

Effect of Steric Hindrance on Hydrogen-Bonding Interaction Between Polyesters and Natural Polyphenol Catechin

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ABSTRACT: The phase behaviors for the blends of poly(3-hydroxypropionate) (PHP), poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(D,L-lactide) (PDLLA) with catechin were investigated by differential scanning calorimetry. In PLLA/catechin, PDLA/catechin, and PDLLA/catechin blends, two glass transitions were detected when the catechin content was ≥ 40 wt %, whereas in PHP/catechin blends only one glass transition was observed over the whole range of blend compositions. The former and the latter results should reflect the inhomogeneous and the homogeneous nature of the blends, respectively, in the amorphous phase. These different phase behaviors should arise from the differences in the chemical structures between PHP and PLLA/PDLA/PDLLA, which dominates the strength

and the number of intermolecular hydrogen-bonding interactions between the ester carbonyl groups of polyesters and the phenol groups of catechin. As detected by FTIR spectroscopy, in comparison with PHP, the steric hindrance of side-chain methyl groups of PLLA, PDLA, and PDLLA might restrain the formation of hydrogen bonds between their ester carbonyl groups and the phenol hydroxyl groups of catechin, even weakening the strength of such hydrogen bonds. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3565–3573, 2004

Key words: blends; FTIR; polyesters; phase behavior; differential scanning calorimetry (DSC)

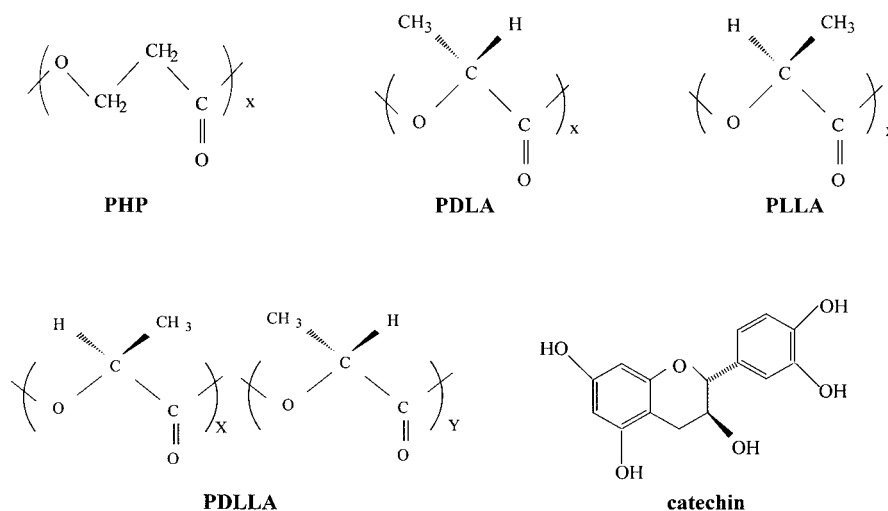
INTRODUCTION

Biodegradable polyesters have attracted much attention from industry and individual investigators.^{1–6} The biodegradable polyesters have two major applications: (1) as biomedical materials that contribute to the medical care of patients and (2) as ecological polymers that keep the earth's environment clean. To promote biomedical applications, a significant amount of work has been devoted to introduce hydrogen-bonding interactions into biodegradable polyesters to modify their mechanical and thermal properties.^{7,8} In a series of previous publications, we presented the results of FTIR and differential scanning calorimetry (DSC) studies on a number of binary compatible biodegradable polyester blends with low molecular weight polyphenols.^{10–13} It is interesting to note that almost all the biodegradable polyesters studied have the ability to interact with low molecular weight phenols by hydrogen bonds. The main reason for this is that these polyesters contain carbonyl groups in their

backbones, which can form hydrogen bonds with the hydroxyl groups of low molecular weight phenols. However, not all the polyesters can form equally strong or numerous hydrogen bonds with such phenols, given that the strength and the extent of hydrogen bonding depend on the chemical as well as stereochemical structures of polyesters. It is scientifically interesting and practically important to investigate the dependency of the formation and the strength of polyester–polyphenol hydrogen bonds on the structure of polyesters.

In this research, to elucidate the relationships between the formation of polyester–polyphenol hydrogen bonds and the chemical as well as the stereochemical structures of polyesters, and moreover between the miscibility of polyester–polyphenol blends and the strength of hydrogen bonds, the phase behavior and intermolecular interaction were investigated for the blends of polyesters with low molecular weight polyphenol. Here, catechin was used as a low molecular weight polyphenol. Catechin is a kind of biodegradable and biocompatible natural polyphenol, originating from green tea. It is a free-radical scavenger, preventing free-radical-mediated damage in a variety of biological systems.⁹ As proton-accepting polyesters,

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Scheme 1 Chemical structures of PDLLA, PDLA, PLLA, PHP, and catechin.

poly(3-hydroxypropionate) (PHP), poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(D,L-lactide) (PDLLA) were used here. PDLLA is a copolymer of D- and L-stereo dimer of lactic acids. Because randomly distributed D- and L-repeating units break the stereoregularity of backbone, PDLLA is amorphous, whereas PLLA and PDLA are highly crystalline. It is expected that the number of intermolecular hydrogen bonds in PDLLA/catechin blends will be higher than that in PLLA/catechin blends because there is no PDLLA crystalline phase in the PDLLA/catechin system. The molecular formula of PHP is similar to that of poly(lactide), but there is no side-chain group in the backbone of PHP, whereas poly(lactide) contains a side-chain methyl group in every repeating unit. The reason for including PHP in this research was to elucidate the steric effect of the methyl groups on the formation of intermolecular hydrogen bonds. The chemical structures of PDLLA, PDLA, PLLA, PHP, and catechin are shown in Scheme 1.

