Preparation and Characterization of PLA/ZnS Nanocomposites via an *In Situ* Solvothermal Process

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ABSTRACT: Homogenous poly(lactic acid) (PLA)/zinc sulfide (ZnS) nanocomposites were successfully prepared via a solvothermal method with lactide, zinc acetate, and carbon disulfide as precursors. In this process, the cationic ring-opening polymerization of lactide and the formation of ZnS nanoparticles were taken place simultaneously, and PLA/ZnS nanocomposites were obtained *in situ* way. The effect of reaction temperature, time, and zinc acetate content on the molecular weight of PLA was discussed. Ubbelohde viscometer, TEM, UV–vis, TGA, and fluorophotometer were used to characterize the obtained nanocomposites. It was found that homogonous PLA/ZnS nanocomposites could be obtained at 160°C for 8 h with toluene as reaction medium. Comparing to pure PLA, the molecular weight of PLA in the obtained nanocomposites increased, and ZnS nanoparticles with the size about 10 nm in diameter were dispersed well in PLA matrix without any dispersan. The PLA/ZnS nanocomposites have ultraviolet resistant. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: PLA; ZnS; nanocomposites; *in situ* solvothermal reaction

INTRODUCTION

Demand for biodegradable polymers with excellent properties is growing at a rapid rate.[1] In this area, poly(lactic acid) (PLA) is one of the most promising and widely used in surgery (sutures, orthopedic applications, tissue engineering) and packaging field,[2–4] because it is thermoplastic, biodegradable, biocompatible, and have good mechanical properties and processability.

However, some properties of PLA (e.g. hydrophilicity, impact strength, heat distortion temperature, etc.) are often not good enough for various applications.[5] This encourages people to engage in modifying PLA materials through various ways, such as copolymerization, grafting, and blending.[5–8] In recent years, extensive research efforts have been devoted to the modification of PLA, through adding inorganic nanofillers, to enhance its physical properties and improve its degradation characteristics.[1] On the other hand, the introduction of inorganic materials can also endow PLA with new functionalities, and some of PLA/inorganic hybrids have been extensively studied, such as PLA/silica,[9] PLA/TiO₂,[10] PLA/Fe₃O₄,[11] PLA/montmorillonite,[12] and PLA/hydroxyapatite.[13]

Zinc sulfide (ZnS) has attracted much attention because of its excellent physical properties, for example, wide bandgap ($\sim$ 3.6 eV in bulk),[14] high refractive index ($n = 2.36$ at 620 nm), and low absorption coefficient over a broad wavelength range.[15,16] Thus, ZnS semiconductor and its nanoparticles have been widely used in flat-panel displays, electroluminescence devices, infrared windows, sensor,[17–20] and optical fields.[21] Recently, some ZnS/polymer hybrid materials have been prepared to make use of the functional properties of ZnS nanoparticles and to combine the advantages of organic polymers, such as PTU/ZnS,[22] PVA/ZnS,[23–25] PVP/ZnS,[26] PS/ZnS,[27] PMMA/ZnS,[28] and PVDF/ZnS.[29] These composites can be used as high refractive index materials, semiconductor, photoluminescence, and electroluminescence materials and so on. And various methods were developed to prepare hybrids or nanocomposites, such as sol–gel method, precursor method, and *in situ* synthesis.[30] However, few studies on the PLA/ZnS hybrids have been reported.

In general, solvothermal synthesis is carried out in a pressure vessel where the commonly used solvents, for example, toluene and alcohol, will be stable beyond their boiling points under a high pressure.[4] Under this condition, the dissolution and reaction activity of reactants would greatly increase so
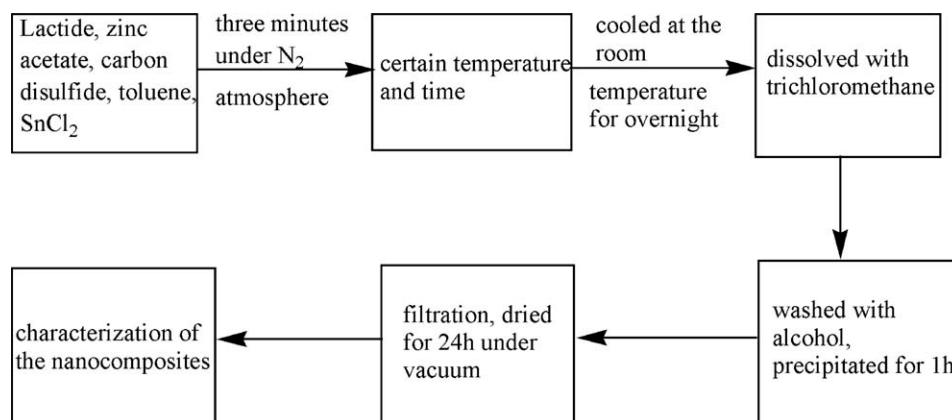
Scheme 1   The process of the whole reaction.

