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HALLOYSITE NANOTUBES/POLYSTYRENE (HNTs/PS) NANOCOMPOSITES VIA IN SITU BULK POLYMERIZATION

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Serials of halloysite nanotubes/polystyrene (HNTs/PS) nanocomposites with different contents of organo-modified halloysite nanotubes (organo-HNTs) were successfully prepared by the in situ bulk polymerization of styrene with the organo-HNTs as macromonomers. The percentage of grafting (PG%) of more than 230% was achieved, calculated from the results of the thermogravimetric analysis (TG). The TG results also showed that the thermal stabilities of the HNTs/PS nanocomposites prepared via the bulk polymerization were better than the pure polystyrene. And the maximum thermal degradation temperature of the nanocomposites increased with the increasing of the amount of the HNTs fillers added.

Keywords: *bulk polymerization, halloysite nanotubes, nanocomposites, polystyrene, thermal stability*

Introduction

In the past decades, polymer nanocomposites reinforced with lower volume fraction of nano-scale materials such as nanoparticles, carbon nanotubes and layered silicate clays have attracted steadily growing interest due to their peculiar and fascinating properties as well as their unique applications in commercial sectors [1–6]. The incorporation of nanomaterials such as layered silicate clays, calcium carbonate or silica nanoparticles arranged on the nanometer scale with a high aspect ratio and/or an extremely large surface area into polymers improves their mechanical performances significantly. The layered silicate clays had been widely applied for the polymer nanocomposites because of the inexpensive resources [7–10].

The properties of nanocomposites depend greatly on the chemistry of polymer matrices, nature of nanofillers, and the way in which they are prepared. The uniform dispersion of nanofillers in the polymer matrices is a general prerequisite for achieving desired mechanical and physical characteristics. So the surface modification techniques had been developed to improve the physical and chemical properties of the nanosurfaces, with small organic molecules or polymers [11–13]. It was also found that the presence of covalent bonds between the nanofillers and polymer matrices could improved markedly the thermal and mechanical properties of the resulting polymer nanocomposites [14–16]. However, the percentage of grafting (PG%) of the polymer nanocomposites was lower than 30% [17] except for living polymerization techniques [18].

Halloysite nanotubes (HNTs) is a kind of aluminosilicate clay with hollow nanotubular structure (about 20–50 nm in diameter and several hundreds nanometers in length) mined from natural deposits in countries such as China, America, Brazil, France, etc. [19]. Typically, HNTs are used in the manufacture of high quality ceramic white-ware [20]. In recent years, HNTs have been used as nanotemplates or nanoscale reaction vessels instead of CNTs or boron nitride nanotubes (BNNTs) [21, 22]. Most recently, the authors attempted to utilize HNTs as nanofillers in polymers, such as natural rubber, nitrile rubber and polypropylene [23]. It was found that with the incorporation of HNTs in a polymer, the thermal stability and flame retardancy of the nanocomposites were increased significantly.

In this work we reported a novel technique for the preparation of halloysite nanotubes/polystyrene nanocomposites (HNTs/PS) with much higher PG%. And the effect of the coupling agent on the thermal stabilities of the resulting nanocomposites was also discussed.

Experimental

Materials

Raw materials

The raw halloysite clay obtained from Hebei, China. γ-Methacryloxypropyltrimethoxysilane (KH-570) (Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) was used without further purification. The mo-

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nomer, styrene (St, analytical reagent, Tianjin Chemicals Co. Ltd., China) was dried over CaH_2 and distilled under reduced pressure. The initiator, 2,2'-azobis(isobutylonitrile) (AIBN) (Tianjin Chemicals Ltd. Co. Tianjin, China) was re-crystallized from ethanol before use. Other reagents used were analytical grade.

Pretreatment of halloysite clay

The raw halloysite clay 250 g and 500 mL water were mixed and milled with SF400 type wit sand-grinding dispersing machine at 4000 rpm for 2 h. The HNTs suspension was pre-centrifuged (3000 rpm for 3 min) to throw away the deposit. The stable suspension was dried by infrared light for further experiments.

Organo-HNTs

The certain amounts of HNTs and KH-570 were dispersed into 50 mL of toluene in a 100 mL flask via ultrasonic irradiation for 1 h. Then the mixture was heated to 80°C and was conducted with electromagnetism stirring at the same temperature for 10 h. The superfluous KH-570 was washed with toluene for several times, and dried in vacuum for the further experiments.

