

단신

양친성 그래프트 공중합체의 탄소나노튜브 분산제로의 이용

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Use of Amphiphilic Graft Copolymer as Dispersant for Carbon Nanotubes

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초록: 탄소나노튜브(CNT)는 뛰어난 전기적, 물리적인 특성으로 인해 차세대 소재로서 관심을 끌고 있다. 그러나 탄소나노튜브들 사이에는 본질적으로 강한 소수성 상호작용이 내재하여 불규칙한 결합체를 생성하기 때문에 다양한 분야의 응용이 어려웠다. 본 연구에서는 양친성 가지형 공중합체, poly(vinyl chloride)-*graft*-poly(oxyethylene methacrylate), PVC-*g*-POEM를 합성하였고 극성 용매에서 단일벽 탄소나노튜브를 분산시킬 수 있는 용이한 방법을 제시하였다. PVC-*g*-POEM은 원자전달 라디칼중합(ATRP)으로 중합되었고 gel permeation chromatography (GPC)와 ¹H NMR spectroscopy를 통해 성공적인 합성되었음을 확인하였다. 단일벽 탄소나노튜브는 분산제인 PVC-*g*-POEM와의 친화력으로 인해 극성 용매 dimethylsiloxane (DMSO)에서 균일하게 분산되었으며 transmission electron microscopy (TEM) 분석으로 단일벽 탄소나노튜브와 PVC-*g*-POEM의 상호작용으로 생성된 나노복합체의 분산 형태를 관찰하였다. 또한 용매증발 과정을 거쳐 우수한 균질성을 보이는 free-standing 나노복합체 막을 제조하였다.

Abstract: Carbon nanotubes (CNTs) draw attention as promising materials due to their excellent electrical and mechanical properties. However, the intrinsic strong interaction between CNTs presents a challenge to their use in various applications. Here, we present a facile method to disperse single-walled carbon nanotubes (SWCNTs) in a polar solution using a graft copolymer, poly(vinyl chloride)-*graft*-poly(oxyethylene methacrylate), PVC-*g*-POEM. The graft copolymer was synthesized via atom transfer radical polymerization (ATRP), as confirmed by gel permeation chromatography (GPC) and ¹H NMR spectroscopy. The SWCNTs were uniformly dispersed in a polar solvent such as dimethylsiloxane (DMSO) using PVC-*g*-POEM as a dispersant, due to interaction between CNT and the graft copolymer, as revealed by transmission electron microscopy (TEM) analysis. Upon removal of the solvent, free standing nanocomposite films with good homogeneity were obtained.

Keywords: graft copolymer, atom transfer radical polymerization (ATRP), carbon nanotubes (CNT), nanocomposite.

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Introduction

Carbon nanotubes (CNTs) such as multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) have drawn great interest due to their high electrical conductivity, electrochemical catalytic effect, large aspect ratio (300~1000), and excellent mechanical properties. Over the last decades, CNTs have been utilized in various applications such as thermoelectric materials for power generation,¹ counter electrodes,² electrolytes³ of dye sensitized solar cells (DSSC) and electrolyte membranes for fuel cells.⁴

One of the critical problems in employing CNTs is aggregation resulting from their strong intrinsic van der Waals attraction between nanotubes.^{5,6} The bundles of CNTs decrease the surface area and electrical properties of CNT. It has been a key issue to suspend CNTs uniformly for optimizing the electrical properties and processibility of CNTs. Various attempts have been made to disperse CNTs uniformly using high energy sonication⁷ and covalent surface modification of CNTs by chemical reaction or acid/base treatment.⁸ However, the sonicated CNTs or strong acid-treated CNTs often led to irregular fractured structures, some defects on their surface and reduced aspect ratio, which was detrimental to the CNT properties.

Recently, the use of amphiphilic copolymer such as block copolymer as a dispersant has been considered a promising approach as a facile and nondestructive process.⁹⁻¹¹ Kang *et al.* have demonstrated that the encapsulation of SWCNTs with crosslinkable amphiphilic block copolymer enhanced the dispersion of nanotubes in a variety of polar solvents and polymer matrices.¹⁰ Shin *et al.* also used amphiphilic block copolymer, polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP), as a dispersant for SWCNTs. Stabilization of SWCNTs by adhering block copolymer micelles was achieved in either a polar or nonpolar solvent due to the amphiphilic property of PS-*b*-P4VP.¹¹ This method is challenging due to the tendency of SWCNTs to agglomerate during slow solvent evaporation, leading to inhomogeneous distribution of the nanotubes in the polymer matrix.

