Polymer 49 (2008) 2071–2076

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Location-selective incorporation of multiwalled carbon nanotubes in polycarbonate microspheres

Rira Jung, Won-Il Park, Soon-Min Kwon, Hun-Sik Kim, Hyoung-Joon Jin *

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

A R T I C L E I N F O

Article history:
Received 31 December 2007
Received in revised form 23 February 2008
Accepted 28 February 2008
Available online 2 March 2008

Keywords:
Multiwalled carbon nanotubes
Polycarbonate
Location-selective incorporation

A B S T R A C T

In this study, we describe a process to produce polycarbonate (PC) microspheres and incorporate multiwalled carbon nanotubes (MWCNTs) within them location-selectively. The process, an oil-in-water (O/W) emulsion method, entails the formation of an aqueous phase with poly(vinylpyrrolidone) (PVP) and a methylene chloride phase that dissolves PC. Uniform PC microspheres were prepared by forming a stable emulsion using a homogenizer and a steric stabilizer, PVP. With this process, MWCNTs can be location-selectively incorporated in PC microspheres to afford the required properties such as electrical conductivity and thermal stability. When MWCNTs were dispersed in an aqueous phase using PVP, they were incorporated only on the surface of the PC microspheres. However, PC microspheres incorporating MWCNTs inside them were fabricated when the MWCNTs were dispersed in methylene chloride by functionalizing them via alkylation.

1. Introduction

Following the discovery of carbon nanotubes (CNTs), polymer/CNT nanocomposites have generated a great deal of interest in research and industrial communities [1–5]. As CNTs exhibit extraordinary mechanical properties, thermal stability, and electrical conductivity, they can be used to enhance the properties of polymeric matrices through various compounding methods such as in situ polymerization, solution casting, and adsorption [6–8]. To produce high performance polymer composites, however, the CNTs should be highly dispersed without bundles or aggregation. Recently, much attention has been paid to the preparation of CNT dispersions via the chemical treatment, plasma treatment, and polymer wrapping of CNTs [9–11]. It is also important to incorporate the CNTs at the proper locations according to the projected use of the polymer composites. For example, while the uniform dispersion of CNTs in polymeric matrices enhances the mechanical properties of the polymer/CNT nanocomposites, their electrical conductivity is generally low [7,12]. In contrast, polymeric nanocomposites having surfaces covered with CNTs exhibit superior electrical conductivity at the same concentration of CNTs, because the CNTs can readily construct a network of electrical pathways on the surface [8,13].

Polycarbonate (PC) is a typical engineering thermoplastic polymer that exhibits good optical transparency, outstanding dimensional and thermal stability, and high impact strength, as well as excellent moldability [14,15]. Due to their extraordinary properties, PC and PC based composite materials have been widely applied in diverse areas such as lenses, compact discs, bottles, and displays. However, additional processing is necessary to produce PC in the form of a perfectly spherical shape with a uniform size. In contrast, PMMA and PS are directly polymerized in the form of microspheres via suspension, emulsion, and dispersion polymerization.

In this study, we used an O/W emulsion system to incorporate MWCNTs in PC microspheres at the desired locations, as well as to manufacture PC in the form of microspheres. The O/W emulsion system consists of two immiscible liquids, water and methylene chloride, and is stabilized using a steric stabilizer to afford a uniform emulsion, while retaining the uniform size of the microspheres. During this process, PC/MWCNT microspheres having two different conformations were produced by dispersing MWCNTs in either an aqueous phase or organic phase.

2. Experimental part

2.1. Materials

PC was supplied by LG-DOW Polycarbonate Ltd. (Korea) with the commercial designation of PC 201-22. Methylene chloride (DC Chemical Co. Ltd., Korea) was used without further purification. Polyvinylpyrrolidone (PVP, Mw: 360,000 g/mol, Aldrich, USA) was used as a steric stabilizer of the O/W emulsion system. The MWCNTs used in this study were supplied by Iljin Nanotech Co., Korea. They were synthesized by thermal chemical vapor deposition (CVD), and their purity was more than 90%.