EXPERIMENTAL

Materials

PDLLA (isotactic diad fraction = 0.50) and PLLA samples were kindly supplied by Shimadzu Corp. (Tokyo, Japan) and were used as received. PDLA was prepared by the ring-opening polymerization of D-lactide using tin octoate as a catalyst. The chemically synthesized PHP sample, prepared by a ring-opening polymerization of propiolactone, was kindly supplied by Tokuyama Co. (Japan), and was purified from chloroform solution by precipitation in *n*-heptane. The molecular characteristics of PLLA, PDLA, PDLLA, and PHP samples, determined by GPC, are tabulated in Table I. Catechin (Lot No. 120k1194) was purchased from Sigma-Aldrich Co. (St. Louis, MO).

Preparation of blend samples

A series of blend samples of polyesters with catechin were prepared by solvent-casting techniques on Teflon petri dishes with dioxane solution of the polyesters and catechin in appropriate concentration, 10 mg/mL. The solvent was allowed to evaporate slowly at room temperature, and then the samples were dried under vacuum at 70°C for 3 weeks to remove the residual solvent before physical analysis. Sample films with thickness suitable for the measurements of FTIR spectra were prepared by casting the sample solution directly onto the surface of a silicon wafer, which was transparent for the IR incident beam and used as the substrate. To indicate the different weight contents of the samples, the following codes were used: LAC10, DAC10, DLAC10, HPC10, and so on. The numbers refer to the weight percentage of catechin in the blend sample: LAC, DAC, DLAC, and HPC indicated PLLA/catechin, PDLA/catechin, PDLLA/catechin, and PHP/catechin blend system, respectively; and LA, DA, DLA, and HP indicated pure PLLA, PDLA, PDLLA, and PHP, respectively.

Analytical procedures

Samples were measured by a Tosoh HLC-8020 GPC instrument with a Tosoh SC-8010 controller, refractive

TABLE I
Characteristics of Polyester Samples

Sample	M_w ($\times 10^{+5}$)	M_w/M_n
PHP	1.54	2.32
PLLA	1.38	1.65
PDLA	2.58	1.64
PDLLA	1.06	2.45

detector, and TSK gel G2000HXL and GMHXL columns. Polystyrene standards with narrow molecular-weight distribution were used to construct a calibration curve, and then the number-average and weight-average molecular weights (M_n , M_w) and polydispersity (M_w/M_n) were calculated.

FTIR measurements were carried out on a Spectra 2000 (Perkin–Elmer Japan Co., Tokyo), a single-beam IR spectrometer with a digital temperature controller. All the spectra were recorded under a given temperature (without clear indication, normally 30°C) at a resolution of 4 cm⁻¹ with an accumulation of 16 scans. A curve-fitting program, based on the Gauss–Newton iteration procedure, was applied here for the line-shape analysis of the FTIR carbonyl-vibration spectra. With the least-squares parameter-adjustment criterion, the bands of carbonyl vibration could be quantitatively (or at least semiquantitatively) resolved into three parts: the amorphous, the crystalline, and the hydrogen-bonded components. This fitting adjusted the peak position, the line shape, the peak width, and the height in such a way that the best fit between experimental and calculated spectra was obtained.

DSC thermograms were recorded on a Seiko DSC 220 system connected to a SSC5300 workstation. A sample (~ 5 mg) was encapsulated into an aluminum pan. In the first heating run, the samples were heated from -50 to 200°C at a scanning rate of 20°C/min. Then, they were quenched with liquid nitrogen to -50°C, and again reheated to 200°C at the same scanning rate (the second heating run). The glass-transition temperature T_g was taken as that indicated by the top point of DDSC (differential of DSC) peak recorded in the second heating run.

RESULTS AND DISCUSSION

Phase behavior

Figure 1(a) and (b) show the DSC thermograms of PLLA/catechin and PDLLA/catechin binary blend systems observed in the second heating scans. Each of these blends shows just a single glass transition when the catechin content was <50%, while showing two transitions when the catechin content increased to ≥50%. For PDLA/catechin blends, as shown in Figure 1(c), the phase separation occurs when the catechin content is ≥40%. These results indicate that PLLA, PDLA, and PDLLA are somewhat compatible with catechin, but not miscible with catechin over the whole composition range. The possible reason for this should be that the interaction between these polyesters and catechin is not strong enough to prevent phase separation. In these binary blend systems, catechin molecules are able to form two kinds of association: (1) the self-association through hydrogen-bonding interaction between their hydroxyl groups and (2)

the intermolecular association through hydrogen-bonding interaction between the hydroxyl groups of catechin and the carbonyl groups of polyesters. The phase behavior of the blends depends on the competition of the two kinds of association, which can be described by the association model suggested by Coleman.¹⁴ Among the three blend systems, it should also be noted that the PDLA/catechin blend system shows phase separation. At 40% catechin content, the PDLA/catechin blend shows two glass transitions, whereas the PLLA/catechin and PDLLA/catechin show a single glass transition. For poly(lactide)s/catechin blend systems, the higher T_g (simplified as T_g^H) and the lower T_g (simplified as T_g^L) should belong to the catechin-rich phase and the polyester-rich phase, respectively. As shown in Table II, it is obvious that T_g^L of poly(lactide)s/catechin binary systems increases substantially with the catechin content, suggesting the presence of weak interactions in these binary systems.

