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# Miscibility and Phase Structure of Binary Blends of Poly(L-lactide) and Poly(vinyl alcohol)

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**ABSTRACT:** Blend films of poly(L-lactide) (PLLA) and poly(vinyl alcohol) (PVA) were obtained by evaporation of hexafluoroisopropanol solutions of both components. The component interaction, crystallization behavior, and miscibility of these blends were studied by solid-state NMR and other conventional methods, such as Fourier transform infrared (FTIR) spectra, differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD). The existence of two series of isolated and constant glass-transition temperatures ( $T_g$ 's) independent of the blend composition indicates that PLLA and PVA are immiscible in the amorphous region. However, the DSC data still demonstrates that some degree of compatibility related to blend composition exists in both PLLA/atactic-PVA (a-PVA) and PLLA/syndiotactic-PVA (s-PVA) blend systems. Furthermore, the formation of interpolymer hydrogen bonding in the amorphous region, which is regarded as the driving force leading to some degree of component compatibility in these immiscible systems, is confirmed by FTIR and further analyzed by  $^{13}\text{C}$  solid-state NMR analyses, especially for the blends with low PLLA contents. Although the crystallization kinetics of one component (especially PVA) were affected by another component, WAXD measurement shows that these blends still possess two isolated crystalline PLLA and PVA phases other than the so-called cocrystalline phase.  $^{13}\text{C}$  solid-state NMR analysis excludes the interpolymer hydrogen bonding in the crystalline region. The mechanical properties (tensile strength and elongation at break) of blend films are consistent with the immiscible but somewhat compatible nature of these blends. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 762–772, 2001

**Key words:** biodegradable blends; miscibility; crystallization; mechanical properties; poly(vinyl alcohol); poly(L-lactide)

## INTRODUCTION

Traditional plastics are commonly made from polyolefin or other nondegradable polymers, and large-scale use of these polymers has already re-

sulted in very serious environmental problems all over the world.<sup>1–3</sup> Therefore, development of biodegradable polymeric materials replacing the traditional and nondegradable polymers is of very great importance. In addition to their being used as environmentally friendly materials, biodegradable polymers are believed to be suitable for agriculture (as mulch film), biomedical implants and controlled drug release, and absorbable surgery sutures. The increasing research interest in biodegradable polymers over the past two decades has led to the availability of a large variety of novel polymers with claims of biodegradability.<sup>4</sup>

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Current commercial biodegradable polymers are predominantly limited to aliphatic polyesters, polyether, poly(vinyl alcohol), and native polysaccharides.<sup>5,6</sup> Among these, the most important biodegradable polymers typically are aliphatic polyesters including, for example, poly(L-lactide) (PLLA), poly(glycolide), poly( $\epsilon$ -caprolactone) (PCL), poly(3-hydroxy butyrate) (PHB), and poly(butylene succinate), whose susceptibility to hydrolytic or enzymatic degradation makes these polyesters suitable as biodegradable materials. According to the literature reports, these polyesters were prepared by biosynthesis<sup>7,8</sup> and chemosynthesis,<sup>9–11</sup> such as polycondensation and either ring-opening anionic or coordination polymerization of various lactones. Although many investigations have been carried out on the properties and applications of these polyesters, many properties of these polymers still have been found to fall short of the required properties for many practical applications.<sup>12</sup>

The properties of these polymers might be improved through several approaches including blending<sup>13–16</sup> and copolymerization.<sup>17–19</sup> Blending is a relatively simple and fast way compared to copolymer synthesis. Up to now many blends, containing at least one of three kinds of polyesters, PLLA, PCL, and either isotactic-PHB (i-PHB) or atactic-PHB (a-PHB), have been reported. Among these blends, only some of them are completely biodegradable systems consisting of all-degradable components, for example, the following binary blends: i-PHB and PLLA,<sup>20</sup> i-PHB and PCL,<sup>21,22</sup> i-PHB and PVA,<sup>23</sup> i-PHB and a-PHB,<sup>24</sup> i-PHB and biosynthesized poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (known as PHBV),<sup>25–29</sup> PHBV and PCL,<sup>30</sup> PCL and PVA,<sup>31</sup> i-PHB and poly(ethylene oxide) (PEO),<sup>32,33</sup> PLLA and PEO,<sup>34</sup> and so forth. However, many other blends belong to partially biodegradable systems, comprised of one of these three kinds of polyesters and at least one nonbiodegradable component, such as poly(vinyl acetate) (PVAc),<sup>21,35</sup> poly(methyl methacrylate) (PMMA),<sup>36</sup> and poly(*p*-vinylphenol) (PVPh).<sup>37</sup>

Admittedly, miscibility of components in blends should be of great concern because it is usually a key factor in determining the properties of the blends. On one hand, the high interfacial energy between two immiscible phases is always one cause for bad mechanical properties of the polymer blends.<sup>38</sup> On the other hand, it has been demonstrated that, for both completely<sup>14</sup> and partially<sup>39</sup> degradable blends, the biodegradation be-

havior of a blend is affected not only by the biodegradability of each component but also by the miscibility of blend components. Taking the biodegradation and miscibility jointly into account, it is of very great importance to develop some miscible and completely biodegradable polymer blends that possess optimized comprehensive properties compared to those of an individual polymer. However, the number of miscible and completely biodegradable polymer pairs based on polyesters is quite limited.

