

Miscibility and Thermal Properties of PLLA-based Blends

*Fang-Chyou Chiu¹⁾ and Chen-Tsyr Lo²⁾

^{1), 2)} *Department of Chemical and Materials Engineering, Chang Gung University,
Taoyuan 333, Taiwan*

¹⁾ maxson@mail.cgu.edu.tw

ABSTRACT

This work examined the miscibility and thermal properties of three melt-mixed blend systems, including PLLA/PET, PLLA/PTT, and PLLA/PBT blends. The miscibility study showed that there were certain interactions between the two counterparts in the PLLA/PET and PLLA/PBT blends; however, little interaction was observed in the PLLA/PTT blend. The presence of PLLA resulted in the different degrees of melting temperature depression of the respective aromatic polyesters. XRD analyses showed that there was no new crystal structure developed in each of the three blends. DSC results indicated the crystallizability of PET declined in the blend; the crystallizability of PTT and PBT increased in the blends. TGA results revealed that adding PLLA in the blends increased the degradation activation energies of PET and PTT, but decreased the activation energy of PBT.

1. INTRODUCTION

Because of their potential to exhibit tailor-made properties, polymer blends continue to attract much interest both academically and industrially during the past decades. (Utracki 1998) Hence, investigations on various polymer blends have been conducted. As it is recognized, the miscibility between the components plays an important role in the final performance of the blend products. For blends with crystalline component(s), their crystallization kinetics and crystalline morphology will have influences on the resultant properties as well. Poly(L-lactide) (PLLA) is a well-known biodegradable and biocompatible thermoplastic which can be produced from renewable resources. (Bogaert 2000) It has favorable mechanical properties, and exhibits potential for use in biomedical applications and industrial packaging. From an ecological viewpoint, the versatility of PLLA has to be enhanced. To approach this goal, fabrication of PLLA-based blends is an effective route, and the blends are expected to exhibit a wide range of features. The study on the miscibility and physical properties of PLLA-based blends has been carried out. (Lai 2004) Nevertheless, the blends of PLLA with engineering-grade aromatic polyesters are less investigated. (Acar 2007, Chen 2009) In the present study, PLLA was blended with PET, PTT and PBT, respectively, to form three binary blend systems. The miscibility, crystallization behavior, melting behavior and crystalline

¹⁾ Professor

²⁾ Graduate Student

morphology of the three systems were characterized, and compared with one another.

2. EXPERIMENTAL

2.1. Materials and Blends Preparation

PLLA (Resomer® L-209S) used in this study was purchased from Boehringer Ingelheim. Its intrinsic viscosity is around 3.0 dl/g. PET with an intrinsic viscosity of 0.84 dl/g was supplied by Nan Ya Plastics Corporation (Taiwan). PTT with an intrinsic viscosity of 0.92 dl/g was purchased from Shell Company. PBT used was manufactured by ShinKong Synthetic Fiber Corporation, and it has an intrinsic viscosity of 0.92 dl/g. Three blends of PLLA/PET, PLLA/PTT, and PLLA/PBT with weight ratio of 50:50 were prepared through a melt mixing process by a Laboratory Mixing Molder (Atlas). For comparative purposes, neat components were also treated through the same melt processing procedure.

2.2. Characterizations

The T_g , crystallization and melting behaviors of the samples were measured using a TA DSC Q10 analyzer equipped with an inter-cooler. The thermal stability of the samples was characterized using a TA TGA Q50 system. Phase morphology of the three blends was examined by a Hitachi S-3000N SEM system. For the crystal structure examination, wide angle x-ray diffraction (WAXD) patterns of the samples were recorded at room temperature using a Siemens D5005 X-ray unit. The X-ray used was $CuK\alpha$ radiation with a wavelength of 0.154 nm.

3. RESULTS AND DISCUSSION

The T_g s of the liquid nitrogen-quenched samples were determined by DSC to evaluate the miscibility of the three blends. Two T_g s were observed for each of the blends, indicating the immiscible feature of the blends. Nevertheless, the T_g of PLLA in the blends declined slightly compared with the neat PLLA. Figure 1 shows the SEM images of the three blends. Two-phased morphology was observed for each blend. The PLLA was recognized to dominate the matrix role, and the aromatic polyesters formed the dispersed phase. The average size of the dispersed phase in the blends followed the order of PLLA/PTT>PLLA/PBT>PLLA/PET. XRD diffraction patterns of the 10 °C/min-cooled samples were collected at room temperature. The characteristic diffractions of both PLLA and polyester components exhibited in the patterns, which indicated the crystal structure of the components remained in the blends.

