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SHORT COMMUNICATION

Bulk polymerized polystyrene in the presence of multiwalled carbon nanotubes

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Abstract The in situ bulk polymerization method was applied to synthesize composites of multiwalled carbon nanotubes (MWNTs) and polystyrene (PS) under ultrasonication to open π-bonds in the MWNTs. Morphology of the composite products was studied by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thermal properties and molecular weight of the PS synthesized in the presence of the MWNTs were examined by thermogravimetric analysis (TGA) and gel permeation chromatography (GPC), respectively. The MWNTs were observed to play an important role as initiator consumers during the polymerization reaction. Electrical conductivity of a film-type sample of the PS/MWNT nanocomposite was found to increase with increased amount of MWNTs added, following the percolation theory.

Keywords Carbon nanotube · Polystyrene · Nanocomposite · Bulk polymerization · Sonochemistry

Introduction

Since their discovery, carbon nanotubes (CNTs) have been widely adopted in many novel engineering and technological applications [1], due to their remarkable electrical and mechanical properties, and their good chemical stability. CNTs are very thin tubes with diameters of a few nanometers, but they can have micron-sized lengths. Therefore, they can possess excellent mechanical, chemical, thermal, and electrical properties [2–4] and have potential applications in various fields such as energy storage, field emitting devices, transistors, electroactive materials and polymeric composite materials [5–9]. Among these applications, CNTs have been used as a filling material for polymeric composites, due to a high aspect ratio of their shape, which allows the filler to have a strong effect even for very low filler fractions. Dalton et al. [10] introduced a unique method of constructing composites consisting of single-walled CNTs and poly(vinyl alcohol) which contain long fibers and are very strong. In spite of these advantages, CNTs aggregate easily, so that, it is difficult for them to be dispersed in a polymeric matrix, due to strong van der Waals forces among the tubes stemming from their large aspect ratio and surface areas. Meanwhile, the CNTs are commonly blended into polymers via melt-mixing, solution-mixing, and in situ polymerization method of the monomer [11].

Recently, we prepared suspension polymerized poly (methyl methacrylate)/MWNT nanocomposite particles and studied their electrorheological (ER) performance under an applied electric field when dispersed in an insulating silicone oil [12]. These ER fluids, which are suspensions of polarizable particles in a nonconducting liquid, exhibit drastic changes in their rheological properties under an applied electric field. By tuning the fibrillar structures with controlled electric field strength, a microstructural transition from a liquid-like to a solid-like state is obtained. Polarizable particles, under an external electric field, behave as electric dipoles, which attract each other to form chain and column structures aligned along the field direction [13–15].

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In this study, we synthesized multiwalled carbon nanotube (MWNT)/polystyrene (PS) composites by an in situ bulk polymerization with simultaneous application of ultrasonic treatment to achieve high dispersion quality of the MWNTs in the polymeric medium. The ultrasonication enhanced polymerization of the PS. We also characterized their morphological, thermal, and electrical properties by focusing on the role of an initiator, 2,2-azobis (isobutyronitrile) (AIBN), during the process of polymerization.

