



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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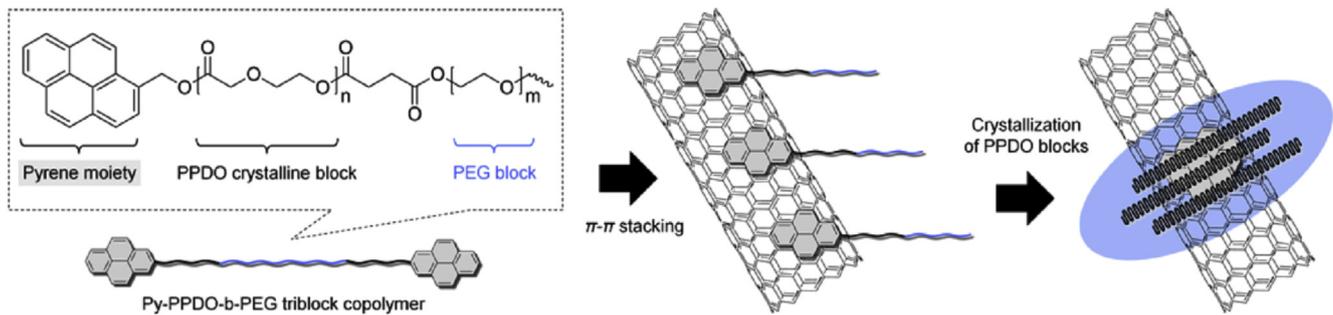


Fig. 1. Schematic representation of sparsely partial wrapping of CNTs.

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

the mass fraction of the filler, m_c is the mass percolation concentration, and t is an exponent which fits the data and is used to predict the mechanism of electrical network.

A tensile testing machine SANS CMT4104 (SANS Group, China) was used to measure the tensile properties of the nanocomposites at a cross-head speed of 30 mm/min. All samples for tensile testing were prepared at room temperature and vacuum drying for 3 days. The measurement was conducted at room temperature (25 °C). Each sample did six parallel.

3. Results and discussion

PPDO-b-PEG copolymers with or without pyrene end groups can self-assemble into nanoparticles in selective solvent (DMF and THF) owing to the crystallization of PPDO blocks (Fig. 2A), PPDO blocks, cannot crystallize when using CHCl_3 as solvent. In order to demonstrate the role of PPDO crystallization and the π - π stacking interactions in the formation of the hybrid structures, we conducted two control experiments. In the first one, Py-PPDO-b-PEG was replaced by PPDO-b-PEG which had no pyrene moieties. In the second, CHCl_3 was used as the solvent. In both cases, the stability of MWCNTs in solution is very poor (Fig. 2B). These control experiments clearly prove that both π - π stacking interactions and crystallization induced self-assembly are essential to the formation of stable Py-PPDO-b-PEG@MWCNTs hybrid nano-aggregates. Only induced by the π - π stacking interactions between pyrene moieties and MWCNTs, the Py-PPDO-b-PEG copolymers can be absorbed on the surface of MWCNTs and then induce the crystallization of PPDO blocks in selective solvent, resulting in very stable Py-PPDO-b-PEG@MWCNTs hybrid nano-aggregates. Nevertheless, when using CHCl_3 as solvent, PPDO blocks cannot crystallize and the interactions between Pyrene end-capped copolymer and MWCNTs are not strong enough for stabilizing the MWCNTs.

