Electrically Conducting Polymeric Microspheres fabricated from Carbon Nanotube Dispersions

탄소나노튜브 분산용액을 이용한 전기전도성 고분자 마이크로 입자의 제조에 관한 연구

2009 年 2 月

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Electrically Conducting Polymeric Microspheres fabricated from Carbon Nanotube Dispersions

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Abstract

Polymer/carbon nanotube (CNT) microspheres were synthesized using a variety of methods. Poly(methyl methacrylate) (PMMA), polycarbonate (PC), and multiwalled carbon nanotubes (MWCNTs) were used. The PMMA/MWCNT microspheres were prepared successfully using *in-situ* dispersion polymerization in an alcohol phase in which acid-treated MWCNTs had been dispersed prior to polymerization. The diameter of the PMMA/MWCNT microspheres decreased from approximately 11.6 to 6.0 \( \mu \text{m} \) with increasing MWCNT content from 0 to 0.03 wt%. In addition, PC/MWCNT microspheres were fabricated using an oil-in-water emulsion method, which involved the formation of an aqueous phase with poly(vinyl pyrrolidone) and a methylene chloride phase that dissolved the PC. With this process, MWCNTs can be incorporated location-selectively in PC microspheres to afford the required properties, such as electrical conductivity and thermal stability. In addition, this study examined the morphological, physical and electrical properties of the polymer/MWCNT microspheres as well as the performance of the polymer/MWCNT microspheres in various applications.
국문요약
고분자와 탄소나노튜브를 복합화하여 고분자/탄소나노튜브 마이크로입자를 다양한 방법을 통하여 제조하였다. 제조된 고분자/탄소나노튜브 마이크로입자는 그 제조방법에 따라 마이크로입자의 크기 및 크기분산성이 달라질 뿐만 아니라 모양 및 물리적·전기적 특성이 달라진다. 본 연구에서는 폴리메틸메타크릴레이트, 폴리카보네이트를 각각 동시분산중합 그리고 oil-in-water 에멀젼방법을 이용하여 탄소나노튜브가 도입된 마이크로입자를 제조하였다. 분산중합으로 제조한 폴리메타메틸레이트/탄소나노튜브 마이크로입자는 균일한 크기를 가지면서 최대 $6.5 \times 10^{-6}$ S/cm의 전기전도성을 나타내었다. 폴리카보네이트/탄소나노튜브 마이크로입자의 경우 제조과정에서 탄소나노튜브를 유기상 혹은 물상에 분산시킴에 따라 폴리카보네이트 마이크로입자의 내부 및 외부에 탄소나노튜브의 위치를 선택적으로 조절할 수 있었으며 그 결과 마이크로입자의 전기전도성이 다양하게 나타날 수 있었다. 따라서 본 연구에서는 전기전도성 고분자/탄소나노튜브 마이크로입자의 제조를 통해 고분자 고유의 물성을 보완하여 다양한 분야에서의 고부가가치 재료로서의 가능성을 보여주었다.
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PART Ⅰ.

Preparation of Poly(methyl methacrylate)/Multiwalled Carbon Nanotube Microspheres via In-Situ Dispersion Polymerization
1. INTRODUCTION

Generally, the most common type of electrorheological (ER) fluid is a colloid of conductive or polarizable micron-sized and monodispersed solid particles dispersed in insulating fluids as silicone oil. The rheological properties of ER fluids are controllable and can reversibly change through the application of an electric field [1]. The ER fluids show Newtonian fluid behavior when an applied electric field is zero. On the other hand, ER fluids when an electric field is applied to several kilovolts per unit length show Bingham characteristic with a yield stress. That is, the formation of particle chains in the direction of the applied field produces the observed rheological changes. Also, Goodwin reported the range of particle conductivity to ER response is $10^{-9} - 10^{-1}$ S/cm under 50 Hz electric fields at water-free system [2]. Various particles as suspended materials have been used to prepare ER fluid. They have been reported like pumice [1], phosphate cellulose [3], Chitosan [4], silica [5], conducting polymer [6] and carbonaceous particles [7].