Preparation of HNTs/PS nanocomposites

The calculated amounts (Table 1) of St and organo-HNTs, and a certain amount of AIBN (0.3 mass% of styrene) were mixed into a 25 mL glass tube with ultrasonic vibrations for 30 min, bubbling with N_2. Then the tube was sealed and placed in the center of an oven heated to 80°C and was shimmied 20 min^{-1} for 20 h. After the products were cooled to the room temperature, the polystyrene grafted HNTs (HNTs-PS) were separated from the non-grafted PS by the following procedure reported previously [24]: the HNTs/PS nanocomposites were extracted with toluene using a Soxhlet apparatus until no PS was eluted in the refluxing solvent (no precipitation was observed when the toluene solution was poured into ethanol). The solid products of the HNTs-PS were separated by the centrifugation ($1\cdot10^4$ rpm for 30 min). Then the precipitates were dried at 40°C in vacuum.

Table 1 The HNTs amounts added for the HNTs/PS nanocomposites

Sample	Mass ratios of St/HNTs added	HNTs contents/ mass%
HNTs/PS 1	19.9/0.1	0.5
HNTs/PS 2	19.8/0.2	1.0
HNTs/PS 3	19.6/0.4	2.0
HNTs/PS 4	19.4/0.6	3.0

Methods

A Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared spectroscopy analysis (FTIR). Thermogravimetric analysis (TG) was used for the thermal stability of the HNTs/PS and HNTs-PS nanocomposites, performed with a Perkin-Elmer TGA system from room temperature to 800°C in N_2 at a scan rate of 10°C min^{-1}. The morphologies of the raw HNTs, organo-HNTs and the HNTs/PS were characterized with a JEM-1200 EX/S transmission electron microscope (TEM). The bare halloysite nanotubes were dispersed in water and the HNTs/PS nanocomposites were dispersed in toluene in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated carbon film.

The percentage of grafting (PG%) and the grafting efficiency (GE%) were calculated from the results of the TG according to the following relationships:

$$PG\%=\text{grafted PS (g)}/\text{HNTs used (g)}\cdot100\%$$

$$GE\%=\text{grafted PS (g)}/\text{total PS (g)}\cdot100\%$$

Results and discussion

Functional organic silanes and quaternary ammonium salts were widely used for the surface modification of silicate clays. In the study, the functional organic silane with polymerable group of C=C, γ-methacryloxypropyltrimethoxysilane (KH-570), was used for the organo-modification of the halloysite nanotubes with their surface hydroxyl groups via chemical bonds. The absorbance bands at 1723 cm^{-1} of ester groups, 1470 cm^{-1} of $(CH_2)_3$ group, 1637 cm^{-1} of C=C group and 2924 cm^{-1} bands of methyl were all found in the FTIR spectrum of the resulting organo-HNTs (Fig. 1).

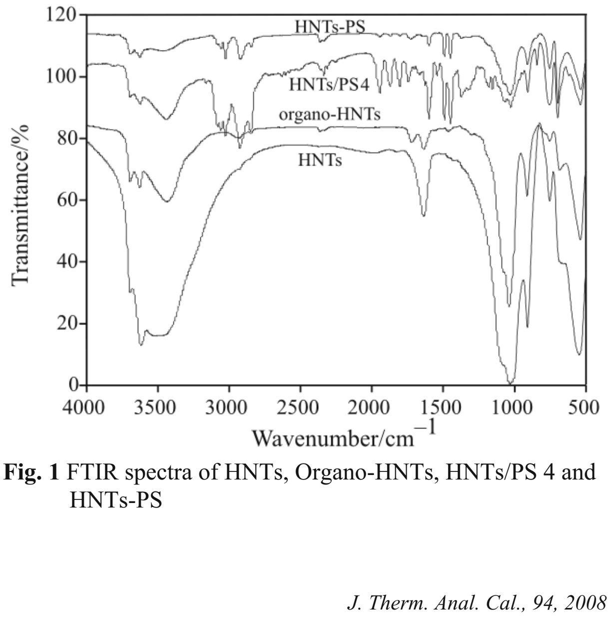


Fig. 1 FTIR spectra of HNTs, Organo-HNTs, HNTs/PS 4 and HNTs-PS

The organo-modification of the halloysite nanotubes was also testified by the TG analysis (Fig. 2a). The main mass loss of raw halloysite nanotubes about 13% at the temperature range of 350–500°C was attributed to the release of the crystal water. However, the mass loss of the organo-HNTs at the temperature range of 300–500°C was found to be about 24%. The amount of the anchored functionality of organo-HNTs was 1.06 mmol g^{-1} calculated from the TG results.