that the synthesis of compounds and polymers can be achieved. This technique was widely used in the synthesis of inorganic compounds such as ZnO, Co_3O_4,[31] and ZnS.[32] We also had synthesized PLA with high molecular weight[4] and prepared the grafting copolymer of high grafting degree via solvothermal method in our previous works.[33,34] The addition of ZnS nanoparticles is a feasible method to obtain high molecular weight of PLA, and the as-prepared nanocomposites can be used in the field of food packaging due to its ultraviolet resisting property, which can prevent the damage of UV to the photosensitive food, maintain the appearance and the taste, and further extend the shelf life of food. In this study, PLA/ZnS nanocomposites have been synthesized in one step through solvothermal method because the formation of ZnS and the synthesis of PLA have similar reaction conditions. In other words, ZnS nanoparticles were formed under elevated temperatures and high pressures and dispersed in the lactide simultaneously. At the same time, cationic ring-opening polymerization of lactide was occurred, and PLA/ZnS nanocomposites were obtained *in situ* polymerization. Furthermore, the effect of temperature, reaction time, and the amount of ZnS on the nanocomposites was also investigated. The properties of PLA/ZnS composites were characterized through Ubbelohde viscometer, TEM, UV–vis, and TGA. The results show that the obtained PLA/ZnS nanocomposites have the enhanced ultraviolet resisting property.

EXPERIMENTS

Materials

L-lactide (95%) was purchased from Nanjing Lihan Chemical (China), and it was recrystallized twice from ethyl acetate and dried under high vacuum at 45°C for 4 h before use. $SnCl_2$, ethyl acetate, and carbon disulfide (Sinopharm Chemical Reagent, China)

of analytic grade were used as received. Trichloromethane and toluene of analytic grade were purchased from Shanghai Lingfeng Chemical Reagent, China. Zinc acetate (Xingtameixing Chemical Factory, China) and alcohol (Yonghua Fine Chemical Factory, China) of analytic grade were used.

Synthesis of PLA/ZnS nanocomposites

In a typical process, lactide (15 g), zinc acetate (2.29 g), carbon disulfide (1.8 mL), and toluene (10 mL) were introduced into a 50-mL high-pressure reaction vessel. After 4% wt $SnCl_2$ (0.06 g) being added as catalyst, the reaction system was purged with nitrogen for more than 3 min to remove oxygen. Then the vessel was put into an oven under 160°C. After being reacted for 8 h, the reaction vessel was taken out and cooled to room temperature. Then the product was taken out of vessel, dissolved with trichloromethane, and precipitated in alcohol, respectively. And then, the obtained products were subsequently washed with alcohol for several times to remove the unreacted reactants. The purified composites were dried for 24 h under vacuum. The process was shown in Scheme 1.

Characterization

Viscosity Average Molecular Weight (M_η)

Viscosity method is used to determine the molecular weight of PLA, and the steps are given as followings: (1) Taking about 1 g sample into 25 mL volumetric flask with trichloromethane as solvent, and then the solution being centrifuged and filtrated before molecular weight measurement. (2) Taking 10.00 mL solution by pipette into Ubbelohde Viscometer (Liang Jing Glass Instrument, shanghai), which was washed and dried, and then put into 30°C thermostatic water bath for 10 min. The viscometer constant is 0.01894 mm^2/s^2, inner diameter of capillary is 0.6–0.7mm. (3) Absorbing solution to

