and the tensile strength can raise 25% [36]. And the presence of CNTs in the matrix may alleviate many drawbacks of conventional fiber composites, especially longitudinal compression and interlaminar properties [37–39].

PREPARATION OF MULTI-SCALE HYBRID COMPOSITES

Because of high performance of CNTs, a lot of investigations have been done recently on design and preparation of the CNT/fiber hybrid composites. And there are many methods to prepare the multi-scale hybrid composites, and several methods to fabricate the composite of them have been developed, e.g., solution casting [40–43], melt-mixing and in situ process through polymerization of monomers with the presence of the CNTs [37, 44, 45]. But in this study, four kinds of commonly used methods are mainly introduced. Figure 3 shows the architectures of CNT-carbon fiber hybrid composites. Figure 4 exhibits a
schematic of the experimental set-up for the closed-mould vacuum-assisted resin transfer moulding (VARTM) process [46].

Chemical Vapor Deposition (CVD)

At present, some research groups are working on growth of CNTs by chemical vapor deposition (CVD) directly onto a carbon fiber surface [29, 47]. And the CVD route has been established as the most effective and practical route to synthesize CNTs [36]. Matsuda et al. [48] used direct current (DC) plasma CVD method on the submicron-sized dot-catalyst array substrate which was fabricated by electron beam lithography for the purpose of developing nano-sized electron field emitters. Experimental results showed that multi-walled carbon nanotubes (MWNTs) grown from Ni-C composite nanoclusters have become narrower than those from Ni evaporated thin film. Their diameters were reduced from 50–100 nm to 5 nm or less. Guo et al. [49] used CVD method to synthesize hybrid composites. Ni foil with thickness of 0.2 mm was used as a catalyst for CNT growth. The Ni foil was placed in a thermal CVD system using a gas mixture of acetylene and hydrogen. The as-prepared CNTs were processed to field emission emitter by screen-printing method. Figure 5a shows a photograph of typical CNTs mat scraped from nickel foil substrate. And as shown in Fig. 5(b), the mat comprises of high purity nanotubes with different diameters.

Although the CVD process is an efficient technique for the growth of CNTs on a variety of surfaces, the use of high temperatures and predeposited catalysts, taken together with the difficulties in processing large panels, imposes serious limitations on the practical application of this technique for the fabrication of CNT-reinforced structural composites [50]. CVD can produce well-aligned single wall carbon nanotube (SWNTs) or MWNTs but can also yield entangled CNTs [51]. And many difficulties need to be solved, such as homogeneous dispersion of CNTs in polymeric matrix and strong interfacial interaction so as to affect load transfer from polymeric matrix to CNTs [37]. Moreover, the properties of pristine fiber are seriously injured because of the catalyst and prophetic gas environment.

Chemical Grafting

He et al. [30] presented a new chemical method used for preparation of the CNT/carbon fiber multi-scale reinforcement, which combines micrometric fibers with nano-metric CNTs. MWNTs functionalized with hexamethylene diamine at the end caps were grafted onto the surfaces of carbon fibers treated by acyl chloride using the fiber surface grafting technique [30, 52–54]. Laachachi et al. [47]...
developed a simple method for grafting CNTs onto a carbon fiber surface. CNTs and carbon fiber underwent an oxidation treatment. Oxidation generated oxygen, like carboxyl, carbonyl, or hydroxyl groups on nanotube and carbon fiber surface. Functionalized CNTs were dispersed in a solvent and deposited on carbon fibers. The bonds between CNTs and carbon fibers were operated by esterification or anhydridation of the chemical surface groups (see Fig. 6).

The grafted MWNTs stuck to the carbon fiber surface at different angles and were uniformly distributed along the outer edges of the grooves in the fiber surface. The grafting increased the weight of the carbon fiber by 1.2%, and it was implied that a considerable amount of MWNTs were graft onto carbon fiber surface [30]. But this method may damage the strength of the fiber during the fiber surface functionalization.

**Surface Coating**

Zhu et al. [55] developed a coating method for distributing a very small amount of CNTs on the woven fiber to facilitate the fabrication of large scale nanocomposites compatible with the traditional composite manufacturing processes (see Fig. 7). He added a small amount of SWNTs in nanocomposite to improve Z-axis properties, particularly, interlaminar shear strength. The glass fiber fabric was coated by CNTs and then was processed into vinyl ester composite laminates. Figure 8 shows the glass fiber coated with CNT-epoxy nanocomposite.

