Fabrication and Properties of sc-PLA/SiO$_2$ Composites

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Abstract. Stereocomplex poly(lactic acid) /SiO$_2$ (sc-PLA/SiO$_2$) composites were prepared through solution mixing followed by vacuum drying. In the composites, good dispersion of SiO$_2$ particles could be obtained when the loading was less than 3wt%. Crystallization properties of sc-PLA were improved due to the addition of SiO$_2$. The maximum of both melt crystallization temperature ($T_{mc}$) and crystallinity ($X_c$) simultaneously occurred when the loading of SiO$_2$ was 1wt%. Furthermore, thermal stability of the composites was not affected greatly by agglomeration in a certain range. The initial decomposition temperature increased by 75°C (5wt% loading of SiO$_2$) compared with the crude.

Keywords. sc-PLA; SiO$_2$; Crystallization; Thermal-stability

1. Introduction

As a plant-derived biodegradable polyester, poly(lactic acid) (PLA) is widely used as engineering plastics, pharmaceutical, wrapping films, etc[1]. The enhancement of crystallization rate and heat-resistance of semicrystalline PLA is crucial to the broadening of the scope of application. Stereocomplex PLA (sc-PLA) prepared from PLLA and PDLA has been investigated as advanced PLA to some special applications. The most valuable attraction of sc-PLA is the melting point (up to about 230°C), which is about 50°C higher than that of the homocrystals [2]. However, the crystallization rate and heat-stability of sc-PLA still need great improvement for some plastic application.

One of the most effective methods to improve the properties of sc-PLA is nano-modification. For instance, Brzezinski [3] prepared PLA stereocomplexes from equimolar mixtures of PLLA and PDLA in the presence of MWCNT-g-PLA. In this case, crystallization of stereocomplexes from molten state was completely reversible, without formation of any homocrystallites. Yukiko Furuhashi [4] mixed equimolar PLLA and PDLA with addition of organo-modified montmorillonite in solution. Homocrystallization and stereocomplexation of PLAs both enhanced after annealing of the blends.

As one of the most commonly used modifier, nano-SiO$_2$ has been widely used in plastic and paint. Liu [5] prepared PLA/nano-SiO$_2$ composites by in-situ polycondensation. Thermal stability and tensile strength increased compared with the crude. However, the effect of nano-SiO$_2$ on other properties of sc-PLA has not been investigated to our best knowledge. This paper explores in detail the effect of
nano-SiO$_2$ on the crystallization and thermal stability of sc-PLA, in order to find an effective method to obtain high thermal-stability PLA composites to optimize the application of PLA materials.

2. Experimental

2.1 Materials

L-lactic acid (90%) and D-lactic acid (90%) were purchased from Musashino (Jiangxi Province, China). Stannous dichloride dehydrate (SnCl$_2$·2H$_2$O), p-toluenesulfonic acid monohdrate (TSA) were obtained from Tianjin Guangfu Technology Company. Dichloromethane and alcohol were from Beijing Chemical Works. Nano-SiO$_2$ was supplied by Nanjing Haitai nano Material Co.

2.2 Polymerization

2.2.1 Preparation of PLA

The linear PLLA and PDLA enantiomeric polymers were synthesized according to known procedure [6]. Take PLLA as an example, mixture of OLLA (50 g) with SnCl$_2$·2H$_2$O (0.05 g) and TSA (0.05 g) in a three-necked flask was heated at 180$^\circ$C under reduced pressure of 13.3×10$^{-2}$ Pa for 3-5 h. The crude product was purified through two dissolve-precipitation cycles in chloroform and ethanol, respectively. The relative weight-averaged molecular weight ($M_w$) of PLLA in white solid powder ranged between 2 and 3×10$^4$. PDLA was prepared with the same procedure.

2.2.2 Preparation of sc-PLA/SiO$_2$ composites

SiO$_2$ was pre-dispersed in DMF through high speed ball-milling procedure lasting for about 7 hours. PLLA and PDLA were respectively dissolved in dichloromethane at a concentration of 1 g/dl. SiO$_2$ dispersion solution was added drop by drop into the solution mixture of PLLA and PDLA under vigorously stirring. The solvent was evaporated off under ambient temperature or vacuum oven.

2.3 Measurements

A DSC-6200 (Seiko Instruments Inc) analyzer was used for analyzing the thermal properties of polymer samples under a nitrogen atmosphere. The samples were heated from 30 to 240$^\circ$C at a heating rate of 80$^\circ$C/min (the 1st heating scan). Then the samples stayed at 240$^\circ$C for 2 min and then cooled at 10$^\circ$C/min (cooling scan), followed by heated from 30 to 240$^\circ$C at a rate of 10$^\circ$C/min (the 2nd heating scan). TG209F1 (Netzsch) was used for analyzing the thermal stability. In the procedure, the temperature rised form 40 to 400$^\circ$C at a heating rate 10$^\circ$C/min. FE-TEM (Tecnai G$^2$ F20) was used to investigate dispersion of SiO$_2$ at an acceleration voltage of 200KV.

