Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 2, 553–557

THERMAL STABILITY AND GLASS TRANSITION BEHAVIOR OF PANI/α-Al_2O_3 COMPOSITES

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Polyaniline/α-Al_2O_3 (PANI/α-Al_2O_3) composites were synthesized by in situ polymerization through ammonium persulfate ($(NH_4)_2S_2O_8$, APS) oxidized aniline using HCl as dopant. XRD and FTIR were used to characterize the PANI/α-Al_2O_3 composites. The thermal stabilities and glass transition temperature (T_g) of PANI/α-Al_2O_3 composites were tested using thermogravimetric (TG) method and modulated differential scanning calorimetry (MDSC) technique. The results of TG showed that the thermal stability of PANI/α-Al_2O_3 composite increased and then decreased with the increase in α-Al_2O_3 content. The derivative thermogravimetry (DTG) curves showed one step degradation of PANI when the α-Al_2O_3 content was lower than 52.5 mass%, and exhibited two steps degradation when the α-Al_2O_3 content was higher than 63.6 mass%. The MDSC curves showed that the T_g of PANI/α-Al_2O_3 composites increased and then decreased with the augment of α-Al_2O_3 for the interaction between PANI chains and the surface of α-Al_2O_3.

Keywords: *glass transition, modulated differential scanning calorimetry, PANI/α-Al_2O_3 composite, thermal stability*

Introduction

In recent years, conducting PANI has attracted much attention for its novel properties of easy preparation and environmental stability, as well as its potential applications in electronics [1, 2] and sensors [3, 4]. When PANI compounded with inorganic nanoparticles, the PANI composites usually exhibited more special properties than pure PANI [5–8]. For example, PANI/Fe_3O_4 nanocomposite was more promising electromagnetic wave absorbers than pure PANI and pure Fe_3O_4 particles [9]. PANI with addition of MnO_2 and ZrO_2 nanoparticles could change to be water-dispersible [10, 11]. Furthermore, PANI/TiO_2 nanocomposites [12, 13] with high piezoresistivity and PANI/MWNT composites with high shear stress [14] have also been found.

These special properties of PANI composites came from the combination of PANI chains and inorganic nanoparticles. Therefore inorganic nanoparticles with special properties [15] could improve some poor properties like thermal stability of PANI. Some researchers have paid attention to this aspect. Yoshimoto [16] and Wang [17] studied the effect of montmorillonite and Co_3O_4 nanoparticles on the thermal properties of PANI. And found that the thermal stability of PANI both increased with the addition of up two inorganic nanoparticles. Kazimso [18] studied the T_g of PANI/Te nanocomposites and found that the Te nanoparticles could decrease the T_g of PANI. And our previous work showed that the γ-Al_2O_3 nanoparticles could improve the thermal stability and increase the glass transition temperature of PANI [19]. So it would be interesting to study the effect of more thermal stable nanoparticles–α-Al_2O_3 on the thermal stability and T_g of PANI. In our present work, the PANI/α-Al_2O_3 composite was synthesized by in situ polymerization, the XRD patterns and FTIR spectra were studied to confirm constitutes of the composites. Thermal analytical experiments were performed to confirm the content of the PANI in the composites and the thermal properties (thermal stability and T_g) of PANI/α-Al_2O_3 composites

Experimental

Materials

Aniline obtained from Shenyang Federation Reagent Factory was purified twice by vacuum distillation and then was stored in refrigerator for using. Ammonium persulfate ($(NH_4)_2S_2O_8$, APS) used as an oxidant was purchased from Tianjin Jizhun Chemical reagent Co. Ltd., hydrochloric acid (HCl) was provided by Harbin Chemical Reagent Co. and α-Al_2O_3 nanoparticles with particle size of approximately 80 nm was obtained from Nanjing Haitai Technology Nano-Co. Ltd. All chemical reagents were analytical grade.