Carbon nanotubes (CNTs) have unique electrical and mechanical properties. Thus, CNTs have been using as reinforcing materials for various polymers. Polymer/CNT composites show increasing properties than intrinsic properties of polymer, and it can be application in various industrial fields. However, they have two problems. One is poor dispersion in polymer matrix due to van der waals force both CNTs, the other is poor interfacial adhesion with polymer for good load transfer [8]. A many methods to solve these problems have been reported as if surface modification of CNT though acid-treatment or novel self-assembling techniques for CNTs, etc. [9].

In previous study, CNTs were adsorbed at surface of polystyrene (PS) and poly(methyl methacrylate) (PMMA) particles [10]. The conductivity of CNT absorbed particles was reported between $10^5$ and $10^4$ S/cm. However, in case of absorption technique, CNTs not present at inside of particle, only observed surface of particle. Thus, it is prospected that
mechanical properties are not increased due to the physical incorporation of CNTs in particles. On the other hand, in case of *in-situ* polymerization technique, CNTs can present both inner and surface of polymer. Also, among several polymerization techniques, the dispersion polymerization method is one of the most popular methods for prepare the uniform sized microspheres [11, 12]. In a dispersion polymerization, the medium is chosen to be a solvent for the monomer, and a non-solvent for the resultant polymer. In common case using alcohol solvents as continuous phase, and using styrene or methyl mechacrylate (MMA) as monomer to be polymerized. In addition, a surfactant is used to produce a colloidly stable dispersion [13].

In this study, we prepared multi-wall carbon nanotubes (MWCNTs) dispersed methanol solution and then synthesized microspherical PMMA/MWCNT composite by *in-situ* dispersion polymerization. We observed that MWCNTs were appeared not only embedded inside the microspheres but also the surface of microspheres. In addition, the PMMA/MWCNT microspheres have also been adopted as an ER fluid material.
2. EXPERIMENTAL DETAILS

2.1 Materials

The MWCNTs (purity of 95%, supplied by Iljin Nanotech Co., Korea.) produced by thermal chemical vapor deposition (CVD) were used in this study. Methyl methacrylate (MMA, DC chemical co. Ltd., Korea) and Polyvinylpyrrolydone (PVP, M_w: 360,000 g/mol, Aldrich, USA) were used as a monomer and stabilizer without further purification. 2,2-Azobisisobutyronitrile (AIBN, Junsei, Japan) was used as an initiator and was dissolved ethanol to remove inhibitor, precipitated at -10 °C, and stored in a refrigerator before polymerization. Methanol (DC chemical co. Ltd., Korea) was used as the polymerization media.

2.2 Preparation of MWCNT Dispersed Alcohol Solution

To eliminate impurities in the MWCNTs such as metallic catalysts, MWCNTs were treated with acid and underwent the following typical procedure [14]. The MWCNTs were treated in acid mixture (sulfuric acid/nitric acid = 3:1 (v/v)) at 60 °C for 24 h. As a result of the purification process, the carboxylic and hydroxyl functional groups are introduced onto the surface of the MWCNTs [15]. The acid treated MWCNTs were dispersed in methanol without surfactants for dispersion polymerization. The MWCNTs solution looks like black color ink, MWCNTs were well dispersed and stable in the methanol.

2.3 Synthesis of the PMMA/MWCNT Microspheres

Dispersion polymerization was carried out in a 250 mL round flask with a mechanical stirring at 80 rpm under nitrogen atmosphere at 60 °C for 48h. Pre-weighed MWCNTs and methanol solution were loaded in the reactor and followed by the addition of MMA and PVP. Then, AIBN dissolved in methanol was added as initiator. During the polymerization, parts of the reaction mixture were withdrawn from the reactor to examine the conversion upon reaction time and the characteristics of the microspheres. The withdrawn polymerization products were
rinsed off with methanol, centrifuged repeatedly to remove the non-reacted MMA and PVP. Then PMMA/MWCNT microspheres were dried in vacuum oven at room temperature for 48 h [16].

