MECHANICAL PROPERTIES OF MULTI-WALLED CARBON NANOTUBE/PEEK POLYMER COMPOSITES AT NANO SCALE

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Keywords: Carbon nanotubes, nano-scaled mechanical properties, PEEK composites

ABSTRACT

This study presents the micro- and nano-scaled mechanical properties of multi-walled carbon nanotubes (MWCNTs)/poly ether ether ketone (PEEK) nanocomposites. Micro-scaled mechanical properties were tested on thin composites film with 6.5 wt% MWCNTs loading. An *in-situ* tensile testing setup was successfully accommodated inside FE-SEM and nano-sized tensile specimens were fabricated using focused ion beam (FIB). Tensile strength of the as-prepared specimens was increased up to 380.74 MPa experimentally demonstrating prominent size effect on composites mechanical properties when reduced to nanoscale. Meanwhile, composites deformation mechanism was also recorded by the *in-situ* tensile testing.

1 INTRODUCTION

Single-walled (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes have been widely studied since the discovery by Iijima in 1991 [1]. Due to their excellent thermal, electrical and mechanical properties [2–5], CNTs are considered as an ideal filler for polymers to strengthen their properties, especially in mechanical properties. For the past decades, numerous publications have shown that CNTs can be dispersed into various thermoplastic polymers, such as poly-styrene (PS) [6], poly-methyl-methacrylate (PMMA) [7] and poly-ether-ether-ketone (PEEK) [8–10]. Improved strength, toughness and elastic modulus have been shown in those CNTs/polymer nanocomposites with small amount (<10%) of CNTs added.

PEEK is a high performance semi-crystalline thermoplastic polymer with great mechanical properties, thermal stability and chemical resistance [11–13]. Due to its high glass transition and melt temperature, PEEK has been widely used in the fields of aerospace, electronics and chemical industry. PEEK reinforced with MWCNTs has presented improved mechanical properties. Rong et al. reported that, by adding 5% CNTs nanofillers, Young's modulus and tensile strength of composites were increased by 20% and 3%, respectively [10]. Davies et al. studied CNTs/PEEK composites fabricated through extrusion deposition method. The tensile strength of 5% CNTs reinforced composites was enhanced by 21% [14]. Deng et al. also reported that the tensile modulus of MWCNTs/PEEK composites was improved by 90% for a dispersion of 15 wt% CNTs [15].

Nonetheless, the Halpin-Tsai model predicts that tensile modulus of CNTs/PEEK composites can reach up to 26 GPa [16]. This gap between the simulation and experiment results has been proposed to be due to the unfavourable effects from dispersion, alignment and interfacial interactions between CNTs and the polymer matrix.

So far, there is limited knowledge in the nano-scaled force/deformation process of those CNT reinforced nanocomposites. Direct observation has hardly been achieved either on how CNTs act in nanocomposites or how CNTs contribute to the enhanced mechanical properties under external forces. To gain insights into CNTs performance at nanoscale, here we report a development of *in-situ* SEM technique involving FIB-preparation of nano-size MWCNTs/PEEK nanocomposites specimens and *in-situ* mechanical test to observe and record the interactions between single CNT fibre and the surrounded polymer in the nanocomposites.

2 EXPERIMENTAL METHOD

2.1 MATERIALS

MWCNTs/PEEK nanocomposites were prepared by dispersing 6.5 wt% MWCNTs in the PEEK polymer matrix. Multi-walled carbon nanotubes were synthesized by chemical vapour deposition approach and obtained from Bussan Nanotech Research Institute Inc. Average length of the MWCNTs was a few micrometres and the diameter was in the range of 20-100 nm. Two-axis extruder was used to mix PEEK and 6.5 wt% MWCNTs and thin nanocomposites film was extruded.

2.2 CHARACTERIZATIONS

The surface morphology and microstructure of the MWCNTs/PEEK were examined with a ZEISS Auriga 60 focused ion beam/field emission scanning electron microscope (FIB/FE-SEM). The secondary electron and back scattered electron images were taken under 3 kV acceleration voltages. Tensile tests were conducted on Shimadzu AGS-X Universal Tester with 1 N load cell under a constant displacement rate of 0.5 mm/min at room temperature. Specimen size was cut to 0.6 mm in width and 20 mm in overall length.

