INVESTIGATION OF THE DEFORMATION MECHANICS IN CARBON NANOTUBES-POLYMER COMPOSITES AT MICROSCOPIC AND ATOMISTIC LEVEL

Fei DENG*, Toshio OGASAWARA, Nobuo TAKEDA***
[F. DENG] dengfei@smart.k.u-tokyo.ac.jp

*** The University of Tokyo**
****Advanced Composite Technology Center Japan Aerospace Exploration Agency (JAXA),**

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Abstract

Multi-walled carbon nanotubes were dispersed throughout a thermoplastic polymer, poly ether ether ketone. The results of tensile testes showed an increase in the elastic modulus and the yield strength, and decrease in the failure strain. Scanning electron microscope and transmission electron microscope images showed that the MWNTs were well dispersed in the polymer matrix. At room temperature, the addition of 15 wt% MWNTs increased the tensile modulus (at 0.1 ～ 0.3% strain) by 89% and the yield stress by 19%. Above the glass transition temperature, they increased by 163% and 42%, respectively.The tensile tests were also done inside transmission electron microscopy for observation of the atomistic level of the deformation in the interface.

1 Introduction

Single wall carbon nanotubes (SWNTs) and multi-wall carbon nanotubes (MWNTs) have been widely studied in basic and applied experiments because of their specific mechanical properties, as well as their excellent electrical and thermal properties. Recently, it is believed that SWNTs, MWNTs and carbon nanofibers (CNFs) can be used as filler in polymer matrices leading to composites with many enhanced properties, especially in mechanical properties [1]. The effects of these additions on mechanical, thermal and electrical properties have been investigated for various kinds of thermoplastic and thermosetting polymers. Increases in strength, elastic modulus, and electrical conductivity have been found. Furthermore, the cost of carbon nanotubes (CNTs) has been drastically decreasing, because many companies have been devoting a great amount of efforts for development of the mass production. If the cost of CNTs will be on the downward trend, CNTs will be no longer special materials in the near future [2].

The effective utilization of CNTs in composite applications depends strongly on the ability to disperse the CNTs homogeneously throughout the matrix without destroying the integrity of the CNTs. Furthermore, good interfacial bonding is required to achieve load transfer across the CNTs-matrix interface, a necessary condition for improving the mechanical properties of polymer composites [1]. However, there are only a few experiments has been studied the interface between CNTs and matrix directly [4,8], because it is difficult to perform the manipulation and to simultaneously observe tensile deformation at micro and nano meter scale.

In this study, the PEEK/MWNTs nano composites containing 0, 6.5, 9, 12 and 15wt% MWNTs were fabricated, and the properties were characterized by dynamic mechanical thermal analysis (DMA) and tensile tests at room temperature, 100 ^{o}C and 200 ^{o}C. The microscopic of deformation process was observed by using *in situ* scanning electron microscopy (SEM) and the atomistic level was observed in transmission electron microscopy (TEM).

2 Experimental materials and methods

2.1 Composites preparation

Multi-walled carbon nanotubes synthesized by a chemical vapor deposition process were obtained from Bussan Nanotech Research Institute Inc.

(XNRI), which is a subsidiary of Mitsui Corporation (Tokyo, Japan). The diameter of the MWNTs was in the range of 20–100 nm, and the average length was a few micrometers. The PEEK/MWNTs master batches containing 0, 6.5, 9, 12 and 15 wt% MWNTs were provided from XNRI. The Master batches were made by mixing PEEK (151G, Victrex, UK) and MWNTs using a two-axis extruder. The tensile specimens were formed by injection molding using the master batches, and it is conformable to JIS K7152 (ISO 294).

2.2 Dynamic mechanical thermal analysis

In order to characterize the thermal mechanical properties, composites with different MWNTs concentrations were tested with a dynamic mechanical thermal analyzer (DMA). A TA Instruments Q800 was used in the single cantilever beam test mode with a 17.5 mm span length, 4 mm width, and 1 mm thick. Tests were run from 40 to 350 ^{o}C at 2 ^{o}C/min with a cycling rate of 1 Hz, and a strain of 0.1%.