---

* Corresponding author. Tel.: +82 32 860 7483; fax: +82 32 865 5178.
E-mail address: hjjin@inha.ac.kr (H.-J. Jin).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.02.045

2.2. Functionalization of MWCNTs

The MWCNTs were purified by treating them in 3 M HNO_3 at 60 °C for 12 h, followed by refluxing in 5 M HCl at 120 °C for 6 h. Acid treatment is an effective means of introducing carboxylic and hydroxyl functional groups onto the surface of the MWCNTs [16]. The acid-treated MWCNTs were filtered and washed with a large amount of deionized water and then vacuum-dried at room temperature overnight. To disperse the MWCNTs in methylene chloride, the acid-treated MWCNTs were alkylated using lithium and alkyl halide in liquid ammonia (NH_3, 2.0 M solution in methanol, Aldrich, USA). The reaction was carried out as described in a previous study [9]. To a 100 mL three-neck round-bottom flask 20 mg of the acid-treated MWCNTs was added. Then 60 mL of NH_3 was added into the flask followed by the addition of 231 mg of lithium metal. After addition of 6.4 mmol of 1-iodooctane (Aldrich, USA), the reaction mixture was stirred overnight. During the process, NH_3 slowly evaporated. The flask was then cooled in an ice bath and methanol was added slowly followed by water. After acidification with 10% HCl, the alkylated MWCNTs were extracted into hexane and washed several times with water. The hexane was filtered through a 0.2 μm PTFE membrane filter with ethanol, and dried in a vacuum oven at 80 °C overnight.

2.3. Preparation of PC microspheres via O/W emulsion system

PC microspheres were fabricated via an O/W emulsion system as follows. PC (4 wt%) and PVP were dissolved in methylene chloride and deionized water, respectively, at room temperature. The PC solution and aqueous PVP solution were mixed at a 20/80 (wt/wt) ratio, as shown in Fig. 1a. To form a stable emulsion, the mixture solution was homogenized at 2000 rpm for 2 min using an Ultra-Turrax® T25 (Ika Labortechnik, Staufen, Germany). The methylene chloride in the emulsion was then extracted in vigorously stirred methanol, followed by filtering through a 0.5 μm nylon membrane filter with ethanol and water. The PC microspheres were then dried at room temperature overnight.

2.4. Preparation of S-PC/MWCNT and I-PS/MWCNT microspheres

The PC microspheres with MWCNTs on their surface (S-PC/MWCNT microspheres) were prepared as follows. The process was fundamentally the same as the previously mentioned method of preparing the PC microspheres. However, 0.03 wt% of the acid-treated MWCNTs was dispersed in 4 wt% of aqueous PVP solution. Ultrasound was then applied to the aqueous MWCNT dispersion for 2 h at 25 °C using an ultrasonic generator (Kodo Technical Research Co., Korea) having a nominal frequency of 28 kHz and a power of 600 W. To the aqueous MWCNT dispersion 20% (wt/wt) of methylene chloride (4 wt% PC) was added, as shown in Fig. 1b. The mixture was homogenized at 2000 rpm for 2 min, and then added to methanol under vigorous stirring. The S-PC/MWCNT microspheres were filtered through a 0.5 μm nylon membrane filter with ethanol and water, and dried at room temperature overnight.

The I-PC/MWCNT microspheres denote the PC microspheres incorporating MWCNTs inside the microspheres. The I-PC/MWCNT microspheres were prepared via a similar method to the S-PC/MWCNT microspheres. However, 0.03 wt% of the alkylated MWCNTs was dispersed in methylene chloride instead of water, followed by the application of ultrasound for 2 h at 25 °C. PC (4 wt%) was dissolved in the MWCNT dispersion, which was added to an 80% (wt/wt) aqueous phase (4 wt% PVP), as shown in Fig. 1c. The mixture was processed in accordance with the procedures described above, including stirring, washing, and drying.

2.5. Characterization

The functional groups of the MWCNTs and the structure of PC were verified using a Fourier transformed infrared spectrometer (FT-IR, VERTEX 80v, Bruker Optics, Germany). The morphology of

