J Mater Sci (2008) 43:5609–5617
DOI 10.1007/s10853-008-2804-x

Synthesis of poly(ethylene glycol) functionalized MWNTs and their inclusion complexes with α-cyclodextrin

Yexiang Wang · Hua Xiong · Yong Gao · Huaming Li

Received: 13 March 2008 / Accepted: 12 June 2008 / Published online: 28 June 2008

Abstract Poly(ethylene glycol) (PEG) functionalized multiwalled carbon nanotubes (MWNTs), prepared by coupling of isocyanate-decorated MWNTs with PEG of different molecular weights (M_n = 400, 1000, 2000, and 4000 g/mol), were used to form inclusion complexes (ICs) with α-cyclodextrin (α-CD) through the grafted PEG chains being threaded with α-CD rings in aqueous solution. The FTIR, TGA, UV-Vis, and scanning electron microscopy (SEM) techniques were employed to characterize the formed ICs. The ICs formation time was monitored by UV-Vis spectroscopy, and the results indicated that the inclusion interaction between MWNT surface anchored PEG chains and α-CD was dependent on the molecular weight of PEG. The grafted PEG with molecular weights of 4000 and 2000 g/mol, respectively, can form ICs with α-CD, while the grafted PEG with molecular weights of 1000 and 400 g/mol, respectively, are difficult to form ICs with α-CD due to the steric hindrance from nanotubes. The stoichiometry value determined by TGA indicated that the ratio of ethylene glycol (EG) unit to α-CD in the resulted ICs was about 15:1. In addition, the morphology of the ICs was observed by SEM and transmission electron microscopy (TEM).

Introduction

Carbon nanotubes (CNTs) are unique nanostructured materials with remarkable physical, mechanical, and electronic properties [1–3]. These properties make them attractive for applications in many scientific and technological fields such as electronic structures [4], polymer composites [5], and biological systems [6]. Among them, the exploration of CNTs in biomedical applications, including biosensing and drug delivery, is just underway. Although some of these applications can be realized through in situ growth, many others will require aqueous solution-phase processing and manipulation [7, 8]. Aqueous solution-phase processing, however, has proved to be problematic due to their inherent insolubility and low dispersibility in aqueous solvent. Recently, several approaches to the functionalization of CNTs, including covalent sidewall coupling reactions, end-group reactions, and non-covalent exohedral interactions, have been developed to prepare water-soluble CNTs [9–11]. Among these approaches, covalent sidewall functionalization of CNTs with polymeric structures has been shown effective in improving the solubility of nanotube-polymer conjugates, even with a relatively low degree of functionalization [12–15].

Current methods for the preparation of water-soluble polymer-CNT conjugates include "grafting from" method using initiator-functionalized CNTs [16, 17], as well as "grafting to" method involving reaction with surface-bound carboxylic acid groups on oxidized CNTs. For example, oxidized CNTs can be functionalized with poly(ethylene oxide) derivatives [18], sugar moieties [19], oligonucleotides [20], and peptides [21], nucleic acids [22], or proteins [23]. We have recently developed an efficient method for solubilizing CNTs using toluene 2,4-diisocyanate (TDI) as coupling agent [24]. By carefully choosing

---

Y. Wang · H. Xiong · Y. Gao · H. Li (✉)
Institute of Polymer Science, Chemistry College, Xiangtan University, Xiangtan 411105, Hunan Province,
People's Republic of China
e-mail: lihuaming@xtu.edu.cn

H. Li
Key Lab of Environment-Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan 411105,
People's Republic of China

the polymers, it is possible to obtain water-soluble CNT derivates for further study.

Cyclodextrins (CDs) are cyclic oligosaccharides with D-(+)-glucose as the repeating unit coupled by 1,4-α-linkages. α-, β-, and γ-CDs are commonly available forms which consist of 6, 7, and 8 glucose units, respectively [25]. During the past years, CDs have been extensively studied as host molecules in supramolecular chemistry due to the existence of hydrophobic cavity, and it can form host–guest complex with varied guest polymer molecules [26–35]. For example, poly(ethylene glycol) (PEG) can form ICs with α-CD molecules through the polymer chains being threaded with α-CD rings in aqueous solution. Recent researches indicate that there are many interested findings when CNTs are incorporated into the ICs system. Wang et al. [36] have reported a novel hydrogel hybridized with single-walled carbon nanotubes (SWNTs); such hybrid hydrogel was prepared through mixing an aqueous solution of α-CD with an aqueous dispersion of SWNTs stabilized by Pluronic copolymer. Ogoshi et al. [37] have also reported the preparation of a supramolecular SWNTs hydrogel by host–guest interactions between SWNT surface absorbed β-CD moieties and dodecyl groups of poly(acrylic acid).

As far as we knew, there have been few studies dealing with the ICs between polymer covalently functionalized multi-walled carbon nanotubes (MWNTs) and CDs. Herein, we report a facile strategy to incorporate MWNTs into the ICs system through host–guest interactions between the PEG functionalized MWNTs (MWNT-PEG) and α-CDs. Compared with polymers non-covalently functionalized CNTs, the nanotubes applied here have a unique structure; that is, the density and the length of polymer chains linked to CNT surface can be roughly adjusted. Furthermore, the host–guest interactions between CNT surface bound polymers and α-CDs are different due to steric hindrance from the tubes. The purpose of this report is to explore whether such PEG grafted MWNTs can form ICs with α-CDs. A series of water-soluble MWNT samples were synthesized by grafting PEG onto the nanotube surfaces using 2,4-toluene diisocyanate (TDI) as coupling agent, and the IC samples were prepared from these materials and α-CDs. The ICs formation time was monitored by UV-Vis spectroscopy. The morphology of the ICs was observed by scanning electron microscopy (SEM). The hybrid supramolecular structure may produce materials with novel properties such as stimuli responsive and, therefore, have great potential in biological and biomedical applications.

