Preparation and Structural Characterization for Polyacrylonitrile/Carbon Nanotubes Composites Treated with Concentrated Nitric Acid

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The multi-walled carbon nanotubes were modified by conc. HNO_3, the composite of multi-walled carbon nanotube and poly(acrylonitrile) (PAN) was manufactured by aqueous deposited polymerization method. The effect of multi-walled carbon nanotube on the thermal and crystallization properties of poly(acrylonitrile) composites was discussed. It is demonstrated that the preoxidation temperature of PAN/CNTs composites is in advance to a certain extent than those of pure poly(acrylonitrile) polymers, its heat release reduces obviously and the crystallization degree for polymers decreases a little but not changing the basic structure of polymer films. Consequently, the homogeneously-dispersed PAN/CNTs composites are achieved and the compatibility between the polymer and carbon nanotubes is improved remarkably.

Key Words: Multi-walled carbon nanotubes, Polyacrylonitrile, Concentrated nitric acid, Thermal properties, Crystallization.

INTRODUCTION

Carbon nanotubes (CNTs), with eminent mechanical strength and independent electrical conductivity, were discovered by Iijima[1]. Today the main research fields of CNTs include electron device, biological engineering and polymer composites. It is tempting to use CNTs to obtain new materials with unusual mechanical properties. Accordingly, many polymers are being explored as host matrices with CNTs. However, because of large length-diameter ratio and high specific surface of CNTs[2-4], developing the compatibility between CNTs and polymer chains is difficult, which impedes the application of CNTs in composites[5-7]. It was investigated that fabricating homogeneous polymer nanocomposites remains a major challenge, which is also dependent on the chemical nature of the polymer host. Various methods are used to disperse CNTs into polymer matrices, such as melt mixing[8], *in-situ* polymerization[9] and solution blending[10]. Purification and *in situ* polymerization of CNTs were an effective method for preparing polymer/CNTs composites. Moniruzzaman and Winey[11] and Liu *et al.*[12] found that carboxyl group could be introduced into CNTs after the length of CNTs was shortened by mixed acid. Guo *et al.*[13] and Liu *et al.*[14] observed that poly(acrylonitrtile) composite films produced with CNTs showed that the potential to disperse CNTs well throughout the matrix. Guo *et al.*[15] thought that a composite film exhibited good mechanical and electrical properties at 35 wt % CNTs loading and the property improvements were rationalized in terms of the CNTs surface area.

EXPERIMENTAL

Multi-walled carbon nanotube (MWCNT) (diameter 10-20 nm, length 10-20 μm, L/D ratio 1.502×10^3) were prepared. Acrylonitrile (AN) was purified by alkali washing, followed by distillation under 76-78 ºC. Itaconic acid (IA) was recrystallized twice from water. Ammonium persulfate (APS) was also refined before polymerization. Deionized water (H_2O).

Purification of MWCNT: 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, filtered, vacuum dried at 60 ºC for 4 h.

Preparation of PAN/MWCNT composites: A given mass of purified MWCNT were mixed with deionized water and water-solubility ammonium persulfate, sonicated using a bath sonicator and stirred periodically using a bio-homogenizer at room temperature for 2 h. The solution/dispersion was then transferred to a round-bottom flask and the excess solvent water was boiled off to obtain the desired final MWCNT/APS initiator volume, where the concentration of ammonium persulfate was 0.8 wt %. Copolymerization of acrylonitrile with itaconic acid

was carried out in a three-necked flask at 60 ºC under nitrogen atmosphere, deionized water as a reaction medium and the total monomer concentration was 22 wt %. The reaction was stopped after 2 h and the precipitate mixture was filtrated, washed and dried under vacuum at 60 ºC. The polymer composite obtained by MWCNT/APS initiator was defined as PAN-2, where the content of MWCNT was 0.5 % of monomer. As comparison, the polymer composite prepared with only APS initiator was defined as PAN-1.

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). DSC curves of the polymer composite were recorded on NETZSCH DSC404 Chermal analyzer (which was made in Germany) in air flow using a heating rate of 5 ºC/min in the temperature range from 30-400 ºC. The X-ray diffraction patterns were collected by Rigaku D/max-RC X-ray diffractometer (made in Japan), using Ni-filtered, CuK$_\alpha$ radiation. A 2θ was made from to 4-40º. The planar spacing d can be calculated by Bragg formula[16]:

$$d = \frac{\lambda}{2 \sin \theta}$$

The degree of crystallization C can be calculated by the Hinrichen formula[17]:

$$C = \frac{A_c}{A_c + A_a} \times 100 \%$$

where λ = 1.541 Å, A_c is the integral area of crystallization, A_a is the integral area of non-crystallization.