2.3 *IN-SITU* TENSILE TESTING

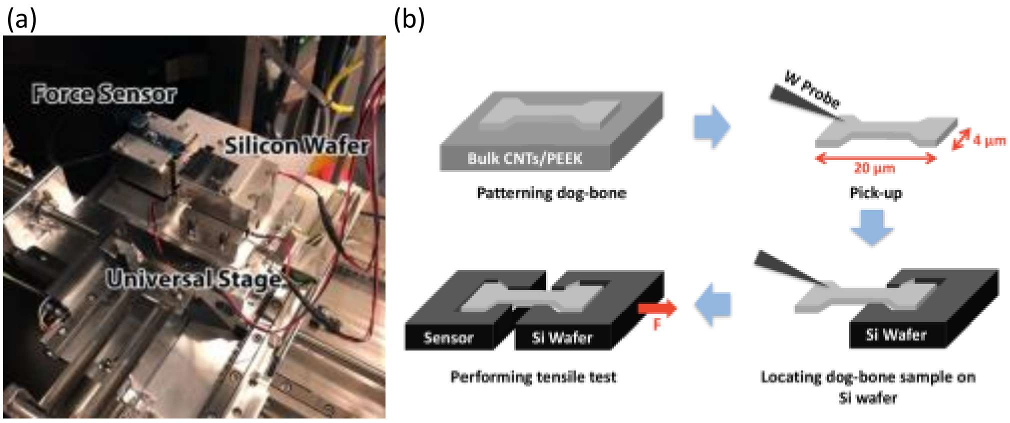

Figure 1: Universal *in-situ* tensile testing (a) setup accommodated inside FE-SEM. (b) scheme of microscopic scale dog-bone sample preparation and performing tensile testing.

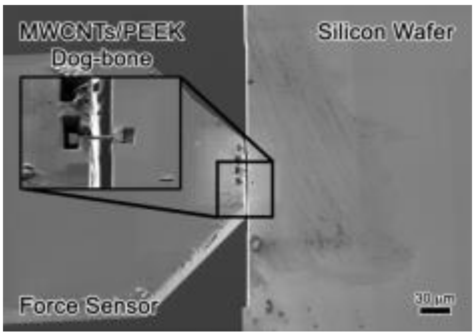

Figure 2: SEM image of tensile testing before performing.

A universal *in-situ* tensile testing setup was accommodated and performed inside the ZEISS Auriga 60 FIB/FE-SEM. Nanoscale dog-bone specimens of 20 µm by 4 µm and ~700 nm in thickness, were prepared from MWCNTs/PEEK nanocomposites with NanoPatterning and Visualization Engine (NPVE) using Ga focused ion beam and picked up by a tungsten manipulator, as shown in Figure 1.

The tensile test sample was then located between force sensor and silicon wafer. Both force sensor and silicon wafer were fixed on the piezo stage. When silicon wafer moves away from force sensor with 0.1 um/s, a tension force was applied to the specimens. During the test, a video was recorded for monitoring the elongation of specimen; meanwhile, the force variation was also obtained by a LabVIEW program. The cross-sectional area of the fracture surface was imaged and measured with SEM. As a result, the tensile strength of the nanoscale specimen could be calculated. Figure 2 presents a SEM image of force sensor and silicon wafer (a nano dog-bone holder) right before the test. A nano-sized dog-bone of MWCNTs/PEEK composite bridged between the force sensor and Si wafer (inserted in Figure 2).

3 RESULTS AND DISCUSSION

Figure 3 shows SEM images of fracture surface of pure PEEK and nanocomposites specimens. The fractured pure PEEK shows a smooth and uniform fracture surface but the failed MWCNTs/PEEK showed pull-out MWCNTs and crack deviation on the PEEK. The crack deviation by MWCNTs and pull-out mechanism improve the ability of nanocomposite to absorbed more energy [17,18]. Meanwhile, the clean surface of individual MWCNT with no residual PEEK attached may explain that the poor adhesion between MWCNTs and polymer matrix results in the lack of efficient load transfer.

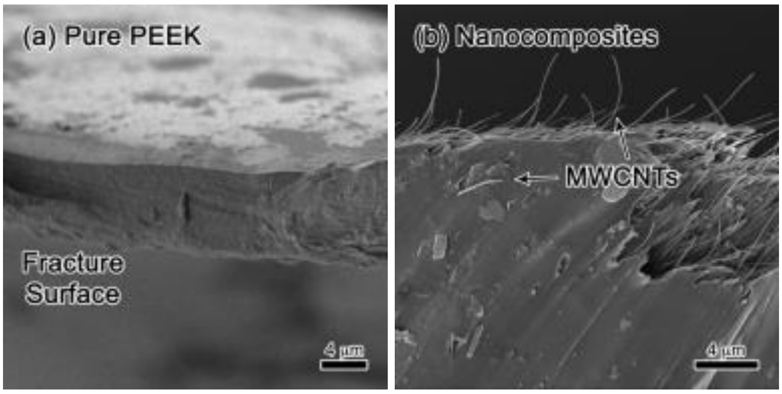

Figure 3: Fracture surface of (a) pure PEEK and (b) 6.5 wt% MWCNTs/PEEK specimens.

