

Preparation of carbon nanotubes/poly(lactic acid) nanocomposites using a non-covalent method

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Abstract The polymeric composites with four-armed star poly(lactic acid) (PLA) immobilized on the surface of carbon nanotubes (CNTs) were constructed by a simple ultrasonic process using non-covalent method. The four-armed star poly(lactic acid) was prepared by ring-opening polymerization of lactide using zinc *p*-tetraaminophenylporphyrin (ZnP) as initiator and stannous octoate as catalyst. Due to the strong π - π interactions between CNTs and zinc porphyrin of star PLA, the CNTs/PLA composites can be easily obtained while the intrinsic graphitic structure of CNTs is retained. The CNTs/PLA nanocomposite was studied via infrared spectrum (IR) and thermogravimetric (TG) analysis. UV-Vis and fluorescence demonstrate that the porphyrin probably strongly anchored on the side walls of the nanotubes. Optical studies further promise the non-covalent interactions. Meanwhile, morphology studies with scanning electron microscope (SEM) show that CNTs are dispersed well in the polymer. This convenient non-covalent method may be useful for the preparation of CNTs-polymer hybrid without the destruction of the intrinsic graphitic structure of the pristine CNTs.

Keywords Star poly(lactic acid) · Carbon nanotubes · Polymeric composites · Nanocomposites

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Introduction

With unique structural and transport properties, such as excellent strength, modulus, electrical and thermal conductivities along with a low density, CNTs have attracted much interest as the reinforcement for polymer matrix composites [1–4]. However, the expectations concerning their mechanical reinforcement potential have not been fully confirmed so far. This is mainly attributed to the difficulties of dispersing CNTs in polymer materials [5, 6]. It is very difficult to disperse CNTs in most solvents as CNTs usually exist as ropes or bundles to form a highly dense structure [7, 8]. This makes it much more challenging to achieve a good dispersion level of the nano-scale fillers in polymer composites. In recent years, many efforts have been focused on the chemical modification of CNTs to improve their solubility, processability and performance by covalent method [9–12], which can efficiently improve the dispersion of the CNTs in solvent. However, the covalent functionalization partially destroys the π -conjugated structure of CNTs, which is undesirable. To establish an efficient approach to disperse CNTs without destruction of the CNTs structure, non-covalent functionalization based on the π - π stacking interactions has been exploited [13]. The polymers used in this strategy usually contain conjugated moieties such as pyrene, porphyrin, etc., [14, 15]. Pan prepared polymeric composite using pristine multi-walled carbon nanotubes and triphenylene core PLA with a non-covalent functionalization method [16]. It makes CNTs dispersible in a variety of organic solvents. However, there are few works reported on the preparation of CNTs/PLA nanocomposites with non-covalent functionalization method up to now. Researchers are still facing challenges to achieve homogeneous dispersion of CNTs to enhance the CNTs/polymer interfacial interactions [17].

As is well known, porphyrin derivatives are widely used in preparation nanocomposites by non-covalent functionalization method for their π - π interactions with CNTs [14, 15]. Here we report the preparation of CNTs/PLA nanocomposites with non-covalent method. The star PLA with a ZnP core is synthesized through a similar method described in our previous work [18] except that ZnP was used as initiator as shown in Fig. 1. It will afford us with an alternative approach to improve the solubility of CNTs in organic solvents and provide a novel idea to prepare CNTs/PLA nanocomposites without the destruction of the intrinsic graphitic structure of pristine CNTs.