RESULTS AND DISCUSSION

FT-IR spectra analysis of polymer composite: The FT-IR spectra of polymers with different content CNTs are shown in Fig. 1. It has been reported that the obvious and sharp characteristic peaks appeared at 1075, 1180, 1250-1230, 1360, 1451, 1628, 1737, 2243, 2937 and 3600 cm^{-1} in the spectrum. In the finger zone, the stretching mode at 778 cm^{-1} is the stretching vibration of S-O single bond because of the ammonium persulfate introducing sulfate end-groups to the polymer chains. The weak C=O stretching sharp absorption peak at 1180 cm^{-1} is contributed to C-O stretching and the absorption bands at 1250 and 1230 cm^{-1} are stereo-specific due to the wagging mode of the methine(CH) group coupled with rocking mode of the methylene (CH$_2$) group. The bands with peak values at around 1075, 1360 and 1451 cm^{-1} are assigned to the C-H vibrations of different modes, the band at 1628 cm^{-1} owned to NH$_2$ bending in polymers are likely caused by the hydrolysis of C≡N and the strong band at 1737 cm^{-1} is due to the C=O stretching introduced by carboxyl group in CNTs or in IA comonomer. But there are no remarkable changes for the position of the two peaks between PAN-1 and PAN-2. The position of the C≡N absorption band at 2243 cm^{-1}, which is the strongest absorption band in polymers, indicating the presence of uninterrupted long sequences AN units in polymers. The broad band in the range 3100-2700 cm^{-1} with its maximum at 2937 cm^{-1} was assigned to CH$_2$ stretching vibration. Beside it, the absorption peak at 3600 cm^{-1} was possibly attributed to the O-H stretching of IA in the polymer chains or the NH$_2$

stretching lead by the hydrolysis of C≡N, also might be induced by water absorbed.
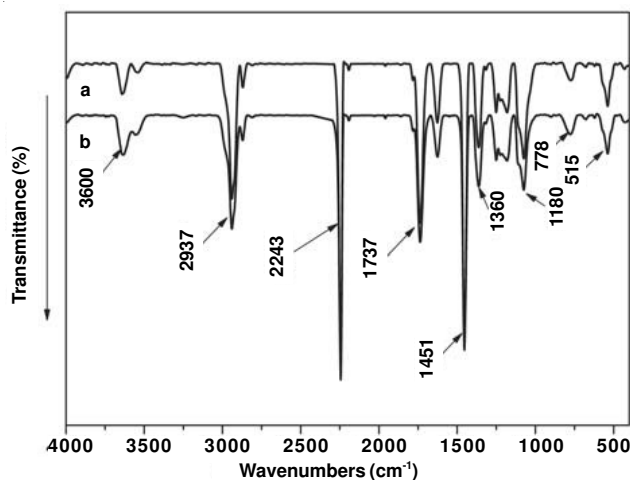

Fig. 1. FTIR spectra of (a) PAN-1, (b) PAN-2 polymers

Generally speaking, the ratio between the two intensities of the absorption peak at 2244 and 1737 cm^{-1}, respectively can be defined the relative content of IA in the polymers the intensity ratio of a spectral line of PAN-1(I_{1737}/I_{2244} = 0.47) is less than that of PAN-2 (I_{1737}/I_{2244} = 0.521), so it can concluded that the oxygenic functional groups in the surface of CNTs take part in chemical reaction with itaconic acid and the polymer was successfully grafted to surface of CNTs by covalent bond.

Effect of CNTs on the thermal properties of polymers: Effect of CNTs on the thermal properties of polymers was investigated in Fig. 2 and the various parameters obtained from two DSC exotherms, viz., initiation temperature (T_i), peak temperature (T_p), termination temperature (T_f), temperature difference between T_i and T_f (ΔT) and heat evolved (ΔH) are tabulated in Table-1.

TABLE-1
DSC DATA OF (a) PAN-1; (b) PAN-2 POLYMERS

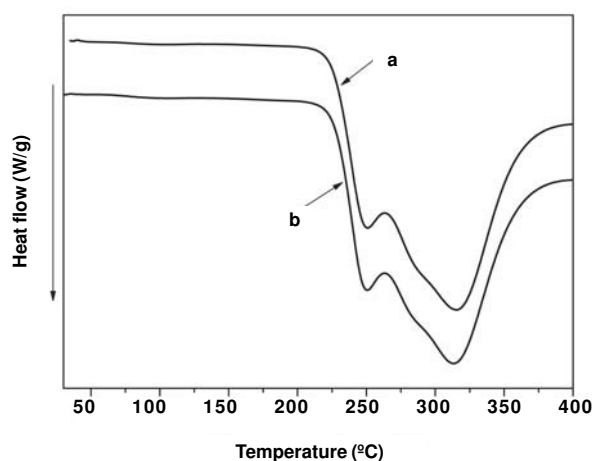| Sample	T_i (ºC)	T_{p1} (ºC)	T_{p2} (ºC)	T_f (ºC)	ΔT (ºC)	ΔH (J g^{-1})	ΔH/ΔT (Jg^{-1} K^{-1})
PAN-1	228	249	316	377	149	5052	33.9
PAN-2	219	250	314	374	155	4789	30.9