To compare the effects of chemical structures of polyesters to specific interaction, thermal properties were also investigated for the PHP/catechin blends. The PHP repeating unit contains the same kinds and the same number of atoms as poly(lactide)s, although it has no side-chain groups. Figure 1(d) shows the DSC traces of PHP/catechin binary system with various compositions in the second heating scans. All samples show a single T_g that lies between the glass-transition temperatures of pure PHP and catechin.¹⁵ The T_g value of pure PHP is -16°C, and it increases to 38°C as the catechin content increases to 50%. A single glass transition observed for the blends is generally accepted as a criterion of the miscibility for the binary system. It also indicates the existence of strong inter-association between the two blend components.

The T_g values as a function of the blend compositions can be described by a number of equations, such as the Gordon–Taylor equation¹⁶; the Jenkel–Heush equation¹⁷; and the equations proposed by Fox,¹⁸ Couchman,¹⁹ and Kwei.²⁰ Among these equations, the Kwei equation can satisfactorily describe the single T_g behavior of binary polymer blend systems, especially that of hydrogen-bonded systems. The Kwei equation is composed of the traditional Gordon–Taylor equation and a specific interaction term, qw_1w_2 :

$$T_g + \frac{w_1T_{g1} + kw_2T_{g2}}{w_1 + kw_2} + qw_1w_2 \quad (1)$$

where q is a parameter corresponding to the strength of the specific interaction between the two components; T_g , T_{g1} , and T_{g2} are the glass-transition temperatures of the blend and of two pure components, respectively; and w_1 and w_2 are the weight fractions of two pure components. The T_g values observed by DSC and those predicted by the Kwei equation are plotted

