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Controlling stereocomplexation, heat resistance and mechanical properties of stereocomplex polylactide films by using mixtures of low and high molecular weight poly(D-lactide)

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Abstract: Stereocomplex polylactide (scPLA) films were prepared by blending poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) solutions before solvent evaporation. The PLLA/PDLA ratios were 80/20 and 60/40 (w/w). PDLAs with low and high molecular weights (M.W.) were used as PDLA mixtures. The scPLA films with different low/high M.W. PDLA ratios were investigated for both the 80/20 and 60/40 (w/w) scPLA film series. Stereocomplexation, heat resistance and the mechanical properties of the scPLA films were studied by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and tensile testing, respectively. The results indicated that low M.W. PDLA can enhance the stereocomplexation and heat resistance of scPLA films while the high M.W. PDLA can improve tensile properties of scPLA films. It was concluded that the stereocomplexation, heat resistance and tensile properties of scPLA films could be controlled by adjusting the low/high M.W. PDLA ratio in PDLA fraction.

Keywords: crystallization; heat resistance; mechanical properties; polylactide; stereocomplexation.

1 Introduction

In recent decades, stereocomplex polylactides (scPLAs), prepared by blending poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), have been extensively investigated for potential use in high-performance bioplastic applications (1, 2). The scPLA exhibited better hydrolysis resistance, heat resistance and mechanical properties than PLLA (2–4). The stereocomplex crystallites of scPLA are different from the homo-crystallites of PLLA and PDLA that have faster crystallization and higher melting points due to the stereocomplex crystallites having CH₃ · · · O=C interactions between enantiomeric PLA (5–8).

The stereocomplexation behaviors of PLAs strongly depended on the molecular weight (M.W.) of each PLLA and PDLA components. The low M.W. PLAs have been shown to be more efficient in forming the stereocomplex crystallites than the high M.W. PLAs. This is due to its good chain diffusion for stereocomplex crystallization (8). The higher melting temperature and faster crystallization of stereocomplex crystallites enhanced heat resistant properties of the PLA. The scPLA films exhibited better mechanical properties than the PLLA films because of a high density of tie chains between the stereocomplex crystallites that act as physical cross-linkers (9, 10). The mechanical properties of all PLLA, PDLA and scPLA films strongly depended on their M.W. values (11). The high M.W. PLAs improved the mechanical properties of these films. However, more “fine tuning” is still required in stereocomplexation, heat resistance and the mechanical properties of the scPLA. Moreover, the stereocomplexation-heat resistance-mechanical property relationship of scPLA remains to be identified.

To the best of our knowledge, mixtures of low and high M.W. PDLAs have not been used to form the scPLA. Thus, the purpose of this work was to investigate the influence of the mixtures of low and high M.W. PDLAs on stereocomplex formation, heat resistance and the mechanical properties of scPLA films. For this purpose, high M.W. PLLA, low M.W. PDLA and high M.W. PDLA were synthesized. Then, 80/20 and 60/40 (w/w) PLLA/PDLA blend film series were prepared by solution blending followed with a solvent evaporation. The PDLA fractions were mixtures of low and high M.W. PDLAs with different weight ratios (100/0, 75/25, 50/50, 25/75 and 0/100). The scPLA films were characterized by the use of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and tensile testing. The results were also compared with the pure PLLA film.
2 Experimental

2.1 Materials

L-lactide (LLA) and D-lactide (DLA) monomers were prepared from L-lactic acid (88%, Purac, Rayong, Thailand) and D-lactic acid (90%, Haihang Industry Co., Ltd., Jinan, China), respectively, using a direct polycondensation followed with a thermal depolymerization. Both LLA and DLA monomers were purified by re-crystallization 4 times from ethyl acetate before being dried in a vacuum oven at 55°C for 24 h. 1-Dodecanol (98%, Fluka, Buchs, Switzerland) was purified by distillation under reduced pressure before use. Stannous octoate [Sn(Oct)₂, 95%, Sigma, St. Louis, USA] was used without further purification. All reagents used were analytical grade.

2.2 Methods

The PLLA and PDLA were synthesized by ring-opening polymerization in bulk at 165°C for 2.5 h under a nitrogen atmosphere using Sn(Oct)₂ (0.01 mol%) and 1-dodecanol as the initiating system. The 1-dodecanol contents of 2.8 and 0.14 mol% were used to synthesize PLAs with theoretical M.Ws of 5 and 100 kg/mol, respectively. The PLLA with a theoretical M.W. of 100 kg/mol and the PDLAs with theoretical M.W. of 5 and 100 kg/mol were then synthesized. The obtained PLAs were granulated before drying in a vacuum oven at 110°C for 3 h to remove any un-reacted monomers.