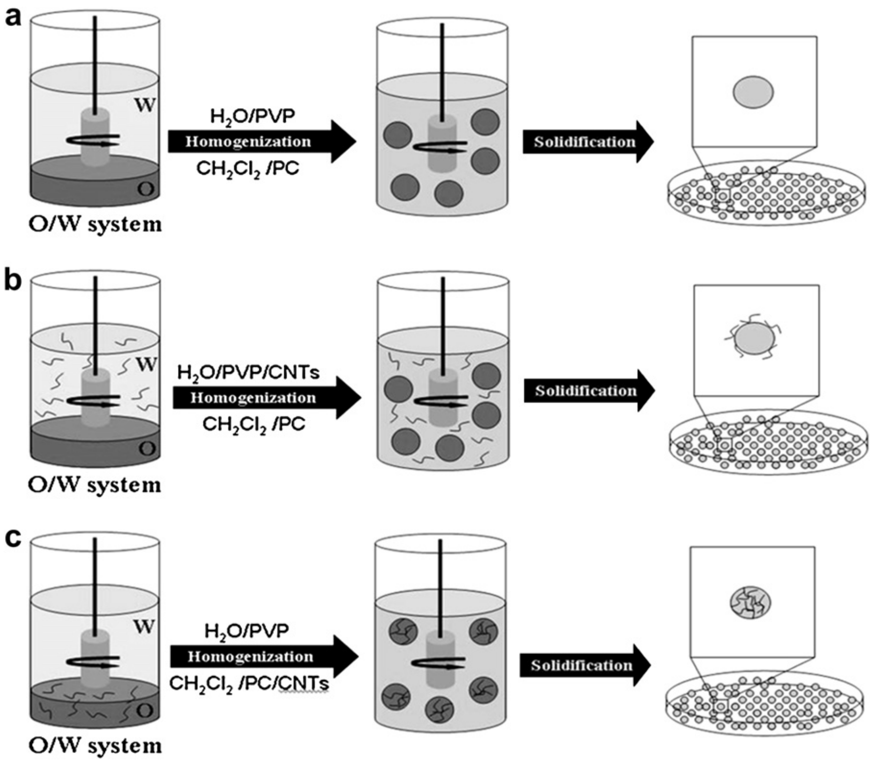

Fig. 1. Schematic representation of preparation of (a) PC microspheres; (b) S-PC/MWCNT microspheres; (c) I-PC/MWCNT microspheres.

the microspheres was observed via field emission scanning electron microscopy (FESEM, S-4200, Hitachi, Japan) at an accelerating voltage of 15 kV after precoating the sample with a homogeneous Pt layer by ion sputtering (E-1030, Hitachi, Japan). The location of the MWCNTs incorporated in the PC microspheres was observed by transmission electron microscopy (TEM, CM200, Philips, USA) at an accelerating voltage of 100 kV. The microspheres were placed in an epoxy resin and hardened in an oven at 60 °C for 2 days. A microtomed slice of the microspheres embedded in epoxy resin was placed on a copper grid and observed by TEM. The amounts of functional groups attached to the MWCNTs and MWCNTs incorporated into the PC microspheres were calculated using thermogravimetric analysis (TGA, Q50, TA instruments, UK) by scanning from 20 to 900 °C at a heating rate of 20 °C/min under a nitrogen atmosphere. The electrical conductivities of the S-PC/MWCNT microspheres and I-PC/MWCNT microspheres were measured by the four-probe method using a picoammeter with an internal voltage source (487, Keithley, USA) and an impedance analyzer (4284A, HP, USA). The samples were prepared in the form of disc-type pellets with a thickness of 0.8 mm by applying a pressure of 1000 kg at room temperature using a Carver laboratory press.

3. Results and discussion

CNTs usually form bundles or aggregates in solvents as a result of van der Waals forces. However, the preparation of well dispersed CNTs is of importance to produce polymer/CNT nanocomposites [8]. To obtain high quality MWCNT dispersions, we functionalized the MWCNTs using two methods. In the first method, the MWCNTs were functionalized by acid treatment, whereby hydroxyl and carboxylic acid groups were introduced on their side walls. In the second method, in order to disperse the MWCNTs in an organic solvent (methylene chloride in the present work), the acid-treated MWCNTs were alkylated using alkyl halide and lithium metal. The FT-IR spectra were analyzed to verify the functionalization of the MWCNTs. Fig. 2 shows the FT-IR spectra of the MWCNTs and the functionalized MWCNTs with carboxylic acid and alkyl groups. In contrast to Fig. 2a, the acid-treated MWCNTs exhibit a broad band at 3700–3300 cm^{-1} due to the O–H stretching vibration and the characteristic peak of the C=O stretching at 1711 cm^{-1} (Fig. 2b). After the acid-treated MWCNTs were modified by alkylation, their spectra exhibit peaks corresponding to C–H stretching and –CH$_2$– scissoring at 2914 cm^{-1} and 1452 cm^{-1}, respectively, which corresponds to the functionalized alkyl groups on the acid-treated MWCNTs (Fig. 2c).