Although well-defined graft copolymers can possess amphiphilic properties similar to block copolymers, there are only a few reports using graft copolymer as a dispersant for CNT.^{12,13} Graft copolymer is more attractive than block copolymer in terms of its low cost and simple synthesis. Here, we report on the use of amphiphilic graft copolymer, poly(vinyl chloride)-*graft*-poly(oxyethylene methacrylate) (PVC-*g*-POEM) as a dispersant for CNT. PVC-*g*-POEM was synthesized via atom transfer radical polymerization (ATRP) and characterized using gel permeation chromato-

graphy (GPC) and ^1H NMR spectroscopy. The properties of solutions and films consisting of SWCNTs and PVC-*g*-POEM are reported.

Experimental

Materials. Single-wall carbon nanotubes (SWCNTs, 40~60 wt% carbon basis, diameter=2~10 nm, length=1~5 μm), poly(vinyl chloride) (PVC, $M_w=62000$ g/mol, $M_n=35000$ g/mol), poly(oxyethylene methacrylate) (POEM, poly(ethylene glycol) methyl ether methacrylate, $M_n=475$ g/mol), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper(I) chloride (CuCl, 99%), tetrahydrofuran (THF), *N*-methyl pyrrolidone (NMP) and dimethyl sulfoxide (DMSO) were purchased from Aldrich and used as received without further purification.

Synthesis of PVC-*g*-POEM. PVC-*g*-POEM was synthesized according to a previously reported procedure.^{14,15} 6 g of PVC was dissolved in 50 mL of NMP for 24 h at room temperature and then 30 mL of POEM, 0.1 g of CuCl and 0.23 mL of HMTETA were added to the PVC solution in NMP. After 30 min of N_2 purging, the mixture was placed in an oil bath at 90 $^\circ\text{C}$ for 24 h. The resulting polymer solution was precipitated into methanol three times and the final polymer was dried in an oven at room temperature for 24 h.

Preparation of PVC-*g*-POEM/CNT Nanocomposite. PVC-*g*-POEM was dissolved in DMSO to make 5% polymer solution. SWCNTs were added to the polymer solution with various amounts, i.e. 5, 10, 15, 20, 30, 40 and 50 wt% with respect to the polymer. After vigorous stirring and sonication for 20 min, the mixture was casted on the Teflon dish (1.5 cm \times 3 cm).

Characterization. ^1H NMR measurements were performed with 600 MHz, high resolution NMR spectrometer (AVANCE 600 MHz FT-NMR, Germany, Rucker). The GPC data were measured using instrument (YongLin, Korea) at the flow rate of 1 mL/min and 35 $^\circ\text{C}$. THF was used as a solvent and polystyrene (from Shodex) was used as a calibration standard. TEM pictures of samples were obtained using a Libra1 20 (Carl Zeiss, Germany) by drop casting the dilute solution (~2 wt%) on copper TEM grid.

Results and Discussion

The PVC-*g*-POEM graft copolymer was synthesized using the chlorine atom of PVC main chains as an ATRP initiation site. It was reported the labile chlorines of PVC are formed as structural defects during the radical polymerization, which act as initiation sites for direct grafting

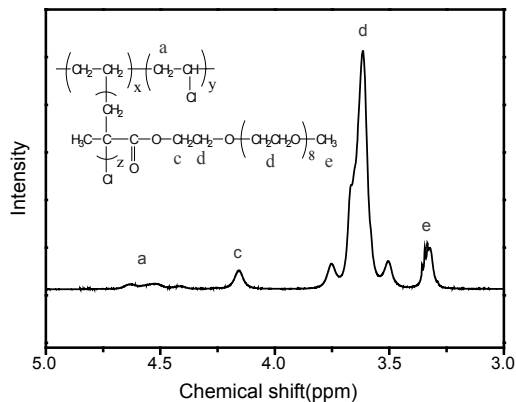


Figure 1. ^1H NMR spectra of PVC-*g*-POEM graft copolymer.

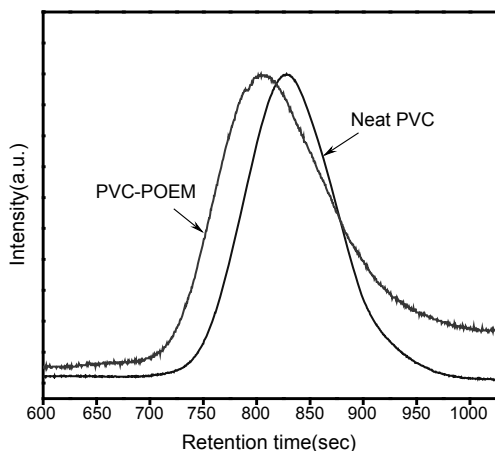


Figure 2. GPC data of neat PVC and PVC-*g*-POEM graft copolymer.

of PVC.^{16,17} The ^1H NMR spectrum of PVC-*g*-POEM graft copolymer is shown in Figure 1. The three peaks at 4.6–4.4 ppm are attributed to the CHCl group in PVC whereas the peaks at 4.2, 3.6 and 3.4 ppm are derived from the ethylene oxide units of POEM.^{18,19} Upon comparing the integral areas of each peak, the composition of PVC-*g*-POEM graft copolymer was determined to PVC:POEM=30:70 wt ratio.