The advantage of this coating method is that it could be implemented in a straightforward manner by conventional composite processing like resin transfer molding. The method can also be easily extended to other polymer based composite systems. However, it is very difficult to control the homogeneous dispersion of the CNTs by using this method.

**Electrophoresis**

Electrophoresis is a simple and versatile technique that can be readily automated and utilized for industrial application. On the basis of the ability of CNTs to respond to an electric field, Bekyarova et al. [50] developed the method for the deposition of CNTs on the surface of carbon fibers by using of electrophoresis. It was found that CNTs were deposited uniformly on the surface of a carbon fiber from aqueous nanotube dispersions upon applying a DC potential between the carbon fibers and the counter electrode. Because of their negative charge, CNTs migrate toward the positive carbon fiber electrode and are subsequently deposited on the fiber surface (see Fig. 9). The negative charge is attributed to the carboxylic acid groups introduced into the nanotubes during the nitric acid treatment [57], and the adsorption of hydroxyl anions from the dispersion may also contribute to the net negative charge [58]. Figure 10 shows the images of carbon fibers with CNTs deposited by electrophoresis.

By using this method, the manufactured multi-scale hybrid composites reinforced with CNT-coated carbon fabric showed ~30% enhancement of the interlaminar shear strength, and importantly, they have preserved in-plane mechanical properties. However, this method required relatively harsh conditions and the CNTs can get...
a homogeneous dispersion on the fiber/fabric surface but can not disperse homogeneously in the inner-fabric.

MECHANICAL PERFORMANCE OF MULTI-SCALE HYBRID COMPOSITES

Adding the CNTs in the composite can significantly improve the composite mechanical properties and the improvement in mechanical properties can be mainly attributed to the following characteristics of this new type of interface structure. First, stress can be efficiently transferred from the matrix to the reinforcements. Second, the matrix surrounding the reinforcement particles is reinforced by CNTs. Finally, CNTs may promote formation of microcracks in the interface [15]. Figure 11 shows mechanical property improvement of carbon fiber reinforced plastic (CFRP) by incorporation of CNTs.

Tensile Strength and Modulus

The tensile properties are some of the most important indicators to reflect the composite mechanical properties. In the composites, different reinforcement may cause different tensile properties. Adding the CNTs in the glass fiber/epoxy composites can improve the tensile properties. Qiu et al. [60] fabricated three different composite samples based upon conventional epoxy/glass-fiber composites: (1) 1 wt% functionalized MWNT-reinforced multi-scale composites; (2) 1 wt% pristine MWNT-reinforced multi-scale composites; (3) conventional epoxy/glass fiber composites without adding MWNT. The tensile tests on these three samples showed that for pristine MWNT-reinforced composites, both tensile modulus and shear modulus were improved by about 8%, but the tensile strength and shear strength decreased. However, all the properties of multi-scale composites using functionalized MWNTs showed significant enhancement. Modulus along fiber orientation was enhanced by 27.2%, while tensile strength was enhanced by 15.9%. Siddiqui et al. [56] showed that the 0.3 wt% CNT-epoxy nanocomposite coating gave rise to a significant increase in tensile strength of the single fiber for all gauge lengths, which was better than the neat epoxy coating. The results on glass fiber roving also indicated a clear beneficial effect of composite impregnation on tensile strength.

However, adding the CNTs in the carbon fiber/epoxy composites can’t improve the tensile properties significantly. Bekyarova et al. [50] had carried out some tensile tests on the carbon fiber/epoxy and multi-scale MWNT/carbon fiber/epoxy composites and found that the tensile strength and tensile modulus of the composites prepared with MWNT deposited carbon fiber are similar to those of the composites made with carbon fiber alone. Kim et al. [61] showed that the longitudinal tensile modulus and transverse tensile modulus of epoxy/carbon fiber composite were 221.3 and 13.08 GPa, however, after adding the CNT in the epoxy/carbon fiber composite the longitudinal tensile modulus and transverse tensile modulus were
221.4 and 14.15 GPa, respectively. It is indicated that the CNTs can’t significantly improve the composites tensile properties.