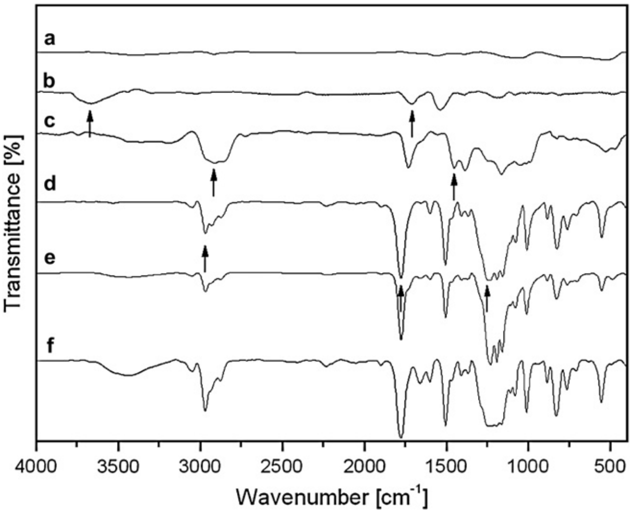

Fig. 2. FT-IR spectra of (a) raw MWCNTs; (b) acid-treated MWCNTs; (c) alkylated MWCNTs; (d) PC microspheres; (e) S-PC/MWCNT microspheres and (f) I-PC/MWCNT microspheres.

The FT-IR spectra of the PC microspheres revealed strong characteristic bands at 1780 cm^{-1} and 1245 cm^{-1} due to the C=O and C–O–C stretching vibrations, respectively (Fig. 2d). The spectra also show a band at 556 cm^{-1} due to the C–H out-of-plane vibration, indicating the presence of *p*-substituted aromatic rings. As shown in Fig. 2e, the S-PC/MWCNT microspheres had the characteristic bands of both PC and acid-treated MWCNTs; it is noted, however that, the intensities of the acid-treated MWCNT bands were relatively small, because of the low content of MWCNTs. The I-PC/MWCNT microspheres also showed the same bands as the PC microspheres and alkylated MWCNTs. This indicates that the MWCNTs were well incorporated into the PC microspheres, causing any significant change in the molecular structure of PC.

TGA experiments were performed to analyze the amounts of functional groups and MWCNTs in a nitrogen atmosphere. There is one inflection at ∼470 °C in the TGA curve of the acid-treated MWCNTs, which indicates that the MWCNTs begin to decompose at this temperature, as shown in Fig. 3a [17,18]. A weight decrease of the acid-treated MWCNTs is observed from 150 to 400 °C, which is attributed to the loss of oxygen-containing functional groups, such as carboxylic groups [19,20]. Thus, the acid-treated MWCNTs used in this study contain approximately 3.2 wt% carboxylic acid sites. This value is similar to the result reported in a previous study [21]. The TGA curves of the alkylated MWCNTs show an obvious weight loss at ∼280 °C, which is attributed to the loss of alkyl groups. The weight loss from 280 to 470 °C can be used to estimate the contents of alkyl groups attached to the MWCNTs [17,18]. From Fig. 3a, the amount of alkyl groups attached to the alkylated MWCNTs used in the composite synthesis in this study is determined to be approximately 11.6 wt%. Clearly, the MWCNTs were functionalized with carboxylic acid and alkyl groups, which indicated that the acid-treated and alkylated MWCNTs are soluble in water and organic solvents. Also, the content of MWCNTs incorporated into the PC microspheres was determined by TGA measurements, as shown in Fig. 3b. The PC microspheres start to lose weight at ∼350 °C, and are completely decomposed by ∼600 °C. Thus, the contents of MWCNTs incorporated in the S-PC/MWCNT and I-PC/MWCNT microspheres were 7.6 and 2.9 wt%, respectively. The content of MWCNTs incorporated in the I-PC/MWCNT microspheres was much lower than that in the S-PC/MWCNT microspheres. It should be noted that the ratio of methylene chloride to aqueous phase was 20/80 (wt/wt) even though the concentrations of the two MWCNT dispersions were the same. In addition, the I-PC/MWCNT microspheres start to lose weight at ∼405 °C, which indicates that the thermal stability of the PC microspheres was increased due to the incorporation of the MWCNTs inside of the PC microspheres. Fig. 4 shows the FESEM images of the PC microspheres produced via the O/W emulsion system. Water is immiscible with methylene chloride, which is a good solvent of PC, and consequently the two solutions form an emulsion when they are mixed using a homogenizer. PVP dissolved in water was employed as a steric stabilizer for this O/W emulsion system. PVP is a conventionally used stabilizer for emulsion or dispersion polymerization. It is believed that the amphiphilic structure of the PVP molecules facilitates the stabilization of the emulsion. Under the hypothesized mechanism, the vinyl groups on the PVP molecules would head organic droplets and form adsorbed layers on the interfaces between the organic droplets and aqueous phase. As a result, the organic droplets stabilized by PVP would not attach to each other. Moreover, the pyrrolidone components of the PVP molecules that extend into the aqueous phase would be repulsive toward each other, thus effectively helping to maintain the distance between the organic droplets. Consequently, the organic droplets including the

PC homogeneously were fabricated into PC microspheres with uniform size by extraction of methylene chloride in methanol. The average diameter of the PC microspheres was 1.1 ± 0.4 μm, as measured by counting 100 individual microspheres from the FESEM images using image analyzer software. The PC microspheres were quite spherical and had clear surfaces without impurities.

