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Weakening effect of nickel catalyst particles on the mechanical strength of the carbon nanotube/carbon fiber junction

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ABSTRACT

Carbon fiber reinforced composites have been accepted as a newly-developing structural material widely used in the automotive and aerospace industries owing to its lightweight and good mechanical performances. The growth of carbon nanotubes (CNTs), catalyzed by metal nanoparticles, on the fiber surface is a promising way to mitigate the stress concentration around the fibers but requires strong bonds between the tubes and the fiber surface. Yet, details regarding the fiber/CNT bonding remain largely unknown. In this work, ReaxFF based reactive molecular dynamic simulations have been performed to predict the grafting strength between single wall carbon nanotubes (SWCNTs) and graphene layers in the presence of pure and oxidized nickel nanoparticles. These multi-material interfaces were loaded in tension and mechanical properties were calculated. The system without nanoparticle shows the largest stress at failure whereas the presence of a pure nickel nanoparticle weakens the SWCNT/Graphene junction up to 50%, while the SWCNT/graphene junction remains strong in the presence of an oxidized nickel nanoparticle. A detailed analysis of the formation and breakage of chemical bonds between the carbon, oxygen, and nickel atoms during the tensile tests enables us to elucidate the roles of the nanoparticle on the failure mechanisms.

1. Introduction

Carbon fiber reinforced polymer composites draw significant interest as they demonstrate at the same time high mechanical properties and low weight [1,2] and are thus considered as a prime material in the automotive and aerospace industries continuously seeking for ways to reduce the fuel consumption of cars and aircrafts. To further improve the mechanical properties of these materials [3], especially their toughness and transverse properties, discontinuous reinforcements [4,5] such as carbon nanotubes (CNTs) with outstanding intrinsic Young's modulus, high strain and stress at failure, and low weight can be integrated into the conventional composite materials. CNTs can be added to polymer composites in three different ways: in the matrix but poor dispersion and uncontrolled alignment of CNTs usually lead to negligible positive or even detrimental effect [6], deposited on the fiber surface when incorporated in a coating solution [7] or directly grown by means of a catalytic Chemical Vapor Deposition (CVD) [8] technique or a combustion flame oxy-acetylene method [9]. During the CVD process, the formation process of the CNTs can be described by a dissociation-diffusion-precipitation mechanism [10]. Between 500 °C and 900 °C, the carbon source, usually hydrocarbon (acetylene, ethylene, etc.) in vapour phase, is dissociated and carbon is absorbed by a metal catalyst nanoparticle, composed of a transition metal or its metal oxide, such as nickel, iron or their oxides. These carbon atoms diffuse to the surface away from the reaction gas and precipitate to form CNTs. The type and size of these nanoparticles (NPs) not only control the properties of the CNTs [11,12] but also the type of the growth modes, i.e. tip-growth or bottom-growth.

Understanding and predicting the properties of a CNT grown on a carbon fiber (CF) surface is therefore complex as it requires a comprehensive view on the interactions between three different materials i.e. the CNT, the CF surface, and the catalyst NP. Although most of the studies focused on CNTs, much less attention has been paid to this 3-component system.

Imaging and testing the mechanical properties of individual CNTs can be accomplished via techniques such as Atomic Force Microscopy (AFM) or High Resolution Transmission Electron

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Microscopy (HRTEM). Using a vibration amplitude method based on the observation of the displacement of individual nanotube tips inside a transmission electron microscope (TEM), Treacy et al. [13] were the first to measure the Young's modulus of arc-grown SWCNTs and multi wall CNTs (MWCNTs) with average values of respectively 1.3 and 1.8 TPa. The reproducibility of the experiments was however limited as values from 0.9 TPa to 1.9 TPa for the SWCNTs and from 0.4 TPa to 4.15 TPa for the MWCNTs were measured. This emphasizes the extreme difficulty to characterize individual nanotubes which may also have different levels of defectiveness. Ruoff et al. [14] then measured stress at failure of about 800 GPa for defect-free SWCNTs. However, the authors again pointed out that the modulus of MWCNTs was not constant making it difficult to reliably measure the strength of MWCNTs. Yu et al. measured successfully the strength of MWCNTs by following a sword-in-sheath failure mode using two AFM tips [15]. Values ranging between 11 GPa and 63 GPa, significantly lower than the values obtained for perfect SWCNTs, were obtained. It was hypothesized that the presence of structural defects known to greatly influence strength measurements played here a key role. The variations of the Young's modulus and strength measured experimentally, even when using the same methodology, is remarkably large. The presence of defects in different distributions and concentrations along the entire length of the tube may explain these discrepancies. Other mechanical properties like bending strength and bulk modulus [16] can also be studied but are even much more difficult to obtain.

Although several groups have been successful in growing CNTs around CFs [8,9,17–19] - and to eventually characterize their effects on the mechanical properties of the polymer composites materials at the macroscale [20], only a few experimental studies have focused on the junction between the CF surface and the CNTs due to the extreme difficulty to characterize and to image it. First the growth mode is now accepted to be mostly controlled by the adhesion between the substrate and the NP, strong adhesion leading to the bottom-growth mode and weak adhesion to the tip-growth mode [21]. For a CF substrate and Ni NP, contradictory conclusions are given by Kim et al. [21] (tip-growth mode) and Wang et al. [22] (bottom-growth mode).