**Compressive Properties**

There are a large volume of works concentrating on buckling of CNTs by themselves, but there have been relatively few studies on the compressive behavior of CNTs when embedded in composites. However, adding some CNTs in the composites affects not only the tensile properties but also the compressive properties [62–67]. Cho and Daniel [65] showed that adding 0.5 wt% and 1.0 wt% CNTs in carbon fiber/epoxy composites, the in-plane compressive strength increased by 39 and 26%, respectively. Zhu et al. [55] indicated that in glass fiber reinforced vinyl ester composites, the compressive strength is 27 MPa. The addition of 0.1 wt% SWNTs and 0.2% SWNTs in the composites, the compressive strength is about 39 and 33 MPa, respectively. So, it is proper to add right amount of CNTs in the composites to improve compressive properties. Yokozeki et al. [66] showed that in composite laminates, the compressive strength of composites with 5% CNTs increased to 501 MPa, and the compressive strength of composites with 10% CNTs is 539 MPa.

**Flexural Properties**

Although the conventional composites have been widely used in many industries, the flexural properties always blocked its development. However, the conventional composites with CNTs can make up for this defect. Song [68] tested the flexuous properties of aramid fiber/epoxy composite and CNT/aramid fiber/epoxy composite. It was found that the flexuous properties of the aramid/epoxy composites with CNTs were slightly improved. Zhou et al. [69] showed that the carbon fabric/epoxy composites with 0.3% CNTs can slightly improve the composites flexuous properties. Yokozeki et al. [66] added the cup-stacked carbon nanotubes (CSCNTs) in the CFRP laminates composites, and he found that adding 5 wt% CSCNTs in the composites can improve the composites flexural properties, and the flexural strength is 912 MPa. At the same time, adding the CNTs in the matrix can also improve the properties of the matrix. When 0.3 wt% reactive CNTs were added in the matrix, the flexural strength, modulus and breaking strain of the epoxy systems increased by 32, 9, and 70%, respectively [70]. Yan [71] tested five specimens of glass fiber reinforced epoxy composites, and found that glass fiber/epoxy composites with or without SWNTs had no obvious change on the flexural properties of composites. However, the SWNTs/glass fiber/epoxy composites containing SWNTs treated with Volan or both Volan and BYK-9076, the flexural strength of composite improved dramatically by 2.64 or 16.11%. The reasons of these results can be separated into two factors, one is that the dispersing agents can improve the dispersion of SWNTs and the other one is that the Volan can improve the interface property between SWNTs or glass fiber and epoxy resin. Kepple et al. [8] found that after woven carbon fiber laminates were functionalized in situ with CNTs, the flexural modulus of carbon/epoxy composites actually increased by a slight 5%
due to the addition of the CNT on the surface of the carbon fiber. The flexural properties of different composites are shown in Table 1.

### Interlaminar Shear Strength and Interface Adhesion

The composite interlaminar adhesion is one of the most important mechanical properties. So, there are considerable amount of research groups devoting to improve it. The interlaminar strength of the conventional composites is very weak; however, adding some CNTs in the composites can remove this defect. On the basis of the concept that inter-laminar carbon-nanotube forests would provide enhanced multifunctional properties along the thickness direction [72], the hybrid laminate showed an improvement of 69% with respect to the unreinforced laminate [69]. Zhu et al. [55] showed that interlaminar shear strength is one of the most interesting Z-axis properties for composite laminates, and made the conclusion that adding 0.1% SWNTs in the glass fiber reinforced vinyl ester composites can improve the interlaminar properties significantly. For the fabricated 3D composites with MWNT forests (Fig. 12), remarkable improvement was found in the interlaminar fracture toughness, hardness, delamination resistance and in-plane mechanical properties. The flexural modulus, strength, and toughness of 3D composites were increased by 5, 140, and 424%, respectively [73].

