

SURFACE COVALENT ENCAPSULATION OF MULTI-WALLED CARBON NANOTUBES BY POLYMER GRAFT

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Abstract

Hydroxyl groups present on the surface of multi-walled carbon nanotubes (MWCNTs) treated with a mixture of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ (1:1, v/v), were first directly used as reaction sites to covalently functionalize MWCNTs through grafting active polymer onto the MWCNT surface. MWCNTs were covalently grafted with poly (acryloyl chloride) (PACl) via esterification reaction of acyl chlorides. It was reasonable to believe that only a small fraction of acyl chloride groups was consumed in the attachment of PACl to MWCNTs, and the major part of acyl chloride groups remained intact. These high active groups possess various derivability of chemistry, and were readily subjected to esterification reaction with poly (ethylene glycol) (PEG), leading to surface grafted polymer chains. Thus grafted MWCNTs were characterized using Fourier transform infrared spectrometer, transmission electron microscopy, and X-ray photoelectron spectroscopy. Thermogravimetric analysis showed that the weight fraction of grafted polymers amounted to 80% of the modified MWCNTs. The polymer-grafted MWCNTs have good dispersibility in chloroform, tetrahydrofuran, dimethylsulfoxide and dimethylformamide, and the resulting dispersions in these solvents were very stable without any observable black deposit from these dispersions for long time. Thanks to high reactivity of acyl chloride groups of grafted PACl, other polymer with reactive groups as well as PEG can be used to covalent graft.

Introduction

Recently the studies on polymer-multiwalled carbon nanotubes (MWCNTs) composites and hybrid materials have attracted increasing interest due to their excellent mechanical and electronic properties of MWCNTs. It is believed that the incorporation of MWCNTs in polymer matrices should provide unique properties. However, it is difficult to well disperse MWCNTs in the polymer matrix; on the other hand the atomically smooth surface of MWCNTs provides poor interfacial adhesion to the matrices, which limited effective load transfer from the matrices to MWCNTs. As a result, the surface modification of MWCNTs is essential to improve the dispersion in media and the interfacial adhesion to the matrix. Currently increasing researches have demonstrated that the covalent grafting of polymer chains onto the surface of MWCNTs constituted an effective methodology of surface modification.

Treatment of MWNT with strong acids has been proven to be an effective way to generate hydroxyl, carbonyl and/or carboxylic groups on the MWNT's surface. According to researches performed by Yu et al, oxidation of MWCNTs with a mixture of concentrated H_2SO_4 and HNO_3 (1:1, v/v) resulted in a relatively large number of hydroxyl functional groups present at the MWCNTs surface besides carboxylic groups.

In order to effectively attach characteristic polymers, especially comb, brush and graft chains, a two-step approach was proposed in this paper. First, using hydroxyl groups present at the surface of acid-treated MWCNTs as the reaction sites, linear poly (acryloyl chloride) with high reactive acyl chloride side groups was covalently grafted. Subsequently, the acryloyl chloride groups on the graft were allow to link with poly (ethylene glycol) generating a grafted-chain structure, which is also called polymer analogous reactions. Such polymer usually serve as polyelectrolytes in batteries, stabilizers in dispersion or emulsion systems, antistatic agents, drug carriers, additives for stabilization of polymer blends or for surface modification of organic materials, and so on.

Thanks to high reactivity of acyl chloride groups of grafted poly (acryloyl chloride), other polymer or organic molecules with reactive groups as well as PEG can be used to form these polymers on the MWCNTs surface. Therefore, this reasons the work present in this paper constitutes a model for a variety of such modifications.

Methods and procedures

A suitable amount of raw MWNT (purity \geq 95%, diameter 10-20nm and length 0.5-500 μm) was suspended and refluxed in concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture (20ml/20ml) for 1 hour at 140 $^\circ\text{C}$, followed by dilution of this suspension with deionized water (500ml). The acid-treated MWNT was retrieved and washed repeatedly with deionized water, and dried in vacuum. The hydroxyl groups generated on the surface of MWNT were characterized with XPS.