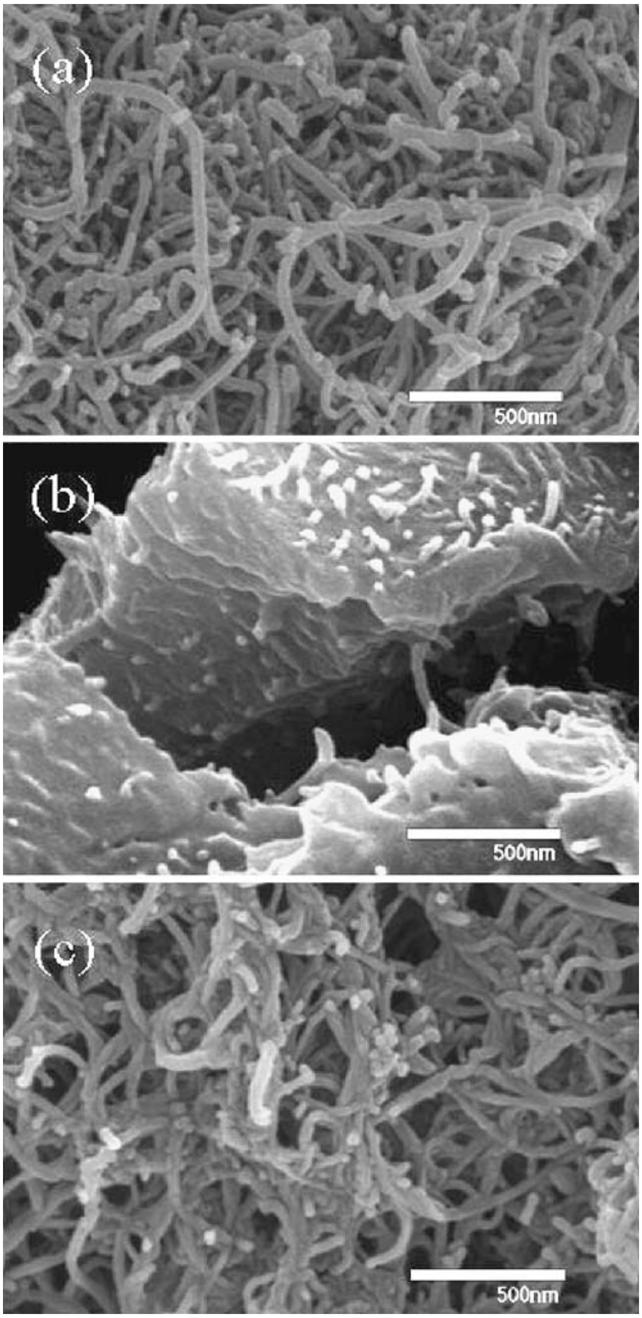


Fig. 1 SEM morphology of **a** pristine MWNT, **b** fractured surface for PS/MWNT (2 wt%) nanocomposites, **c** PS-g-MWNT

Experimental section

We used MWNTs with a purity of ~95 wt% which were synthesized via a thermal chemical vapor deposition method (Iljin Nanotec, Korea). To improve purity of these purchased MWNTs before their use, they were treated both in 3 M HNO_3 and 5 M HCl by sequential reflux processes for 24 h at 60 °C and 6 h at 120 °C, respectively [16]. Purity of the acid-treated MWNTs was found to be about 99 wt% using thermogravimetric analysis (TGA, Polymer Lab., TGA1000, UK). Even though this acid-treatment method has been known to shorten length of the MWNTs and introduce hydroxylic functional groups [17], we were

