

Structural Characterization for Carbon Nanotubes Treated with Concentrated Nitric Acid

BAO-HUA JI

Shandong Provincial Key Laboratory of Functional Macromolecular Biophysics, Dezhou University, 566 Daxuexilu, Dezhou 253023, Shandong Province, P.R. China

Corresponding author: E-mail: jbh1971@126.com

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In order to improve the compatibility between multi-walled carbon nanotubes and polymer chains and obtain well-dispersed composite polymers. Multi-walled carbon nanotubes were modified by concentrated nitric acid and the effect of concentrated nitric acid on the chemical structural changes of multi-walled carbon nanotubes was investigated by means of FT-IR spectrometer, Raman spectra, thermogravimetric analysis and scanning electron microscope. It was demonstrated that the acidized treatment can not only remove impurities inside carbon nanotubes, but also bring in the carboxyl groups into the surface of carbon nanotubes while not destroying the integral structure.

Key Words: Multi-walled carbon nanotubes, Concentrated nitric acid, Structural characterization.

INTRODUCTION

Carbon nanotubes (CNTs) were discovered by Iijima¹. Attributed to its eminent mechanical strength, independent electrical conductivity and the potential application in the future high-tech fields, they had become a research hotspot worldwide. At present, the main research of CNTs is focused on the field including electron device², biological engineering³ and polymer composites⁴. It is a new trend to use CNTs to obtain new materials with unusual mechanical properties and many polymers are being explored as host matrices with CNTs. However, developing the compatibility between the CNTs and the polymer chains is difficult, which can be ascribed to the large length-diameter ratio and high specific surface of CNTs⁵⁻⁷. The compatibility is directly related to achieving homogeneously-dispersed polymer composites, which impedes the application of CNTs in the composites⁸⁻¹⁰. Thus it is still a major challenge to modify the structure of multi-walled carbon nanotubes (MWCNT) to improve the compatibility between multi-walled carbon nanotubes and the polymer chains.

EXPERIMENTAL

Multi-walled carbon nanotubes (MWCNT) (with a diameter of 10-20 nm, length 10-20 μm and L/D ratio 1.502×10^3) were prepared, which had high purity and uniform diameter distribution. Acrylonitrile was purified by alkali washing, followed by distillation in the temperature of 76-78 $^{\circ}\text{C}$. Itaconic acid was recrystallized twice from water, which was obtained by Tianjin Chemical Resin Industry (Tianjin, China). Ammonium

persulfate was also refined before polymerization. Deionized water (H_2O) was adopted as the polymerization medium.

Purification of multi-walled carbon nanotube: 2 g MWCNT were mixed with 250 mL concentrated nitric acid in the 1000 mL of beaker, the mixture was entailed stirring under room temperature after dispersing MWCNT in an ultrasonic bath and the certain amount of conc. HNO_3 was added into the beaker each 2 h. A given mass of MWCNTs were taken out at 5 and 24 h, respectively, washed by deionized water and filtered, vacuum dried at 60 $^{\circ}\text{C}$ for 4 h, to ensure all water and impurity were removed from the system.

Characterization: Bruker Vector22 type FT-IR spectrometer was used to characterize the selected PAN polymers (VERTEX-70, data collection frequency 4000-370 cm^{-1} , made in Germany BRUKER optical spectrum instrument). Raman spectra were collected using a Holoprobe Research Raman Microscope equipped with a 785 nm excitation laser (made by Horiba Jobin Yvon Inc. France). Thermogravimetric analysis (TGA) of powdery polymer composites was conducted on TGC-40 (manufactured by TA Instruments, Inc. Japan) in air at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The resultant polymers were examined by Hitachi Model 8010 (manufactured by Hitachi, Inc. Japan), a scanning electron microscope (SEM), at 25 kV accelerating potential.

