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Effect of wet jet milling of carbon nanotube on electrical properties of polymer nanocomposites

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HIGHLIGHTS

- Wet-type jet milling (WJM) pre-treatment on CNT as electrical conductive filler.
- Large percolation critical exponent with WJM-CNT nanocomposites.
- Two-fold higher σ_{DC} with WJM-CNT at 0.5 wt% CNT.
- Complicated local structure suggested by detailed AC impedance analysis.

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ABSTRACT

Wet-type jet milling (WJM) was used as a pre-treatment procedure for carbon nanotube (CNT) which was utilized as electrical conductive filler for polymer nanocomposites. Nanocomposites were prepared by dispersing WJM treated CNT (WJM-CNT) or as-received CNT (AR-CNT) in isotactic polypropylene matrix, and the effect of WJM pre-treatment on nanocomposite properties was investigated. Dispersion structure of CNT was observed by SEM and electrical property was studied by impedance spectroscopy. DC conductivities (σ_{DC}) showed different CNT concentration dependences, which were characterized by the percolation critical exponents. At 0.5 wt% of CNT, σ_{DC} increased two-fold by using WJM-CNT. Analysis of imaginary part of impedance spectra and complex dielectric permittivity suggested the WJM-CNT nanocomposites had much complicated local structure as compared to the AR-CNT counterparts. These electrical properties were discussed in relation to the dispersion structure of CNT.

1. Introduction

Carbon nanotube (CNT) has been attracting intensive research interests as fillers for polymer nanocomposites owing to superior electrical and mechanical properties in combination with its dimensional feature [1–4]. CNT has also been utilized to improve properties of advanced structural composite materials [5,6]. In the composite system of electrically conductive filler in insulating matrix, critical behavior on the formation of percolation network of conductive fillers is decisive to achieve DC conductivity [7]. Extremely high aspect ratio of CNT gives a possibility of quite low percolation threshold. As-synthesized CNT tends to have bundled, entangled and aggregated form. Therefore, in addition to the type of CNT (single-, double-, or multi-walled) and quality such as crystallinity and purity, control of the dispersion state affects crucially on the properties of the CNT nanocomposites. Properties of CNT are also sensitive to the degree of defects formation [8,9]. Proper choice of dispersion process is important because it affects both the state of dispersion and degree of deterioration.

Wet-type jet milling (WJM) technology is relatively novel method for dispersion of nanomaterials [10]. In the WJM process, particulate material suspended in liquid medium is passed through a narrow channel at high pressure. Dispersion of material is enhanced by complex shear force from turbulent flow in the channel and cavitation from abrupt pressure change. Applied pressure is the parameter to be controlled in order to optimize the intensity of treatment which decides the degree of dispersion and deterioration. In addition, ability of continuous treatment makes WJM attractive as industrially productive process. We have found that WJM allows the formation of stable dispersion of nanomaterials by inhibiting the deterioration of particle surface during processing [11–13]. This feature makes the WJM technology attractive for controlled processing of CNT. Recently, WJM have

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been applied for the dispersion of CNT in polymer composite system [14–17].

In the present study, electrical conducting properties of CNT nanocomposites were studied, focusing on the effect of WJM treatment of CNT. Nanocomposites with isotactic polypropylene (iPP) were prepared by melt kneading process. Electrical conductivity is examined by AC impedance spectroscopy. Percolating behavior in DC conduction as well as relaxation process in AC domain was investigated in detail.

2. Materials and methods

2.1. Wet-type jet mill treatment of CNT

In this work, single walled carbon nanotube synthesized by the super growth method [18] was used as CNT. Tertiary butanol (tBA) was employed as a medium for WJM treatment because of its wettability to CNT and ease of removal by freeze drying. 0.15 g of CNT was pre-dispersed in 100 mL of tBA by stirring vigorously with a magnetic stirrer for 14 h. Then the dispersion was treated by the wet-type jet mill (GENUS PY, GENUS Co., Ltd.) at 60 MPa. Collected dispersion was freeze dried to remove tBA without re-aggregation of CNT. EYELA freeze dryer FDU-810 (Tokyo Rikakikai, Co., Ltd.) was used. The completion of freeze drying was confirmed by achieving the constant absolute pressure below 2 Pa.

Effect of WJM treatment on chemical structure of CNT was evaluated by Raman spectroscopy (Renishaw inVia Raman microscope, excitation at 514.5 nm).

2.2. Preparation of iPP/CNT nanocomposites

Different concentrations of the wet-type jet mill treated CNT (WJM-CNT) or the as-received CNT (AR-CNT) were kneaded with isotactic polypropylene (Novatec-PP MA3, Japan Polypropylene, Corp.) by using a twin screw extruder (HAAKE MiniLab) equipped with a counter-rotating conical screw under nitrogen atmosphere at 200 °C. This extruder has a "cycle" mode, which allows repeated mixing before extrusion. In the cycle mode, kneaded sample flows through an integrated backflow channel and is kneaded again repeatedly. After a certain kneading period, the sample was collected by extrusion. Several different kneading time conditions were tried to study the effect of repeated mixing.