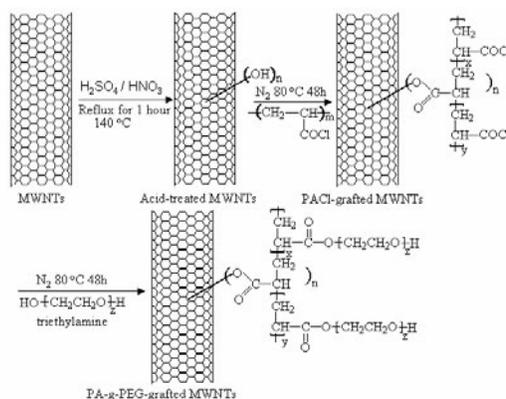
Poly (acryloyl chloride) was prepared via free radical polymerization of acryloyl chloride, referred to the method employed by Strohriegel et al. In a 20ml dry Schlenk tube equipped with a magnetic stirring bar, a solution of acryloyl chloride (1.5ml) and 2, 2'-azobisisobutyronitrile (AIBN, 25mg) in anhydrous dioxane (1.5ml) was stirred for 48h at 60 $^\circ\text{C}$ protected with dry nitrogen atmosphere.

The solution of poly (acryloyl chloride) obtained above was introduced into a suspension of acid-treated MWCNTs (50mg) in anhydrous 1, 4-dioxane (100mL), then the mixture was kept vigorously stirring at 80 $^\circ\text{C}$ under nitrogen atmosphere

for 48h. The solid product was collected and washed 5 times with anhydrous THF, and finally was placed in dry nitrogen atmosphere. All the procedures were carried out under nitrogen protection. PACl-grafted MWCNTs were obtained.

The poly (acryloyl chloride)-grafted MWCNTs were suspended in 50ml of anhydrous dioxane and subjected to sonication for 2 hours. Subsequently the suspension was added dropwise to a solution of PEG (26g) and triethylamine (2.7ml) in anhydrous dioxane (100ml) at 0°C under nitrogen atmosphere with vigorously stirring. After the addition, the system was heated to 80°C and kept vigorously stirring for 24h. Upon vacuum filtration, the remaining black product was washed several times with ethanol and was re-dispersed in THF by sonication for 2h and allowed to stand for 24h. Repeating the filtration, wash and dispersion with THF procedures for 8 times, the final product was dried under vacuum for 8 h at 50°C. The reactions mentioned above were shown in Scheme 1.

Results and discussion



Scheme 1. Synthetic procedure of PA-g-PEG-grafted MWCNTs.

Figure 1 shows deconvolution of high-resolution XPS spectrum of C_{1s} for acid-treated MWCNTs. The peak centered at 284.2eV was assigned to both sp^2 -hybridized graphite-like and hydrogen bound carbon atoms. The peak at 285.1eV originated from sp^3 -hybridized diamond-like carbon atoms. Peaks at 286.2, 287.7, and 288.9eV were assigned to the C1s of hydroxyl carbon, carbonyl carbon, and carboxyl carbon, respectively, because carbon atoms bound to oxygen atoms lead to higher binding energies of C1s. The peak at 290.9eV was commonly assigned to the π - π^* transition levels (free electrons of the graphitic plane). Based on above assignment, the ratio of hydroxyl, carbonyl and carboxyl functional groups was calculated to be about 14mol%, 13mol%, and 7mol%, respectively, in which the hydroxyl groups were further used as the reaction sites for esterification.

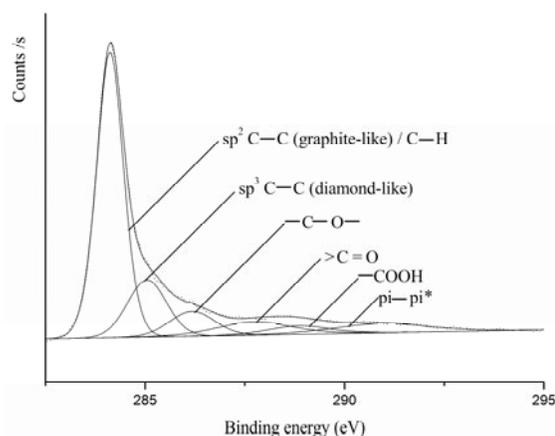


Figure 1. High-resolution XPS spectrum of C_{1s} for acid-treated MWCNTs. Back dots express experimental data curve, and solid line is fitting curve from deconvolution for C_{1s} spectrum.