PVA is a favorite polymer frequently chosen in research of biodegradable polymer blends.<sup>14,31,35,40</sup> PVA is biodegradable, biocompatible, inexpensive compared to costs of polyesters, and both hydrophilic and highly flexible, in spite of the high crystalline structure. Moreover, PVA theoretically has the potential of forming hydrogen bonding with the oxygen atom of the ester group. Taking advantage of this specific interaction that may exist in the blends, miscibility or partial miscibility might be achieved between polyester and PVA. Consequently, the flexibility and hydrophilicity of those brittle and hydrophobic polyesters may be improved through blending with PVA.

The binary blends of i-PHB and PVA with different degrees of tacticity were intensively studied by Inoue et al.<sup>14,41,42</sup> It was found that i-PHB and PVA are partially miscible<sup>14</sup> in the amorphous region, and the hydrogen bonding between PVA and i-PHB in the amorphous phase, revealed by solid-state <sup>13</sup>C-NMR, was proposed to be the driving force leading to compatibility between the two components. The crystallization of the minor component in the blends was found to be much suppressed, and the biodegradation of the blends was accelerated as a result of the reduced crystallinity in the blends.

In this investigation, the blends of PLLA with PVA, which to our knowledge have not been reported on so far, were studied concerning both the miscibility of two components and the thermal/mechanical properties of these blends. It was anticipated that the blending of PLLA and PVA might be an effective way of obtaining completely biodegradable PLLA-based materials with improved flexibility compared to that of PLLA.

## EXPERIMENTAL

### Preparation of Blend Films of PLLA and PVA

Atactic PVA (a-PVA: degree of polymerization 2000; degree of saponification 99%; triad tacticity

22% mm, 50% mr, 28% rr) was purchased from Nacalai Tesque (Tokyo, Japan). Syndiotactic PVA (s-PVA: degree of polymerization 1690; degree of saponification 99%; triad tacticity 14% mm, 49% mr, and 37% rr) was kindly donated by Kuraray Co. (Kurashita, Japan). PLLA ( $M_n = 1.33 \times 10^5$ ;  $M_w/M_n = 1.7$ ) was kindly donated by Mitsui Chemicals (Tokyo, Japan).

PLLA and PVA (a- or s-PVA) were codissolved in hexafluoroisopropanol (HFIP), after which the blend solutions [concentration  $\sim 2.5\%$  (w/v)] were cast onto Teflon dishes. The solvent was allowed to evaporate at room temperature for 2 weeks and films were subsequently dried *in vacuo* for 3 weeks at 60°C.

### Instrumentation

FTIR spectra were recorded at room temperature on a Perkin–Elmer Spectrum 2000 spectrometer (Perkin–Elmer Japan, Yokohama, Japan) at a resolution of  $2\text{ cm}^{-1}$ . All sample films, prepared for FTIR measurement by directly casting the sample solutions onto silicon wafers, were thin enough so that the Beer–Lambert law was obeyed within an absorbance range of the measurement.

A Seiko DSC 220U differential scanning calorimeter (Seiko Instruments, Tokyo, Japan), calibrated with indium, was used to analyze the thermal properties of the blends. The sample was heated from a low temperature (established in accordance with sample, e.g.,  $-100^\circ\text{C}$ ) to a high temperature (established in accordance with sample, e.g.,  $250^\circ\text{C}$ ) at a heating rate of  $20^\circ\text{C}/\text{min}$ . It was annealed for 1 min and quenched to a low temperature (established in accordance with sample, e.g.,  $-120^\circ\text{C}$ ). The sample was subsequently heated again to a high temperature (established in accordance with sample, e.g.,  $250^\circ\text{C}$ ) at a heating rate of  $10^\circ\text{C}/\text{min}$ . The thermograms of the first and the second DSC heating runs were both recorded. The cold crystallization temperatures ( $T_{cc}$ 's) and the melting temperatures ( $T_m$ 's) were taken as the top values of crystallization and melting endotherms, respectively. The enthalpies of fusion ( $\Delta H_f$ 's) were calculated from the integral of endothermic melting peaks in DSC curves. The glass-transition temperatures ( $T_g$ 's) in the second-heating run DSC curves were taken as indicated by DDSC (differentiation of DSC) peak.

The crystallization behavior of PLLA/PVA blends was studied by wide-angle X-ray diffraction (WAXD) measurement in addition to DSC measurement. WAXD patterns were recorded on

Rigaku Ru-200 (50 kV, 180 mA) and Rigaku IP R-Axis-DS3 systems (Rigaku Co., Tokyo, Japan) using nickel-filtered  $\text{CuK}_\alpha$  radiation in a  $2\theta$  range of  $5\text{--}40^\circ$ .

Solid-state  $^{13}\text{C}$ -NMR spectra were measured at 67.9 MHz on a JEOL GSX-270 NMR (JEOL, Tokyo, Japan) or at 100 MHz on a Varian Unity 400 spectrometer (Varian Associates, Palo Alto, CA) equipped with a cross-polarization/magic angle spinning (CPMAS) accessory.  $^{13}\text{C}$ -CP MAS NMR 67.9-MHz spectra were measured with a contact time of 2 ms, a 5-s pulse repetition, a spectral width of 40 kHz, 1 K data points (zero-filled to 8 K), and 1024–2048 accumulations. All spectra were acquired with high-power dipolar decoupling (DD) of 50 kHz and MAS at 2.6–3.0 kHz.  $^{13}\text{C}$  chemical shifts were calibrated by the methyl resonance of solid hexamethylbenzene (17.36 ppm relative to tetramethylsilane). Pulse saturation transfer (PST) MAS NMR spectra (100 MHz) were also measured to investigate especially the interpolymer interaction in the amorphous region of the blends. Saturation of  $^1\text{H}$  magnetization was carried out with 400  $90^\circ$  pulses (the pulse interval was 10 ms). The  $^{13}\text{C}$  signal was observed with a  $45^\circ$  pulse at 5-s pulse-repetition time and 2048 accumulations.

