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Improvement of tensile properties of poly(methyl methacrylate) by dispersing multi-walled carbon nanotubes functionalized with poly(3-hexylthiophene)-*graft*-poly(methyl methacrylate)

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ABSTRACT

Poly(methyl methacrylate) (PMMA)/multi-walled carbon nanotube (MWCNT) composites are prepared using poly(3-hexylthiophene) (P3HT)-*graft*-PMMA as a compatibilizer. Fluorescence emission and Raman spectra indicate that the P3HT part of the compatibilizer strongly interacts with the surface of MWCNT. Addition of the compatibilizer results in well-dispersed PMMA/MWCNT composite with enhanced mechanical properties, whereas PMMA/MWCNT composite prepared without addition of the compatibilizer shows an aggregation of MWCNT in PMMA matrix. Particularly, PMMA/MWCNT composites prepared in the presence of the compatibilizer do not exhibit the trade-off of mechanical properties, whereas PMMA/MWCNT composites without the compatibilizer exhibit the trade-off behavior.

1. Introduction

The exceptional mechanical properties of carbon nanotubes (CNTs) have led to their use as effective reinforcing filler for polymer composites [1–3]. However, to fully realize the potential of CNTs for this purpose, they have to be homogeneously dispersed in polymer–matrix and have a strong interfacial interaction with polymer–matrix so as to achieve efficient load transfer across the polymer–CNT interface [4–9]. Therefore, it is a prerequisite for effective reinforcement of polymer with CNTs to improve compatibility between them. For this reason, a number of studies on polymer–CNT composites have focused on improving the compatibility between CNTs and matrix–polymer.

One of the most widely used approaches for improving the compatibility between them is to directly graft polymer chains onto the surface of CNT using ‘grafting from’ [10–12] or ‘grafting to’ method [13–15]. Although this approach based on the covalent functionalization of the surface of CNTs is very effective to enhance the compatibility between CNTs and matrix–polymer, it is inevitably accompanied with complicate chemical reactions in order to introduce functional groups on the surface of CNTs. Furthermore, it usually destroys the π-electron system of CNTs, which results in detrimental effect on improvement in electrical and mechanical properties of the resultant polymer-CNT composites. Hence, as an alternative, the introduction of compatibilizer which non-covalently interacts with CNTs has recently been attempted [4,6,9]. Although this approach based on non-covalent functionalization of the surface of CNTs has also been successful for improving the compatibility between CNTs and matrix–polymer, the systematic strategy to design and synthesize an effective compatibilizer for a specific system has not been reported. In particular, few studies has reported on the use of compatibilizer composed of block copolymer or graft copolymer which has been widely used as a compatibilizer in polymer blend systems [16]. As expected, block copolymer or graft copolymer can act as an effective compatibilizer for polymer–CNT composites if each component of block copolymer or graft copolymer can be designed to have favorable interaction with CNTs and matrix–polymer. With this in mind, we previously synthesized a new compatibilizer, poly(3-hexylthiophene)-*graft*-poly(methyl methacrylate) (P3HT-*g*-PMMA), and found it to be very effective to disperse multi-walled carbon nanotube (MWCNT) in poly(styrene-*co*-acrylonitrile) (SAN) matrix [17,18]. Since it has been identified that the effectiveness of P3HT-*g*-PMMA for SAN/MWCNT composites arises from both the strong π–π interaction between P3HT backbone and the surface of MWCNT and the miscibility between PMMA graft and SAN matrix, it is natural to use the P3HT-*g*-PMMA as a compatibilizer for preparation of PMMA/MWCNT composite.

PMMA has been widely used in architecture, automobile, air and railway transport systems due to its superior optical and mechanical properties. This wide range of applications of PMMA can be even more extended by incorporation of CNTs into PMMA matrix, because well-dispersed CNTs may enhance various physical properties of PMMA. For this reason, several researchers have attempted to disperse CNTs in PMMA [19–25]. However, most of their studies are based on the in situ polymerization of MMA in

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the presence of CNTs and/or the chemical modification of surface of CNTs to homogeneously disperse CNTs in PMMA matrix, which is accompanied with complicate chemical reactions. Unlike the above cases, the use of P3HT-*g*-PMMA as a compatibilizer for preparation of PMMA/MWCNT composite is basically to adopt noncovalent functionalization of MWCNT which is more facile and practical approach for functionalization of CNTs. In this work, we report the use of P3HT-*g*-PMMA as a compatibilizer for preparation of PMMA/MWCNT composite.

2. Experimental

2.1. Materials and synthesis of P3HT-**g**-PMMA

MWCNT with a diameter range of 25–70 nm and PMMA were supplied from Jeio Co. and Polyscience Co., respectively and were used as received. Fig. 1 shows chemical structure of P3HT-*g*-PMMA used as a compatibilizer. P3HT-*g*-PMMA was synthesized and characterized according to method presented in our previous study [18,19]. The molecular characteristics of polythiophene backbone and P3HT-*g*-PMMA are listed in Table 1.

2.2. Preparation of PMMA/MWCNT/P3HT-g-PMMA composite films

All of PMMA/ MWCNT/P3HT-*g*-PMMA composites with different loadings of MWCNT were prepared by solution blending. A typical procedure of PMMA/MWCNT/P3HT-*g*-PMMA composite containing 0.1 wt% of MWCNT is as follows: A dispersion of 2 mg of P3HT-*g*-PMMA and 2 mg of MWCNT in 20 ml of chloroform was sonicated for 1 h. Then, the dispersed solution was added to a solution containing 2 g of PMMA in 20 ml of chloroform. The mixture was sonicated for an additional 10 min and precipitated in excess *n*-hexane. The precipitate was collected by filtration and washed subsequently with *n*-hexane. The filter cake (PMMA/MWCNT/P3HT-*g*-PMMA composite) was dried at 30 °C under vacuum for 24 h. For comparison, PMMA/MWCNT composites in the absence of P3HT-*g*-PMMA were also prepared under the same procedure.