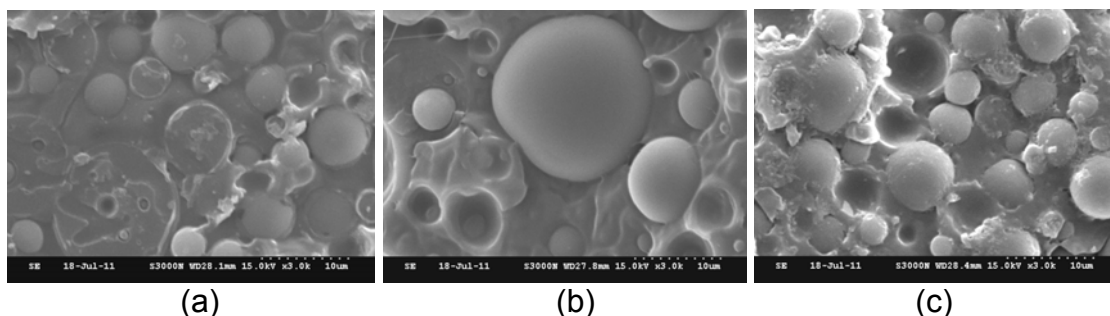


Fig. 1 SEM images of (a) PLLA/PET, (b) PLLA/PTT, (c) PLLA/PBT blends.

Figure 2(a) shows the DSC cooling curves of the blends and their polyester components at a 20 °C/min cooling rate in the range of 160 °C to 235 °C. It is noted that the presence of PLLA slightly increased the crystallization peak temperature (T_p) of PTT and PBT, but decreased the T_p of PET. These results revealed that PLLA enhanced the crystallization ability of PTT and PBT, but retarded PET's crystallization ability. Figure 2(b) depicts the DSC cooling curves in the range of 40 °C to 150 °C. The crystallization of PLLA was observed in the neat state and in the PTT- and PBT-blends. The curve of PLLA/PET blend is not included in the figure due to the absence of PLLA crystallization. In the figure, PTT was noted to enhance slightly the crystallization of PLLA. The PBT evidently enhanced the crystallization ability of PLLA. The isothermal crystallization behavior of the polyesters in the neat state and in the blends was investigated as well. Figures 3(a) and 3(b) show typical DSC crystallization curves of PTT and PLLA/PTT blend at different crystallization temperatures (T_c s). In the study, crystallization peak time (t_p) was defined as the time crystallization exotherm minima occurred. Figure 4 shows t_p^{-1} as a function of T_c for the three blends and their polyester components. t_p^{-1} is proportional to the overall crystallization rate. The results show that at identical T_c s the presence of PLLA decreased the overall crystallization rate of PET and PTT. On the contrary, PLLA enhanced the crystallization of PBT, especially at low T_c s.