To incorporate them into the PC microspheres, the MWCNTs were introduced into either methylene chloride or water. When the MWCNTs were dispersed in the aqueous phase, they located on the surface of the PC/MWCNT nanocomposite microspheres (Fig. 5a). The acid-treated MWCNTs were homogeneously dispersed in water using PVP. PVP functions as a dispersant for the aqueous MWCNT dispersion by enclosing the MWCNTs, as well as acting as a steric stabilizer of the emulsion [10,22]. We suggest that the PVP molecules with the MWCNTs serve as a steric stabilizer of the O/W emulsion system in the same manner as in the preparation of the PC microspheres. It is projected that the PVP molecules proceed onto the surface of organic droplets consisting of PC and methylene chloride. Therefore, the MWCNTs could be located on the surfaces of the S-PC/MWCNT microspheres.

In contrast to the S-PC/MWCNT microspheres, very few MWCNTs were observed on the surfaces of the I-PC/MWCNT microspheres. Most of the MWCNTs were embedded in the I-PC/MWCNT microspheres, as shown in Fig. 5b. The I-PC/MWCNT microspheres were fabricated by dispersing the MWCNTs into the methlyene chloride phase before dissolving PC. The MWCNTs were functionalized with alkyl groups in order to be able to disperse them in methylene chloride, as previously mentioned. The alkylated MWCNTs produced a much better dispersion, as also noted in previous studies [17,23]. The dispersed MWCNTs were well compounded with PC in the solution state, so that they could be located inside the organic droplets under the O/W emulsion system. This explains why the

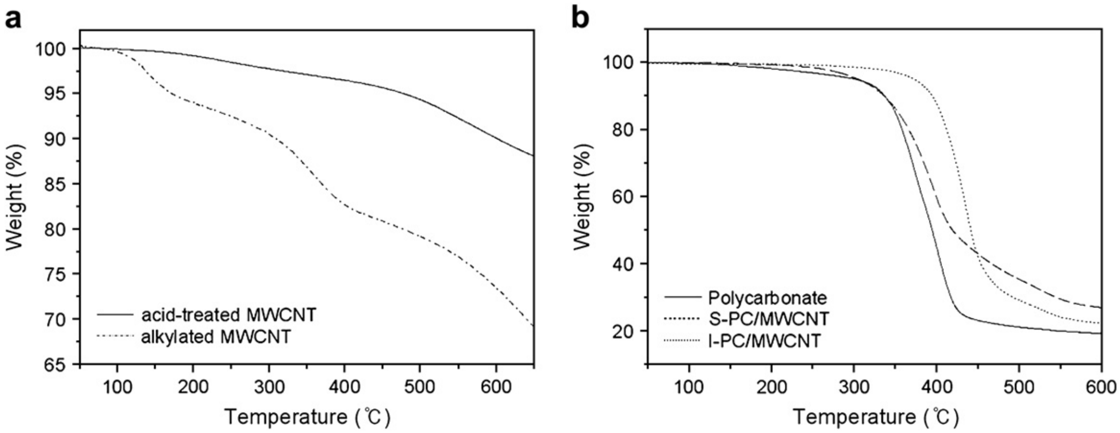

Fig. 3. TGA curves of (a) acid-treated MWCNTs and alkylated MWCNTs and (b) PC microspheres, S-PC/MWCNT microspheres, and I-PC/MWCNT microspheres.