Because the mechanical properties of composites depend on not only the properties of the constituent materials but also the nature of the interfacial bond and the mechanism of load transfer, the topic of the fiber/matrix interface, or "interphase" has been the subject of considerable research [74]. And efforts have been made to improve the interfacial adhesion using various methods, by either enhancing the chemical activity of the fiber surface or increasing the surface area [75–78]. For carbon fibers, a number of surface treatments have been used to improve adhesion at the fiber/matrix interface, and it was found that the presence of CNTs at the fiber/matrix interface can improve the interlaminar shear strength of the composites [29]. Downs and Baker [77] investigated the interfacial properties of the composites with carbon nano-fiber-grafted carbon fibers through single fiber fragmenta-

### Fracture Toughness

The dispersion of CSCNT resulted in the enhancement of 90° stiffness and strength and the decrease of residual thermal strain in composite laminates. Fracture toughness associated with the matrix crack onset was evaluated using the analytical models and experimental results, and about 40% increase of the fracture toughness in CFRP filled with CSCNT was indicated [80]. Godara et al. [50] demonstrated the influence of CNTs on the fracture toughness of the UD composite laminates and showed

![FIG. 11. Scenario of mechanical properties improvement of CFRP by incorporation of CNTs [59].](image)

<table>
<thead>
<tr>
<th>Composite samples</th>
<th>Flexural modulus (GPa)</th>
<th>Flexural strength (MPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon fiber/epoxy</td>
<td>39.5 ± 2.1</td>
<td>626.4 ± 78.2</td>
<td>[61]</td>
</tr>
<tr>
<td>Carbon fiber/CNT/epoxy</td>
<td>44.1 ± 1.6</td>
<td>740.6 ± 73.2</td>
<td></td>
</tr>
<tr>
<td>Carbon fabric/epoxy</td>
<td>63.0 (± 5.5%)</td>
<td>608 (± 4.7%)</td>
<td>[69]</td>
</tr>
<tr>
<td>Carbon fabric/0.3 wt%CNT/epoxy</td>
<td>66.1 (± 5.6%)</td>
<td>626 (± 5.7%)</td>
<td></td>
</tr>
<tr>
<td>Aramid fiber/epoxy</td>
<td>31.2</td>
<td>1,450</td>
<td>[68]</td>
</tr>
<tr>
<td>Aramid fiber/CNT/epoxy</td>
<td>31.8</td>
<td>1,470</td>
<td></td>
</tr>
<tr>
<td>CFRP laminates</td>
<td>53.0</td>
<td>875</td>
<td>[66]</td>
</tr>
<tr>
<td>CFRP laminates with 5%CSCNT</td>
<td>55.1</td>
<td>912</td>
<td></td>
</tr>
<tr>
<td>CFRP laminates with 10%CSCNT</td>
<td>55.8</td>
<td>888</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 1. The flexural properties of different composites.
that even at relatively low CNT concentration (0.5 wt%) in the epoxy matrix (~0.2–0.25 wt% in the final three phase composite) there was a significant improvement in the fracture toughness. He et al. [81] added 1.5 wt% CNTs and 0.3 wt% Ni in the CNT(Ni)-Al2O3 composite, and found that the toughness of the composites increased 67% over pure alumina, and the introduction of 1.5 wt% CNTs into alumina matrix improved the hardness from 17.1 to 20.1 GPa. He characterized that the improvement of the fracture toughness and hardness was attributed to the network structure of CNT(Ni)-Al2O3, which ensured homogenously dispersed CNTs in the matrix and tight interfacial bonding between CNTs and alumina matrix, and thus led to a good stress transfer between the nanotube and alumina matrix. Kepple et al. [8] found that the CNTs as-grown on the woven carbon fiber were shown to substantially improve the fracture toughness of the cured composite on the order of 50%.

Fiedler et al. [82] reviewed the fracture properties of the CNT/epoxy composites with CNT volume contents below 1%. It was shown that the fracture toughness $K_{IC}$ can be increased by 45% by adding only 0.3% of amino-functionalized double-walled carbon nanotubes. This illustrated the huge potential of CNTs for improving the fracture performance of polymer composites. Therefore, it is possible to add CNTs into the matrix of a laminated composite to improve its poor interlaminar properties [73].

**FUNCTIONAL PROPERTIES OF MULTI-SCALE HYBRID COMPOSITES**

Composites with CNTs can not only offer extraordinary theoretical mechanical properties [83–88], but also offer functional properties such as electrical conductivity and thermal properties.