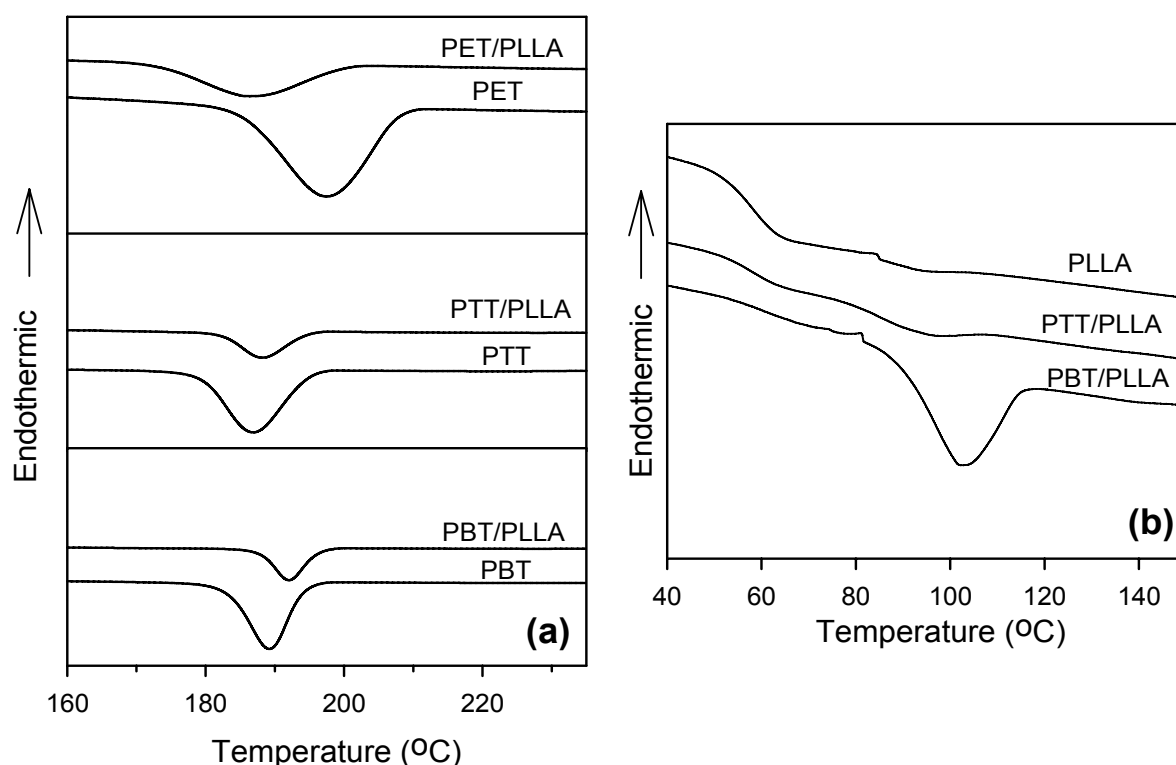


Fig. 2 DSC cooling curves of the samples in the (a) high temperature (160 °C~235 °C) range and (b) low temperature (40 °C~150 °C) range.

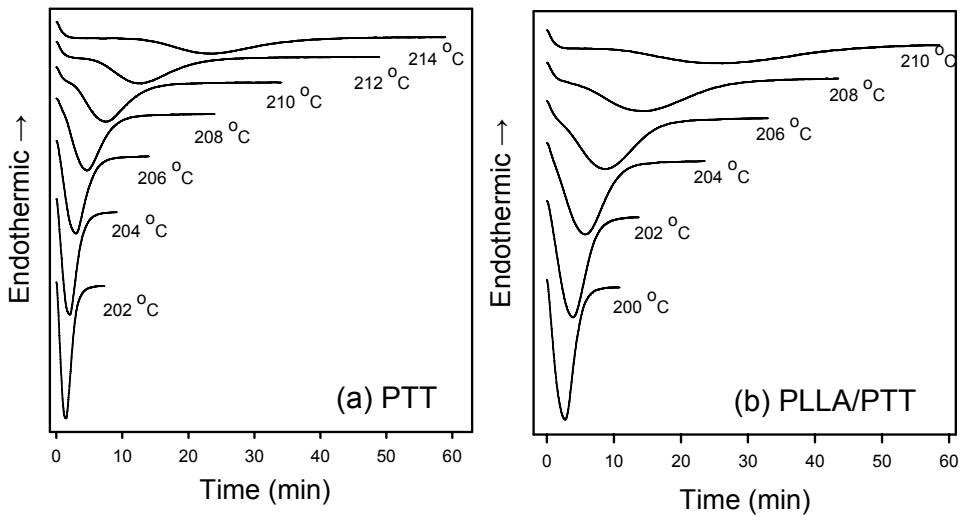


Fig. 3 DSC isothermal crystallization curves of (a) PTT and (b) PLLA/PTT blend.

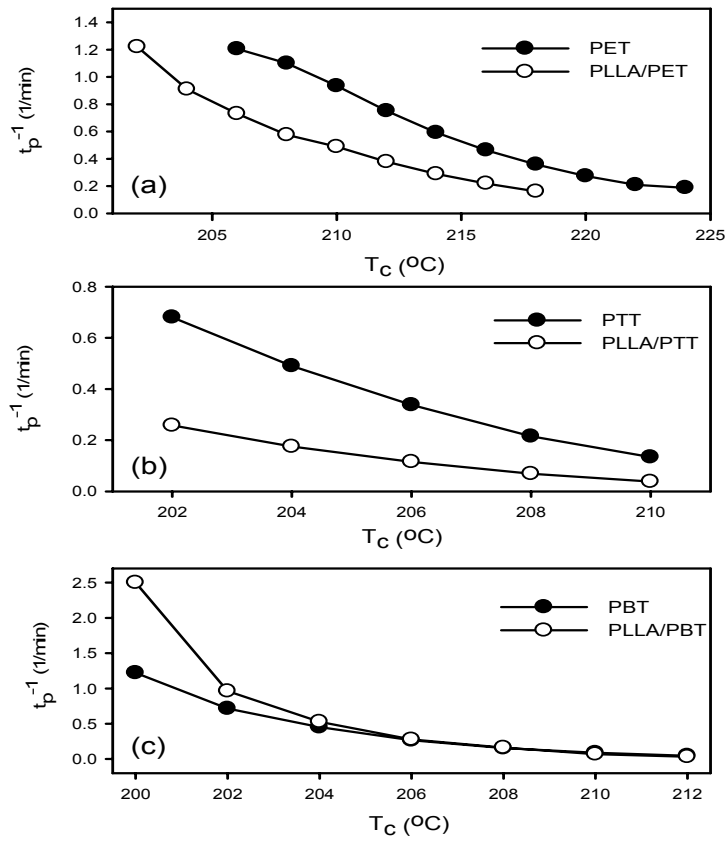


Fig. 4 t_p^{-1} as a function of T_c for different systems.