$$Zn(CH_3COO)_2 + S^{2-} \xrightarrow[\text{high pressure}]{\text{high temperature}} ZnS + 2CH_3COO^-$$
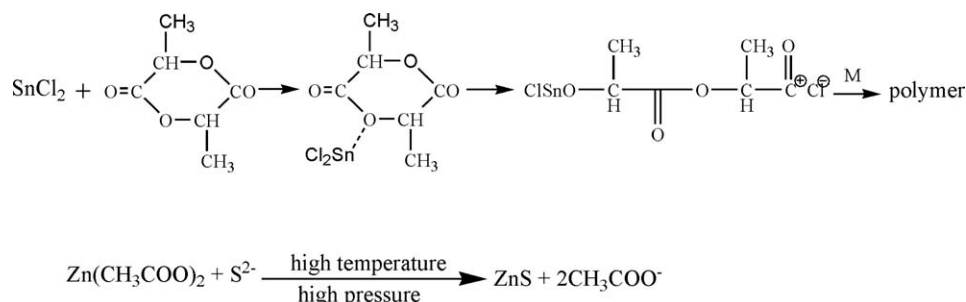
Scheme 2 The ring-opening polymerization of lactide and the formation of ZnS.

wash measuring pipette for several times. (4) Measuring the time of solution which flows from up liquid level to down liquid level, the procedure was repeated three times. (5) Adding 2 mL trichloromethane and putting into thermostatic water bath for 5 min, then using the ear washing bulb repeatedly to mix the liquid and washing the measuring pipette. (6) Repeating step (4). (7) Repeating steps (5) and (6) two times. (8) Pouring the solution, then washing the measuring pipette by trichloromethane, lately adding about 10 mL trichloromethane and keeping the constant temperature 10 min. (9) Repeating steps (3) and (4). (10) Calculating the viscosity of sample:

$$\log[\eta] = \log K + a \log M_\eta \qquad (2.1)$$

where η is the viscosity, K and a are the constants, and M_η is the viscosity molecular weight.

UV–Vis

The obtained composite was analyzed by ultraviolet-visible spectrophotometer (UV-2450, Shimadzu, Japan). The products were grinded into power, and taken 0.4 g to mix with 2.0 g $BaSO_4$, and then the mixtures were performed to analyze.

TGA

Thermogravimetric analysis (Q5000IR, TA Instruments, USA) was used to measure the thermo-stability of the obtained composite and the content of ZnS. About 5 g sample was heated from room temperature to 800°C via the heating rate of 20°C/min under the atmosphere of nitrogen.

TEM

Transmission electron microscopy (TEM) measurements were carried out on a JEM 2100 microscope (JEOL, Japan). Before testing, the obtained composite was made into dilute solution whose concentration was about 0.3%, then dropping the dilute solution

over water, lately dragging the film onto copper mesh. The dried films were observed by TEM.

RESULTS AND DISCUSSION

The molecular weight of PLAs

In this study, it can be designed that the polymerization of lactide and the formation of ZnS will be taken place at the same time and nanocomposites were obtained by the *in situ* polymerization. Scheme 2 gives the possible reactions in solvothermal processing. To obtain high molecular weight of PLA, it is crucial to find the optimum factors. Here we studied the impact of the various factors on the molecular weight of PLAs.

Our precious work had investigated the effect of catalyst usage, different solvents, and their content on the molecular weight of PLAs, so 10 mL toluene was chosen as solvent in this study and the amount of catalyst $SnCl_2$ was 0.06 g.[4] From Scheme 2, it can be also known that the polymerization of lactide and the formation of ZnS were taken place at the same time, so the zinc salts and sulfur source were considered to avoid their effect on the polymerization of PLAs. ZnS generally forms from hydrogen sulfide and zinc salts, but PLAs are easily degraded in the acidic condition.[35] Carbon disulfide was selected because it can be easily dissolved in chloroform and insoluble in water, which is benefit for removing the residual carbon disulfide. On the other hand, the boiling point of carbon disulfide is low so that the generation of S^{2-} is relatively easy. As for zinc salts, zinc acetate is soluble in ethanol so that it can be removed during the purification and it does not affect the degradation of PLAs. Therefore, carbon disulfide as sulfur source and zinc acetate as zinc salt were used. On the following section, the effects of different factors on the molecular weight of PLAs were investigated, respectively.

