Miscibility and Phase Structure of Binary Blends of Polylactide and Poly(methyl methacrylate)

GUOBAO ZHANG, JIANMING ZHANG, SHENGUO WANG, DEYAN SHEN

State Key Laboratory of Polymer Physics & Chemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, Peoples Republic of China

ABSTRACT: Blends of amorphous poly(DL-lactide) (DL-PLA) and crystalline poly(L-lactide) (PLLA) with poly(methyl methacrylate) (PMMA) were prepared by both solution/precipitation and solution-casting film methods. The miscibility, crystallization behavior, and component interaction of these blends were examined by differential scanning calorimetry. Only one glass-transition temperature (T_g) was found in the DL-PLA/PMMA solution/precipitation blends, indicating miscibility in this system. Two isolated T_g's appeared in the DL-PLA/PMMA solution-casting film blends, suggesting two segregated phases in the blend system, but evidence showed that two components were partially miscible. In the PLLA/PMMA blend, the crystallization of PLLA was greatly restricted by amorphous PMMA. Once the thermal history of the blend was destroyed, PLLA and PMMA were miscible. The T_g composition relationship for both DL-PLA/PMMA and PLLA/PMMA miscible systems obeyed the Gordon–Taylor equation. Experiment results indicated that there is no more favorable trend of DL-PLA to form miscible blends with PMMA than PLLA when PLLA is in the amorphous state. © 2002 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 41: 23–30, 2003

Keywords: polylactide; poly(methyl methacrylate); miscibility; blends; crystalline

INTRODUCTION

In the family of aliphatic polyesters, polylactides (PLAs) have been considered as one of the most interesting and promising biodegradable materials. Because of its good biocompatibility and nontoxicity, PLAs and their copolymers have been used for biomedical applications, such as drug-delivery systems,[1] implant materials for bone fixation,[2] and surgical surture.[3] These materials have the advantage of no retrieval of the device after usage because their degradation products can be metabolized in the body.[4] The increasing use of biodegradable polymers in medicine, together with specific properties required for specific applications, has promoted intensive research into new material with potential applications in this field. The control of the degradation behavior and mechanical performance on the basis of the structure/morphology/property is the driving force of these studies.

Several approaches can be used to improve the properties of PLA including blending and copolymerization. Extensive effort has been devoted to the study of the effect of copolymerization of PLA on the physical and chemical properties of the final products. The optimization of properties such as the rate of biodegradation, mechanical properties, and hydrophilic–hydrophobic balance has been mainly achieved by copolymerization with other monomers or oligomer of poly(ethylene glycol) (PEG).[5–9] For example, copolymers of PLA and poly(glycolic acid) have been produced to con-

trol the degradation rate, and the degradation time of this polymeric material can be varied from months to years through compositional modification.[10,11] Hydrophilicity can be modified by inserting PEG in the backbone of PLA, and the rates of drug release can be modified by balancing the amount of hydrophobic–hydrophilic segments in the copolymer chain.[5]

Blending of polymers is a relatively simple and more cost-effective method as compared with copolymer synthesis to modify polymer properties, and it can represent, in some cases, an alternative to copolymerization. Generally, blends exhibit advantageous physical and chemical properties that each individual polymer does not possess. Through an opportune choice and the composition of the second component of the blend, a tailor-made material with some specific properties can be obtained. A number of studies have focused on the bending of PLA with other polymers or copolymers. These blends include PLA with poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate),[12,13] blends of PLA with PEG,[14–16] and blends of PLA with poly(ϵ-caprolactone) poly(glycolide).[17,18] Properties of blends depend not only on the chemical composition of the blend but also on the compatibility or miscibility of the components; however, most of the blends are immiscible. Gajria et al.[19] found that amorphous PLA is miscible with poly(vinyl acetate), but it seems immiscible with ethylene-vinyl acetate copolymer.[20] Recently, Shuai et al.[21] examined the blends of PLA with poly(vinyl alcolol) and found that the blends are partially miscible because of the specific interaction of intermolecular hydrogen bonding.

Poly(methyl methacrylate) (PMMA) is a synthetic polymer with good chemical and physical properties. In this article, the blends of both poly(L-lactide) and poly(DL-lactide) with PMMA were investigated. Miscibility, crystallinity, and the morphological structure of two components are the key factors that determine the properties of the blends. This article centers on these subjects. It is expected that blending of PLA and PMMA may be an effective method for obtaining PLA-based materials with improved properties as compared with PLA.

