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RESEARCH ARTICLE

Improvement of thermal properties of poly (L-lactic acid) by blending with zinc lactate

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Abstract: Zinc lactate (RSX) was synthesised from zinc acetate and L-lactic acid, and the structure was characterised using X-ray diffraction (XRD). Thermal decomposition showed that the decomposition temperature of RSX is higher than the processing temperature of composites based on poly (L-lactic acid) (PLLA). Single factor experiments certified that the optimum reaction conditions are a reaction temperature of 80 ^{o}C, and a reaction time of 4 hours. Addition of RSX could significantly decrease the half-time of overall PLLA crystallisation. Compared to pure PLLA, the half-time of PLLA with 7 % RSX decreased from 2359.91 seconds to 152.68 seconds at 115 ^{o}C. The kinetics of isothermal crystallisation of PLLA/RSX composites can be described using the Avrami equation.

Keywords: Crystallisation kinetics, isothermal crystallisation, poly (L-lactic acid), thermal decomposition, zinc lactate.

INTRODUCTION

Zinc lactate (RSX) is an important nutrient used to overcome zinc deficiency in food. It is often used in cosmetics and toothpaste (Cao *et al*., 2002). Continuous studies have been made on the crystallisation and dissolution behaviour of RSX (Zhang *et al*., 2010; 2012). RSX will also find applications in many fields. Effects of stirring and ultrasonic waves on the crystallisation of RSX have already been investigated (Cao *et al*., 2002). The results show that stirring could improve dissolution of crystallized RSX, and ultrasonic waves do not influence the crystallisation process.

Poly (L-lactic acid) (PLLA), is an important biodegradable polymer material widely investigated by researchers and has been used in many ways such as in packaging (Longano *et al*., 2012), automobile industry (Jo *et al*., 2012) and drug delivery (Campardelli *et al*., 2014). To widen the application of PLLA in food packaging, PLLA/montmorillonite nanocomposites have been fabricated by melt processing. The results show that PLLA/montmorillonite composite films could exhibit enhancement in oxygen and water vapour barrier properties (Kotiyar *et al*., 2011).

A few disadvantages occur to restrict the application of PLLA, such as slow crystallisation rate, low degree of crystallisation and poor heat resistance (Cai *et al*., 2014). A wider range of applications would be possible if the thermal properties of PLLA could be improved. Usually, blending with some functional additives is often used to improve the thermal properties of PLLA. For example, addition of ethylene bis-12-hydroxystearamide significantly improves the crystallisation rate and crystallinity of PLA. Compared to pure PLA, only the half-time of PLA with 1 % ethylene bis-12-hydroxystearamide at 105 ^{o}C decreased from 18.8 minutes to 2.8 minutes, and the crystallinity of PLA with 1 % ethylene bis-12-hydroxystearamide is 35 % after 5 minute heat treatment (Tang *et al*., 2012).

In this study, RSX was synthesised to add to PLLA matrix using melting blending technology. The thermal properties of PLLA/RSX composites were investigated in detail to elucidate the role of RSX in enhancement of thermal properties of PLLA/RSX. This study may also help researchers to obtain more functional additives for PLLA.

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METHODS AND MATERIALS

Materials

Poly(L-lactic acid) (2002D) was purchased from Nature Works L.L.C., USA. Zinc acetate and L-lactic acid of analytical grade were purchased from Chengdu Kelong Chemical Reagents Company (Sichuan Province, China), and ethanol of analytical grade was purchased from Tianjin Kemiou Chemical Reagents Company (Tianjin, China).

Synthesis of RSX

Six grams of zinc acetate was dissolved in 180 mL of ethanol and 5 mL of water. The mixture was heated at 80 °C for 3 h while stirring. Then 2.5 mL of L-lactic acid was added slowly into the mixture and kept at 80 °C for 4 h while stirring. The reaction mixture was cooled to room temperature and filtered. The obtained crude product was washed with ethanol and water, and the resulting product was dried under vacuum at 45 °C.

Preparation of PLLA/RSX composites

The preparation process of PLLA/RSX composite was similar to the process of preparing other PLLA materials as reported previously (Cai, 2013).