Experimental

General procedures

MWNTs with 1.06 wt% concentration of hydroxyl groups (MWNT-OH) purchased from the Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Science, were dried in vacuum at 100 °C for 12 h before use. The preparation details for the MWNT-OH have been protected by Chinese patent (CN1463919). PEG with different molecular weights ($M_n = 400$, 1000, 2000, and 4000 g/mol) were dried at 120 °C under vacuum for 12 h before use. TDI was freshly distilled prior to use and α-CDs were dried in vacuum at 60 °C for 48 h before use. Toluene was reflux with sodium and then distilled. All other chemicals were used as received. FTIR spectra in KBr pellets were recorded on a Perkin-Elmer Spectrum One FTIR spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a STA 449C instrument with a heating rate of 5 °C/min in flowing N_2. Ultraviolet-visible (UV-Vis) spectra were measured using a PE Lambda 20 spectrophotometer. Transmission electron microscopy (TEM) was conducted using a JEM 3010 electron microscope. SEM images were recorded using a JSM 6700F electron microscope. The specimens were loaded on a mica surface, previously sputter-coated with a homogeneous gold layer for charge dissipation during the SEM imaging.

Preparation of isocyanate-functionalized MWNTs

In total, 100 mg of MWNT-OH (0.0624 mmol of hydroxyl group) was dispersed in 50 mL of TDI (0.352 mol) under stirring and the functionalization was endured in a dry nitrogen atmosphere at 80 °C for 72 h. The functionalized MWNTs were then filtered through a PTFE (200 nm pore size) membrane to recycle TDI. The collected solid was washed with anhydrous toluene to completely remove the residual TDI. After being dried in vacuum at 40 °C for 24 h, the functionalized MWNTs containing isocyanate groups were obtained. FTIR (KBr pellets, cm^{-1}): 2270, 1651, 1634, 1592, 1538, 1298, 1221, 1076. The mass loss of TDI functionalized MWNTs at 500 °C was about 8.5 wt% as determined by TGA, suggesting that the isocyanate graft density was about 0.59 mmol/g of neat MWNTs.

Preparation of PEG functionalized MWNTs (MWNT-PEG)

In a typical experiment, isocyanate-functionalized MWNTs (50 mg, 0.0244 mmol of isocyanate group) and PEG (10 equiv/mol of isocyanate group) were sonicated in 100 mL of anhydrous toluene for 10 min to give a homogeneous suspension. Then, the mixture was stirred at 100 °C in a nitrogen atmosphere for 48 h. After cooling to room temperature, the mixture was filtered through a PTFE (200 nm pore size) membrane and washed thoroughly with methanol and distilled water. The black solid was collected and dried in vacuum at 60 °C for 24 h.

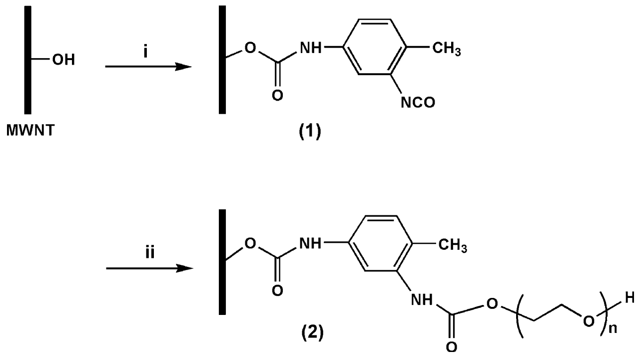
Preparation of MWNT-PEG and α-CDs inclusion complexes

A vial charged with 10 mg of MWNT-PEG and 10 mL of distilled water was sonicated for 10 min. After centrifuging at 8000 rpm for 30 min, the vial was allowed to stand undisturbed overnight. The supernatant was carefully separated and then mixed with α-CD aqueous solution at room temperature by sonicating for 10 min. The mixture was again allowed to stand at room temperature. The solid inclusion complex was isolated by centrifugation at 8000 rpm, washed with water, and dried in vacuum at 60 °C for 24 h.

Results and discussion

Preparation of PEG functionalized MWNTs

In the present study, MWNT-OH with 1.06 wt% concentration of hydroxyl groups was used to react with TDI to produce isocyanate-functionalized MWNTs as depicted in our previous article [24]. Subsequently, polymer coupling to the nanotubes to produce MWNT-PEG was accomplished by reacting isocyanate-functionalized MWNTs with PEG of different molecular weight as shown in Scheme 1. A series of MWNT-PEG samples with almost similar graft density, as determined by TGA, were synthesized and used for further studies (Table 1). The coupling reaction was accomplished in dry toluene at 100 °C. In a typical experiment, isocyanate functionalized MWNTs (50 mg) and PEG (10–50 equiv/mol of isocyanate groups) were mixed with dry toluene (100 mL). After sonicating at room temperature for 10 min, the resulting mixture was stirred at 100 °C for 48 h under nitrogen. The functionalized MWNT derivatives were isolated by filtration through a 200 nm pore Teflon membrane, followed by washing with MeOH, and H_2O. In this study, excess PEG was used in order to exclude the possibly existed crosslinking reaction. This excess PEG was easily removed after each reaction by ultra-filtration and prolonged washing with water.



