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Synthesis and characterization of polycaprolactone-grafted carbon nanotubes via click reaction

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Polycaprolactone (PCL) was covalently grafted on the surface of carbon nanotubes by a simple click reaction of propargyl-terminated PCL (propargyl-PCL) and carbon nanotubes (CNTs) containing azide groups (MWNT-N\textsubscript{3}). Propargyl-PCL was synthesized by the ring-opening polymerization of \(\varepsilon\)-caprolactone using propargyl alcohol and stannous octoate. MWNT-N\textsubscript{3} was prepared from MWNT having 2-bromoisobutyryl groups (MWNT-Br) with sodium azide by azidation. The melting temperature of propargyl-PCL was shifted to the high temperature in PCL-grafted MWNT. The thermal stability of PCL-grafted MWNT was enhanced as compared to that of propargyl-PCL. PCL was coated on the surface of MWNT with a high density of PCL chains, which showed good solubility of PCL-grafted MWNT in organic solvents. PCL-grafted MWNT was characterized with FT-IR, \textsuperscript{1}H NMR, Raman, differential scanning calorimetry, thermogravimetric analysis, and scanning electron microscopy.

Keywords: polycaprolactone (PCL); carbon nanotubes; ring-opening polymerization; thermal stability; PCL-grafted MWNT

1. Introduction

Carbon nanotubes (CNTs) have attracted great attention in both academic and industrial fields because of outstanding mechanical and chemical properties derived from their unique structure.[1–3] Various modifications of CNTs with organic groups or polymer chains make it easier to improve the solubility of CNTs and hence to facilitate the potential applications in hybrid nanotechnology.[4,5] The research regarding the functionalization of CNTs has focused more on polymer chains than on small organic molecules due to the polymer effect. The incorporation of polymer into CNTs to prepare polymer/CNT nanocomposites was conducted using covalent linkage or non-covalent interactions between polymer and CNTs. Covalent bonding such as esterification, amidation, or radical coupling as well as non-covalent bonding such as hydrogen bonding, ionic, or \(\pi-\pi\) interactions were utilized to make CNT-based nanocomposites. In addition to polymer, various materials such as metals or inorganic nanoparticles were applied to CNTs for hybrid materials based on CNTs. We have already explored various CNT-based hybrid materials with polymer or inorganic nanoparticles.[6–11] To prepare CNT-based nanocomposites, it is an important point to deposit polymer chains on the
surfaces of CNTs. ‘Grafting to’ or ‘grafting from’ approaches are normally employed to functionalize the surfaces of CNTs.

Polycaprolactone (PCL) is gaining an increasing interest in materials science because of its biocompatibility and biodegradability. Also, the low cost, nontoxicity, and good solubility of PCL has led to the numerous applications in the drug delivery system, biomedical engineering, and so on.[12,13]

This work describes the grafting of PCL on the surfaces of MWNT using a click chemistry between propargyl-terminated PCL (propargyl-PCL) and CNTs containing azide groups (MWNT-N3). ‘Click chemistry’ has been mainly used in organic synthesis, but recently began to use in materials science and polymer chemistry for fabricating new molecular design.[14–16] Various attempts for employing click chemistry to CNTs have been achieved. Likewise, click chemistry was used to prepare polymer-functionalized MWNT in this study.[17–19] There are already several reports dealing with PCL and MWNT. Wang et al. synthesized MWNT/PCL composites by the solution evaporation technique for bone tissue engineering application.[20] Park and Saeed reported the good electrical properties of MWNT/PCL nanocomposites by in situ polymerization.[21] Yan et al. presented the synthesis of PCL-grafted MWNT by ‘grafting from’ method.[4] In above literatures, MWNT/PCL composites were prepared by the solution mixing with different MWNT/PCL weight ratios, whereby MWNT was used as a reinforcing material. But the poor miscibility of PCL and MWNT causes the phase separation and low loading of MWNT as filler, which results in the degradation of MWNT/PCL composites. To overcome the above problems, the surfaces on MWNT were incorporated with PCL. PCL-grafted MWNT can be used to make hybrid composites with various polymers because of the enhanced miscibility between PCL-grafted MWNT and various polymers. PCL with alkynes moieties was prepared by the ring-opening polymerization of ε-caprolactone using propargyl alcohol. Azido-terminated MWNT was synthesized by the reaction of MWNT having 2-bromoisobutyryl groups with sodium azide. Copper-catalyzed click chemistry was applied to prepare PCL-grafted MWNT via the ‘grafting to’ approach. That is, PCL was well grafted on the surfaces of MWNT using simple click chemistry. To the best of our knowledge, the introduction of PCL on the surfaces of MWNT via click chemistry has not yet been explored. This approach for modifying the surfaces of MWNT with polymer can be utilized to fabricate various hybrid materials with physical bonding between polymer-grafted MWNT and polymer or nanoparticles.