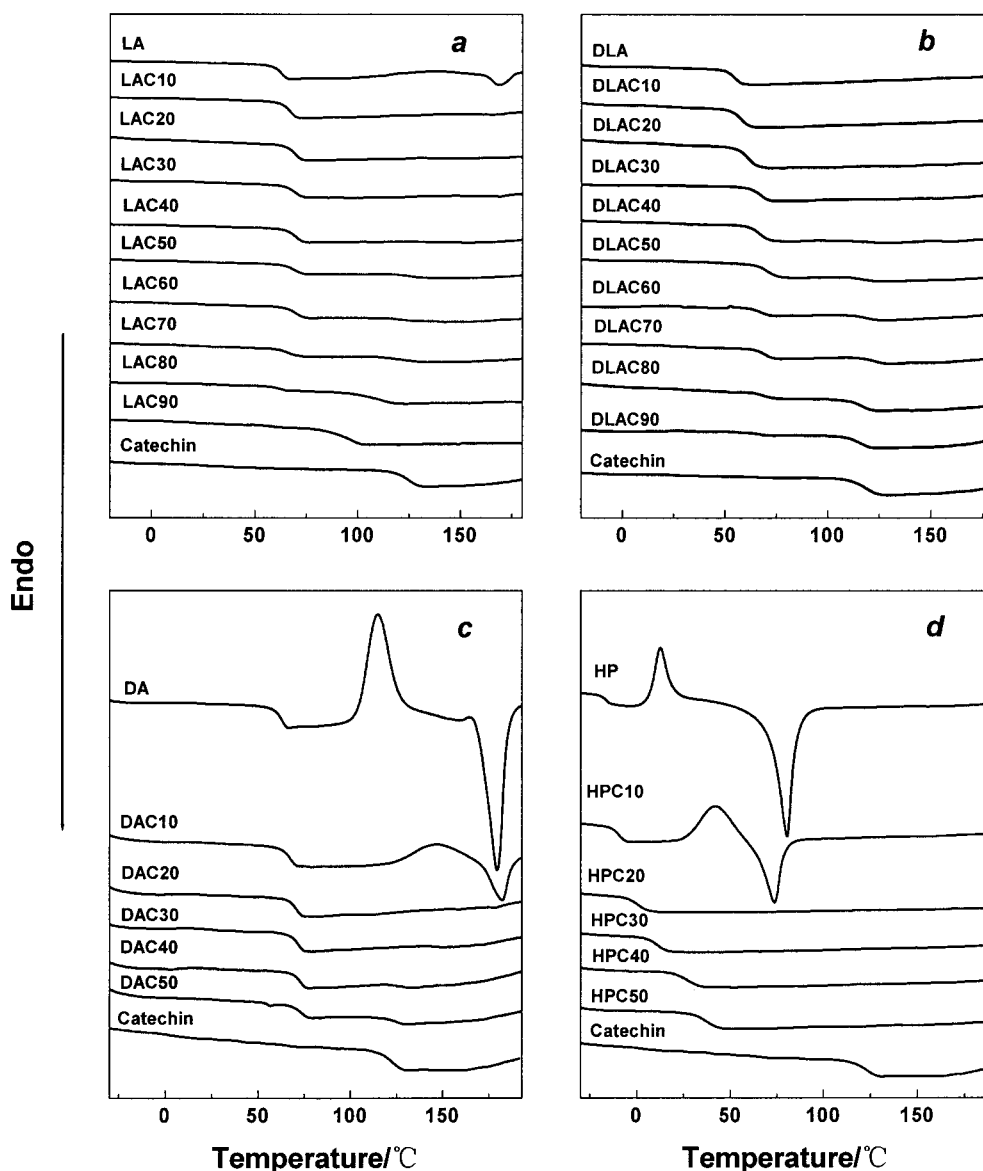


Figure 1 DSC traces of polyester/catechin blends observed in the second heating scan: (a) PLLA/catechin; (b) PDLA/catechin; (c) PDLLA/catechin; (d) PHP/catechin.

against the catechin content in Figure 2 for PHP/catechin binary system. It is clear that the Kwei equation can satisfactorily predict T_g with the q and k values, -64.0 and 1 , respectively.

By comparing the results for the PHP/catechin system with those for the PLLA/catechin, PDLA/catechin, and PDLLA/catechin binary systems, it can be suggested that PHP, which has no side-chain methyl group, seems to be more easily involved in the specific interaction with catechin, leading to miscibilization of the two components. On the contrary, PLLA, PDLA, and PLLA all contain a side-chain methyl group adjacent to the hydrogen-accepting carbonyl group in each segment, most likely interfering with the interaction between the carbonyl groups of poly(lactide)s and the hydroxyl groups of catechin.

Hydrogen-bonding interaction

As is well known, FTIR is used extensively in the study of polymer complexes to determine the presence of specific interactions between various chemical groups because of the sensitivity of the force constants to intermolecular and intramolecular interactions. FTIR is also able to provide both qualitative and quantitative information on specific interactions between polymers and low molecular weight compounds.

For polyester-catechin complexes, there are two main absorption ranges in the infrared spectra that are sensitive to the hydrogen-bond formation: (1) the hydroxyl-stretching region located within $3000\text{--}4000\text{ cm}^{-1}$ and (2) the carbonyl-stretching region within $1660\text{--}1780\text{ cm}^{-1}$. A $\nu_{\text{C=O}}$ stretching mode of polyes-

TABLE II
Thermal Properties of Polyester–Catechin Binary Blend Systems Detected in the DSC Second Scan

Sample	Thermal properties ^a (°C)	Catechin (wt %)										
		0	10	20	30	40	50	60	70	80	90	100
PLLA	T_g^L	63	66	70	68	70	69	70	66	63	60	
	T_g^H						123	122	123	111	96	124
	T_c	138	143									
	T_m	169	166									
PDLA	T_g^L	63	67	71	72	73	73					
	T_g^H					124	123					
	T_c	115	147									
	T_m	180	182									
PDLLA	T_g^L	55	58	61	68	67	70	67	70	69	68	
	T_g^H						116	118	123	116	116	124
PHP	T_g	-16	-10	0	11	28	38					
	T_c	13	42									
	T_m	81	74									

^a T_g , T_g^L , T_g^H , T_c , and T_m are the glass-transition temperature, the lower T_g of phase-separated blends, the higher T_g of phase-separated blends, the cold crystallization temperature, and the melting point, respectively.

ters appears at around 1750 cm^{-1} , whereas catechin shows no absorption in this region. Therefore, any changes observed in this region should be directly attributed to the changes in the carbonyl-group environment of polyesters, such as the formation of hydrogen-bond complexes.

Figure 3(a) shows the carbonyl-stretching spectra of PHP, catechin, and their blends with different compositions. When PHP is blended with catechin, a new band appears at about 1717 cm^{-1} , which is lower than that of pure PHP at about 1740 cm^{-1} . This new band is attributed to the hydrogen-bonded carbonyl groups. With an increase of catechin content in the blends, the relative absorbance of the hydrogen-bonded carbonyl

increases. Figure 3(b) shows the hydroxyl-stretching spectra of PHP, catechin, and their blends with different compositions. The main band of catechin, centering at 3324 cm^{-1} , is attributed to the self-associated hydroxyl group because of its position at a low wavenumber. For pure PHP, only a very weak band centering at 3448 cm^{-1} is observed in this region, which should be attributed to the stretching of the chain-end hydroxyl groups of PHP. Because of its low intensity compared with that of catechin, the contribution of this band to the total spectrum can be neglected when the weight content of catechin is sufficiently high. By blending PHP and catechin, a new band centering at about 3426 cm^{-1} appears, which should be induced by the formation of the hydrogen bonds. The relative intensity of this new band increases with an increase in catechin weight content. Compared with the wavenumber of self-associated pure catechin, this band lies in the higher wavenumber region, indicating that the strength of these polyester–catechin intermolecular hydrogen bonds is weaker than that of the catechin–catechin ones.

