



## Preparation of Novel Polystyrene-Layered Hydroxide Zinc Benzoate Nanocomposites by Bulk Polymerization

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Received: 2 July 2014;

Accepted: 15 September 2014;

Published online: 27 April 2015;

AJC-17178

Novel polystyrene-layered hydroxide zinc benzoate nanocomposites were prepared by bulk polymerization with azobisisobutyronitrile initiator. The well dispersion of layered hydroxide zinc benzoate in matrix was observed. The presence of filler shields polystyrene from thermal oxidation and brings to a reduction of 50 % in heat release rate during combustion with 1 wt. % loading. The research successfully exemplified the feasibility of layered hydroxide benzoate as fillers in polymeric nanocomposites.

**Keywords:** Nanocomposite, Layered hydroxide salts, Polymerization.

### INTRODUCTION

Polymer-layered inorganic nanocomposites are one of the most significant breakthroughs in polymer and materials science and have potential applications in such as electronics, transportation, construction and consumer products. The dispersion of a low loading (about 5 wt. %) of micro- or nano-scale reinforcements into organic polymers is current interest and challenge for the preparation of novel composite materials with enhanced mechanical, gas barrier and flame retardant properties when compared with those of the individual components or polymers<sup>1-5</sup>.

Layered inorganic materials possess unique intercalate and exchange properties and can be active as fillers in polymeric nanocomposites. There is a wide range of layered materials available, such as silicate, phosphates, sulfide, titanates, layered double hydroxides, but only a few have found use in polymer nanocomposites<sup>6,7</sup>. Much work has been reported on the use of ionic-exchanging montmorillonites clays as fillers of polymeric nanocomposites. Up to now, less attention has been paid to anionic-exchanging layered inorganics hydroxide salts (LHSs) especially Zn type LHSs, even if these latter materials compare favourably with natural clays in terms of purities, control of crystallinity and particle size, wider possibility of functionalization<sup>8-10</sup>. Although there has been some work reported on synthesis, structure analysis and anion-exchange reactions of Zn type LHSs, Zn type LHSs compounds have less explored as fillers in polymeric nanocomposites<sup>11-15</sup>. Recently, a typical zinc type LHSs *i.e.*, layered hydroxide zinc

benzoate (LHZB) as fillers was selected to examine the feasibility of Zn type LHSs as fillers in polymeric nanocomposites.

In this paper, the polystyrene-LHZB (PS-LHZB) nanocomposites were prepared by the bulk polymerization of styrene. The dispersion of LHZB in the matrix and the effect of LHZB loading on properties of the PS-LHZB were discussed.

### EXPERIMENTAL

Styrene was used after further purification including retarder removal, water removal and reduced pressure distillation. Other starting materials used in this work are analytical reagent grade.

**General procedure:** In this experiment, layered hydroxide zinc benzoate (LHZB) was synthesized by hydrothermal technique under 120 °C for 24 h with zinc oxide and benzoic acid. Different amounts of LHZB were mixed with the 15 g of styrene monomer under ultra-sonic stirring for 20 min. When the LHZB was completely dispersed, the 1 % by weight of azobisisobutyronitrile (AIBN) was added and stirred to form a stable suspension. Then the suspension was polymerized at 60 °C for 10 h under a nitrogen atmosphere. The viscous mixture was then poured into a mould and kept at 70 °C for 12 h in oven. After drying and removing unpolymerized monomer in a vacuum oven at 80 °C, PS-LHZB nanocomposites were obtained. This preparation procedure was also used for pure polystyrene.

The structure of the samples were measured by X-ray diffraction (XRD) measurement on a PW3040/60 diffractometer

equipped with graphite mono-chromatized  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406$  nm). Thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA851 thermal analyzer operating in a dynamic mode at heating rates of  $10$  °C/min. The conditions were the sample weight,  $10$  mg and air. HRTEM images were obtained with a JEOL JEM-2200FS instrument operating at an accelerating voltage  $200$  kV. The samples morphologies were observed by a scanning electron microscope (SEM) using JEOL JSM 6300 microscope, at an acceleration voltage of  $10$  kV.