The number average molecular weights (Mₙ) of the high M.W. PLLA, low M.W. PDLA and high M.W. PDLA were 90 kg/mol (PLLA90k), 5.7 kg/mol (PDLA6k) and 85.4 kg/mol (PDLA85k), respectively, as determined by gel permeation chromatography in tetrahydrofuran at 40°C. Their poly-dispersity indices (PI) were 2.8, 1.9 and 2.1, respectively. The L-enantiomer contents of the PLLA90k, PDLA6k and PDLA85k obtained by polarimetry in chloroform at 25°C were 96.5%, 3.8% and 4.2%, respectively.

The scPLA films were prepared by solution blending before film casting. Each PLLA and PDLA solution in chloroform (0.01 g/ml) was separately prepared before mixing together with vigorous stirring. The blended solutions were dried at room temperature for 24 h before being dried in a vacuum oven at room temperature for a week. Film thicknesses were in range 0.15–0.25 mm. The PLLA/PDLA ratios of 20/80 and 60/40 (w/w) were chosen to study effect of PDLA6k/PDLA85k ratio on properties of scPLA films with non-complete and complete stereocomplexation, respectively.

3 Results and discussion

The 80/20 and 60/40 (w/w) PLLA90k/(PDLA6k + PDLA85k) blend or scPLA films with different PDLA6k/PDLA85k ratios were successfully prepared by solution blending before film casting except the 60/40 (w/w) scPLA film prepared with PDLA6k/PDLA85k ratio of 100/0 (w/w). The latter film was highly brittle due to the largest stereocomplexation and the highest fraction of low M.W. PDLA. The PLLA/PDLA ratios of 20/80 and 60/40 (w/w) were chosen to study effect of PDLA6k/PDLA85k ratio on properties of scPLA films with non-complete and complete stereocomplexation, respectively.

3.1 Stereocomplexation

The stereocomplexation of scPLA films was determined from the second heating scan DSC thermograms as shown in Figure 1. The glass transition temperatures
were similar in range, 55–60°C. The peaks of cold crystallization temperature ($T_{cc}$), melting temperature of homo-crystallites ($T_{m,hc}$) and melting temperature of stereocomplex crystallites ($T_{m,sc}$) were detected. The $T_{cc}$ peaks significantly shifted to higher temperature with the PDLA85k ratio for both 80/20 and 60/40 (w/w) scPLA film series. This was attributed to the longer PDLA85k chains retarding the crystallization of PLA matrices due to its low chain mobility (8). The $T_{cc}$ peaks of homo- and stereocomplex crystallites overlapped each other (12). Thus, the degrees of crystallinity of both homo- and stereocomplex crystallites could not be determined because of the $T_{cc}$ peaks of homo- and stereocomplex crystallites could not be separately estimated. It is interesting that the $T_{cc}$ peaks of scPLA films with 50/50 (w/w) PDLA6k/PDLA85k had shoulder peaks for both the 80/20 and 60/40 (w/w) scPLA films. The results suggested the almost cold crystallization of stereocomplex crystallites occurred at lower temperature than the homo-crystallites. It may be said that the $T_{cc}$ peaks in ranges 81–89°C and 101–102°C were pre-dominantly stereocomplex and homo-crystallization, respectively. Their $T_{m,sc}$ and $T_{m,hc}$ values were in ranges 168–175°C and 217–224°C, respectively. It should be noted that the 60/40 (w/w) scPLA films with 100/0 and 75/25 (w/w) PDLA6k/PDLA85k in Figure 1 (below) presented only $T_{m,sc}$ peaks. This indicates the two latter scPLA films were complete stereocomplexation due to higher PDLA ratio (40 wt%) and greater PDLA6k content (100 and 75 wt%).

The enthalpies of cold crystallization ($\Delta H_{cc}$) as well as enthalpies of melting of homo-crystallites ($\Delta H_{m,hc}$) and stereocomplex crystallites ($\Delta H_{m,sc}$) are summarized in Table 1. It is clearly seen that the $\Delta H_{cc}$ and $\Delta H_{m,hc}$ steadily increased as well as the $\Delta H_{m,sc}$ decreased as the decreasing PDLA6k ratio. It has been reported that the shorter PDLA chains enhanced better stereocomplexation than the longer PDLA chains because the shorter PDLA chains had good chain mobility for stereocomplex formation (8–10). In addition, the 60/40 (w/w) scPLA films showed higher $\Delta H_{m,sc}$ than the 80/20 (w/w) scPLA films for the same PDLA6k/PDLA85k ratio.