Scheme 1 Synthesis of PEG functionalized multiwalled carbon nanotubes: (i) TDI, 80 °C; (ii) PEG, toluene, 100 °C

Table 1 Grafting density and solubility for MWNT-PEGs

Samples[a]	Mass contents (wt%)	Graft density (mmol/g)	Solubility (mg/L)
MWNT-PEG04k	19.7	0.069	137
MWNT-PEG1k	22.6	0.063	169
MWNT-PEG2k	27.3	0.067	346
MWNT-PEG4k	32.5	0.056	485

[a] PEG of four molecular weights (M_n = 400, 1000, 2000, and 4000 g/mol) were used to functionalize MWNTs, giving the products referred to as MWNT-PEG04k, MWNT-PEG1k, MWNT-PEG2k, and MWNT-PEG4k, respectively

FTIR spectroscopic analysis provided evidence that the MWNT surface modification proceeded as illustrated in Scheme 1. Figure 1 shows the FTIR spectra of MWNT-OH (a), isocyanate-functionalized MWNTs (b), and MWNT-PEG (c). The very weak absorbance at around 3500 cm^{-1} in spectrum (a) is attributed to the surface OH groups of MWNT-OH [38]. Conversely, clearly discernable bands at 2270 and 1634 cm^{-1} are observed in the spectrum (b), which can be assigned to asymmetric stretching of the appended terminal isocyanate groups and the aromatic C–C stretch, respectively. The surface isocyanate functionalities could then be treated with PEG in anhydrous toluene at 100 °C to graft polymer onto the nanotube surfaces (Scheme 1). This functionalization reaction was again followed by FTIR spectroscopy to monitor the appearance of C–H stretches at 2929 and 2860 cm^{-1} from the alkyl portions of the attached polymer (Fig. 1c). Although the isocyanate

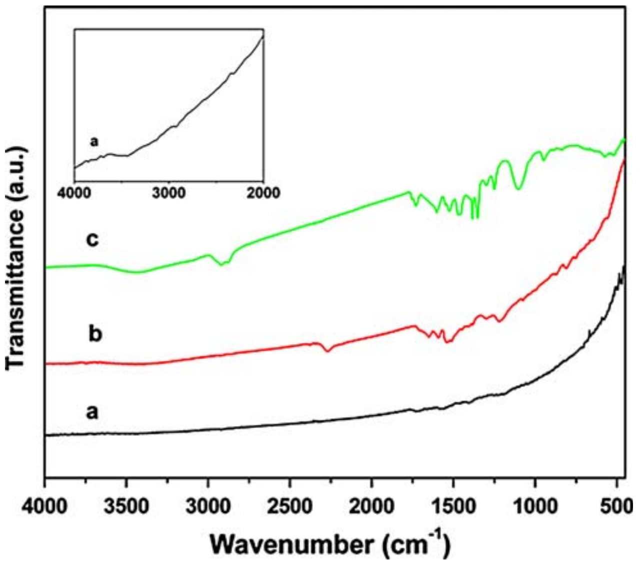


Fig. 1 FTIR spectra of (a) MWNT-OH, (b) isocyanate-functionalized MWNTs, and (c) MWNT-PEG

signal at 2270 cm^{-1} is weak, the spectra clearly indicate that the isocyanate signal is not present prior to reaction with TDI or after the addition to PEG. Compared with the FTIR spectrum of isocyanate-functionalized MWNTs, the disappearance of the isocyanate stretch after the addition to PEG indicates that most of the isocyanates must have been consumed during this reaction, although the low intensity of this FTIR absorption leaves some uncertainty. These results indicate that PEG chains have successfully grafted onto the MWNT surfaces.

To gain a quantitative picture of the extent of nanotube functionalization, the degree of MWNT solubility in water as a result of functionalization was estimated by UV-Vis spectroscopy following a procedure published by Adronov and co-workers [39]. The MWNT-PEG sample (10 mg) was dissolved in 10 mL of distilled water by sonication for 10 min and then centrifuged at 8000 rpm for 30 min followed by standing undisturbed for at least 12 h. The supernatant was collected and diluted for UV-Vis absorption measurements. The absorption values at 500 nm were plotted against nanotubes concentration (Fig. 2). TGA was employed to determine the weight percent of nanotubes within the polymer-functionalized materials, allowing the calculation of the exact amounts of nanotubes present within the dissolved material used in the absorption experiment. This specific extinction coefficient is found to be 0.0151 L mg^{-1} cm^{-1} at 500 nm and can be used to estimate the concentration of nanotube solutions. The data in Table 1 provide an indication that polymer molecular weight has a significant impact on the solubility of the conjugate materials. As expected, the polymer at a molecular weight of 4000 g/mol imparts the highest solubility at 485 mg/L.

High-resolution TEM analysis of the PEG functionalized MWNTs was performed by placing a single drop of the aqueous solution onto a holey carbon-coated copper grid. Figure 3 depicts representative TEM images for the PEG functionalized MWNTs. Figure 3a is the image of the starting MWNTs, in which the tube surface is relatively smooth and clean. Figure 3b–d shows the images of the polymer functionalized MWNTs in the different magnifications. In the lower magnification images (b and c), it can be clearly found that the tube is enwrapped by several nanometers of polymer chains, although the outer layer of polymer phase is incontinuous. In addition, the bamboo-like structure of MWNTs is maintained after the modification process. Under higher magnification, the boundary between the tube and the polymer layer becomes distinct due to the differing electron contrast of the MWNTs and PEG.

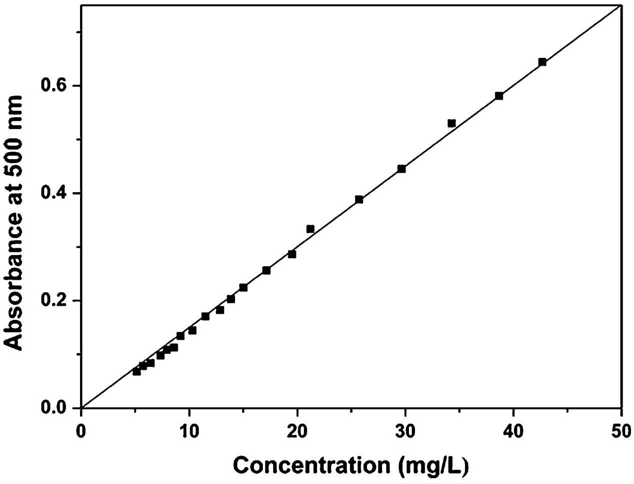


Fig. 2 Optical density at 500 nm of MWNTs in distilled water at different concentrations