## RESULTS AND DISCUSSION

The structure of the hydrothermal synthesized sample of LHZB was measured by X-ray diffraction (XRD) in Fig. 1. The sample is composed of main layered phase of  $1.45$  nm and shows main diffraction peaks with  $d$  value of  $0.72$ ,  $0.48$ ,  $0.36$  and  $0.29$  nm, which is very close to the value reported by Ogata *et al.*<sup>16</sup>. The diffraction peak with  $d$  value of  $1.32$  nm is observed. It suggests that the sample have mixed layered phase. The morphology of the sample of LHZB was examined with scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) (Figs. 2 and 3). Here, the unique wire-like morphology of LHZB is regarded as an important factor that influences properties of the material. The nanowire could interact with more functional groups around it within the length scope. This is benefit to sufficient dispersion in polymer matrix. Therefore, fewer LHZB are needed to the formation of interpenetrating network.

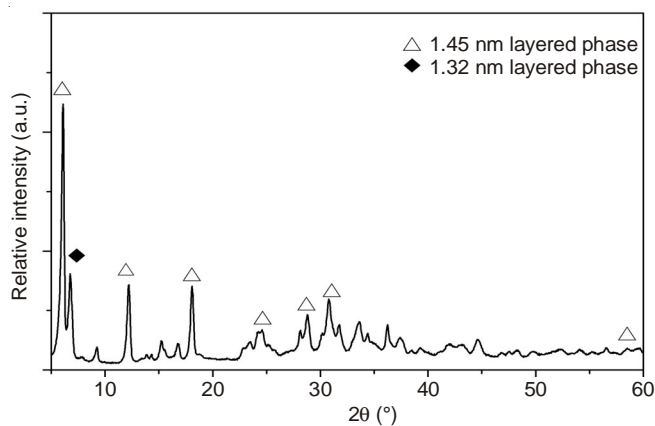


Fig. 1. XRD pattern of the synthesized LHZB

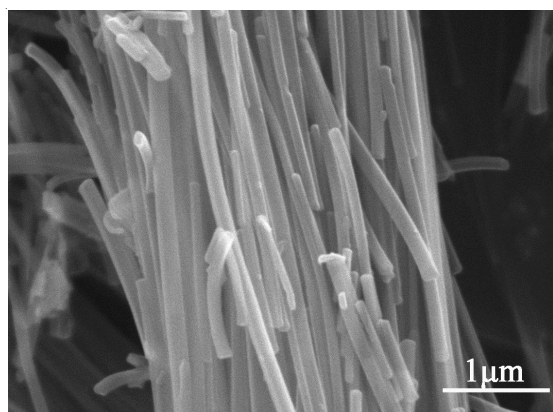


Fig. 2. SEM image of the synthesized LHZB

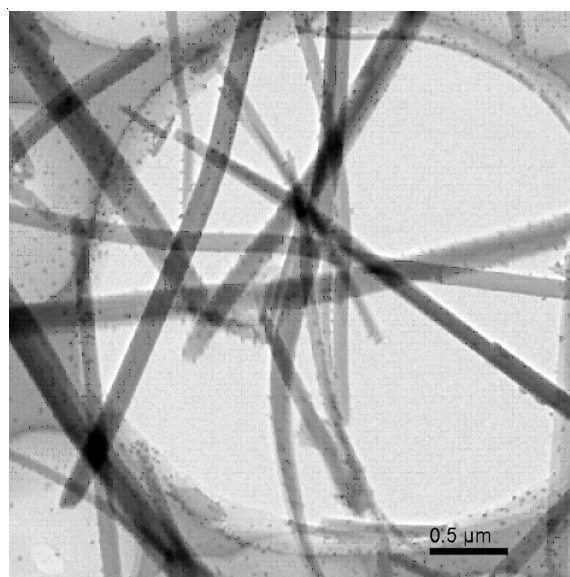


Fig. 3. TEM image of the synthesized LHZB

X-Ray diffraction patterns of PS-LHZB composites are shown in Fig. 4 in the range of  $2\theta = 2$ - $10$ °. These diffraction patterns reveal the structural changes of the samples with different loadings of LHZB. The basal spacing of the LHZB powder sample (Fig. 4 LHZB) is measured to be  $1.45$  nm from the (001) diffraction peak at  $2\theta = 6.06$ °. The shifting of this peak to lower angles indicates an increase of interlayer spacing due to the intercalation of polymer (PS-3 wt. % LHZB and PS-5 wt. % LHZB nanocomposites). For PS-LHZB composite containing 3 wt. % LHZB, the strong (001) plane peak corresponding to  $d_{001}$  (about  $3.4$  nm) (Fig. 4 PS3) is clearly observed, resulting from this