Films of PMMA/MWCNT/P3HT-*g*-PMMA composite were prepared by solution casting: A solution of PMMA/MWCNT/P3HT-*g*-PMMA in chloroform was poured onto a glass plate and then a doctor blade was used to prepare a solution film. Then, the solvent was slowly evaporated at room temperature for 6 h and the film was thoroughly dried under high vacuum at 30 °C for 24 h. Films of PMMA/MWCNT composite were also prepared under the same procedure.

2.3. Measurements

The π–π interaction between P3HT of P3HT-*g*-PMMA and MWCNT is identified by comparing the fluorescence emission spectrum of P3HT-*g*-PMMA with that of PMMA/MWCNT/P3HT-*g*-PMMA composite in chloroform solution and solid state. The fluorescence emission spectra were obtained from a fluorescence spectrometer (QM-4, Photon Technology International). Raman spectra of MWCNT, PMMA/MWCNT, and PMMA/MWCNT/P3HT-*g*-PMMA composite were also obtained to identify the π–π interaction between P3HT of P3HT-*g*-PMMA and MWCNT. Raman measurements were carried out on the powder samples using a Jobin Yvon (T64000) with Ar laser at excitation wavelength of 514 nm.

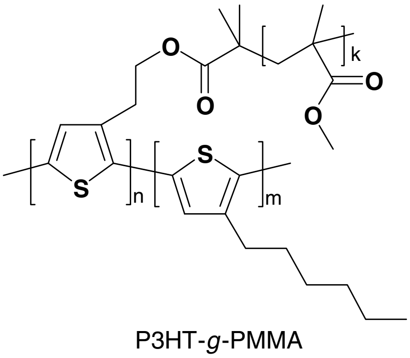

Fig. 1. The chemical structure of the compatibilizer, P3HT-*g*-PMMA.

The fracture surfaces of PMMA/MWCNT and PMMA/MWCNT/P3HT-*g*-PMMA films were observed for analysis of dispersion state of MWCNT using a Jeol JSM-6330F field emission-scanning electron microscopy (FE-SEM), operated at an accelerating voltage of 5 kV. The sample films for FE-SEM observation were ultramicrotomed with a diamond knife at room temperature to produce the smooth fracture surface.

The tensile properties of PMMA, PMMA/MWCNT, and PMMA/MWCNT/P3HT-*g*-PMMA films were measured with a universal testing machine (Instron-5543) with a 1 kN load cell at a constant cross-head speed of 3 mm/min. At least five specimens were tested for each sample, and the tensile properties are reported on average.

3. Results and discussion

3.1. Photoluminescence analysis

A specific interaction between P3HT-*g*-PMMA and MWCNT is a prerequisite to accomplish the aim of this study. Hence, the π–π interaction between P3HT of P3HT-*g*-PMMA and MWCNT is verified by the fluorescence emission spectroscopy. Fig. 2 shows the fluorescence emission spectra of P3HT-*g*-PMMA and PMMA/MWCNT/P3HT-*g*-PMMA in chloroform when the samples are irradiated at 420 nm corresponding to the excitation wavelength of P3HT-*g*-PMMA. As can be seen in Fig. 2, the strong fluorescence of P3HT-*g*-PMMA is thoroughly quenched in PMMA/MWCNT/P3HT-*g*-PMMA. This quenching arises mainly from an efficient energy transfer between P3HT of P3HT-*g*-PMMA and MWCNT via the strong π–π interaction [26,27]. Furthermore, when the fluorescence emission of PMMA/MWCNT/P3HT-*g*-PMMA film is measured to confirm whether or not the quenching is still available in solid state, as shown in Fig. 3, it reveals that the strong fluorescence of P3HT-*g*-PMMA is also completely quenched in PMMA/MWCNT/P3HT-*g*-PMMA film, indicating the strong π–π interaction between P3HT-*g*-PMMA and MWCNT is still available in solid state.

3.2. Raman analysis

The π–π interaction between P3HT-*g*-PMMA and MWCNT in solid state is also confirmed by Raman spectroscopy. Generally, it is well known that the strong attachment of polymer onto the surface of CNTs leads the absorption wavenumber of tangential G-band of MWCNT to shift toward higher wavenumber due to an increase in the elastic constant of the harmonic oscillator of the polymer-coated CNTs [28]. Therefore, it can be easily expected that the strong π–π interaction between P3HT-*g*-PMMA and MWCNT leads to upshift in the tangential G-band of MWCNT. When the Raman spectra of MWCNT, PMMA/MWCNT, and PMMA/MWCNT/P3HT-*g*-PMMA are compared, as shown in Fig. 4, it is realized that the tangential G-band of pristine MWCNT at 1570 cm^{-1} shifts to higher wavenumber in PMMA/MWCNT/P3HT-*g*-PMMA by 6 cm^{-1} while the tangential G-band of MWCNT in PMMA/MWCNT remains unchanged, which suggests that the upshift of the tangential G-band of MWCNT in PMMA/MWCNT/P3HT-*g*-PMMA is attributed to the strong π–π interaction between P3HT-*g*-PMMA and MWCNT. Thus, both the fluorescence emission and Raman spectra strongly