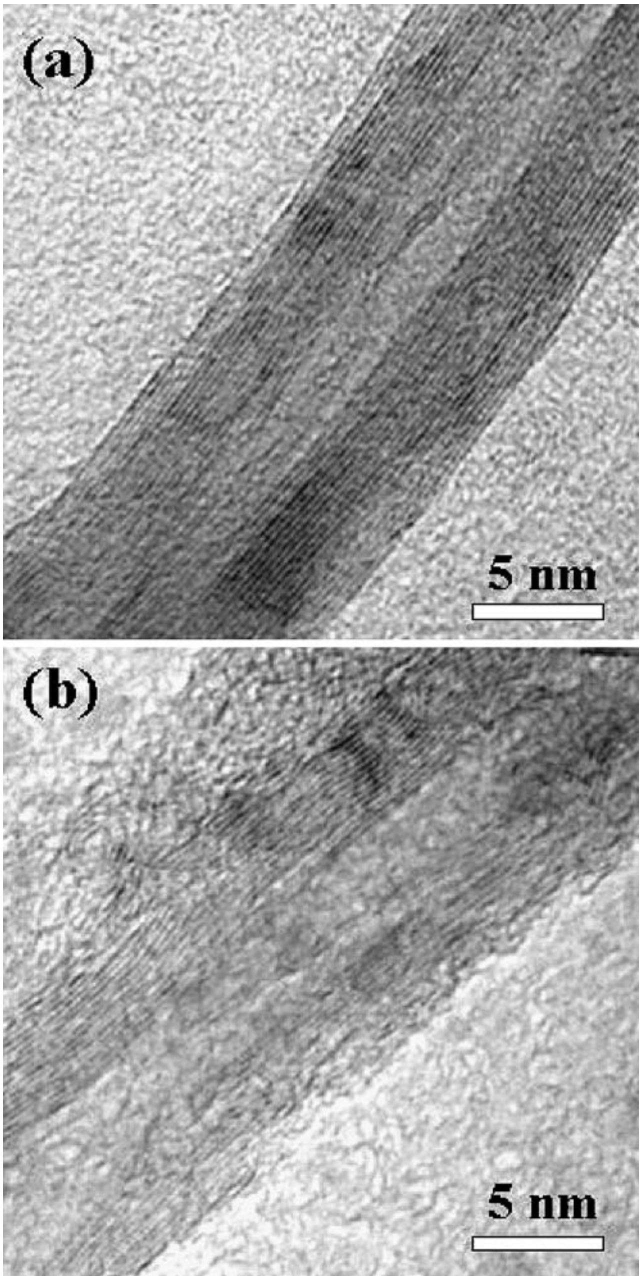


Fig. 2 TEM morphology of **a** pristine MWNT, **b** PS-g-MWNT

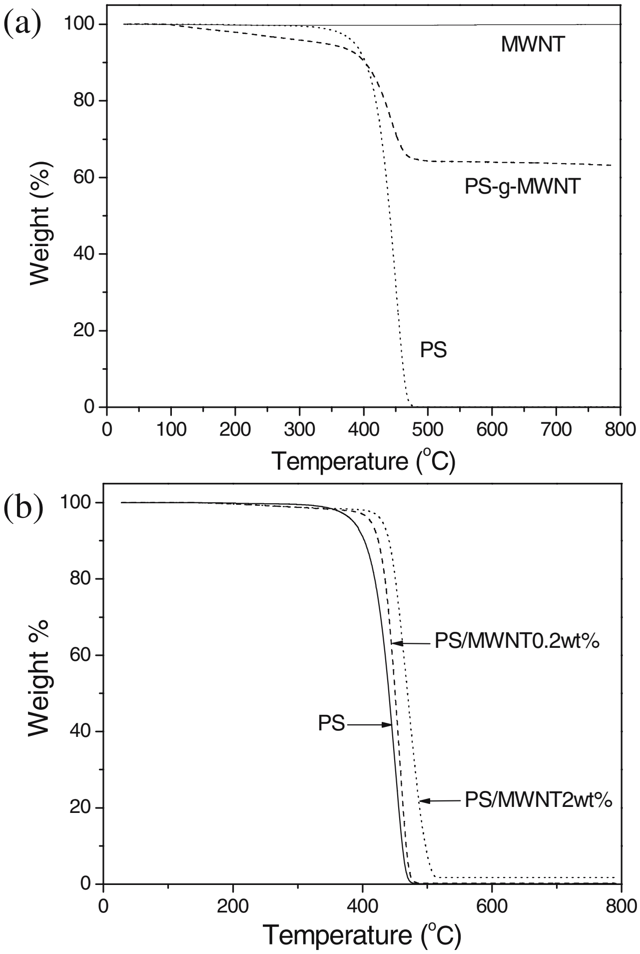


Fig. 3 TGA curves of **a** PS, pristine MWNT, and PS-g-MWNT and **b** PS, PS/MWNT (0.2 wt%), and PS/MWNT (2 wt%) (20 °C /min under N_2)

able to purify them without any damage of the MWNTs [16]. The desired amount of acid-treated MWNTs was dispersed in styrene monomer using an ultrasonic generator (G2806, Kyungil Ultrasonic, Korea) which has a nominal frequency of 28 kHz, with a power of 600 W for 4 h at 25 °C. The AIBN was added to form a stable suspension, and the styrene monomers were polymerized under ultrasonic treatment at 80 °C. To carefully investigate the role of the AIBN in the formation of the MWNT composites, we also separately synthesized PS/MWNT composites via a sonochemical method at 80 °C without adding AIBN as an initiator. It is well known that applying sonication to