2.4 Characterization

The number-average diameter ($D_n$) and the coefficient of variation ($C_v$) of microsphere diameter were defined using the following equations by counting at least 50 individual microspheres from SEM microphotographs.

$$D_n = \left( \frac{\sum n_i d_i}{n_i} \right)$$

$$C_v = \left( \frac{\left( \sum (d_i - \frac{\sum n_i d_i}{\sum n_i})^2 / \sum n_i \right)}{\left( \sum n_i d_i / \sum n_i \right)} \right)^{1/2} \times 100$$

where $n_i$ is the number of microspheres with $d_i$, and $d_i$ is the diameter of microspheres [11].

The molecular weight of the synthesized PMMA microspheres was measured by gel permeation chromatography (GPC, Waters 410 detector, USA) with THF as a solvent and polystyrene as the standard. The morphology of the PMMA and PMMA/MWCNT were observed using scanning electron microscopy (SEM, Hitachi S-4300, Japan) after pre-coating the sample with a homogeneous Pt layer by ion sputtering (Hitachi, E-1030, Japan). The internal structures of the PMMA/MWCNT microspheres were observed by transmission electron microscopy (TEM, Philips CM200, USA) at an accelerating voltage of 100 kV. All of the ultrathin sections were microtomed using a MTX ultramicrotome (Tucson, AZ, USA) with a diamond knife. The surface of the PMMA/MWCNT microspheres was observed by atomic force microscopy (AFM, SPA400, Seiko Instrument Incorporated, Japan). AFM operated in the tapping mode. Thermogravimetric analysis (TGA, TA instruments, Q50, UK) was used to measure the MWCNT content in the PMMA/MWCNT microspheres. It was analyzed under a heating rate of 20 °C/min from room temperature to 900 °C and a dynamic nitrogen flow of 10 cm$^3$/min. For measuring the electrical conductivity of the PMMA/MWCNT microspheres, they
were prepared in the form of disc-type pellets with thickness of 0.7 mm by applying a pressure of 1 ton at room temperature using a Carver laboratory press (Model #3912, Carver Inc., Wabash, IN, USA). Its electrical resistances of the PMMA/MWCNT microsphere were measured by a four-probe method with resistivity meter (Hiresta-up MCP-HT450, Mitsubishi chemical corporation, Japan). Finally, the ER fluid was prepared by dispersing the PMMA/MWCNT microspheres in the silicone oil by ultrasonic generator (Kodo technical research co. Ltd., Korea). The gap between the two parallel electrodes was fixed precisely at 398 μm. The microstructure image of the ER fluid was obtained by optical microscopy (BX51, Olympus, Japan). Such a particle concentration (10 vol%) of PMMA/MWCNT microspheres corresponds to about 0.03 wt% of MWCNT in the ER fluid in this study.
3. RESULTS AND DISCUSSION

3.1 MWCNT dispersion in methanol

![Figure 1](image.png)

**Figure 1.** Photo images of (a) the acid-treated MWCNTs dispersed in methanol and (b) pristine MWCNTs dispersed in methanol.

It is well known that acid treatments introduce functional groups such as carboxyl groups on the surfaces of CNTs [17]. In this way, they can be dispersed better in organic solvents or aqueous media, because of their increased solubility. As shown in Figure 1, after ultrasonication, the acid-treated MWCNTs were highly dispersible in methanol. The resulting dispersions were homogeneous and stable, and jet-black colored. Moreover, the dispersed MWCNTs in methanol did not precipitate at the bottom of the vials after more than 120 h, whereas the pristine MWCNTs in methanol sedimented rapidly and completely, forming large aggregations [Fig. 1(b)]. We believe that the MWCNTs were able to be easily dispersed in methanol, because of the oxygen groups that were introduced on their surface after the acid treatment [17].
Figure 2. SEM images of (a) pristine MWCNTs cast from methanol and (b) acid-treated MWCNTs cast from methanol.