GPC trace of poly (methyl acrylate) indicated a number-average degree of polymerization of 140. Since the poly (methyl acrylate) was obtained via the reaction between excess amount of methanol and poly (acryloyl chloride), the obtained degree of polymerization was supposed to be equal to that of the latter.

The infrared spectra of various species were presented in Figure 2. The acid-treated MWNT (2a), the broad peak at 3414cm^{-1} was assigned to O-H stretch vibration in hydroxyl groups, the peak at 1704cm^{-1} corresponded to the carboxylic C=O stretch vibration, and the one at 1565cm^{-1} was attributed to C-C stretch vibration of the bulk MWNT. The peaks at

2918 cm^{-1} and 2848 cm^{-1} can be assigned to C-H stretch vibration of methylene at the defect sites of acid-treated MWNT surface. The neat PACl was featured by the C=O stretch vibration of acyl chloride group at 1801 cm^{-1} (4b). After functionalization with PACl, the new peaks appeared in the spectrum of PACl-grafted MWNT, compared with acid-treated MWNT. The broad peak at 2925 cm^{-1} was assigned to C-H stretch vibration of polymer backbone, and the peaks at 1803 and 1756 cm^{-1} originated from C=O stretch vibration of acyl chloride. Since the PACl-grafted MWCNTs samples were repeatedly washed with THF, the IR features suggested that PACl was covalently attached to the surface of MWNT instead of physically absorbing.

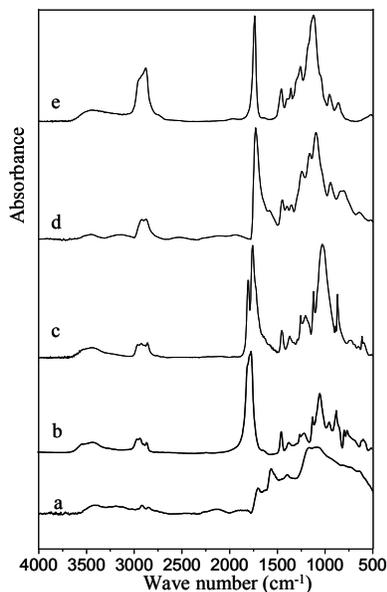


Figure 2. FTIR of acid-treated MWCNTs (a), poly (acryloyl chloride) (b), PACl-grafted MWCNTs (c), PA-g-PEG-grafted MWCNTs (d) and PA-g-PEG (e).

It was reasonable to believe that only a small fraction of acyl chloride groups was consumed in the attachment of poly (acryloyl chloride) to MWCNTs, and the major part of acyl chloride groups remained intact, which was ready to react with poly (ethylene glycol) (PEG), leading to surface grafted polymers. The reaction procedure was shown in the EXPERIMENTAL section. During the addition of the suspension of PACl-grafted MWCNTs in dioxane into PEG solution, a slow dropping rate was necessary to avoid crosslinking between polymers. The FTIR spectrum of the polymer-grafted MWNT was shown in Figure 2 (d). The peak at 3444 cm^{-1} was assigned to side terminal hydroxyl groups in the grafted polymer. The peak at 1724 cm^{-1} was attributed to the C=O stretching vibrations of the ester carbonyl group. The peaks at 1092 and 1240 cm^{-1} were attributed to the characteristic C–O–C stretching vibrations of the repeated –OCH₂CH₂ units of PEG and the –COO–bonds stretching vibrations, respectively. All the features for C–H stretching were centered at 2916 and 2871 cm^{-1} . The characteristic vibrations of acyl chloride groups at 1803 cm^{-1} were no longer shown in Figure 2d indicating all the PACl-bound acyl chloride groups were esterified. A comparison between the traces of 2d and 2e (for neat PA-g-PEG) confirmed that the PA-g-PEG was indeed covalently attached onto the surface MWCNTs.