2. Experimental

2.1. Materials

Pristine MWNTs were obtained from the Iljin Nanotech Inc (diameter: 10–20 nm, length: 10–50 μm, >90 vol% of purity). Stannous octoate (Sn(Oct)2), sodium azide (NaN3), ε-caprolactone, copper bromide (CuBr), and propargyl alcohol were purchased from Aldrich. Organic solvents such as DMF, chloroform, and toluene were obtained from Merck Chemical with HPLC grade.

2.2. Analytical methods

1H NMR spectra were obtained on a 400 MHz AVANVE 400FT-NMR (BRUKER) spectrometer at room temperature with CDCl3 as a solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet IR 200 (THERMO) spectrometer in the range between 500 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹ using the KBr disk method. The thermal
behavior and decomposition were examined by thermogravimetric analysis (TGA) (TGA S-1000, SCINCO) in the temperature range of 30–600 °C with a heating rate of 10 °C/min in a nitrogen flow (70 mL/min). Differential scanning calorimetry (DSC) experiments were carried out on a DSC 2000 (TA INSTRUMENTS) in the temperature range of 25–150 °C with a heating rate of 10 °C/min in a nitrogen flow (70 mL/min). The morphologies and structures of PCL-grafted MWNT were observed by field-emission scanning electron microscopy (FE-SEM) equipped with an energy dispersive spectrometer (EDX) (JSM-6700 JEOL), and the samples were loaded onto silicon surface.

2.3. Material preparation

2.3.1. Propargyl-terminated PCL

Propargyl alcohol (0.14 g, 2.5 mmol), ε-caprolactone (20 g, 175.2 mmol), and stannous octoate (0.5 g, 1.2 mmol) were added to 80 mL of toluene in a flask. The solution was stirred at 80 °C for 6 h. The solution was concentrated and then precipitated in diethyl ether. The polymer was obtained and dried under vacuum overnight. The degree of polymerization and absolute molecular weight (Mn) calculated on the basis of 1H NMR result were 18 and 2107, respectively.

2.3.2. CNTs containing azide groups (MWNT-N3)

MWNT having 2-bromoisobutyryl groups (MWNT-Br) was synthesized by a method described previously by our group.[8] The obtained MWNT-Br (1.0 g) was dissolved in DMF (100 mL), and then sodium azide (3.3 g, 50.8 mmol) was added to the mixture and stirred at room temperature for 4 h. The mixture was collected by filtration and washed thoroughly with DMF, and MWNT-N3 was dried under vacuum overnight.

2.3.3. PCL-grafted MWNT via copper-catalyzed alkyne–azide click chemistry

0.05 g of MWNT-N3 and 50 mL of DMF were introduced to a 100 mL of flask and the mixture was sonicated for 2 h. Then, propargyl-PCL (0.5 g) and CuBr (30 mg, 0.2 mmol) were added to the solution. The mixture was stirred at room temperature for 24 h. The mixture was collected by filtration. The obtained PCL-grafted MWNT was dried under vacuum overnight.

3. Results and discussion

The purpose of this study is to prepare PCL-grafted MWNT by copper-catalyzed click chemistry between azide-grafted MWNT and alkyne-functionalized PCL (Scheme 1). Azide-grafted MWNT was prepared by the simple reaction of MWNT-Br with sodium azide. Alkyne-functionalized PCL was synthesized by the ring-opening polymerization of ε-caprolactone under the co-initiation of propargyl alcohol and stannous octoate.