However, for poly(lactide)/catechin blends, neither the position nor the shape of the carbonyl-stretching band changes (not shown here), when the catechin content increases from 0 to 50%. This suggests that few or no hydrogen bonds form in the poly(lactide)/catechin blends. The DSC and FTIR results seem somewhat confusing. The DSC results suggest that a weak interaction should exist between poly(lactide)s and catechin because poly(lactide) blends with catechin content less than 40% shows only one glass transition. These conflicts can be explained by the phase behavior of the blend samples for the FTIR measurements. In this research, the samples for the measurements of transmission-mode infrared spectra were prepared by casting the solution of the blends directly onto the

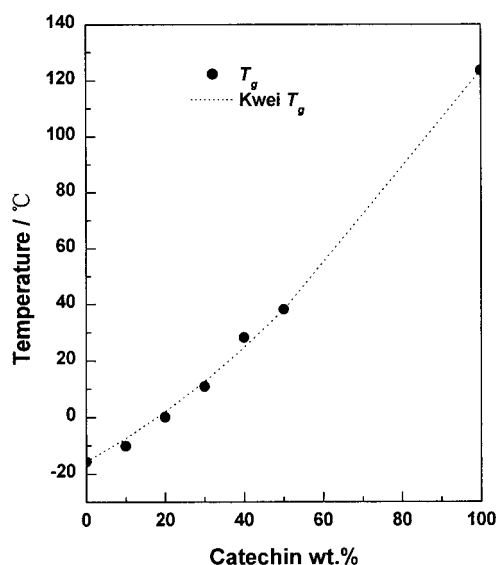


Figure 2 Experimental T_g (●) and theoretical T_g predicted by the Kwei equation for the PHP/catechin blends plotted against the catechin weight content.

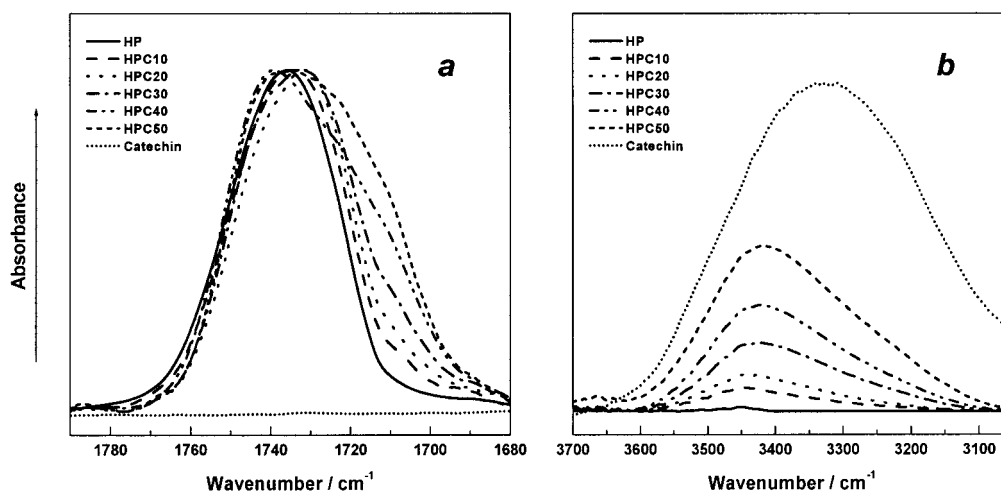


Figure 3 FTIR spectra for the blends of PHP/catechin at room temperature: (a) carbonyl-stretching band; (b) hydroxyl-stretching band.

surface of the silicon wafer to ensure that the sample films were thin enough to be in the range where the Beer-Lambert law is applicable.²¹ In addition, it is often assumed that intimate mixing of two polymers can be achieved by such a casting technique. Nevertheless, it is well known that the type of solvents used for casting exerts major effects on the phase behavior of polymer blends. In fact, if the interaction of one of the component polymers with solvent is very different from that of the other polymer, a phase separation may occur during the casting procedure.²² In this research, poly(lactide)/catechin samples for the FTIR measurements were prepared by casting dioxane solution. Major differences can be anticipated between the interaction of poly(lactide) carbonyl groups/dioxane ether groups and that of catechin hydroxyl groups/dioxane ether groups, where the hydroxyl-ether intermolecular interaction is significantly stronger²³ than the carbonyl-ether intermolecular interaction.²⁴ Accordingly, it is reasonable to assume that poly(lactide)/catechin FTIR samples are phase separated.

To confirm this assumption, especially to detect the formation of hydrogen bonds in poly(lactide) blends, appropriate conditions for intimate mixing should be applied to these blends. The melting point of semicrystalline PLLA is about 172°C, so if the temperature for FTIR measurements increases above 172°C, the phase-separated blends might be able to revert to a single phase. Here, the FTIR spectra were measured at 190°C, which is higher than both the glass-transition temperature of amorphous PDLLA and the melting points of PLLA and PDLA. Figure 4(a) shows the FTIR behavior of LAC40 blends under different thermal conditions. Under nitrogen purge, with increasing the temperature from 30 to 190°C, the band of the LAC40 in the carbonyl-stretching region shifts to a lower wavenumber position and the top shape of the band

becomes wider. This indicates that a part of the carbonyl groups are involved in hydrogen-bond formation at higher temperature; that is, the phase-separated phases tend to revert to a single phase at the temperature above the melting points of the blends, so that hydrogen bonds are formed. The quenched samples, obtained by cooling from 190 to 30°C with liquid nitrogen, clearly show the integrated FTIR spectra keeping almost the same shape and position as those observed at 190°C. Given that the temperature 30°C is much lower than the T_g value, the amorphous nature at 190°C should remain in the quenched sample at 30°C. Thus, the results from the quenched sample again confirm the plausibility of the explanation. The PDLA/catechin and PDLLA/catechin blends also show a similar behavior, as shown in Figure 4(b) and (c).

