AN OVERVIEW ON THE INTERFACIAL INTERACTIONS BETWEEN CNTs AND THE POLYMER MATRIX

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ABSTRACT

Because of their nanoscale dimensions, low density, intrinsically superior mechanical properties, and remarkable electrical and thermal properties, carbon nanotubes (CNTs) are expected to be one of the most potential components for the composites. At the same time, more and more people focus on the idea of incorporating CNTs into conventional fiber reinforced polymer composites. Actually the properties of the constituent materials as well as the characteristics of the interface(s) between matrixes and fibers have impacts on the mechanical behavior of composites. The interface between fibers and matrixes has been regarded as a critical element in controlling the overall performance of conventional polymer composites. In this paper, we review recent advances about interfacial interactions between CNTs and the polymer matrix and effect of the geometrical properties of the CNTs on the interfacial behavior of epoxy/CNT composites, including length, diameter, chirality and waviness.

1 INTRODUCTION

The breakthrough discovery in the 1990s of the unique properties of carbon nanotubes, including their extremely high elastic modulus, tensile strength and resilience, has sparked the exploration of their possible use in composites. It was conjectured that nano-composites toughness and strength is found to increase with enhanced interfacial adhesion, because its larger surface area contribute to massive stress transfer and energy dissipation [1]. It is thus possible to improve the mechanical properties of nano-composites by adjusting the molecular property of its interface and the CNTs characteristics. We mainly review the latest research of the interfacial behaviors of CNTs to make the functions of CNTs in polymer composites.

2 EFFECT OF CARBON NANOTUBES ON THE INTERFACIAL SHEAR STRENGTH

It has been found that the interfacial shear strength between CFs and the matrix in a polymeric composite could be greatly improved by growing CNTs onto the surfaces of CFs. Grafting CNTs on carbon fibers was observed to contribute to interfacial load transfer [2]. The interfacial shear strength (IFSS) of the composites increased by around 4.75 times (in the best case) was first reported in 2002 [3]. And coating with multi-walled carbon nanotubes (MWCNTs), the pitch-based carbon fibers would get an improvement in IFSS, assuming that the strength of the fibers would not be affected by the CVD processing [2]. At the same time, after performed the single fiber-micro droplet tensile test, the IFSS of a composite with an epoxy matrix and a novel CNT/CF multi-scale reinforcement is as high as 106.55
MPa, which is 150% higher than that of the as-received T300 fiber composites [4]. In addition, it is found that the IFSS of two kinds of T650 carbon fibers, which grafted oriented MWCNT and aligned respectively, would increase by 71% and 11%. It is estimated that due to the presence of the nanotubes, both the adhesion of the matrix to the fiber and the interphase shear yield strength increase a lot. As for the increase in interphase shear strength observed for the randomly oriented MWCNT case, it is most likely due to the alignment of MWCNTs with the principal tensile stress direction in the interphase [5].

After grafting CNTs on carbon fibers, the interfacial adhesion and interfacial shear strength would be greatly improved. The main interfacial reinforcing mechanism of this novel composite could be attributed to chemical bonding, Van der Waals binding, mechanical interlocking, and surface wetting. As the composites bear shear force, all of these kinds of interaction between CNTs and matrix contribute to the higher resistance.

3 EFFECT OF THE GEOMETRICAL PROPERTIES OF THE CARBON NANOTUBES ON THE INTERFACIAL BEHAVIOR

In recent years, many scientists pay great attention to how the geometrical properties of the CNTs influence the properties of composites. Pull-out experiments and modeling approaches have been widely used to analyze this issue.

Many groups have tried to perform pull-out experiments to measure IFSS of CNTs based nano-composites directly. The scanning probe microscope (SPM) was used to observe the process of pulling out MWCNTs from an epoxy matrix, obtaining IFSS values ranging from 376 to 35 MPa [6]. It is also suggested that the embedded length of CNTs have great impact on IFSS, which means that higher values of IFSS would be obtained for small embedded length and the increase of the CNTs content can lead to a sharp fall of IFSS. An ineffective length over which most of the shear stress transfer occurs is considered to cause this behavior. The shear lag theory developed by Cox is coherent with this result [7]. In addition, pullout tests of MWCNTs from a polyethylene butene matrix using an AFM-based technique are also performed. The maximum pullout force and embedded length were used to estimate the total interfacial fracture energy in the pullout process. The results suggest the existence of a relatively strong interface, with higher fracture energy for smaller diameter nanotubes and tougher composites [8-10].

