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Preparation and Characterization of Poly(methyl methacrylate)-functionalized Carboxyl Multi-walled Carbon Nanotubes†

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An in situ polymerization process was used to prepare poly (methyl methacrylate) (PMMA)-functionalized carboxyl multi-walled carbon nanotubes using carboxylate carbon nanotubes and methyl methacrylate as reactants and benzoyl peroxide as an initiator agent. The functionalized multi-walled carbon nanotubes were characterized using transmission electron microscope, scanning electron microscope, nuclear magnetic resonance, Fourier transform infrared spectroscopy, thermogravimetric analysis and Raman. The results indicate that the PMMA chains are covalently linked with the surface of carboxylate carbon nanotubes. The surface morphology is controlled by the content of carboxylate carbon nanotubes in the reactants. The PMMA functionalized multi-walled carbon nanotubes are soluble in deuterated chloroform. The storage modulus and tanδ magnitude increase as the content of CCNTs increases up to 0.3%.

Key words: Carbon nanotube, Methyl methacrylate, in situ polymerization, Morphology, Solubility

I. INTRODUCTION

Since discovered by Iijima in 1991 [1], carbon nanotubes (CNTs) have attracted more and more attention due to their excellent mechanical [2], thermal, and magnetic properties etc. [3]. Two main types of carbon nanotubes (CNTs) have high structural perfection. Single-walled nanotubes (SWNT) consist of a single graphene sheet seamlessly wrapped into a cylindrical tube. Multi-walled nanotubes (MWNT) comprise an array of nanotubes that are concentrically nested. The Young’s modulus of a SWNT is as high as 5 TPa. Young’s modulus of MWNTs is as high as 1.8 TPa and bending strengths as high as 14.2 GPa [4]. CNTs are able to withstand repeated bending, buckling and twisting, which result in building lightweight nanocomposites matrix. CNTs has been widely considered as attractive candidates for important composition hybrids for fabricating novel materials with desirable properties. The key problem for CNT/polymer composite elaboration is the dispersion, compatibilization, and stabilization of the CNTs in the polymer matrix. Grafting macromolecules onto the convex walls of CNTs has been explored for several years. It has been reported that water-soluble carbon nanotubes can be functionalized with polystyrene [5], poly(acrylic acid) [6], poly(n-butyl methacrylate) [7], poly(N-isopropylacrylamide) [8], poly(tert-butyl acrylate) [9], poly(sodium 4-styrylresulfonate) [6], poly(N-vinylcarbazole) [10], crown ethers [11], glucosamines [12], biological molecules such as DNA [13], peptides [14], and proteins [15], etc. through sidewall functionalization [16]. Poly (methyl methacrylate) (PMMA) is a very important thermoplastic. PMMA-CNTs nanocomposites could be prepared by solution mixing [17], melt blending [18], in situ polymerization [19] and atom transfer radical polymerization (ATRP) [20]. In this work, PPMACN were prepared by in situ polymerization approach. The surface morphology and solubility of poly (methyl methacrylate)-functionalized carboxyl carbon nanotubes (PPMAMCN) were investigated.

II. EXPERIMENTS

Carboxylic multi-walled carbon nanotubes (CCNTs) were obtained from Institute of Organic Chemistry in Chengdu of the Chinese Academy of Sciences. The CCNTs were made by the oxidative acid treatment of the as-produced CNTs.

Benzoyl peroxide (BPO) was purified by dissolving in chloroform and re-precipitating with methanol. Methyl methacrylate (MMA), obtained from the Development Center of Chemical Agents in Tianjin, was washed with 5% sodium hydroxide aqueous solution, dried with anhydrous calcium chloride for 24 h, and vacuum distilled. Other reagents were obtained from the Development Center of Chemical Agents in Tianjin and were used without further purification. In this process, the predetermined amount of CCNTs and the BPO were added into MMA. The mixtures were fully mixed ultrasonically and stirred for 20 min. Then heated to 80-85 °C, a BPO molecule decomposed into two free radicals, the C=C double bond in MMA molecule and CCNTs would be opened [21], and then linked with

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each other to form a long chain of PMMA molecules on the surfaces of the CCNTs. The reaction lasted for 30 min. The poly(methyl ethacrylate)-functionalized carbon nanotubes samples containing 0.1%, 0.3%, 0.5%, 1%, and 2% of CCNTs were synthesized. After being poured into the little test tube, the viscous mixtures of PMMACN were heated to 40-45 °C, held for 20 h. After then the mixtures were stepped up to 100 °C for 2 h, and cooled to room temperature.