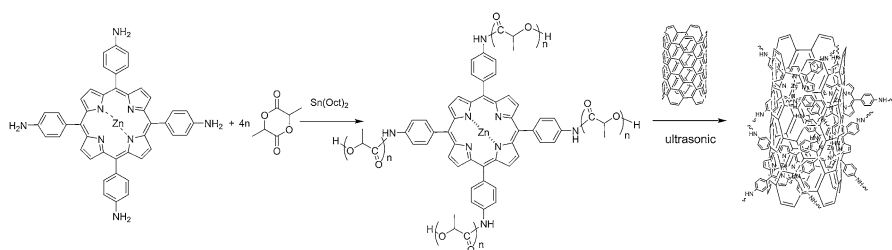


Fig. 1 Preparation route for the polymeric composite

Experimental section

Preparation of four-armed star PLA with a zinc porphyrin core

ZnP (30 mg, 0.04 mmol) in 2 mL of dry dichloromethane and lactide (5.76 g, 40 mmol) were added into a glass tube equipped with a magnetic stirrer. A nitrogen exhausting/refilling process was performed three times. Stannous octoate (81 mg, 0.2 mmol) in 1 mL of dry dichloromethane was added, and the exhausting–refilling process was carried out again to remove the dichloromethane. The tube was sealed under vacuum, and was put into an oil bath at 140 °C for 24 h. Then the product was dissolved in dichloromethane, and methanol was used to precipitate the product. The product was isolated and dried under vacuum at 40 °C overnight. Yield: 87 %, $M_{n,NMR} = 11,800$, $M_{n,GPC} = 73,000$, PDI = 1.97.

Preparation of the CNTs–PLA composite

In a typical experiment, the polymer (300 mg) was firstly dissolved in tetrahydrofuran (THF, 30 mL). A certain amount of CNTs was added into the above solution and the mixture was sonicated for 60 min. After centrifugation of the solution at 1000 rpm for 5 min, a clear solution was obtained. The solution was concentrated under vacuum, and the CNTs–PLA composite was obtained.

Materials and characterizations

The CNTs (diameter <2 nm, length 5–15 μm , Shenzhen Nanotech Port Co., Ltd, China) were used without further purification. Compound ZnP was prepared according to the literature [19]. ^1H NMR spectra were measured on a Bruker Avance 500 MHz spectrometer using tetramethylsilane (TMS) ($\delta = 0.00$) as an internal chemical shift standard. UV–Vis absorption spectra were performed on a PerkinElmer Lambda 35 spectrometer. Fluorescence spectra were determined by PerkinElmer LS 50B luminescent spectrometer. Thermal gravity analyses (TGA) were carried out on a TA Instrument Q600 analyzer with a heating rate of 10 °C/min under nitrogen atmosphere. The field emission scanning electron microscope (SEM) was performed on a FSEM, A TMX 840 instrument.

Results and discussions

The characterization of the star PLA is similar to that in our previous work [18]. Figure 2a represents a typical ^1H NMR spectrum of the star PLA. The signals at δ -8.97(a), 8.18(c) and 8.06–8.07(b) are assigned to the protons in porphyrin core. The methine proton next to terminal hydroxyl group is located at δ -4.37(h). The signal at δ -5.55(e) is assigned to the protons in the $-\text{NHCOCH}(\text{CH}_3)$ group near to the phenyl group of porphyrin in PLA chain, which confirms that four-armed star PLA with porphyrin core should be formed.

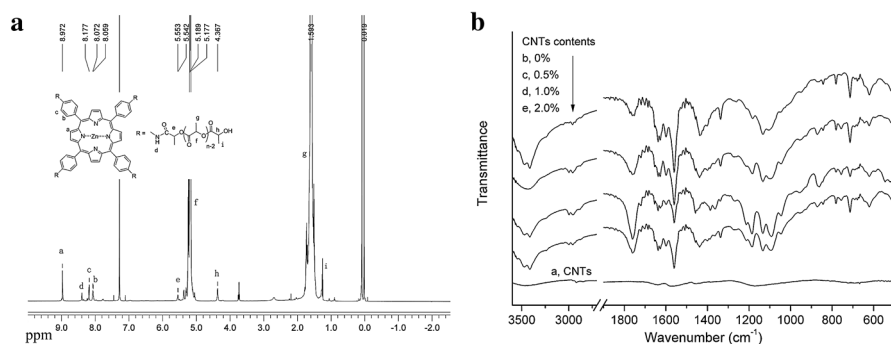


Fig. 2 **a** ¹H NMR spectra of the star PLA and **b** FTIR spectra of the CNTs–PLA composites

To verify the structure of the CNTs–PLA composites, their FTIR spectra were measured. Figure 2b represents typical FTIR spectra of the pristine CNTs and the CNTs–PLA composites. From spectra of CNTs/PLA and pure PLA, the stretch absorption peaks of C = O at 1760 cm^{-1} can be clearly observed, and the stretch absorption peaks of C–H bond at 2920 cm^{-1} are also strong. The peak at 1598 cm^{-1} is the absorption band of phenyl group of porphyrin. Combining with the FTIR spectra of PLA and CNTs–PLA composites, the amine carbonyl stretching band at 1643 cm^{-1} and the N–H stretching band at 3413 cm^{-1} are the typical absorption bands of star PLA with porphyrin core.