The melting behaviors of non-isothermally and isothermally crystallized samples were subsequently studied. The PLLA influenced the melting behavior of aromatic polyesters evidently. The conventional Hoffman-Weeks (HW) extrapolative method was employed to determine the equilibrium melting temperature (T_m°) of the aromatic polyester in the blend and in the neat state. The T_m° of each aromatic polyester was determined to be lower in the blend than that in the neat state. The depression in T_m° of the aromatic polyester in the blend indicated that certain interactions existed between the PLLA and individual polyester, though two-phased morphology was observed. The thermal stability of the blends and their components were compared through TGA analyses. Figure 5 illustrates the typical TGA results scanned at 20 °C/min under nitrogen environment. For the components, PLLA showed the lowest thermal stability, and PET possessed the highest thermal stability. PTT and PBT had similar degradation results. The temperature (T_{dmax}) at the fastest degradation rate for each sample was determined from the derivative TGA data. It is noted that T_{dmax} of each component decreased slightly in the blend. These results indicate that the blending approach hardly increased the thermal stability of the PLLA.

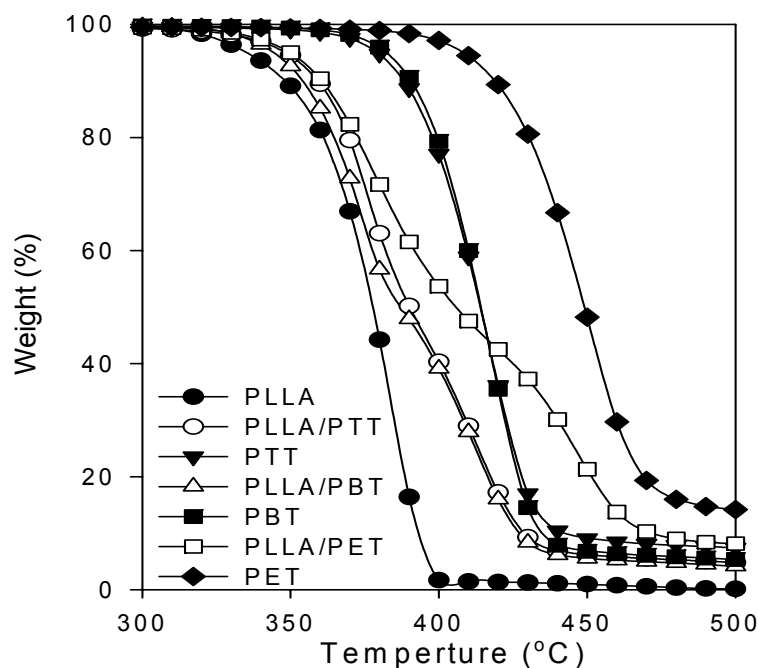


Fig. 5 TGA curves of the samples in N_2 .

4. CONCLUSIONS

Three PLLA/aromatic polyester (PET, PTT, PBT) blend systems were prepared through a conventional melt mixing procedure. The presence of PLLA affected the crystallization and melting behaviors of the individual polyester to different degrees. The crystallization ability of PBT was enhanced with the incorporation of PLLA. The crystallization ability of PET was retarded by the addition of PLLA. The T_m° of each aromatic polyester was determined to be lower in the blend than that in the neat state.

The blends exhibited two-phased morphology, indicating their immiscible feature. The thermal stability of the blends' components declined slightly in the blends.

REFERENCES

- Acar, I., Durmuş, A. and Özgümüş, S. (2007), "Nonisothermal crystallization kinetics and morphology of poly(ethylene terephthalate) modified with poly(lactic acid)", *J. Appl. Polym. Sci.*, **106**, 4180-4188.
- Chen, H., Pyda, M. and Cebe, P. (2009), "Non-isothermal crystallization of PET/PLA blends", *Thermochim. Acta*, **492**, 61-66.
- Bogaert, J.C. and Coszach, P. (2000), "Poly(lactic acids): A potential solution to plastic waste dilemma", *Macromol. Symp.*, **153**, 287-303.
- Lai, W.C., Liao, W.B. and Lin, T.T. (2004), "The effect of end groups of PEG on the crystallization behaviors of binary crystalline polymer blends PEG/PLLA", *Polymer*, **45**, 3073-3080.
- Utracki, L.A. (1998), *Commercial Polymer Blends*, Chapman & Hall, New York.