

Preparation and Characteristics of Polystyrene/Attapulgite Composites Via In-situ Suspension Polymerization

Kunyan WANG

Department of Materials Chemistry, Huzhou University, Huzhou, 313000, China

wky@hutc.zj.cn¹

Abstract. A series of polystyrene/attapulgite composites were synthesized through suspension polymerization. The composites were characterized by Fourier transform infrared spectroscopy, thermal gravimetric analysis, and X-ray diffraction. FTIR results show that there was no significant change in the peak positions and the peak intensity for polystyrene/attapulgite composites compared to the pure polystyrene. There is a rise in thermal stability of composites compared to pure polystyrene. Attapulgite acts as an effective thermal barrier and thereby hinders the degradation of polystyrene.

1. Introduction

Polymer-matrix composites have attracted much attention of researchers due to creation of materials with improved physical and chemical properties. A number of studies have been performed aimed at improving the thermal stability and mechanical properties of polystyrene (PS) by compounding it with organic or inorganic particles[1-3], such as multi-wall carbon[4], clay[5] and graphene[6]. For example, P. Pereira et.al[7] compared the impact of fullerenes and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) on the thermal stability of melt processed polystyrene, and reported that the PS-PCBM have higher thermal than the corresponding PS-C₆₀. A. Krishnan et. al.[8] investigated the effect of cellulose nanofibers on the mechanical and morphological properties of polypropylene/polystyrene blend.

Comparatively, the polymer-modified clay minerals possess more excellent dispersibility and good property than others. Attapulgite (ATP), natural Mg-Al silicate clay mineral with one-dimension crystal morphology, have recently received a great deal of attention. Attapulgite play important role in modifying the desirable properties of polymers and reducing the costing of their composites. To ensure interfacial interactions of the layered silicate with other polymer matrices, the layered surface must be converted to an organophilic surface. Organic attapulgite is one of the most important clay. Polymer/organic attapulgite composites have been attracting great interest because of their improved properties.

In this work, the attapulgites were used for the polystyrene-based composites via suspension polymerization. The effects of attapulgite loading on the properties of the polystyrene and the thermal degradation were confirmed by FTIR, XRD and TGA.

* Corresponding author:wky@hutc.zj.cn

2. Experimental Section

2.1 Materials

The monomer of styrene and dibenzoyl peroxide (BPO) as a free radical initiator were purchased from aladdin Co. Ltd. (China). Poly(vinyl pyrrolidone) (PVP) was used as stabilizing agent. The attapulgite which is one of natural fibrillar minerals was supplied by the Jiuchuan Nano-material Technology Co. Ltd.

2.2 Specimens Preparation

A series of polystyrene/attapulgite composites were synthesized through suspension polymerization. Attapulgite concentrations were 1, 3, and 5 wt% of monomer total weight. 0.3g of BPO, 0.14g attapulgite, and styrene were placed in the three-necked flask. The attapulgite were dispersed by sonication for 10min. Then 20ml 1.5% PVP and deionized water were added to three-necked flask. under constant stirring at 90 °C for 2h. Finally, PS/attapulgite particles were collected on a filter, washed with deionized water and dried in a vacuum drying chamber at 60 °C.

2.3 Characterizations

Fourier-transform infra-red (FTIR) spectroscopy has been used to monitor the chemical reactions. For the infrared measurement a small portion of the samples were grind to a fine powder, mixed with potassium bromide (KBr) powder and pressed into a pellet by hand press. FTIR were recorded by nicolet NEXUS-670 IR spectrometer in the wavelength range of 4000-400 cm^{-1} .

X-ray diffraction patterns were recorded in XD-6 X-ray diffractometer (China). The length and width of all test samples are 20mm and 15mm, respectively. The wavelength of the monochromated X-ray from Cu K α radiation is 0.154056nm. The scanning 2θ range was 10-60° with a scanning rate of 2°/min.

Thermogravimetric analysis (TGA) was carried out on a HTC-1 TG (China). The mass of each specimen was about 6 mg. Thermogravimetry analysis curves were recorded in the course of heating from 25°C to 500°C at a heating rate of 10°C/min.

