

## THERMAL STABILITY AND GLASS TRANSITION BEHAVIOR OF PANI/MWNT COMPOSITES

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Polyaniline/multi-walled carbon nanotube (PANI/MWNT) composites were prepared by in situ polymerization. Transmission electron microscope (TEM), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) were used to characterize the PANI/MWNT composites. Thermal stability and glass transition temperature ( $T_g$ ) were measured by thermogravimetry (TG) and temperature modulated differential scanning calorimetry (TMDSC), respectively. The TG and derivative thermogravimetry (DTG) curves indicated that with augment of MWNTs content, the thermal stability of PANI/MWNT composites increased continuously. While,  $T_g$  increased and then decreased with the MWNTs content increasing from 0 to 20 mass%.

**Keywords:** composites, MWNTs, polyaniline,  $T_g$ , thermal stability

### Introduction

Carbon nanotubes (CNTs) have attracted much attention for their potential applications in electronic devices [1], hydrogen absorption materials [2] and nanocomposites [3]. Recently, many polymer/CNT composites have been prepared and studied for CNTs unique structure, mechanical and electrical properties [4–6]. Polystyrene/MWNT composites were synthesized and characterized; the results indicated that MWNTs increased the conductivity and rheological parameters of polystyrene [7]. The study on the chitosan/MWNT composite indicated that MWNTs improved the mechanical properties of chitosan [8]. Besides these two polymer/CNT composites, polyethylene/CNT [9], poly(methyl methacrylate)/MWNT [10], poly(ether ketones)/MWNT [11], PANI/CNT and polypyrrole/CNT composites were also investigated.

Among all the polymers, PANI has widest potential applications for its environmental stability, easy preparation and conductive property [12]. Accordingly, the researches on the preparation and characteristics of PANI/CNT composites were obtained more interests. Deng *et al.* [13], Wu *et al.* [14], Gopalan *et al.* [15] and Ginic-Markovic *et al.* [16] studied the different synthesis methods and their effects on PANI/CNT composites. It was found that MWNT could enhance the electrical conductivity and thermal stability of PANI [17]. In the same time, effective PANI/CNT composites electrode for

supercapacitor [18] and PANI/CNT pH sensor [19] had also been investigated. However, the study on the thermal properties, which is very important for the applications of PANI/CNT composites, had not been done systematically. So, in this paper, we prepared the PANI/MWNT composites by in situ polymerization and holistically studied effect of the content of MWNT on thermal stability and glass transition behavior of PANI by TG and TMDSC, respectively.

### Experimental

#### Materials

MWNTs (diameter: <10 nm and length range: 5–15  $\mu\text{m}$ , purity  $\geq 95\%$ ) were supplied by Shenzhen Nanotechnologies Co. Ltd. Aniline (Ani) obtained from Shenyang Federation Reagent Factory was purified twice by vacuum distillation and then was stored in refrigerator for using. Ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , APS) used as an oxidant was purchased from Tianjin Jizhun Chemical reagent Co. Ltd. And the other reagents, such as methanol, HCl,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  were analytical grade and used without further purification.

#### Preparation of PANI/MWNT composites

Before compounded with PANI, MWNTs were purified and functionalized by sonication in a 3:1 mixture of

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concentrated H<sub>2</sub>SO<sub>4</sub>: HNO<sub>3</sub> at 50°C for 22 h like reference [20]. The PANI/MWNT composites were synthesized by in situ polymerization, which was similar to reference [14]. Firstly, 0.5 mL aniline was injected into 17 mL 2 M HCl solution, stirred for 0.5 h. And then different amounts of MWNTs after treatment were added into the clear solution with stirring and ultrasonic action to reduce the aggregation. After 5 h, a known volume of APS solution was dropped into the above solution with stirring. The reaction mixture was continuously stirred at room temperature for 12 h. The productions were then washed thoroughly with methanol and deionized water repeatedly till the filtrate was colorless. The product was dried in vacuum at 80°C for 24 h. For each experiment, the molar ratios of Ani to APS were retained at 1:1. The MWNT contents (as to Ani) were 0, 2, 5, 10 and 20 mass%, respectively.

