The effect of fibrous dimension on the electric conductivity of polymer-based nano-composites

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Introduction

Since the discovery[1] and bulk synthesis[2],[3] of carbon nanotubes, a great interest has been stimulated for their potential applications[4-7] in nanoscale devices and materials,[8] field emission[9] and scanning probe microscopy. Large quantities of fibrous nanocarbons (carbon nanotubes and carbon nanofibers) now can be synthesized by either arc-discharge method, or laser ablation. The main limitation of the arc-discharge process is that the size of carbon nanotubes is relatively small and that the low yield of the process makes the product expensive. On the other hand, catalytic production overcomes these difficulties. The catalytic production method is simple and has a higher productivity than the arc-discharge process. Carbon nanotubes are a new form of carbon, consisting of concentric cylinders of graphite layers. Carbon nanotubes occur in two discrete forms, single-walled nanotubes (SWNT), which are composed of graphene sheets rolled into cylinders and multiwalled nanotubes (MWNT), which consist of multiple concentric graphene cylinders. For MWNT, the strength is limited by the ease with which individual graphene cylinders slide with respect to each other. [10] Such carbon nanotubes usually afford the higher conductivities after making the polymer composites. However, high cost of carbon nanotube is still beyond the applications to the advanced polymer matrix composites. Compared to carbon nanotubes, carbon nanofibers (CNFs) showed no hollow tubes inside of fiber and have relatively larger diameters of over 100 nm. Recently, very thin carbon nanofibers were commercialized by NEXENnanotech Co. Ltd in Korea and supplied relatively low cost.

In this work, the conductivities of PC and PVA based composites prepared with the carbon nanofibers of 3 different diameters were examined. The ball-mill type mechanical dispersion was employed for a homogeneous dispersion of carbon nanofibers into polymer matrix for the exact estimation of the dimension effects. The diameters of present carbon nanofibers which were produced by the commercial base in NEXENnanotech Co. Ltd. were controlled by the change of the preparation temperature.

Experimental

Materials

Table 1 summarized the preparation conditions and some properties of carbon nanofibers used in this work. Polyvinyl alcohol (PVA, general grade of N-type, Nippon Gosei co. Ltd.) and polycarbonate (**PC-300**™, **BPI) were used as** matrix polymers.

Table 1 Preparation conditions and some properties of carbon nanofibers used in this work

Sample code	Preparation conditions				Properties			
	Catalyst Wt%	Gas(vol/vol) sccm	Temperature (oC)	Time (h)	Yield (Product/catalyst)	Average Diameter (nm)	XRD properties	
							d_{oo2} (nm)	Lc(002) (nm)
NEXCAR2	Fe/Ni (2/8)	Ethylene/H2 (1/1)	480	2	80	22	0.3444	3
NEXCAR4	Fe/Ni (2/8)	Ethylene/H2 (1/1)	540	2	140	45	0.3434	3
NEXCAR6	Fe/Ni (2/8)	Ethylene/H2 (1/1)	600	2	180	120	0.3422	4

Preparation of polymer-CNF composite films

5 parts (5 wt %) of CNF and polymer were put into the appropriate solvent and ball-milled for 3 days with the shaking type ball-mill apparatus. The packing of glass beads for milling in the bottle was controlled 50 volume %. After ball-milling, the mixed solution was casted into the glass plate and dried for a day in the air atmosphere.

Test of electric conductivity

The electric conductivity of composites film was carried out according to ASTM F84 standard four probe method.

Results and Discussion

Figure 1 showed the electric conductivities of carbon nanofibers used in this work.
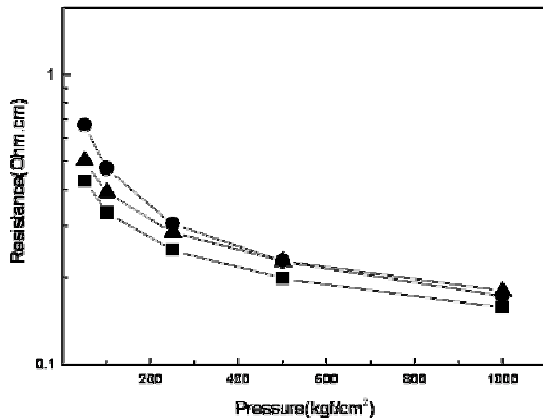
Fig. 1 Electric conductivities of various carbon nanofibers estimated by powder pressure method; ●:NEXCAR2, ▲:NEXCAR4, ■:NEXCAR6)

Carbon nanofibers showed relatively well developed graphitic structures and highly conductivities. NEXCARB6 showed highest electric conductivity as a powder form because of well developed graphitic structure.

Table 2 showed the electric conductivities of CNF/polymer films.

Table 2 Electric conductivities of CNF/polymer films

Carbon Materials	PVA matrix		PC matrix	
	Conductivity (S/cm)	Dispersion	Conductivity (S/cm)	Dispersion
NEXCARB2	8.63×10^{-2}	Good	9.25×10^{-1}	Good
NEXCARB4	3.37×10^{-3}	Excellent	7.82×10^{-2}	Excellent
NEXCARB6	2.62×10^{-3}	Excellent	6.40×10^{-2}	Excellent
Ketjen	9.84×10^{-2}	Good	9.44×10^{-1}	Poor

The obtained films showed very high electric conductivities. Film conductivity increased with decreasing the diameter of CNF. Especially, thinner NEXCAR2 showed higher conductivity than the film made by the same dispersion of Ketjen EC carbon black. The conductivity of film was higher in the PC matrix composites compared to that of PVA.
The dispersion properties of carbon nanofibers are excellent in our mechanical dispersion system, being superior to carbon black. Such better dispersion may contribute to the smooth surface of resultant CNF/polymer composites. Fig. 2 showed low magnified micrographs of prepared CNF/polymer composite films. Prepared CNF/polymer composite films showed very smooth surface with luster. Such lustrous surface did not appear in the surface of carbon black/polymer film.

NEXCAR2/PVA 5wt%

NEXCAR2/PC 5wt%

Fig. 2 Surface properties of polymer-CNF composites

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