In addition, it is reasonable to observe that the shape of carbonyl-stretching spectra within the range from 1690 to 1710 cm^{-1} for the quenched sample at 30°C is slightly wider than that for the melted sample at 190°C, suggesting stronger and more hydrogen bonds are formed in the quenched sample at 30°C. As is well known, the decrease of thermal energy is in favor of the buildup of hydrogen bonds. That is, when the measurement temperature decreases below T_g (as shown in Table II), the decrease of thermal energy serves to increase the average strength of intermolecular interaction and the number of interactions. This hypothesis is further substantiated by observing the FTIR hydroxyl-stretching bands. As shown in Figure 5, the main peak of the hydroxyl-stretching spectrum for the LAC40 measured at 30°C lies at 3328 cm^{-1} , almost the same as that of pure catechin. The main peak can be attributed to the self-association. Besides the main peak, a small peak emerges at a lower position centering at 3508 cm^{-1} , which may correspond to the free hydroxyl groups with respect to the corre-

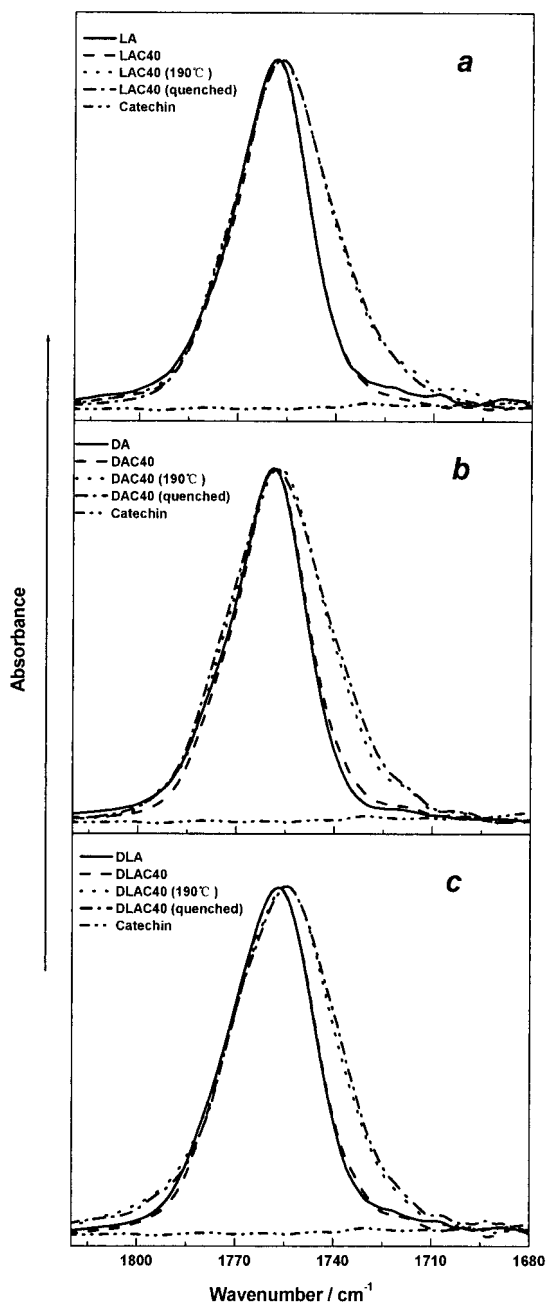


Figure 4 FTIR spectra in the carbonyl-stretching region for poly(lactide)/catechin blends with different thermal histories: (a) LAC40; (b) DAC40; (c) DLAC40.

sponding carbonyl stretching. When the sample temperature increased to 190°C, the hydroxyl-stretching band of LAC40 shifted to almost 3508 cm^{-1} , the same as the free-hydroxyl stretching. However, the bands are not symmetrical, which, in effect, besides free hydroxyl groups, should be a superposition of numerous curves representing a range of strength of interassociated and self-associated hydroxyl groups. When the sample was quenched to 30°C, the hydroxyl-stretching band of the quenched LAC40 sample shifted to a lower wavenumber than that of LAC40 at 190°C, which indicates the strength and the number of inter-

associated interaction are increased by the decrease of thermal energy. As shown in Figure 5(b) and (c), similar results may be observed for DAC40 and DLAC40 samples. Thus, based on these results, it can be concluded that the hydrogen bonds can be formed between PLLA, PDLA or PDLLA, and catechin.