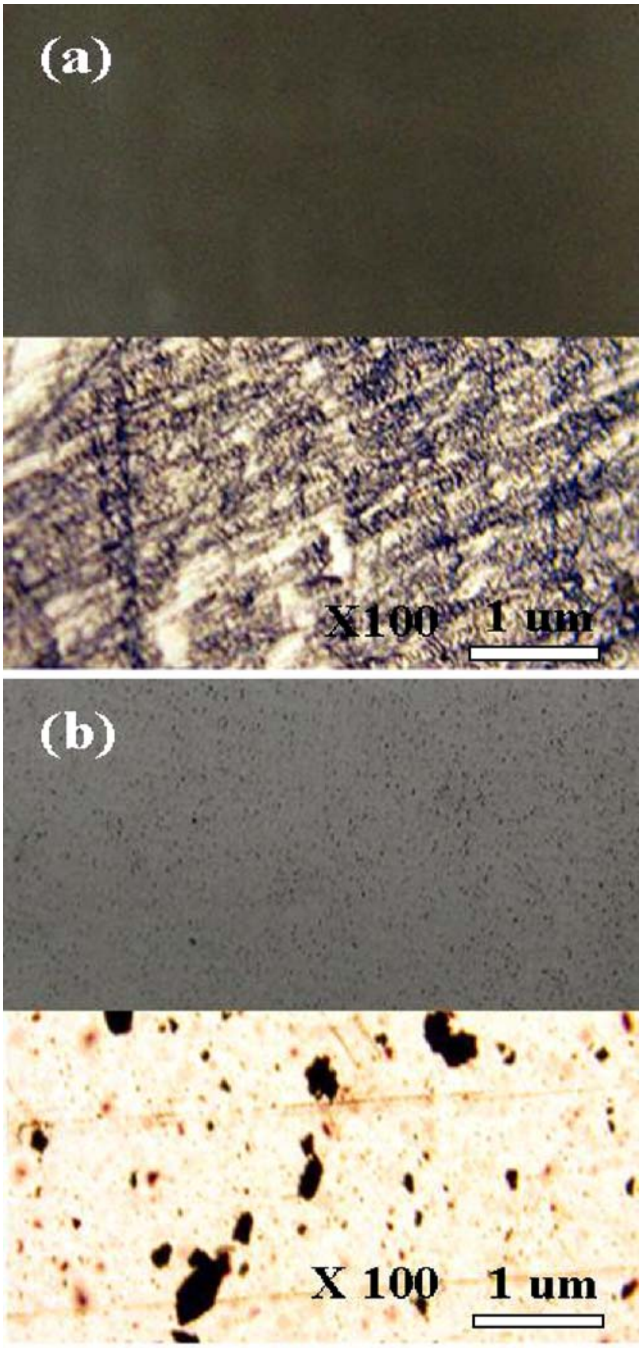
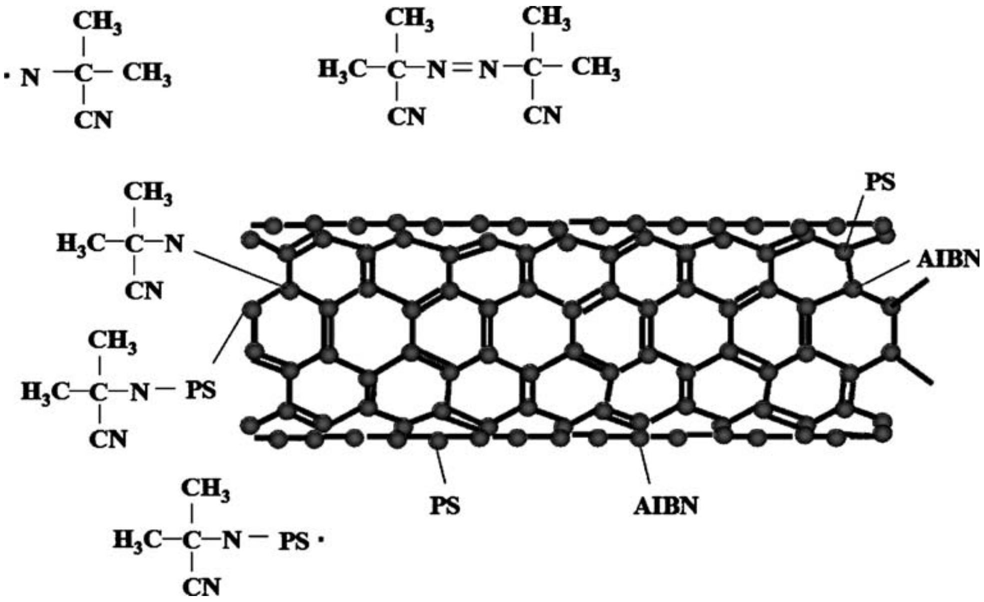


