Solvothermal Synthesis of Organically Modified α-Zirconium Phosphate-Based Polystyrene Nanocomposites and Thermal Stability

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ABSTRACT: Polystyrene/α-zirconium phosphate (PS/OZrP) nanocomposites were prepared based on the organically modified α-ZrP(OZrP) with hexadecyltrimethyl ammonium bromide (C16) by solvothermal technique and solution refluxing. The structure of the PS/OZrP composites was characterized by X-ray diffraction and high-resolution electronic microscopy. The thermal behaviors of the composites obtained were investigated by thermogravimetric analysis. The maximum decomposition temperatures ($T_{\max}$) of PS/OZrP nanocomposites prepared by solvothermal method increased gradually from 431 to 458°C with the increase of the OZrP loading from 0 to 20 wt %, and the amounts of the charred residue at 600°C (char wt %) had a remarkable increase from 1.6 to 17.1 wt %, respectively. Moreover, the TG results of the nanocomposites prepared by solvothermal method have more obvious enhancement in the thermal stabilities and especially in the amount of charred residue at 600°C (char wt %), which has a double increase from 4.2 to 8.5 wt % at the content of 10 wt % OZrP than by solution refluxing. All results suggested that the solvothermal method is an effective way for the preparation of PS/OZrP nanocomposites with the intercalated nanostructure, which led to the obviously improved thermal stability. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 593–598, 2011

Key words: polystyrene; nanocomposites; thermal properties; synthesis

INTRODUCTION

In the recent years, polymer/layered inorganic nanocomposites have been extensively studied because of their unique properties including mechanical, thermal, and gas barrier properties compared to their conventional counterparts.[1–5] However, the studies about these kinds of nanocomposites have been mainly focused on the polymer/layered silicate systems, especially montmorillonite, while the layered metal phosphate systems have been much less reported in the literature.[6–9] As a kind of the synthetic-layered inorganic compounds, crystalline α-zirconium phosphate (α-ZrP) was first prepared in 1964 by Clearfield and Stynes.[10] α-ZrP has a much higher ion exchange capacity of 600 mmol/100 g than silicate, and its quite narrow particle size distribution and high aspect ratio can be controlled by altering reaction conditions.[11] So, α-ZrP is an excellent host for the preparation of organic/inorganic hybrids. However, during the past few years, much attention has been paid to the preparation of metal oxide pillared α-ZrP intercalated compound and polyelectrolyte/α-ZrP composite film, whereas the polymer/α-ZrP systems have rarely been studied.[12–14] In 1995, Ding[15] reported their work on the modification of α-ZrP using amino acids to prepare nylon 6/α-ZrP nanocomposite. Sue and coworkers[16,17] reported their study about the preparation and fracture behavior of α-ZrP-based epoxy nanocomposites by modifying α-ZrP with monoamine-terminated polyether (Jeffamine M715). Lately, Yang[18] investigated the synergistic effect of layered α-ZrP in intumescent fire-retardant polypropylene systems. To the best of our knowledge, no other related research works have been found focusing on the preparation of the polymer/α-ZrP nanocomposites.

Polystyrene (PS) is one of the most widely used thermoplastics in many fields such as electrical appliances, packaging, and building materials because of its low cost, rigidity, high transparence, and chemical stability. Yet, the applications of PS are also limited due to its poor thermal stability and mechanical property. Although several efforts have been reported on the preparation of PS/layered silicate nanocomposites with improved properties by