*Methods*

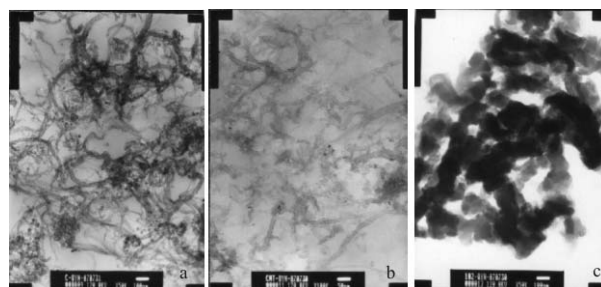
The morphology of PANI/MWNT composite was conducted by TEM on JEM-2000EX instrument. The XRD patterns of MWNTs and PANI/MWNT composite were recorded on a PANalytical X'Pert MPD PRO diffractometer fitted with CuK<sub>α</sub> radiation (λ=1.5404 nm) at 40 kV and 40 mA, with a scanning speed of 10° min<sup>-1</sup>. FTIR absorption spectra of pure PANI, MWNTs and PANI/MWNT composite were performed on a Bruck Equinox 55 spectrophotometer in the wavelength range of 4000–400 cm<sup>-1</sup>.

TG of pure PANI and PANI/MWNT composites were performed using a thermogravimetric analyzer DT-20B instrument. TG curves were obtained under air atmosphere at a heating rate of 10°C min<sup>-1</sup> from room temperature to 800°C. The gas flow rate was 30 mL min<sup>-1</sup>. The T<sub>g</sub> of pure PANI and PANI/MWNT composites were measured by TMDSC on a Q1000 from TA Instruments, in a temperature range from 50 to 270°C, at a heating rate of 3°C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Standard modulation conditions were amplitude A<sub>T</sub> of 0.5°C and a period of 40 s.

**Results and discussion**

*Structure characterization of PANI/MWNT composites*

Figure 1 shows TEM images of raw MWNTs, MWNTs treated by acid and PANI/MWNT (5 mass%) composite. It can be seen that after acid treatment, sidewalls of MWNTs were much rougher. These rougher sidewalls helped the MWNTs dispersing in water and supported more defect sites to adsorb aniline [21]. Ani absorbed on the sidewalls of MWNTs and polymerized under APS oxidation,

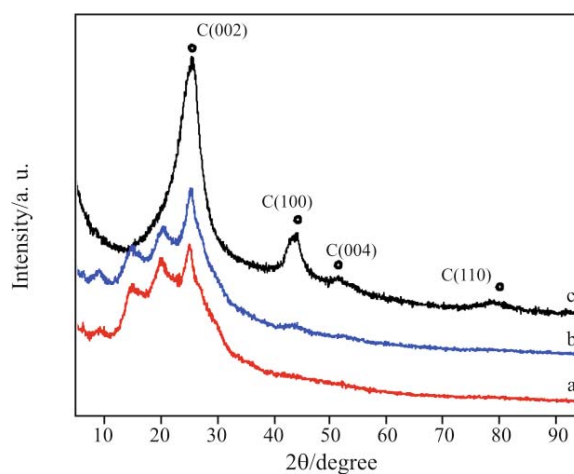


**Fig. 1** TEM images of a – MWNTs, b – MWNTs treated by acid and c – PANI/MWNT (5 mass%) composite

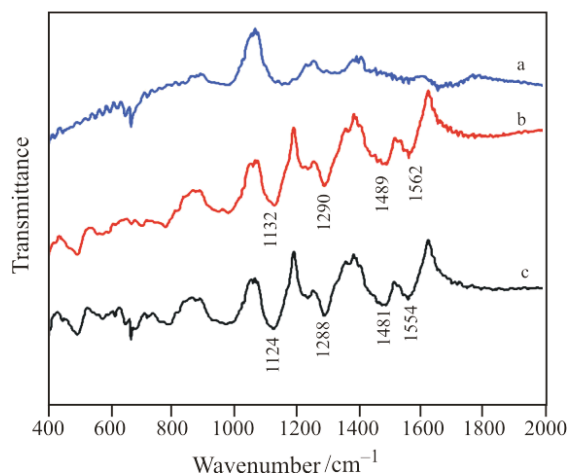
which made MWNTs wrap by PANI. This phenomenon got the MWNTs look wider as seen in Fig. 1c.