Characterisation

X-ray diffraction (XRD): XRD analyses of RSX were performed on a X-ray diffractometer (D/MAX2550, Rigaku, Japan) using Cu K_α radiation (wavelength, 1.54 Å) in the range of 2θ = 5-80º with a scanning rate of 2º/min.

Thermogravimetric analysis (TGA): Thermogravimetric analysis of RSX was performed using a thermal analysis Q500 (TA Instrument-Waters L.L.C., USA) with a heating rate of 5 °C/min under air flow (50 mL/min) from 40 °C to 800 °C.

Depolarized-light intensity measurement: The overall isothermal crystallisation of PLLA was investigated by a GJY-III optical depolarizer with a range of 100 °C to 120 °C. The electronic signals transformed from the measured optical depolarizer were amplified and then recorded for further analysing.

RESULTS AND DISCUSSION

Structure of RSX

The structure of zinc lactate was characterised first using XRD. As shown in Figure 1, the strongest diffraction peak is at 2θ = 10°, and the diffraction peak position is similar to that in literature (Wang *et al*., 2011), which indicates that RSX has been successfully prepared. The observations from polarization optical microscopy shows that RSX has an approximate spherical structure (Figure 2). However, literature reports that RSX has a nano-wire structure when RSX was prepared using the same

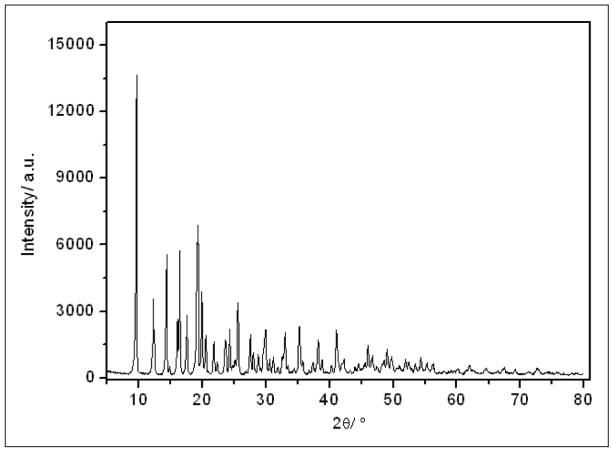