The transmission electron microscope (TEM) measurements were carried out using a Philips Tecnai F20 analytical electron microscope with a field emission source. The accelerating voltage was 20 kV. TEM samples were prepared by ultrasonic dispersion of the CCNTs in ethanol, placing a drop on a copper grid and drying at room temperature. The morphologies of the surfaces of the PMMACN were observed using scanning electron microscope (SEM, Quanta 200 in Czech). Thermogravimetric analysis (TGA) experiment was performed with NETZSCH STA409 PC/PG TG-DTA thermal analyzer system under N₂ flow at a heating rate of 10 °C/min. FT-IR spectra of the samples were obtained using a VECTOR22 FT-IR spectrometer. The sample was dissolved in acetone and formed a liquid film for measurement. The samples were dispersed in CDCl₃ and stayed. To extract the defecated solution in the test tube, ¹H-NMR spectroscopy in CDCl₃ was recorded at 300 MHz on a BRUKER 300 UltraShield at 295 K. The Raman measurements were carried out on a microRaman system (Instruments Invia, Renishaw) using a spectra-physics argon ion laser at an excitation wavelength of 514.5 nm (2.41 eV). The characterization peak of CDCl₃ appears at δ=3.6 ppm ascribes to methyl proton of ester.

III. RESULTS AND DISCUSSION

Figure 1 shows the TEM image of CCNTs. The CCNTs are curved and coiled. They are central hollow tubes in the center, with 5-10 nm in internal diameter, 10-20 nm in external diameter, 0.5-500 μm in length, and 10-30 graphite layers. CCNTs are partially oxidized via acid treatment and have carboxylic functionalities and double bond [22] in the open ends, sidewalls and defect sites. The CCNTs contain approximately 2% carboxylic groups according to the product description. In higher resolution, small quantities of impurities are presented in the form of amorphous carbon and multi-shell carbon nanocapsules. The surface of the CCNTs indicates the presence of some defects associated with the formation of carboxylic groups and double bond on the surface [21,22]. The open end is destroyed by oxidation of the strong acid, and the exterior carbon layer appears fractured.

In order to investigate the interaction and compatibility between CCNTs with PMMA chains, the morphologies of cross section and profile section of PMMACN in various contents of CCNTs were observed using SEM. Figure 2 shows the SEM images of the PMMACN for 0.1%, 0.3%, and 0.5% concentration in cross section. Figure 3 shows the SEM images of the PMMACN for 0.3% concentration in profile section.

Several features can be noticed as follows. First, for the concentration of 0.1% CNTs (Fig.3(a)), PMMACN show a relatively regular pane structure. The similar structure is not reported in former literatures [17-20]. The inside of the pane is somewhat darker than the rim. No aggregation of CCNTs is observed on different areas of the sample. In the 0.3% concentration sample (Fig.3(b)), the relatively regular pane structures are destroyed and a little amount of dendritic structures appear. The results show that the CCNTs are not simple aggregation and they probably are linked with each other by the PMMA chains. For the concentration of 0.5% (Fig.3(c)), we notice more regular dendritic structures of CCNTs. In specific area of cross section, we find that the CCNTs are covered with PMMA chains (Fig.3(d)). The dendritic structures are self-organized of CCNTs with PMMA chains. In Fig.3, we also notice a uniform distribution of CCNTs, and good compatibility between the CCNTs with PMMA chains.