The size of self-assemblies of Py-PPDO-b-PEG in selective solvent are determined by the crystallization conditions. As shown in Fig. 2C, both size and polydispersity of neat Py-PPDO-b-PEG self-assemblies increased with the elevated crystallization temperature. Therefore, by adjusting the crystallization temperature of PPDO blocks, the morphology and nano-structure of the Py-PPDO-b-PEG@MWCNTs could be easily and precisely tailored. Fig. 3A–C are TEM images of Py-PPDO-b-PEG@MWCNTs prepared at different temperature. “Shish-kebab”-like partial wrapping morphology with MWCNTs as the shish and self-assemblies of Py-PPDO-b-PEG as the kebab was observed for all three samples. These flake-like self-assemblies had an incompact inner structure composed of

both amorphous PPDO and some crystallized PPDO lamellae stacked in a layer-by-layer fashion. Generally, the none-covalent wrapping of CNTs has no region selectivity, and the polymers should wrap evenly on the CNTs surface. However, with the crystallization of PPDO blocks, the loose and amorphous molecular chains gradually turned into compact and chain-folded crystalline, lead to a volume shrinkage and redistribution of the wrapping shell, and the partial wrapping morphology was achieved. High crystallization temperature may promote the crystalline growth but is not in favor of nucleation. Therefore, the size of Py-PPDO-b-PEG aggregates increased while the density of partial wrapping decreased with the increase of temperature. For hybrid nano-aggregates prepared at 55 °C, many bare MWCNTs without any wrapping were observed (Fig. 3C). Comparatively, the Py-PPDO-b-PEG@MWCNTs prepared at 40 °C has optimized partial wrapping morphology, as shown in Fig. 3D–F. Almost all of MWCNTs in this sample have been partially wrapped by at least one Py-PPDO-b-PEG self-assemblies which renders good stability for MWCNTs, while there are still sufficient bare sections of MWCNTs. For PPDO-b-PEG copolymer without pyrene moieties, it cannot form stable hybrid nano aggregates with MWCNTs, and the dispersion of PPDO-b-PEG/MWCNTs divided into two layers very quickly after sonication. As shown in Fig. S1, only self-assemblies of PPDO-b-PEG were found in the supernatant, while both aggregated MWCNTs and a few self-assemblies were observed in the precipitate, suggested that there is no obvious inter-particle interactions between PPDO-b-PEG and MWCNTs.

The DSC heating scan of Py-PPDO-b-PEG@MWCNTs freeze-dried from water dispersion (Fig. S2) also demonstrated that the crystallization of PPDO blocks is responsible for the formation of anisotropic flake-like nano aggregates. Moreover, the temperature exhibit important influence on the PPDO crystallization behavior.

The room temperature volume conductivities of PCL and its nanocomposites with MWCNTs are shown in Fig. 4A. The black hollow block connected by dotted line in Fig. 4 displays the volume conductivity of PCL/MWCNTs with different MWCNTs contents, which is consistent with those results of PCL/MWCNTs composites in previous published research prepared by directly melt compounding [25]. MWCNTs without any wrapping has a strong tendency to agglomerate, relatively high MWCNTs content was needed for formation of percolation network. Moreover, large deviation in conductivity measured from the different sides of PCL/MWCNTs film especially at high MWCNTs content also suggested that the MWCNTs without any surface modification had very poor dispersity. After wrapped by Py-PPDO-b-PEG, the volume conductivity