Inclusion complexation of MWNT-PEG with α-CDs

Researchers have demonstrated that PEG of various molecular weights can form ICs with α-CD in high yield [26]. The key factor of inclusion process is the size matching between the cross-sectional area of polymer chain and the inner diameter of CD's cavity as well as the hydrogen bonding of neighboring CDs, which serves as the driving forces [35]. Herein, we present inclusion studies between MWNT-PEG and α-CDs. PEG of four molecular weights (M_n = 400, 1000, 2000, and 4000, respectively) was used to chemically functionalize MWNTs. In order to investigate the effect of the length of PEG chains that covalently linked to CNT surface on the inclusion complexation behavior, a series of MWNT-PEG samples with almost similar graft densities were prepared as shown in Table 1. Furthermore, a relatively lower grafting density was controlled to avoid the rapid formation of α-CD/MWNT-PEG ICs.

The simplest qualitative test to determine whether the MWNT surface bound PEGs can form ICs with α-CDs involved checking for solubility of the product in aqueous solvent. We first choose MWNT-PEG4k sample (Table 1) for this study; thus, nanotube and α-CD aqueous solutions were prepared separately followed by mixing together, and their concentrations in the mixed solution were fixed at 137 and 145 mg/mL, respectively. It was found that mixed solution became turbid and precipitates were obtained, indicating the formation of complexes. The process of ICs formation between MWNT-PEG4k and α-CDs was then recorded by an optical camera as shown in Fig. 4. Dark precipitates were observed in the MWNT-PEG4k and α-CD mixed aqueous solution system after standing for 48 h, and colorless supernatant was obtained over 100 h. Conversely, the MWNT-PEG4k aqueous solution without α-CDs remains stable for a period of at least 1 month. As reported in the literature [26], the formation of the complex is reversible. Similarly, the resulted complexes can be

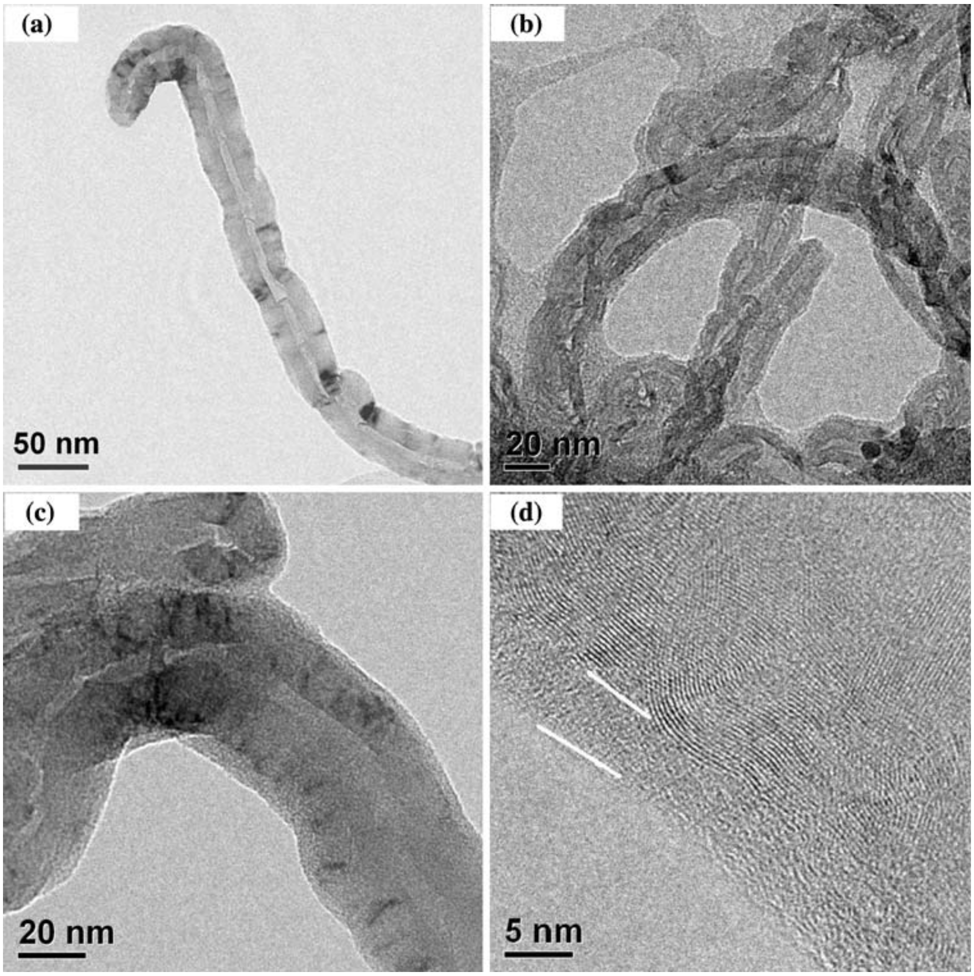


Fig. 3 Representative TEM images of MWNT-OH (**a**) and MWNT-PEG (**b–d**)

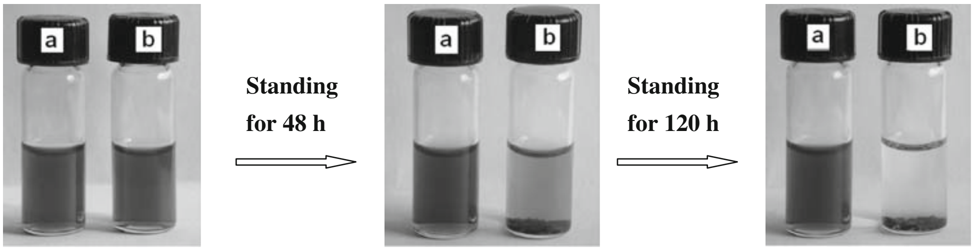


Fig. 4 Evolvement of ICs formation traced by a digital camera comparing with the native solution. (a) The aqueous solution of MWNT-PEG4k and (b) the aqueous solution of MWNT-PEG4k mixed with α-CD

redissolved in water by sonicating. Again, the addition of an excess amount of urea, which is thought to be a competitive inhibitor to the suspension of the complex, resulted in solubilization of the complex.