Figure 4 shows the micro-scale tensile test results of pure PEEK and MWCNTs/PEEK nanocomposites. The elongation of composites, compare to pure PEEK, was reduced since the nano-fillers constrain the extent of plastic deformation [19]. Strains of both pure PEEK and nanocomposites thin film are dramatically increased compared to that of bulk composites [14,15]. Thin film materials with higher degree of freedom to deform parallel to the load direction suggests that composites polymer chain is dominantly oriented perpendicular to the thickness direction. Spivack found that parylene N polymer thin film increased in ultimate elongation by 27.5% as thin film thickness decreases from 25.4 μm to 0.945 μm [20].

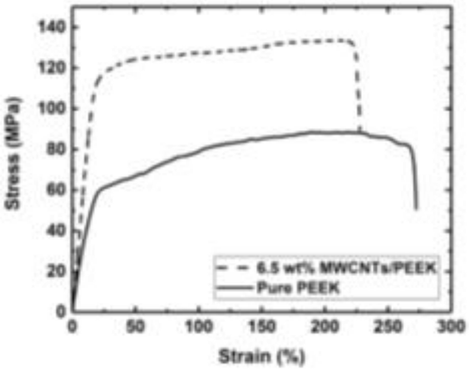

Figure 4: Stress-strain curve of pure PEEK and nanocomposites thin film.

Moreover, the average tensile strength of the as-prepared MWCNTs/PEEK nanocomposites and the pure PEEK are measured to be 133.71 MPa and 88.45 MPa, respectively. Compared to that of the pure PEEK, tensile strength of nanocomposites with 6.5 wt% MWCNTs was enhanced by 51.17%. This demonstrates the reinforcement effects of MWCNTs and that load can be transferred from matrix to MWCNTs.

However, experimentally measured tensile strength is usually lower than the theoretical calculations due to many factors, such as size and degree of dispersion of the nano fillers, bonding at the CNT/polymer interface and defects distribution [16,21,22]. As a result, this study performs tensile test inside SEM to observe how MWCNTs reinforce PEEK polymer and to understand how defects distribution affect mechanical properties.