3. Results and Discussion

3.1 Chemical Structure of Polystyrene/Attapulgite Composites

FTIR spectral analysis was performed to confirm the chemical structure of polystyrene and polystyrene/attapulgite composites. The FTIR spectra of polystyrene and polystyrene/attapulgite composites were shown in Fig.1. The absorption peak at about 3500 cm^{-1} was assigned to the absorption of water inside the PS. The peak at about 3000 cm^{-1} corresponding to the asymmetrical and symmetrical stretching vibrations of $-\text{CH}_2$ could be observed. The peak at 1500 cm^{-1} was assigned to aromatic C-H stretching. There was no significant change in the peak positions and the peak intensity for polystyrene/attapulgite composites, indicating that the composite have the same structural properties.

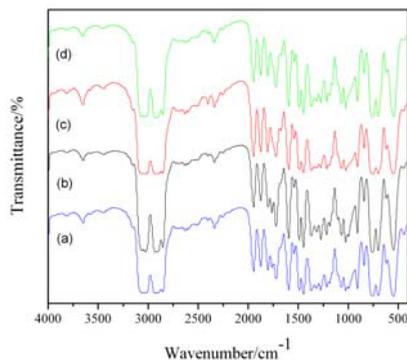


Fig.1 Infrared spectra of polystyrene (a) and polystyrene/attapulgite composites with different content of attapulgite, (b) 1wt%, (c) 3wt%, (d) 5wt%.

3.2 X-ray Diffraction Analysis

Fig. 2 shows the XRD patterns of polystyrene and polystyrene/attapulgite composites. Both polystyrene and polystyrene/attapulgite composites exhibit a broad diffraction peak and its location does not change.. It can be seen that the reflexes associated with attapulgite are absent in XRD patterns of composite. This is due to that the concentration of attapulgite in the studied composites is inadequate for the occurrence or the weak aggregation of attapulgite.

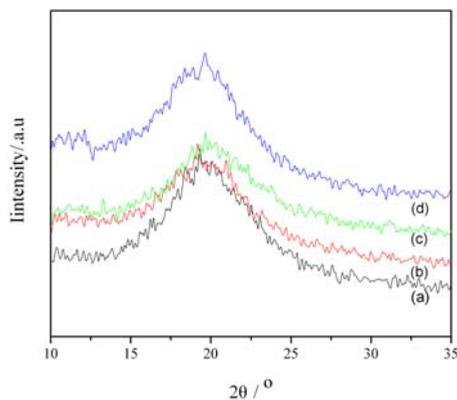


Fig. 2 XRD patterns of polystyrene (a) and polystyrene/attapulgite composites with different content of attapulgite, (b) 1wt%, (c) 3wt%, (d) 5wt%.

3.3 Thermal Degradation of Composites

Fig. 3 shows the TG curves from the thermal degradation of the effect of attapulgite on the decomposition behavior of polystyrene. Both polystyrene and polystyrene/attapulgite composites decomposed in a one step process. The TGA curves showed that polystyrene and composites undergo massive thermal degradation after 320 °C. The TGA curve profile of the composites shifted towards a higher temperature compared to pure polystyrene. There is a

rise in thermal stability of composites compared to pure polystyrene. Attapulgite acts as an effective thermal barrier and thereby hinders the degradation of polystyrene. Fig. 4 shows the DTA of TGA, which gives the peak temperature at which the maximum weight loss occurred. The DTA curve shows a single prominent rate of weight loss peak, which indicated that the thermal degradation consisted of one main weight loss step.

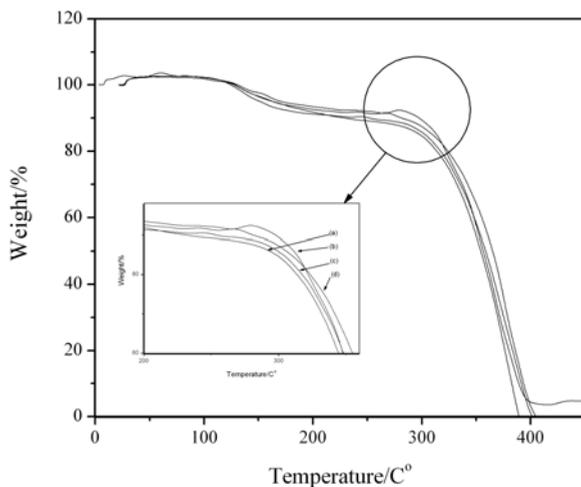


Fig.3 TG curve of polystyrene (a) and polystyrene/attapulgite composites with different content of attapulgite, (b) 1wt%, (c) 3wt%, (d) 5wt%.

