Thermal and Mechanical Properties of Poly(L-Lactic Acid) Composites Based on Sodium Alginate

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The melting behaviour at different conditions, thermal stability and mechanical properties of poly(L-lactic acid)/sodium alginate (PLLA/SA) composites were investigated. The results showed that the melting behaviour was affected by heating rate, crystallization temperature and crystallization time and the double melting peaks is in accord with the melting recrystallization and remelting process. Meantime, the melting behaviour also further confirmed that sodium alginate could improve the crystallization of PLLA. Thermal stability of PLLA composites indicated that PLLA decomposed fast and completed in one stage above 300 °C and the decomposition process of PLLA/2%SA composites was similar to that of PLLA, but the onset decomposition temperature was lower than that of PLLA. Upon addition of 2 % sodium alginate, comparing with the neat PLLA, the tensile strength and modulus increase from 49.8 Mpa and 2329.4 Mpa to 72.7 Mpa and 3434.5 Mpa. However, the elongations at break of PLLA/2%SA composites decreased from 2.89 to 2.15 %.

Key Words: Poly(L-lactic acid), Sodium alginate, Melting behaviour, Thermal stability.

INTRODUCTION

It is well-known that the native poly(L-lactic acid) (PLLA) material without additives is difficult to use. Thus, the composites based on PLLA have become more and more important for development of society due to lower energy consumption, non-toxic to the environment of PLLA and PLLA composites was applied in more and more industries such as packaging materials¹, bone implants², surgical sutures³, etc. Yan *et al.*⁴ reported that grafted SiO₂ was prepared by grafting L-lactic acid oligomer onto the surface silanol groups of silica nanoparticles. The loading of grafted SiO₂ nanoparticles in PLLA matrix greatly improved the toughness and tensile strength of this material. Thermal analysis showed that grafted SiO₂ nanoparticles could serve as a nucleating agent for the crystallization of PLLA in the composites. Yu *et al.*⁵ investigated the properties of new poly(L-lactide)/poly(3-caprolactone)/organically modified montmorillonite nanocomposites. Their results showed that adding organically modified montmorillonite improved the thermal stability and crystalline abilities of nanocomposites and increasing content of organically modified montmorillonite reduced the domain size of phase-separated particles.

To investigate the effect of filler on properties of PLLA, more and more PLLA composites with different filler were

prepared. Sodium alginate (SA) is an important polysaccharide and widely applied in materials^{6,7}. In our previous paper⁸, sodium alginate is effective nucleating agent for the crystallization and can increase the overall crystallization rate of PLLA. With the addition of 3 % sodium alginate, the crystallization half-time of PLLA/SA composites decrease from 26.5 to 1.4 min at 105 °C. However, the other properties of PLLA/SA composites was not reported. Thus, in this paper, the melting behaviour at different conditions, thermal stability and mechanical properties of PLLA/SA composites were investigated.

EXPERIMENTAL

Poly(L-lactic acid) (2002D) was purchased from Nature Works LLC, USA. The sodium alginate was procured from Chengdu Kelong Chemical Reagents Company.

Preparation of PLLA/sodium alginate composites: Blending of PLLA and sodium alginate was performed on a counter-rotating mixer and the preparation process of PLLA/SA composites was reported in our previous paper⁸.

Differential Scanning Calorimeter (DSC): The melting behaviour of PLLA/SA composites was measured by DSC Q2000 (TA Instruments-Waters LLC, USA). The temperature and heat flow at different condition were calibrated using an indium standard.

Thermal stability testing: Thermogravimetric analysis (TGA) was performed using a thermal analysis Q500 from TA Instruments-Waters LLC with a heating ramp of 10 °C/min under air flow (60 mL/min) from room temperature to 500 °C.

Tensile testing: Dumbbell-shaped tensile test specimens with effective dimensions of 25 mm × 6 mm × 1.0 mm were prepared by pneumatic-controlled impact shaping machine. Normal tensile tests were conducted on a D&G DX-10000 electronic tensile tester at the speed of 50 mm/min at room temperature. The tensile strength, elastic modulus and elongations at break were obtained by averaging over five specimens.