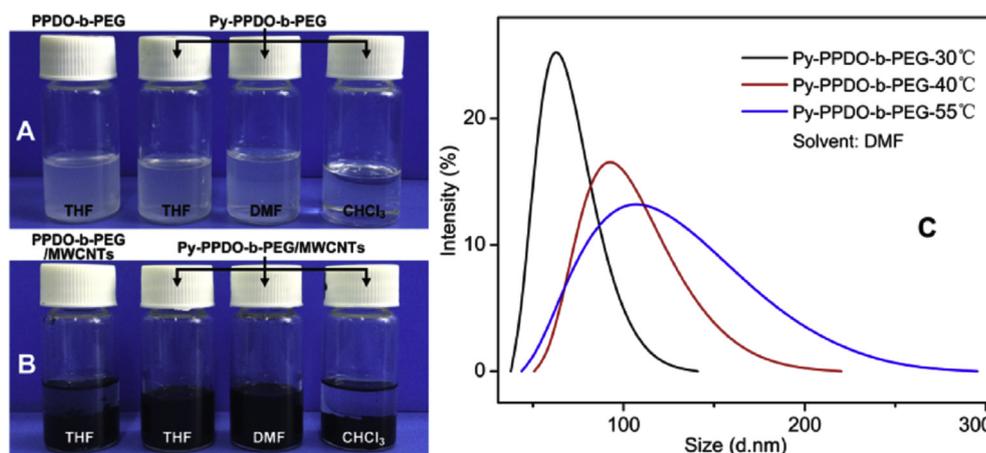


Fig. 2. Digital photos of dispersion of (A) PPDO-b-PEG copolymer end capped with or without pyrene moieties and (B) incorporated with MWCNTs in different solvents; DLS curves (C) of Py-PPDO-b-PEG nano-aggregates prepared at different temperatures.

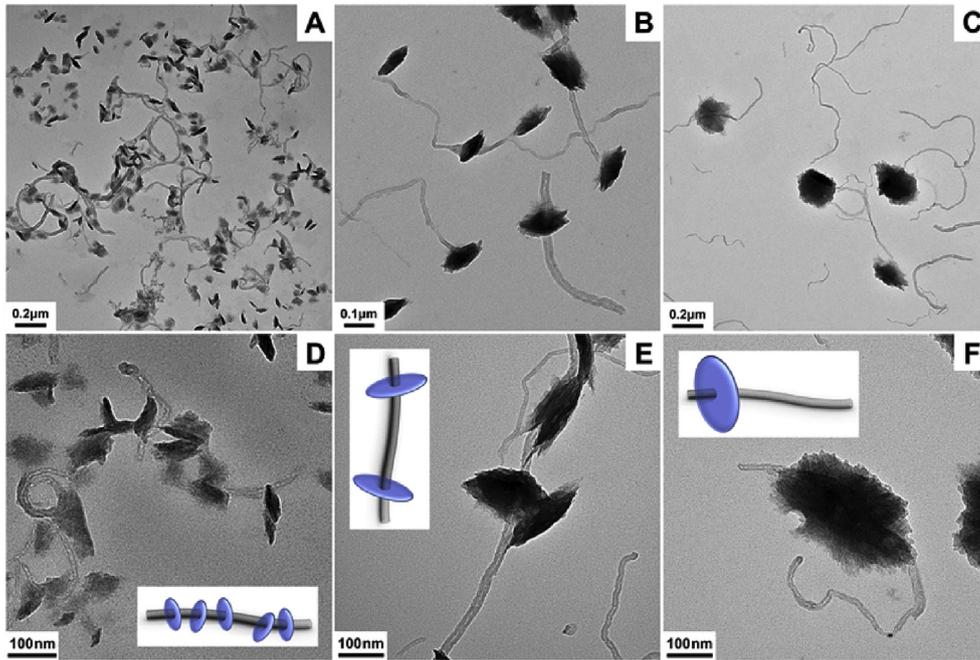


Fig. 3. TEM images of Py-PPDO-b-PEG@MWCNTs hybrid nano-aggregates prepared at (A,D) 30 °C, (B,E) 40 °C, and (C,F) 55 °C; while the insert pictures in (D–F) are graphic illustration of the wrapping density.

