Asian Journal of Chemistry; Vol. 25, No. 16 (2013), 9269-9271

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15392

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

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(*Received*: 27 February 2013; *Accepted*: 20 September 2013) AJC-14159

The melting behaviour at different conditions, thermal stability and mechanical properties of poly(L-lactic acid)/sodium alginate (PLLA/SA) composities 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 composities indicated that PLLA decomposed fast and completed in one stage above 300 ºC and the decomposition process of PLLA/2%SA composities 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 composities 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 composities was applied in more and more industries such as packaging materials[1], bone implants[2], surgical sutures[3], *etc*. Yan *et al.*[4] reported that grafted SiO_2 was prepared by grafting L-lactic acid oligomer onto the surface silanol groups of silica nanoparticles. The loading of grafted SiO_2 nanoparticles in PLLA matrix greatly improved the toughness and tensile strength of this material. Thermal analysis showed that grafted SiO_2 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 composities with different filler were prepared. Sodium alginate (SA) is an important polysaccharide and widely applied in materials[6,7]. In our previous paper[8], 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 composities decrease from 26.5 to 1.4 min at 105 ºC. 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 composities 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 paper[8].

Differential Scanning Calorimeter (DSC): The melting behaviour of PLLA/SA composites was measured by DSC Q2000 (TA Instrumrnts-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 ºC/min under air flow (60 mL/min) from room temperature to 500 ºC.

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 composities at different heating rate after isothermal crystallization for 3 h at 100 ºC: Fig. 1 shows the melting behaviour of PLLA/2%SA composities at different heating rate after isothermal crystallization for 3 h at 100 ºC. 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 process[9]. Concerning the melting recrystallization, the low-temperature melting peak is attributed to the primary crystallites and high-temperature melting peak reflect the relatively prefect lamella stacks results from recrystallization during the heating scan. It is observed from Fig. 1 that the low-temperature melting peak hardly move with 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 ºC 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.

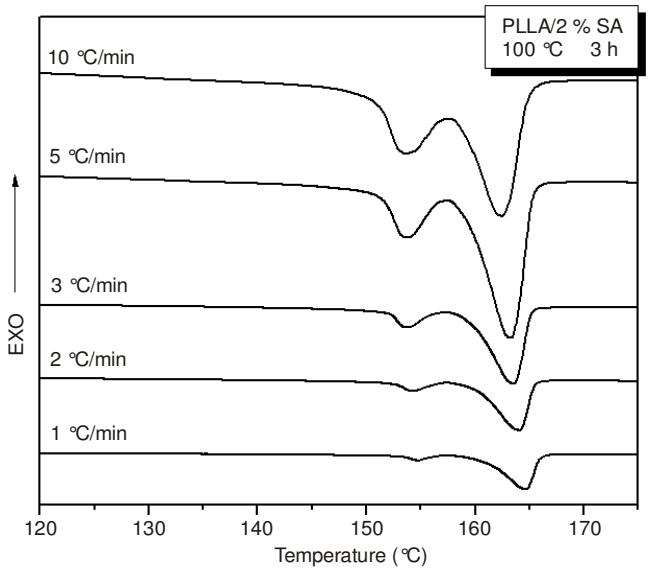

Fig. 1. Melting behaviour of PLLA/2%SA composities at different heating rate after isothermal crystallization for 3 h at 100 ºC

The melting behaviour of PLLA/2%SA composities at different heating rate after isothermal crystallization for 3 h at 100 ºC 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 composities after isothermal crystallization at 100 ºC 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 composities after different isothermal crystallization time. Fig. 2 shows melting behaviour of PLLA/2%SA composities at heating of 10 ºC/min after isothermal crystallization at 100 ºC 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.

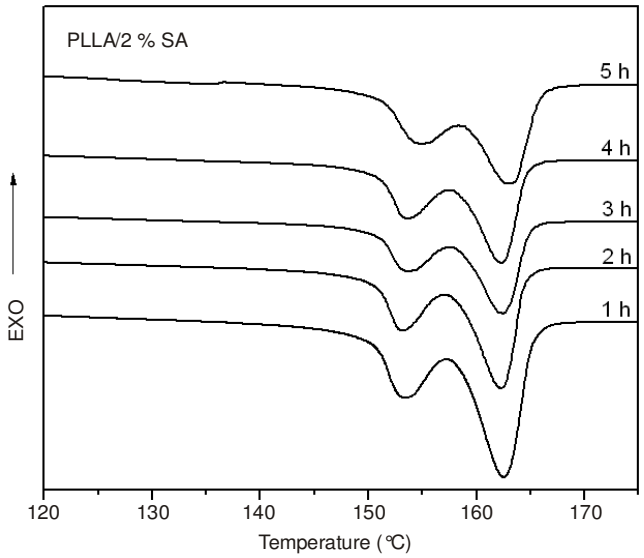

Fig. 2. Melting behaviour of PLLA/2%SA composities after isothermal crystallization at 100 ºC for different time

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

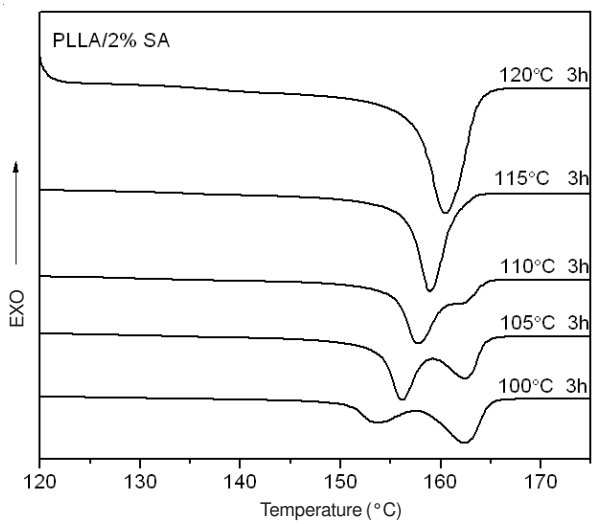

Fig. 3. Melting behaviour of PLLA/2%SA composities after different crystallization time for 3 h