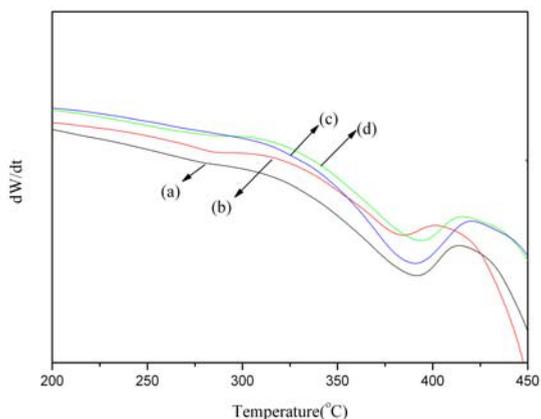


Fig.4 DTA curve of polystyrene (a) and polystyrene/attapulgite composites with different content of attapulgite, (b) 1wt%, (c) 3wt%, (d) 5wt%.

4. Conclusions

In this work, polystyrene and polystyrene/attapulgite composites were prepared through in situ suspension polymerization. The polystyrene/attapulgite composites were characterized by Fourier transform infrared spectroscopy, thermal gravimetric analysis, and X-ray diffraction. FTIR results show that there was no significant change in the peak

positions and the peak intensity for polystyrene/attapulgite composites compared to the pure polystyrene. TGA results show that the attapulgite enhanced thermal properties for polystyrene. Attapulgite acts as an effective thermal barrier and thereby hinders the degradation of polystyrene.

5. Acknowledgements

The authors would like to acknowledge financial support by the Natural Science Foundation of Zhejiang province of China (LQ14B040003).

References

1. K.Chrissafis, E. Pavlidou, E. Vouvoudi, D. Bikiaris, Decomposition kinetic and mechanism of syndiotactic polystyrene nanocomposites with MWCNTs and nanodiamonds studied by TGA and Py-GC/MS, *Thermochimica Acta*. 582(2014)15-24.
2. L. Blanco, L. Abate, F.A. Bottino, P. Bottino, Thermal behavior of a series of novel aliphatic bridged polyhedral oligomeric silsesquioxanes (POSSs)/polystyrene (PS) nanocomposites: The influence of the bridge length on the resistance to thermal degradation, *Polymer Degradation and stability*. 102(2014)132-137.
3. L. Saghatforoush, M. Hasanzadeh, N. Shadiou, Polystyrene-graphene oxide modified glassy carbon electrode as a new class of polymeric nanosensors for electrochemical determination of histamine, *Chinese Chemical Letters*. 25(2014)655-658.
4. P. Slobodian, V. Pavlínek, A. Lengálová, P. Sába, Polystyrene/multi-wall carbon nanotube composites prepared by suspension polymerization and their electrorheological behavior, *Current Applied Physics*. 9(2009)184-188.
5. M.A.B.S. Nunes, L.S. Galvao, T.P.M. Ferreira, E.J.F.T. Luiz, Y.L.M. Bastos, A.S.F. Santos, Reprocessability of high impact polystyrene/clay nanocomposites in extrusion, *Polymer Degradation and Stability*. 125(2016)87-96.
6. R.Gu, WZ. Xu, P.A. Charpentier, Synthesis of graphene-polystyrene nanocomposites via RAFT polymerization, *Polymer*. 55(2014)5322-5331.
7. P. Pereira, H. Gaspar, L. Fernandes, G. Bernardo, Impact of fullerenes on the thermal stability of melt processed polystyrene and poly(methyl methacrylate) composites, *Polymer Testing*. 47(2015)130-136.
8. A. Krishnan K, C. Jose, K.E. George, Sisal nanofibril reinforced polypropylene/polystyrene blends: morphology, mechanical, dynamic mechanical and water transmission studies, *Industrial Crops and products*. 71(2015)173-184.