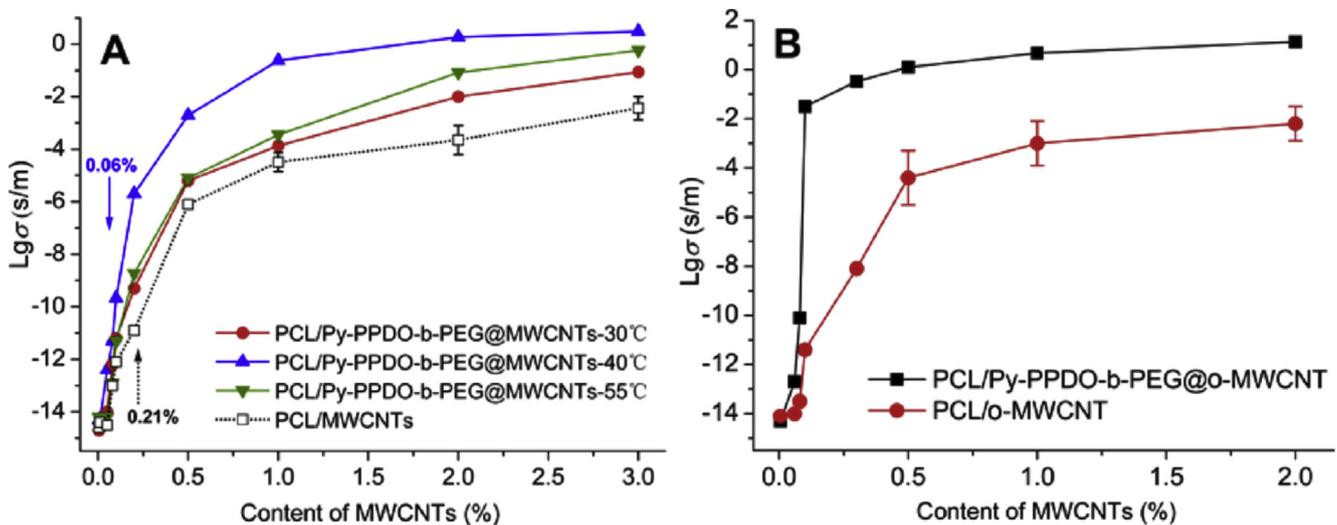


Fig. 4. Electrical conductivity of (A) PCL/Py-PPDO-b-PEG@MWCNTs and (B) PCL/Py-PPDO-b-PEG@o-MWCNTs composite films with different MWCNTs contents.

of films obviously increased especially when content of MWCNTs were lower than 0.5 wt%. Compared to PCL/MWCNTs composite films at same MWCNTs content, the volume conductivities of PCL/Py-PPDO-b-PEG@MWCNTs films prepared at 40 °C increased over 3–5 orders of magnitude in range from 0.1 to 3 wt% of MWCNTs contents. According to the percolation theory [26], the percolation threshold of this sample is 0.06 wt% (also marked by blue arrow in Fig. 4A) which is much lower than that of PCL/MWCNTs (0.21 wt%). The distinct increase in volume conductivity and decrease in percolation threshold of PCL/Py-PPDO-b-PEG@MWCNTs-40 °C compared to other samples demonstrated that this sample have more efficient percolation network which provides much more channels for the electrons transferring throughout the whole matrix.

The aforementioned MWCNTs used for preparing composite film have been purified with dilute HNO_3 solution, which may inevitably decrease the length of MWCNTs [27]. Although shorter CNTs affords the advantage of efficient dispersion, longer CNTs helps in reducing the number of contact points necessary between CNTs along the electrical conduction path. Therefore, we also used the original MWCNTs (marked as *o*-MWCNTs), which have only been purified with water and their length may well-preserved, for preparing the composite films. As we expect, the volume conductivities of composite films prepared from partially wrapped *o*-MWCNTs are further increased. The volume conductivity of PCL/Py-PPDO-b-PEG@*o*-MWCNTs film reached to 0.035 S/m when only 0.1 wt% of *o*-MWCNTs was added, which is 11 orders of magnitude higher than that of PCL/*o*-MWCNTs composite films at same *o*-