EXPERIMENTAL

Materials

The PLLA samples used in this study were synthesized in our laboratory according to the literature.[22] The viscosity-average molecular weight was 55 kg/mol, as determined by measuring the intrinsic viscosity [η] in chloroform solution at 30 °C. DL-PLA and PMMA were purchased from Sigma and used as received. The weight-average molecular weights of DL-PLA and PMMA were 150 and 1000 kg/mol, respectively, relative to polystyrene standards of narrow dispersity, as determined by gel chromatography (GPC) with a PL-210 GPC with tetrahydroforan as the eluent.

Sample Preparation

Three polymer solutions in dioxane were prepared separately at a concentration of 1% (w/v). Predetermined amounts of the solutions were mixed and precipitated into magnetically stirred fivefold volume petroleum ether. After decanting, the polymer was dried in vacuum at about 50 °C for 48 h and then stored in a desiccator until use. Samples prepared by casting from chloroform solution were also used.

Measurement

A Mettler–Toledo-822e differential scanning calorimeter (DSC), calibrated with indium, was used to analyze the thermal properties of the blends. The samples were first heated from room temperature to 200 °C at the heating rate of 20 °C/min and were annealed for 1 min at this temperature to erase previous thermal history followed by quenching in liquid nitrogen. The samples were subsequently heated again to 200 °C at the heating rate of 10 °C/min. The thermograms of the first and second DSC heating runs were both recorded. The glass-transition temperature (T_g) was taken as the temperature at the midpoint of the corresponding heat-capacity jump in the second heating runs. The melting temperature (T_m) and the apparent enthalpy of fusion (ΔH_f) of each sample were determined from the maximum and the area of the melting endothermic peaks in the first scans, respectively. All the DSC measurements proceeded under N_2 of 20 mL/min.

RESULTS AND DISCUSSION

DL-PLA/PMMA Blends

For polymer blends, samples prepared by different methods will have different results. In this work, blends prepared by both solution/precipita-
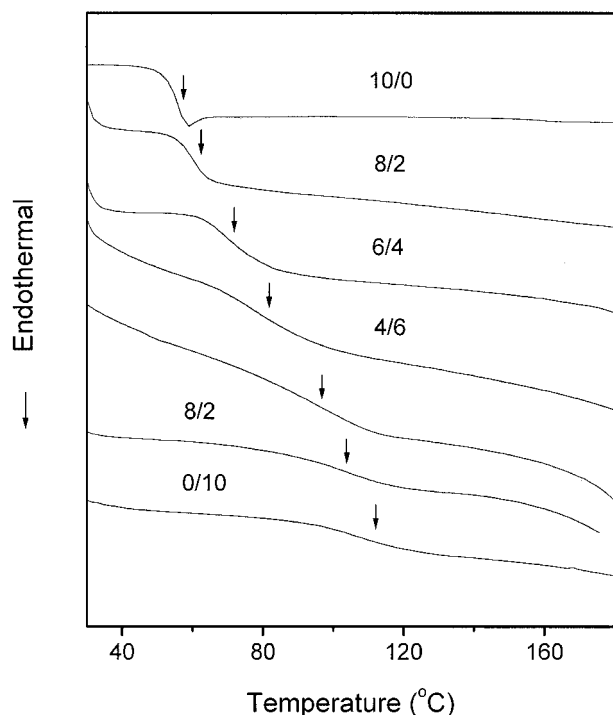
Figure 1. DSC thermograms in the second heating runs for solution/precipitation DL-PLA/PMMA blends with compositions from 100:0 to 0:100.

tion methods and solution-casting films are discussed. Figure 1 illustrates the thermograms obtained in the second DSC heating run for DL-PLA/PMMA solution/precipitation blends with different compositions.

The T_g of a polymer blend is one of the most important criteria for the miscibility of components. Miscibility between any two polymers in the amorphous state is detected by the presence of a single T_g intermediate between those of the two component polymers. Immiscibility of two polymers is demonstrated by the retention of the T_g values of both individual components. In Figure 1, the blends of two polymers exhibit a single T_g in the whole composition range situated between the T_g's of the individual components. The location of the blend T_g appears to be more or less proportional to the composition of the blend. This is a clear indication of miscibility of the two polymers.