Figure 2 shows the SEM images of the pristine and acid-treated MWCNTs dispersed in methanol. The length distributions of the pristine MWCNTs and acid-treated MWCNTs were $3.4 \pm 0.9$ and $0.9 \pm 0.4 \, \mu m$ ($N = 100$), respectively. In the case of the acid-treated MWCNTs, the length of the individual tubes was drastically decreased by up to four times, because of the strong chemical oxidation and ultrasonication [18]. Furthermore, while the pristine MWCNTs formed extremely large agglomerates, the acid-treated MWCNTs were individually separated from each other.

3.2 Morphologies of PMMA/MWCNT microspheres

We synthesized PMMA/MWCNT microspheres by the in situ dispersion polymerization of MWCNTs dispersed in methanol media (0.01, 0.02, and 0.03 wt % of MWCNTs). The inner and surface morphologies were observed by TEM, SEM, and AFM. Figure 3 shows the TEM images of the PMMA/MWCNT microspheres. MWCNTs inside the PMMA/MWCNT microspheres were observed by TEM, as shown in Figure 3(a). Figure 3(b) shows a larger magnification image of the inner structure which indicates that the MWCNTs were embedded in the PMMA/MWCNT microsphere. It has often been reported that poly-meric stabilizers such as PVP used in dispersion polymerization are not only physically adsorbed on the surface of the microspheres, but also chemically bound by
forming a covalent bond with the polymer molecules [19,20]. It is believed that the MWCNTs were incorporated into the PMMA microsphere surfaces with PVP during the polymerization. However, MWCNTs were not observed on the surfaces of the PMMA/MWCNT microspheres in the TEM images. We considered that the MWCNTs which existed on the surfaces of the microspheres were pulled out during the ultramicrotoming procedure performed in preparation for the TEM observation. Thus, the surfaces of the microspheres were observed by SEM and AFM to confirm the existence of MWCNTs.

Figure 3. TEM images of (a) PMMA/MWCNT microspheres at an MWCNT concentration of 0.03 wt % (b) with a higher magnification.

Figure 4. SEM micrographs of PMMA and PMMA/MWCNT microspheres prepared by in situ dispersion polymerization: (a) PMMA, (b) PMMA/MWCNT (0.01 wt %), (c) PMMA/MWCNT (0.02 wt %), (d) PMMA/MWCNT (0.03 wt %).
Figure 4 shows the SEM images of the PMMA and PMMA/MWCNT microspheres. The PMMA/MWCNT microspheres were successfully prepared with a spherical shape, and their diameter depended on the MWCNT content. The average MWCNT content in the PMMA/MWCNT microspheres was measured by TGA. The MWCNT content in the PMMA/MWCNT microspheres increased as the MWCNT loading in alcohol increased. The contents of the MWCNTs in the PMMA/MWCNT microspheres were 0.2, 1.7, and 3.7 wt % when using the 0.01, 0.02, and 0.03 wt% MWCNT dispersions, respectively.

The AFM images in Figure 5 show the morphology on the surface of the PMMA and PMMA/MWCNT microspheres. In Figure 5(a), the image shows that the surface of the PMMA microsphere is very clear and slick. No impurities were observed on the surface of the PMMA microspheres. However, MWCNTs were observed on the surface of the PMMA/MWCNT microspheres, as shown in Figure 5(b). As shown in the AFM images, the MWCNTs were embedded in the microspheres and attached to their surface. These results confirmed those provided by the SEM images.

![AFM images](image.png)

**Figure 5.** AFM images on surface of PMMA and PMMA/MWCNT microsphere with an MWCNT concentration of 0.03 wt %: (a) PMMA microsphere at an image size of 2 μm × 2 μm and (b) PMMA/MWCNT microsphere at an image size of 1 μm × 1 μm.
3.3 Properties of PMMA/MWCNT microspheres

Figure 6 shows the average diameter and $C_v$ value of the PMMA/MWCNT microspheres at various concentrations of MWCNTs. The average diameters of the PMMA/MWCNT microspheres decreased as the MWCNT loading was increased from 0 to 0.03 wt %. The average diameters of the PMMA microspheres and the PMMA/MWCNT microspheres with MWCNT contents of 0.01, 0.02, and 0.03 wt % were 11.6, 7.3, 6.2, and 6.0 μm, respectively, as determined by counting at least 50 individual microspheres (Fig. 4). Dispersion polymerization is a well known method of preparing monodispersed microspheres [21]. However, the $C_v$ value of the PMMA/MWCNTs microspheres increased from 8 to 14 when the amount of MWCNTs was increased from 0 to 0.02 wt %. When 0.03 wt % of MWCNTs was added, however, the size of the microspheres was slightly decreased compared to those with an MWCNT content of 0.02 wt %.

