EFFECT OF SILANE FUNCTIONALIZATION ON THE MECHANICAL PROPERTEIS OF MWNT / EPOXY COMPOSITES

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1. Introduction

A great amount of effort has been devoted to application of carbon nanotubes (CNTs) to polymer reinforcement for the last 15 years. As a result, it has been understood that the mechanical properties, which are inferior to theoretical estimations, are mainly attributable to poor dispersion and weak interfacial load transfer between CNTs and the polymer matrix. The improvement of interfacial shear strength is one of the key technologies to enhance the mechanical properties [1]. Therefore a lot of studies regarding functionalization for the CNT surfaces have been conducted. Silane functionalization is one of the promising methods, and the effect of mechanical and electrical properties were investigated in detail [2].

The objective of this study is to investigate the effect of silane functionalization on the mechanical properties of CNT/epoxy composites. The CNTs were chemically functionalized using aminosilane coupling agent, and dispersed into epoxy by 0.25 wt%. The stress-strain behaviour and dynamic mechanical behaviour were evaluated.

2. Experimental procedures

3.1 Starting Materials

Multi-walled carbon nanotubes (VGCF) were provided from Showa Denko (Tokyo, Japan) [3]. The diameter ranged from 150 to 200 nm, and the average length was a few micrometers. An SEM photograph is shown in Fig. 1

3.2 Silane functionalization (Silanization)

Carboxylic groups (-COOH) were grafted onto the surface of CNTs immersing in a 3:1 volume concentrated solution of HNO_3/H_2SO_4 for 5 h [4]. The CNTs were washed with water until PH=7, and then dried at 80ºC for 12 h. The carboxylic grafted CNTs were immersed in a 3-(2-Amino-ethylamino) propyl-triethoxy-silane / toluene solution at 100 ºC for 10 min in ultrasonic bath, and then hold at 110 ºC for 5 h. The silane-functionalized CNTs, which is designated as SC-CNTs, were washed using acetone, ethanol and water until PH=7, and dried at 80 ºC for 12 h.

The chemical formula of the aminosilane coupling agent and the expected reaction at the surface of the CNTs are shown in Fig.2 and 3, respectively.

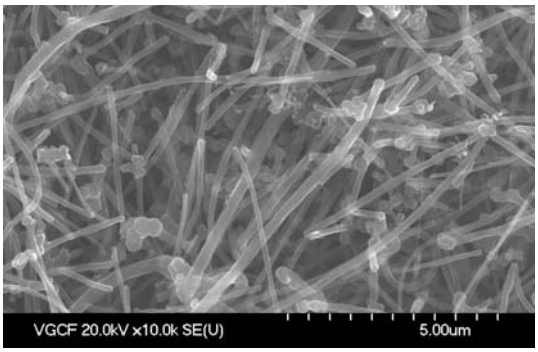

Fig. 1 SEM photograph illustrating MW-CNT used in this study (VGCF, Showa Denko)

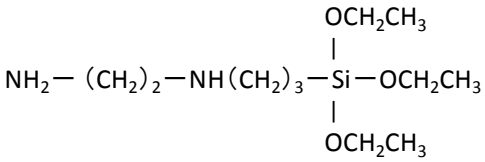

Fig. 2 Chemical formula of 3-(2-Aminoethylamino) propyltriethoxy silane

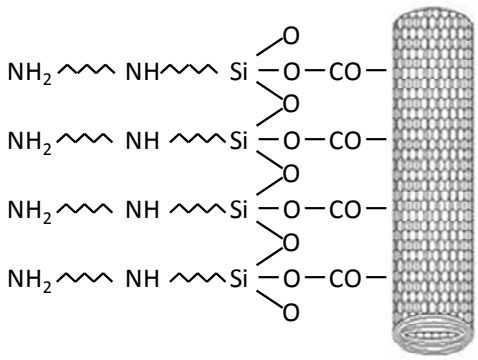

Fig. 3 Expected reaction at the surface of the CNTs

3.2 Composite processing

The resin system consists of bisphenol-F type epoxy (Epikote 807) and amine hardener (Epomate B002, Japan Epoxy Resins) in a ratio of 2:1 weight resin to curing agent. The CNTs were incorporated into the Epikote 807 as the concentrations of 0.25 wt % of total resin system. The CNT / epoxy composites were processed by mixing the nanotubes in the epoxy for 10 min at room temperature (RT) using a mechanical mixer (Mazerustar, Kurabo, Japan). After adding hardener, the resin was molded, cured at 65 ºC for 90 min, and post-cured at 100 ºC for 60 min. The specimen size was 1 mm thickness, 10 mm width, and 100 mm overall length.

3.3 Mechanical testing

Tensile tests were conducted on a servo-hydraulic testing rig (Model 8501, Instron, USA) under a constant displacement rate of 1 mm/min at room temperature. Longitudinal strain was measured using a contact type extensometer with a gage length of 25 mm.

Dynamic mechanical behavior was evaluated using a single cantilever mode under 1Hz with 0.1 % of strain on a dynamic mechanical analyzer DMA (Q800, TA Instruments).