Measurements on mechanical properties of specimens were performed at room temperature with a Shimadzu EZ Test machine (Shimadzu, Kyoto, Japan) at a cross-head speed of 3 mm/min. Each value reported is an average of three specimens.

## RESULTS AND DISCUSSION

The results of DSC measurements for a-PVA/PLLA and s-PVA/PLLA blends are listed in Tables I and II, respectively. Figures 1 and 2 show the thermograms obtained in the second DSC heating run for a-PVA/PLLA and s-PVA/PLLA blends with different compositions.

It is well known that the glass-transition temperature ( $T_g$ ) of a polymer blend is one of the most important criteria for the miscibility of components. The definition for miscible and partially miscible blends has been well established.<sup>43</sup> As far as the binary blends are concerned, if components are miscible at the level of 5–10 nm in the main chain, usually only one  $T_g$  will appear in DSC thermograms at an intermediate temperature compared to that of the  $T_g$  value of each pure polymer. This solitary  $T_g$  of blend should obey the

**Table I DSC Measurement Results of Blends of a-PVA and PLLA**

Composition <sup>a</sup> PLLA/a-PVA	PLLA <sup>b</sup>					a-PVA <sup>b</sup>			
	$T_{cc}^{2nd}$ (°C)	$T_g^{2nd}$ (°C)	$T_m^{1st}$ (°C)	$\Delta H_f^{1st}$ (J/g <sub>PLLA</sub> )	$\chi_c$ (%)	$T_g^{2nd}$ (°C)	$T_m^{1st}$ (°C)	$\Delta H_f^{1st}$ (J/g <sub>a-PVA</sub> )	$\chi_c$ (%)
100/0	132.2	61.4	164.4	29.7038	31.94				
90/10	126.7	60.4	165.0	29.9708	32.23	nd <sup>c</sup>	217.2	39.7639	26.16
70/30	121.4	59.6	164.0	28.4771	30.62	74.2	218.2	32.7176	21.52
50/50	128.3	60.8	155.5	19.1663	20.61	76.5	211.1	39.0244	25.67
30/70	nd	59.4	158.0	14.4374	15.52	76.9	207.6	41.3011	27.17
10/90	nd	nd	nd			74.9	205.1	46.9174	30.87
0/100						80.3	224.5	51.1504	33.65

<sup>a</sup> Indicates weight ratio.<sup>b</sup> 1st = first-heating run in DSC measurement; 2nd = second-heating run in DSC measurement.<sup>c</sup> nd = not detected.

Fox equation describing the relationship between the  $T_g$  value, of the blend and its composition, as well as  $T_g$  values of components in the pure state.<sup>43</sup> Even if two components are only partially miscible, the  $T_g$  value of each component phase should be affected by the other one, and it is usually composition dependent.

In the DSC thermograms of blends of PLLA with a- and s-PVA recorded during the second-heating run, there obviously exist two isolated  $T_g$  series corresponding to the PLLA-rich phase and the PVA-rich phase, respectively. It is indicated by DDSC that the  $T_g$  values of the PVA-rich phase (especially in the a-PVA/PLLA blends) seem to be changed somewhat toward lower temperatures upon blending PVA with PLLA. However, these decreases of PVA  $T_g$  are not very convincing if we notice that the glass transition of the PVA-rich

phase in blend is obscure and quite wide. Therefore, we can hardly be sure of any composition-dependent change for each series of  $T_g$ 's. From these results and analyses, it is concluded that PLLA is immiscible, or at least not miscible, with a-PVA and s-PVA over the whole composition range investigated.

Tables I and II show the degrees of the crystallinity of a-PVA and PLLA calculated by the following equation:

$$\chi_c = \Delta H_f / (\Delta H_f^0 W)$$

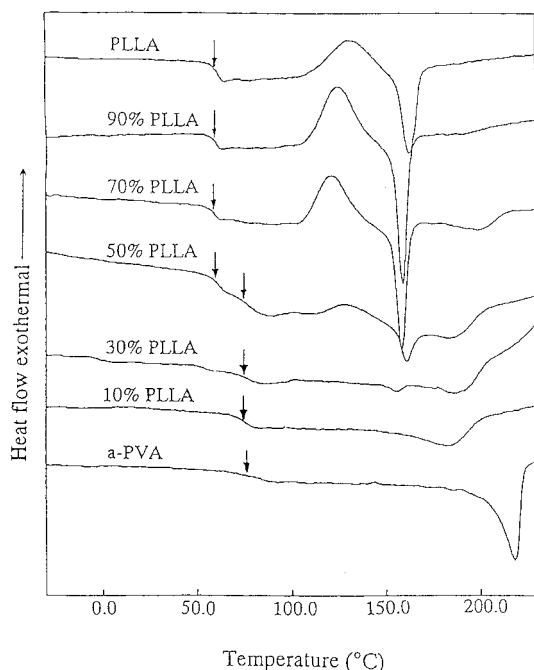
where  $\Delta H_f$  is the apparent enthalpy (indicated in DSC thermograms as melting enthalpy per gram of blend) of fusion corresponding to the component,  $W$  is the weight fraction of the component,