In spite these few successful experimental approaches can be used to analyze the effect of the geometrical properties of the carbon nanotubes on the interfacial behavior of epoxy/CNT composites, there is a challenge to measure it directly because of difficulties on manipulation of CNTs and experimental scattering of results. Therefore, many researchers tend their attention to modeling approaches. The modified Cox model [7] was used to investigate the effects of tube length and diameter on the distributions of tensile stress and interfacial shear stress of a single-walled carbon nanotubes (SWCNTs) in epoxy matrix [11]. The result showed that a more effective reinforcement requires a smaller tube diameter and an optimal tube length at which reinforcement reaches its top value. Figure 1 shows the influence of nanotubes diameter, wall thickness and length on the reinforcement of the tubes. It is suggested that with the tube diameter decreasing, the total shear force in the composite gradually increases. Moreover, there is an optimal tube length at which the total shear force reaches its maximum. Figure 2 shows the variation of δ (stress transfer efficiency) with the tube length L, diameter d and wall thickness t. It is clear that with L increasing, the value of δ goes up gradually and approaches its saturation value δs, when L tends to be infinite. It is also indicated that a larger d or a smaller t can
contribute to raising $\delta_s$. On the other hand, the chirality of the single walled nanotubes is also regarded as an important factor of reinforcement in the interfacial shear stress by performing a local density approximation model [12]. In the meanwhile, finite elements method (FEM) has already confirmed that the fiber-embedded length greatly affects the shear stress [13]. And atomistic simulations are also widely used as a modeling method to analyze interfacial interactions. By using a molecular mechanics/molecular dynamics (MM/MD) approach, it has been investigated the effect of the geometrical parameters (length, diameter and chirality) of CNTs on the interfacial behavior of epoxy/CNT composites. It is reported that the length of the models of CNTs plays a vital part in the IFSS values compared other parameters. And the effective shearing transfer region is up to 500–1000 nm from the border of the nanotubes [14].

Figure 1: Total shear force $F_s$ per unit of composite volume, $V_c$, as a function of tube length under various tube diameters and wall thicknesses when nanotube volume fraction is kept constant [11].
According to these studies, we can conclude that among the geometrical parameters (length, diameter and chirality) of CNTs, the length of CNTs is a key factor that influences on the interfacial behavior of epoxy/CNT composites, which mainly reflect on the IFSS value. And there exists an optimal tube length at which the reinforcement is maximized. In the meanwhile, a decreasing trend was also found on the IFSS when the radius increased. And the chirality of the SWCNTs has a small influence on the IFSS with armchair SWCNTs showing slightly higher values than in the case of zigzag nanotubes.

4 EFFECT OF CNT WAVINESS ON INTERFACIAL STRESS TRANSFER CHARACTERISTICS

In general, many experiments confirm that embedded CNTs significantly appear in the form of non-straight shapes in nanotubes reinforced polymer composites [15, 16] Figure. 3 reveals the practical appearance of CNTs in the composites, which clearly exists in a curved shape. It is observed that the waviness is one of the important mechanisms elements the reinforcing efficiency in CNT-based composites. Xiao measured curvature distribution of the CNTs, which shows in Figure. 4 with a mean value of 0.0074 nm⁻¹ and a standard deviation of 0.0009 nm⁻¹. He reported that the reason why the superior property of high tensile modulus of MWNTs has not been fully utilized in the composites is the curving and coiling nature of the nanotubes [18].
Figure 3: Variation in reinforcement scales from millimeters to nanometers: (from left) from woven fabric of yarn bundles, to a single carbon fiber with entangled carbon nanotubes grown on the surface [2], to the nanometer diameter and wall structure of the carbon nanotubes [17].

