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# EFFECTS OF DIFFERENT FUNCTIONALIZATION SCHEMES ON THE INTERFACIAL STRENGTH OF CARBON NANOTUBE POLYETHYLENE COMPOSITE**

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**ABSTRACT** The mechanical performance of carbon nanotube (CNT) reinforced polymer composites is primarily controlled by the dispersive capacity and interfacial shear strength of CNTs in polymer matrices. CNT functionalizations will improve dispersion and strengthen interfacial bonding of CNTs in matrices. To understand the effects of different functionalization schemes on the interfacial strength of CNT-polymer composites, pullout of the covalent, noncovalent, and mixed functionalized single-walled carbon nanotube (SWCNT) from polyethylene (PE) matrix was simulated by using molecular dynamics, respectively. The results show that the SWCNT-PE interfacial shear strength is significantly improved by SWCNT functionalizations, particularly by mixed functionalization.

**KEY WORDS** interfacial shear strength, carbon nanotubes, nano composites, molecular dynamics

## I. INTRODUCTION

With ultrahigh elastic modulus and tensile strength, excellent thermostability and chemical stability, carbon nanotubes (CNTs) are anticipated as an ideal filler for future advanced composites[1]. Similar to those conventional microfiber-polymer composites, the mechanical performance of CNT reinforced polymer composites is mainly controlled by interfacial interactions, as well as dispersion and alignment of CNTs in the matrix[2–4]. As evidenced by bare CNTs being pulled out of polymer matrix[5], pristine (non-functionalized) CNTs may have a weak interfacial interaction with polymer matrix, while their functionalized counterparts have polymer clumps on the outside of the walls after pullout[6], which indicates the possibility of introducing functional groups onto CNT surface to enhance CNT-polymer interactions. Prone to aggregation and insoluble in most solvents, pristine CNTs are difficult to disperse

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in matrix materials[6]. CNT aggregation may cause inter-tubular slippage in tension and decreases the load transfer efficiency of CNTs to the host polymer matrix[7,8]. For this reason, certain functionalization schemes[9,10] should be introduced.

CNT functionalizations can be categorized into two groups: covalent and non-covalent. Covalent functionalization[11,12] is in general performed by oxidizing CNTs in acid, to attach carboxylic or hydroxyl groups onto the end-caps or defect sites of CNTs, and further grafting other specific functional groups onto the former. Although experimental[2,3] and computational[13,14] results have demonstrated that strong CNT-matrix bonding can be achieved by covalent reaction, this process will result in $sp^3$ hybridization defects on the CNT walls, which impairs their mechanical performance. Hence only a few defect sites are allowed during covalent grafting, leading to incomplete coverage of covalent functional groups on CNT surface, which may prove insubstaintial to the improvement of CNT dispersion in matrix[7]. Noncovalent functionalization or polymer wrapping[15,16], however, is able to attach large amounts of functional molecules onto CNT walls without altering their presumed perfect structures, and those CNTs can successfully solubilize in various solvents afterwards[10,17]. Although noncovalent functionalization can remarkably improve CNT dispersion in the polymer matrix, noncovalent binding between functional groups and CNTs is much weaker than covalent bonds. Therefore it is interfacial detachment rather than slippage that dominates the failure of the CNT-polymer composites[18] during CNT pullout.

In classical mechanics, static friction is the force to keep a motionless object from being pushed or pulled over a surface, and kinetic friction the force to resist the motion of an object sliding across a surface. Having studied the interfacial adhesion in CNT-polymer composite through molecular dynamics (MD) simulations, Wei[19] found that the interfacial shear stress through van der Waals interactions increases linearly with applied tensile strain, then decreases in a staircase-like manner when the noncovalent bonds between CNTs and surrounding polymer break successively. We may refer to the shear stress before the noncovalent bonds breakage as the ‘static friction’, and after as the ‘kinetic friction’. To be precise, the static friction force is the minimum force to initiate sliding, and the kinetic friction is the force required to maintain sliding. Contrary to a simple slipping process where larger adhesion leads to higher friction, Zhang and co-workers[20] found that the friction is not directly related to the adhesion energy, but to the change of the adhesion energy while sliding. Furthermore, Lordi and Yao[15] computed the binding energies and sliding frictional stresses between pristine CNTs and polymers by means of molecular simulations, and compared them with experimental results of fiber-pullout. They found that helical polymer conformation is the key factor in determining the strength of the CNT-polymer interface, whereas interfacial binding energies are just slightly correlated with adhesion in actual composites. According to these studies, we believe that detachment and slippage coexist in the pullout process of CNTs in CNT-polymer composites and the detachment relates to polymer’s morphological change. It must be pointed out that detachment has a greater tendency to occur than slippage because in detachment only the interfacial binding energy localized at the front of the detachment needs to be overcome. If the detachment is preventable, with high aspect ratio the friction building up along the axial direction of a CNT will accumulate sufficiently for load transfer, despite weak noncovalent binding. Therefore we have devised a mixed scheme for CNT functionalization[18] in which complete noncovalent polymer wrapping is adopted to improve CNT dispersion in the matrix, while a small quantity of covalent functional groups are introduced onto the CNT surfaces as anchors to pin the noncovalent polymer wrapping against detachment. Reference [13] suggests that only a few covalent functional groups will suffice for interface pinning and furthermore, Reference [21] shows that the number of defects on a single-walled carbon nanotube (SWCNT) will not affect its performance if they are located outside a so-called ‘indifference length’, over which the defects do not feel the existence of each other. Hence by utilizing this mixed scheme, possible negative effects of covalent functionalization on CNT structures are limited.

Interfacial shear stress is a critical parameter controlling the efficiency of load transfer which determines some of the important mechanical properties of composites, such as elastic modulus, tensile strength, and fracture toughness. Pullout tests are always used to evaluate the interfacial strength of microfiber-polymer composites[22] and, similarly, the CNT-polymer interaction was quantified by dragging nanotubes with atomic force microscopy (AFM) tip[23,24]. Direct pullout of a single MWCNT from