Figure 1 shows the 1H NMR spectrum of propargyl-PCL, which has characteristic peaks at 4.7 ppm for methylene protons of propargyl group, 2.3 ppm for alkyn groups, and 4.1 ppm for PCL repeating units. The degree of polymerization of PCL can be calculated by the integration ratio of signals at 4.7 ppm (a) and that of signal at 1.7 ppm (c). The degree of polymerization of propargyl-PCL was 18. The azidation of MWNT and click chemistry between propargyl-PCL and MWNT-N3 were confirmed by FT-IR as shown in Figure 2.
The spectrum of MWNT-N₃ shows new azide peak at 2100 cm⁻¹ after the reaction of MWNT-Br with sodium azide. The absorption peak of C=O stretching peak at 1726 cm⁻¹ derived from propargyl-PCL was observed in PCL-grafted MWNT, but the absorption peak of azide group at 2100 cm⁻¹ derived from MWNT-N₃ was completely disappeared in PCL-grafted MWNT. This result confirms that PCL is successfully attached to the surface of MWNT by click chemistry.

Raman spectroscopy was used to verify the grafting of PCL on the surface of MWNT as shown in Figure 3. Two characteristics bands at 1340 cm⁻¹ (D band) and 1579 cm⁻¹ (G band) were attributed to the defects mode from disorder of sp³ carbon in MWNT and in-plane bond-stretching motion of sp² carbon in MWNT, respectively. The increase in the band intensity ratio (I_D/I_G) of functionalized MWNT (MWNT-Br (1.067), MWNT-N₃

![Scheme 1. Synthesis scheme of PCL-grafted MWNT.](image)

![Figure 1. ¹H NMR spectrum of propargyl-PCL.](image)
(1.074), and PCL-grafted MWNT (1.331)) compared to that of pristine MWNT (1.039) reflects the defects and disorder in MWNT resulting from the functionalization on MWNT.

SEM images of PCL-grafted MWNT were strong evidence that PCL was well coated on the surface of MWNT as shown in Figure 4. As compared to the images of MWNT-Br and MWNT-N₃, PCL-grafted MWNT has significantly rougher and thicker surface, indicating the successful PCL modification to the surface of MWNT via click chemistry. Also, the image of PCL-grafted MWNT shows that PCL phase on the surface of MWNT becomes more continuous.
Figure 5 shows DSC thermograms of propargyl-PCL and PCL-grafted MWNT. According to the surface modification with PCL to the surface of MWNT, melting temperature of propargyl-PCL was shifted to the high temperature in PCL-grafted MWNT. This result was derived from PCL chemically attached to the surface of MWNT. Generally, polymer–silica hybrid nanocomposites present the disappearance or increase of glass transition temperature or melting temperature of polymer due to the silica-based inorganic materials.[22,23] MWNT was acted as an inorganic material in this hybrid system which PCL is functionalized to the surface of MWNT.

Figure 6 shows TGA curves of pristine MWNT, MWNT-N₃, propargyl-PCL, and PCL-grafted MWNT under nitrogen atmospheres. TGA results provide the evidence for the functionalization of MWNT with PCL. Clearly, pristine MWNT has no obvious decomposition up to 600 °C. Propargyl-PCL was completely decomposed at around 320 °C. The difference in the weight loss at 600 °C between PCL-grafted MWNT and MWNT-N₃ shows that polymer grafting amount is about 53%. The graph of PCL-grafted MWNT was shifted to the right, indicating that the thermal stability of PCL-grafted MWNT was higher than that of propargyl-PCL. This result suggests that PCL was well deposited on the surface of MWNT through the click reaction between MWNT-N₃ and Propargyl-PCL. PCL was coated on the surface of MWNT with a high density of PCL chains, which showed good solubility of PCL-grafted MWNT in organic solvents such as THF and chloroform.
4. Conclusions

The simple ‘click chemistry’ was successfully applied to prepare PCL-grafted MWNT which meant that PCL was covalently deposited on the surface of MWNT. That is, PCL-grafted MWNT were synthesized by the copper-catalyzed azide–alkyne cycloaddition between MWNT-N₃ and propargyl-PCL. PCL-grafted MWNT showed higher...
thermal stability as compared to propargyl-PCL. The morphology of PCL-grafted MWNT revealed rough and thick MWNT surface as well as the continuous structure of PCL phase, indicating that PCL was well deposited on the surface of MWNT via click chemistry. This grafted PCL not only provides the good solubility of PCL-grafted MWNT in various solvent but also promises the enhanced miscibility of PCL-grafted MWNT to prepare hybrids with various polymers.

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