![Figure 6](image)

**Figure 6.** Effect of MWCNT content on the average diameter (solid symbol) and $C_v$ (open symbol) in the dispersion polymerization.

The PMMA and PMMA/MWCNT microspheres have a molecular weight of 143,000–110,000 g/mol. The molecular weight of the PMMA and PMMA/MWCNT microspheres continuously decreased as the MWCNT loading was increased, while their PDI decreased (4.3,
4.3, 3.7, and 3.2 at MWCNT contents of 0, 0.01, 0.02, 0.03 wt %, respectively), as shown in Figure 7. These results indicate that the MWCNTs participate in the polymerization process. Namely, during the polymerization, radicals were created by the initiator transferred to the surface of the MWCNTs. Therefore, PMMA and the MWCNTs have strong interfacial adhesion caused by covalent bonding [6]. However, the MWCNTs inhibit the polymerization of MMA, because they are consumed by the radicals which are needed to polymerize the monomer [22–24].

![Figure 7. Effect of MWCNT content on the weight average molecular weight ($M_w$, solid symbol) and the polydispersity index (PDI, open symbol) of the PMMA and PMMA/MWCNT microspheres.]

Also, we believe that the MWCNTs influence only limited parts of the reaction system at a low concentration, causing the size distribution of the microspheres to vary widely. On the other hand, when their concentration is sufficient, the MWCNTs influence the growth of the microspheres homogeneously throughout the reaction system, causing their size to be decreased and monodisperse. As can be observed in the SEM and AFM images, the PMMA microspheres have a clear and slick surface. MWCNTs were observed on the surface of the PMMA/MWCNT microspheres. Some of the MWCNTs in these composite particles appeared
to be embedded in the microspheres, while others were attached to their surface.

### 3.4 Electrorheological (ER) properties

![Optical microscopic image of the PMMA/MWCNT microspheres dispersed in silicone oil](image)

**Figure 8.** Optical microscopic image of the PMMA/MWCNT microspheres dispersed in silicone oil (a) which formed chain-like structures along the direction of the applied electric field (b).

The electrical conductivity of the PMMA and PMMA/MWCNT microspheres was measured by the four-probe method at room temperature. The electrical conductivity of the PMMA microspheres was \(1.0 \times 10^{-16}\) S/cm and those of the PMMA/MWCNT microspheres were \(4.4 \times 10^{12}\), \(2.3 \times 10^{12}\), and \(6.5 \times 10^{6}\) S/cm at MWCNT contents of 0.01, 0.02, and 0.03 wt %, respectively. In the theoretical models of ER fluids, the suspended ER particles are normally assumed to be monodisperse and spherical particles. Therefore, we expected that the PMMA/MWCNT (0.03 wt %) microspheres would make good ER fluids, because they have a uniform spherical form and their electrical conductivity was about \(10^{6}\) S/cm, which is an acceptable conductivity value for ER fluids [25]. In addition, polymeric microspheres in the range of size from 1 to 10 µm are known to exhibit superior ER performance provided that they all have similar electrical properties [12]. The applied electric field was maintained for a
few minutes at room temperature to obtain an equilibrium columnar structure [26]. The formation of a microsphere chain (which is called fibrillation) was demonstrated under an applied electric field of 2.5 kV/cm [Fig. 8(b)], as compared with the random distribution of the dispersed microspheres before the application of the electric field [Fig. 8(a)]. This appearance is due to the electrostatic interaction between the conductive particles, which is caused by the mismatch of the dielectric constants between the conductive particles and oil [25,27]. The PMMA/MWCNT microspheres form dense chains of particles within seconds after the application of an electric field, and the chain-like structure remained stable as long as the electric field was applied. It is possible that the fibrillated chain structures might provide a path for the transport of electrons, and thereby contribute to the conducting behavior of the ER fluids. Moreover, we also observed that partial electrophoresis, which was caused by the reduction in the microsphere density between the two electrodes, was observed for these ER fluids during the formation of the particle chain after the application of an electric field [26].
4. CONCLUSIONS