For the CNT growth, Ni NPs are usually preferred to Fe NPs [23] as they do not form a stable carbide [24] and remain catalytically active over a wide temperature range even if Fe tends to yield CNT forests of higher densities. The NP generally undergoes a chemical change during the CVD growth process. Whereas it is oxidized prior to the exposure to the reducing reaction gas, a complete (or an almost complete) reversion to pure and metallic crystalline NP occurs during the CNT growth. The precise chemical state of the NP strongly depends on the interaction with the underlying substrate [25], but in the case of CFs the oxidation is less likely. Moreover, NPs with diameter in the range of 20 nm–100 nm in diameter are found to be partially embedded in the graphitic layers (up to a penetration depth of 78 nm) [26] and can act as local defects reducing the tensile strength of CFs. The use of smaller NPs or a Al_2O_3 protective layer tend to eliminate this detrimental effect. Finally, the type of bonds, chemical or physical, formed between the CNT and the CF surface is crucial as it controls the strength of the junction. Using a combination of SEM and AFM techniques, Wang et al. [22] and Du et al. [27] measured the force required to detach an individual CNT from a CF surface but without elaborating on the failure mechanisms. Zhang et al. also showed [28] that the strength of the junction is determined by the strength of the covalent bonds between the CNTs and the substrate whereas Vinod et al. [29] observed the formation of a 3D network at the junction. Large variations of measured bonding forces ranging from 6 to 1400 nN [22,30–32] for an individual CNT indicate that either van der Waals forces or C–C covalent bonds dominate. Significant improvements of the interfacial properties can however only be achieved if strong connections, i.e. covalent bonds, are formed. The resulting grafting strengths, between 5 and 90 MPa [26,31] remains up to now much lower than the properties of the CNTs, clearly indicating that there is a need to better design the CNT/NP/CF junction. At the macroscale (fabric), Guignier et al. [33,34]. designed and implemented friction and adhesion tests obtaining contradictory results.

The effect of the catalyst NP –present or absent at the junction depending on the bottom- or tip-growth mode– on the stress at failure and Young's modulus has so far been overlooked. As recently demonstrated by means of aberration-corrected high resolution transmission electron microscopy, Ni NPs interact more strongly with the outer graphitic plane of MWCNTs than Cu and possibly form new covalent Ni–C bonds [35]. Direct imaging of defects present on the CNT wall, just beneath the NP, evidenced a potential detrimental effect of the NP on the integrity of the CNT basal plane. The complexity of interactions between metal NPs and CNTs could partly be revealed by studying the electron beam mediated interaction of metal NPs encapsulated in CNTs inside a TEM [36–38]. Rodriguez-Manzo et al. succeeded to measure the tensile strength of a junction between a cobalt NP and a MWCNT end-contact. The tensile strength at the point of failure was in the range of 5 GPa indicating formation of strong covalent Co–C bonds [38], although the direct influence of the electron-beam on the chemical bonds formed remained unclear. Nevertheless, such measurements of the fracture strength of a junction has been rather exceptional due to the difficulty of manipulation inside a TEM as well as that of precise tuning of the electron-beam welding for formation of such junctions.

Computer simulations predicting the behavior of nanoscale systems with a large number of atoms have become an important tool to obtain a better understanding of the fundamental mechanisms controlling the properties of materials. There are mainly three types of numerical methods to model CNTs: atomistic modelling, especially molecular dynamic simulations (MD), continuum modelling and nanoscale continuum modelling [39]. MD simulations (discrete particle modelling) use force fields or ab-initio derived forces to predict the position of atoms [40], while continuum modelling and nanoscale continuum modelling methods consider CNTs as a continuous structure by replacing the C–C bonds with continuum elements [39].

At the atomic scale, the MD method was the first method to be applied to predict the properties of CNTs [41]. This method is especially relevant to predict the mechanical properties for CNTs submitted to external loads [39,42–44]. For example, Zhang et al. (Morse potential and Tersoff-Brenner force field) [45], Liew et al. [46], Agrawal et al. [47], WenXing et al. [48] (all three with the REBO force field), and Odegard et al. [49] (ReaxFF force field [50]) have predicted various mechanical properties of SWCNTs and MWCNTs.

ReaxFF has also been used to model the failure mode of graphene [51] and to describe the formation of CNTs with different catalyst particles [52]. A good accuracy was reported when the ReaxFF was used to predict the binding characteristics of Co, Ni and Cu atoms to hydrocarbon fragments and when applied to study the activity of metal atoms to initiate the growth of nanotubes. Jensen et al. [49] have however recently shown that the simulations using the $ReaxFF_{CHO}$ parameter set may overestimate the Young's modulus of graphene and CNTs and that the revised version of the parameter set defined by Srinivasan et al. [53], including Density Functional Theory (DFT)-derived mechanical data for diamond and graphite ($ReaxFF_{C\text{-}2013}$) allows for a better transferability providing more accurate predictions for CNTs and graphene. This novel parameter set was also tested successfully to describe the mechanical properties of systems composed of Ni, C, O and H atoms