

In-situ 벌크 초음파합성에 의한 MWNT/PS의 유변학적 거동과 특성

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Characteristics and rheological behavior of multiwalled carbon nanotube/polystyrene composites prepared by in-situ bulk sonochemical polymerization

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Introduction

Carbon nanotubes (CNTs)/polymer composites have attracted scientific interest due to their potential engineering applications in various areas such as automobile industry, aerospace technology and energy storage [1-4]. CNTs have a large aspect ratio (nanometer scale diameter vs. micrometer scale length) with low density, which can enhance not only the electrical conductivity of polymeric composites, but also mechanical properties. Therefore, CNTs are regarded to be an ideal filler for composites. However, it is difficult to disperse CNTs well in the polymer matrix due to the strong Van der Waals force among its tubes stemming from large aspect ratio and surface area. In order to solve these problems ultrasound are usually used, because bubbles are implisively collapsed in the liquid, when solutions are treated by strong ultrasound. This collapse results in the creation of very high temperature (thousands of Kelvin) and pressures (hundreds of atmosphere) at the centre of the bubbles, in which not only disperse CNTs very well but also irradiate any chemical reaction [5]. For example, Xia reported polymer-encapsulated Carbon Nanotubes through ultrasonically initiated in emulsion polymerization [6].

In this study, we prepared the MWNT/PS composites by in-situ bulk polymerization under the application of ultrasonication to open the π -bonds in the MWNT. The bulk polymerization was performed with and without (w/o) initiator 2,2-azobis (isobutyronitrile) (AIBN). In addition, we investigated the influence of AIBN exception on the rheological properties of the MWNT/PS composites.

Experimental

MWNTs with purity of ~95 wt%, synthesized by a thermal chemical vapor deposition method (Iljin Nanotec Co., Korea), were used in this study. To improve the purity of MWNT, we treated them in 3M HNO₃ and 5M HCl by sequential reflux processes for 24 h at 60°C and 6h at 120°C, respectively[7]. The HNO₃ treatment produced carboxylic groups on the surface of the MWNT [8-10], without any damage of MWNT [7]. It was confirmed that the purity of MWNT was improved up to 99 wt% after the acid-treatment by using the

thermogravimetric analysis (TGA, Polymer Lab., TGA1000, UK).

The acid-treated MWNT were dispersed in styrene monomer followed by treatment with ultrasonic generator (G2806, Kyungil Ultrasonic Co., Korea) which has a nominal frequency of 28 kHz, with a power of 600 W, to form stable suspension. Then AIBN was added into the suspension, and monomer was polymerized under ultrasonic treatment at 80°C. Also, we synthesized composites of MWNT and PS by the sonochemical method without adding AIBN at 80°C.

After polymerization, morphology of MWNT/PS composites was characterized by a scanning electron microscope (SEM) (Hitachi S-4300, Japan) and a transmittance electron microscope (TEM) (Phillips CM200, NL). The TEM specimens was prepared by solvent casting of the composite solution, after the composites were etched with toluene. Fourier transform infrared spectrometer (FT-IR, Perkin-Elmer, spectrum 2000 explorer spectrometer, USA) was used to investigate the chemical structure. Rheological measurements were performed by using a rotational rheometer (Physica MCR 300, Germany) with 25mm parallel plate measure at 230°C under air atmosphere.

Results and discussion

Figure 1 showed the SEM images of MWNT/PS composites with and without AIBN. MWNTs were observed to be sufficiently wetted in PS matrix. By comparing Fig. 1 (a) and (b) carefully, we can find MWNT poor dispersion forming clusters in Fig. 1(a) very clearly, and the surface of the Fig.1(b) is much smoother than that of Fig.1(a). It indicates that PS was grafted onto the MWNT well in the MWNT/PS composites without the AIBN.

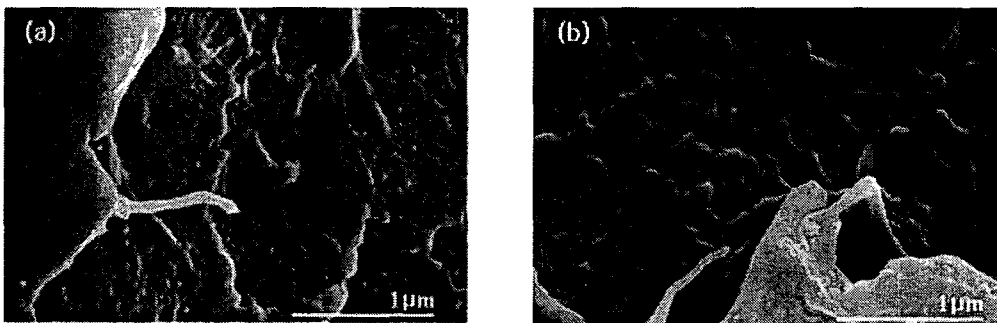


Fig.1 SEM image of (a) MWNT/PS composites with AIBN,(b) MWNT/PS composite w/o AIBN.

In the Fig.2, the TEM image showed the internal structure of the composite. The diameter of the composite was measured to 30 nm. Also, it was found that the polymer shell still existed at the surface of MWNT, although the composites etched with toluene. That indicates there are chemical bonds between MWNT and PS.

The composition of PS/MWNT were analyzed by FT-IR spectrometer in Fig. 3. A new peak at 1655 cm^{-1} was observed in the composites. It might originate from a C-C bond between MWNT and PS, which was formed during polymerization initiated by the radicals on MWNT [11].