In this study, PMMA and PMMA/MWCNT microspheres were successfully fabricated by *in-situ* dispersion polymerization in methanol which dispersed acid-treated MWCNTs before polymerization. The SEM, AFM, and TEM micrographs confirmed that the MWCNTs were not only embedded inside the microspheres, but also present on their surface. Through TGA measurements, we also found that the amount of MWCNTs included in the PMMA/MWCNT microspheres increased with increasing concentration of the MWCNTs dispersed in methanol. The diameter of the PMMA/MWCNT microspheres was smaller than that of the PMMA microspheres and their molecular weight was lower. The electrical conductivity of the PMMA/MWCNT microspheres was $6.5 \times 10^{-6}$ S/cm at an MWCNT content of 3.692 wt%. The PMMA/MWCNT microspheres exhibited ER properties. The reversible behavior of the chain-like structure was demonstrated under an applied electric field of 2.5 kV/cm.
5. REFERENCES


PART II.

Location-selective Incorporation of Multiwalled Carbon Nanotubes in Polycarbonate Microspheres
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 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 chemical treatment, plasma treatment, and polymer wrapping of CNTs.[9-11] It is also important to control incorporation of CNTs at proper locations according to the projected uses of the polymer composites. For example, while the uniform dispersion of CNTs in polymeric matrices enhances mechanical properties of polymer/CNT nanocomposites, the polymer/CNT nanocomposites generally show low electrical conductivity as a result of embedding CNTs in the polymeric matrices.[7,12] In contrast, polymeric nanocomposites having surfaces covered with CNTs exhibit superior electrical conductivity at the same concentration of CNTs, because 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 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 applied O/W emulsion system to incorporate MWCNTs in PC microspheres at 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 while retaining uniform size by homogenization and use of a steric stabilizer to retain uniform emulsion. 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 DETAILS

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. MWCNTs used in this study were supplied by Iljin Nanotech Co., Korea. They were synthesized by thermal chemical vapor deposition (CVD), and the purity was more than 90%.

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] 20 mg of the acid-treated MWCNTs was added to a 100 mL three-neck round-bottom flask. 60 mL of NH$_3$ was then added into the flask followed by the addition of 231 mg of lithium metal. After 6.4 mmol of 1-iodooctane (Aldrich, USA) was added, the reaction mixture was stirred overnight. During the process, NH$_3$ was 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. 4 wt.-% PC and PVP were dissolved in methylene chloride and deionized water, respectively, at room temperature. 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 Basic (Ika Labortechnik, Staufen, Germany). 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. PC microspheres were then dried at room temperature overnight.

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

Figure 1. Schematic representation of preparation of (a) PC microspheres; (b) S-PC/MWCNT microspheres; (c) I-PC/MWCNT microspheres.
PC microspheres with MWCNTs on their surface (S-PC/MWCNT microspheres) were prepared as follows. The process was fundamentally the same as previously mentioned PC microspheres preparation. 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 (Kyungill Ultrasonic Co., Korea) having a nominal frequency of 28 kHz and a power of 600 W. 20% (wt/wt) of methylene chloride (4 wt.-% PC) was added to the aqueous MWCNT dispersion, as shown in Fig. 1b. The mixture was homogenized at 2000 rpm for 2 min, and then added to methanol under vigorous stirring. S-PC/MWCNT microspheres were filtered through a 0.5 μm nylon membrane filter with ethanol and water, and dried at room temperature overnight.