For ideal systems that are miscible and amorphous over the whole composition range, the relationship between the T_g and the composition of the blend can be predicted by simple equations, for example, the Gordon–Taylor equation[23]

$$T_g = T_{g1} + kw_2(T_{g2} - T_{g1})/(w_1 + kw_2) \qquad (1)$$

where w_i refers to the weight faction of component i, and T_{gi} is its glass-transition temperature. Subscripts 1 and 2 are used to designate components 1 and 2. In this article, 1 and 2 represent PLA and PMMA, respectively. k is an adjustable parameter that has often been interpreted as a miscibility measure because it has been related to the interaction strength between the components in a blend.

Figure 2 shows the variation of the observed and calculated T_g data (with the Gordon–Taylor equation) as a function of the percentage of PMMA in DL-PLA/PMMA solution/precipitation blends. Where the solid line corresponds to the Gordon–Taylor prediction for this system with $k = 0.5$, the dashed line represents the weight average and the solid circles are the experimental results. The figure demonstrates that the observed and calculated values agree. The k value is a miscibility measure that can be used to represent the interaction between two polymers. The low k value (<1) often indicates weak interaction between two polymers. From the experimental results, all T_g values are below weight average. On the basis of the lower k values and negative T_g deviation from the weight average, although the blend system is miscible, no stronger interaction occurs between DL-PLA and PMMA.

Figure 3 outlines the thermograms obtained in the second DSC heating run for DL-PLA/PMMA
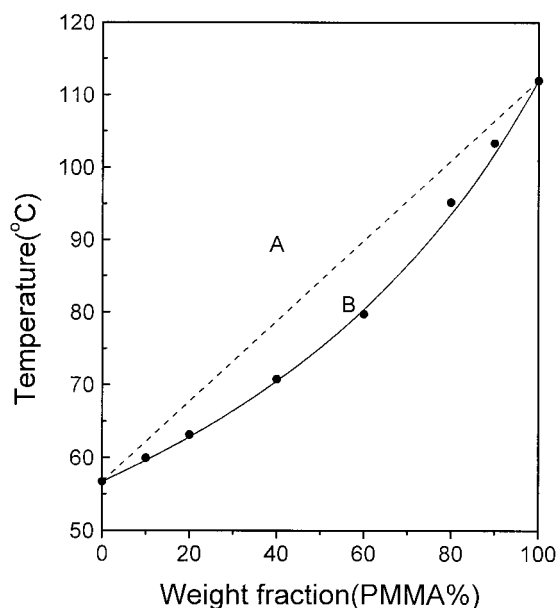

Figure 2. T_g versus composition in solution/precipitation DL-PLA/PMMA blends. (●) Experimental results. Line A corresponds to the weight average, and line B is drawn according to eq 1 with $k = 0.5$.

solution-casting blends with different composi-
tions. Two isolated T_g series exist that correspond
to the DL-PLA-rich phase and the PMMA-rich
phase, respectively, suggesting that DL-PLA/
PMMA blends prepared by solution-cast film are
immiscible. For an immiscible blend showing par-
tial miscibility, the T_g value of each component
phase should be affected by the other one, and
they should be shifted toward each other. Such
behavior is due to some degree of molecular mix-
ing at the interface between the two polymeric
phases. Figure 4 portrays the composition depen-
dence of T_g for DL-PLA/PMMA. The T_g values of
the DL-PLA-rich phase increase slowly with an
increasing PMMA content in the blends, suggest-
ing the presence of PMMA in the DL-PLA phase.
The T_g values of the PMMA-rich phase relevant
to the blend compositions are very particular. The
blend with a higher DL-PLA content does not
indicate a lower T_g value as compared with those
of lower DL-PLA content blends. Its lowest value
seems to exist when the DL-PLA content is 10%
in the blend.