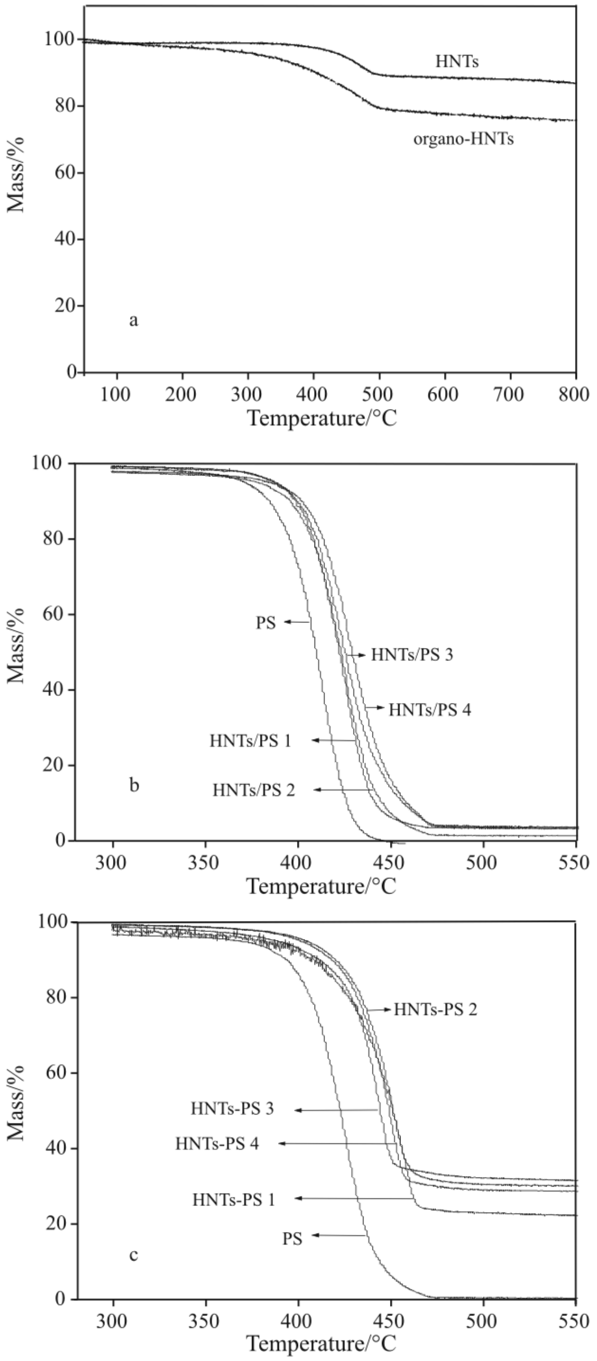


Fig. 2 TG curves of a – raw HNTs and organo-HNTs, b – free PS and nanocomposites (HNTs/PS 1-4) and c – free PS and PS grafted HNTs (HNTs-PS 1-4)

After the radical copolymerization of styrene with the organo-HNTs as macromonomers via the present bulk polymerization method, styrene had polymerized completely. Then the polystyrene grafted halloysite nanotubes (HNTs-PS) were separated from the free non-grafted polystyrene by the extraction of the halloysite nanotubes/polystyrene nanocomposites (HNTs/PS) with toluene. The characteristic absorbance bands of polystyrene, polystyrene aromatic C–H stretching vibrations at 3003, 3026, 3059, 3081, 3105, 755 and 697 cm^{-1}, the aliphatic C–H stretch at 2924 and 2851 cm^{-1} and styrene C–C vibrations at 1450 and 1493 cm^{-1}, were all found in the FTIR spectrum of the resulting HNTs-PS (Fig. 1). It showed that the polystyrene had been grafted onto the surfaces of the halloysite nanotubes successfully and it could improve the dispersibility of the halloysite nanotubes in polystyrene or organic solvent such as toluene.

The effects of the amounts of the organo-HNTs added on the PG% and the GE% were calculated from the TG results of the HNTs-PS nanocomposites (Fig. 2b) and the results were shown in Fig. 3. It clearly shows that the grafting efficiency (EG%) increased with the increasing of the amounts of the organo-HNTs added. However, the percentage of grafting (PG%) was found to be more than 230% for the amounts of the organo-HNTs added of 0.5 to 3.0%. They were much higher than those works reported previously [17]. This may be due to the crosslink reactions of the polystyrene grafted because of the higher functional groups contents of the organo-HNTs. The crosslink reactions were occurred especially in the inner spaces of the halloysite nanotubes. It is concluded from the transmission electron microscope (TEM) images (Fig. 4). The HNTs-PS showed the cluster morphology after dispersed in toluene. And the hollow nanotubes were observed in the