The effect of reaction temperature on the molecular weight of PLAs

As shown in Scheme 2, the polymerization of PLA is a reversible reaction,[36] so the polymerization and
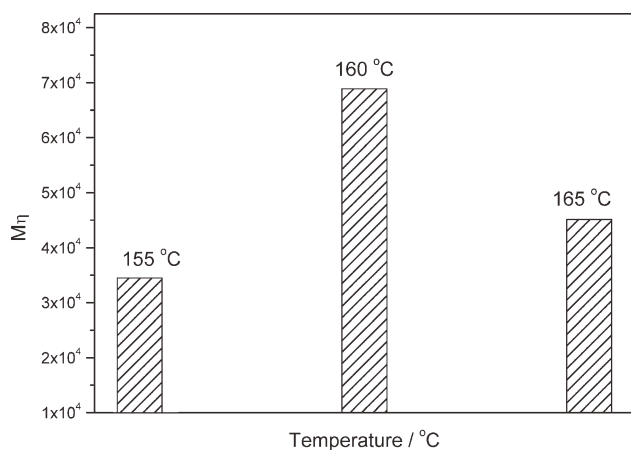
Figure 1 The molecular weight of PLAs under different reaction temperature. (Lactide: 15 g, SnCl2: 0.06 g, zinc acetate: 2.29 g, reaction time: 8 h, toluene: 10 mL, CS2: 1.8 mL).

depolymerization of PLA are concurrent, and the investigation of reaction temperature is necessary. Figure 1 shows the effect of reaction temperature on the molecular weight of PLAs. As shown in Figure 1, the molecular weight of polymer increases with the temperature rising before 160°C, while the molecular weight decreases with the temperature rising after 160°C. This is because the catalytic polymerization and catalytic thermal degradation is a pair of competitive reaction. In other words, the rate of catalytic polymerization is greater than that of thermal degradation at lower reaction temperature, while the molecular motion aggravates with the polymerization temperature increasing, which is in favor of growing of active center and the molecular weight of polymer increases. When the reaction temperature continues to increase until it exceeds the critical point, the rate of catalytic polymerization is lower than that of ther-
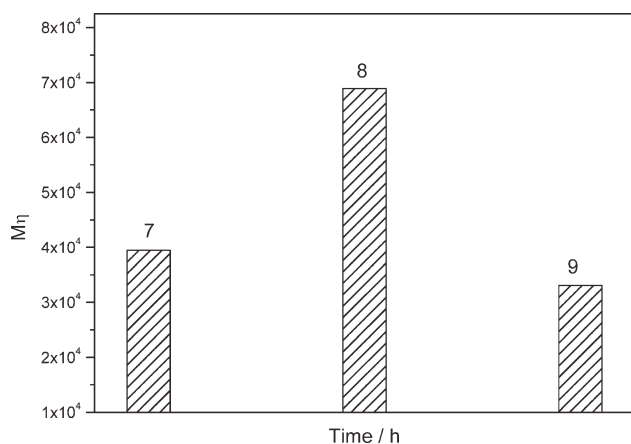
mal degradation, which would make the molecular weight of polymer decrease.[4,37,38]

The effect of reaction time on the molecular weight of PLAs

The relationship between the reaction time and the molecular weight of PLAs is shown in Figure 2, from which it can be seen that the molecular weight initially increases and reaches the maximum when the reaction time is 8 h, and then it decreases with the reaction time increasing. During the reaction, the extension of time is favorable to obtain longer polymer chains which would make the molecular weight increase. However, the monomers in the process are fewer with the reaction carrying out, which leads to decline in the reaction rate. What is more, the rate of depolymerization rises.[4,39] Thus, the longer reaction time would lead to the fracture of the long-chain of PLA and the degradation of polymers, which would further lead to obtain the lower molecular weight and wider molecular weight distribution of PLAs.

The effect of zinc acetate content on the molecular weight of PLAs

As mentioned above, the polymerization of PLA and the formation of ZnS are taken place simultaneously, so the existence of Zn^{2+} may affect the molecular weight of PLAs. Figure 3 shows the relationship of zinc acetate content and the molecular weight of PLAs. From Figure 3, it can be seen that the molecular weight increases compared to that of pure PLA and reaches the maximum value until the amount of Zn^{2+} is 5% wt. However, the molecular weight of PLAs decreases when the amount of Zn^{2+} further increases. This is because Zn^{2+} could combine with hydroxyl of lactide to form precursor via ionic bond, and the