Semiquantitative analysis of the fractions of hydrogen-bonded carbonyl groups

As shown above, FTIR spectra confirmed the existence of intermolecular hydrogen bonds between the car-

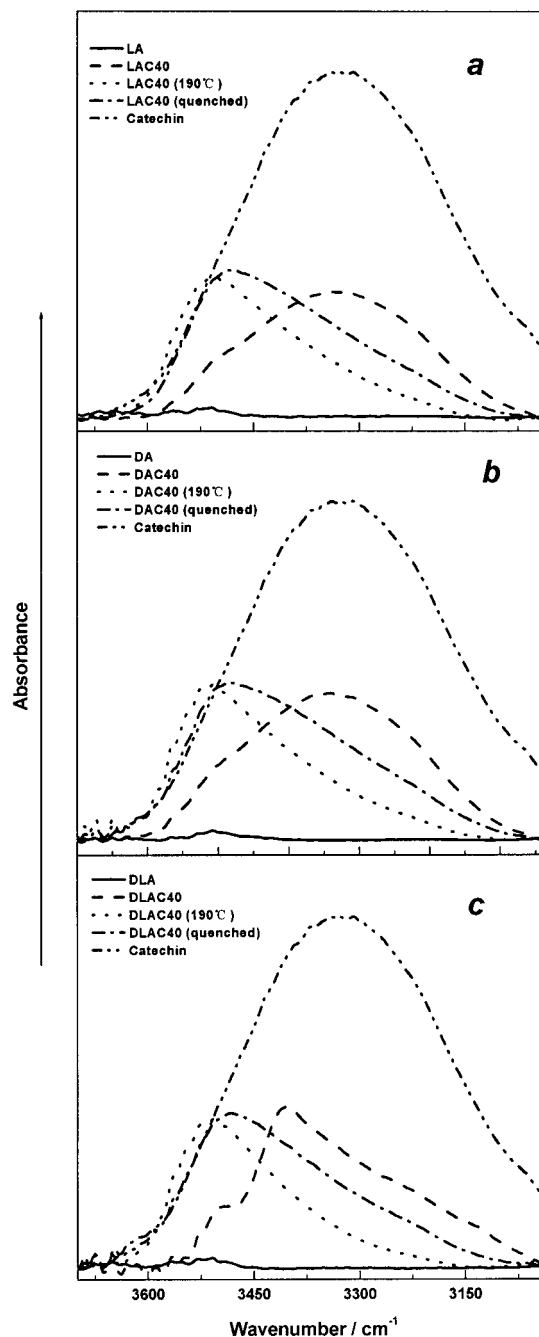


Figure 5 FTIR spectra in the hydroxyl-stretching region for poly(lactide)/catechin blends with different thermal histories: (a) LAC40; (b) DAC40; (c) DLAC40.

TABLE III
Relative Intensities and Fractions of Hydrogen-Bonded Carbonyl Groups for Polyester/Catechin Blends

Sample	Free carbonyl						Hydrogen-bonding carbonyl			F_b (%)
	Amorphous			Crystalline			ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	$A_{(b,CO)}$ (%)	
	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	$A_{(a,CO)}$ (%)	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	$A_{(c,CO)}$ (%)				
PHP	1743	23	60	1729	19	40				0
HPC10	1743	23	51	1729	19	32	1717	32	17	12
HPC20	1743	23	40	1729	19	33	1717	32	27	20
HPC30	1743	23	40	1729	19	24	1717	32	36	27
HPC40	1743	23	43	1729	19	14	1717	32	43	33
HPC40 ^a	1743	23	50	1729	19	0	1717	32	50	40
		ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)		$A_{(a,CO)}$ (%)					
LAC40 ^a		1758	34		82		1736	38	18	13
DAC40 ^a		1758	34		89		1736	38	11	8
DLAC40 ^a		1758	34		84		1736	38	16	11

^a Quenched sample.

bonyl groups of polyesters and the hydroxyl groups of catechin. Besides carbonyl groups, carboxyl oxygens also tend to form hydrogen bonds. Thus, use of only the carbonyl-stretching region may lead to an underestimation of the number of hydrogen bonds. However, as for similar systems,²⁵ no clear FTIR certification has been found for the existence of hydrogen bonds between the carboxyl oxygen and the hydroxyl group of catechin in our systems; thus, only the carbonyl-stretching region is referred to in this section. For comparison of the fraction of hydrogen-bond number among the four kinds of polyester blends, a curve-fitting program was used to analyze quantitatively the carbonyl-stretching bands. By applying the curve-fitting procedure,¹²⁻¹⁴ and based on the Beer-Lambert law, the integrated intensity of the carbonyl-stretching band of PHP/catechin samples can be divided into three components: (1) the amorphous [$A_{(a,CO)}$], (2) the crystalline [$A_{(c,CO)}$], and (3) the hydrogen-bonded [$A_{(b,CO)}$]. Because the quenched HPC40, LAC40, DAC40, and DLAC40 samples are amorphous, the carbonyl-stretching bands of these samples were resolved into the amorphous and hydrogen-bonded bands. The fraction of hydrogen-bonded carbonyl groups of PHP/catechin blends (F_b) can be expressed as

$$F_b = A_{(b,CO)} / [A_{(b,CO)} + \gamma_{b/c} A_{(c,CO)} + \gamma_{b/a} A_{(a,CO)}] \quad (2)$$

For quenched HPC40, LAC40, DAC40, and DLAC40 samples, the value of F_b can be calculated as

$$F_b = A_{(b,CO)} / [A_{(b,CO)} + \gamma_{b/a} A_{(a,CO)}] \quad (3)$$

where $\gamma_{b/a}$ and $\gamma_{b/c}$ are the absorption coefficients, which take into account the difference among the absorptivities of the amorphous, hydrogen-bonded, and crystalline carbonyl groups. Compared with the absorption coefficients of similar polyester sys-

tems,^{14,26,27} the ratio of two absorptivities, $\gamma_{b/c}$, $\gamma_{b/a}$ or $\gamma_{b/fr}$ were reasonably assumed to be 1.5.