Figure 1: XRD curve of prepared RSX

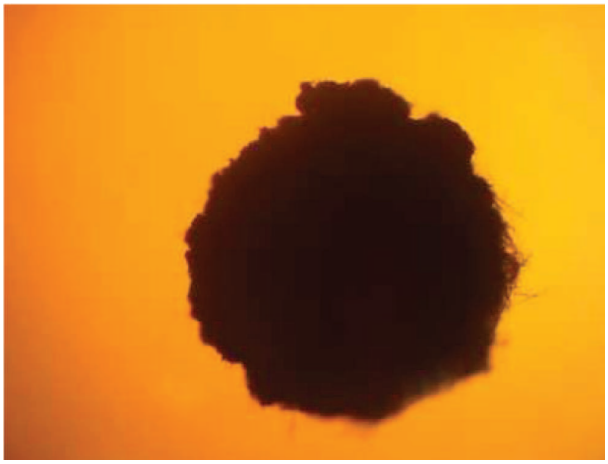

Figure 2: Morphology of RSX observed using microscopy

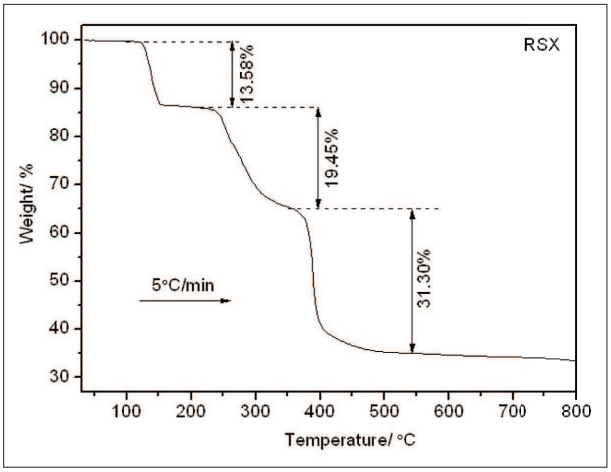

Figure 3: The TGA curve of RSX at a heating rate of 5 °C/min

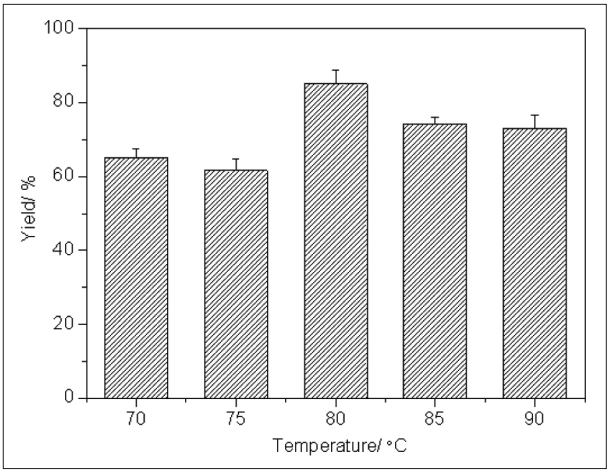

Figure 4: Effect of reaction temperature on yield of RSX

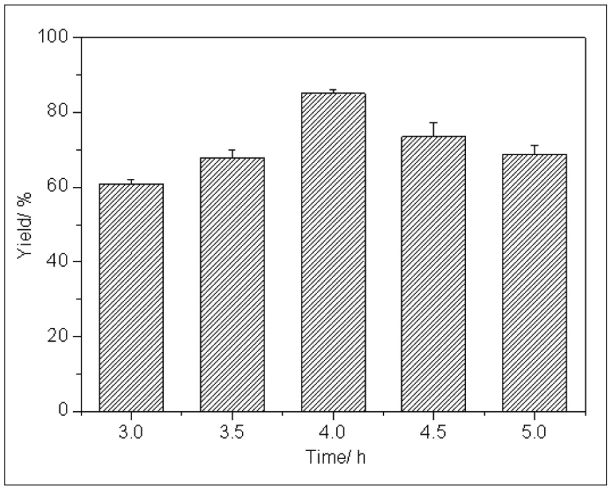

Figure 5: Effect of reaction time on the yield of RSX

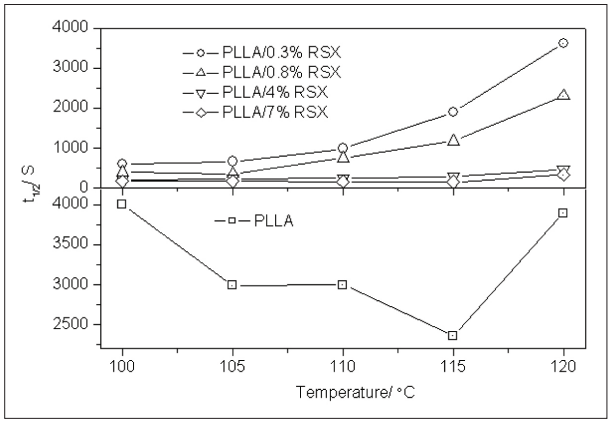

Figure 6: The $t_{1/2}$ of PLLA and PLLA/RSX composites with T_c

Table 1: Isothermal crystallisation parameters of PLLA and PLLA/RSX

Sample	T_c /°C	n	logK
PLLA	100	1.5	- 06.03
	105	2.9	- 10.17
	110	3.3	- 11.69
	115	4.4	- 15.27
	120	5.1	- 20.61
PLLA/0.3 % RSX	100	4.9	- 13.77
	105	6.2	- 17.89
	110	6.3	- 18.95
	115	5.0	- 16.41
	120	3.3	- 11.91
PLLA/0.8 % RSX	100	5.3	- 13.97
	105	5.6	- 14.63
	110	6.4	- 18.60
	115	4.4	- 13.55
	120	4.2	- 14.23
PLLA/4 % RSX	100	5.2	- 12.17
	105	5.1	- 12.24
	110	5.4	- 13.02
	115	5.2	- 12.93
	120	5.1	- 13.97
PLLA/7 % RSX	100	6.2	- 14.19
	105	5.5	- 12.33
	110	5.3	- 11.90
	115	4.9	- 10.80
	120	4.2	- 10.88

synthesis method (Song *et al*., 2012), depending upon the stirring modes and stirring rate. Compared to normal RSX, RSX with high specific surface area has more advanced nucleation ability for PLLA (Song *et al*., 2012).