A series of CNTs/PLA composites were prepared according to Table 1. The contents of CNTs in the composites were calculated from TGA curves under nitrogen atmosphere. In Fig. 3, the weight loss of the first range ($150\text{--}300\text{ }^{\circ}\text{C}$) is associated with the loss of water about 5 wt%, whereas the second range ($300\text{--}350\text{ }^{\circ}\text{C}$) corresponds to the thermal degradation of PLA. Further, the TGA analysis also shows the different thermal stability of CNTs and CNTs/PLA composites. Pristine CNTs are thermally stable from 150 to $600\text{ }^{\circ}\text{C}$. The star PLA shows the lowest thermal stability without any CNTs addition. TGA curves of CNTs/PLA composites containing 0.5–2 % contents of CNTs show higher thermal stability than the pure polymer, which indicate that the CNTs can enhance the thermal stability of PLA polymer.

To explore the dispersion stability of CNTs/PLA composites in organic solvent, 5.0 mg of CNTs/PLA composite was charged into 5.0 mL organic solvent. Figure 4 shows the dispersion stability of CNTs/PLA in THF solution. The CNTs/PLA composites yielded soluble samples and showed good stability in THF solution. No

Table 1 Feed ratio of the CNTs/PLA composites

Sample code	CNTs weight (mg)	PLA weight (mg)	Theoretical contents of CNTs (%)	Contents of CNTs in the composites ^a
1	1.51	300	0.5	0.42
2	3.03	300	1.0	0.86
3	6.12	300	2.0	1.78

^a Contents of CNTs calculated from TGA

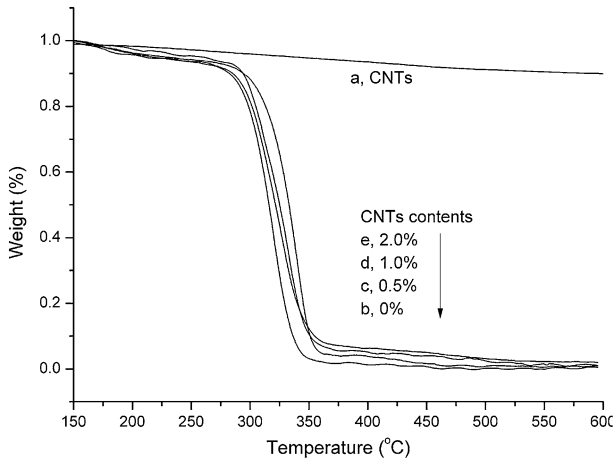


Fig. 3 TGA curves of the CNTs–PLA composites

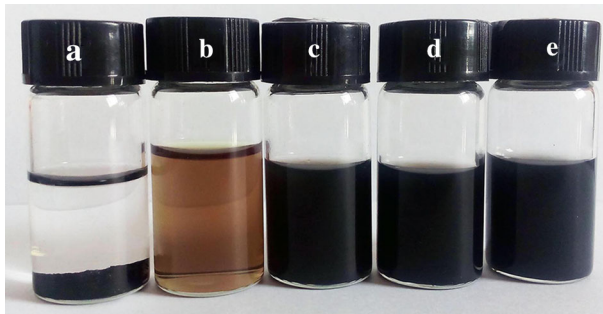


Fig. 4 Dispersion of CNTs/linear poly(lactic acid) (a), star PLA (b), 0.5 % content (c), 1.0 % content (d), and 2.0 % content (e) of CNTs in composites in THF solution, respectively

deposition was found even after 2 weeks. To confirm that this result was not due to adsorption of PLA onto CNTs, the mixture of pure linear PLA and pristine CNTs was prepared. In contrast, CNTs cannot be dispersed stably in linear PLA THF solution, and the mixture could not disperse stably in more than 1 day. The result confirms that the combination between PLA and CNTs is not just a simple physical process.