Fig. 4 The cast films made of **a** PS/MWNT (0.1 wt%) nanocomposite, **b** PS/MWNT (0.1 wt%) prepared from solution mixing for 3 h under ultrasonic treatment

Table 1 The GPC result for MWNT/PS composites with and without AIBN

	Radical polymerization with AIBN				Sonochemical polymerization without AIBN			
MWNT (wt%)	0	0.05	0.1	0.2	0	0.01	0.1	0.5
M_n (g/mol) ($\times 10^5$)	0.230	0.212	0.206	0.180	3.90	3.73	3.58	2.77
M_w (g/mol) ($\times 10^5$)	0.459	0.463	0.648	0.906	10.5	10.4	10.2	9.0
Polydispersity index (M_w/M_n)	1.99	2.18	3.14	5.03	2.70	2.79	2.86	3.25

Scheme 1 PS radicals and MWNT



styrene leads to the generation of styrene radicals which initiate its polymerization into polystyrene [18].

After polymerization, the PS/MWNT nanocomposite product was washed and filtered with excess chloroform several times to remove ungrafted PS chains. After vacuum drying, we obtained PS grafted MWNTs (PS-g-MWNTs), as confirmed by TGA. Morphology of the nanocomposites was observed by both scanning electron microscopy (SEM, Hitachi S-4300, Japan) and transmission electron microscopy (TEM, Phillips CM200, NL). We also used gel permeation chromatography (GPC, Waters 40 RI detector, Waters 510 HPLC pump, USA) to characterize the molecular weights of the PS in the nanocomposites using tetrahydrofuran as a solvent. Electrical conductivity vs MWNT content in the MWNT/PS nanocomposite film was measured by a four-probe method (237 high voltage source-measurement unit, Keithley, USA).

Results and discussion

The morphology of the resulting PS/MWNT (2 wt%) composites was observed with SEM (Fig. 1b), in which the MWNTs were observed to be sufficiently wetted, rather than being aggregated in the PS matrix. Grafted PS chains onto the MWNTs or the wrapped MWNTs play an important role in disjoining the MWNT bundles. After we removed ungrafted homo PS chains from the PS/MWNT composites, even though the PS-g-MWNTs (Fig. 1c) reaggregated, they were quite different from the pristine MWNTs (Fig. 1a).

TEM images of the pristine MWNTs and PS-g-MWNTs are shown in Fig. 2. From the TEM micrographs of the PS-g-MWNT samples, we can clearly confirm the presence of PS adhering to the MWNTs. In the case of the pristine MWNTs, the tube surface is relatively smooth (Fig. 2a), which is quite different from that of the PS grafted MWNTs (Fig. 2b).

The amount of grafted PS on the MWNTs was studied by TGA, by heating them up to 800 °C at a heating rate of 20 °C/min in an N_2 atmosphere (Fig. 3a). The weight of the pristine MWNTs hardly changed as the temperature was raised to 800 °C, whereas the weight of the PS-g-MWNTs decreased rapidly near 400 °C because of the decomposition of PS. According to the TGA curves, PS content in the PS-g-MWNTs was nearly 37 wt%. This indirectly demonstrates that 37 wt% of the PS was covalently linked to the MWNTs in the PS-g-MWNTs. In addition, as the MWNT content was increased, the degradation temperature was shifted to a higher temperature than that obtained only with

