표면 개질된 탄소나노튜브/에폭시 나노복합재료의 유변학적 거동과 물성

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Effect of Surface Modificaion on the Rheology and Property of CNTs/Epoxy Nanocomposites

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Abstract

Multi-walled carbon nanotubes (MWNTs) produced by chemical vapor deposition were treated with acidic solution for purification and oxidization of CNTs. The surface modification of the oxidized CNTs was achieved by amine treatment and oxygen plasma treatment. The functionalized CNTs were embedded in the epoxy resin by sonication method and the resulting composite was investigated by FESEM. Rheological and mechanical properties of nanocomposites were measured by AR2000 and Instron. The rheological properties and dispersion of modified CNTs/epoxy composites were improved as CNTs were modified, because the modification of CNTs led to a improvement interaction between the CNTs and the epoxy resin. In addition to this, mechanical properties are also improved because of the effective stress transfer between the CNTs and the polymer.

Key Words: Multi-walled carbon nanotube, nanocomposite, surface modification, sonication

1. Introduction

The cabon nanotubes, discovered in 1991 by Iijima, have unique atomic structure, very high aspect ratio and mechanical properties (modulus and strength). Because of their unique properties, CNTs have been used for reinforcing materials in polymer based composites. Polymer based nanocomposites filled with CNTs have superior electrical property and high strength at relatively low concentration of fillers.

In order to achieve optimal enhancement of the property of CNTs/polymer nanocomposites, two important factors should be fulfilled, which are the homogeneous dispersion of CNTs and strong interfacial interaction between the CNTs and the polymer. Carbon nanotubes are generally entangled in the form of curved agglomerates due to the synthesis method and the intermolecular Van der Waals force, which disturb the homogeneous dispersion of CNTs in polymer matrix. The aggregation problems have been usually solved by using melt mixing, bulk polymerization, and sonication during the CNTs dispersion process. In addition to the homogeneous dispersion, surface modifications are essential in order to improve interaction between CNTs and matrix material. Surface treatments may roughly be divided to two categories: the use of the nanotube-bound carboxylic acids and a direct attachment of functional groups to the graphitic surface. In the first category, chemical oxidation and amine treatment were included. The CNTs are opened at the end and a terminal carbon converts to carboxylic acids by

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oxidation in concentrated sulfuric and nitric acids. Jian Chen and co-workers reported on the use of acid group by attaching long alkyl chain with an octadecylamine to the carbon nanotube surface [1]. The second category includes a gas plasma treatment. The plasma treatment is a useful method because it modifies surfaces without changing the characteristics of CNTs.

In this study, CNTs were modified through amine treatment and plasma oxidation. The surface modified CNTs/epoxy nanoconposites were prepared by sonication method and characterized by FESEM. And rheological properties of nanocomposites were investigated in shear and extensional flow.

2. Experimental

2.1 Materials

The multi-walled carbon nanotubes used in this studies were supplied by Iljin Nanotech Co. The MWNTs synthesized by the chemical vapor deposition(CVD) method had the average diameter of 13 nm and the length of 10 m. Epoxy resin (YD 128) and hardener(TH 432), which are based on diglycidyl ether of bisphenol-A and midified aromatic amine, respectively were obtained from Kukdo Chemical.

2.2 Surface Modification

The CNTs were heated in an excess mixture of sulfuric and nitric acid in order to remove impurities. These purified CNTs were separated by micro-filtration and washed with distilled water. Then some purified CNTs were heated in octadecylamine (ODA) for 5 days. These modified CNTs were rinsed with ethanol and micro-filtrated. The rest of purified CNTs were treated by using atmospheric-pressure oxygen plasma.

2.3 Preparation of Nanocomposites

The untreated CNTs and chemically modified CNTs were dispersed in ethanol under sonication for 2 hours. But the plasma treated CNTs were directly mixed into the epoxy resin. After mixing the ethanol-based solution into the epoxy resin, the suspensions were sonicated with an ultrasonic bar for 1 hour at 80℃. In order to evaporate the ethanol, the mixture were placed in a vacuum oven at 80℃ for 5 days. After adding the hardener, the mixture was stirred for 30 minutes under sonication. For mechanical tests, the epoxy resin loaded with the CNTs was injected into a mold and cured for 3 days. The specimens have length of 150 mm, width of 20 mm and thickness of 3 mm.

2.4 Characterization

FESEM (JEOL JSM-6330F) was used for the exact characterization of the morphology of nanocomposites. AR2000 was used to examine rheological behavior of CNTs/epoxy nanocomposites in shear flow. The mechanical properties of nanocomposites were measured by Instron 5584. Tensile tests were carried out at room temperature and at constant cross-head speed of 2mm/min.