GPC traces for pristine PVC and PVC-*g*-POEM graft copolymer are shown in Figure 2. The grafting of POEM from PVC main chains resulted in distributions shifted up in molecular weight relative to the PVC homopolymer (6.6×10^4 to 10.1×10^4 g/mol) and the increase of PDI value from 1.8 to 2.3. The molecular weight distribution for PVC-*g*-POEM graft copolymer was unimodal, implying no evidence of homopolymer contamination or coupling reactions.¹⁸ These ^1H NMR and GPC results are strong evidence for successful graft polymerization via ATRP.

TEM analysis was carried out to characterize the morphology of graft copolymer and SWCNTs, as shown in Figure 3. Because of the large difference of electron densities in PVC and POEM chains, the unstained TEM sample

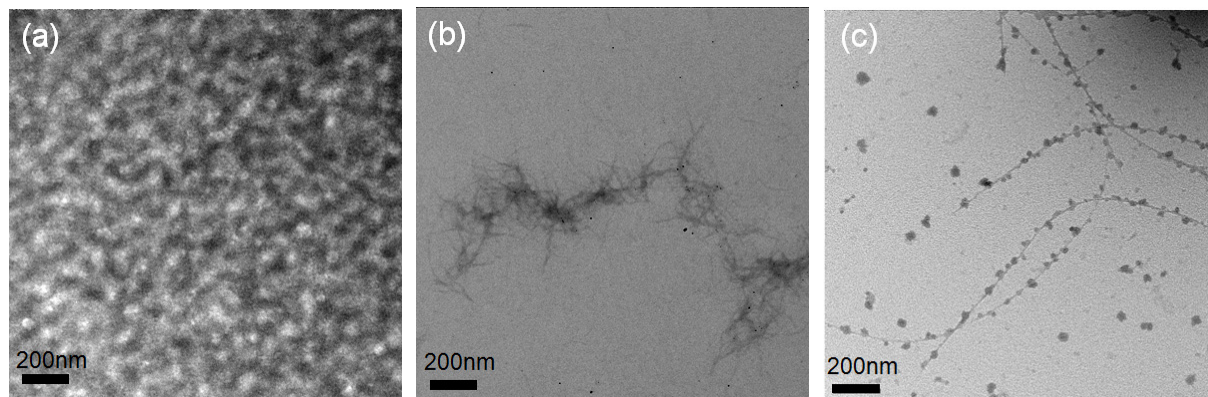
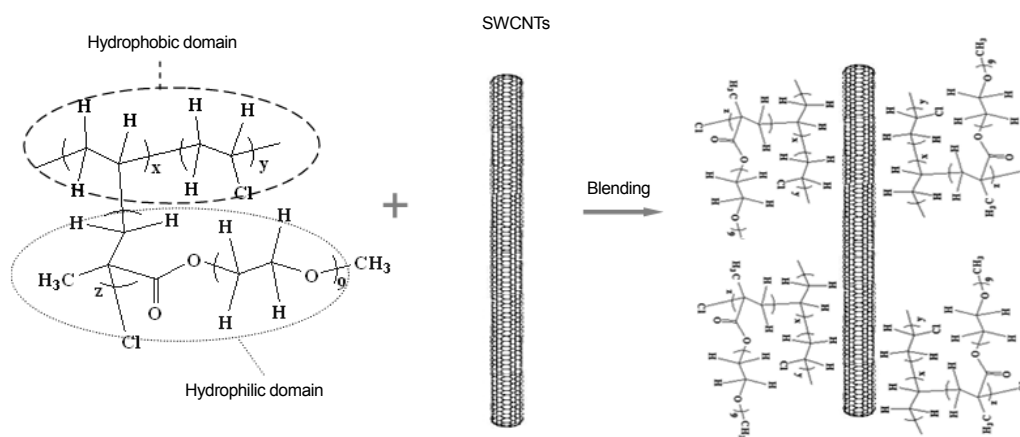


Figure 3. TEM images of (a) PVC-*g*-POEM; (b) pristine SWCNTs; (c) SWCNTs/PVC-*g*-POEM.



