



Construction of conductive percolation network with high efficiency in composite film via a novel sparsely partial wrapping strategy



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ABSTRACT

Carbon nanotubes (CNTs) is a great potential reinforcing additives or conductive fillers for polymer composites. It is well known that interfacial properties between CNTs and polymer matrix have a critical effect on the properties of composites. Here, we demonstrate a novel strategy for preparing high efficient percolation networks of CNTs in polymer composite by partially wrapping of MWCNTs with crystallization induced self-assembly of pyrene end-capped poly(*p*-dioxanone)-block-poly(ethylene glycol) (Py-PPDO-*b*-PEG). The wrapped surface can prevent the aggregation of CNTs, while the bare surface may still induce enough interconnection of CNTs, resulting in high efficient percolation network. The wrapping density, which could be easily engineered by control the crystallization temperature of PPDO block, is essential to the formation of percolation networks. The composite film prepared from Py-PPDO-*b*-PEG@MWCNTs and PCL exhibited much improved conductivity especially at very low nanotube concentration compared to those from neat MWCNTs without any wrapping. Especially using Py-PPDO-*b*-PEG@MWCNTs prepared at 40 °C as the precursors, the composite film exhibits both best electrical conductivity (3–11 orders of magnitude higher than that of PCL/MWCNTs composites films at same MWCNTs contents) and mechanical properties, which could be attributed to the optimized wrapping density of this sample. Dense or excessively sparse wrapping may impede the interconnection and dispersity of the MWCNTs, respectively, and therefore resulted in decreased conductivities.

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1. Introduction

The unique chemical structure and high aspect ratios of carbon nanomaterials (CNMs), such as carbon nanotubes (CNTs), can enhance the overall performance of polymer/CNMs composites. It has attracted tremendous attention due to their excellent mechanical, electrical, and thermal characteristics [1–4] and has been developed for applications such as sensors [5], stretchable conductors [6], shape memory materials [7], and oil/water separation [8]. The key issue of conductivity is the formation of percolation networks of CNTs in polymer matrix, which is essential to construct conductive path through the composite [9]. The morphological studies verified that CNTs can be triggered to form conductive network under engineered processing conditions, such as polymer blends [10], shear forces [11], latex particle [12], electric field [13],

nanoimprint lithography [14], and preformed scaffold [15]. However, unless the interface between nanotubes and polymer is carefully modified, the agglomeration of CNTs may inevitably occur due to their intrinsic poor dispersibility and processability, and lead to deterioration and fluctuations in properties [16]. Therefore, under most conditions, surface modification of CNTs has become an essential step for its applications [17]. Covalent functionalization and non-covalent wrapping are generally adopted methods [18–20]. It is important to emphasize that, although a well surface modification indeed improve the stability and dispersity of CNTs in solvent or polymer matrix, it is not in favor of the formation of percolation networks because the polymers or surfactants fully covered on the CNTs surface may prevent the interconnection of CNTs, (Fig. 1). Up to now, it is still a great challenge to construct conductive percolation networks in polymer/CNTs composites with high efficiency through a facile and wide applicable strategy.

In this work, we demonstrate a novel sparsely partial wrapping strategy for constructing percolation networks in this article. As

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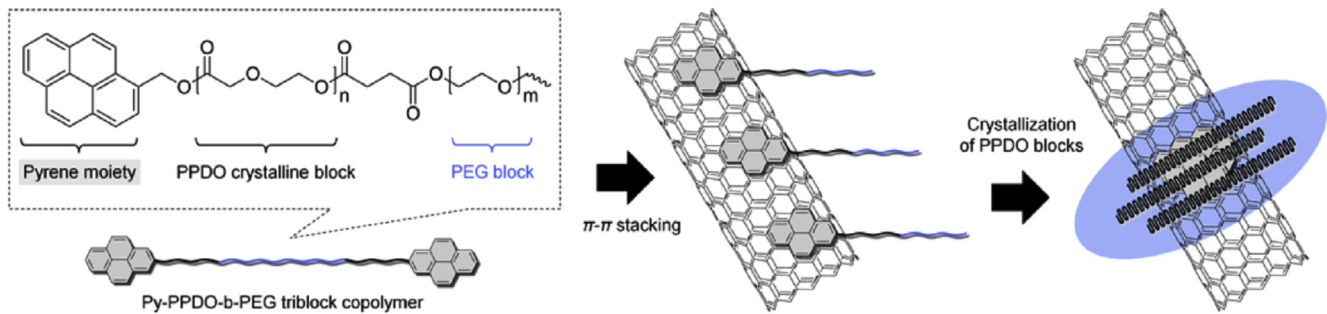


Fig. 1. Schematic representation of sparsely partial wrapping of CNTs.

illustrated in Fig. 1, the wrapped sections can prevent the aggregation of CNTs, while the bare (not wrapped) sections are long enough to induce the interconnection of CNTs and therefore form continuous pathways for charge transport with very high efficiency. Therefore, the engineered nanostructure of CNTs with rational balance between wrapped and bare sections is the prime issue to be addressed. Recently, researches have demonstrated that CNTs can be decorated with polymer lamellar crystals, resulting in trans-crystalline structures [21]. Owing to the relatively small size of single crystals, the periodicity of functionalization/patterning on CNTs prepared by this method should be controlled in the range of several to dozens of nm, in consideration of the stability of hybrids. However, for constructing percolation networks in polymer matrix, relatively sparse wrapping density and long length of bare CNTs sections are necessary because of the steric hindrance effect of polymer crystalline grown on CNTs. In our previous work, we reported that the amphiphilic copolymers of poly(*p*-dioxanone) (PPDO) tend to form anisotropic nano-aggregates in selective solvents due to the crystallization of PPDO blocks [22–25]. When functionalized with pyrene moieties at the chain end of PPDO blocks, the copolymer can form hybrid nano-aggregates together with CNTs, which have very good stability and dispersity in solution. (Fig. 1). Hence, this novel method was utilized for preparing partially wrapped CNTs.