In Table III are listed the results of curve-fitting, including absorption intensity (A_i) and peak width at half height ($W_{1/2}$). For PHP/catechin blends, the fraction of hydrogen-bonded carbonyls obviously increases with the increase of catechin content. In addition, by comparison of the fraction of hydrogen-bonded carbonyls among the quenched DLAC40, DAC40, LLAC40, and HPC40 samples, it is clear that poly(lactide)s form fewer hydrogen bonds than PHP, which should arise from, as mentioned earlier, the steric hindrance of the side-chain methyl group of poly(lactide)s.

Figure 6 illustrates the hydroxyl-stretching bands of the quenched HPC40, LAC40, DAC40, DLAC40, and catechin, respectively. The peak lies between the free-

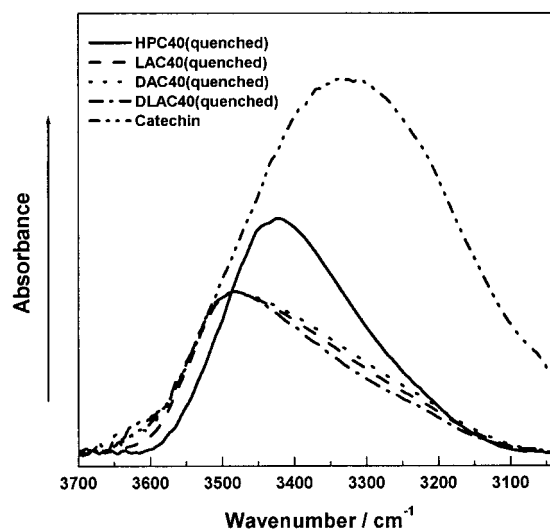


Figure 6 Comparison of the FTIR spectra in the hydroxyl-stretching region for polyester/catechin blends quenched from fusion.

hydroxyl stretching and self-associated hydroxyl stretching, suggesting the peak may be assigned as the position of interassociated hydrogen bonds. The bands of catechin hydroxyls in the self-associated catechin, and PHP–catechin, PLLA–catechin, PDLA–catechin, and PDLLA–catechin blends centered at 3328, 3426, 3484, 3482, and 3483 cm^{-1} , respectively. It is clear that the band position is in the order of catechin > HPC40 > LAC40 \approx DAC40 \approx DLAC40. The hydroxyl-stretching bands with the lower position correspond to the stronger strength of hydrogen-bonding interaction. Coleman et al.²⁸ used the frequency difference ($\Delta\nu$) between the hydrogen-bonded hydroxyl absorption and the free hydroxyl absorption to investigate the average strength of the intermolecular interaction. However, in this case, the free hydroxyl absorption is completely overlapped by the widely distributed self-associated hydroxyl absorption. Therefore, we used the frequency distance between the hydrogen-bonded hydroxyl-stretching and the self-associated hydroxyl-stretching band to distinguish the strength of four kinds of polyester–catechin interactions. The results are in the order of PHP–catechin (98 cm^{-1}) > PDLLA–catechin (152 cm^{-1}) \approx PDLA–catechin (154 cm^{-1}) \approx PLLA–catechin (156 cm^{-1}).

CONCLUSIONS

As investigated by DSC measurements, it was found that PLLA/catechin, PDLA/catechin, and PDLLA/catechin blends showed two glass transitions when the catechin content was high (40%), whereas PHP/catechin blends showed only one glass transition over the whole range of blend compositions. The different phase behavior should result from the different capabilities of forming hydrogen bonds. In the PLLA/catechin and the PDLLA/catechin blend systems, neither a wavenumber shift nor a shape change of the carbonyl-stretching band, indicating the formation of hydrogen bonds, was detected at room temperature by FTIR measurements, whereas in the PHP/catechin blends a distinct new band, which was attributed to the hydrogen-bonding interaction, appeared in the carbonyl-stretching region. Weak hydrogen bonds were found in the quenched poly(lactide)/catechin blend samples. Hence, the blend samples, which originally were phase separated, reversed to a single phase when the measurement temperature was higher than the melting point or the glass transition. With a curve-fitting program, the carbonyl-stretching bands of quenched LAC40, DAC40, DLAC40, and HP/cate-

chin blends were analyzed semiquantitatively. It is clear that PHP can form more and stronger hydrogen bonds with catechin than can poly(lactide)s, indicating that the steric hindrance of the side-chain methyl group of poly(lactide)s prevents the formation of strong hydrogen bonds. Moreover, almost no difference in the ability of hydrogen-bond formation with catechin was found among PLLA, PDLA, and PDLLA, which suggested that the steric configuration had no effects on the formation of hydrogen bonds with catechin in the weak-interaction blend systems.

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