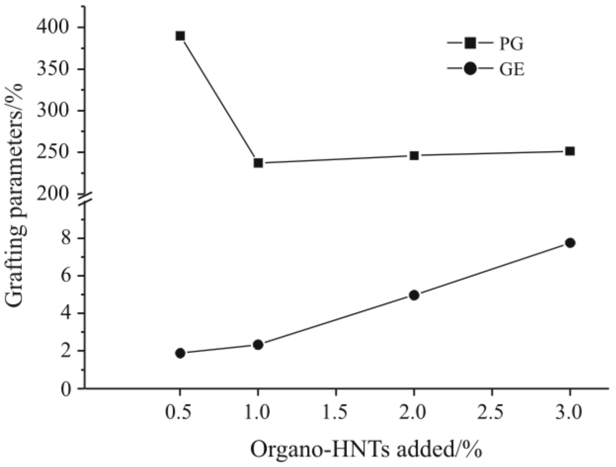
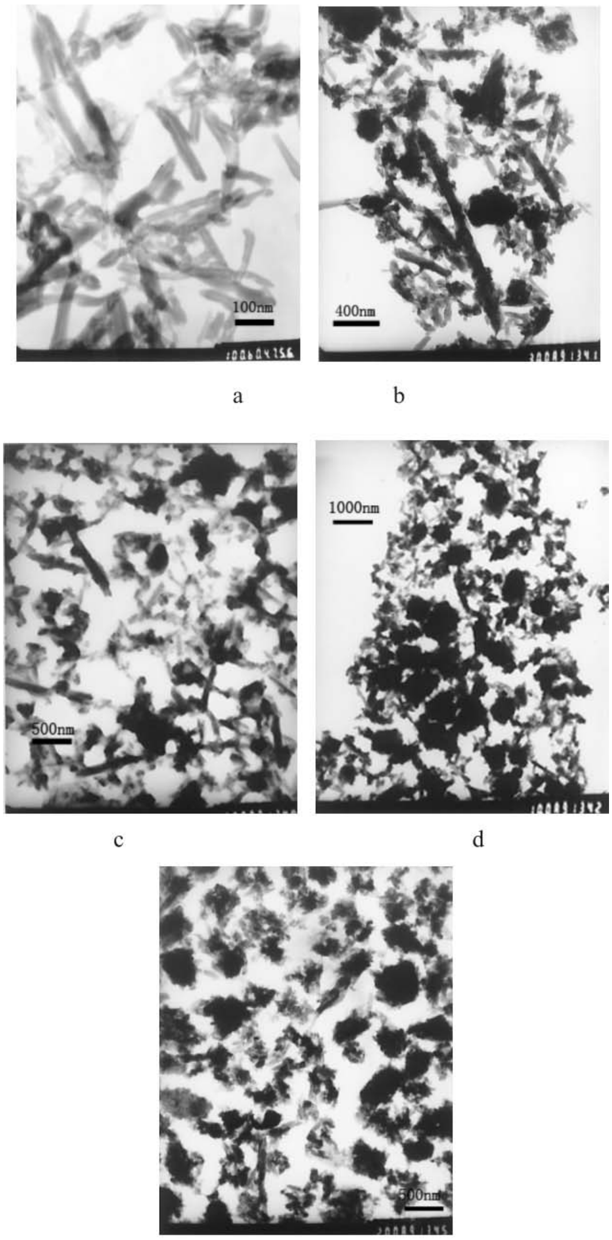


Fig. 3 Effect of the HNTs contents on the PG% and the GE% of the HNTs/PS nanocomposites

raw halloysite nanotubes. However, the solid structures were found in the TEM images of the HNTs-PS. It showed that the crosslink reactions were occurred also between the halloysite nanotubes to joint several halloysite nanotubes each other as an aggregation.

The thermal stabilities of the HNTs/PS and the HNTs-PS nanocomposites with different amounts of the organo-HNTs added in the bulk copolymerizations were compared with that of the pure polystyrene in Figs 2b and c, respectively. The thermal stabilities of the HNTs/PS nanocomposites were improved by copolymerization with the organo-HNTs. It is the same conclusion as the works reported previously. However, the thermal stabilities of the HNTs-PS nanocomposites were also higher than the pure polystyrene. The polymer grafted nanoparticles had lower thermal stabilities than the pure polystyrene because of the lower molecular mass of the grafted polymers [24]. This also showed that the crosslink reactions were occurred in the grafted polystyrene chains.



a b

c d

e

Fig. 4 TEM images of raw HNTs and PS grafted HNTs
a – HNTs, b – HNTs-PS 1, c – HNTs-PS 2,
d – HNTs-PS 3 and e – HNTs-PS 4

Conclusions

In the work, the unusually high percentage of grafting (PG%) of more than 230% was achieved in the halloysite nanotubes/polystyrene (HNTs/PS) nanocomposites with different amounts of the organo-HNTs added by the present bulk polymerization of styrene with organo-modified halloysite nanotubes (organo-HNTs) as macromonomers. It was explained with the cross-link reactions of the grafted polystyrene chains in the inner hollow space of the halloysite nanotubes and between the halloysite nanotubes each other. So the resulting nanocomposites HNTs/PS and HNTs-PS showed higher thermal stabilities than that of the pure polystyrene.

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