intercalation reaction,[19,20] no attempt has been conducted on the intercalation of α-ZrP with PS by solvothermal method. Generally, polymer/layered inorganic nanocomposites can be synthesized by various methods, including solution intercalation, *in situ* polymerization, or melt intercalation. Among these methods, solution intercalation is an extensively used way, by which the polymer molecule can be directly introduced into the gallery of layered inorganic. The key of the solution method is to select a suitable solvent for both dissolution of polymer and dispersion of inorganic and to provide an environment for the effective diffusion and transfer of the chemicals. Also, layered inorganic hosts usually need to be organically modified before the intercalation with polymer. In addition, the solvothermal method is a powerful technique for preparing materials under a pressure–temperature domain condition, which conduces to the diffusion and transfer of chemicals.[21] In this work, α-ZrP was modified by hexadecyltrimethyl ammonium bromide (C16) to obtain the organophilic C16/α-ZrP-intercalated compound (named OZrP), which was used as a precursor for the preparation of PS nanocomposites by solvothermal method. For comparison, the PS/α-zirconium phosphate (PS/OZrP) composites were synthesized by solution refluxing. Then, on the basis of the preparation and characterization, the thermal behaviors of PS/OZrP nanocomposites and composites were investigated using thermogravimetric (TG) analysis.

EXPERIMENTAL

Materials

Hexadecyltrimethyl ammonium bromide (C16) and other reagents were purchased from Shanghai Chemical Reagent Corp. PS resin (492j, $M_w = 7.5 \times 10^4$) was supplied as pellets by Yangzi Petrochemical Company (Nanjing,China). All these commercial chemicals were used as received without further purification. Pristine-layered α-ZrP powder was prepared by hydrothermal synthesis under the optimum condition according to our previous work.[22]

Teflon-lined stainless steel autoclave was used for solvothermal synthesis. The ultrasonic treatment was carried out by a KS-900 ultrasonic generator (Ningbo Kesheng) at room temperature under air atmosphere.

Synthesis

Preparation of organophilic α-ZrP

Because α-ZrP has a small interlayer distance of 0.76 nm and high-layer charge density, unlike layered

montmorillonite, it is hard to be exfoliated in water. But it is easy to be exfoliated with polar alkylamines or alcohol amines,[23] by which the interlayer charge density was decreased, and the interlayer distance of α-ZrP was increased, resulting in forming exfoliated system, which would be beneficial to the intercalation reaction. To obtain organophilic α-ZrP (OZrP), the hexadecyltrimethyl ammonium bromide (C16), a kind of an ammonium salts with long alkyl chains was used as a modifier and introduced into the gallery of α-ZrP by exfoliation–intercalation method described as follows. First, ethylamine (EA) was chosen as a colloidal reagent for the exfoliation of α-ZrP. A certain amount of α-ZrP powder was dispersed in distilled water in a liquid/solid ratio of 100 mL g^{-1}, followed by adding EA aqueous solution of 0.2 mol L^{-1} in a mole ratio of 2.0 of amine/α-ZrP. After ultrasonic treatment for several minutes, α-ZrP-exfoliated system was obtained. Then, a desired amount of C16 aqueous solution of 0.2 mol L^{-1} was added dropwise into the α-ZrP-exfoliated system and subsequently stirred vigorously at room temperature for several hours. The white precipitate as-prepared was washed with hot deionized water and centrifuged repeatedly several times to remove the residual C16 surfactant. The filtrate was titrated with 0.1 mol L^{-1}AgNO$_3$ until no precipitate of AgBr was formed so as to ensure the complete removal of bromide ions. The product was placed in a vacuum drying oven at 60°C for 12 h and was ground to obtain white organophilic α-ZrP powder (i.e., OZrP).[24]

Preparation of PS/OZrP nanocomposites

A certain amount of OZrP powder was homogeneously dispersed in toluene in a liquid/solid ratio of about 20 mL g^{-1}at room temperature. At the same time, a desired amount of PS resin and toluene was added into a Teflon-lined stainless steel autoclave of 60-mL capacity. The autoclave was sealed and maintained at 150°C for 1 h to obtain the swelled PS in toluene. Then, the above OZrP toluene dispersion was poured into the cooled autoclave containing the swelled PS. Subsequently, the autoclave was put in an oven and maintained at 150°C for 3 h. After cooling to room temperature naturally, the product was poured into a flat mold and dried at 80°C under vacuum overnight to volatilize toluene. Finally, the pale yellow PS/OZrP nanocomposite was obtained. For comparison, the mixture of PS and OZrP in toluene was refluxed at 115°C for 8 h to obtain the PS/OZrP composite.