Thermal stability of PLLA/SA composities: 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 composities at heating rates of 10 ºC/min are presented in Fig. 4, PLLA decomposes fast and completes in one stage above 300 ºC. 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 ketene[10]. 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 H_2O and the decomposition of sodium alginate at second stage is fast. However, up to 500 ºC, there still exists about 40 % mass. The TGA curve of PLLA/2%SA composities is similar to that of PLLA, but the onset decomposition temperature is lower than that of PLLA.

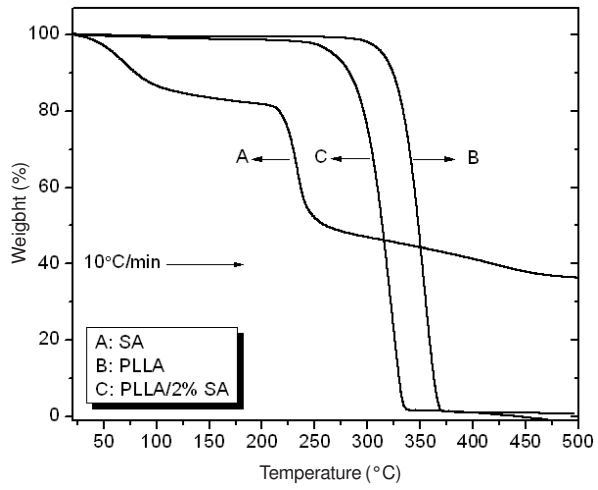

Fig. 4. TGA curves of thermal decomposition for PLLA, sodium alginate and PLLA/2%SA composities at heating rates of 10 ºC/min

Mechanical properties: The mechanical properties of polymer is affected by filler. Thus, study on mechanical properties of PLLA composities also help to understand the role of filler in polymer matrix. Fig. 5 shows the stree strain curve of PLLA and PLLA/2%SA composities. It is observed that sodium alginate makes PLLA become brittler. 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 composities decrease from 2.89 to 2.15 %, resulting from improving crystallization of PLLA in the presence of sodium alginate.

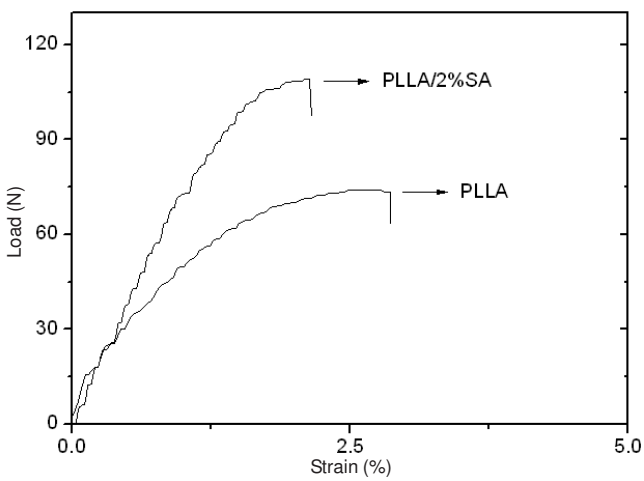

Fig. 5. The stress strain curve of PLLA and PLLA/2%SA composities

ACKNOWLEDGEMENTS

This work was supported by China Postdoctoral Science Foundation (Project No. 2013M531937), National Nature Science Foundation of China(Project No. 21101136), Natural Science Foundation Project of CQ CSTC (Project No. cstc2012jjA50001), Postdoctoral Science Foundation Project of ChongQing (Project No. XM20120035), Foundation of ChongQing Municipal Education Commission (Project No. KJ131202) and ChongQing University of Arts and Sciences (Project No. R2012CH10, 2012PYXM04).

REFERENCES

1. M. Viljanmaa, A. Södergård and P. Törmälä, *Int. J. Adhes. Adhesiv.*, **22**, 219 (2002)
2. Y. Shikinami, Y. Matsusue and T. Nakamura, *Biomaterials*, **26**, 5542 (2005).
3. D.S. Keskin, A. Tezcaner, P. Korkusuz, F. Korkusuz and V. Hasirci, *Biomaterials*, **26**, 4023 (2005).
4. S.F. Yan, J.B. Yin, Y. Yang, Z.Z. Dai, J. Ma and X.S. Chen, *Polymer*, **48**, 1688 (2007).
5. Z.Y. Yu, J.B. Yin, S.F. Yan, Y.T. Xie, J. Ma and X.S. Chen, *Polymer*, **48**, 6439 (2007).
6. M. Sajjan, B.K.J. Kumar, A.A. Kittur and M.Y. Kariduraganavar, *J. Membr. Sci.*, **425**, 77 (2012).
7. P. Rani, S. Mishra and G. Sen, *Carbohyd. Polym.*, **91**, 686 (2013).
8. Y.H. Cai, *Asian J. Chem.*, **25**, 3005 (2013).
9. Z.Z. Su, Q.Y. Li, Y.J. Liu, G.H. Hu and C.B. Wu, *J. Polym. Sci., Part B: Polym. Phys.*, **47**, 1971 (2009).
10. Y.H. Cai, S.F. Yan, Y.Q. Fan, Z.Y. Yu, X.S. Chen and J.B. Yin, *Iran. Polym. J.*, **21**, 435 (2012).