2.3 Tensile testing inside *in-situ* SEM and TEM

Microscopic observations were performed by using a SEM with a tensile testing stage in the specimen room (Hitachi, S-2150). Details of this method have been reported elsewhere [5,6], and a brief summary is described in the following. The specimen for tensile testing was placed on a support stage, which connected to a mechanical motor to perform the tensile test in the specimen room of SEM. The observation accelerating voltage was 25 kV. In situ nano tensile deformation was observed using a TEM (JEM-3000F, JEOL, Japan) with a contact type specimen holder which was developed by Kizuka et al [7]. Figure 1 shows an optical micrograph of the contact type specimen holder (Fig. 1(a)), and the illustration of principle of the tensile system inside TEM (Fig. 1(b)). In the specimen area of the contact type holder, the right side is the mobile side and the left side is the fixed side. The mobile side is connected with a tube-type piezoelectric device for atomistic order displacement in three directions i.e., x, y and z directions; and a micro screw motor for coarse x displacement. To perform the tensile testing inside TEM, an aluminium plate (0.1 mm in thickness, 1 mm in width, and 8 mm in length) was mounted between the mobile and fixed sides by silver past for easy handling. And a fined rectangular hole (10 μm in with, 50 μm in length) was drilled in the middle of

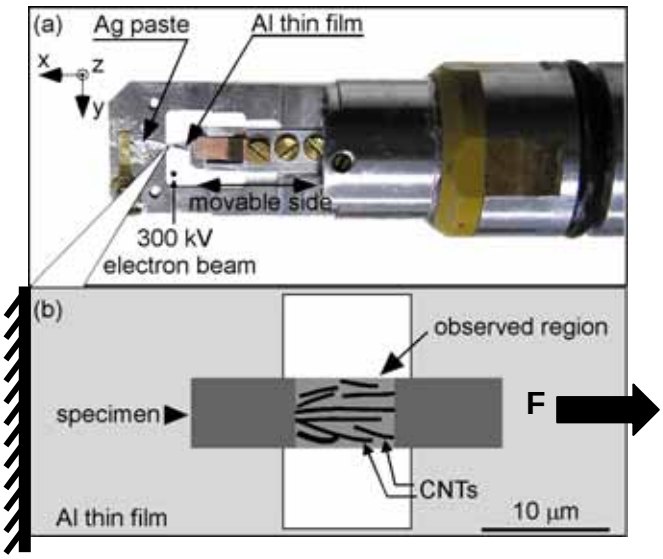

Fig. 1. Optical micrographs of the contact type specimen holder for TEM (a), and the illustration of principle of the tensile system inside TEM (b).

the bridging aluminium plate by focused ion beam (JEM-9310FIB, JEOL, Japan) to place a PEEK/MWNTs composite specimen. The composite film whose thickness was less than 100 nm was made for in situ TEM observation by using FIB method [10], and was bonded with the aluminium plate by epoxy adhesive. When the aluminium plate was stretched, the load was applied on the composite. The deformation of this process was observed at an accelerating voltage of 300 kV, and recorded by a TV system [7].

Microscopic observations were performed by using a SEM with a tensile testing stage in specimen room, and a TEM. In situ micro tensile deformation was performed by a SEM (Hitachi, S-2150). In situ nano tensile deformation was observed using a contact type specimen holder in a TEM (JEOL, Ltd., JEM-3000F). The specimen size is ~100 nm in thickness thinned by focused ion beam (JEOL, Ltd., JEM-9310), 1 mm in width, and 8 mm in overall length. High-resolution imaging was obtained at an accelerating voltage of 300 kV with a TV-rate system. The base pressure of the specimen chamber of the microscope was 10^{-5} Pa.