**Table II DSC Measurement Results of Blends of s-PVA and PLLA**

Composition <sup>a</sup> PLA/a-PVA	PLLA <sup>b</sup>					s-PVA <sup>b</sup>		
	$T_{cc}^{2nd}$ (°C)	$T_g^{2nd}$ (°C)	$T_m^{1st}$ (°C)	$\Delta H_f^{1st}$ (J/g <sub>PLLA</sub> )	$\chi_c$ (%)	$T_g^{2nd}$ (°C)	$T_m^{1st}$ (°C)	$\Delta H_f^{1st}$ (J/g <sub>s-PVA</sub> )
100/0	138.1	63.9	164.9	25.1012	26.99			
90/10	134.2	62.4	161.4	25.7437	27.68	nd <sup>c</sup>	246.7	69.8711
70/30	121.0	64.0	162.2	24.2465	26.07	nd	246.5	67.0463
50/50	130.2	62.3	157.6	15.7437	16.93	nd	243.4	74.6452
30/70	nd	59.8	nd			85.1	242.4	73.3201
10/90	nd	nd	nd			87.0	240.6	69.1066
0/100						88.5	248.4	66.3261

<sup>a</sup> Indicates weight ratio.<sup>b</sup> 1st = first-heating run in DSC measurement; 2nd = second-heating run in DSC measurement.<sup>c</sup> nd = not detected.





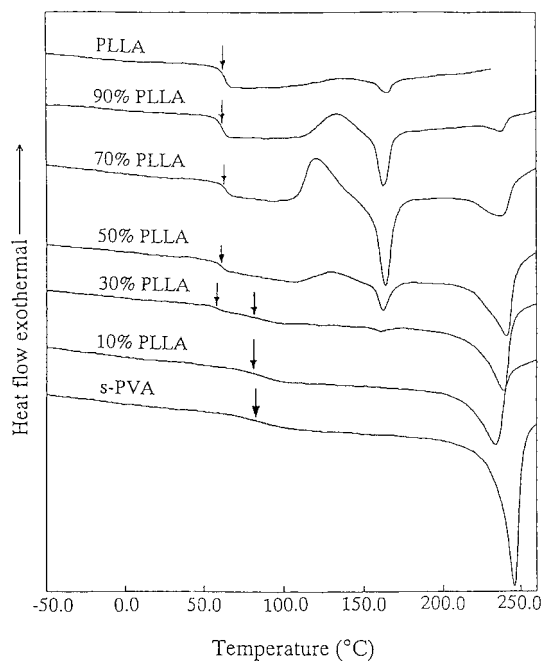
**Figure 1** Second heating run DSC thermograms of PLLA, a-PVA, and PLLA/a-PVA blends.

and  $\Delta H_f^0$  is the enthalpy of fusion per gram of the component in its completely crystalline state (93 J/g for PLLA<sup>44</sup> and 152 J/g for a-PVA<sup>31</sup>).

For polymer blends containing a crystalline component, the variations in values of  $T_m$ ,  $T_{cc}$ , and  $\chi_c$  are usually assigned to the interactions between components.<sup>20,37,41</sup> We concluded from the  $T_g$  measurements that PLLA and PVA (a-PVA and s-PVA) are immiscible in the amorphous region of blends prepared in the present research. However, there is still some obvious evidence that indicates interactions between PLLA and PVA. For solution-cast films, the melting enthalpy corresponding to the s-PVA phase in various s-PVA/PLLA blends is quite constant and may be regarded as composition independent; in contrast, slight decreases in the crystallinity, corresponding to the a-PVA phase in the PLLA/a-PVA blends, were detected. Moreover, it seems that what really matters is the addition of PLLA (other than the amount of PLLA added in the blends), because there is no obvious difference in the  $\chi_c$  values corresponding to those of the a-PVA phase when the PLLA content increases from 10 to 90%. For both of the s-PVA/PLLA and a-PVA/PLLA blends, no manifest change depending on the composition may be detected in the  $\chi_c$  values of the PLLA phase when the PLLA content is high (more than 70%). In the case in which the blend

contains a relatively small fraction of PLLA (less than 30%), the melting endotherm of the PLLA phase becomes relatively weak. On one hand, this might indicate some depression of the PLLA crystallinity upon blending with a large amount of PVA but, on the other hand, makes it very difficult to calculate the accurate  $\chi_c$  value of the PLLA phase in these blends. Therefore, the  $\chi_c$  values of PLLA listed in Tables I and II may indicate that the crystallization of PLLA in the blends is somewhat affected by PVA. Such an implication, however, is not very reliable in evaluating the component interactions. Theoretically, the increase or decrease of  $T_{cc}$  changes of a component may indicate that the crystallization of this component becomes more difficult or easier, respectively, upon blending with another component.<sup>32</sup> As to the present PVA/PLLA blends, no significant composition-dependent change is detected in the  $T_{cc}$  values of the PLLA phase; thus, we can neither confirm nor exclude the component interaction based on  $T_{cc}$  values.