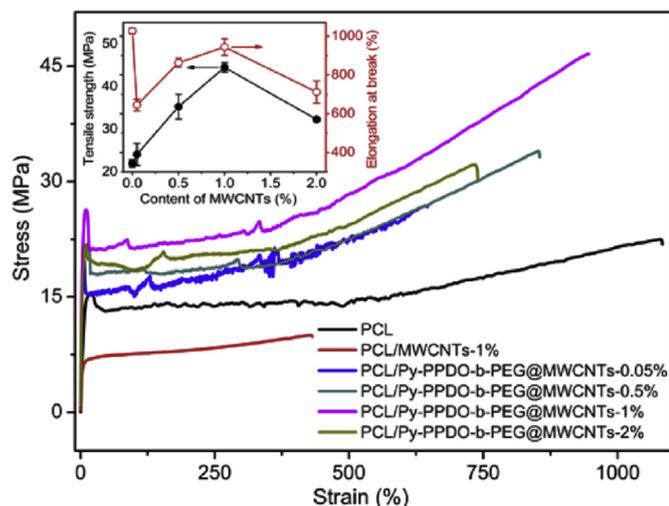


Fig. 5. Stress-strain curves of PCL, PCL/MWCNTs, and PCL/Py-PPDO-b-PEG@MWCNTs films with different MWCNTs contents; the insert graph is mechanical property parameters obtained from stress-strain measurement.

MWCNTs content (Fig. 4B), while is also 8 orders of magnitude higher than that of PCL/Py-PPDO-b-PEG@MWCNTs-0.1%. We will now show that the percolation networks from partial wrapping MWCNTs form highly efficient charge transport pathways even at very low nanotube concentration.

The openness of the nanohybrid structure is the main reason responsible for the efficient formation of percolation network [28]. However, the wrapping density of the hybrid structure also plays very important role. The Py-PPDO-b-PEG@MWCNTs hybrid nano-aggregates prepared at 30 °C have a dense wrapping morphology (Fig. 3A and D), which may impede the interconnection of the MWCNTs, and therefore the composite films based on them exhibit lower conductivities than those composite films using Py-PPDO-b-PEG@MWCNTs prepared at 40 °C. Moreover, the electrical

conductivities of this sample are very close to those of PCL nanocomposites using surface modified CNTs with surfactant [29] or polymer [30], suggested that the dense wrapping of CNTs has similar effect as complete surface modification. Meanwhile, excessively sparse wrapping of CNTs (Py-PPDO-b-PEG@MWCNTs-55 °C, Fig. 3C and F) may also lead to decrease in conductivities because of the poor dispersity.

The mechanical properties of the composite films also showed a dependency on the percolation network. The films with higher volume conductivity exhibit better mechanical properties (Fig. 5). For composite films using Py-PPDO-b-PEG@MWCNTs prepared at 40 °C, the tensile strength reached 44.5 MPa with 1.0 wt% MWCNTs loading, which corresponded to about 100% reinforcement compared to the neat PCL film. The high reinforcement could be attributed to the effective network structure as well as homogeneous dispersion of the MWCNTs in the PCL matrix, which maximized the area of the load transfer from one nanotube to its neighbor and between the MWCNTs and PCL. This is a very representative example showing a remarkable reinforcement of PCL and prominent improvement of the conductivity from partially wrapped CNTs by a noncovalent modification. For PCL/MWCNTs and PCL/Py-PPDO-b-PEG@MWCNTs-55 °C films, MWCNTs tend to agglomerate and result in high surface tension. Therefore, these samples showed very poor mechanical properties. The addition of larger quantities of MWCNTs in conductive polymer composites (CPCs) is not favorable to the mechanical properties, and the reason for this behavior is not completely understood yet. A possible explanation is that MWCNTs in large amounts results in the formation of a weak interface and leading to poor mechanical properties [31].