Figure 2 The molecular weights of PLA under different reaction time. (Lactide: 15 g, SnCl2: 0.06 g, zinc acetate: 2.29 g, temperature: 160°C, toluene: 10 mL, CS2: 1.8 mL).
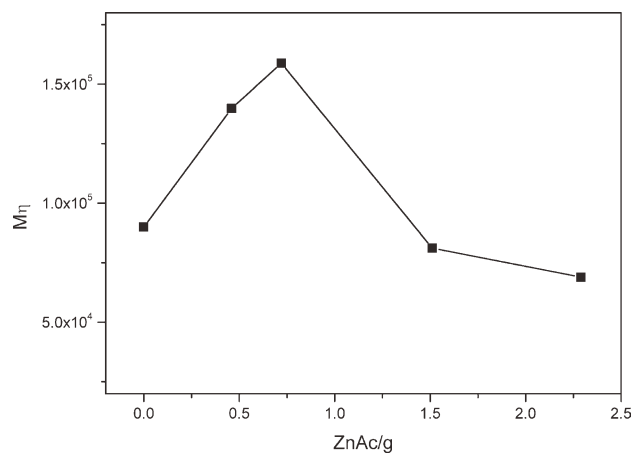

Figure 3 The relationship between the amount of zinc acetate (ZnAc) and the molecular weight of PLAs (lactide:15 g, SnCl2:0.06 g, toluene: 10 mL, temperature: 160°C, reaction time:8 h, CS2: 1.8 mL).
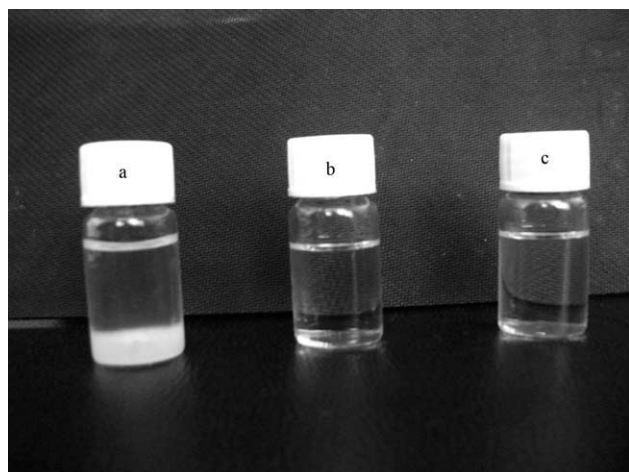
Figure 4 The phenomenon of pre-prepared pure ZnS/ PLA mixture and PLA-ZnS nanocomposites in chloroform. (a) The simple mixture of pre-prepared pure ZnS and PLA, (b) PLA-ZnS nanocomposites (zinc acetate: 1.51 g), and (c) PLA-ZnS nanocomposites (zinc acetate: 4.58 g).

precursor is homogeneous and stable in toluene when the amount of Zn^{2+} is low. Then the Zn^{2+} would further react with S^{2-}, and ZnS nanoparticles are quickly generated under the reactive temperature. The presence of Zn^{2+} would act as a kind of catalysts and promote the rate of reaction in some way.[23] Thus the molecular weight of PLAs increases. When more amount of zinc acetate is used, the depolymerization is easier to take place, thus polymer chains fracture, which would lead to the molecular weight of PLAs decrease.

Microstructure of PLA/ZnS nanocomposites

The dissolution properties of the obtained PLA/ZnS nanocomposites were also investigated. Figure 4 shows photographs of the simple mixture of the pre-prepared pure ZnS and PLA, and PLA-ZnS nanocomposites in chloroform. From Figure 4(a), one can see a clear stratification for the simple mixture of pre-prepared pure ZnS and PLA. The upper layer is clear liquid, while the lower layer is turbidity, which is consistent with the properties of PLA and ZnS. This is because ZnS nanoparticles cannot dissolve in the chloroform and PLA has a good solubility in chloroform. And the poor effect between ZnS and PLA in the simple mixture leads to the stratification. While, the chloroform solution of PLA/ZnS nanocomposites (from one-step *in situ* polymerization) is clear and transparent [in Fig. 4(b,c)], and no precipitation is observed [Fig. 4(b,c)], which suggests that the obtained nanocomposites can be dissolved easily in chloroform. The possible explanation is following: (1) The PLA/ZnS nanocomposites were formed *in situ* way, ZnS nanoparticles dispersed well in PLA matrix and some stronger effects existed between ZnS and PLA because of the coordinating

effects of Zn^{2+} and –OH of PLA. (2) The long molecular chains of PLAs increase the steric hindrance, so the collision ratio of nanocomposites reduces.