Fig. 2. DSC curves of (a) PAN-1, (b) PAN-2 polymers

With regards to PAN-2, its peak-like of DSC exotherms become broader than that of PAN-1, its T_i lowered about 9 ℃ but T_f was in advance, its heat release reduced and the rate of heat release also slowed down, which prevented the concentrative exotherm during the oxidation process. Ge *et al.*[18] explained that CNTs were intertwined by many poly(acrylonitrile) molecular chains in the polymerization. In other words, the electron cloud of cyano-group in PAN molecular chains started to shift, which can be attributed to "nanometer effect" of CNTs. The capacity of attracting electron enhanced, which caused the facilitation of decomposition and cyclization of cyano-group in poly(acrylonitrile) molecular chains and alleviated the oxidation process of polymers.

Effect of CNTs on the crystallinity of polymers: Fig. 3 shows the XRD patterns of PAN-1 and PAN-2 polymers. The various parameters induced from Fig. 3 are tabulated in Table-2, f_{whm} is the half-width of the diffraction peak at about $2\theta \approx 17°$ was calculated from the intensity distribution.
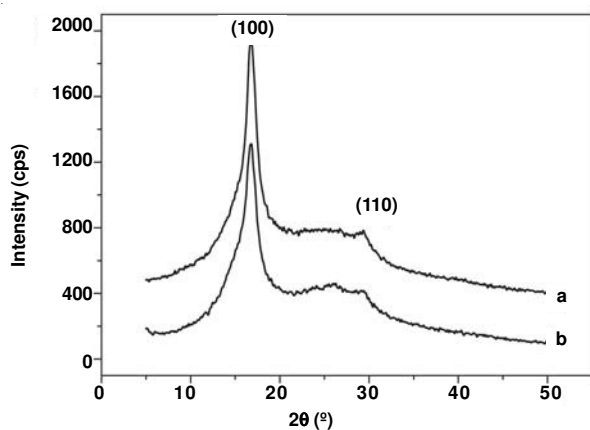

Fig. 3. XRD curves of (a) PAN-1; (b) PAN-2 polymers

TABLE-2
XRD DATA OF (a) PAN-1; (b) PAN-2 POLYMERS

Sample	2θ (°)	d (nm)	f_{whm} (°)	C (%)
PAN-1	16.72	0.5302	1.4847	36.2
PAN-2	16.73	0.5299	1.4085	31.1

It is obvious that the strongest diffraction peak from the polymers appearing at about $2\theta \approx 17°$, corresponded to a crystalline planar spacing d = 0.5302 nm for PAN-1 and d = 0.5299 nm for PAN-2, respectively, which could be attributed to a (100) crystalline plane of the hexagonal lattice. At the same time, a weak diffraction peaks at about $2\theta \approx 29°$ appeared, which was owned to the (110) crystalline plane of the hexagonal lattice. As seen from Fig. 3 and Table-2, the position of the peaks for PAN-1 and PAN-2 polymers did not change, so it can affirmatively be concluded that the preparation method did not induce an alteration of the crystal form of the polymer chains. But the intensity of the diffraction peak from the PAN-2 polymers appearing at *ca.* $2\theta \approx 17°$ obviously lowered when compared with that of PAN-1 and it is the same for the intensity of weak diffraction peaks at about $2\theta \approx 29°$, which increased the amorphous zone of polymers. Moreover, it can be seen that the crystallization degree for PAN-2 was lower than that for PAN-1, which reduced from 36.2-31.1 % by the calculation in Table-2. This result was opposite with that of Zhang *et al.*[19]

and the reason should be that the preparation method was different. As we know, the CNTs have high aspect ratio[20] which can be considered as a structure with long-range order and the diameter of the CNTs is several nanometers[21], which is close to the crystal size of poly(acrylonitrile), then the CNTs can induce the growth of poly(acrylonitrile) crystallites. On the other hand, the half width and the planar spacing for PAN-2 reduced, which can be attributed to the movement and nucleation of poly(acrylonitrile) molecular chains were impeded by the CNTs.

Conclusion

The polymer is successfully grafted to surface of CNTs by aqueous deposited copolymerization and well-dispersion composite is obtained. Adding CNTs to polymers causes the facilitation of decomposition and cyclization of cyano-group in poly(acrylonitrile) molecular chain, the preoxidation temperature of PAN/CNT composites is in advance to a certain extent than those of pure poly(acrylonitrile) polymers and its heat release is obviously reduced, which prevents concentrative exotherm during the preoxidation process. It also causes the intensity of the diffraction peak and the crystallization degree to reduce, but does not induce an alteration of the crystal form of the polymer chains in nature.

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