RESULTS AND DISCUSSION

FT-IR Spectra characterization of multi-walled carbon nanotube: Fig. 1 shows the changes in the FT-IR spectra of

MWCNT treated with different time. It has been reported that the same characteristic of the intense peaks for the three types of MWCNT is 3440 cm^{-1} band, which is a symbol of -OH functional group¹¹. It can be attributed to the defective CNTs, which can be easily oxidized in the air. For untreated MWCNT the absorption peak of around the band 1747 cm^{-1} has not been found in the figure¹², in contrast with the appeared absorption peak for the treated MWCNTs. It has been demonstrated that carboxyl group can exist in the surface of CNTs treated. Moreover, with prolonging the processing time, the intensity of carboxyl group is becoming stronger. The characteristic absorption peak found at 1220 cm^{-1} is assigned to C-O stretch vibration¹³ and the peak around 1630 cm^{-1} is regarded as the C-C skeleton of CNTs itself¹⁴, so it can be suggested that the other oxygenic functional groups emerge in the surface of CNTs treated with conc. HNO_3 .

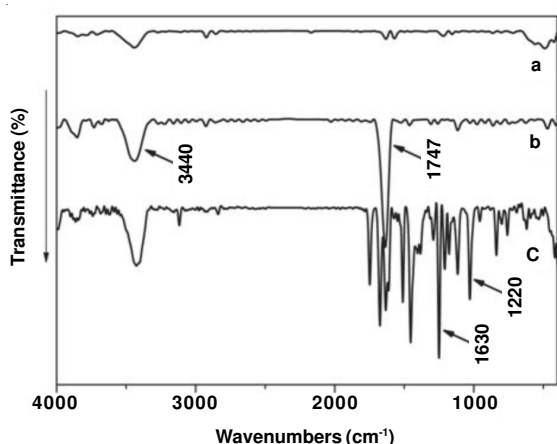


Fig. 1. FTIR spectra of MWCNT: (a) untreated; (b) treated for 5 h; (c) treated for 24 h

Raman spectra characterization of multi-walled carbon nanotube: Raman spectroscopy is a non-destructive technique to characterize graphite materials, in particular to determine the defects, the ordered and disordered structures of CNTs. The Raman spectra of the MWCNTs treated and untreated are shown in Fig. 2. In the Raman spectrum, the peak at 1569 cm^{-1} which is termed as G peak belongs to the Raman-allowed phonon mode E_{2g} , which involves out-of-phase displacements¹⁵. The peak at 1353 cm^{-1} which is termed as D peak appears through the disorder-induced phonon mode due to the infinite size of crystals and defects¹⁶. The G peak is less sharp and the D peak higher than the corresponding peaks of graphite, which indicates that the present MWCNT are characterized by a low degree of graphitization. Interestingly, the location of two peaks both change little but their intensity varied a little, which can illustrate that the structure of CNTs did not change. The intensity ratio of the D-band against the G-band shows the dependence both on the degree of graphitization and the orientation of graphite in the surface of CNTs. As calculated from Fig. 2, the intensity ratio of a spectral line $I_D/I_G = 1462/4880 = 0.299$ is less than that of b spectral line $I_D/I_G = 679/1393 = 0.487$. It can be ascribed to the processing of treatment with acid cause more defect turn up in the surface of CNTs; in the meantime, carboxyl group and other functional group have been brought in.