Supporting evidence for the conclusion that the formation of ICs between MWNT-PEG4k and α-CD comes from a comparison of the FTIR spectra of starting materials and that of the ICs. Figure 5 shows the FTIR spectra of α-CD, MWNT-PEG4k, and their ICs. It is interesting to find that the spectrum of ICs is similar to that of the pure α-CD. The extremely broad band in the 4000–3000 cm^{-1} region is assigned to the symmetric and asymmetric O–H stretching. On the other hand, the bands observed in the 3000–2000 cm^{-1} region for pure α-CD and the ICs are slightly different. The band at around 2850 cm^{-1} appeared in the ICs spectrum, which is different from the α-CD spectrum, can be attributed to the included PEG segments in their IC sample. A new band appeared at 1732 cm^{-1} in the ICs spectrum due to the carbonyl stretching from carbamate linkage is observed, which is absent from the α-CDs' spectrum. Bands in the 1200–800 cm^{-1} region are very similar for both α-CDs and ICs. These bands are referred to as stretching modes of the glucosidic group coupled with C–C and C–O stretching modes [40].

The successful threading α-CD molecules onto MWNT surface bound PEG chains prompted us to investigate the

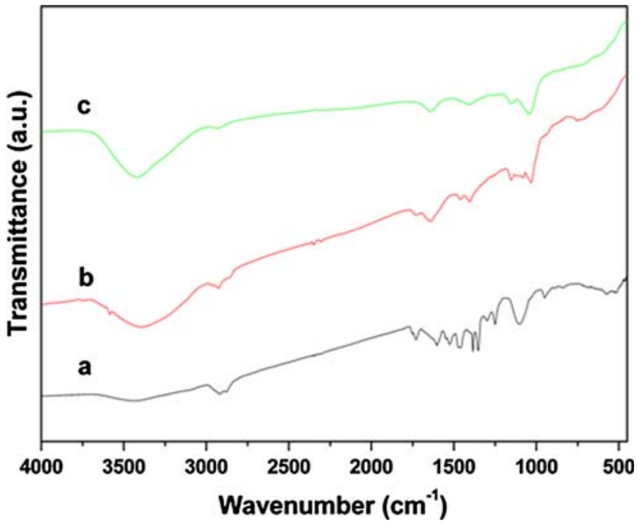


Fig. 5 FTIR spectra of (a) MWNT-PEG, (b) α-CD/MWNT-PEG4k ICs, and (c) purer α-CD

effect of polymer molecular weights on the inclusion complexation behavior. Previous studies indicated the rate of the α-CD/PEG complex precipitation depends on the molecular weight of PEG [26]. This conclusion was further proved by inclusion complexation between comb-like PEG grafted polymers and α-CD, where α-CD could form crystalline ICs with grafted polymers for long PEG side chains ($M_n > 475$ g/mol), but failed to form ICs for short PEG side chains ($M_n \leq 300$ g/mol) [35]. In this study, UV-Vis spectroscopy was employed to track the formation process of ICs between MWNT-PEG and α-CD. The ICs formation time was followed by absorbance at 500 nm with pure α-CD aqueous solution as reference (Fig. 6a), where the concentrations of MWNTs and α-CD were fixed at 137 and 145 mg/mL, respectively. Figure 6b shows the effect of the molecular weights of grafted PEG on the time of turbidity development after mixing the MWNT-PEG and α-CD solutions. Clearly, the absorbances of the mixed α-CD/MWNT-PEG4k and α-CD/MWNT-PEG2k solutions revealed a dramatic decrease with the increase of standing time. On the other hand, only a little change in absorbance was observed for the mixed solution of α-CD/MWNT-PEG1k and α-CD/MWNT-PEG04k even after standing for about 5 days. These results indicate that the time needed for the complexation was dependent on the polymer chain length that linked to MWNT surfaces. The long chains facilitate the complexation formation. Therefore, such grafted PEG chains can form ICs with α-CD, but short grafted chains are more difficult to be threaded than the long ones due to the steric hindrance from the tubes. Furthermore, the complexes are in equilibrium between the complex and its component in solution, compared with the long PEG chains, CDs can easily slide out from the short ones and no ICs can be stabilized.

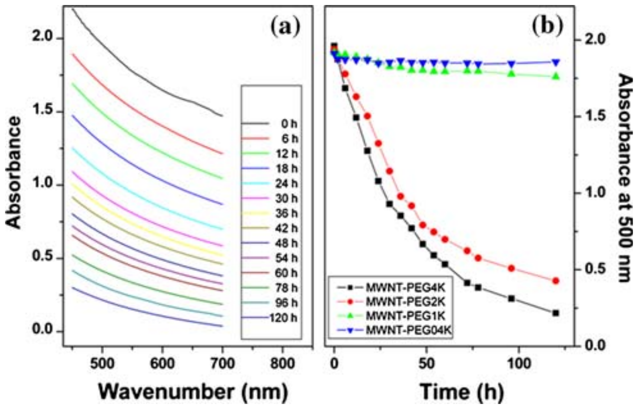


Fig. 6 The effect of the molecular weight of the grafted PEG on the ICs formation time development after mixing the MWNT-PEG and α-CD solutions. (**a**) The UV-Vis absorption spectra of α-CD/MWNT-PEG4k aqueous solution system at different standing time and (**b**) the relationship between optical density at 500 nm and standing time for α-CD/MWNT-PEG aqueous solution system as a function of the molecular weight of PEG. The initial concentrations of MWNTs and α-CD in the mixed solution were fixed at 137 and 145 mg/mL, respectively