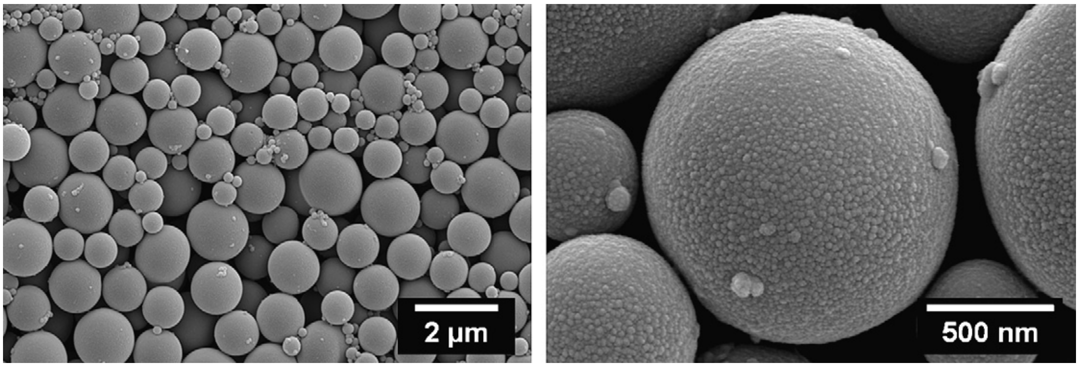

Fig. 4. FESEM images of PC microspheres produced by O/W emulsion method at two different magnifications.

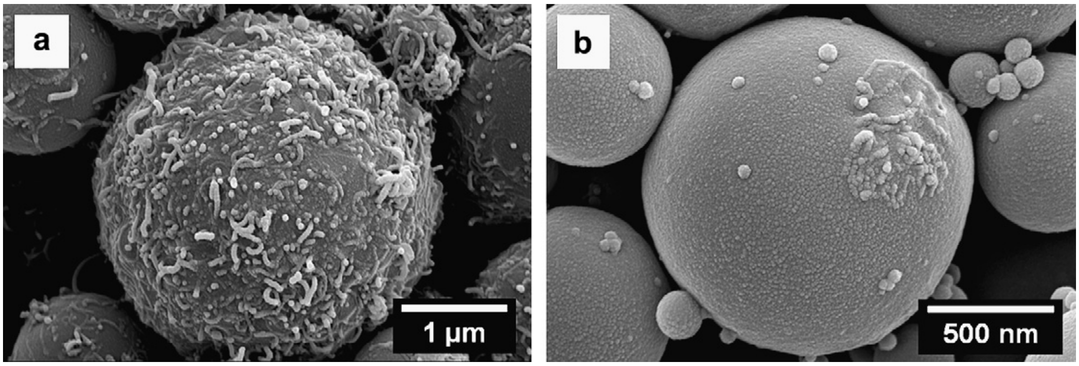

Fig. 5. FESEM images of (a) S-PC/MWCNT microspheres and (b) I-PC/MWCNT microspheres.

MWCNTs cannot be detected in the FESEM images of the I-PC/MWCNT microspheres. The average diameters of the S-PC/MWCNT microspheres and I-PC/MWCNT microspheres were $2.2 \pm 0.9\ \mu m$ and $1.3 \pm 0.4\ \mu m$, respectively. It appears that the MWCNTs layers, thermodynamically wrapped by the PVP molecules, increase the size of the S-PC/MWCNT microspheres while also inducing an irregular morphology. Namely, a part of PVP was wrapped around the MWCNTs and the size of the O/W emulsion droplets was increased due to the PVP wrapped MWCNTs acting as a steric stabilizer.

The locations of the MWCNTs incorporated in the PC microspheres were verified by observing the TEM images. As expected, the MWCNTs were located only on the surface of the S-PC/MWCNT microspheres (Fig. 6a). As shown in Fig. 6b, the MWCNTs incorporated on the S-PC/MWCNT microspheres were interconnected, thus leading to the formation of MWCNT layers. The electrical conductivity was as high as 5.1×10^{-2} S/cm. This high electrical conductivity at a low content also indicates that most of the incorporated MWCNTs were located on the surfaces of the microspheres and that they formed an outstanding network of electrical pathways [24].

Fig. 7 presents the cross-section of the I-PC/MWCNT microspheres. In contrast with Fig. 6, most of the incorporated MWCNTs were found inside the PC microspheres. This is consistent with the previous discussion related to Fig. 5b. Compared with Fig. 6a, a clear interface can be seen between the S-PC/MWCNT microspheres, whereas the interface is not clear enough to identify the individual I-PC/MWCNT microspheres in Fig. 7a. We considered that the MWCNTs which existed on the surfaces of the S-PC/MWCNT microspheres formed the interface. However, the MWCNTs in the I-PC/MWCNT microspheres were situated inside the microspheres. Therefore, the interface was not as clear, due to the similar contrast to PC and epoxy resin used for the TEM observation. The electrical conductivity of the I-PC/MWCNT microspheres was 7.2×10^{-13} S/cm, which was far lower than that of the S-PC/MWCNT microspheres. The source of this discrepancy might be that only a small amount of MWCNTs was incorporated and that the MWCNTs in the I-PC/MWCNT microspheres also tended to aggregate in the microspheres, as shown in Fig. 7b. We suggest that the dispersity of the MWCNTs decreased, due to the extraction of the methylene chloride dispersed MWCNTs during the solidification of PC.