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1388–6150/$20.00

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Preparation of PANI/α-Al_2O_3 composites

The PANI/α-Al_2O_3 composites were synthesized by in situ polymerization, which was similar to our previous work [19]. Firstly, a known volume of aniline was injected into 10 mL 2 M HCl aqueous solution, stirred for 0.5 h. And then α-Al_2O_3 nanoparticles were added into the clear solution with stirring and ultrasonic action to reduce the aggregation of α-Al_2O_3 nanoparticles. 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 aniline to HCl and to APS were retained at 1:0.5 and 1:1, respectively.

Methods

Characterization

The XRD patterns of α-Al_2O_3, pure PANI and PANI/α-Al_2O_3 composites were recorded on a PANalytical X'Pert MPD PRO diffractometer fitted with CuK_α radiation (λ=1.5404 nm) at 40 kV and 40 mA, with a scanning speed of 10° min^{-1}. Fourier transform infra-red (FTIR) absorption spectra of pure PANI, α-Al_2O_3 nanoparticles and PANI/α-Al_2O_3 composites were performed on a Bruck Equinox 55 spectrophotometer in the wavelength range of 4000–400 cm^{-1}. The specimen substrate was a KBr disc.

Thermal properties

The thermogravimetry of pure PANI and PANI/α-Al_2O_3 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^{-1} from room temperature to 700°C. The gas flow rate was 30 mL min^{-1}. The T_g of pure PANI and PANI/α-Al_2O_3 composites were measured by MDSC on a Q1000 from TA Instruments, in a temperature range from 50 to 270°C, at a heating rate of 3°C min^{-1}.

Results and discussion

Structure characterization of PANI/α-Al_2O_3 composites

Figure 1 shows the XRD patterns of pure PANI, PANI/α-Al_2O_3 composite [55.5/44.5 (*w*/*w*)] and α-Al_2O_3 nanoparticles. It can be seen that the pure PANI exhibited two broad peaks at 2θ angles around 20 and 26°, which indicated that the pure PANI had crystallinity to a certain extent [20]. α-Al_2O_3 nanoparticles showed ten peaks at 2θ angles from 20 to 70°. The XRD pattern of PANI/α-Al_2O_3 composite [55.5/44.5 (*w*/*w*)] integrated the characters of PANI and α-Al_2O_3 nanoparticles. It means that the α-Al_2O_3 nanoparticles existed in the composite. While, compared with pure PANI and α-Al_2O_3 nanoparticles, the peaks intensity of the composite decreased, which showed that the α-Al_2O_3 nanoparticles addition decreased the crystallinity extent of PANI.

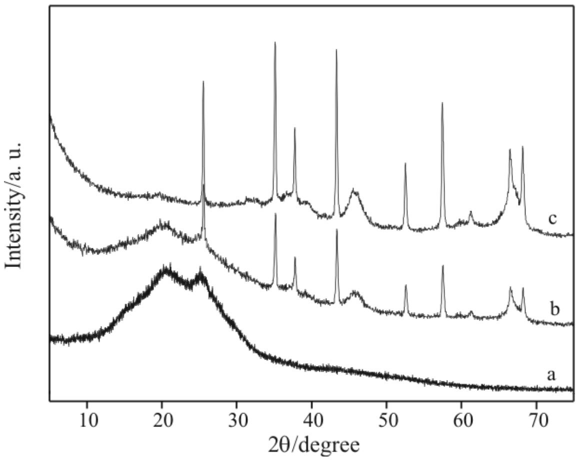

Fig. 1 XRD patterns of a – pure PANI, b – PANI/α-Al_2O_3 composite [55.5/44.5 (*w*/*w*)] and c – α-Al_2O_3 nanoparticles