To sum up, we are reluctant to declare compatibility between PLLA and a-PVA or s-PVA based on the  $T_{cc}$  and  $\chi_c$  results; however, the  $T_m$  changes of components in the PVA/PLLA blends strongly suggest some degree of interaction between PLLA and PVA. It is known that  $T_m$  of the crystalline component in a blend depends on both morpho-



**Figure 2** Second heating run DSC thermograms of PLLA, s-PVA, and PLLA/s-PVA blends.

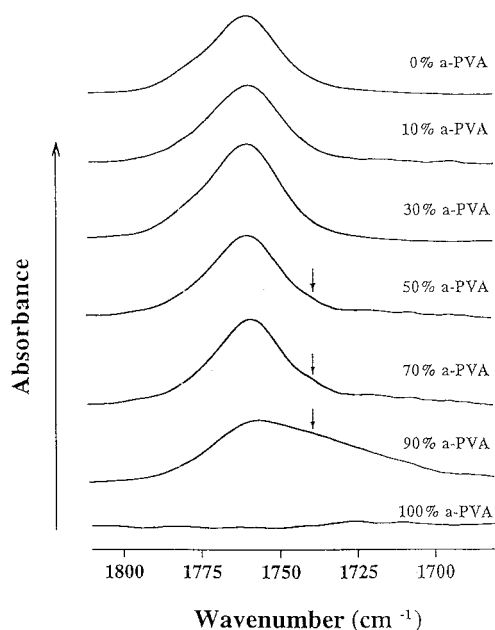
logical and thermodynamic factors. Considering that all blends are prepared under the same conditions in the present report, the  $T_m$  changes of components depending on composition could be seen as a result of interaction between components, referring to the literature reports.<sup>31,37</sup> As shown in Tables I and II, and Figures 1 and 2, the  $T_m$  values of the PLLA phase were slightly decreased with the increase of PVA content. The  $T_m$  changes of the PVA phase relevant to the blend compositions are very particular and much more significant ( $T_m$  depression more than 19°C for the 90% a-PVA-containing blend, obtained from the first DSC heating run) than those of the PLLA phase. It is noteworthy that the high content PLLA-containing blends do not show a large depression in  $T_m$  of PVA in comparison with those of low PLLA content. When the PLLA content increases to be higher than a critical value (e.g., 70%, as indicated by DSC measurement results), the blends, independent of composition, seem to have rather constant but slightly reduced  $T_m$  values of the PVA phase relative to those of pure PVA. This may indicate that increasing PLLA content does not help in the interpolymer interaction. In contrast, the  $T_m$  of the PVA phase is greatly composition dependent when the PLLA contents are lower than this critical value.

Let us tentatively forget the true immiscible nature of the studied blends and assume a miscible (of course, not true) or a partially miscible PVA/PLLA blend system. A general outcome imaginable should be that the lower the PLLA content, the less the depression in  $T_m$  of the PLLA phase, according to the outcome of other miscible or partially miscible blend systems reported in literature.<sup>37,41</sup> Interestingly, for the PLLA/PVA blends with PLLA contents less than the critical value mentioned earlier, an opposite result was observed in that, the lower the PLLA content, the larger the depression in  $T_m$  of the PLLA phase. Therefore, this result more or less supports the conclusion that PLLA is immiscible with both a-PVA and s-PVA, and indicates the special character of component-dependent interpolymer interaction. That is to say, in these blends with very low PLLA contents, the interaction between PVA and PLLA, unlike cases of normal immiscible or partially miscible blending, might become stronger with the decrease of PLLA content. Consequently the compatibility of PLLA with PVA was increased and the lamellae of PVA became thinner with the decrease of PLLA content. In these cases, it is very likely that the PLLA domains

were more finely dispersed in the continuous PVA phase as a result of the interpolymer interaction, which will be further confirmed.

Theoretically, PVA has the potential to form hydrogen bonds with carbonyl or amide-containing polymers. Because of this kind of interpolymer interaction of hydrogen bonding, PVA has been found to be miscible or partially miscible with some polymer counterparts.<sup>35,41</sup> FTIR spectroscopy is a very useful and convenient technique in research of polymer blends because it can provide information on interpolymer interaction. In the FTIR spectra of polymer blends especially, the functional groups involved in strong interpolymer hydrogen bonding often exhibit obvious shifts in their vibration frequencies.