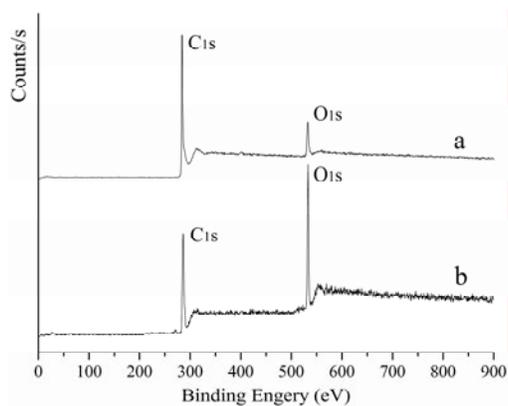


Figure 3. Survey XPS spectra of acid-treated MWCNTs (a) and PA-g-PEG-grafted MWCNTs (b).

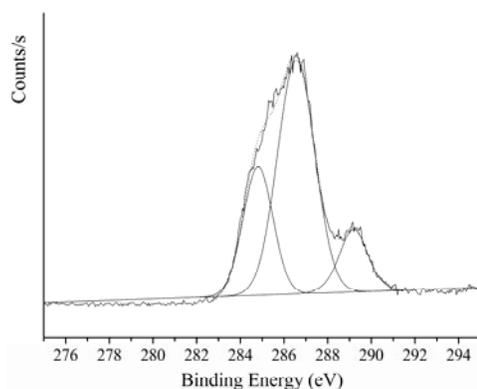


Figure 4. High-resolution XPS spectrum of C_{1s} for PA-g-PEG-grafted MWCNTs. Black solid curve expresses experimental data curve, and black dots are fitting curves from peaks deconvolution for spectrum.

Figure 3 was the XPS trace for the PA-g-PEG-grafted MWNT. Compared with that for the acid-treated ones in Figure 3 (a), the peak of O_{1s} in Figure 3 (b) became obviously stronger, which can be attributed to the PEG side chains. The relative atomic concentrations of carbon and oxygen became 70% and 30% respectively. In Figure 4 the C_{1s} peak was deconvoluted into three contributions. The peak at 284.8eV was assigned to both carbon atoms bound to hydrogen atoms on the grafted polymer chains and graphitic carbon atoms of MWCNTs. The peak at 286.6eV arose from the C_{1s} of etheric carbons (C-O-C) in the grafted polymer branches chains. The peak at 289.1eV was attributed to the C_{1s} of the ester carbon atoms (O-C=O) in the grafted polymer. However the $\pi\text{-}\pi^*$ transition peak at 290.9eV disappeared in this C_{1s} spectrum, indicating some covalent bonds were formed between the nanotube surface and grafted polymer. The XPS spectra provided a strong evidence for the formation of PA-g-PEG polymer in nanotube surface.

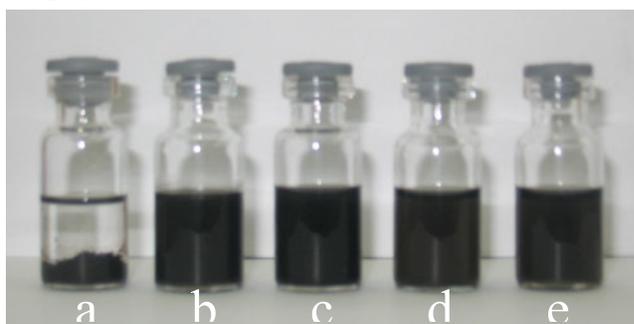


Figure 5. Suspensions of MWCNTs in various solvents: acid-treated MWCNTs in $CHCl_3$ (a) and PA-g-PEG-grafted MWCNTs in $CHCl_3$ (b), THF (c), DMSO (d) and DMF (e).