3. Result and discussion

3.1 Morphology

As shown in Figure 1, the microstructures of the composites were characterized by TEM. Nanoparticles can be well dispersed in DMF through milling. However, there exists some hard agglomeration when the content of SiO$_2$ reaches to1wt%. Hard agglomeration phenomenon becomes more obvious with increasing loadings. As a result, the crystallization and other properties of the composites decreased. In other words, solution-casting was one of several possibilities, but not the optimum one. Moreover, such phenomenon might be greatly improved by in-situ polymerization in our follow-up research.
3.2 Crystallization

As demonstrated in the data in Figure 2 and Table 1, nano SiO₂ obviously played a role of heterogeneous nucleating agent in sc-PLA, which can accelerate the crystallization rate of PLA. The nanoscaled SiO₂ provides large specific surface due to their small size and thus it is reasonable to consider that they acted as efficient nucleating agent. However, it should be noted that the samples appear double-melting peaks in the second heating scan except the pure sc-PLA. The double melting peaks for semicrystallization polymer usually are attributed to melt-reorganization (recrystallization)-remelt mechanism. Both the maximum melt crystallization temperature (T_{mc}) and the maximum crystallinity (X_c in second heating) occurred when the loading of SiO₂ was 1wt%. These should be contributed from good dispersion of nano SiO₂ in the matrix, which offers high efficiency for SiO₂ to be as nucleating agent. When the addition reached to 5wt%, agglomeration of nanoparticles became obvious. Therefore, the advantage of high specific surface and nucleation role declined greatly.

Figure 1 TEM image of SiO₂ dispersed in DMF (a) and in sc-PLA with different contents 0.5wt%(b), 1wt%(c), 3wt%(d) and 5wt%(e)
Figure 2. DSC traces of sc-PLA and sc-PLA/SiO$_2$ composites (Top: cooling scan from the melt; Bottom: the second heating scan)

Table 1. Thermal Properties of sc-PLA and sc-PLA/SiO$_2$

| SiO$_2$(wt%) | $T_{mc}$ (℃) | $T_m$ (℃) | $\Delta H_m$(J/g) | $X_c$(%) |
|--------------|--------------|-----------|------------------|--------|
| 0            | 116          | 199.7     | 46.6             | 30.1   |
| 0.5          | 126          | 197.5     | 208.9            | 68.9   | 44.5   |
| 1            | 131          | 203.4     | 212.8            | 76.3   | 49.2   |
| 3            | 128          | 197.4     | 207.7            | 71.3   | 46     |
| 5            | 120          | 200.8     | 211.1            | 70     | 45.2   |

3.3 Thermal Stability

Thermal stability of sc-PLA has been improved greatly after SiO$_2$ being loaded [7]. As shown in Figure 3, both the initial decomposition temperature and the final decomposition temperature increased. Initial decomposition temperature was 75 ℃ higher than sc-PLA at the addition of 5wt% despite of agglomeration. It was also found that such initial decomposition temperature can be as high as PLA with which molecular weight reached to $10^5$. Therefore, a simple process for preparing low molecular weight PLA with high thermal-stability polyester by low molecular was achieved. A grid or net structure possibly formed through the hydroxyl function of SiO$_2$, especially in the presence of high SiO$_2$ loading. The network might suppress the mobility of the volatile substance, leading to a delay in decomposition. In addition, we need to explore the improvement with high molecular sc-PLA in detail in future study.

Figure 3. TG curves of sc-PLA and sc-PLA/SiO$_2$ composites
4. Conclusion

In the present study, well dispersed SiO$_2$ was obtained by milling in PLAs when the loading was lower. The involved SiO$_2$ can obviously improve the crystallization of sc-PLA, indicated by the DSC scans. The optimum addition to improve the crystallization behavior was 1 wt%. Thermal stability of sc-PLA increased greatly with the addition of SiO$_2$, despite of some agglomeration in the matrix.

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References:

[1] Yang Bin, Polylactic acid [M]. Beijing: Chemical Industry Press, 2007, 12-18

[2] Hideto Tsuji, SuongHyu Hyon, Yoshito Ikada. Stereocomplex Formation between Enantiomeric Poly(lactic acid)s. 3. Calorimetric Studies on Blend Films Cast from Dilute Solution. Macromolecules, 1991, 24: 5651-5656

[3] M. Brzezinski, M. Bogusawska, M. Ilicikova. Unusual Thermal Properties of Polylactides and Polylactide Stereocomplexes Containing Polylactide-Functionalized Multi-Walled Carbon Nanotubes. Macromolecules, 2012, 45: 8714–8721

[4] Yukiko Furuhashi, Kousuke Morioka, Hideyuki Tamegai, Naoko Yoshie. Preparation and Some Properties of Stereocomplex-Type Poly (lactic acid)/Layered Silicate Nanocomposites. J. Appl. Polymer. Sci., 2013, 127: 1615–1622.

[5] Liu Lizhu. Preparation and properties of polylactide/nano$_2$ silica in situ composites. Journal of Beijing University of Chemical Technology, 2008, 35(1): 66-69

[6] S.-I. Moon, C.-W. Lee, I. Taniguchi, M. Miyamoto. Melt/solid polycondensation of l-lactic acid: an alternative route to poly(l-lactic acid) with high molecular weight. Polymer, 2001, 42: 5059–5062

[7] H. Yamane, K. Sasai. Effect of the addition of poly (D-lactic acid) on the thermal property of poly(L-lactic acid). Polymer, 2003, 44: 2569–2575