XRD patterns for PANI, PANI/MWNT (10 mass%) composite and MWNTs treated by acid are shown in Fig. 2. The peaks of PANI at 2θ angles around 15, 20, 25° indicated PANI crystallization to a certain extent. The characteristic peaks of carbon (Fig. 2c) expressed that the structure of MWNTs did not change after acid treatment [22]. The XRD pattern for PANI/MWNT (10 mass%) composite (Fig. 2b) showed both peaks of PANI and MWNTs. The peak at 25° for PANI became much sharper for the peaks superimposition of PANI and MWNTs [13]. The peaks intensity of MWNTs was a little weaker for its lower content in the PANI/MWNT composite.

Figure 3 exhibits the FTIR spectra of MWNTs treated by acid, PANI and PANI/MWNT (10 mass%) composite. It can be obviously seen that the peaks of pure PANI were in good agreement with those reported in the literature [23]. The characteristic peaks at 1562 and 1489 cm<sup>-1</sup> for emeraldine salt form of PANI are ascribed to C=C stretching vibration of quinoid rings and benzenoid rings, respectively. The presence of absorption band at 1290 cm<sup>-1</sup> is corresponding to the C–N stretching mode for benzenoid unit, while the band at 1132 cm<sup>-1</sup> is attributed to C–H in plane bending vibra-



**Fig. 2** XRD patterns for a – PANI, b – PANI/MWNT (10 mass%) composite and c – MWNTs treated by acid

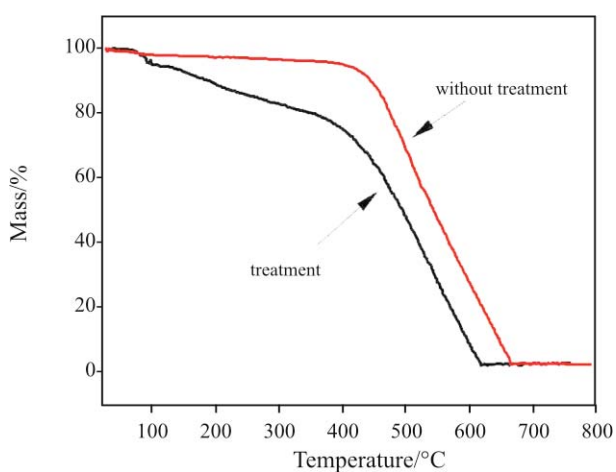


**Fig. 3** FTIR spectra of a – MWNTs treated by acid, b – PANI and c – PANI/MWNT (10 mass%) composite

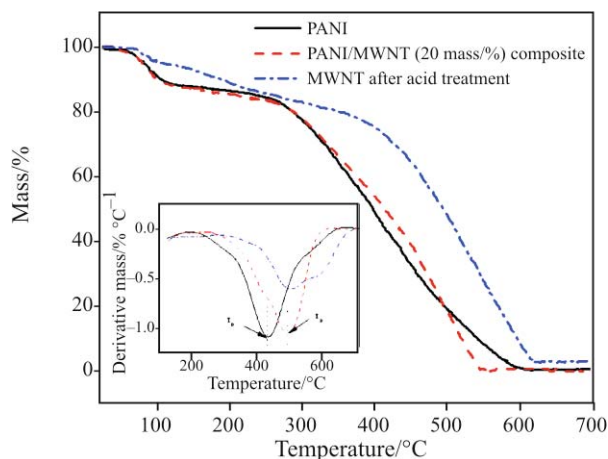
tion of quinonoid unit. In the FTIR spectra of PANI/MWNT (10 mass%) composite, the characteristic peaks of PANI shifted to lower wavelength, which were 1554, 1481, 1288 and 1124 cm<sup>-1</sup>, respectively, as seen in Fig. 2c. This phenomenon was similar to reference [17] because of the interaction between MWNTs sidewalls and PANI chains.