In order to figure out the mechanism of enhancement in conductivity, the microstructure of MWCNTs network in PCL/Py-PPDO-b-PEG@MWCNTs films with different wrapping densities were investigated by TEM, as emphasized by Fig. 6. For PCL/MWCNTs composite, obvious aggregation of MWCNTs were observed (Fig. 6A, see also in SEM images of cryogenic fracture surface of composite films in Fig. 6E). For composite film using Py-PPDO-b-

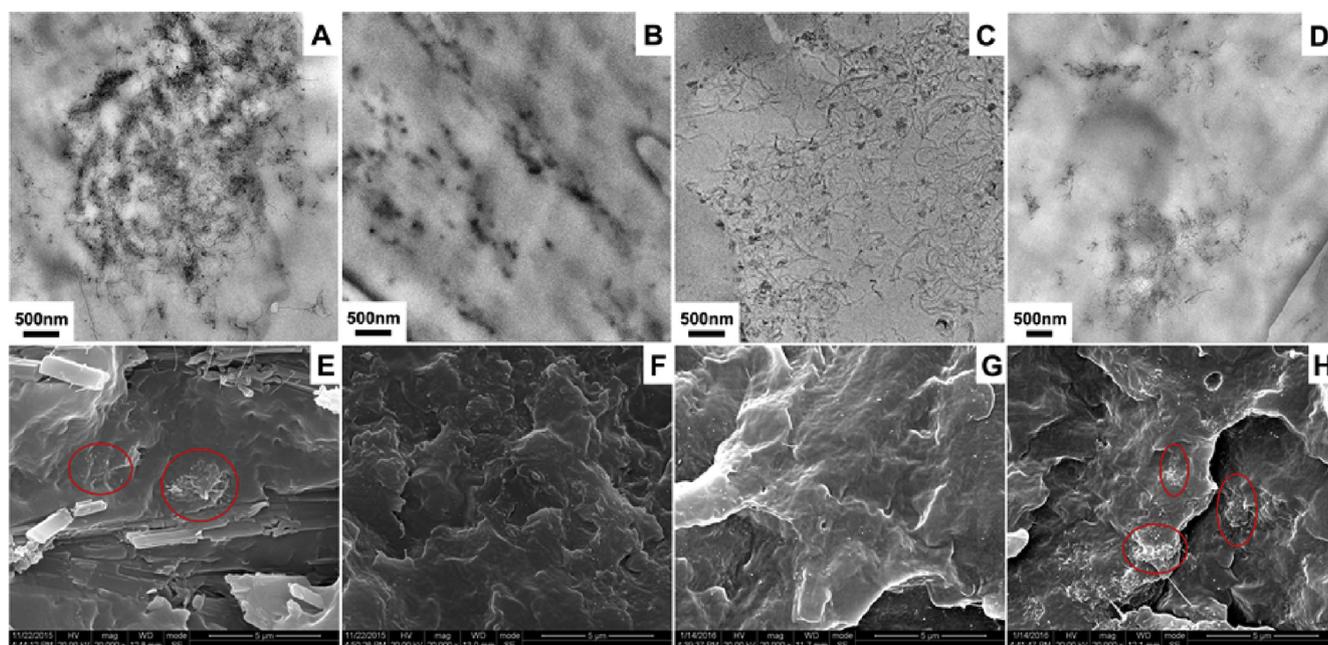


Fig. 6. TEM images (A–D) of composites films and SEM images (E–H) of cryogenic fracture surface of (A,E) PCL/MWCNTs; (B,F) PCL/Py-PPDO-b-PEG@MWCNTs-30 °C; (C,G) PCL/Py-PPDO-b-PEG@MWCNTs-40 °C; (D,H) PCL/Py-PPDO-b-EG@MWCNTs-55 °C.