Figure 5 shows the TEM micrographs of PLA/ZnS nanocomposites. As shown in Figure 5(a), only a small amount of ZnS nanoparticles are generated in the matrix of PLA via *in situ* polymerization, the particle size is about 10 nm. However, when the amount of Zn^{2+} is 10% wt [Fig. 5(b)], it can be obviously seen that the dispersion is homogeneous without adding dispersants and the particle size is about 10 nm. This is because the metal Zn^{2+} ions combine with hydroxyl of lactide to form precursor via ionic bond, so lactide acts as a dispersant due to its complexation. It reduces the probability of collisions between ions and the steric hindrance increases when the macromolecular generates continually. Moreover, the end of macromolecular has the opposite charges with metal ions, thus the free macromolecular are absorbed on the particles surface (Scheme 1).
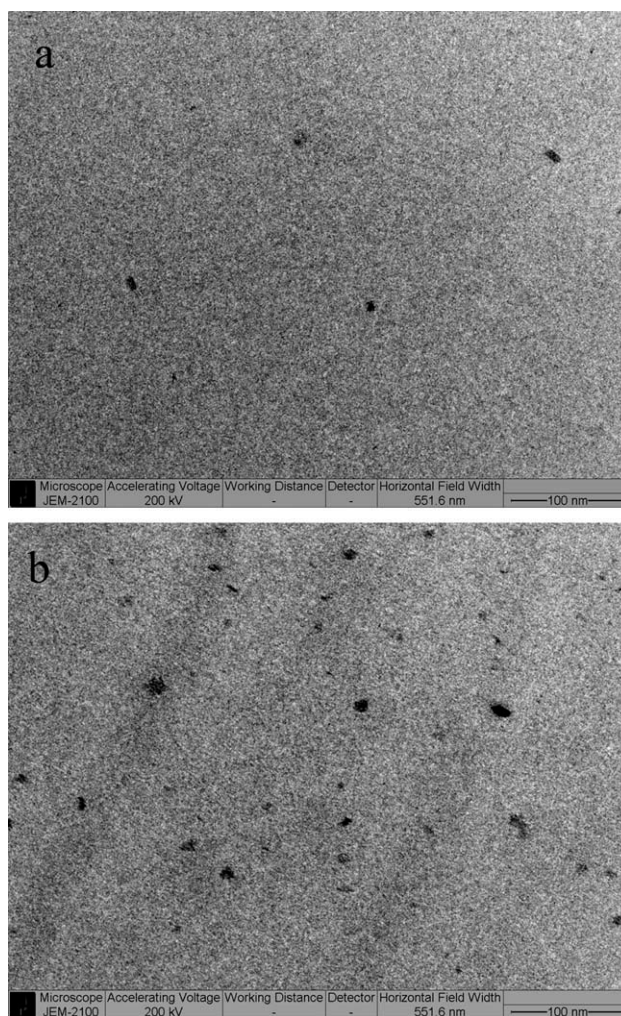

Figure 5 TEM micrographs of PLA/ZnS nanocomposites. (a) PLA-ZnS (zinc acetate: 0.46 g) and (b) PLA-ZnS (zinc acetate: 1.51 g). (lactide: 15 g, SnCl2: 0.06 g, toluene: 10 mL, temperature: 160°C, reaction time: 8 h, CS2: 1.8 mL).
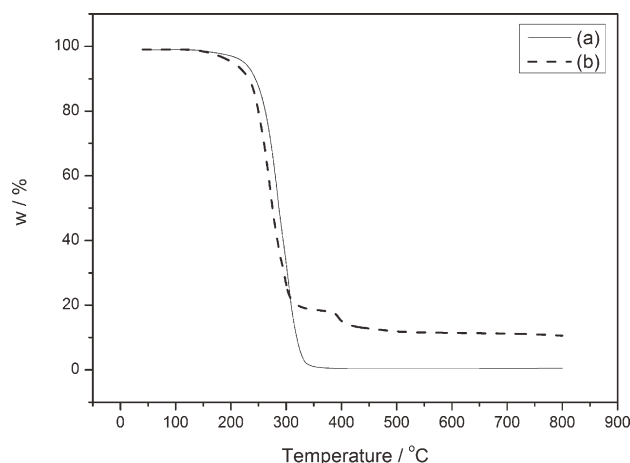
Figure 6 TGA curves for (a) pure PLA and (b) PLA-ZnS (zinc acetate: 2.29 g). (Reaction condition: lactide: 15 g, SnCl2: 0.06 g, toluene: 10 mL, temperature: 160°C, reaction time: 8 h, CS2: 1.8 mL).