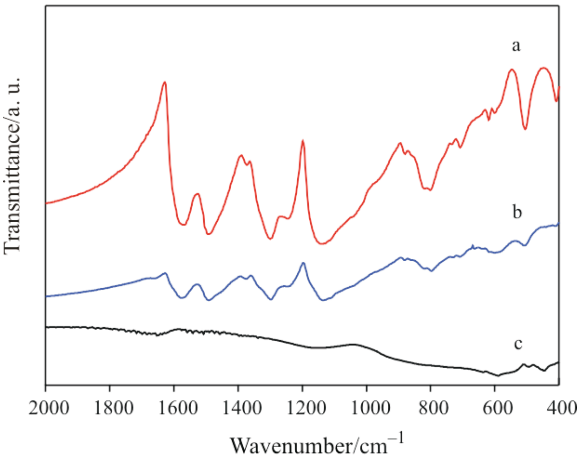

Fig. 2 FTIR spectra of a – pure PANI, b – PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] and c – α-Al_2O_3 nanoparticles

FTIR spectra of pure PANI, PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] and α-Al_2O_3 nanoparticles are shown in Fig. 2. It can be seen that the FTIR spectra of α-Al_2O_3 nanoparticles exhibited some small peaks in the range of 400 to 2000 cm^{-1}. And the peaks at 1572, 1492, 1295, 1130 and 804 cm^{-1} in the spectra of PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] were in accordance with the FTIR spectra of pure PANI, which was the same to the similar study [21]. It means that the α-Al_2O_3 nanoparticles had not much influence on the structure of PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)].

Thermal stability of PANI/α-Al_2O_3 composites

It is well known that TG was an important measurement to estimate the component content in the composite [22]. Figure 3 shows the TG and DTG (inset) curves of pure PANI, PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] and α-Al_2O_3 nanoparticles. From Fig. 3, it can be seen that in the temperature range of 20 to 700°C, the mass loss of α-Al_2O_3 nanoparticles was ca. 8.5%, which was due to the volatilization of impurity [23]. In the same temperature range, the mass loss of pure PANI was ca. 97.3% and the total mass loss of PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] was ca. 75.9%. So the PANI mass content in the composite was (75.9–8.5)%=67.4%, the α-Al_2O_3 nanoparticles mass content was (100–67.4)%=32.6%.

TG curves of pure PANI and PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] showed two steps mass loss. For pure PANI, the first step was from 45 to 130°C, which was attributed to the volatilization of H_2O and HCl. The second step occurred from 250 to 650°C was due to the degradation of PANI chains. The temperature ranges of two steps mass loss of PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] were similar to the pure PANI. But the initial degradation temperature (T_i) of PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] was (298.7°C) a little higher than that of pure PANI (297.4°C). It means that the PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] was more thermal stable than pure PANI. The peak temperature of composite degradation (T_p) is another criterion for thermal stability. The peak at 414.4°C in DTG curves (inset in Fig. 3) of PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] was corresponding to the degradation of PANI chains, which was higher than that of pure PANI (405.0°C). It was also exhibited that the thermal stability of the PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] was higher than pure PANI.

Figures 4 and 5 show the TG and DTG curves of PANI/α-Al_2O_3 composites with different contents. The T_i of TG and T_p of DTG data for the PANI/α-Al_2O_3 composites are listed in Table 1. From Fig. 4 and Table 1, it can be seen that with the increase in content of α-Al_2O_3, the T_i of PANI/α-Al_2O_3 composites increased when the α-Al_2O_3 content was lower than 63.6 mass%. It was because that the interaction between PANI chains and the surface of α-Al_2O_3 nanoparticles obviously strengthened with the content of α-Al_2O_3 nanoparticles increasing, which increased the thermal stability of PANI [24]. But when the α-Al_2O_3 content was higher than 63.6 mass%, the α-Al_2O_3 aggregation occurred and the free PANI in the