In an attempt to alter the complexation time, while maintaining a relatively rapid ICs formation rate, the graft density for MWNT-PEG4k was changed from 0.036 to 0.125 mmol/g neat MWNTs, corresponding to the PEG mass contents ranged from 28 to 45 wt%. Using these MWNT-PEG4k materials and fixing the concentrations of nanotubes and α-CD at 137 and 145 mg/mL, respectively, in the mixed solutions, it was possible to quantitatively investigate the effects of graft densities on the time of ICs formation. Figure 7 shows the relationships between the grafted PEG contents and the ICs formation time development after mixing the MWNT-PEG4k and α-CD solutions. The ICs formation time is monitored by UV-Vis

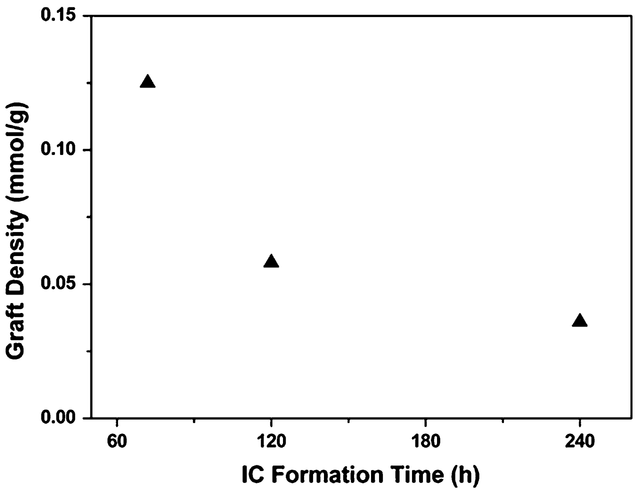


Fig. 7 The relationship between PEG grafting density and the ICs formation time development after mixing the MWNT-PEG4k and α-CD solutions

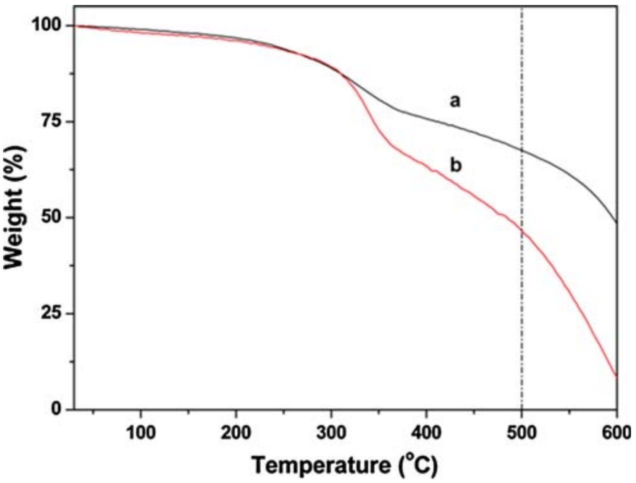


Fig. 8 Thermogravimetric analysis data for (a) MWNT-PEG4k and (b) α-CD/MWNT-PEG4k ICs, acquired under nitrogen at a ramp of 5 °C/min

absorbance of the mixed solution at 500 nm as mentioned previously, and is defined as the total time required to lower the absorbance of the solution from its initial value to a given absorbance, i.e., 0.2. Clearly, higher PEG contents on the MWNT surface led to the rapid formation of ICs, whereas lower content resulted in slow rate.

To gain a quantitative picture of the mass content of α-CD in the ICs, TGA analysis was performed on the α-CD/MWNT-PEG4k complex as depicted in Fig. 8. For comparison, the TGA plot of native MWNT-PEG4k was also shown in Fig. 8, and indicated a gradual mass loss of around 33 wt% as the temperature reaches 500 °C. Similarly, there was a distinct mass loss region between 200 and 500 °C for the complex. If the mass loss of the MWNT-PEG4k at 500 °C is used as the reference, the mass loss of the complex at 500 °C is about 53 wt%. This result indicates that there is about 20 wt% of α-CDs that have been threaded onto the nanotube bound PEG chains. Considering that the starting tube has a PEG graft density of about 0.056 mmol/g neat MWNTs, the TGA result indicates that the ratio of EG unit to α-CD of the resulted ICs is about 15:1. It has reported that the stoichiometry for a fully threaded linear PEG/α-CDs IC is 2:1, which means that two EG repeat units are threaded by one α-CD ring. Compared to the linear PEG, the fact that fewer α-CDs were threaded by grafted PEG chains demonstrated that some of EG units, presumably those near the nanotubes, were difficult to be threaded by α-CDs due to the steric hindrance between tube and grafted chains. Furthermore, some α-CD rings may slide out from the PEG chains when washed with water.

Figure 9 displays the SEM images of MWNT-PEG4k and the ICs sample. The MWNTs were clearly observed and the convex surfaces of PEG functionalized MWNTs seemed to be relatively smooth due to relatively low degree of functionalization. In contrast, in the SEM image of ICs, the polymer almost formed a continuous phase, and the MWNTs were submerged in the polymer phase (Fig. 9b), suggesting that there is a significant amount of polymers in the ICs precipitate. In addition, the ICs SEM image also show that the PEG functionalized nanotubes became thicker after being threaded with α-CDs. These results demonstrate that the α-CD rings have been threaded onto the MWNT surface bound PEG chains.

In order to get a closer structural investigation of the ICs, TEM analysis of the α-CD/MWNT-PEG4k complex was performed by placing a single drop of the ethanol suspension onto a holey carbon-coated copper grid. Figure 10 shows the representative TEM micrograph of the ICs. It is very evident that the nanotubes encapsulated by ICs are tangled together (Fig. 10a, b). Under higher magnification, the TEM image (Fig. 10d) shows that the tube is enwrapped by a ICs layer that is several nanometers thick, again suggesting the PEG functionalized nanotubes became thicker after being threaded with α-CDs.