TGA of PLA/ZnS nanocomposites

The thermal properties of the products were investigated with TGA. Figure 6 showed TGA curves of pure PLA and PLA/ZnS nanocomposites. From Figure 6(a), we can know that the initial decomposition temperature of pure PLA was about 280°C. The decomposition temperature was slightly earlier after incorporating ZnS nanoparticles in suit polymerization [Fig. 6(b)]. The possible reason is that Zn^{2+} acts as catalyst under certain temperature. Because the ring-opening polymerization of PLA is a reversible reaction, the depolymerization is occurred under the existence of Zn^{2+}. So the decomposition temperature was in advance. However, it can be seen in Figure 6(b) there is another weight loss during the temperature range of 300 and 400°C, which might be attrib-
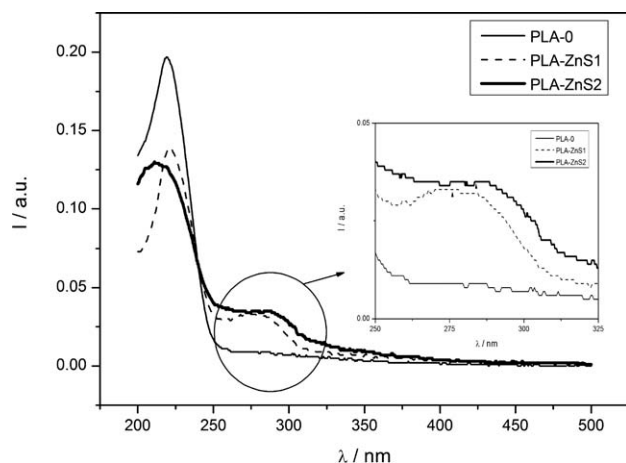

Figure 8 The UV–vis absorption spectra of nanocomposites under different temperatures. (Lactide: 15 g, SnCl2:0.06 g, zinc acetate: 2.29 g, reaction time: 8 h, toluene: 10 mL, CS2: 12 mL. The thickness of all the samples was the same).

uted to the interfacial interactions between PLA and ZnS can be enhanced when ZnS nanoparticles were formed in suit in PLA matrix.[11] From the curve of Figure 6(b), it can also be seen that the proportion of ZnS in the composite was about 18% wt, which was similar to the initial additive amount of Zn^{2+}. Thus it suggested that ZnS nanoparticles did exist in the matrix of PLA and the PLA/ZnS composites were obtained via in suit solvothermal reaction in one step.

Ultraviolet-visible spectra of PLA/ZnS nanocomposites

Figure 7 shows the UV–vis absorption spectra of PLA-0 and PLA/ZnS nanoconposites. From the spectra of PLA-0, one can see that there is a strong