2.3. Electrical impedance measurement

The iPP/CNT nanocomposites were compression molded at 200 °C to prepare films with a thickness of approximately 300 μm. For electrical impedance measurement, Au electrodes (ϕ3 mm, t50 nm) were deposited on both sides of the film by an ion sputter.

Electrical impedance measurements were carried out by two electrode method using an Agilent 4294A precision impedance analyzer attached with a 16034E test fixture in a frequency range of 40 Hz–40 MHz. Complex impedance Z^* was measured as a function of frequency f, and then it was converted to complex resistivity (impeditivity), $\rho^* = Z^* \times A/d$, where A is electrode area and d is sample thickness. Then complex conductivity, $\sigma^* = 1/\rho^* = \sigma' + i\sigma''$, was calculated. Eight pieces were measured for each sample to study the variation of the electrical responses.

2.4. Microscopic morphology observation

Scanning electron microscopy (SEM) observation of CNT before and after WJM treatment and nanocomposites was carried out by using a Hitachi field emission SEM S-4300. For microscopic observation of internal structure of the nanocomposites, surface of the films was dry etched for 3 h by using an UV/O_3 surface processor (SSP16-110, SEN Lights Corp., Japan).

3. Results and discussion

3.1. Morphological effect of WJM treatment on CNT

Fig. 1 shows FE-SEM micrographs of CNT before and after WJM treatment. As-received super growth CNT has an axial length of approximately 680 μm. The white arrow in Fig. 1a indicates the axial direction. Diameter of the super growth CNT is reported to be 3.0 nm [18]. Extremely large aspect ratio was confirmed. Magnified view in Fig. 1b indicates bundles with a diameter of several tens of nanometers were formed and all of them were aligned to the same direction in the AR-CNT.

WJM treatment of CNT/tBA dispersion at 60 MPa gave viscous slurry with no tendency of sedimentation. Freeze dried CNT had a bulk density of 1.6 mg/mL, which was much lower than 37 mg/mL of the raw material [19]. FE-SEM observation in Fig. 1c shows that originally aligned CNT was disrupted by the WJM treatment to give bulky structure. Magnified view in Fig. 1d indicates that there was little change on the smallest bundle size, but the aligned structure was completely disordered and the bundles formed entangled network.

Effect of WJM treatment on chemical structure of CNT was evaluated by Raman spectroscopic analysis. Peak intensity ratios between D (disordered) band at 1342 cm^{-1} and G (graphitic) band at 1587 cm^{-1} were D/G = 0.16 ± 0.06 for AR-CNT and 0.20 ± 0.02 for WJM-CNT, respectively. Although the averaged ratio of disordered structure increased slightly after WJM, it was within a fluctuation of data. It indicates that there was no severe deterioration of CNT structure under the current WJM treatment condition.

3.2. DC conductive properties of nanocomposites

Fig. 2 shows the representative real part of complex electrical conductivity, σ', as a function of frequency. Above 0.05 wt% of CNT, σ' values showed plateau in lower frequency region [20,21]. The plateau is extrapolated to 0 Hz and reported as DC conductivity, σ_{DC}, hereafter. 0.05wt% nanocomposite showed no such plateau, indicating insulating behavior at DC.

Fig. 3 shows variations of σ_{DC} of 0.5 wt% CNT nanocomposites as a function of kneading period. With AR-CNT, saturation was reached after 90 min of kneading. By applying WJM treatment to CNT, the period was shortened to 60 min. It is considered that the WJM treatment acts as pre-dispersion process. Based on this result, fixed kneading period of 90 min was employed for further conductivity studies. At 0.5 wt% of CNT, the nanocomposite prepared from WJM-CNT showed twice higher saturated σ_{DC} than that from AR-CNT.

Fig. 4a shows CNT concentration dependence of σ_{DC}. For both WJM-CNT and AR-CNT, drastic increases of σ_{DC} were observed at 0.1 wt%, indicating the formation of electrically conductive percolation networks. At 0.05 wt%, both were insulating. In the transition region between 0.05 and 0.1 wt%, nanocomposites showed measurable but quite low and scattering σ_{DC}, indicated by the large error bars. This implies only limited conduction pass was formed at these concentrations [22]. From the percolation theory [7], it is known that the conductivity above percolation threshold follows the scaling relation described as $\sigma_{DC} = \sigma_0(\rho - \rho_c)^t$ for $\rho > \rho_c$, where ρ is CNT concentration, ρ_c is percolation threshold concentration, and t is critical exponent, respectively. Fig. 4b shows the log–log plot of σ_{DC} against $\rho - \rho_c$, and the regression lines for the above equation are also shown. The ρ_c value of 0.05 wt% was used in the calculation for both samples. It is obvious from Fig 4a that the true ρ_c value lays