Conclusion

PEGs with different molecular weights were covalently coupled onto MWNT surfaces by “grafting to” approach using TDI as coupling agents. The water-soluble PEG

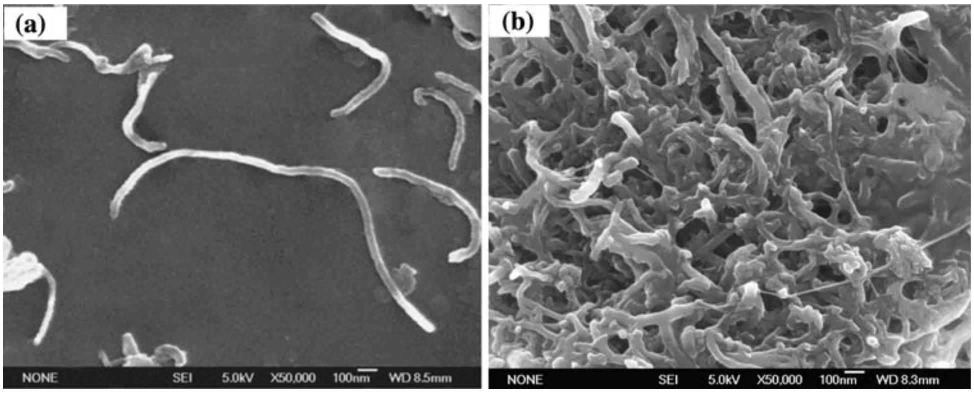


Fig. 9 SEM images of MWNT-PEG4k (**a**) and α-CD/MWNT-PEG4k ICs (**b**)

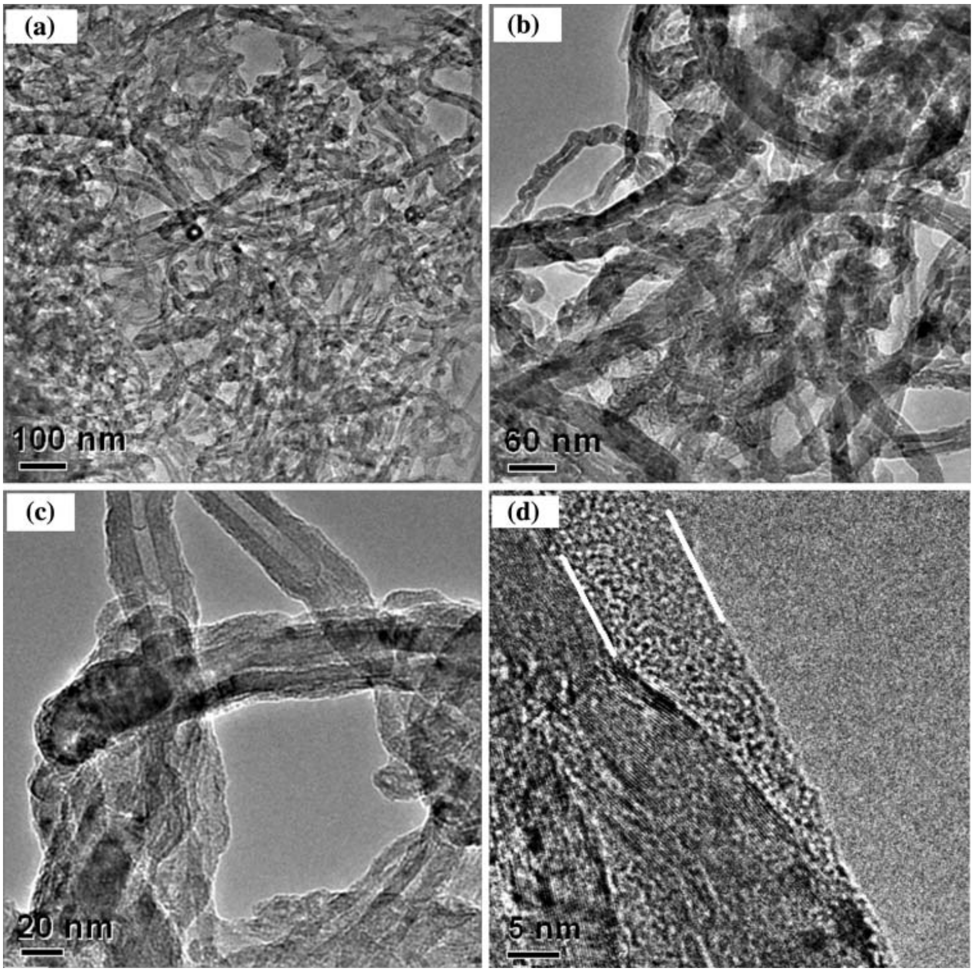


Fig. 10 TEM images of α-CD/MWNT-PEG4k ICs

functionalized MWNTs were confirmed by FTIR, UV-Vis, TGA, and TEM techniques. The ICs between PEG functionalized MWNTs and α-CD were successfully prepared and characterized. The ICs formation time was monitored by UV-Vis spectroscopy, and the results indicated that the inclusion interaction between MWNT surface anchored PEG chains and α-CD was dependent on the molecular weight of PEG. The grafted PEG with molecular weight of 4000 and 2000 g/mol, respectively, can form ICs with α-CD, while the grafted PEG of 1000 and 400 g/mol, respectively, were difficult to form ICs with α-CD due to the steric hindrance. The stoichiometry value determined by TGA indicated that the ratio of EG unit to α-CD in the resulted ICs was about 15:1. In addition, the morphology of the ICs was observed by SEM. The complexation of CDs with such kind of nanotube surface bound polymers is highly interesting and is the focus of our ongoing investigations.