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

2.5 Characterization

Functional groups of MWCNTs and the structure of the PC were verified using a Fourier transformed infrared spectrometer (FT-IR, VERTEX 80v, Bruker Optics, Germany). The morphology of 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 MWCNTs incorporated in the PC microspheres was observed by transmission electron
microscopy (TEM, CM200, Philips, USA). The microspheres were placed in an epoxy resin and hardened in an oven at 60 °C for 2 days. A microtomed slice of microspheres embedded in epoxy resin was placed on a copper grid and observed by TEM. The amounts of attached functional groups to MWCNTs and incorporated MWCNTs to PC microspheres were calculated using a 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 conductivity of the S-PC/MWCNT microspheres and I-PC/MWCNT microspheres, respectively, was 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 thickness of 0.8 mm by applying a pressure of 1000 kg at room temperature using a Carver laboratory press.
3. RESULTS AND DISCUSSION

3.1 Characteristics and properties of functionalized MWCNTs

Figure 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.

CNTs usually form bundles or aggregates in solvents as a result of van der Waals force. However, preparation of well dispersed CNTs is of importance to produce polymer/CNT nanocomposites.[8] To obtain high quality MWCNT dispersions, we functionalized MWCNTs through two methods. First, MWCNTs were functionalized by acid treatment, whereby hydroxyl and carboxylic acid groups were introduced on side walls of the MWCNTs. 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 MWCNTs. Fig. 2 shows the FT-IR spectra of MWCNTs and the functionalized MWCNTs with carboxylic acid and alkyl groups. Differently from Fig. 2a, the acid-treated MWCNTs exhibit a broad band at 3700-3300 cm\(^{-1}\) due to O-H stretching vibration and a characteristic peak of C=O stretching at 1711 cm\(^{-1}\) (Fig. 2b). After
the acid-treated MWCNTs were modified by alkylation, it is seen that the alkylated MWCNTs exhibit 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).

The results from 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 C-H out-of-plane vibration, indicating the presence of $p$-substituted aromatic rings. As shown in Fig. 2e, S-PC/MWCNT microspheres had both characteristic bands of 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. It is indicated that MWCNTs were well incorporated into PC microspheres while they did not make any change in the molecular structure of PC.

![Figure 3. TGA curves of (a) acid-treated MWCNTs and alkylated MWCNTs and (b) PC microspheres, S-PC/MWCNT microspheres, and I-PC/MWCNT microspheres.](image)

TGA experiments were performed to analyze the contents of functional groups and of MWCNTs in the nitrogen atmosphere. There is one inflection at $\sim 470 \, ^\circ C$ 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 $^\circ C$ that is attributed to loss of oxygen-containing functional groups,
such as carboxylic groups.[19,20] Thus, the acid-treated MWCNTs used in this study are contain approximately 3.2 wt.-% carboxylic-acid sites. This value is similar results with that of reported before.[21] The TGA curves of the alkylated MWCNTs show obvious weight loss at ~280 °C, which should be 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 contents of attached alkyl groups in the alkylated MWCNTs used in the composite synthesis in this study are determined to 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 the water and organic solvents. Also, the content of incorporated MWCNTs to PC microspheres was determined by TGA measurements, as shown in Fig. 3b. PC microspheres start to lose weight at ~350 °C, and is completely decomposed by ~600°C. Thus, the content of incorporated MWCNTs in the S-PC/MWCNT and the I-PC/MWCNT microspheres were 7.6 and 2.9 wt.-%, respectively. The content of incorporated MWCNTs in the I-PC/MWCNT microspheres was much lower than that of MWCNTs in the S-PC/MWCNT microspheres. Note 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 PC microspheres was increased according to incorporating of MWCNTs at innerness of PC microspheres.

3.2 Morphologies of PC, I-PC, and S-PC microspheres

Fig. 4 shows 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 PVP molecules facilitate stabilization of the emulsion. Under the hypothesized mechanism, the vinyl groups on PVP molecules would head organic droplets and form adsorbed layers on the interfaces between organic droplets and aqueous phase. As a result, the organic droplets stabilized by PVP would not attach to each other. Moreover, pyrrolidone components of PVP molecules that extend into the aqueous phase would be repulsive, thus effectively help a distance between the organic droplets to maintain. Consequently, the organic droplets including PC homogeneously fabricated 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 FESEM images using image analyzer software. The PC microspheres were quite spherical and had clear surfaces without impurities.