In the case of partial miscibility, Fox's law
could be used to determine the composition of the
phases.[24] Because two T_g values were discovered
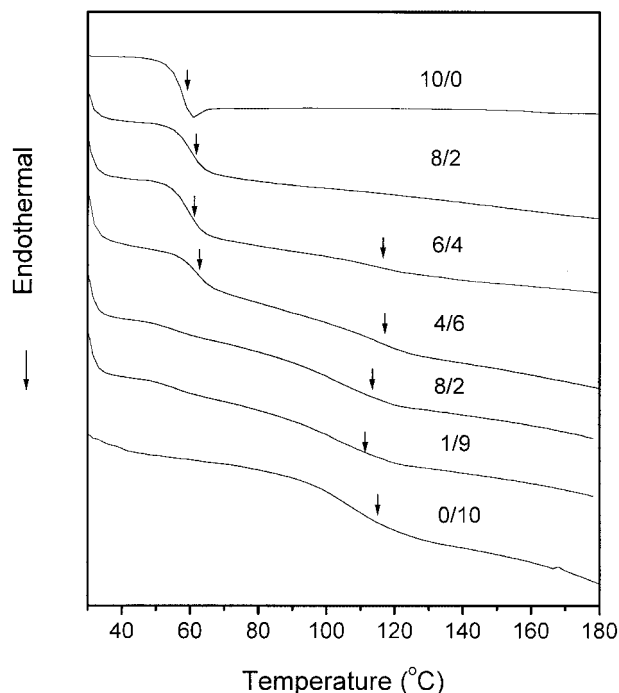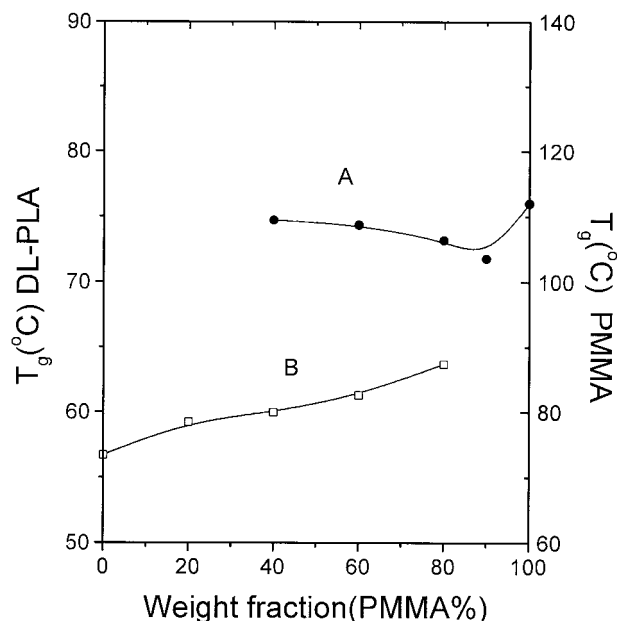in the DL-PLA/PMMA blends, DL-PLA-rich

Figure 4. T_g versus compositions in solution-cast DL-PLA/PMMA blends. Lines A and B correspond to the PMMA-rich and DL-PLA-rich phases, respectively.

phases and PMMA-rich phases were assumed.
The compositions of these two phases are com-
puted in Fox's equation

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \qquad (2)$$

where T_g, T_{g2}, T_{g2}, W_1, and W_2 have the same
meaning as before. Equation 2 can be rearranged
as

$$W_1 = T_{g1}(T_{g2} - T_g)/[T_g(T_{g2} - T_{g1})] \qquad (3)$$

$$W_2 = T_{g2}(T_g - T_{g1})/[T_g(T_{g2} - T_{g1})] \qquad (4)$$

Applying eqs 3 and 4 to the T_g values of DL-PLA/
PMMA blends, the weight fractions of DL-PLA in
the DL-PLA-rich phase (W_1) and PMMA in the
PMMA-rich phase (W_2) were calculated. The re-
sults are listed in Table 1. The blends with DL-
PLA compositions ranged from 80 to 20%; the
blends behave similarly and separate into a DL-
PLA-rich phase, with DL-PLA compositions of
86.7–76.8%. For the DL-PLA/PMMA blends with
a high DL-PLA concentration (>80%), the blends
are miscible. Similarly, when blends with PMMA
compositions range from 80 to 40%, PMMA-rich
phases can be observed with PMMA compositions
of 94.3–97.2%. However, when PMMA concentra-

Figure 3. DSC thermograms in the second heating runs for solution-cast DL-PLA/PMMA blends with compositions from 100:0 to 0:100.

tions are higher than 90%, the DL-PLA domain may be segmentally dispersed in the continuous PMMA phase; as a result, a miscible blend is observed.

The question is why DL-PL/PMMA blends prepared by different methods present totally different thermal-analysis results. In polymer–polymer mixtures, the entropy of mixing is very small because of the small number of molecules involved. Miscibility generally requires some favorable interactions such as hydrogen bonding, donor–acceptor interaction, charge transfer, and so forth, resulting in a negative exchange interaction contribution to the free energy of mixing. However, for the DL-PLA/PMMA blends, no such strong specific interaction exists; only some kind of weak dipolar interaction could take place owing to the chemical structure of two polymers.