3. Results and discussion

Typical true stress - true strain curves of the epoxy, CNT/epoxy, and SC-CNT/epoxy are presented in Fig. 4. The Young's modulus (E), ultimate tensile strength (UTS), and failure strain (ε_f), are summarized in Table 1. In spite of the same material constituent, two kinds of SC-CNT/epoxy were obtained. One has higher failure strain (180% increase, type-A), and the other has higher strength (28% increase, type-B) as compared with the original epoxy. Number of type-A specimens was 3, whereas that of type-B specimens was 5 among the total 8 specimens. Although the substantive reason why the different property appeared has not been understood even now, it may be due to the difference in the dispersion of CNTs.

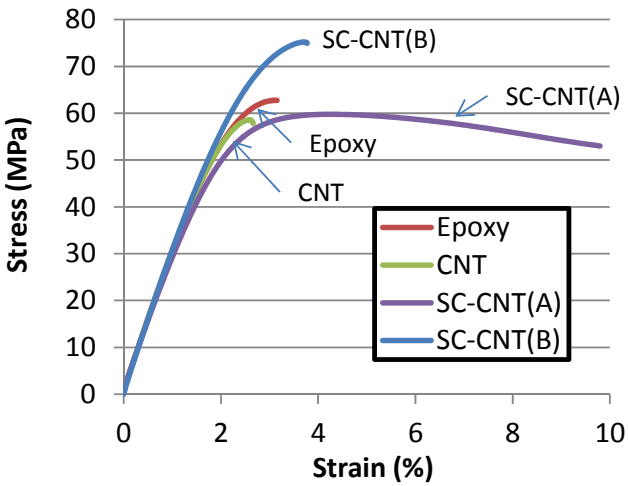

Fig.4. Typical stress-strain curves of Epoxy, CNT/Epoxy, and SC-CNT/Epoxy composites

Table 1 Mechanical properties of epoxy, CNT/epoxy, SC-CNT/epoxy (A) and (B)

	Epoxy	CNT/ Epoxy	SC-CNT (A)	SC-CNT (B)
E (GPa) *	3.1	3.1	3.0	3.2
UTS (MPa)	57.3	58.9	57.3	69.7
ε_f (%)	3.0	2.6	8.5	3.8
Tg (º C)**	65.7	70.4	72.0	74.3
Number of specimen	2	4	3	5

* Tensile test (strain 0.1 % - 0.3 %)

** DMA (the onset temperature of E' decrease)

Fig. 5 depicts storage modulus (E') as a function of temperature. The glass transition temperature (Tg), which was defined as the onset temperature of E' decrease, is presented in Table 1. The Tg of SC-CNT/epoxy increases by 6 K for type-A, and 8 K for type-B. This implies that the cross-link density of matrix resin in SC-CNT/epoxy composites slightly increases. The reason why the ductility in SC-CNT/epoxy type-A specimens was improved is not due to the lower cross link density of epoxy.

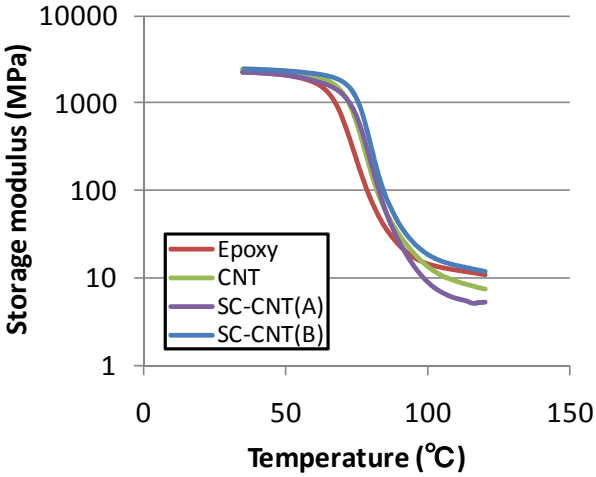

Fig.5 Storage modulus of epoxy, CNT/epoxy, and SC-CNT/epoxy composites as a function of temperature

It has been believed that the failure strain decreases with CNT dispersions, because the CNT clusters act as defects. A considerable improvement in failure strain by incorporating a small amount of SC-CNTs (0.25 wt%) has not been reported in the past literatures except the reference [5]. The increase in the failure strain may be caused by the microscopic toughening mechanisms such as crack bowing, deflection, and interfacial debonding like fullerene dispersion [6].

4 Conclusion

The effect of surface modification for multi-walled carbon nanotube (CNTs) on the mechanical properties of CNT dispersed epoxy. Monotonic tensile tests were carried out to evaluate the stress-strain behaviors. The elastic modulus (E) of an as-received-CNT (0.25 wt%) dispersed epoxy increases by 4.0 %, and the failure strain decreased by 23%, respectively. In spite of the same material constituent, two kinds of SC-CNT/epoxy were obtained. One has higher failure strain (180% increase, type-A), and the other has higher strength (28% increase, type-B) as compared with the original epoxy. Number of type-A specimens was 3, whereas that of type-B specimens was 5 among the total 8 specimens.

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