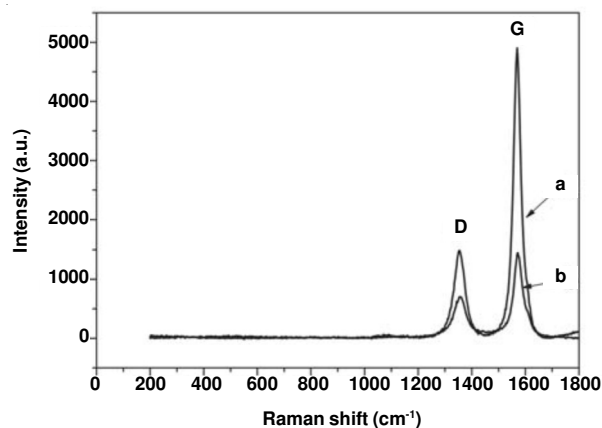


Fig. 2. Raman curves of MWCNT: (a) untreated; (b) treated for 24 h

Thermogravimetric analysis of multi-walled carbon nanotubes: There are many impurities inside CNTs itself, so it must be purified before using and their TGA curves are shown in Fig. 3. The obvious difference can not be found in the figure before $450\text{ }^\circ\text{C}$, but after $450\text{ }^\circ\text{C}$ the weight loss ratio of PAN-2 is higher than that of PAN-1, which can be attributed to many impurity including metal substance and amorphous carbon, which could be oxidated in the high-temperature oxidation process. The impurity content in the CNTs treated reduced obviously, so acidizing was an effective method to get rid of impurity inside CNTs. On one hand, the purpose of purification can be reached; on the other hand, the integral structure can not be destroyed while importing the other functional group into its structure.

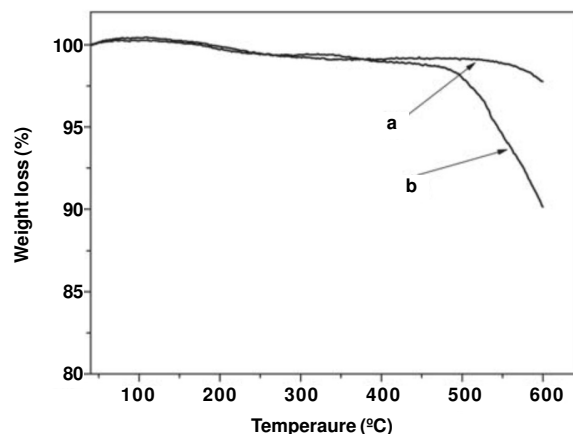


Fig. 3. TG curves of MWCNT: (a) untreated; (b) treated for 24 h

SEM Characterization of multi-walled carbon nanotube: Fig. 4 shows SEM images of MWCNT treated with conc. HNO_3 in different processing time. It can be seen that the intertwining degree of CNTs alleviates a little but the surfaces of some CNTs are becoming more uneven with prolonging the time of treating and the amorphous carbon islands are completely removed from the sample. However, some CNTs keep higher L/D ratio all the time, which is favorable for the polymer to be grafted successfully to the surface of CNTs. It was implied that such CNTs easily dispersed in the MWCNT/ammonium persulfate initiator though more sonication time, which resulted in a good dispersion in the polymer composites.

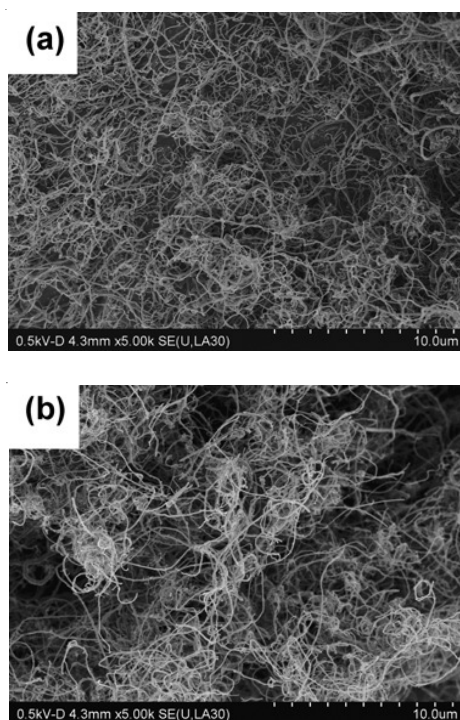


Fig. 4. SEM images of MWCNT: (a) untreated; (b) treated for 24 h

Conclusion

The acidized treatment can not only remove impurities inside CNTs, but also bring in carboxyl groups into the surface of CNTs while not destroying the integral structure. Some CNTs keep higher L/D ratio all the time, which is favorable for the polymer to be grafted to surface of CNTs and results in a good dispersion in polymer composites.

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