RESULTS AND DISCUSSION

Melting behaviour of PLLA/2%SA composites at different heating rate after isothermal crystallization for 3 h at 100 °C: Fig. 1 shows the melting behaviour of PLLA/2%SA composites at different heating rate after isothermal crystallization for 3 h at 100 °C. Fig. 1 showed that there exists double melting peaks during heating scan. As to double melting peaks of semicrystalline PLLA, there exists two mechanism including melting of crystals of different stability and the melting recrystallization and remelting process⁹. Concerning the melting recrystallization, the low-temperature melting peak is attributed to the primary crystallites and high-temperature melting peak reflect the relatively perfect lamella stacks results from recrystallization during the heating scan. It is observed from Fig. 1 that the low-temperature melting peak hardly move with increasing of heating rate, which indicates that the heating rate hardly affect the melting behaviour of primary crystallites of PLLA. However, the high-temperature melting peak shifts to low-temperature with increasing of heating rate and the ratio of peak area between low-temperature melting peak and high-temperature melting peak gets small. These results show that the crystallization of PLLA at 100 °C for 3 h is not perfect. On the other hand, increasing of heating rate makes the crystallization degree of PLLA decrease during heating scan, resulting in less perfect crystallization of PLLA.

Fig. 1. Melting behaviour of PLLA/2%SA composites at different heating rate after isothermal crystallization for 3 h at 100 °C

The melting behaviour of PLLA/2%SA composites at different heating rate after isothermal crystallization for 3 h at 100 °C shows that the possible mechanism of double peaks of PLLA is in accord with the melting recrystallization and remelting process.

Melting behaviour of PLLA/2%SA composites after isothermal crystallization at 100 °C for different time: In order to investigate the effect of different condition on the melting behaviour of PLLA, we investigate the melting behaviour of PLLA/2%SA composites after different isothermal crystallization time. Fig. 2 shows melting behaviour of PLLA/2%SA composites at heating of 10 °C/min after isothermal crystallization at 100 °C for different time. With increasing of crystallization time, the low-temperature melting peak shifts to high temperature, but high-temperature melting peak do not shift to higher temperature, resulting from the same second crystallization of PLLA at same heating rate. However, the ratio of melting peak area between low-temperature melting peak and high-temperature melting peak is small. The reason is that the crystallization degree of PLLA at longer crystallization time is higher and the crystal is more perfect.

Fig. 2. Melting behaviour of PLLA/2%SA composites after isothermal crystallization at 100 °C for different time

Melting behaviour of PLLA/2%SA composites after different crystallization temperature for 3 h: Crystallization temperature is very important to melting behaviour of PLLA. Thus, the melting behaviour of PLLA/2%SA composites after different crystallization time for 3 h was investigated. As seen in Fig. 3, with increasing of crystallization temperature, the melting peak of PLLA changes from double melting peaks to single melting peak, which further confirms the important effect of crystallization temperature on melting behaviour. The possible reason is that higher crystallization temperature and enough crystallization time make PLLA form more primary crystallites and there exists no crystal at second heating scan. The melting peak becomes more and more sharper with increasing of crystallization temperature, the higher the crystallization temperature is, the more perfect the crystal of PLLA is. The more perfect crystal makes the melting peak becomes sharper.

Fig. 3. Melting behaviour of PLLA/2%SA composites after different crystallization time for 3 h

Thermal stability of PLLA/SA composites: It is very important to investigate thermal stability to obtain the information useful for industrial applications of PLLA. Thermogravimetric curves of thermal decomposition for PLLA, SA and PLLA/2%SA composites at heating rates of 10 °C/min are presented in Fig. 4. PLLA decomposes fast and completes in one stage above 300 °C. The main degradation products of PLLA are oligomers together with some lactide, but there are also other volatile products such as acetaldehyde, carbon dioxide, carbon monoxide and ketene¹⁰. As to sodium alginate, there exists more than two decomposition stages and the onset decomposition temperature is low. The first stage may be decomposition of H₂O and the decomposition of sodium alginate at second stage is fast. However, up to 500 °C, there still exists about 40 % mass. The TGA curve of PLLA/2%SA composites is similar to that of PLLA, but the onset decomposition temperature is lower than that of PLLA.

Fig. 4. TGA curves of thermal decomposition for PLLA, sodium alginate and PLLA/2%SA composites at heating rates of 10 °C/min

Mechanical properties: The mechanical properties of polymer is affected by filler. Thus, study on mechanical prop-

erties of PLLA composites also help to understand the role of filler in polymer matrix. Fig. 5 shows the stress strain curve of PLLA and PLLA/2%SA composites. It is observed that sodium alginate makes PLLA become brittle. Upon addition of 2 % sodium alginate, comparing with the neat PLLA, the tensile strength and modulus increase from 49.8Mpa and 2329.4Mpa to 72.7 Mpa and 3434.5 Mpa, respectively. However, the elongations at break of PLLA/2%SA composites decrease from 2.89 to 2.15 %,resulting from improving crystallization of PLLA in the presence of sodium alginate.

Fig. 5. The stress strain curve of PLLA and PLLA/2%SA composites

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