The chemical structures of PMMACN were examined by ¹H NMR and FT-IR spectra. In the ¹H-NMR of CCNTs, the characteristic peak of CDCl₃ appears at δ=0.02 ppm, δ=1.56 ppm, and δ=7.28 ppm (Fig.4(a)). There are no characteristic peaks of CCNTs in ¹H-NMR, since only the defecated solution is used. It indicates that the CCNTs do not dissolve in CDCl₃. In the spectrum of PMMACN, the characteristic peaks of PMMA, δ=3.6 ppm ascribes to methyl proton of ester.
FIG. 2 SEM images of PMMACN with different concentration of CCNT (a) 0.1%, (b) 0.3%, and (c), (d) 0.5% in cross section.

FIG. 3 SEM images of PMMACN for 0.3% concentration of CCNT in profile section.

unit and $\delta=1.0-2.1$ ppm ascribes to the methylene associated with the backbone of the grafted PMMA chain. The result is similar to that reported by Xu and coworkers [23]. Notably, the peaks clearly appearing in the spectrum at $\delta=7.5-7.6$ ppm and $\delta=8.1$ ppm respectively are similar to the peaks of polycyclic aromatic hydrocarbon. We suppose that these peaks ascribe to the hydrogen species of CCNTs. This result shows that the PMMA functionalized CCNTs are dissolved in CDCl$_3$, the PMMA chains are linked with the CCNTs.

The CCNTs were insoluble in CHCl$_3$. The PMMACN are soluble in CHCl$_3$ and showed good solubility in CHCl$_3$, forming a gray solution which is stable for weeks. The stability suggests that the CCNTs are covalently bound grafted PMMA and not adsorbed polymer. Such linkage strongly influences the physical properties of the tubes. Xu and coworkers also prepared a fascinating nanoobject, which are diblock polymer brushes with a hard core of MWNTs and a relatively soft shell of PMMA-block-polystyrene. The products are soluble in CHCl$_3$ and insoluble in H$_2$O. And the polymer content of the samples influences the solubility in organic solvents [24].

In the FT-IR spectrum of PMMACN (unshown), the peak heights of PMMACN are lower than that of PMMA. A sharp peak at 1726 cm$^{-1}$ corresponds to C=O stretching mode of the carboxylic group. The absorption bands at 1140 cm$^{-1}$ is assigned to C–O stretch. The peak at 2934 cm$^{-1}$ is assigned to the C–H stretch of the alkyl groups. All of the characteristic peaks of PMMA appeared in the spectrum of PMMACN. The peak at 1656 cm$^{-1}$ exists in PMMA and PMMACN. Park and Jia thought a peak at 1650 cm$^{-1}$ of FT-IR spectrum of PMMACN composite showed C–C bond for MWNT and PMMA [25,26].

Figure 4 shows the Raman spectra of CCNTs, PMMA, and PMMACN. The peak at 1340 cm$^{-1}$ (D-band) is assigned to the disorder graphite structure or sp$^3$ hybridized carbons of the nanotubes, and the high frequency peak at 1568 cm$^{-1}$ (G-band) corresponds to a splitting of the $E_{2g}$ stretching mode of graphite, which reflects the structural intensity of the sp$^2$ hybridized carbon atoms. The relative degree of functionalization or defects in the nanotubes can be evaluated by

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FIG. 4 Raman spectra of CCNTs (a), PMMA (b), and PMMACN (c).

the intensity ratio of the D-band and G-band ($I_G/I_D$). The Raman G/D ratios for CCNTs and PMMACN are 1.30 and 1.10 respectively. The $I_G/I_D$ of PMMACN is smaller than that of the CCNTs, which reveals the formation of defects or functional groups on the nanotubes surface after polymerization. The characteristic peak of PMMA appears on the spectra of PMMACN. Moreover, compared with CCNTs, a pronounced Raman red-shift (6-21 cm$^{-1}$) of above modified CCNTs is observed because of the increased functional groups. Raman spectra can further confirm the conclusion drawn by $^1$H-NMR and FT-IR.