3 Results and Discussion

3.1 Dynamic mechanical properties

Figure 2 shows dynamic mechanical properties; storage modulus curves as a function of temperature for different MWNTs loading composites. The glass transition temperature (T_g) is defined as the onset

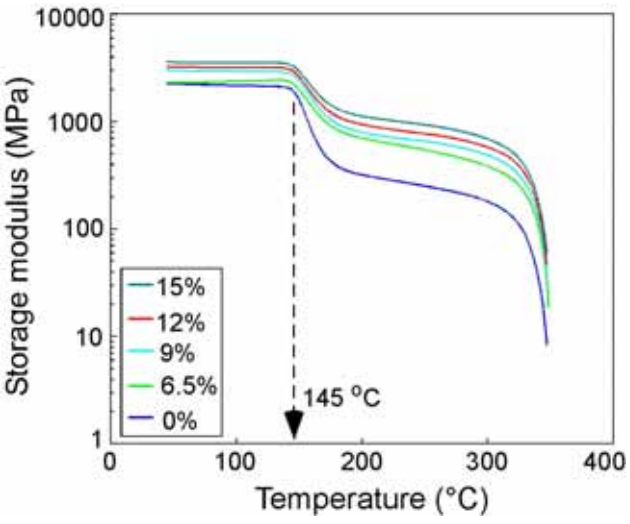

Fig. 2. Dynamic mechanical analysis traces of the PEEK /MWNTs composites

temperature of decrease in the storage modulus, and the estimated glass transition temperature of all composites are around 145 °C. The storage modulus curves show an increase in the modulus in the glassy state region as the loading of the MWNTs increases. At the high-temperature region (above T_g), the storage modulus for 15 wt% PEEK/MWNTs composites is several times higher than pure PEEK.

It is expected that the addition of CNTs for semi-crystalline polymer can improve the thermal stability [2, 11, 12]. Other groups have shown that SWNTs and MWNTs can nucleate crystallization in crystalline polymer [11, 12]. The increasing in the T_g was observed for CNTs/ Tri-A PI composites [2]. On the other hand, it was reported that T_g was not affected by addition carbon nano fibers into PEEK [3]. And our experimental results also indicated that T_g itself was not affected by incorporation of the MWNTs for PEEK. These experimental results suggest that the increase in T_g may be caused by significant interaction between the thermosetting polymers and the CNTs, which is not necessarily the same for thermoplastic polymers.

3.2 Tensile properties

The tensile properties at different temperatures, such as elastic modulus E (estimated from data at 0.1-0.3% strain), ultimate tensile strength σ_{uts} and failure strain ε_{max} are summarized in Table 1. Compared with the pure PEEK, an addition of MWNTs results in increase in the elastic modulus and the yield strength at each temperature, and decrease in the failure strain at room temperature. The tensile modulus of the pure PEEK at room temperature was 4 GPa and increased by 89% to 7.55 GPa for composites containing 15 wt% MWNTs. At 100 °C and 200 °C, they increased by 70% and 163%, respectively. The corresponding tensile strength increased by 19%, 13% and 42%, respectively. According to these results, the improvement of MWNTs is more effective above the glass transition temperature. However, these results typically remain much lower than the theoretical predictions from the rule of mixtures (considered the length and orientation factors) [3, 13]. The simple model assuming the perfect bonding at interfaces, would predict the modulus to be around 24 GPa for the composite loading 15 wt% MWNTs (assuming the modulus of MWNTs is 420 GPa) at room temperature, which is almost three times higher than the experimental results. To understand the reinforcement mechanics of MWNTs, we performed tensile testing inside SEM and TEM, and observed the microscopic deformation of composites in order to explain the mechanical improvement behaviors of CNTs for polymer materials.

3.2 *In-situ* SEM and TEM observation

We performed complementary deformation studies inside a SEM [9] and TEM. Figure 3 shows a time sequence series of SEM images of a tensile deformation process of a composite containing 7

Table 1. Tensile properties of the PEEK/MWNTs composites.