3. Results and discussion

After conducting the tensile experiment of CNTs/epoxy nanocomposites, FESEM images of the fracture surface were observed, which is shown in Figure 1. Plasma treated CNTs are very well-dispersed in epoxy as show in the figure 1-(c). In addition to this, the CNTs are not pulled out and broken due to the strong interfacial bonding between the CNTs and the polymer resin.

Figure 2 shows complex viscosity of untreated and surface modified CNTs/epoxy nanocomposites through small amplitude oscillatory shear test. The epoxy composites embedded with surface modified CNTs have higher complex viscosity than those with untreated CNTs and show strong shear thinning behavior.

Plasma treated CNTs/epoxy nanocomposite have the highest complex viscosity, which is caused by strong interaction between the plasma treated CNTs and the polymer molecular chains.

Mechanical properties of nanocomposite are shown in table 1. Tensile strength, Young's modulus and elongation at break of surface modified CNTs/epoxy composites were higher than those of untreated CNTs/epoxy composite. Because functional groups which are formed on the surface of CNTs by modification are led to the linkage between the CNTs and the surrounding matrix, the linkage enables the effective stress transfer between the polymer and the CNTs. Therefore, the CNTs are not pulled out and broken under tensile loading. From above results, it is obvious that mechanical properties depend on dispersion state and interfacial bonding between the CNTs and the polymer resin.

4. Conclusions

The CNTs were modified by acidic solution, plasma oxidation and amine treatment. The CNTs/epoxy nanocomposites were prepared by sonication method. We have studied local fracture morphologies, rheological properties and mechanical properties of CNTs/epoxy nanocomposites. Apparent strong interfacial bonding between surface modified CNTs and the matrices were observed from the several characterization methods. In particular, plasma treated CNTs/epoxy composites had the best dispersion state and the strongest interfacial bonding compared to the other CNTs/epoxy nanocomposites.

5. Acknowledgement

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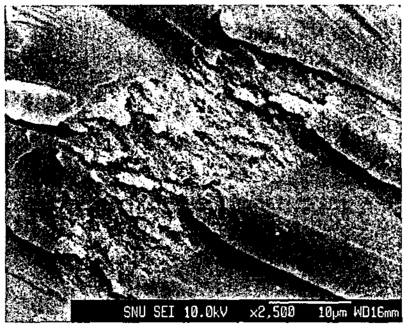
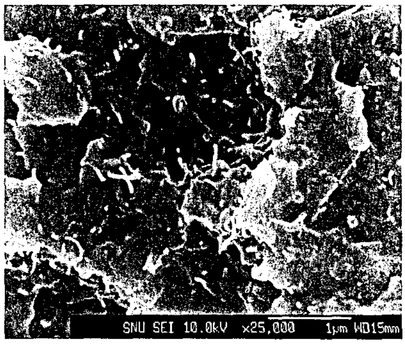


(a)



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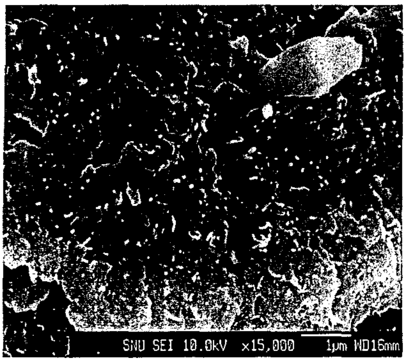

(c)

Figure 1. FESEM image of nanocomposites containing 1 wt% of (a)untreated CNTs (b)acid treated CNTs (c) plasma treated CNTs.

	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Epoxy	26	1.21	2.33
Untreated CNTs	42	1.38	3.83
Acid treated CNTs	44	1.22	4.94
Amine treated CNTs	47	1.23	4.72
Plasma treated CNTs	58	1.61	5.22

Table 1. Mechanical properties of the CNTs/epoxy nanocomposites.

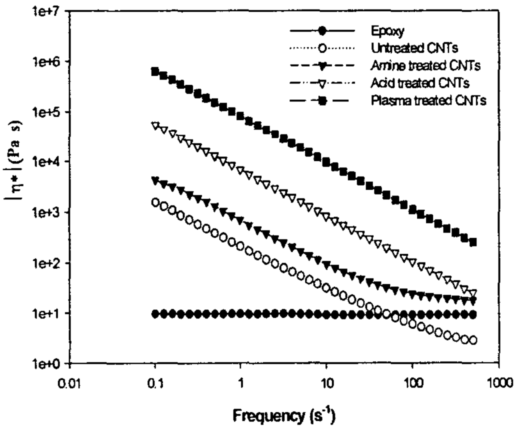

Figure 2. Complex viscosity of the CNTs/epoxy nanocomposites.