#### Thermal stability of PANI/MWNT composites

TG curves of MWNTs before and after acid treatment are shown in Fig. 4. It can be seen that MWNTs without acid treatment exhibited about 5% mass loss before 400°C, which was due to evaporation of the adsorbed water and other impurities. While, after acid treatment MWNTs showed ca. 26% mass loss before 400°C. It was mainly because of elimination of carboxylic group, which introduced to the sidewalls and the ends of MWNTs by the acid treatment. The carboxyl group improved the dispersivity of MWNTs



**Fig. 4** TG curves of MWNTs before and after acid treatment

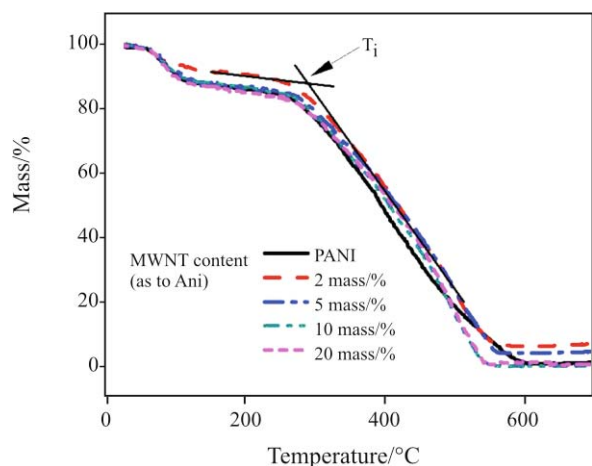


**Fig. 5** TG and DTG (inset) curves of PANI, MWNTs treated by acid and PANI/MWNT (20 mass%) composite

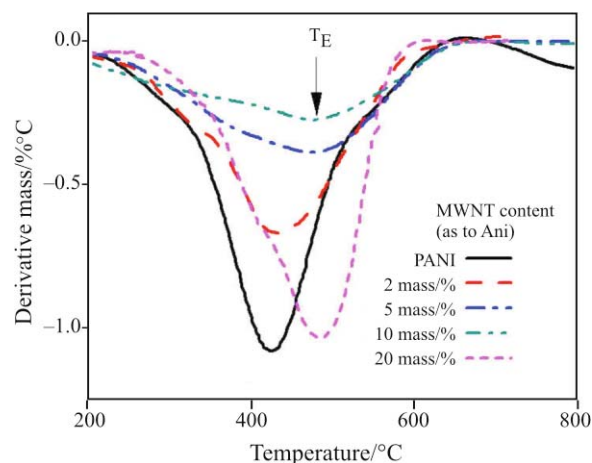
in the HCl solution, and then increased the uniformity of MWNTs in the PANI/MWNT composites.

Figure 5 exhibits the TG and DTG (inset) curves of PANI, MWNTs treated by acid and PANI/MWNT (20 mass%) composite. It can be seen that PANI had two steps of mass loss. The first step was from ca. 50 to 124°C for the volatilization of H<sub>2</sub>O and other impurities [24]. The second step mass loss was ca. 80%, which was from about 254 to 609°C for the degradation of PANI [25]. The TG curve of PANI/MWNT (20 mass%) composite also shows two steps of mass loss. The first step was similar to that of PANI. While the second step was a little different to that of PANI. The mass loss of the second step was the results of degradation of PANI and oxidation of MWNTs. In Fig. 5, it can be also seen that the initial degradation temperature of PANI ( $T_i$ ) was about 283.9°C, which was much lower than that of PANI/MWNT (20 mass%) composite (324.5°C). And the peak temperature of PANI degradation ( $T_p$ ) (obtained from DTG curve in Fig. 5 inset) was also lower than that of PANI/MWNT (20 mass%) composite. The increase in  $T_i$  and  $T_p$  indicated that the addition of MWNTs improved the thermal stability of PANI.