CNT (wt%)	E (GPa)			σ_{uts} (MPa)			ε_{max} (%)		
	RT	100 °C	200 °C	RT	100 °C	200 °C	RT	100 °C	200 °C
0	4.00	3.61	0.40	93.55	64.38	>22.58	>20	>20	>20
6.5	5.32	4.80	0.69	102.15	68.28	>26.74	12.49	>20	>20
9	6.00	5.03	0.74	104.44	72.58	>29.39	10.01	>20	>20
12	6.35	5.35	0.86	107.14	71.06	>30.37	8.28	>20	>20
15	7.55	6.15	1.05	110.90	73.01	>32.11	6.28	>20	>20

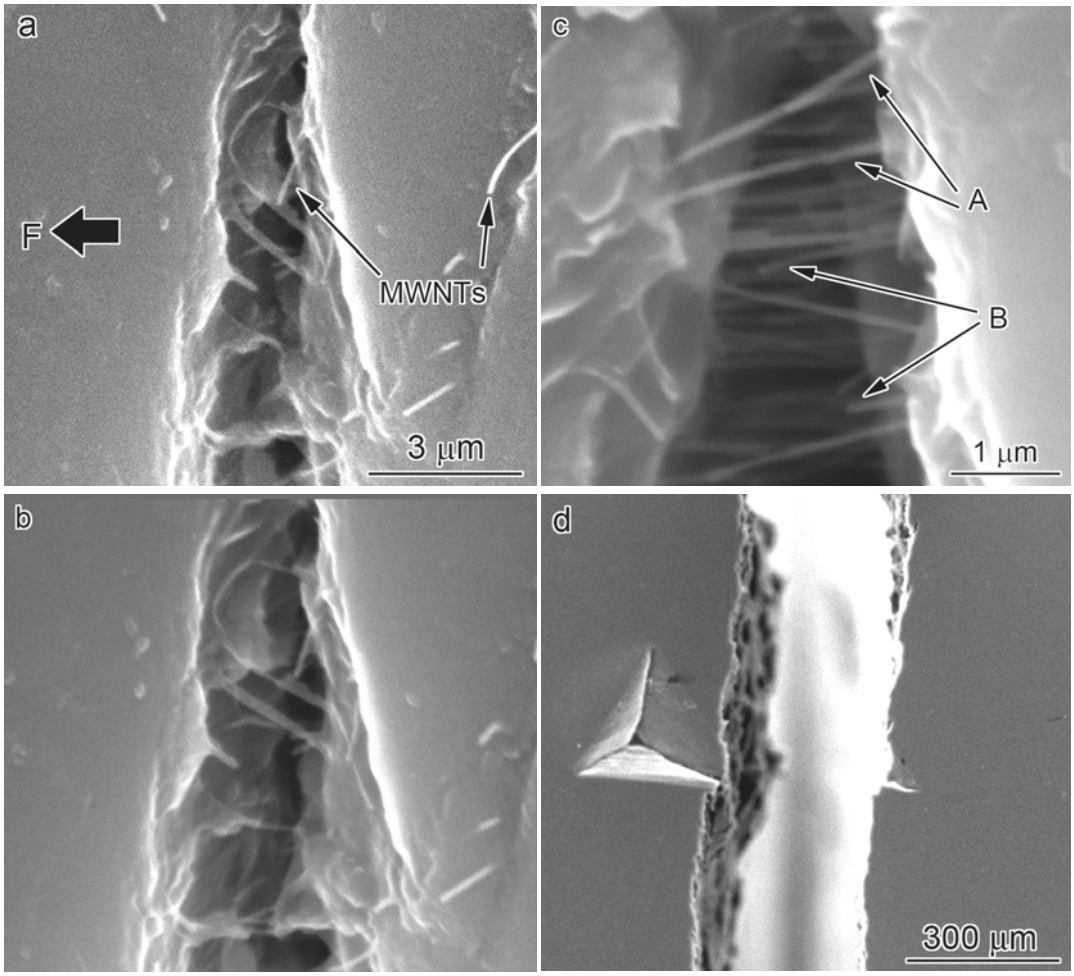

Fig. 3. Time-sequence series of SEM images of a tensile deformation process of a composite containing 7 wt% MWNTs.