The differential solubility parameter ($\Delta\delta$), defined as the difference between the solubility parameters of the components of the blend, is often used to estimate the miscibility of two components.[25] According to this concept, if two materials are thermodynamically miscible, the critical difference $\Delta\delta$ should not exceed 0.5. Because the value of δ for DL-PLA is 10.1 and the value for PMMA is 9.35 (calculated with the group contribution method), DL-PLA/PMMA should not be miscible. This seems to be congruence with the thermal behavior of solution-cast blends. However, experimental evidence suggests that the DL-PLA/PMMA solution/precipitation blend is apparently miscible. Maybe these homogeneous blends do not attain their equilibrium state.

Annealing experiment of polymer blends can be used to examine polymer–polymer phase behavior. After annealing an immiscible blend for a long time above T_g, each polymer relaxes toward its equilibrium. Figure 5 displays the DSC ther-
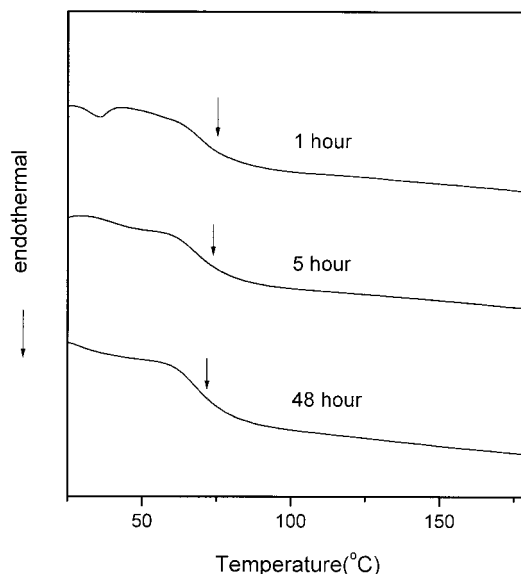

Figure 5. DSC thermograms of solution/precipitation DL-PLA/PMMA blends (60/40) annealed at 115 °C for different times.

mograms of DL-PLA/PMMA 60/40 annealed at 115 °C for different times. Only one T_g is observed even when annealed for 48 h, indicating that the blend is still miscible. Considering that the differential solubility parameter ($\Delta\delta$) of DL-PLA and PMMA is 0.66, which is close to the critical value of miscibility, if some adequate mixing treatments are applied, the miscible blend could be obtained. The solution-casting samples are two-phase segregated. This is because chloroform is a better solvent for PMMA (δ = 9.3); with evaporation of solvent, DL-PLA precipitates first and then a two-phase blend is formed.

PLLA/PMMA Blends

The results of the DSC measurements for PLLA/PMMA solution/precipitation blends are shown in Figures 6–8. Figure 5 displays melting thermograms obtained in the first heating runs for samples with compositions of 100:0–30:70. In contrast with the thermal behavior of DL-PLA/PMMA blends, the blends exhibit a multiphase structure. PLLA is of good crystallinity, and the crystallization tendency of PLLA acts as a driving force for phase segregation and the formation of a segregated crystalline microdomain. In Figure 6, the pure PLLA sample gives a relatively sharp melting endotherm with a peak maximum at 160 °C. With an increasing PMMA content in the

Table 1. Phase Composition of DL-PLA/PMMA Blends

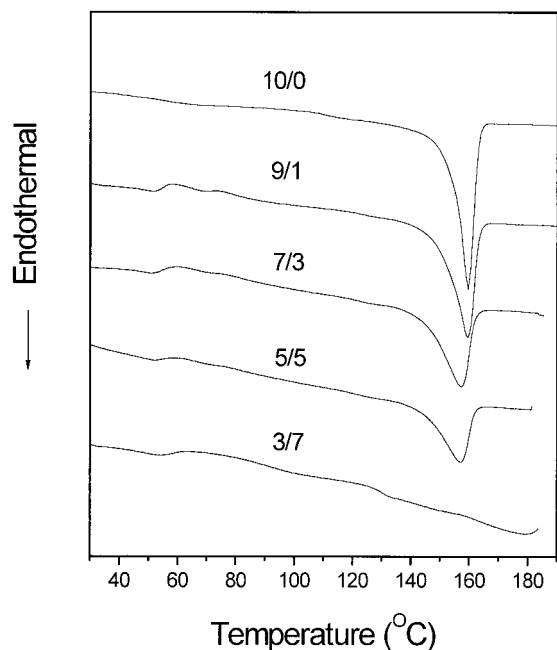| DL-PLA/PMMA (w_1/w_2)	DL-PLA-Rich Phase $W_1\%$	PMMA-Rich Phase $W_2\%$
10/0	100	—
9/1	91.5	
8/2	86.6	—
6/4	83.6	97.2
4/6	80.6	96.7
2/8	76.8	94.3
1/9	—	91.8
0/10	—	100