Figure 7 UV–vis absorption spectra of PLA-0, PLA-ZnS1 (zinc acetate: 1.51 g, CS2: 1.2 mL), and PLA-ZnS (zinc acetate: 2.29 g, CS2: 1.8 mL). (Reactive condition: lactide: 15 g, SnCl2: 0.06 g, toluene: 10 mL, temperature: 160°C, reaction time: 8 h).
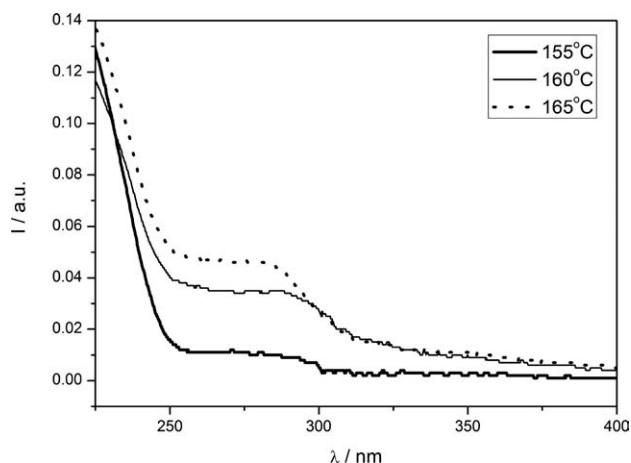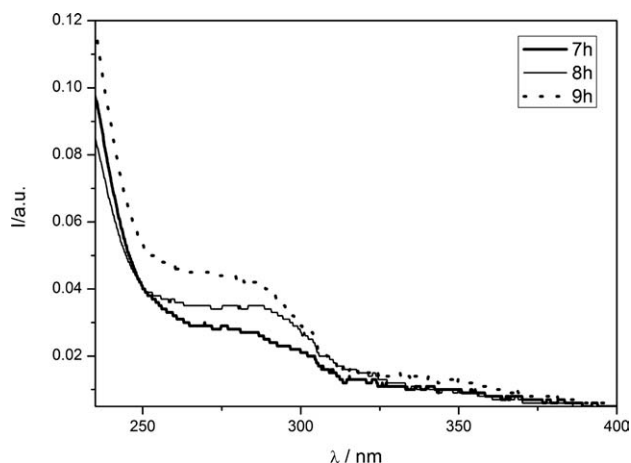

Figure 9 The UV–vis absorption spectra of nanocomposites under different reaction time. (Lactide: 15 g, SnCl2: 0.06 g, zinc acetate: 2.29 g, reaction temperature: 160°C, toluene: 10 mL, CS2: 18 mL. The thickness of all the samples was the same).

absorption peak at 220 nm, and the peak still exists and is weaker after adding ZnS, which can be contributed to the UV absorption peak of PLA. After adding ZnS, an obvious absorption peak at 280 nm can be observed. And the peak shifts to 270 nm but becomes stronger with the increase of ZnS content. The peak at about 280 nm can be determined as a characteristic absorption peak of ZnS.[27] The characteristic absorption peaks of ZnS are shifted with different amount of zinc acetate. This phenomenon comes from quantum size effect. Due to nanoparticle quantum confinement effect, continuous bulk energy band of ZnS turns into separated or partly separated energy-level structure. When particle size decreases, the energy gap between the occupied molecular orbital by electron and unoccupied molecular orbital increases, thus the shift generates.[27,30] Therefore, the addition of ZnS may improve the ultraviolet resistance comparing to the pure PLA.

The effect of various factors on the molecular weight of PLAs had been discussed above. Although the synthesis of PLA and the formation of ZnS were occurred at the same time, the effect of the various factors on the formation of ZnS may be different. So the effect of reaction temperature and reaction time on the formation of ZnS was also investigated, and the results have been given in Figures 8 and 9. As shown in Figure 8, the absorption peak of ZnS at 280 nm became stronger when the temperature increased. The content of one component in the sample can be quantitatively indicated from the absorption peak intensity, so it is favorable for the formation of ZnS with the reaction temperature increasing. When temperature increases, molecular motion aggravates and the collision probability between Zn^{2+} and S^{2-} increases, so it is easier for the formation of ZnS. According to the intensity of the UV–vis absorption peak of ZnS at 280 nm, a higher content of ZnS in the nanocomposites was observed when the reaction time was 9 h (Fig. 9). More opportunities are made for Zn^{2+} and S^{2-} to form ZnS.

CONCLUSION

PLA/ZnS nanocomposites were successfully synthesized through solvothermal method. And ZnS nanoparticles were *in situ* synthesized through the coordination with lactide when PLA formed via cationic ring-opening polymerization in the presence of stannous chloride as catalyst in one step. The effects of the various factors on the molecular weight, morphology, and optical properties have been investigated in detailed. The main results were emphasized below:

1. To obtain the highest molecular weight of PLA, the optimal reaction conditions were as follow-

ings: the toluene was 10 mL, the reaction temperature was 160°C, and the reaction time was 8 h.
2. The *in situ* polymerization was favor for the dispersion of ZnS nanoparticles, and ZnS nanoparticles were homogeneously dispersed in the PLA matrix without any dispersant and its size is about 10 nm.
3. The higher reaction temperature and longer reaction time were the benefits for the formation of ZnS.
4. Comparing to pure PLA, the molecular weight of PLAs and the ultraviolet resistance were improved.

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