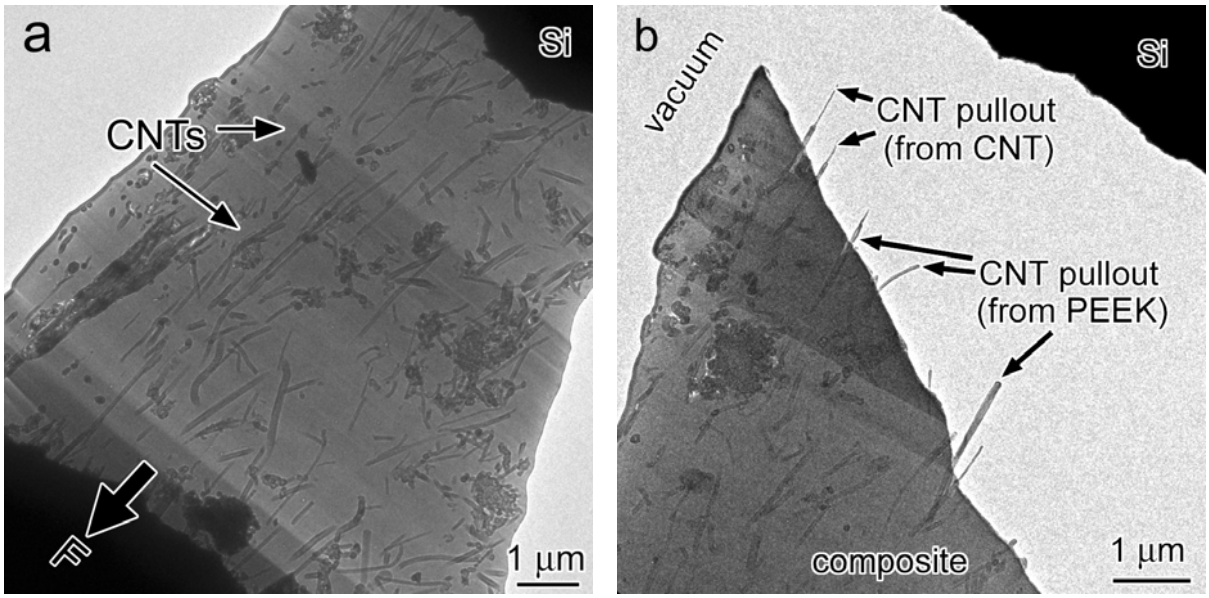

Fig. 4 TEM images of a composite containing 15 wt% MWNTs (a) before, and (b) after fracture due to tensile testing in TEM.

wt% MWNTs. According this observation, we conclude the micro deformation mechanism of composites as below. (1)crack formation (Fig. 3 (a)). (2)crack growth (Fig. 3 (b)). (3)MWNTs bridging between the cracks (see MWNTs A in Fig. 3 (c)). Pull out of MWNTs (see MWNTs B in Fig. 3 (c)). (4) fracture (Fig. 3 (d)).

Figure 4 shows TEM images of a composite containing 15 wt% MWNTs (a) before, and (b) after fracture by tensile deformation inside the TEM. In Fig. 4 (a), MWNTs aligning parallel to the tensile load direction. In figure 4 (b), there are several isolated MWNT, that was pulled out from the PEEK matrix and, pulled out from the MWNT. The surface of these isolated MWNTs are very flat and there is no PEEK bonded. This suggests that the bonding state between MWNTs and PEEK are not sufficient, which will provide imperfect load transfer from matrix to MWNTs. From the high-resolution observation of this process, it is observed slippage occurs between the shells of multi-wall nanotubes and within single-wall nanotube ropes. The graphite layers of MWNTs might have fractured due to the high radial stress. This slippage may limit stress transfer from PEEK to each wall of MWNTs. Thus, the load transfer at the MWNTs-PEEK interface is certainly less than ideal.

4 Conclusion

In this study, we investigated the tensile properties of PEEK/MWNTs composites at room temperature, 100 ^{o}C and 200 ^{o}C. The MWNTs were dispersed homogeneously in a thermoplastic matrix using injection molding. The addition of MWNTs leads to increase in tensile elastic modulus and strength at each temperature, and decrease in the failure strain at room temperature. The improvement of MWNTs was also effective at different temperatures even above the glass transition temperature of pure PEEK. Dynamic mechanical analysis showed no increase in the glass transition temperature with addition of MWNTs, but increased in storage modulus of composites. The micro deformation was observed by *in situ* SEM and TEM. The macroscopic mechanical properties were reasonably well explained through direct observations.

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