Figure 6 shows the TG curves of PANI/MWNT composites with different MWNTs content. The data of  $T_i$  for the composites were listed in Table 1. With the augment of MWNTs content,  $T_i$  increased for the oxidation temperature of MWNTs was higher than the degradation temperature of PANI. The enhancement in  $T_i$  indicated that the thermal stability of PANI increased with the increase in MWNTs content [26]. DTG curves of PANI/MWNT composites are exhibited in Fig. 7. The data of  $T_p$  obtained from DTG curves were also listed in Table 1. It can be seen that  $T_p$  increased with the MWNTs content increasing from 0 to 20 mass%. The increase in  $T_p$  was due to the interaction between PANI chains and MWNTs,



**Fig. 6** TG curves of PANI/MWNT composites with different MWNT content

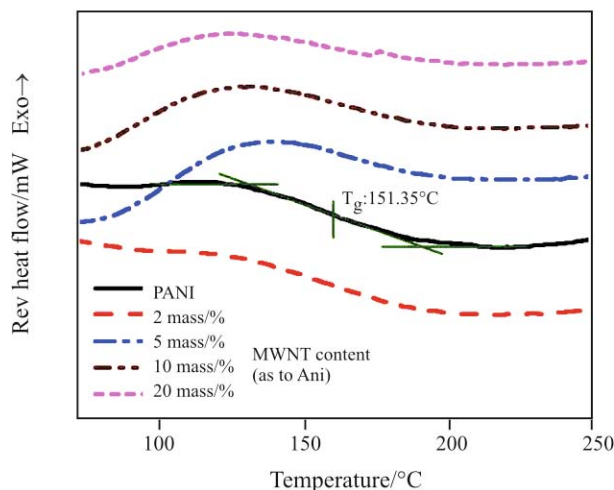


**Fig. 7** DTG curves of PANI/MWNT composites with different MWNT content

**Table 1**  $T_i$  of TG,  $T_p$  of DTG, and  $T_g$  of TMDSC for the PANI/MWNT composites

Sample	MWNT/mass% (as to Ani)	$T_i$ /°C	$T_p$ /°C	$T_g$ /°C
0	0	283.9	424.9	151.35
1	2	287.8	429.0	152.00
2	5	304.1	467.4	161.55
3	10	314.0	471.6	155.01
4	20	324.5	485.0	153.97

which inhibited the degradation speed of PANI. And more MWNTs addition made more chance of the interaction between PANI chains and MWNTs, thus the  $T_p$  increased more; accordingly, the thermal stability of PANI/MWNT composite increased more.



**Fig. 8** TMDSC curves of PANI/MWNT composites with different MWNT content

### Glass transition behavior of PANI/MWNT composites

TMDSC curves of PANI/MWNT composites are shown in Fig. 8. The data of  $T_g$  obtained from Fig. 8 are also listed in Table 1. It can be seen that with MWNTs content increasing,  $T_g$  increased firstly and then decreased. But the  $T_g$  of PANI/MWNT composites were all higher than that of PANI. It may be because that with MWNTs content increasing from 0 to 5 mass%, the quantity of PANI chains, which grew along the sidewalls of MWNTs, increase. The increasing straight chains of PANI induced the  $T_g$  increasing. While, when the content of MWNTs was higher than 5 mass%, the agglomeration of MWNTs occurred. More PANI chains were blocked off by other MWNTs in the PANI chains growing process with more content of MWNTs addition. The short length or ramification of PANI chains formed, which made  $T_g$  decrease.

### Conclusions

PANI/MWNT composites were synthesized by in situ polymerization. TEM images showed that PANI wrapped on the sidewalls of MWNTs. Furthermore, after compounded with MWNTs, the characteristic peaks of PANI in XRD patterns became sharper and the characteristic peaks of PANI in FTIR shifted to lower wavelength due to interaction between PANI chains and MWNTs. The TG and DTG curves indicated that with augment of MWNTs content, the thermal stability of PANI increased. While, with MWNTs content increasing from 0 to 20 mass%, the increase firstly and then decrease in  $T_g$  may be due to the length change of PANI chains.