2. Materials and methods

2.1. Materials

MWCNTs (purity 95%) were purchased from Sigma-Aldrich with a diameter 6–9 nm and a length 5 μm , and purified with 3 M dilute HNO_3 solution. PCL was purchased from Jinan Daigang Biomaterial Co, Ltd with a molecular weight of $1.5 \times 10^5 \text{ g mol}^{-1}$. Pyrene-1-methanol was purchased from Alfa Aesar. *p*-Dioxanone (PDO) (99.9%) was provided by National Engineering Laboratory of Eco-friendly Polymeric Material (Chengdu, China), and distilled under reduced pressure just before use. Poly(ethylene glycol) ether (PEG, degree of polymerization = 90, $M_n = 4 \text{ kDa}$) was purchased from Sigma-Aldrich and dried under vacuum at 40 $^\circ\text{C}$ overnight before use. Stannous octoate $\text{Sn}(\text{Oct})_2$ (95%) was purchased from Sigma-Aldrich (USA), and diluted with dry toluene. CHCl_3 was purchased from Kelong Chemical Reagent Factory (Chengdu, China), washed three times with aqua destillata and dried by refluxing over CaH_2 , and distilled prior to use. All other reagents were analytical grade from Bodi Chemical Factory (PR China) and used as received without further purification. The preparation of Py-PPDO-b-PEG copolymer has been published in our previous work [24]. The average molecular weight of PPDO and PEG blocks of Py-PPDO-b-PEG copolymer triblock copolymer studied in this work, calculated from ^1H NMR spectrum of Py-PPDO-OH and PEG precursors are 1100 g mol^{-1} and 4000 g mol^{-1} , respectively.

2.2. Preparation of Py-PPDO-b-PEG@MWCNTs hybrid nano-aggregates and PCL/Py-PPDO-b-PEG@MWCNTs composite films

In order to control the crystallization of PPDO blocks, the thermal history of Py-PPDO-b-PEG copolymer should be erased. Therefore, DMF was used as the selective solvent for preparing the hybrid nano-aggregates. Py-PPDO-b-PEG copolymer were dissolved at temperature (95 $^\circ\text{C}$) higher than the melting point of PPDO blocks. The MWCNTs were then added to the copolymer solution. The homogeneous dark ink-like dispersion obtained after sonication was then cooled quickly to presented crystallization temperature. After sufficient crystallization, Py-PPDO-b-PEG@MWCNTs hybrid nano-aggregates with high stability and different morphologies were obtained, which can keep stable for at least 48 h in THF and seven days in DMF, respectively. The feed ratio of copolymer to MWCNTs in weight could varied from 4:1 to 8:1. Within this range, the hybrid nano-aggregates have not only good stability in solvent but also ideal wrapping density. In this work, the feed ratio was fixed at 6:1 for further discussion.

Since the DMF has relatively high boiling point, it is not suitable to be used as solvent for casting film. Therefore, a two-step process was adopted for preparing PCL/Py-PPDO-b-PEG@MWCNTs composite films. At first, the Py-PPDO-b-PEG@MWCNTs nano-aggregates prepared in DMF were precipitated by ether, and re-dispersed in THF solution by highly speed stirring after vacuum drying for next step of preparation.

2.3. Characterization

The average size and size distribution of Py-PPDO-b-PEG self-assemblies in DMF were monitored by dynamic light scattering (DLS) on a Malvern Zetasizer Nano ZS90 (Malvern Instruments Ltd) at room temperature (25 $^\circ\text{C}$) after filtering through a Millipore 0.45 μm filter to remove dust.

The morphology of nano-aggregates was examined by Bright-field transmission electron microscopy (TEM). TEM observations were performed on a TecnaiG2 F20 S-TWIN electron microscope (FEI Co.) operated at 200 kV acceleration voltage of 200 kV. The dispersity of MWCNTs was examined by TEM and SEM.

The resistivity measurements (resistance higher than 108 Ω) were monitored with ZC36, samples for resistivity measurements were disk (the diameter is 6 mm). The electrical conductivity of the samples (resistance lower than 108 Ω) was measured using Keithley 2400 electrometer by 2-point-technique. Both ends of the rectangle bars were painted with silver paint to ensure good electrical contact between the bars and the electrodes. Samples for resistivity measurements were prepared in a dimension of $30 \times 10 \times 0.3 \text{ mm}$. Using the percolation concept, the electrical conductivity above the percolation threshold can be correlated as a universal law $\sigma = \sigma_0 (m - m_c)^{-t}$, σ is the conductivity of the mixture with different filler contents, σ_0 is the conductivity of the filler, m is

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