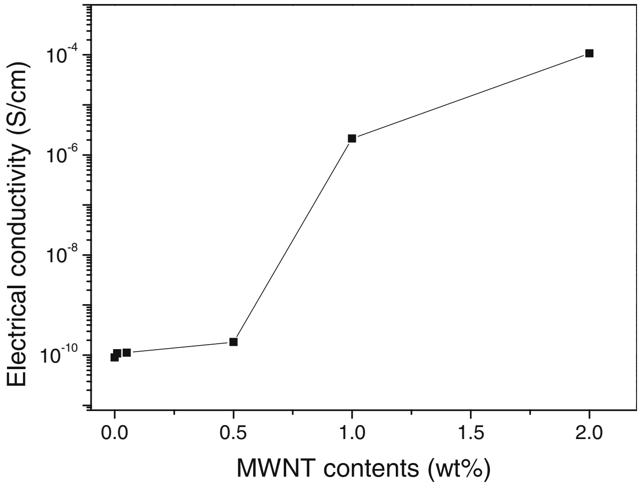


Fig. 5 Electrical conductivity vs weight fraction of MWNT in the nanocomposite

the pure PS (Fig. 3b). These results indicate that the addition of MWNTs to the PS matrix significantly enhanced its thermal stability. Note that the FTIR spectroscopy has been used for providing evidence of covalent linking between MWNT and polymer [19].

Figure 4 shows photographic (upper) and optical microscopic (lower) images for the system consisting of MWNTs dispersed initially in styrene monomers (Fig. 4a) and polystyrene (Fig. 4b). Figure 4a shows the MWNT/PS composites synthesized via the in situ bulk polymerization, and Fig. 4b corresponds to the mixing of the MWNTs and PS under ultrasonic treatment. The MWNTs in Fig. 4a are well dispersed without any agglomeration and have a higher opacity than the other PS/MWNTs system (Fig. 4b) prepared from solution mixing for 3 h under ultrasonic treatment for comparison. This clearly indicates that the in situ polymerization method is better than the simple solution-mixing method in the dispersion of MWNTs, as can be clearly compared between Fig. 4a and b [19].

The GPC results for the MWNT/PS nanocomposites with and without the initiator, AIBN, are summarized in Table 1. Note that in both cases, the number-average molecular weight decreased as the MWNT contents in the nanocomposites increased. The gelation time, during which the polymer chains were under the influence of ultrasound, was increased due to the prolongation of the polymerization caused by the addition of the MWNTs. As a result, the degradation of the PS chains caused by the ultrasonic treatment increased, and the number average molecular weight decreased [20]. In addition, as the MWNT contents increased, we found that the weight-average molecular weights of the PS either increased or decreased, depending on the presence or absence of AIBN, respectively. As previously reported [19], the AIBN was mainly consumed during the polymerization reaction. The additional consumption of the AIBN due to its adsorption onto the MWNTs decreased the number of radicals, thereby, resulting in an increase in the weight average molecular weight of the PS under the same polymerization conditions [21]. Furthermore, it can be also considered that PS radicals and MWNT whose π-bonds were opened by ultrasonic treatment induced chain transfer reaction as shown in Scheme 1 [22], thus, increasing polydispersity index (PDI) with increased MWNT. This could be another supporting evidence for the covalent linking.

Electrical conductivity of a film-typed sample of the MWNT/PS composites is given in Fig. 5 as a function of MWNT content in the PS, showing that the electrical conductivity with MWNT content in the PS was in accordance with a percolation theory [23]. We also found that percolation threshold for the MWNT/PS composites lies between 0.5 and 1.0 wt% because a rapid increase in the electrical conductivity takes place when the MWNT content exceeds 0.5 wt%. At this threshold, enough MWNTs are present for continuously conducting chains to be formed [24].

Conclusion

PS/MWNT nanocomposites were synthesized via an in situ bulk polymerization. The SEM micrographs showed that MWNTs were sufficiently wetted in the PS matrix. After removing PS from the PS/MWNT composites, we were able to determine that PS is covalently linked to the MWNTs during the proposed synthetic procedure via SEM, TEM, TGA, and GPC analyses. Based on the comparison between PS/MWNT composite films from in situ polymerization method and films prepared from solution mixing, the nanocomposites synthesized via the in situ polymerization method were found to provide better uniform dispersion of MWNTs in the PS matrix than those prepared by the solution-mixing method. Furthermore, the ultrasonic treatment can be considered to be an efficient method of dispersing the MWNTs. The GPC analysis also revealed that MWNTs consume AIBN and PS radicals during the polymerization reaction.

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