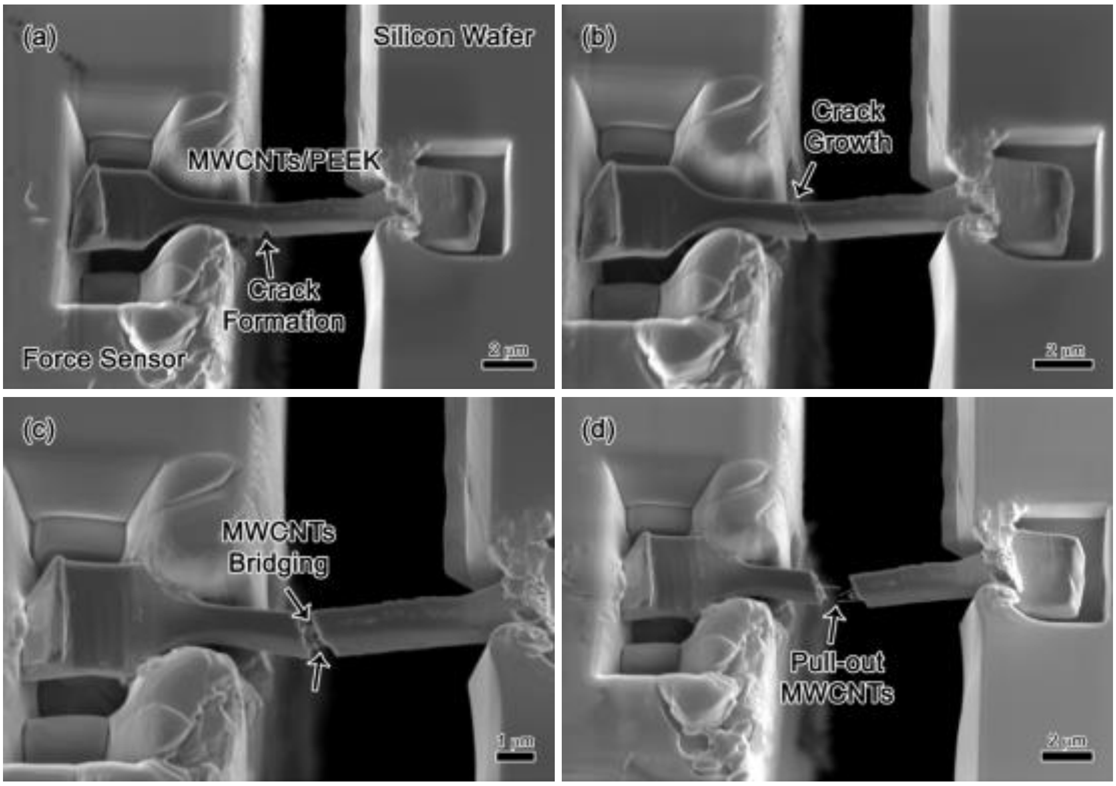

Figure 5: Time-sequence series SEM images of *in-situ* tensile test deformation process on nano-scaled MWCNTs/PEEK dog-bone.

While performing the *in-situ* tensile test, SEM images of the tensile deformation process were recorded, as shown in Figure 5. The deformation phenomenon of composites is observed as follows: (1) A crack initiated on the gauge region (Figure 5(a)); (2) Crack grew perpendicularly to the cross-sectional area (Figure 5(b)); (3) MWCNTs bridged the fracture surfaces (Figure 5(c)) and (4) MWCNTs pulled out (Figure 5 (d)). The test was terminated after the MWCNTs were either pulled out or broken.

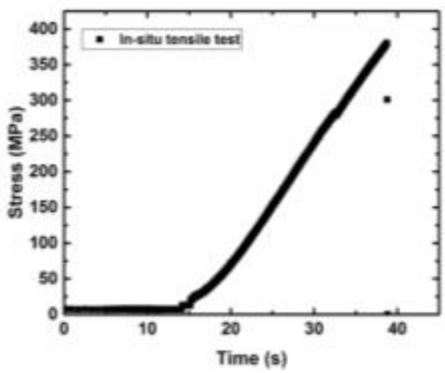

Figure 6: *In-situ* tensile testing time-stress curve.

Figure 6 shows the stress-time curve of *in-situ* test of MWCNTs/PEEK dog-bone with 760 nm in thickness. The yield stress was calculated as 380.74 MPa which is about three-fold higher than that of millimetre thick MWCNTs/PEEK nanocomposites [10,15]. Table 1 summarizes tensile strength of 6.5 wt% MWCNTs/PEEK with different specimen thickness. Strength increases from 102.15 MPa to 380.74 MPa as sample thickness from millimetre decreases to few hundred nanometres scale. Du et al. studied yield strength of polymer thin film with thickness ~ 10 μm by nanoindentation method. They found that the PC and PS thin film were about twice higher than that of bulk materials [23]. Bazant also reviewed the size effect on material strength and proposed that smaller specimen may contain fewer defects such as voids, MWCNTs end, weak nanofiller-matrix interfacial bonding etc. resulting in an enhancement of the tensile strength [24].

Interestingly, unlike macro- and micro-scaled specimens which undergo plastic deformation after yield point, the nano-sized dog-bone specimen behaves in as a brittle manner during the tensile test. As shown in Figure 5, necking does not occur on nanocomposites specimen suggesting that there is fewer dislocation motion and lower defects density necessary for plastic deformation [25].

Specimen scale	Specimen thickness	Tensile strength
	mm	MPa
Bulk[15]	4.0	102.15
Thin film	$1.04x10^{-2}$	133.71
Nano-scale	$7.64x10^{-4}$	380.74

Table 1: Tensile strength of 6.5 wt% MWCNTs/PEEK with different specimen thickness.

4 CONCLUSIONS

This work demonstrates the fabrication process of nano-scaled tensile specimens and *in-situ* tensile testing of nano-scale specimens inside the FE-SEM. Tensile strength was improved with MWCNTs uniformly dispersed in the PEEK matrix. The size effects on tensile strength/strain were studied with 6.5 wt% MWCNTs/PEEK nanocomposites, showing the enhancement of strength as specimen thickness being reduced to nanometer scale. MWCNTs/PEEK nanocomposites present different deformation stages: crack initiation, crack propagation, MWCNTs bridging and MWCNTs pull-out, at nanoscale. In nanscale, the semi-crystalline PEEK nanocomposites fractures in brittle mode and the phenomenon is likely due to the decrease of defect density. This *in-situ* SEM mechanical testing method represents a very promising general capability for probing properties of micro or nanostructures.

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