Scheme 1. Van der Waals interaction between PVC-*g*-POEM and SWCNTs.

of PVC-*g*-POEM is sufficient to provide clear image contrast between the two domains (Figure 3(a)).¹⁵ Dark regions are due to the hydrophobic domains of PVC main chains while bright regions come from the hydrophilic POEM side chains.¹⁵ As seen in the pictures, well-defined microphase-separated morphology between PVC main chains and POEM side chains was obtained. In Figure 3(b), the pristine SWCNTs showed self-aggregation, forming the clusters of SWCNT bundles. As a result, the length of pristine SWCNTs was shorter than that of SWCNTs/PVC-*g*-POEM. The poor dispersion of SWCNTs often results in a marked decline in electrical property of SWCNTs and less applicability to a counter electrode of DSSCs.²⁰ On the other hand, the SWCNTs/PVC-*g*-POEM composite exhibited an interesting morphology consisting of the dangled micelles of PVC-*g*-POEM on the surface of the long SWCNT. The dot-like PVC-*g*-POEM micelles were also found in the background of the Figure 3(c). It is expected that the hydrophilic POEM side chains stretch in a polar solvent such as DMSO whereas the hydrophobic PVC chains contract and wrap around hydrophobic SWCNTs, as illustrated in Scheme 1. It might keep one tube

of SWCNT far enough away from the other tubes to block self agglomeration of SWCNTs. Thus, SWCNTs can be dispersed well in a polar solvent without aggregation upon using PVC-*g*-POEM graft copolymer as a dispersant.

In addition, the dispersed SWCNTs/PVC-*g*-POEM solutions were very stable as shown in Figure 4 and did not precipitate even after two months of storage at room temperature. This demonstrates that PVC-*g*-POEM had an excellent dispersing capability for SWCNTs. This result is comparable to that of sulfonated poly[bis(benzimidazobenzisoquinolinones)] (SPBIBI) polymer that dispersed CNT, as reported by Li *et al.*²¹ When the solvent was evaporated completely, free standing films with good homogeneity were obtained, as shown in Figure 4. The pristine PVC-*g*-POEM film was transparent and flexible, indicating its amorphous and rubbery nature. The addition of SWCNTs to the PVC-*g*-POEM polymer changed the color of film to black but all the films were mechanically strong and flexible. These nanocomposite films will be applicable to various applications such as counter electrode of dye-sensitized solar cells.

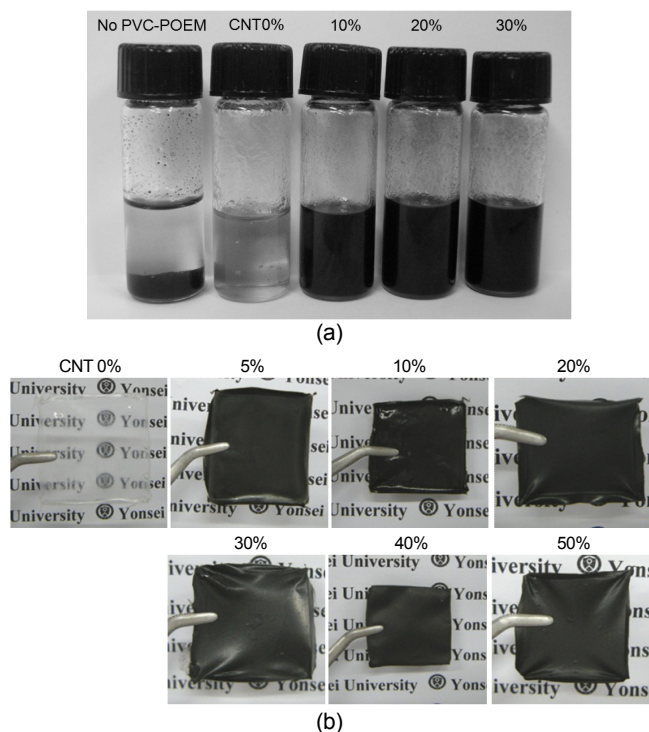


Figure 4. Pictures of SWCNTs/PVC-*g*-POEM solutions in DMSO (a); SWCNTs/PVC-*g*-POEM films after evaporation of solvent (b).

Conclusions

A good dispersion of SWCNTs in a polar solvent such as DMSO was achieved using an amphiphilic graft copolymer synthesized via ATRP. The graft copolymer was comprised of the hydrophobic PVC main chains and the hydrophilic POEM side chains, as confirmed by ^1H NMR, GPC and TEM analysis. The SWCNTs in PVC-*g*-POEM solution showed excellent long-term dispersion stability for more than two months. The hydrophobic force of SWCNTs interacts preferentially with the hydrophobic PVC domain so that the SWCNTs were not aggregated, but uniformly dispersed throughout the whole solution. Our method is useful for the application of SWCNTs to various electrical devices, especially as a counter electrode in DSSC.

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