Figure 6. DSC thermograms in the first heating runs for solution/precipitation PLLA/PMMA blends with compositions from 100:0 to 30:70.

Figure 7. DSC thermograms in the second heating runs for solution/precipitation PLLA/PMMA blends with compositions from 100:0 to 0:100.

blends, the endothermic peak tends to lose its prominence with an accompanying systematic depression in the T_m values. At a blend composition of 30:70, it was difficult to detect the melting endotherm with DSC. The apparent disproportionate reduction in the magnitude of the endothermic peak area corresponds to a rapid decrease of the degree of crystallinity of PLLA in the blends.

Table 2 summarizes the DSC measurement results of blends of PLLA/PMMA in the first and second heating runs. The degrees of crystallinity of L-PLA are calculated by the following equation:

$$X_c = \Delta H_f/(\Delta H_f^o W) \qquad (5)$$

where ΔH_f is the apparent enthalpy (indicated in the DSC thermograms as melting enthalpy per gram of blends) of fusion corresponding to the component, W is the weight fraction of the weight fraction of component, and ΔH_f^o is the enthalpy of fusion per gram of component in its completely crystalline state (93 J/g for PLLA[26]). The data in Table 2 suggest that the crystalline degree of PLLA decreases with an increasing concentration of PMMA.

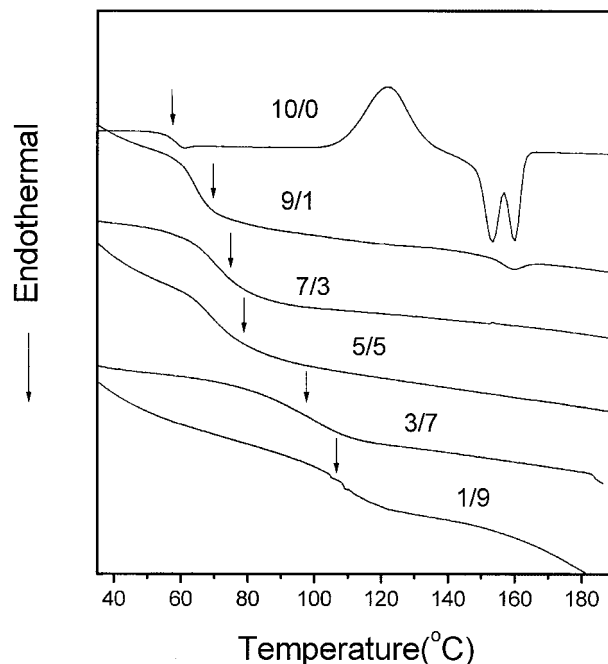T_m of the crystalline component in a blend depends on both morphological and thermodynamic factors. On blending semicrystalline polymers with other polymers, a decrease in T_m is evidence of some degree of miscibility between the components of a blend. As shown in Table 2, the T_m
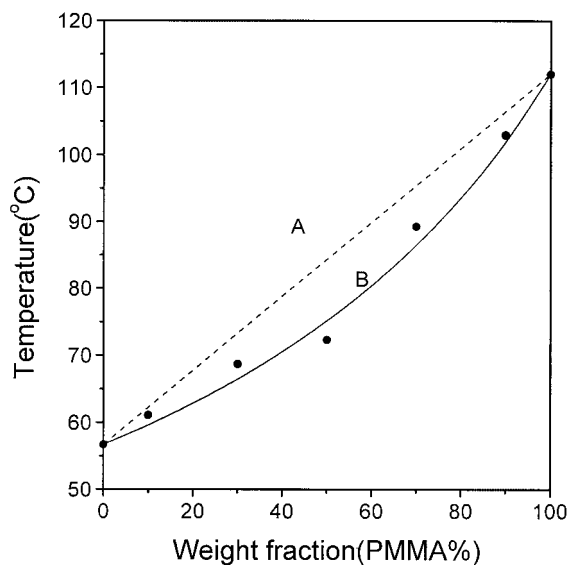

Figure 8. T_g versus composition in solution/precipitation PLLA/PMMA blends. (●) Experimental results. Line A corresponds to the weight average, and line B is drawn according to eq 1 with $k = 0.5$.