Characterization

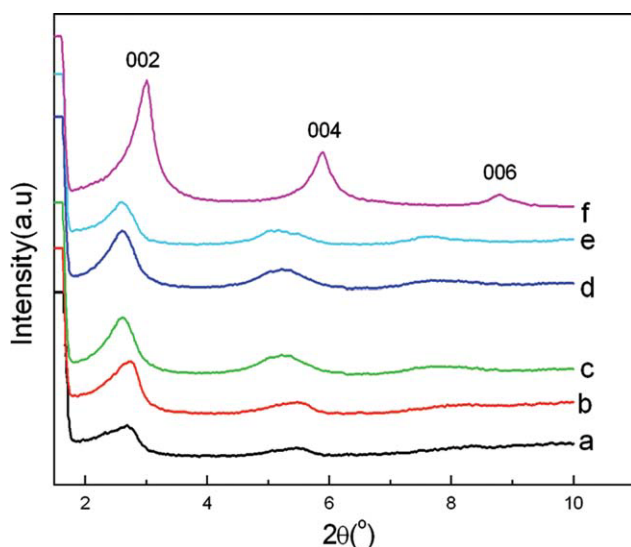X-ray diffraction (XRD) measurements were performed directly on the hybrid samples using a

Figure 1 XRD patterns of OZrP and PS/OZrP nanocomposites with different contents of OZrP: (a) 3 wt %; (b) 5 wt %; (c) 10 wt %; (d) 15 wt %; (e) 20 wt %; (f) precursor OZrP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Rigaku D/max-rA X-ray diffractometer (30 kV and 10 mA) with Cu Kα ($\lambda = 1.54178$ Å) irradiation at a scanning rate of 0.02°/s. The transmission electron microscopy (TEM) images were obtained by H-800 microscope with an acceleration voltage of 100 kV. The high-resolution transmission electronic microscopy (HREM) images were obtained by JEOL-2010 microscope with an acceleration voltage of 200 kV. The specimen for TEM and HREM was cut from an epoxy block with embedded films of compounds at room temperature using an ultramicrotome (Ultracut-1, UK) with a diamond knife. The thermal properties of the materials were investigated by TG analysis using a Netzsch STA-409C thermal analyzer at a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

XRD patterns of OZrP and PS/OZrP hybrids with different inorganic contents prepared by solvothermal method in the optimum conditions (toluene as a solvent, 150°C for 3 h) were shown in Figure 1 in the range of $2\theta = 1.5°–10°$. The basal spacing of the layered OZrP is measured to be 2.9 nm from the (002) diffraction peak at $2\theta = 3.0°$ in Figure 1(f). In the case of Figure 1(a–e), the interlayer distances were expanded effectively to ∼ 3.3 nm corresponding to the (002) diffraction peak at around $2\theta = 2.7°$, which indicated the formation of the intercalated nanostructure of the PS/OZrP nanocomposites. With the increase of the inorganic contents, no distinct changes in the basal spacing of PS/OZrP nanocom-

posites could be seen except the enhancement of the intensity of the diffraction peak corresponding to 002 plane.