As shown in Fig.5, the CCNTs displays weight loss of 4% on the whole weight loss process. It is assigned to the decomposition of free carboxyl groups on the surface of CCNTs. For the PMMACN samples, there are two main weight loss regions. The first weight loss is blow 200 °C. The second weight loss is in the region of 300-400 °C. It might readily be attributed to the decomposition of PMMA chains. The weight loss decreases as the content of CCNTs increases. TGA results give further evidence regarding the content of PMMA chains grafted on CCNTs since the PMMA and CCNTs parts have distinct thermal stabilities.

In an attempt to examine the reinforcing effects of the CCNTs on PMMA, dynamic mechanical properties of the PMMACN composites were measured by the dynamic mechanical analyzer (DMA). As can be seen from Fig.6, the storage modulus of PMMACN increase with increasing content of CCNTs up to 0.3% at the temperature below 125 °C. The storage modulus at −75 °C is up 47% from 150 MPa for pure PMMA to 221 MPa for PMMACN containing 0.3% CCNTs. The reinforcement of the storage modulus of PMMACN after addition of CCNTs is associated with the PMMA grafts, which are compatible with PMMA molecules, on the CCNTs walls. The results are similar to the report of Shieh et al. [27]. These PMMA grafts can physically knot and tangle together with PMMA polymer chains in the matrix. CCNTs serve as the network centers to transfer local stress evenly to all other polymer chains. The mechanical properties of PMMACN can be improved. The reinforcing effects of the CCNTs on PMMA matrix are higher than those on PEO matrix [25]. The interactions between CCNTs and PMMA matrix are strong than that of PEO. The incorporation of 0.5% CCNTs has the least reinforce effect among the three PMMACN samples. The storage modulus is 31 MPa at −75 °C. It is lower than PMMA composite. It is commonly observed that there is an optimum CCNTs content to
achieve the best reinforcing effect on PMMA. Wang et al. reported the optimum effective MWNT content appeared to be 1%-2% for SAN composites [28]. Valentini et al. reported that the incorporation of 0.75% SWNTs enhanced the storage modulus of isotactic polypropylene more than that provided by 1% SWNTs [29]. For polyamide-12/SWNTs composites, the addition of 3% SWNTs (styrene-maleic anhydride copolymer encapsulated) achieved a better strengthening effect than 6% SWNTs did [30]. Zou et al. reported that the tensile strength and Young’s modulus of MWNT-reinforced high density polyethylene (HDPE) reached maximum values at 1% MWNTs over the MWNT content range of 0-3% [31]. In this experiments, the storage modulus is the highest as the content of CCNTs is 0.3%. The incorporation of 0.1% CCNTs moves the tanδ peak to a lower temperature by 28°C, whereas the tanδ peak is the lowest among the PMMACN samples. The tanδ peaks of other PMMACN samples are lower than PMMA. It is likely that the interface formed between CCNTs and PMMA is causing the shift of tanδ peak. The tanδ peak magnitude increase as the content of CCNTs increased up to 0.3%. The CNTs are excellent thermal conductivity, PMMACN have more uniform heat distribution than control sample. The tanδ peak magnitude decreased when the content of CCNTs increased from 0.3% to 0.5%. The molecular mobility is restricted when the content of CCNTs increases. For example, in PAN/SWNT at 10% CNTs loading, the tanδ magnitude decreased significantly [32].

IV. CONCLUSION

The poly(methyl methacrylate) chains were successfully bonded to the surface of carboxylate multi-walled carbon nanotubes by in situ polymerisation. The CCNTs do not congregate each other in the hybrid materials. When the content of CCNTs is 0.1%, PMMA shows the relatively regular pane structure. When the content of CCNTs is 0.3-0.5%, the relatively regular pane structures are destroyed and the dendritic structure appears. The carboxylate carbon nanotubes chemically react and are linked with the PMMA chains. The PMMACN are soluble in deuterated chloroform. The functionalized CCNTs are expected to open up avenue for novel carbon nanotubes materials with designable structures and self-organized properties. The storage modulus and tanδ magnitude increase as the content of CCNTs increases up to 0.3%.