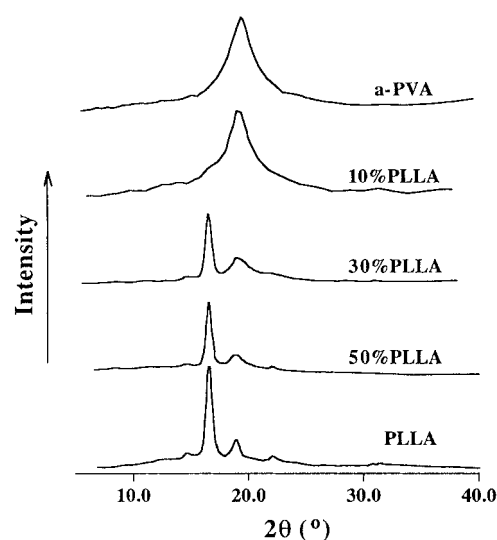
As to the PVA/PLLA blends investigated in the present study, it is difficult to detect the hydrogen bonding between PVA and PLLA from the hydroxyl bands of PVA because PVA is known to be a highly self-associated polymer, which, in the pure state, may form inter- and intramolecular hydrogen bonding. The results come out as expected, that is, no obvious change can be observed concerning the line shape and vibration frequency of the PVA hydroxyl bands. In contrast, the strong and distinct carbonyl absorption of PLLA around 1759  $\text{cm}^{-1}$  should be more indicative, and it is expected that this carbonyl absorption should shift to lower frequency if quite strong interpolymer hydrogen bonding exists in the blends. As shown in Figure 3, no detectable frequency shift of the PLLA carbonyl group can be observed upon blending with a-PVA when the a-PVA contents are less than 50%. This indicates that, within this composition range, there is no, or very weak if present, interpolymer hydrogen bonding in PLLA/a-PVA blends. When a-PVA contents are higher than 50%, a shoulder shifted to lower wavenumber is observed. This shoulder peak becomes more manifest and makes the characteristic carbonyl band broaden toward the low frequency in FTIR spectra with the increase of a-PVA content. This result clearly indicates the formation of new interpolymer hydrogen bonding in the blends with PVA contents higher than a certain value (e.g., 50% for a-PVA/PLLA blends). Moreover, a conclusion for blends within this composition range can be drawn: the higher the a-PVA content, the stronger the interpolymer hydrogen-bonding interactions. These composition-dependent behaviors of interpolymer hydrogen bonding support the DSC measurement results that were discussed earlier.



**Figure 3** FTIR spectra in the carbonyl stretching region for PLLA/a-PVA blends.

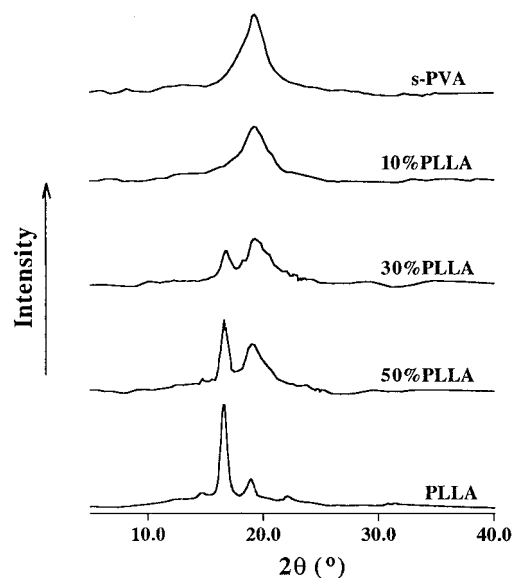
In comparison with a-PVA, s-PVA has a higher capacity to form intermolecular hydrogen bonding. Therefore, it was initially considered that the interpolymer hydrogen bonding might become stronger in the PLA/PVA blends if a-PVA was replaced by s-PVA. Previously, Yoshie et al.<sup>41</sup> found that the compatible composition range of s-PVA/i-PHB blend was wider than that of the a-PVA/i-PHB blend, the reason for which was supposed to be that s-PVA is apt to form hydrogen bonds with i-PHB. However, in the present research, no evidence in the FTIR measurement can support any possibly reinforced hydrogen bonding after a-PVA in blends was replaced by s-PVA. This result is nevertheless consistent with the results of the DSC measurement.

Concerning WAXD patterns, similar results were found between s-PVA/PLLA and a-PVA/PLLA blends (see Figs. 4 and 5), which means that the tacticity of PVA has either no or only a negligible effect on the crystallization of the studied blends. This result agrees well with the results from DSC and FTIR measurements, that no significant variation of interpolymer interaction depending on the tacticity of PVA was detected. From Figures 4 and 5, the blend containing 10% PLLA shows apparently the same diffraction pattern as that of the pure PVA specimen: no diffraction peak assigned to the crystalline PLLA phase is observed. Therefore, it should be reasonable to



**Figure 4** WAXD patterns of PLLA, a-PVA, and PLLA/a-PVA blends.

deduce the much-suppressed PLLA crystallization in the blend of this composition if, in the meanwhile, we consider the FTIR and DSC results that indicated higher compatibility in this composition (10% PLLA content) attributed to hydrogen bonding. In comparison with the pure PVA, the WAXD patterns of blends of two other compositions (30 and 50% PLLA content) appear to be the simple superimposition of the pure PLLA pattern onto that of PVA, except for the changed diffraction intensities. It is thus very



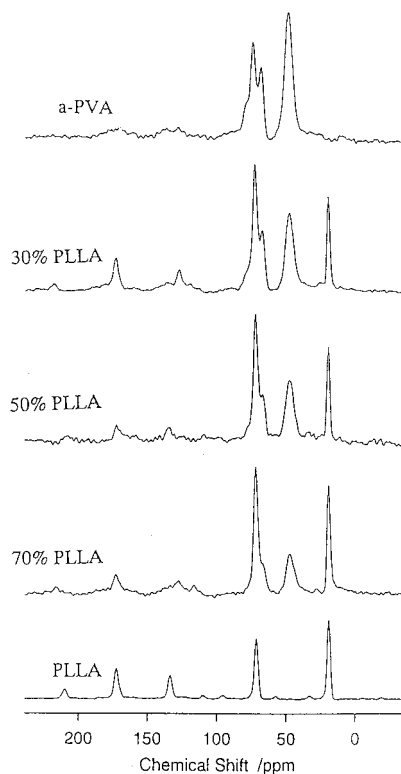
**Figure 5** WAXD patterns of PLLA, s-PVA, and PLLA/s-PVA blends.



clear that two isolated crystalline phases (corresponding to PLLA crystal and PVA crystal), other than the so-called cocrystallization phase, coexist in these blends. Two separate crystalline phases should individually possess the same crystal structure as that of either pure PLLA crystal or pure PVA crystal. Furthermore, there should be no interpolymer interaction existing in the crystalline phase of these blends, as will be further confirmed by  $^{13}\text{C}$ -CP MAS NMR measurement.