TEM observation of PS/OZrP hybrid, as shown in Figure 2(a), demonstrated that the dispersibility of the OZrP layers with a high aspect ratio in nanometer scale was generally homogeneous in the PS matrix. Moreover, the microstructure of PS/OZrP nanocomposite was further confirmed by HREM
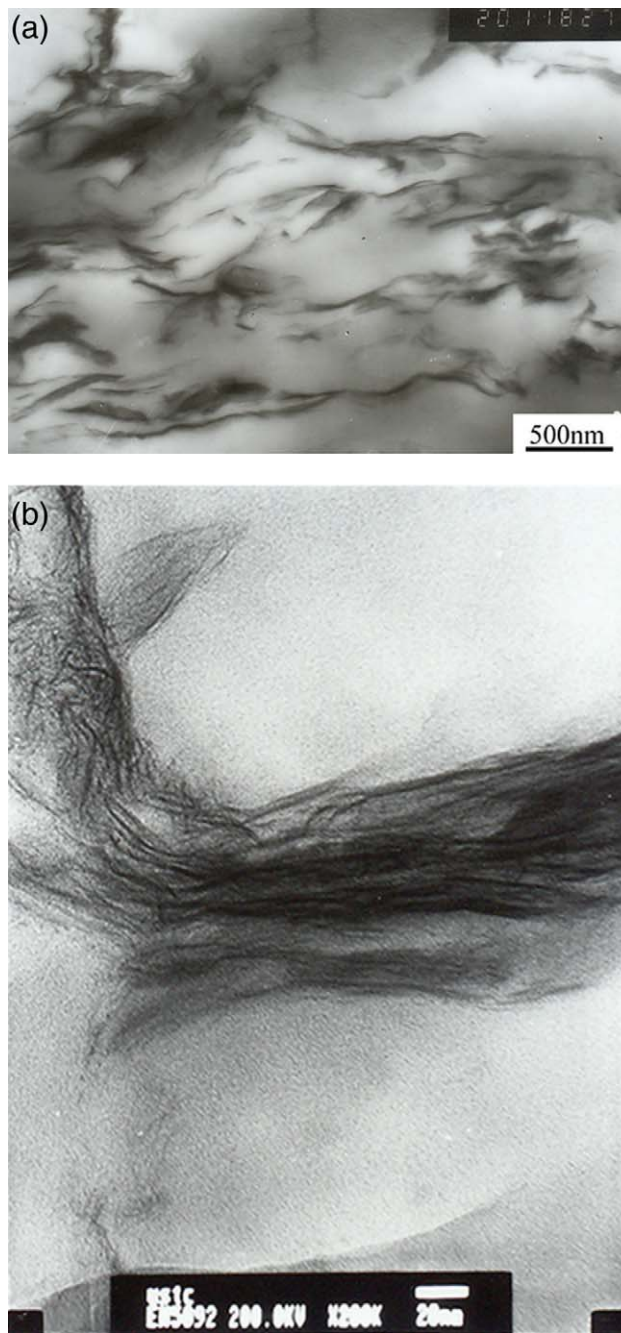

Figure 2 (a) TEM image of PS/OZrP nanocomposite containing 10 wt % OZrP. (b) HREM image of PS/OZrP nanocomposite containing 10 wt % OZrP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
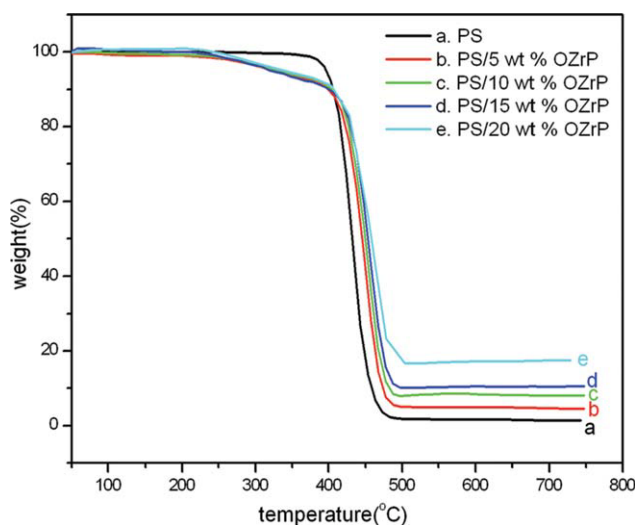
Figure 3 TG curves of pure PS and PS/OZrP nanocomposites with different contents of OZrP: (a) pure PS; (b) 5 wt %; (c) 10 wt %; (d) 15 wt %; (e) 20 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

image from Figure 2(b), wherein the dark lines (the arrow points out) corresponded to the intercalated structure with the interlayer distance of about 4.0 nm. This d_{002} value estimated from HREM is slightly higher than that of the result of XRD (d_{002} = 3.3 nm). The discrepancy is caused by the fact that XRD reveals the result of the statistical average while HREM displays the partial area of the nanocomposite. In fact, the inorganic primary particles dispersed in the polymer matrix are composed of many different single inorganic lamellae with a variety of interlayer distances by the intercalation of polymer molecule.