Table 2.   DSC Measurement Results of PLLA and PMMA Blends in the First and Second Heating Runs

PLLA/PM MA (w/w)	First Heating Run			Second Heating Run				
	T_m (°C)	ΔH_f (J/g)	X_c (%)	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%)
10/0	160	39.6	42.5	56	122	160	39.2	42.2
9/1	159	32.7	35.2	61	—	159	5.2	6.3
7/3	157	18.3	28.3	68	—	—	—	—
5/5	156	10.8	23.4	72	—	—	—	—
3/7	—	—	—	92	—	—	—	—
1/9	—	—	—	104	—	—	—	—

values of the PLLA phase were slightly decreased with an increasing PMMA content. This T_m composition dependence phenomenon indicates that there is some interaction between PLLA and PMMA.

More direct proof of polymer miscibility in blends can be obtained by observing the behavior of the T_g with composition. Figure 7 depicts the DSC thermograms obtained in the second heating runs for samples with compositions of 100:0–30:70. The DSC thermograms of the second heating runs are completely different from those of the first heating runs. The PLA melting point disappears, only one T_g is observed, and its evolution can be described by the Gordon–Taylor law indicating that PLLA and PMMA are miscible in the blends. This result suggests that there is an effect of different DSC runs on the miscibility degree of the polymers. Once the crystalline phase has been melted, high temperature allows two components mixing together.

From the DSC thermogram of pure PLLA in Figure 6, we also see an exothermic peak at about 122 °C; this peak is assigned to the cold crystallization of PLLA. Double melting peaks appear at 155 and 160 °C in a pure PLLA sample, suggesting that two populations of crystals with different lamella thicknesses exist. The lower-temperature peak is due to the melting of less thick crystals than crystals corresponding to the high temperature. According to high-temperature X-ray diffraction measurement performed up to 180 °C, the diffraction pattern of the sample did not change up to T_m; therefore, phase transition did not occur.[27]

One phenomenon is that the melting peaks of PLLA in the second heating runs decrease drastically with an increasing PMMA content. In fact, only when PLLA contents in the blend are higher than 90%, it is possible to observe the crystallization and melting of PLLA crystals in the second run, indicating that the crystalline kinetics of PLLA was highly restricted by amorphous PMMA. This phenomenon could be considered as a typical example of a miscible blend in the amorphous state with a T_g higher than that of the crystalline compounds. In Figure 6, PMMA prevents the crystallization in such a way that only when the content of PLLA in blends is higher than 90%, some degree of crystallization could take place, similar to that obtained in the first run with 30% PLLA.

In Figure 8, the T_g observed in the second heating run versus composition data on PLLA/PMMA blends are replotted and compared with the simple prediction of the Gordon–Taylor equation. Where the solid line corresponds to the Gordon–Taylor prediction for this system, the dashed line represents the weight average and the solid circles are the experimental results. The behavior of the PLLA/PMMA blends resemble that of DL-PLA/PMMA blends. When applying eq 1 to the experimental results, a value of $K = 0.5$ was obtained. The figure agrees with the observed and calculated values. This suggests that there is no more favorable trend of DL-PLA to form miscible blends with PMMA than PLLA does when PLLA is in the amorphous state.

CONCLUSIONS

Blends prepared by different methods appear to exhibit different thermal behavior. On the basis of the DSC results, in solution/precipitation blends, DL-PLA is miscible with PMMA because a single T_g suited between the T_g's of the two pure components at every composition is observed. In

contrast with the behavior of solution/precipitation blends, two isolated T_g's appear in DL-PLA/PMMA solution-casting film blends, suggesting two segregated phases in the blend system, although evidence shows that two components are partially miscible.