The electronic absorption spectra are shown in Fig. 5a. All composites exhibit Soret band at 426 nm and relatively weaker Q-bands in the range of 500–650 nm. No obvious absorption peak of CNTs is observed. In our case, the characteristic features of CNTs/PLA composites are similar to the feature of star polymer. The appearance of the blue-shift Soret band at 404 nm reveals that some H-aggregation forms in the CNTs/PLA composites solution. No red-shifted band is observed, which indicates that J-aggregation did not occur. The result may be due to the steric chain of PLA which prevents ZnP unit J-aggregation but allows their H-aggregation between porphyrin and CNTs [20]. The steady-state fluorescence spectra in Fig. 5b further support the formation of the CNTs/PLA nanocomposites. The fluorescence

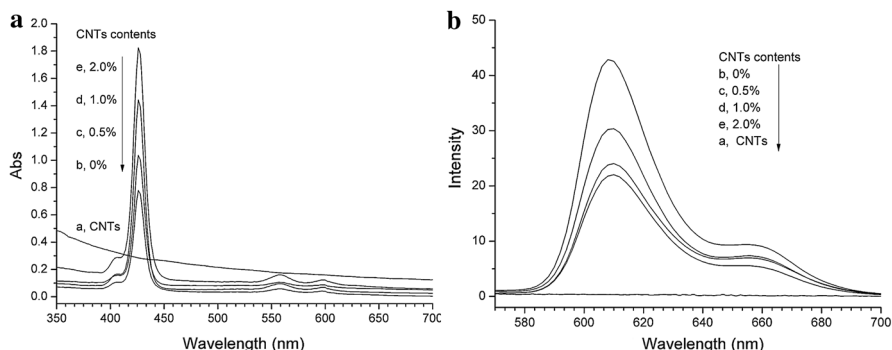


Fig. 5 **a** UV–Vis absorption spectra and **b** fluorescence spectra of the polymer composites upon excitation at 426 nm in THF solution

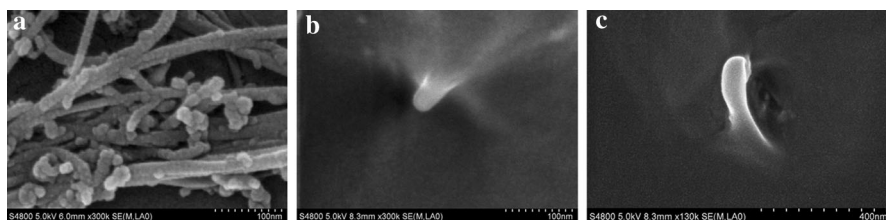


Fig. 6 SEM images of **a** CNTs and **b, c** CNTs–PLA composites with 1.0 % content of CNTs

quenching obtained for composites in THF solution can also be compared with the reported values in the literature for the corresponding materials obtained through non-covalent method [15]. The CNTs quench the emission of ZnP unit of the composite in solution. The fluorescence quenching efficiency of the composites was found to be increased as the CNTs contents increased from 0.5 to 2.0 %. Therefore, photo-induced charge separation through the excited singlet state of ZnP unit is suggested. These results agree well with the results determined in non-covalent π – π interaction supramolecular systems [21]. The non-covalent attachment of PLA to CNTs can be proved by the fluorescence quenching, and the existence of PLA on the CNTs surfaces can further be confirmed.

Morphology studies with SEM are shown in Fig. 6. It is observed that individually CNTs are embedded in the polymer matrix, while many entangled clusters of CNTs are observed in the photograph of pristine CNTs. It means that the CNTs bundles were loosened by the treatment of non-covalent method dispersion and the CNTs are well dispersed in the PLA matrix.

Conclusions

We have prepared CNTs/PLA nanocomposites with star polylactic acid (PLA) immobilized on the surface of CNTs using non-covalent method. CNTs are dispersed well in polymer matrix due to strong interactions in the supramolecular

system. Detailed research by FTIR, UV–Vis and fluorescence spectroscopy demonstrates that the porphyrin cores are probably strongly anchored on the side walls of the nanotubes. The intrinsic graphitic structure of the CNTs is not destroyed. SEM studies reveal that CNTs can be dispersed in the polymer matrix well. This convenient non-covalent method may be useful for the preparation of CNT–polymer hybrid nanomaterials without the destruction of the intrinsic graphitic structure of the pristine CNTs. This study suggests that star PLA with porphyrin core/CNTs composites may find potential application as biological labels.

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