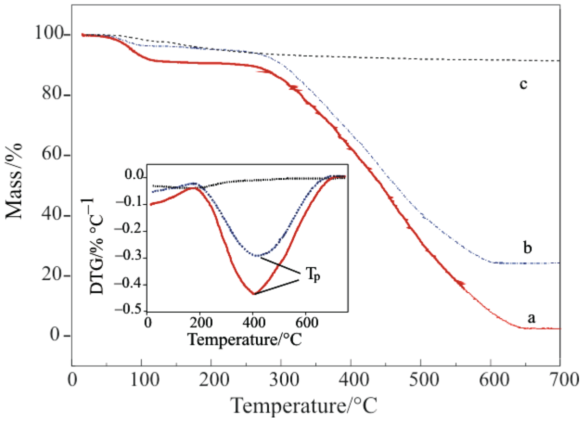

Fig. 3 TG and DTG (inset) curves of a – pure PANI, b – PANI/α-Al_2O_3 composite [67.4/32.6 (*w*/*w*)] and c – α-Al_2O_3 nanoparticles

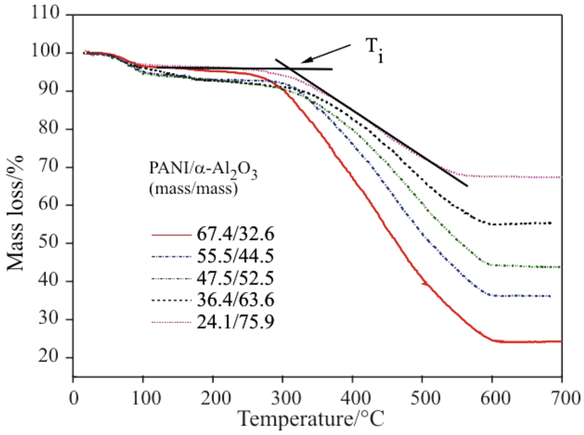

Fig. 4 TG curves of PANI/α-Al_2O_3 composites

Table 1 T_i of TG, T_p of DTG, and T_g of MDSC for the PANI/α-Al_2O_3 composites

Sample	PANI/mass%	α-Al_2O_3/mass%	T_i/°C	T_p/°C	T_g/°C
0	100	0	297.4	405.0	163.19
1	67.4	32.6	298.7	414.4	167.17
2	55.5	44.5	337.3	463.8	171.95
3	47.5	52.5	341.6	478.5	173.10
4	36.4	63.6	363.9	372.9, 512.4	133.86
5	24.1	75.9	313.3	355.8, 434.3	128.06

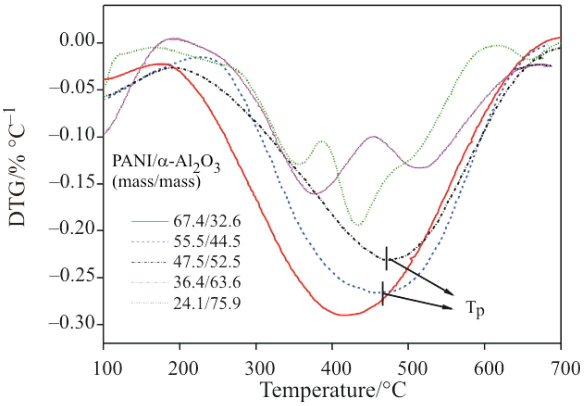

Fig. 5 DTG curves of PANI/α-Al$_2$O$_3$ composites

composite increased which decreased the T_i of the PANI/α-Al$_2$O$_3$ composite. The T_p of PANI/α-Al$_2$O$_3$ composites increased with the α-Al$_2$O$_3$ content increasing when the α-Al$_2$O$_3$ content was lower than 52.5 mass%. And the interesting phenomenon was that when the α-Al$_2$O$_3$ content was higher than 63.6 mass%, the DTG curves showed two peaks in the temperature range of 300 to 600°C. The two T_p represented the degradation of PANI with shorter and longer chains, respectively. Combined with the data of T_i, it can be seen that too much addition of α-Al$_2$O$_3$ nanoparticles (higher than 63.6 mass%) would decrease the thermal stability of PANI.