**Electrical Conductivity**

Composite electrical properties have received much attention due to their potential applications in some special environment. The addition of CNTs can improve the electrical properties of the composites. Bekyarova et al. [50] measured the in-plane and out-of-plane electrical conductivities by the four-probe configuration for two sets of composites prepared with SWNT/carbon fabric and MWNT/carbon fiber reinforced epoxy. The MWNT/carbon fiber/epoxy composites showed an enhancement of the out-of-plane electrical conductivity of ~30% as compared with that of the reference carbon fiber composites. Gojny et al. [89] showed that the GFRP containing 0.3 wt% amino-functionalized double-wall carbon nanotubes exhibited an anisotropic electrical conductivity, whereas the conductivity in plane was one order of magnitude higher than out of plane. Wichmann et al. [90] illustrated that only the glass-fiber-reinforced composites containing 0.3 wt% unfunctionalised double-wall carbon nanotubes and MWNTs exceeded the percolation threshold. A conductivity of up to $1.6 \times 10^{-2} \text{ S.m}^{-1}$ was achieved with the laminate containing 0.3 wt% MWNTs. And the conductivity of the double-wall carbon nanotubes modified composite was measured to $3 \times 10^{-3} \text{ S.m}^{-1}$.

Ounaies et al. [91] tested DC volume and surface conductivities and alternating current (AC) conductivity of the composites, respectively. The DC results showed that a sharp increase of the conductivity value was observed between 0.02 and 0.1 vol%, where the conductivity changed from $3 \times 10^{-17}$ to $1.6 \times 10^{-8} \text{ S.cm}^{-1}$. At 0.5 vol%, the conductivity was $3 \times 10^{-7} \text{ S.cm}^{-1}$. The AC test confirms the percolation behavior. At concentration levels below the percolation threshold, a strong frequency dependence of the conductivity was observed, but as the concentration ratio increased, the frequency dependence disappeared. At 0 and 0.02 vol%, the specific admittance increased linearly with the frequency in a logarithmic scale, exhibiting a typical capacitor behavior. At loadings in excess of 0.1 vol%, the composites exhibited a conductive behavior. This result is in excellent agreement with the findings from the DC conductivity measurements, and further confirms that the critical volume fraction is between 0.02 and 0.1 vol%.

**Coefficient of Thermal Expansion**

The thermal properties of the composites are difficult to control, however, their thermal properties can be improved and become easy to control by adding some CNTs. CNTs themselves have a negative coefficient of thermal expansion [92], so, adding the CNTs in the composites will reduce the coefficient of thermal expansion (CTE) of composites. Godara [80] tested the CTE of carbon fiber/epoxy composites with various CNTs, and found that the MWNTs do not seem to be effective probably because of their low level of interaction or any physical/chemical affinity with the matrix and higher possibility of undergoing the agglomeration. For the composites with

FIG. 12. Schematic diagram of hierarchical MWNTs reinforced 3D composite [73].
thin-MWNTs and functionalized double-wall carbon nanotubes, the CTE is lower than the composites made without CNTs and much lower than the composites with nonfunctionalized MWNTs. Veedu et al. [93] suggested that the presence of CNTs in the thickness direction of the 3D composites reduced the CTE from 123.9 ± 0.4 to 47.3 ± 0.3 ppm·°C⁻¹ (that is, a reduction to 38% of the original value), which was attributed to the effect of interfacial CNTs on resisting expansion of the plies through fastening interactions. He also found that the high thermal conductivity of the CNTs grown in the thickness direction improved the transverse thermal conductivity of the base composite by about 50%.

**SUMMARY**

The presence of CNTs in the composites may alleviate many drawbacks of conventional fiber reinforced composites, and another important application is to use CNTs to modify resin matrix, to enhance the traditional composite mechanical and thermal conductivity properties. However, to really play the importance in the multi-scale hybrid composites, we need to solve the problem of the homogeneous dispersion of CNTs in polymeric matrix, and the orientation of CNTs. Well-behaved dispersion of CNTs in the composites is expected to yield improved materials properties in several areas.

It should be emphasized that the importance of environmentally friendly natural products for industrial applications has become radically crucial in recent years. Therefore, there is a growing urgency to develop new preparations for manufacturing the advanced multi-scale hybrid composites to achieve the multi-scale hybrid composite engineering applications and environmental friendliness. But to achieve its engineering applications, we also need to improve the production efficiency and reduce production costs of the multi-scale hybrid composites. In short, though the vision of the development of the multi-scale hybrid composites increases many challenges and potentials, there is still a lot of space to advance in the integration of science and technology, such as in the combination of research and application.

**REFERENCES**