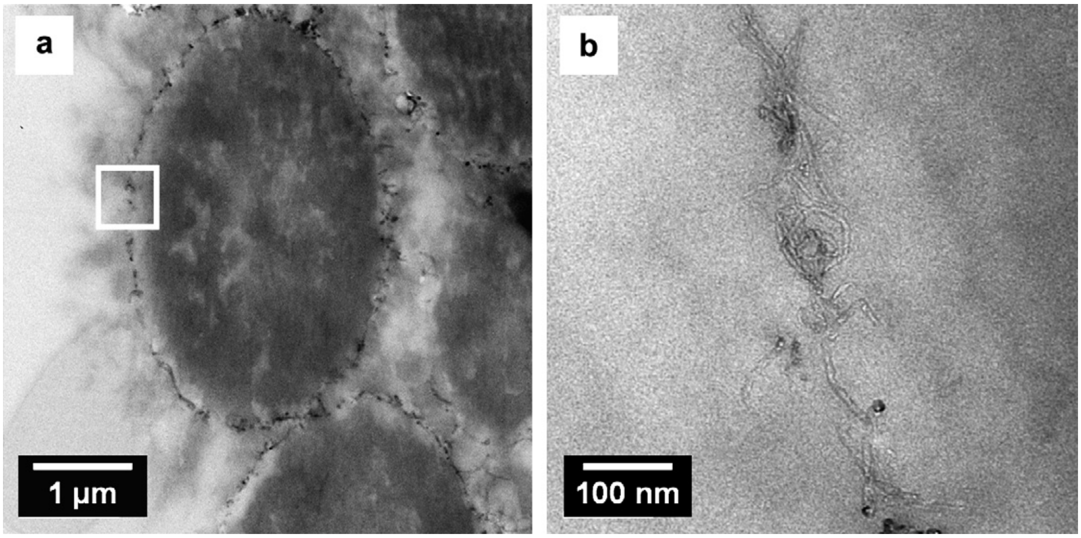

Fig. 6. FETEM images of (a) S-PC/MWCNT microspheres and (b) the MWCNTs in S-PC/MWCNT microspheres.

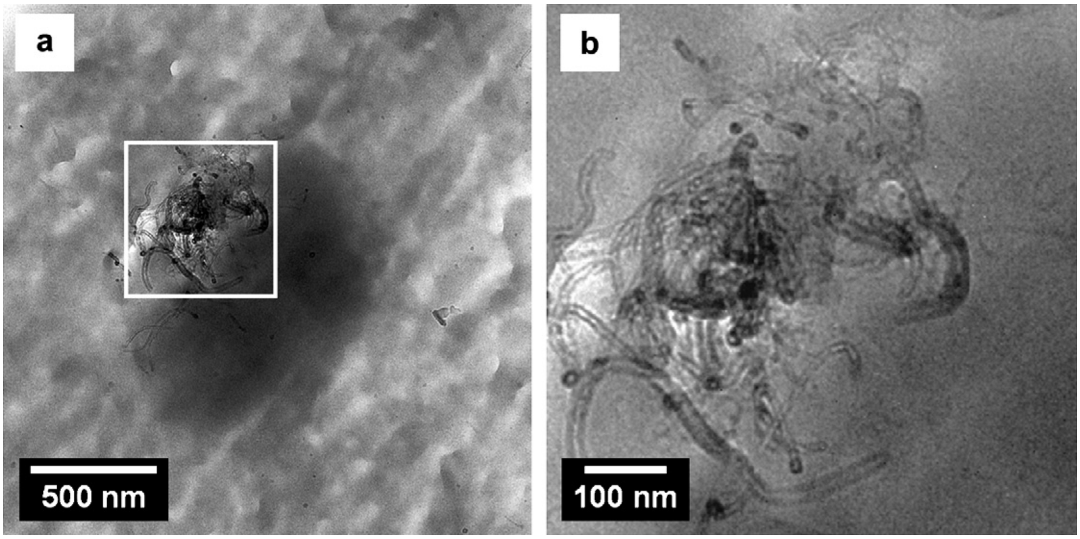

Fig. 7. FETEM images of (a) I-PC/MWCNT microspheres and (b) the MWCNTs in I-PC/MWCNT microspheres.