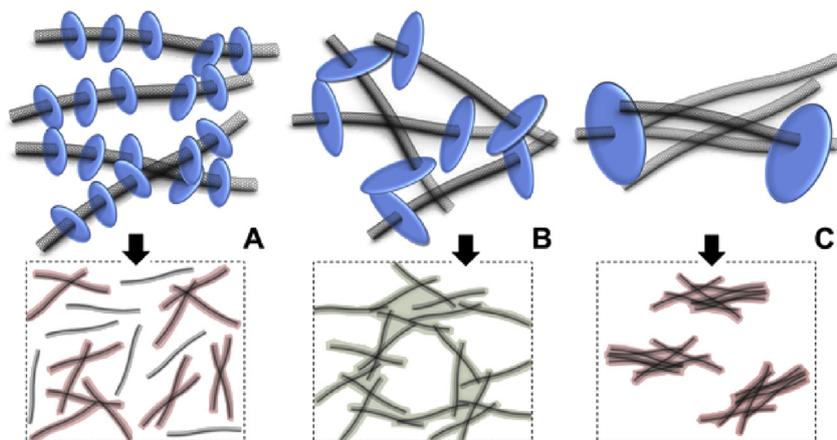


Fig. 7. Schematic illustration of nano-structure and interconnection of Py-PPDO-b-PEG@MWCNTs prepared at (A) 30 °C, (B) 40 °C and (C) 55 °C in polymer matrix.

PEG@MWCNTs prepared at 30 °C as the precursors, the MWCNTs showed good dispersity in the PCL matrix (Fig. 6B and F). However, this sample did not show sufficient interconnection of MWCNTs. As illustrated in Fig. 7A, this phenomenon could be explained by the relatively high wrapping density of Py-PPDO-b-PEG@MWCNTs-30 °C, which results in well dispersion of MWCNTs in PCL matrix. In consideration of the steric hindrance of the self-assemblies wrapping on MWCNTs, the bare sections of Py-PPDO-b-PEG@MWCNTs-30 °C are too short to induce enough interconnection of MWCNTs. The wrapping density of MWCNTs could be reduced by increasing the preparation temperature of Py-PPDO-b-PEG@MWCNTs. At higher temperature, the Py-PPDO-b-PEG tended to form larger self-assemblies induced by crystallization, which leads to longer bare MWCNTs sections.

When using Py-PPDO-b-PEG@MWCNTs-40 °C as the precursors, the MWCNTs exhibits both good dispersity and sufficient interconnection in the composite film (Fig. 6C and G), which could be attributed to the optimized wrapping density of this sample (Fig. 7B). Dielectric spectroscopy (see also in Fig. S3, supporting information) also proved that the MWCNTs have a good dispersion in PCL/Py-PPDO-b-PEG@MWCNTs-40 °C nanocomposites. However, when preparation temperature of Py-PPDO-b-PEG@MWCNTs increased to 55 °C, the existence of MWCNTs without any wrapping resulted in obvious aggregation of MWCNTs in PCL matrix (Fig. 6D and H), and therefore impeded the formation of conductive network (Fig. 7C). These results demonstrate again that the nano-structure, i.e. the wrapping density and length of bare MWCNTs sections plays the key role in determining the formation of percolation networks. Only partial wrapped MWCNTs with proper balance of wrapped and not wrapped sections, which could be effectively tuned by crystallization temperature, can maintain good dispersity and induce sufficient interconnection of MWCNTs simultaneously.

4. Conclusion

In summary, a novel sparse wrapping strategy was developed for preparing CPCs with high efficient percolation networks by using hybrid nano-aggregates of Py-PPDO-b-PEG and MWCNTs as the building block. The wrapping density of the hybrid nano-aggregates, which endues the MWCNTs with both good stability and tendency to form sufficient interconnections in polymer matrix, could be effectively tuned by the crystallization temperature of PPDO blocks. The composite films prepared from Py-PDO-b-PEG@MWCNTs and PCL exhibited much improved conductivity

especially at very low nanotube concentration compared to those from neat MWCNTs without any wrapping. The wrapping density is essential to the formation of percolation networks. When using Py-PPDO-b-PEG@MWCNTs prepared at 40 °C as the precursors, the composite film exhibits both excellent conductivity and mechanical properties, which could be attributed to the optimized wrapping density of this sample. Excessively dense or excessively sparse wrapping may impede the interconnection and dispersity of the MWCNTs, respectively, and therefore resulted in decreased properties.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.compscitech.2016.09.025>.

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