Figure 4: The curvature distribution of the CNTs in the composite [18].

Many experiments suggest that CNTs waviness significantly weakens the capability of CNTs in reinforcement of composites and this reduction would tend to be more obvious with the CNTs content increasing. Young’s modulus of polymer would be enhanced more efficiently with the low contents of CNT, because of the lower level of CNT waviness and agglomeration [19]. It is found that both the waviness and debonding reduce the stiffening effect of the CNTs in a great extent. The effective moduli is very sensitive to the waviness when the latter is small, and this sensitivity decreases with the increase of the waviness [20].
However, some researches show that increase in the waviness of a single aligned long CNT embedded inside a representative volume element reduces the longitudinal Young modulus but increases the transverse Young modulus. And the effect of waviness becomes increasingly prominent with the volume fraction of CNTs increasing[21]. Another conclusion is verified by using a micromechanics model and conducting finite element simulations, which indicates that the nanotubes waviness tends to reduce the elastic modulus and tensile strength but enhance the ultimate strain of the composite [22]. In the meanwhile, the effective fiber model and Mori–Tanaka approach were used to study the effect of the curvature of nanotubes on the elastic properties of nano-composites. Analytical results point out that elastic and shear moduli decreases rapidly with the increase in the value of curvature, and as the weight fraction increases, the effect of nanotubes curvature becomes critical [23]. Recently, it is discovered that the maximum interfacial shear stress of a wavy CNT is higher than that of straight ones and increases with increasing the waviness [24].

The basic conclusion reached in these studies is that though waviness tends to reduce some aspects of CNT/polymer composites, such as the elastic stiffness and tensile strength but it can increase the ultimate strain of the composite and maximum interfacial shear stress. And the curled CNT is found to be more sensitive to the matrix modulus than the straight ones.

5 EVALUATION OF THE EFFECTIVE ELASTIC/PLASTIC PROPERTIES

Over the past decades, many researchers focus on the estimation of effective elastic properties of CNT-reinforced composites. As CNT is not a continuum media, nano-mechanical models has been development to predict the elastic properties instead of using micromechanics rules, such as atomistic modeling, hybrid atomistic–continuum mechanics, and continuum mechanics.

Atomistic modeling, especially techniques of molecular dynamics has been used to simulate interatomic interactions between a single CNT and surrounding polymer chains. In the simulation, the interaction of C-C and C-H in the CNTs and polymer is described by Adaptive Intermolecular Reactive Empirical Bond Order (ARIEBO), and Lennard-Jones pair potential was used to sketch the interaction between the CNTs and polymer [25].These methods can produce accurate results and describe phenomena at nanoscale, but they are very expensive computationally. Another continuum approach is presented by modeling the bonds between two nearest-neighboring atoms as equivalent-beams to investigate the deformation of CNTs. This approach provides a more realistic equivalent model between atomistic and continuum mechanics [26].

And a numerical model in conjunction with micromechanics has been developed to predict effective elastic properties of CNT-reinforced polymers [27]. In this model, effective elastic modulus of CNT/polymer composites is evaluated by using analysis of RVE (Representative Volume Element) containing the multiple CNTs in a polymer matrix with interphase regions. Theoretical results were compared with the finite element model, and two approaches yield a nearly close elastic modulus results.

In addition, other researchers also proposed a 3D FE model of the RVE in their papers. From their reports, they found that nanotubes volume fraction has a greatly impact on all elastic properties and the nanotubes aspect ratio mainly has influence at low values and decreases after the value of 20. They also draw the conclusion that the interface mostly affects the elastic properties in the transverse direction and does not influence reinforcement in longitudinal direction [28].

6 EFFECT OF THE DISPERSION OF CNTS ON SPECIFIC PROPERTIES
The realization of the potentials of CNT-based nano-composites depends on a number of factors. Among all of these factors, the dispersion of CNTs in the nano-composites cannot be disregarded. Due to their strong aggregation tendency, it is still a great challenging issue to disperse these high aspect ratio CNTs into polymer matrices. In order to solve this problem, the entanglement of CNTs produced by the synthesis and agglomerates of the CNTs caused by the intermolecular van der Waals force must be broken [29, 30].