In the PLLA/PMMA blend, the crystallization tendency of PLLA acts as the driving force for phase separation. However, the crystallization of PLLA was greatly restricted by amorphous PMMA; this is a typical example of a miscible blend in the amorphous state with a T_g higher than that of semicrystallization components. Evidence shows there is an effect of different DSC runs on the miscibility degree of the polymers. Once the crystalline phase has been melted, high temperature allows two components mixing together. In addition, the T_g composition relationship for both DL-PLA/PMMA and PLLA/PMMA miscible systems obeys the Gordon–Taylor equation. Experimental results suggested that there is no more favorable tendency of DL-PLA to form miscible blends with PMMA than PLLA does when PLLA is in the amorphous state.

REFERENCES AND NOTES

1. Zhu, K. L.; Xiangzhou, L.; Shilin, Y. J Appl Polym Sci 1990, 39, 1.
2. Bergsma, J. E.; Bos, R. R. M.; Rozema, F. R.; Jong, W. D.; Boering, G. J Mater Sci: Mater Med 1996, 7, 1.
3. Fambri, L.; Pegoretti, A.; Fenner, R.; Incardona, S. D.; Migliarisi, C. Polymer 1997, 38, 79.
4. Bergsma, J. E.; Rozema, F. R.; Bos, R. M.; Boering, G.; Bruijn, W. C.; Pennings, A. J Biomaterials 1995, 16, 247.
5. Han, D. K.; Hubbell, J. A. Macromolecules 1996, 29, 5233.
6. Deng, X. M.; Xiong, C. D.; Cheng, L. M.; Huang, H. H.; Xu, R. P. J Appl Polym Sci 1995, 55, 1193.
7. Cai, Q.; Bei, J. Z.; Wang, S. G. Polym Degrad Stab 2001, 71, 243.
8. Cai, Q.; Bei, J. Z.; Wang, S. G. J Biomater Sci Polym Ed 2000, 11, 273.
9. Barrera, D. A.; Zylstra, E.; Lansbury, P. T.; Langer, R. Macromolecules 1995, 28, 425.
10. Vert, M.; Li, S. M.; Spenlehauers, G.; Guerin, P. J Mater Sci: Mater Med 1992, 3, 432.
11. Holland, S. J.; Tighe, B. J.; Gould, P. L. J Controlled Release 1986, 4, 155.
12. Iannace, S.; Ambrosio, L.; Huang, S. J.; Nicolais, L. J Appl Polym Sci 1994, 54, 1525.
13. Blumm, E.; Owen, A. J. Polymer 1995, 36, 4077.
14. Youngs, H.; Cohen, D. Eur Polym J 1988, 24, 765.
15. Ynag, J. M.; Chen, H. L.; You, J. W.; Hwang, J. C. Polym J 1997, 29, 657.
16. Nakafuku, C.; Sakoda, M. Polym J 1993, 25, 909.
17. Cha, Y.; Pitt, C. G. Biomaterials 1990, 11, 108.
18. Hiljanen-Vaini, M.; Varpomaa, P.; Seppala, J.; Tormala, P. Macromol Chem Phys 1996, 197, 1503.
19. Gajria, A. M.; Dave, V.; Gross, R. A.; McCarthy, S. P. Polymer 1996, 37, 437.
20. Dollinger, H. M.; Sawan, S. P. Polym Prepr (Am Chem Soc Div Polym Chem) 1990, 31, 429.
21. Shuai, X.; He, Y.; Asakawa, N.; Inoue, Y. J Appl Polym Sci 2001, 81, 762.
22. Preparative Methods of Polymer Chemistry; Sorenson, W. R.; Camplell, T. M., Eds.; Wiley: New York, 1961; pp 235–247.
23. Gordon, M.; Taylor, J. S. J Appl Chem 1952, 2, 493.
24. Fox, T. G. J Appl Bull Am Phys Soc 1965, 1, 123.
25. Coleman, M. M.; Graf, J. F.; Painter, P. C. Specific Interactions and the Miscibility of Polymer Blends; Technomic: Lancaster, PA, 1991; pp 49–153.
26. Fischer, E. W.; Sterzed, H. J.; Wegner, G. Colloid Polym Sci 1973, 251, 980.
27. Chitoshi, N. Polym J 1996, 28, 568.
28. Eguiburu, J. L.; Iruin, J. J.; Fernander-Berredi, M. J.; San Roman, J. Polymer 1998, 39, 6891.
29. Zhang, L.; Goh, S. H.; Lee, S. Y. Polymer 1998, 39, 4841.