4. Conclusion

In the present study, we developed an efficient process to produce PC microspheres and incorporate MWCNTs within them location-selectively via an O/W emulsion system. The O/W emulsion system entails an aqueous phase dissolving PVP and a methylene chloride phase dissolving PC. The resulting PC microspheres had a spherical shape and uniform size as a result of the high stability of the emulsion obtained by using a homogenizer and a steric stabilizer, PVP. The S-PC/MWCNT microspheres covered with MWCNTs were prepared by dispersing the MWCNTs in the aqueous phase using PVP. The electrical conductivity of the S-PC/MWCNT microspheres was remarkably high (5.1×10^{-2} S/cm) due to the characteristics of their structure. Conversely, the MWCNTs were incorporated inside the I-PC/MWCNT microspheres, because the MWCNTs were dispersed into methylene chloride after functionalizing them via alkylation. This process provides a location-selective method of incorporating MWCNTs in polymeric microspheres depending on the projected usage. Our ongoing work is focused on improving the dispersity of MWCNTs in the I-PC/MWCNT microspheres and increasing the content of MWCNTs in the I-PC/MWCNT microspheres. The I-PC/MWCNT microspheres including highly dispersed MWCNTs are expected to lend better mechanical and thermal properties to the PC microspheres.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (No. R01-2007-000-10438-0).

References

[1] Xie X-L, Mai Y-W, Zhou X-P. Mat Sci Eng R 2005;49:89–112.

[2] Harris PJF. Int Mater Rev 2004;49:31–43.

[3] Tzavalas S, Drakonakis V, Mouzakis DE, Fischer D, Gregoriou VG. Macromolecules 2006;39:9150–6.

[4] Chen L, Pang X-J, Qu M-Z, Zhang Q-T, Wang B, Zhang B-L, et al. Compos Appl Sci Manuf 2006;37:1485–9.

[5] Eitan A, Fisher FT, Andrews R, Brinson LC, Schadler LS. Compos Sci Technol 2006;66:1162–73.

[6] Kim H-S, Myung SJ, Jung R, Jin H-J. J Nanosci Nanotechnol 2007;7:4045–8.

[7] Jung R, Kim H-S, Jin H-J. Macromol Symp 2007;249–250:259–64.

[8] Jin H-J, Choi HJ, Yoon SH, Myung SJ, Shim SE. Chem Mater 2005;17:4034–7.

[9] Liang F, Sadana AK, Peera A, Chattopadhyay J, Gu Z, Hauge RH, et al. Nano Lett 2004;4:1257–60.

[10] O'Connell MJ, Boul P, Ericson LM, Huffman C, Wang Y, Haroz E, et al. Chem Phys Lett 2001;342:265–71.

[11] Bubert H, Haiber S, Brandl W, Marginean G, Heintze M, Brüser V. Diam Relat Mater 2003;12:811–5.

[12] Sung JH, Kim HS, Jin H-J, Choi HJ, Chin I-J. Macromolecules 2004;37:9899–902.

[13] Kim HS, Jin H-J, Myung SJ, Kang M, Chin I-J. Macromol Rapid Commun 2006;27:146–51.

[14] Yoon PJ, Hunter DL, Paul DR. Polymer 2003;44:5323–39.

[15] Yoo Y, Choi K-Y, Lee JH. Macromol Chem Phys 2004;205:1863–8.

[16] Chen J, Hamon MA, Hu H, Chen Y, Rao AM, Eklund PC, et al. Science 1998;282:95–8.

[17] Qin Y, Shi J, Wu W, Li X, Guo Z-X, Zhu D. J Phys Chem B 2003;107:12899–901.

[18] Qin Y, Liu L, Shi J, Wu W, Zhang J, Guo Z-X, et al. Chem Mater 2003;15:3256–60.

[19] Zhang T, Xi K, Gu M, Jiang ZS. Chinese Chem Lett 2008;19:105–9.

[20] Watts PCP, Mureau N, Tang Z, Miyajima Y, Carey JD, Silva SRP. Nanotechnology 2007;18:175701–6.

[21] Gao J, Itkis ME, Yu A, Bekyarova E, Zhao B, Haddon RC. J Am Chem Soc 2005;127:3847–54.

[22] Li L-J, Nicholas RJ, Chen C-Y, Darton RC, Baker SC. Nanotechnology 2005;16:S202–5.

[23] Li X, Shi J, Qin Y, Wang Q, Luo H, Zhang P, et al. Chem Phys Lett 2007;444:258–62.

[24] Yu J, Lu K, Sourty E, Grossiord N, Koning CE, Loos J. Carbon 2007;45:2897–903.