The crystallization behaviors of the scPLA films were also investigated from the cooling DSC thermograms as shown in Figure 2. The crystallization temperatures ($T_c$) and enthalpies of crystallization ($\Delta H_c$) steadily increased with the PDLA6k ratio for both 80/20 and 60/40 (w/w) scPLA film series. The results supported a conclusion that the scPLA films with higher PDLA6k ratios induced faster crystallization. This is due to the good diffusion ability of short PDLA6k chains accelerating stereocomplex crystallization (8).

### 3.2 Heat resistance

The heat-resistant property of scPLA was determined by DMA. The storage modulus changes have been widely used to study heat resistance of the PLLA and scPLA.
The storage moduli of scPLA films from DMA are given in Figure 3 compared with the pure PLLA90k film. We could not measure the storage modulus for the 60/40 (w/w) scPLA film with 100/0 (w/w) PDLA6k/PDLA85k owing to high brittleness. Probably, the highest $\Delta H_{m,sc}$ value (60.6 J/g, see Table 1) of this scPLA film may have increased its brittleness. The storage modulus of pure PLLA film largely decreased in the range 50–70°C due to glassy-rubbery transition (13). All the scPLA films in Figure 3 exhibited higher storage moduli in range 60–100°C than the pure PLLA90k film attributed to the better heat resistance of scPLA films (15).

Figure 4 compares storage moduli at 90°C of the scPLA films from Figure 3. This was 366 MPa for the pure PLLA90k film prepared in this work. It can be seen that all the scPLA films had higher storage moduli at 90°C than the pure PLLA90k film. The storage moduli at 90°C decreased when the PDLA85k ratio was increased. In addition, the 60/40 (w/w) scPLA film series showed higher storage moduli than those of the 80/20 (w/w) scPLA film series for the same PDLA6k/PDLA85k ratio. The results indicated that the higher PDLA and PDLA6k contents exhibited better heat-resistant property of the scPLA films. It can be concluded that the heat resistance of scPLA films directly related to the $\Delta H_{m,sc}$ in Table 1.
3.3 Tensile properties

The averaged results of tensile properties are presented in Figure 5. The Young’s modulus, stress at break and strain at break of the scPLA films slightly increased with the PDLA85k ratio for both 80/20 and 60/40 (w/w) scPLA film series. The averaged stress and strain at break of the pure PLLA90k film prepared in this work were 31 MPa and 5.8%, respectively. This suggests that the scPLA films with high PDLA6k ratios exhibited similar tensile properties to the pure PLLA90k film. In this work, the density of tie chains between stereocomplex crystallites prepared from the PDLA6k could be too low because of its short chain lengths. Therefore, the high PDLA6k ratios did not improve tensile properties of the scPLA films, although the $\Delta H_{m,sc}$ were increased. Meanwhile the scPLA films with higher PDLA85k ratios showed better tensile properties than the pure PLLA90k film. The longer PLLA and PDLA chains in amorphous regions which linked between stereocomplex crystallites improved its tensile properties (9–11). In addition, the 80/20 (w/w) scPLA films exhibited tensile properties slightly better than those of the 60/40 (w/w) scPLA films for the same PDLA6k/PDLA85k ratio. This is due to the 80/20 (w/w) scPLA films having lower $\Delta H_{m,sc}$.

4 Conclusions

In conclusion, the results presented here show that the low M.W./high M.W. PDLA mixtures of PDLA fraction have the potential to control the stereocomplexation, heat resistance and mechanical properties of PLLA/PDLA blended or scPLA films. Both the higher PDLA and PDLA6k contents showed a significant promoting effect on stereocomplexation and heat resistant property of the scPLA films, while the PDLA85k fraction improved the mechanical properties of the scPLA films. The scPLA films with the highest PDLA6k ratio showed the largest $\Delta H_{m,sc}$ and the best heat resistance but poor mechanical properties. The heat-resistant property were directly related to the $\Delta H_{m,sc}$. The scPLA films with the highest PDLA85k ratio exhibited the best mechanical properties but the lowest $\Delta H_{m,sc}$ and heat-resistant property.

The low M.W. PDLA provided complete stereocomplexation, fast crystallization and good heat resistance of scPLA but induced its highly brittleness. Meanwhile the high M.W. PDLA enhanced mechanical properties but suppressed stereocomplexation, crystallization and heat resistance of the scPLA. This work could provide guidance toward fabrication of scPLA products with balanced stereocomplexation, crystallization, heat resistance and mechanical properties. Moreover, this report will expand the knowledge of scPLA that will provide more application potential for scPLA products.

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References