kind of composite: intercalated nanocomposite or at least intercalated structural shape occupied majority. With the decrease of the LHZB content (from 3 to 1 wt. %), the relative intensity of peak of the (001) plane becomes weaker. Along with LHZB content depression, the diffraction peak of (001) plane is not detectable (Fig. 4 PS1). It declares intercalated morphology is reductive and the exfoliated morphology is incremental. Styrene monomers enter the interlayers and grow to form polystyrene macromolecules going with releasing large quantity of heat. According to the intercalative polymerization mechanism, the interlayer spacing of LHZB should be enlarged and intercalated or exfoliated by the growing polystyrene macromolecule chains<sup>17</sup>.

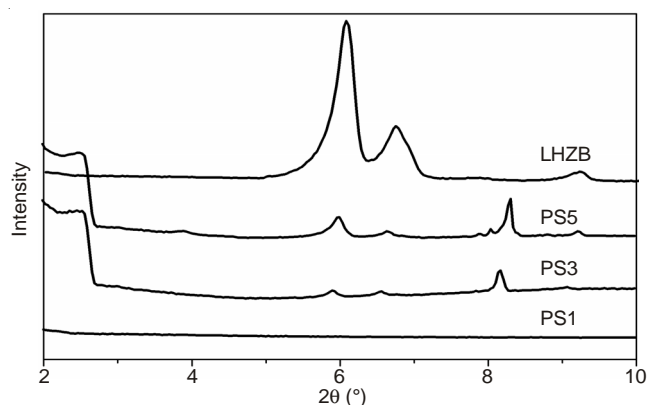


Fig. 4. XRD patterns of PS-LHZB nanocomposites

TABLE-1  
TG DATA OF PURE POLYSTYRENE (PS) AND PS-LHZB NANO-COMPOSITES

Sample codes	LHZB content (%)	$T_{0.1}$ s (°C)	$T_{MAX}$ (°C)	Residue 600°C (wt. %)
PS0	0	361	376	0.03
PS1	1	387	401	1.34
PS3	3	390	407	2.98
PS5	5	391	413	4.71

In order to determine the degree of LHZB dispersion in the polymeric matrix, nanocomposite sample with high inorganic loading (5 wt. %) was cryogenically broken after immersion in liquid nitrogen and the fractured surface is characterized by SEM as shown in Fig. 5. It is evident from SEM images observations that the LHZB nanowire are uniformly dispersed in the polystyrene matrix without macroscopic phase separation, even in high filler content and indicate the formation of interpenetrating network structure between nanowires and polystyrene. Additional and definitive proof of the presence of exfoliated lamellae into the composites will be obtained by transmission electron microscopy analyses in due course.

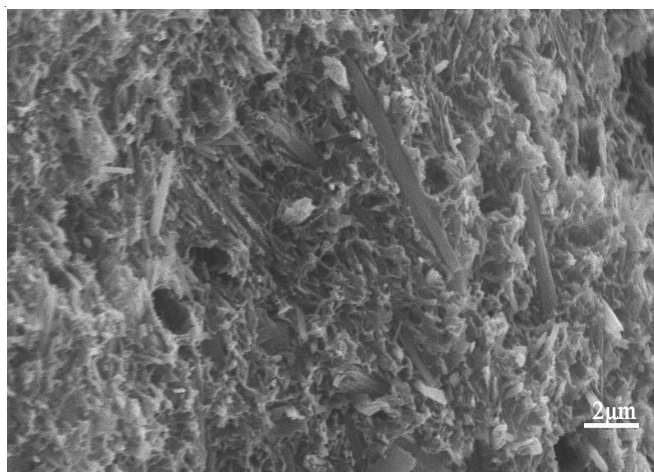


Fig. 5. SEM image of the fractured surface of the nanocomposite sample with high LHZB loading (5 wt. %)