RSX with a spherical structure may significantly enhance the crystallisation properties of PLLA.

Thermal studies of RSX were carried out using TGA. The TGA curve of RSX at a heating rate of 5 °C/min is presented in Figure 3. It is clear that there exists three platforms on the TGA curve (Figure 3). The decomposition temperature of the first stage is 125 °C, resulting from the loss of absorbed water, corresponding to a mass loss of 13.58 %. The decomposition temperature of the second stage is 257 °C, and the mass loss is 19.45 %. The decomposition temperature of RSX is higher than the

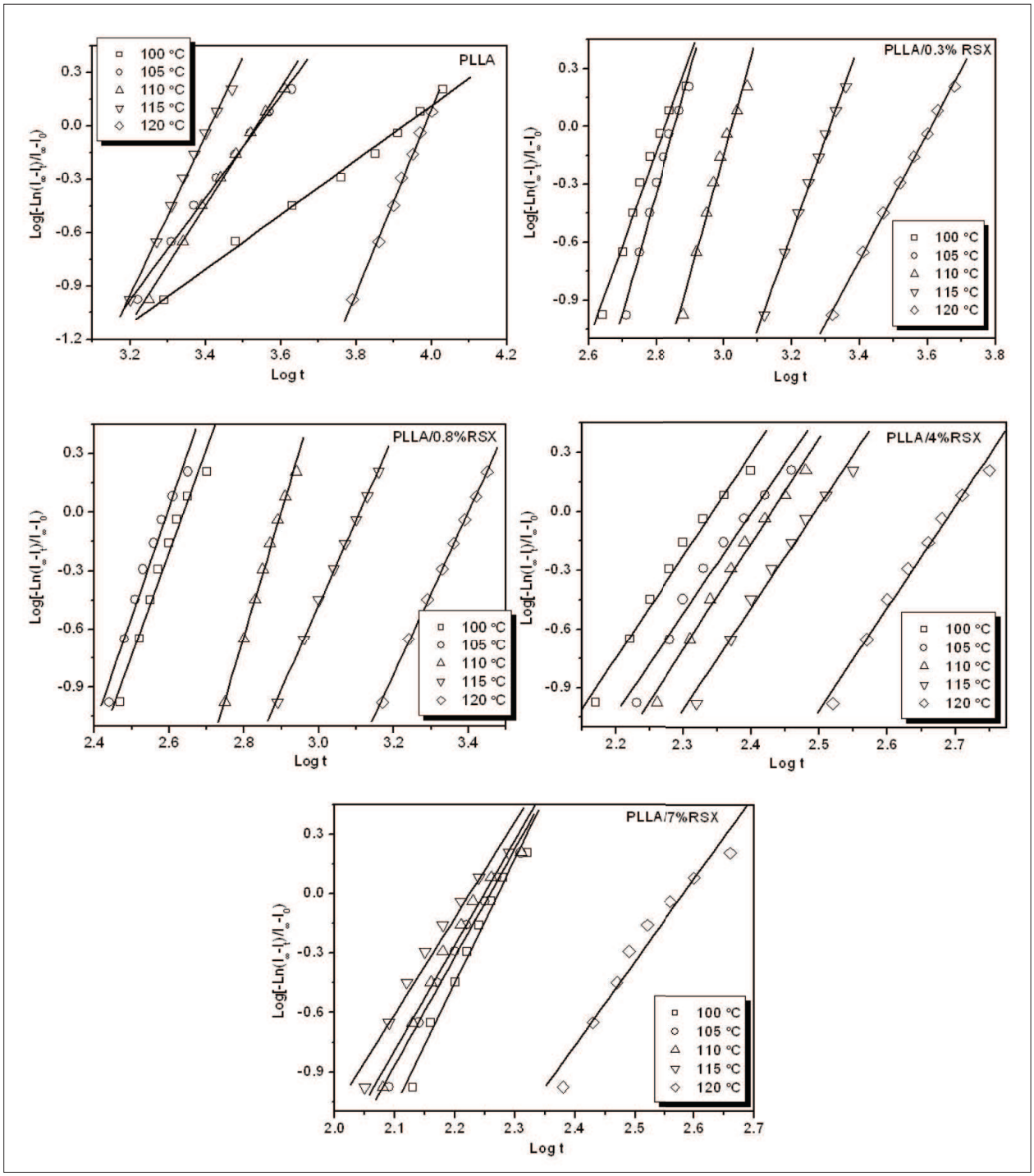

Figure 7: Avrami plots for PLLA and PLLA/RSX at different temperatures

processing temperature of composites based on PLLA, which indicates that RSX can serve as a nucleating agent for PLLA. The maximum mass loss is in the third stage, which is 31.30 %.