By investigating on the dispersion of CNTs in the latex nano-composites, an appropriate method obtaining a satisfactory dispersion have been found, that is putting the carboxylated latex (XSBR) and nanomaterial in low energy ball mill. According to the rheology of nano-composites, milling of latex and CNT with ball mill results in appropriate dispersion of CNTs in the polymer matrix, which ultimately results the improvement in the properties of composites compared with ultrasonication and simple mixing. Besides, due to the interaction of CNT hydroxyl and polymer carboxyl groups, hydroxyl functionalized CNTs (CNTOH) have the more properly dispersion than non-functionalized CNTs. Figure. 5 gives the explanation of the interactions between XSBR hydroxyl group and carboxyl group of CNTOH [31]. And on the other hand, the nano-composites with the poorly dispersed CNTs have higher storage modulus, loss modulus, and complex viscosity compared with ones with the well dispersed CNTs [32]. But the randomness of nanotubes distribution tends to reduce the elastic modulus and tensile strength of composites. Thus, the distribution of nanotubes has a strong influence on the evolution of damage [22]. A case in point is that there is a good improvement in mechanical properties in low-density polyethylene (LLDPE) /CNT fibers with good distribution [33]. In addition, as the well dispersed CNTs can provide conductive paths effectively even at lower loading, it reveals much higher electrical and thermal conductivity than ones embedded with the poorly dispersed CNTs [32].

Figure 5: Mechanism proposed to explain the interactions between XSBR hydroxyl group and carboxyl group of CNTOH [31].

According to the experiments above, we can conclude that composites with the well dispersed CNTs has better mechanical and physical properties, including elastic modulus, tensile strength,
electrical, thermal conductivity. It is a good method that milling of latex and CNTs with ball mill to get better dispersion.

7 CONCLUSIONS

Growing CNTs on the surface of fibers has the potential to modify fiber–matrix interfacial adhesion, enhance the composite delamination resistance, and possibly improve its toughness and any matrix-dominated elastic property as well. A few groups focus on the interfacial interactions between CNTs and the polymer matrix.

- CNTs with appropriate lengths can be grafted to fibres by a simple injection CVD method and it results in a dramatic increase in surface area. We have demonstrated an improvement in interfacial shear strength of carbon fibers coated with CNTs. It is conjectured that the interaction between CNTs and matrix such as chemical bonding, Van der Waals binding, mechanical interlocking, and surface wetting contributes to this improvement.
- Many methods has been developed to measure the IFSS of CNTs based nano-composites, including pull-out experiments, the modified Cox model, finite elements method and atomistic simulations. In conclusion, the optimal length, smaller diameter and chirality could make contribution on the reinforcement in the IFSS. However, their results show that the length of CNTs is the most important element to influence the IFSS values.
- The CNTs waviness significantly reduces the capability of CNTs in reinforcing polymer and this effect would be more obvious with the CNTs content increasing. However, its waviness can enhance the ultimate strain of the composite. The curved CNTs are found to be more sensitive to the matrix modulus compared the straight ones.
- A lot of models are used to evaluate the effective elastic/plastic properties of carbon nanotubes reinforced polymers. Among these, RVE is a practical model to analyze the experimental results. In this model, we can find that nanotubes volume fraction has significant influence on elastic property. The effect of the interface on the elastic property is especially obvious in the transverse direction but there is almost no influence in longitudinal direction.
- The dispersion of CNTs has a great impact on achieving optimal enhancement in the properties of the CNTs/polymer composites. To some extents, the mechanical and physical properties of the nano-composites containing well dispersed CNTs have improved a lot, due to lower storage modulus, loss modulus, complex viscosity higher electrical and thermal conductivity. The good dispersion of CNTs can be achieved by putting the carboxylated latex (XSBR) and nanomaterial in low energy ball mill.

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