The dynamic oscillatory measurement was used to analyze the mesostructure and kept within a linear viscoelastic range. Complex viscosities of pure PS and MWNT/PS composites are shown in Fig. 4, in which the complex viscosity of the nanocomposite

demonstrated a distinct shear thinning behavior by adding MWNT compared to the pure PS, especially at low frequencies. PS/MWNT composites (w/o) AIBN have the higher viscosity than the composites with AIBN even at high frequency with same MWNT content. It is also believed to be PS graft MWNT very well.

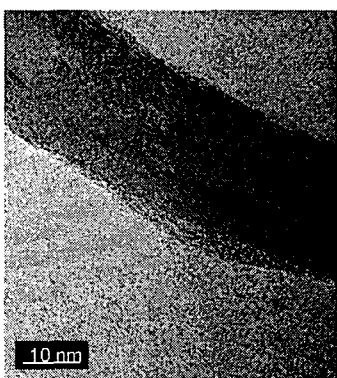


Fig.2 TEM image of MWNT/PS composite

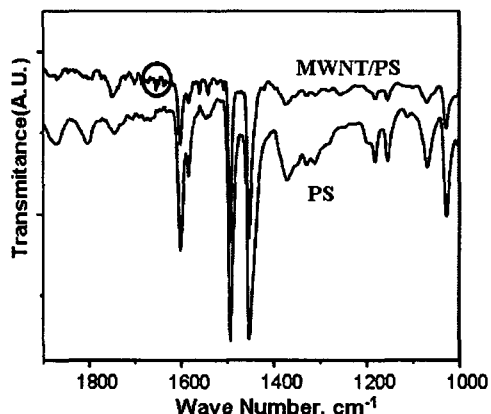


Fig.3 FT-IR spectrum of MWNT/PS composite

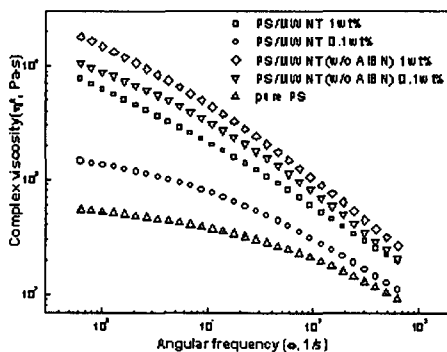


Fig.4 Complex viscosity of MWNT/PS at 230 °C.

The increase in complex viscosity with nanotube composition is primarily caused by an increase in the both of modulus, Fig. 5(a) the storage modulus, G' and the loss modulus G''

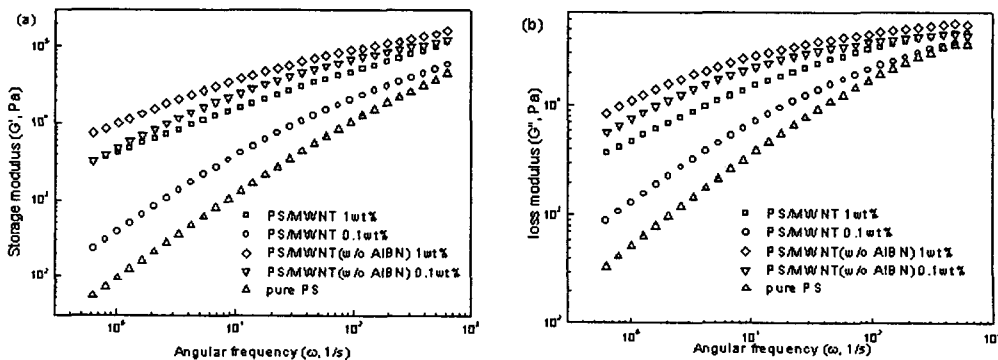


Fig 5 (a) Storage modulus G' (b) loss modulus G'' of MWNT/PS composites at 230 °C.

Fig 5(b). The G' of the composites in the low frequency region increase dramatically with MWNT content increase. With same MWNT content, PS/MWNT composites (w/o) AIBN have high storage modulus G' than the composites with AIBN. This is believed that good dispersion of MWNT and enhanced chemical bonding in composites can influence the dynamics of the polymer chains. Such an enhanced storage modulus of the PS/MWNT composites indicates that the material properties are changing from liquid-like to solid-like behavior as the MWNT content increases [12,13]. The corresponding increase in the loss modulus G'' is much lower than G' as seen in Fig 5(b). Both moduli increase with frequency, however, the rate of increase becomes less at the higher MWNT content.

Conclusions

In summary, PS/MWNT composites were synthesized via an in-situ bulk sonochemical polymerization under the application of ultrasonication to open π -bonds in the MWNT. SEM image showed that the MWNTs were sufficiently wetted in the PS matrix. Through TEM we can see that PS is covalently linked to the MWNT during our method. FT-IR spectroscopy supported the generation of a new C-C bond between MWNT and PS. The rheological behavior of compression molded mixtures of PS and CNTs were investigated using oscillatory rheometry at a constant temperature of 230°C. The viscosity increases significantly with increasing MWNT content, and the viscosity of all of these composites were shown to be dependent upon test frequency. The viscosity increase is with an increase in the elastic melt properties, represented by the storage modulus G' , which is higher than the increase of the loss modulus G'' .

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