Glass transition behavior of PANI/α-Al$_2$O$_3$ composites

T_g is an important property in determining the suitability of a polymer for an engineering application. Figure 6 shows the MDSC curves of PANI and PANI/α-Al$_2$O$_3$ composite. From the MDSC curves, the T_g of PANI/α-Al$_2$O$_3$ composite can be estimated through computer software. The T_g data of PANI/α-Al$_2$O$_3$ composites are also listed in Table 1. With α-Al$_2$O$_3$ content increasing in the composite, T_g increased firstly and then decreased. This trend was similar to that of PANI/γ-Al$_2$O$_3$ composites in our previous work [19, 25], but was opposite to [26] for the different nanoparticles surface. The increase in T_g was because of the decrease in mobility of PANI for the interaction between α-Al$_2$O$_3$ nanoparticles and PANI chains [25]. And the following decrease of T_g was due to the aggregation of α-Al$_2$O$_3$ nanoparticles, which led to the weak interaction between PANI chains and α-Al$_2$O$_3$ nanoparticles [19]. From Table 1 and Fig. 6, it can be even seen that the addition of α-Al$_2$O$_3$ nanoparticles could increase the T_g range of PANI and then increase application range of it.

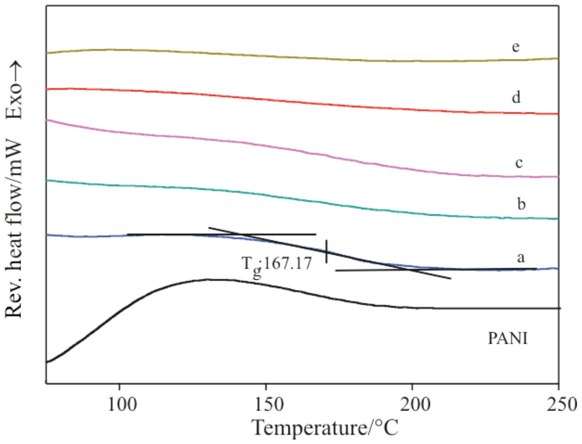

Fig. 6 MDSC curves of pure PANI and PANI/α-Al$_2$O$_3$ (*w*/*w*) composites: a – 67.4/32.6, b – 55.5/44.5, c – 47.5/52.5, d – 36.4/63.6 and e – 24.1/75.9

Conclusions

The PANI/α-Al$_2$O$_3$ composites have been prepared and the thermal properties were examined. The addition of α-Al$_2$O$_3$ nanoparticles had a little influence on the structure of PANI. With the increase in content of α-Al$_2$O$_3$, T_i increased and then decreased for the change of interaction between PANI chains and the surface of α-Al$_2$O$_3$ nanoparticles. The peak for PANI degradation changed from one to two when the α-Al$_2$O$_3$ content was higher than 60 mass%. The T_g of the PANI/α-Al$_2$O$_3$ composites increased firstly and then decreased with augment of α-Al$_2$O$_3$. It was due to the mobility change of PANI and the aggregation of α-Al$_2$O$_3$ nanoparticles, respectively. The suitable content of α-Al$_2$O$_3$ addition could increase the thermal stability and T_g of PANI. Comparing to our previous work [19], when the content of α-Al$_2$O$_3$ in the PANI composite was close to that of γ-Al$_2$O$_3$ nanoparticles, the T_g of the PANI/α-Al$_2$O$_3$ composites were appreciably higher than that of PANI/γ-Al$_2$O$_3$ composites. It means that the effect of α-Al$_2$O$_3$ nanoparticles on the thermal properties of PANI is stronger than that of γ-Al$_2$O$_3$ nanoparticles.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China for financial support to this work under Grant NSFC no. 20573112 and 20473091.

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Received: November 11, 2007
Accepted: May 30, 2008

DOI: 10.1007/s10973-007-8626-2