High-resolution solid-state  $^{13}\text{C}$ -NMR spectroscopy has been known to be a powerful tool in the investigation of interpolymer hydrogen bonding in polymer blends. In general,  $^{13}\text{C}$  nuclei participating in hydrogen bonds exhibit more or less a characteristic downfield shift.<sup>45,46</sup> To further identify the region in which forming of interpolymer hydrogen bonding occurs,  $^{13}\text{C}$ -CP MAS NMR and  $^{13}\text{C}$ -PST MAS NMR measurements were carried out in this research. Considering the similarity of the results obtained from DSC and FTIR measurements between a-PVA/PLLA and s-PVA/PLLA blends, only a-PVA/PLLA blends were selected for the high-resolution solid-state NMR measurements. It is known that  $^{13}\text{C}$ -CP MAS NMR and  $^{13}\text{C}$ -PST NMR spectra are sensitive to the crystalline phase and amorphous phase, respectively.<sup>41</sup> Therefore, these two kinds of solid-state NMR measurements will help us to further identify the region in which the interpolymer hydrogen bonding has been formed.

The  $^{13}\text{C}$ -CP MAS NMR spectra of pure PLLA and a-PVA, as well as of three blends with different compositions, are shown in Figure 6. A triplet ( $\sim 75$ , 70, and 65 ppm) of the methine carbon resonance of PVA, corresponding to two, one, and nonintramolecular hydrogen bonding structures,<sup>47</sup> is well resolved in the spectra of pure PVA and PVA/PLLA blends. If interpolymer hydrogen bonding was formed in these blends, we should observe the changes in chemical shifts of this triplet. In particular, the resonance of the shoulder at 65 ppm, attributed to the methine carbons linked to the hydroxy groups free of PVA intramolecular hydrogen bonding, should be shifted downfield as a result of the higher potential of forming interpolymer hydrogen bonds for these hydroxy groups free of PVA intramolecular hydrogen bonding. However, we should notice the overlap of resonances from PLLA and PVA at the region around 70 ppm in the  $^{13}\text{C}$ -CP MAS NMR spectra. It is better to discuss the interpolymer hydrogen bonding based on the  $^{13}\text{C}$  nuclei resonance of the PLLA carbonyl group, which is well

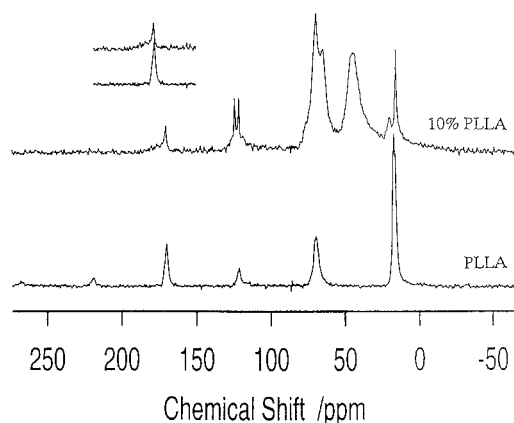


**Figure 6**  $^{13}\text{C}$ -CP MAS NMR spectra of PLLA, a-PVA, and their blends.

separated from the  $^{13}\text{C}$  resonances of PVA and is sensitive to the interpolymer hydrogen bonding.

From Figure 6, no change of the carbonyl chemical shift depending on composition is observed. The chemical shifts of carbonyl groups in various blends are all located at about 171 ppm, the same as that of pure PLLA. Because the  $^{13}\text{C}$ -CP MAS NMR spectra emphasize the resonances from  $^{13}\text{C}$  nuclei in the crystalline phase, two reasonable conclusions can be drawn, based on the  $^{13}\text{C}$ -CP MAS NMR result. First, interpolymer hydrogen bonding detected in FTIR measurement should not exist in the crystalline region of blends. Second, the fact that no detectable interpolymer hydrogen bonding exists in the crystalline phase further demonstrates that each component crystallizes following the crystalline phase separation; therefore, there is no mixed lamellar crystal containing both PVA and PLLA chains in the blends, as also demonstrated by WAXD measurement.