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

Figure 5. FESEM images of (a) S-PC/MWCNT microspheres and (b) I-PC/MWCNT microspheres.
To incorporate MWCNTs in PC microspheres, MWCNTs were introduced into either methylene chloride or water. When 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 employs as a dispersant for aqueous MWCNT dispersion by wrapping MWCNTs as well as a steric stabilizer of emulsion.[10,22] We suggest that the PVP molecules with MWCNTs serve as a steric stabilizer of the O/W emulsion system in the same manner as in the preparation of PC microspheres. It is projected that the PVP molecules proceed to the surface of organic droplets consisting of PC and methylene chloride. Therefore, MWCNTs could be located on the surfaces of the S-PC/MWCNT microspheres.

In contrast with S-PC/MWCNT microspheres, very few MWCNTs were observed on the surfaces of the I-PC/MWCNT microspheres. Most MWCNTs were embedded in the I-PC/MWCNT microspheres, as shown in Fig. 5b. The I-PC/MWCNT microspheres were fabricated by dispersing MWCNTs into methylene chloride phase before dissolving the PC. The MWCNTs were functionalized with alkyl groups to disperse 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 a solution state, so that they could be located inside organic droplets under the O/W emulsion system. This explains why MWCNT 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 ± 0.9 µm and 1.3 ± 0.4 µm, respectively. It appears that the MWCNTs layers, thermodynamically wrapped by PVP molecules, increase the size of the S-PC/MWCNT microspheres while also inducing irregular morphology. Namely, a part of PVP was wrapped MWCNTs and the size of O/W emulsion droplet was increased due to the PVP
wrapped MWCNTs as a steric stabilizer.

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

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

**Figure 7.** FETEM images of (a) I-PC/MWCNT microspheres and (b) the MWCNTs in I-PC/MWCNT microspheres.
Fig. 7 presents a cross-section of 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. Compare with Fig. 6a, S-PC/MWCNT microspheres can see a clear interface between spheres but the interface was not so clear to identify I-PC/MWCNT microspheres in Fig. 7a. We considered that the MWCNTs which existed on the surfaces of the S-PC/MWCNT microsphere were formed interface. However, the MWCNTs in the I-PC/MWCNT microsphere were presented at innerness of microspheres. Therefore, the interface was not so clear due to nearly different of contrast with PC and epoxy resin used for the TEM observation. The electrical conductivity of the I-PC/MWCNT microspheres was $7.2 \times 10^{-13}$ 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 were incorporated and the MWCNTs in I-PC/MWCNT microspheres also tended to aggregate in the microspheres, as shown in Fig. 7b. We suggest that the dispersity of MWCNTs decreased, it is due to extract of the methylene chloride dispersed MWCNTs during the solidification of PC.
4. CONCLUSIONS

In the present study, we have developed an efficient process to produce PC microspheres and incorporate MWCNTs in the microspheres 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 spherical shape and uniform size as a result of retaining high stability of the emulsion using a homogenizer and a steric stabilizer, PVP. S-PC/MWCNT microspheres were covered with MWCNTs by means of dispersing MWCNTs into the aqueous phase using PVP. The electrical conductivity of the S-PC/MWCNT microspheres was remarkably high \(5.1 \times 10^{-2}\) S/cm due to the characteristics of its structure. Conversely, MWCNTs were incorporated inside I-PC/MWCNT microspheres, because the MWCNTs were dispersed into methylene chloride by functionalizing them via alkylation. This process provides a location-selective method of incorporating MWCNTs in polymeric microspheres according to projected uses. Our ongoing work is focused on improving the dispersity of MWCNTs in I-PC/MWCNT microspheres and increasing the content of MWCNTs in I-PC/MWCNT microspheres. I-PC/MWCNT microspheres including highly dispersed MWCNTs are expected to lend better mechanical and thermal properties to PC microspheres.
5. REFERENCES