The grafting of PA-g-PEG onto the MWCNTs surface greatly improved the dispersibility of MWCNTs in solvent. The raw MWCNTs were insoluble in any solvents. Acid-treated MWCNTs, with some hydroxyl and carboxylic functional groups on the surface, can be suspended in chloroform for 2 days without deposit. After 4 days, acid-treated MWCNTs were completely deposited from chloroform, as seen from Figure 5. However, the polymer-grafted MWCNTs have good dispersibility in chloroform, THF, DMSO and DMF, and the resulting dispersions in these solvents were very stable without any observable black deposit from these solutions for 3 months, as shown in Figure 5.

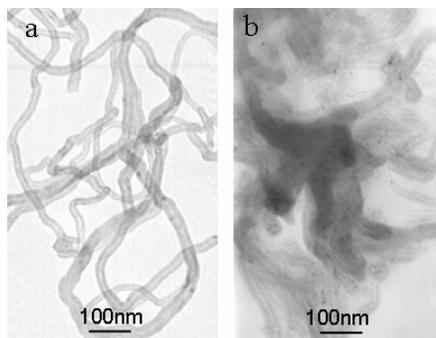


Figure 6. TEM images of acid-treated MWCNTs (a) and PA-g-PEG-grafted MWCNTs (b).

Figure 6 present the TEM micrographs of the morphology of the acid-treated and the polymer-grafted MWCNTs. Before grafted with PACl, acid-treated MWNT exhibited a semi-transparent appearance with somewhat sharp contrast to the background. However, after grafted with PA-g-PEG, the edge of MWNT became blurred. The surface of grafted-MWCNTs looked smeared, likely attributed to a result of swelling of the grafted polymer by the solvent, making a contrast to the smooth surface of acid-treated MWNT. The polymer attached to the surface was never removed away via soaking in solvent for a long time (several weeks), indicating that the polymer was indeed covalently linked to the nanotubes.

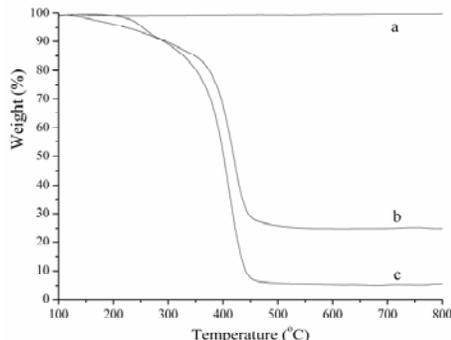


Figure 7. TGA results of raw MWCNTs (a), PA-g-PEG-grafted MWCNTs (b) and PA-g-PEG (c).

Figure 7 was TGA traces for various species. The raw MWNT (trace a) kept stable without significant weight loss until 800°C. Neat PA-g-PEG (trace c) lost about 95% of its original weight before 500°C. In contrast, that of the polymer-grafted MWNT (trace b) was somewhere intermediate between those of the raw MWNT and neat the polymer. There was a shape reduction of weight, which was similar to that of neat the polymer, and a larger weight was retained above 550°C. Two stages of weight loss for the grafted MWNT could be identified, one from 215 to 270°C and the other from 270 to 550°C. Apparently, the first stage was associated with the decomposition of the functional groups on the surface of MWNT. The major weight loss between 270 and 550°C can be undoubtedly assigned to the thermal decomposition of grafted polymer. The plateau in the TGA trace after 550°C was attributed to residue of the grafted polymer and the MWNT. Based on these TGA traces, the amount of the grafted chains on the MWNT could roughly be estimated, and the weight fraction of the polymer chains in the grafted MWNT was calculated to be about 80%.

In summary, Covalent functionalization of multi-walled carbon nanotubes (MWCNTs) with PA-g-PEG has been successfully achieved via covalent formation of polymer on nanotubes surface, which was confirmed with FTIR, XPS spectroscopy, and TEM measurements. Thermogravimetric analysis (TGA) of the grafted MWCNTs showed that the weight ratio of the polymer attached to the nanotubes surface was about 80%. Thanks to high reactivity of acyl chloride groups of grafted poly (acryloyl chloride), other polymers or organic molecules with reactive groups as well as PEG can be used to form the grafted polymer on the MWCNTs surface. Therefore, this reasons the work present in this paper constitutes a model for a variety of such modifications.

Acknowledgements

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