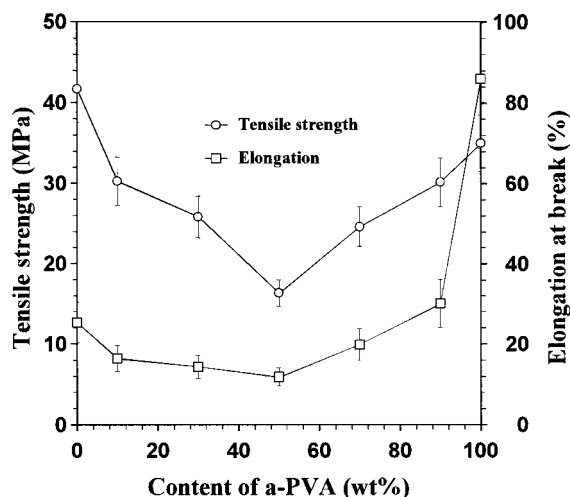
The  $^{13}\text{C}$ -PST MAS NMR spectra of pure PLLA and the a-PVA/PLLA blend containing 10% PLLA are shown in Figure 7. The carbonyl resonance ( $^{13}\text{C}$ , around 171 ppm) of the blend shows not only some downfield chemical shift but also the down-



**Figure 7**  $^{13}\text{C}$ -PST MAS NMR spectra of PLLA and the PLLA/a-PVA (10/90) blend.

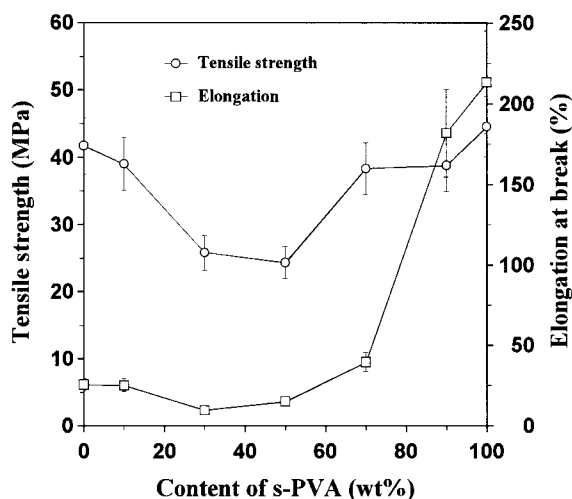
field broadening of the line shape. Because  $^{13}\text{C}$ -PST MAS NMR emphasizes the resonance from the amorphous phase,<sup>41</sup> the above-mentioned changes of the carbonyl resonance ( $^{13}\text{C}$ ) are obviously attributed to the interpolymer hydrogen bonding in the amorphous region. Therefore, the interpolymer hydrogen bonding in the amorphous region is considered to be the driving force leading to some degree of compatibility in the immiscible PLLA/PVA blends, previously discussed based on the results obtained by DSC measurements.

It is known that the mechanical properties of a polymer blend depend not only on the mechanical properties of each component but also on the compatibility of the components as well. Therefore, polymer blending is an effective way to gain new materials with optimized mechanical properties, although it is subject to the compatibility of components. For the blends investigated in the present study, the relationships between the mechanical properties and blend compositions are shown in Figure 8 for PLLA/a-PVA blends and, in Figure 9, for PLLA/s-PVA blends. For both of the PLLA/a-PVA and PLLA/s-PVA blends, the tensile strength first declines and then increases when the PVA content changes from 0 to 100%. The blends with intermediate PVA (or PLLA) contents show much lower tensile strength compared with that of other blends. On the other hand, the elongation at break first declines slightly and then rapidly increases with the increase of PVA content from 0 to 100%. These results are in good agreement with the immiscible, but somewhat compatible, nature of these blends. When PLLA content is high, PLLA will form the continuous phase; otherwise, PVA sets up the continuous



**Figure 8** Tensile strength and elongation versus a-PVA contents in PLLA/a-PVA blends.

phase when the PVA contents are high. In either case, the mechanical properties of blends are determined mainly by one component that makes up the continuous phase but, meanwhile, are affected by another one. In cases in which the contents of the two components are close, the highest degree of phase separation (mainly in the amorphous region) occurs together with the formation of large-size domains and, consequently, the mechanical properties deteriorate. It is noteworthy that both tensile strength and elongation show the tendency of a major increase with increase of PVA content when the PLLA contents are very low, especially for the blend containing 10%



**Figure 9** Tensile strength and elongation versus s-PVA contents in PLLA/s-PVA blends.

PLLA, which exhibits strength or elongation close to that of pure PVA. Considering the higher compatibility and the interpolymer hydrogen bonding in the blends of very low PLLA contents (as revealed in FTIR and DSC measurements), this result is understandable.

## CONCLUSIONS

The formation of interpolymer hydrogen bonding in PLLA/PVA blends with low PLLA contents was demonstrated by FTIR and  $^{13}\text{C}$ -PST MAS NMR measurements. However, there is no evidence indicating any reinforcement of this specific interpolymer interaction when a-PVA in blends is replaced by s-PVA, which theoretically has a higher potential to form interpolymer hydrogen bonding. The amorphous regions of PLA/PVA blends are immiscible because DSC measurements detected two series of isolated and rather composition-independent  $T_g$ 's for both a-PVA/PLLA and s-PVA/PLLA blends. Nonetheless, DSC measurement results still indicate some degree of compatibility between two components attributed to the specific interpolymer interaction identified as hydrogen bonding by FTIR measurement, especially for those blends with low PLLA contents. Furthermore, WAXD and  $^{13}\text{C}$ -CP MAS NMR measurements demonstrate that PLLA and PVA crystallize separately to form isolated PLLA and PVA crystalline phases that are free of interpolymer hydrogen bonding. Interpolymer hydrogen bonding in these blends exists only in the amorphous region, as demonstrated by  $^{13}\text{C}$  solid-state NMR measurements, although it affects the crystalline kinetics of each component. The mechanical properties agree well with the immiscible, but somewhat compatible, nature of these blends.

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