The TG curves of pure polystyrene and PS-LHZB nanocomposites are shown in Fig. 6 and Table-1. The decomposition temperature ( $T_{max}$ ) of nanocomposites is about 25-37 °C higher than that of pure polystyrene. The origin of the noticeable

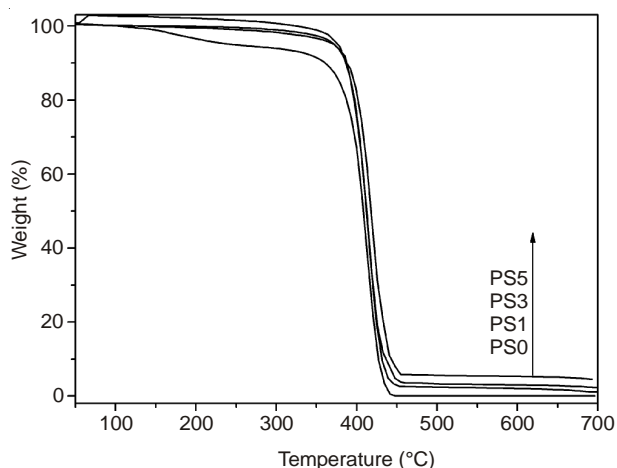


Fig. 6. TG curves of pure polystyrene and PS-LHZB nano-composites

increase in the decomposition temperatures mainly results from strong interaction and possible formation of interpenetrating network structure between polymer and LHZB. These behaviours point out that the presence of the LHZB lamellae produces a barrier effect to oxygen diffusion into the heated polymer.

The formation of this protective layer on the specimen surface is well evident during the combustion in the cone calorimeter test. In Fig. 7, the heat release rate for the pure polymer and its nanocomposite with different loadings of LHZB are displayed. The presence of 1 % of LHZB brings a reduction of 50 % in the maximum of heat release rate (peak HRR). The Fire Growth Index (FGI = peak HRR/TTI) from 6.40 kW/m<sup>2</sup> s for the pure polymeric matrix is decreased to 3.09 kW/m<sup>2</sup> s in the case of the nanocomposite showing a consistent reduction of fire risk.

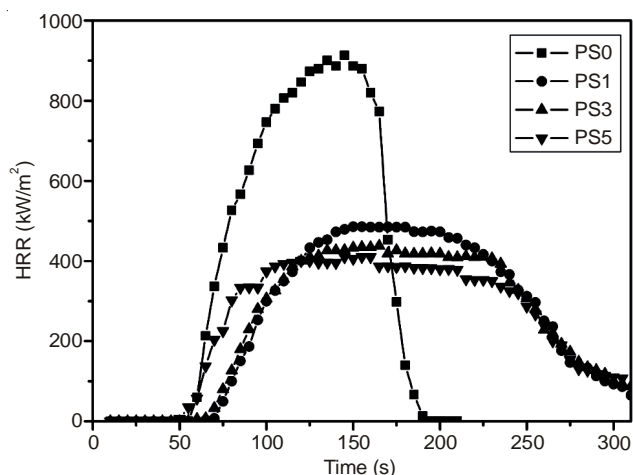


Fig. 7. Heat release rates curves of PS-LHZB nanocomposites

## Conclusion

The PS-LHZB nanocomposites have been successfully synthesized *via* bulk polymerization. The above observations exhibit that the LHZB have expected compatibility with the polystyrene and better thermal stability. The research not only successfully exemplifies the feasibility of layered inorganics hydroxide salts as fillers in polymeric nanocomposites, but also supplies a new way for developing novel polymer-layered inorganic nanocomposites. These nanocomposites have potential applications in heat stabilizer, flame retardant and multifunction additives.

## ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the National Natural Science Foundation of China (51304139) and Liaoning Province Education Administration (L2013089).

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