Acknowledgement Financial support from NSF China (no. 20674065), Program for NCET, SRF for ROCS, SEM, and the Key Project of Scientific Research Funds of Hunan Provincial Education Department (07A072) is greatly acknowledged.

References

1. Ajayan PM (1999) Chem Rev 99:1787. doi:10.1021/cr970102g
2. Dai HJ (2002) Acc Chem Res 35:1035. doi:10.1021/ar0101640
3. Hirsch A (2002) Angew Chem Int Ed 41:1853. doi:10.1002/1521-3773(20020603)41:11<1853::AID-ANIE1853>3.0.CO;2-N
4. Wang G, Li YX, Huang YH (2005) J Phys Chem B 109:10957. doi:10.1021/jp050030u
5. Blake R, Gunko YK, Coleman J, Cadek M, Fonseca A, Nagy JB (2004) J Am Chem Soc 126:10226. doi:10.1021/ja0474805
6. Ramanathan T, Fisher FT, Ruoff RS, Brinson LC (2005) Chem Mater 17:1290. doi:10.1021/cm048357f
7. Wang J, Liu GD, Jan MR (2004) J Am Chem Soc 126:3010. doi:10.1021/ja031723w
8. Kam NWS, Dai HJ (2005) J Am Chem Soc 127:6021. doi:10.1021/ja050062v
9. Chattopadhyay J, Cortez FJ, Chakraborty S, Slater NKH, Billups WE (2006) Chem Mater 18:5864. doi:10.1021/cm0611082
10. Kahn MGC, Banerjee S, Wong SS (2002) Nano Lett 2:1215. doi:10.1021/nl025755d
11. Chen RJ, Zhan YG, Wang DW, Dai HJ (2001) J Am Chem Soc 123:3838. doi:10.1021/ja010172b
12. Fernando KAS, Lin Y, Sun YP (2004) Langmuir 20:4777. doi:10.1021/la036217z
13. Zhao B, Hu H, Haddon HC (2004) Adv Funct Mater 14:71. doi:10.1002/adfm.200304440

14. Sano M, Kamino A, Shinkai S (2001) Angew Chem Int Ed 40:4661. doi:10.1002/1521-3773(20011217)40:24<4661::AID-ANIE4661>3.0.CO;2-V
15. Sun YP, Fu K, Lin Y, Huang WJ (2002) Acc Chem Res 35:1096. doi:10.1021/ar010160v
16. Hong CY, You YZ, Pan CY (2005) Chem Mater 17:2247. doi:10.1021/cm048054l
17. Kong H, Li WW, Gao C, Yan DY, Jin YZ, Walton DRM et al (2004) Macromolecules 37:6683. doi:10.1021/ma048682o
18. Huang W, Fernando S, Allard LF, Sun YP (2003) Nano Lett 3:565. doi:10.1021/nl0340834
19. Pompeo F, Resasco DE (2002) Nano Lett 2:369. doi:10.1021/nl015680y
20. Hazani M, Naaman R, Hennrich F, Kappes MM (2003) Nano Lett 3:153. doi:10.1021/nl025874t
21. Pantarotto D, Partidos CD, Graff R, Hoebeke J, Briand JP, Prato M et al (2003) J Am Chem Soc 125:6160. doi:10.1021/ja034342r
22. Baker SE, Cai W, Lasseter TL, Weidkamp KP, Hamers RJ (2002) Nano Lett 2:1413. doi:10.1021/nl025729f
23. Huang W, Taylor S, Fu K, Lin Y, Zhang D, Hanks TW et al (2002) Nano Lett 2:311. doi:10.1021/nl010095i
24. Yang M, Gao Y, Li HM, Adronov A (2007) Carbon 45:2327. doi:10.1016/j.carbon.2007.07.021
25. Szejtli J (1998) Chem Rev 98:1743. doi:10.1021/cr970022c
26. Harada A, Li J, Kamachi M (1993) Macromolecules 26:5698. doi:10.1021/ma00073a026
27. Harada A, Li J, Kamachi M (1994) J Am Chem Soc 116:3192. doi:10.1021/ja00087a004
28. Harada A, Okada M, Li J, Kamachi M (1995) Macromolecules 28:8406. doi:10.1021/ma00128a060
29. Harada A, Suzuki S, Okada M, Kamachi M (1996) Macromolecules 29:5611. doi:10.1021/ma960428b
30. Harada A, Nishiyama T, Kawaguchi Y, Okada M, Kamachi M (1997) Macromolecules 30:7115. doi:10.1021/ma970680z
31. Huang L, Allen E, Tonelli AE (1998) Polymer (Guildf) 39:4857. doi:10.1016/S0032-3861(97)00568-5
32. Huang L, Allen E, Tonelli AE (1999) Polymer (Guildf) 40:3211. doi:10.1016/S0032-3861(98)00529-1
33. Yoshida K, Shimomura T, Ito K, Hayakawa R (1999) Langmuir 15:910. doi:10.1021/la9812471
34. Kawaguchi Y, Nishiyama T, Okada M, Kamachi M, Harada A (2000) Macromolecules 33:4472. doi:10.1021/ma992103b
35. He LH, Huang J, Chen YM, Liu LP (2005) Macromolecules 38:3351. doi:10.1021/ma047748c
36. Wang ZM, Chen YM (2007) Macromolecules 40:3402. doi:10.1021/ma0702593
37. Ogoshi T, Takashima Y, Yamaguchi H, Harada A (2007) J Am Chem Soc 129:4878. doi:10.1021/ja070457
38. Jia ZJ, Wang ZY, Liang J, Wei BQ, Wu DH (1999) Carbon 37:903. doi:10.1016/S0008-6223(98)00229-2
39. Liu YQ, Yao ZL, Adronov A (2005) Macromolecules 38:1172. doi:10.1021/ma048273s
40. Casu B, Reggiani M (1964) J Polym Sci 7(Part C):171