Thermal stability is an important property in which the nanocomposite morphology plays an important role. TG curves for pure PS and nanocomposites with different OZrP contents were shown in Figure 3. And, the TG analysis results including the 5% weight loss temperature ($T_{-5\%}$), the maximum weight temperatures (T_{max}), and the charred residue amount at 600°C (char wt %) were summarized in Table I. It was obvious that the PS/OZrP nanocom-

posites degraded at a higher temperature, which is similar to the PS/clay intercalated nanocomposites.[25] When the 5% weight loss is selected as a comparison point, the start decomposition temperatures ($T_{-5\%}$) of all PS/OZrP nanocomposites were lower than that of pure PS. According to the Hofmann degradation mechanism,[26] in the initial stage of decomposition, an acid proton on the inorganic surface was formed due to the loss of an olefin and amine driving from the presence of the C16 organically modifier, which facilitated the decomposition and carbonization of polymer by a catalytic effect resulting in the lower decomposition temperature of the PS nanocomposites. When the maximum weight loss is selected as a comparison point, the maximum decomposition temperatures (T_{max}) of PS/OZrP nanocomposites increased gradually from 431 to 458°C with the increase of the OZrP loading from 0 to 20 wt %. At the same time, the amounts of the charred residue at 600°C (char wt %) had a remarkable increase from 1.6 to 17.1 wt %, respectively. These results suggested that PS chains were protected in the degradation process by the intercalated α-ZrP lamellae.

In addition, different preparation methods had different influences on the improvement of the thermal stability of nanocomposites, although no notable changes in the interlayer distance corresponding to the 002 diffraction peak in their XRD patterns could be seen (shown in Fig. 4). Comparing the TG results of the nanocomposites prepared by different methods with the 10 wt % OZR loading (shown in Fig. 5), it could be seen that only by solvothermal
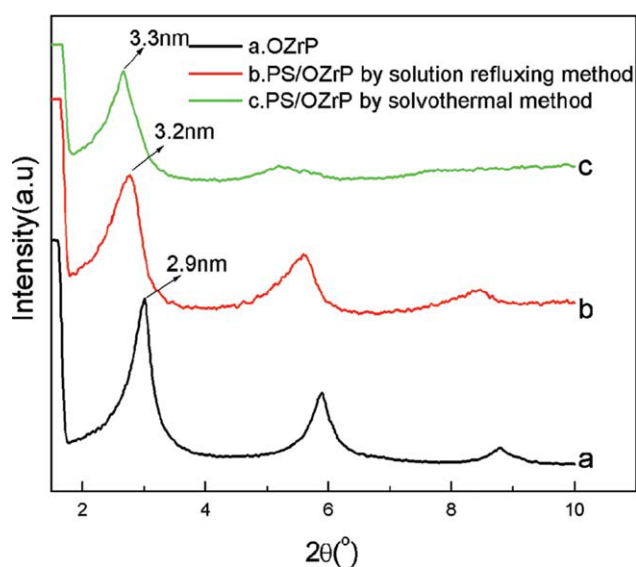
TABLE I
TGA Results for the Thermal Degradation of the Samples

Samples	T_d (−5%) (°C)	T_{max} (°C)	Char at 600°C (wt %)
(a) PS	397	431	1.6
(b) PS/5 wt % OZrP	324	444	5.0
(c) PS/10 wt % OZrP	328	449	8.5
(d) PS/15 wt % OZrP	320	4530	10.4
(e) PS/20 wt % OZrP	337	458	17.1