Synthesis process of RSX

The influence of reaction temperature and reaction time on the yield of RSX was investigated using single factor experiments. First, using a solution with 5 mL of water and 2.5 mL of L-lactic acid, the effect of reaction temperature on the yield of RSX was evaluated for a 4 hour reaction time. The experimental results are shown in Figure 4. The yield of RSX increased with increasing reaction temperature. At the reaction temperature of 80 °C, the yield of RSX has a maximum value of 84.97 %. Appropriately increasing the reaction temperature can improve reaction activity, but higher reaction temperature will also cause the increase of byproducts, resulting in decreased yield.

Using a solution with 5 mL of water and 2.5 mL of L-lactic acid, the influence of reaction time to the yield of RSX was investigated at an optimum reaction temperature of 80 °C. The effect of reaction time on the yield of RSX had a similar trend with that of reaction temperature (Figure 5), and the maximum yield occurs with the reaction time of 4 hours. Thus, the optimum reaction conditions are: reaction temperature of 80 °C and reaction time of 4 hours.

Isothermal crystallisation of PLLA/RSX composites

According to the results of morphological study and thermogravimetric analyses, RSX as nucleating agent may improve the crystallisation of PLLA. Thus, we investigated the isothermal crystallisation behaviour of PLLA/RSX composites. Figure 6 shows the isothermal crystallisation behaviour of PLLA/RSX composites. It is clear that the half-time of composite PLLA crystallisation $t_{1/2}$ becomes low after the addition of RSX. Furthermore, with the increase of RSX content, $t_{1/2}$ becomes lower, which further indicates that RSX can improve the crystallisation of PLLA, and increase the crystallisation rate of PLLA. A high content RSX significantly reduces the half-time of composite PLLA crystallisation. However, the change in the half-time of PLLA crystallisation is not regular with the increase of crystallisation temperature, showing that PLLA/RSX composites have a complicated crystallisation process. Compared to pure PLLA, the half-time of composite PLLA crystallisation $t_{1/2}$ decreases from 2359.91 seconds to 152.68 seconds at 115 °C with the addition of 7 % RSX.

Avrami equation can be used to describe the kinetics of isothermal crystallisation of PLLA/RSX composites. The measure and theoretical basis for isothermal crystallisation have been described previously (Cai *et al*., 2012). Figure 7 shows the Avrami plots of PLLA and PLLA/RSX composites. The relationship of $\log[-\ln(1-X_t)]$ *versus* logt is linear. X_t represents the percentage of relative crystallisation after time t in the measure method. The kinetic parameters *n* and *k* values of pure PLLA and PLLA/RSX composites are listed in Table 1. Usually, *n* is four (4) for a homogeneous nucleation system and three (3) for a heterogeneous nucleation system. However, Table 1 shows that the *n* values of pure PLLA is in the range of 1.5 – 5.1, and the *n* values of PLLA/RSX composites range between 3.3 – 6.4. These results show that the crystallisation process of PLLA and composites based on PLLA are very complicated, and may be affected by RSX, crystallisation temperature, operation process, etc. Furthermore, a similar phenomenon has been reported in other studies (Li *et al*., 2009). But the variation of *k* values has a similar trend as that of $t_{1/2}$ values.

CONCLUSION

Spherical RSX with a high specific surface area was synthesized from zinc acetate and L-lactic acid. Thermal decomposition showed a higher decomposition temperature of RSX. The optimum reaction conditions of RSX were a reaction temperature of 80 °C and a reaction time of 4 hours. Under these optimum conditions, the yield of RSX was 84.97 %. Isothermal crystallisation behaviour indicated that RSX could significantly decrease the half-time of composite PLLA crystallisation. Compared to pure PLLA, the half-time of composite PLLA with 7 % RSX decreased from 2359.91 seconds to 152.68 seconds at 115 °C.

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