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## References

- 1 N. A. Bruque, K. Alam, R. R. Pandey, R. K. Lake, J. P. Lewis, X. Wang, F. Liu, C. S. Ozkan, M. Ozkan and K. L. Wang, *J. Nanoelectron. Optoe.*, 1 (2006) 74.
- 2 F. Fernandez-Alonso, F. J. Bermejo, C. Cabrillo, R. O. Loutfy, V. Leon and M. L. Saboungi, *Phys. Rev. Lett.*, 98 (2007) 215503.
- 3 S. Kim, J. R. Jinschek, H. B. Chen, D. S. Sholl and E. Marand, *Nano. Lett.*, 7 (2007) 2806.
- 4 M. Baldoni, A. Sgamellotti and F. Mercuri, *Org. Lett.*, 9 (2007) 4267.
- 5 J. A. Fagan, J. R. Simpson, B. J. Bauer, S. H. D. Lacerda, M. L. Becker, J. Chun, K. B. Migler, A. R. H. Walker and E. K. Hobbie, *J. Am. Chem. Soc.*, 129 (2007) 10607.
- 6 B. B. Marosfői, A. Szabó, Gy. Marosi, D. Tabuani, G. Camino and S. Pagliari, *J. Therm. Anal. Cal.*, 86 (2006) 669.
- 7 A. K. Kota, B. H. Cipriano, M. K. Duesterberg, A. L. Gershon, D. Powell, S. R. Raghavan and H. A. Bruck, *Macromolecules*, 40 (2007) 7400.
- 8 S. F. Wang, L. Shen, W. D. Zhang and Y. J. Tong, *Biomacromolecules*, 6 (2005) 3067.
- 9 R. Haggemueller, C. Guthy, J. R. Lukes, J. E. Fischer and K. I. Winey, *Macromolecules*, 40 (2007) 2417.
- 10 J. H. Sung, H. S. Kim, H.-J. Jin, H. J. Choi and I.-J. Chin, *Macromolecules*, 37 (2004) 9899.
- 11 J.-Y. Choi, S.-J. Oh, H.-J. Lee, D. H. Wang, L.-S. Tan and J.-B. Baek, *Macromolecules*, 40 (2007) 4474.
- 12 R. Emirkhanian, M. Salvia, J. Ferreira, N. Jaffrezic, L. Chazeau and A. Mazzoldi, *Mater. Sci. Eng. C.*, 26 (2006) 227.
- 13 J. G. Deng, X. B. Ding, W. C. Zhang, Y. X. Peng, J. H. Wang, X. P. Long, P. Li and A. S. C. Chan, *Eur. Polym. J.*, 38 (2002) 2497.
- 14 T. M. Wu and Y. W. Lin, *Polymer*, 47 (2006) 3576.
- 15 A. I. Gopalan, K. P. Lee, P. Santhosh, K. S. Kim and Y. C. Nho, *Compos. Sci. Technol.*, 67 (2007) 900.
- 16 M. Ginic-Markovic, J. G. Matisons, R. Cervini, G. P. Simon and P. M. Fredericks, *Chem. Mater.*, 18 (2006) 6258.
- 17 Y. J. Yu, B. Che, Z. H. Si, L. Li, W. Chen and G. Xue, *Synth. Met.*, 150 (2005) 271.
- 18 V. Gupta and N. Miura, *Electrochim. Acta*, 52 (2006) 1721.
- 19 M. Kaempgen and S. Roth, *J. Electroanal. Chem.*, 586 (2006) 72.
- 20 J. Liu, A. G. Rinzler, H. J. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson et al., *Science*, 280 (1998) 1253.
- 21 H. Zhang, H. X. Li and H. M. Cheng, *J. Phys. Chem. B*, 110 (2006) 9095.
- 22 I. Stamatina, A. Morozaan, A. Dumitru, V. Ciupina, G. Prodan, J. Niewolski and H. Figiel, *Physica E*, 37 (2007) 44.
- 23 H. X. Gao, T. Jiang, B. X. Han, Y. Wang, J. M. Du, Z. M. Liu and J. L. Zhang, *Polymer*, 45 (2004) 3017.
- 24 Y. N. Qi, F. Xu, H. J. Ma, L. X. Sun and J. Zhang, *J. Therm. Anal. Cal.*, 91 (2008) 219.
- 25 D. K. Dash, S. K. Sahu and P. L. Nayak, *J. Therm. Anal. Cal.*, 86 (2006) 517.
- 26 E. N. Konyushenko, J. Stejskal, M. Trchová, J. Hradil, J. Kovářová, J. Prokeš, et al., *Polymer*, 47 (2006) 5715.

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