Figure 4 XRD patterns of the samples: (a) OZrP; (b) PS/10 wt % OZrP composite prepared by solution refluxing; (c) PS/10 wt % OZrP nanocomposite prepared by solvothermal method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 TG curves of the samples: (a) pure PS; (b) PS/10 wt % OZrP composite by solution refluxing; (c) PS/10 wt % OZrP nanocomposite prepared by solvothermal method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
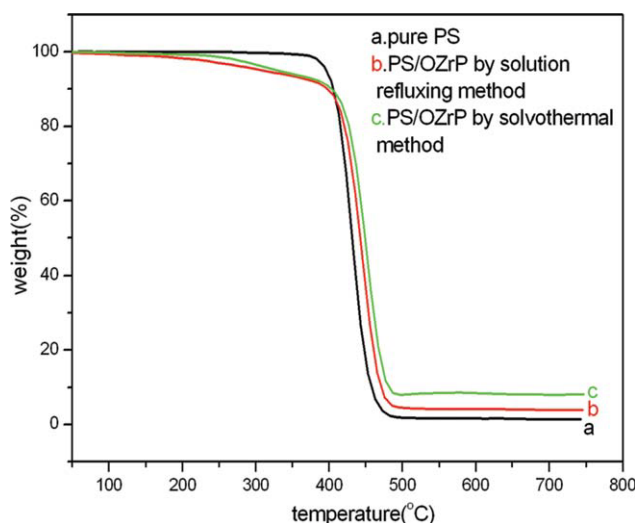
method could one get an obvious enhancement in the thermal stabilities and especially in the amount of charred residue at 600°C (char wt %), which has a double increase from 4.2 to 8.5 wt % than by solution refluxing. Because the solvothermal method provides a pressure–temperature domain condition, the specific physicochemical properties of solvent in solvothermal conditions can markedly improve the diffusion of PS molecular chains in the inorganic layers and effectively facilitate the interaction of α-ZrP layers with polymer. Solvothermal method, therefore, is a powerful way for the preparation of the polymer nanocomposites based on the layered inorganic.

All above results suggested that different preparation methods affected the structure of the nanocomposites, leading to a difference in the improvement of thermal property. The thermal decomposition process and the thermal stability of the nanocomposites were improved because of the effect of layered OZrP lamellae dispersed well in the matrix by creating a protective charring layer on the surface of the materials. At the same time, TGA results also gave an evidence for the formation of the intercalated structure of PS/OZrP nanocomposites.

CONCLUSIONS

In this study, a novel PS/α-ZrP nanocomposites were prepared based on the organically modified α-ZrP(OZrP) with hexadecyltrimethyl ammonium bromide (C16) by solvothermal technique and characterized by XRD, TEM, and HREM. Solvothermal method provided an especial physicochemical condi-

tion, which could effectively facilitate the diffusion of PS molecular chains in the inorganic layers and finally result in the formation of the intercalated nanocomposites. The thermal behaviors of the nanocomposites were investigated by TG analysis. It was found that the structure of the nanocomposites was affected by the different preparation method, which led to a difference in the thermal property. Therefore, solvothermal method is an effective way for the preparation of polymer/layered inorganic nanocomposites with intercalated nanostructure and improved thermal stability.

A short synopsis of the main contributions in this work

PS/OZrP nanocomposites were prepared based on the organically modified α-ZrP(OZrP) with hexadecyltrimethyl ammonium bromide (C16) by solvothermal technique and solution refluxing. The structure of the PS/OZrP composites was characterized by XRD and HREM. The thermal behaviors of the composites obtained were investigated by TG analysis. The maximum decomposition temperatures (T_{max}) of PS/OZrP nanocomposites prepared by solvothermal method increased gradually from 431 to 458°C with the increase of the OZrP loading from 0 to 20 wt %, and the amounts of the charred residue at 600°C (char wt %) had a remarkable increase from 1.6 to 17.1 wt %, respectively. Moreover, the TG results of the nanocomposites prepared by solvothermal method have more obvious enhancement in the thermal stabilities and especially in the amount of charred residue at 600°C (char wt %), which has a double increase from 4.2 to 8.5 wt % at the content of 10 wt % OZrP than by solution refluxing. All results suggested that the solvothermal method is an effective way for the preparation of PS/OZrP nanocomposites with the intercalated nanostructure, which led to obviously improved thermal stability.

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