

Effects of Moisture Content and Heat Treatment on the Physical Properties of Starch and Poly(lactic acid) Blends

TIANYI KE, XIUZHI SUN

Department of Grain Science and Industry, Kansas State University, Manhattan, Kansas 66506

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ABSTRACT: Starch, a hydrophilic renewable polymer, has been used as a filler for environmentally friendly plastics for about 2 decades. Starch granules become swollen and gelatinized when water is added or when they are heated, and water is often used as a plasticizer to obtain desirable product properties. The objective of this research was to characterize blends from starch and poly(lactic acid) (PLA) in the presence of various water contents. The effects of processing procedures on the properties of the blends were also studied. Blends were prepared with a lab-scale twin-screw extruder, and tensile bars for mechanical testing were prepared with both compression and injection molding. Thermal and mechanical properties of the blends were analyzed, and the morphology and water absorption of the blends were evaluated. The initial moisture content (MC) of the starch had no significant effects on its mechanical properties but had a significant effect on the water absorption of the blends. The thermal and crystallization properties of PLA in the blend were not affected by MC. The blends prepared by compression molding had higher crystallinities than those prepared by injection molding. However, the blends prepared by injection molding had higher tensile strengths and elongations and lower water absorption values than those made by compression molding. The crystallinities of the blends increased greatly with annealing treatment at the PLA second crystallization temperature (155°C). The decomposition of PLA indicated that PLA was slightly degraded in the presence of water under the processing temperatures used. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3069–3082, 2001

Key words: cornstarch; poly(lactic acid); gelatinization; thermal properties; mechanical properties

INTRODUCTION

Poly(lactic acid) (PLA) has been studied extensively for use in medical implants, sutures, and drug-delivery systems since the 1980s because of its biodegradability.^{1,2} Its good mechanical prop-

erties^{3,4} have made it attractive for disposable and biodegradable plastic substitutes. However, PLA is still more expensive than conventional plastics, and the degradation rate is not completely satisfactory in some instances (e.g., municipal composting).⁵ Starch has recently been blended with PLA to enhance its degradability and to reduce total raw materials cost.^{6–9}

Starch, a renewable degradable carbohydrate biopolymer, can be purified from various sources. It consists of a glucose monomer joined by α -(1-4) linkages, called *amylose*, and a glucose monomer joined by α -(1-4) linkages with branch points in-

Correspondence to: X. Sun (xss@ksu.edu).

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volving α -(1-6) linkages, called *amylopectin*. Native starch is usually stored in the granular state, in which these polymer molecules are hydrogen-bonded and aligned radially.¹⁰ The starch granule becomes swollen and dispersed in water and becomes gelatinized when heated. During the blending process, the starch is partially or fully gelatinized or destructured in the presence of moisture, heat, and shear force.¹¹ Water has often been used as a plasticizer to destructure starch in its blending with various polymers and to achieve a fine dispersion and, consequently, to obtain desirable product properties.^{12–14}

PLA is a hydrophobic synthetic biopolymer that is depolymerized in the presence of water at elevated temperatures, which results in poor mechanical properties.¹⁵ Therefore, it has been suggested that starch be dried before blending with PLA to avoid PLA degradation. However, in this case, the starch would remain mostly in its granular state in the blends because of the lack of water.¹⁶ Water is a convenient, economical, and effective plasticizer to starch, and the moisture content (MC) in starch would likely affect the morphology and mechanical properties of the blend. The objective of this research was to characterize blends of starch and PLA with various MCs.

EXPERIMENTAL

Materials

Industrial cornstarch (Silver Medal Pearl-1100) was purchased from Cargill, Inc. (Minneapolis, MN). The cornstarch granules contained approximately 75% amylopectin and 25% amylose. PLA was obtained from Shimadzu, Inc. (Tokyo, Japan), had a molecular weight of about 120,000 Da, and was polymerized mainly from L-lactic acid.

Blend Preparation

Starches with six levels of MC (0, 11.9, 20, 30, 40, and 50%) were prepared. For 0% MC, the starch was dried in an air oven at 130°C for 2 h or until no weight loss occurred. The raw starch, which contained 11.9% moisture, was used as one of the MC levels. Distilled water was added into the mixer to increase the MC of the starch from 11.9% to the other four higher levels. The 11.9% MC originally contained in the starch was included for these high-MC-level calculations. The PLA

was ground into small particles of about 2 mm. Next, it was premixed with prepared cornstarch that contained a designed MC with a stand mixer (Ultra Power Kitchen Aid, St. Joseph, MI) at a fixed ratio of 40:60 (dried starch:PLA) at room conditions. The mixture was stored in a polyethylene zippered plastic bag for about 1 h and then blended in a lab-scale, corotating conical, twin-screw extruder (TW-100, Haake, Paramus, NJ) with a screw diameter of 19.1 mm, a length-to-diameter ratio of 25:1, and a constant pitch and flight depth.

The mixture was loaded into a feeding funnel by hand. It was extruded through a rod die with an 8-mm diameter at a temperature profile of 120 (near to the feed inlet), 185, 185, and 185°C (at the die). The screw speed was fixed at 100 rpm. The extruded rods were cut into short cylinders about 10 mm in length and were then ground into small particles of about 2 mm with a mill (model 4 Laboratory Mill, Thomas–Wiley Co., Philadelphia, PA). The ground blends were dried again in the oven at 110°C for 24 h before molding.

Molding and Annealing Treatment

The starch and PLA extrudates were molded into tensile bars with both compression molding and injection molding. For the compression molding, about 4.5 g of the dried ground blends were placed in a dog-bone-shaped tensile bar mold and compression-molded with a Carver hot press (model 3890 Auto M, Carver Inc., Wabash, IN) according to ASTM standard D638. The tensile bar was pressed at 180°C and 4.3 MPa for about 8 min. Then, the mold was removed from the hot press and cooled to room temperature. Finally, the tensile bar was removed with an aluminum foil and zinc stearate mold release.

An injection-molding machine (Boy 22S, Boy Machines, Postfach, Germany) was also used to obtain tensile bars. The premixing screw temperature profile was 150 (near to the inlet), 175, and 175°C, and the molding injection pressure was 150 psi. Injection and cooling times were both 5 s.

To observe the effects of annealing treatment on the properties of the blends, both compression-molded and injection-molded tensile bars were annealed in an air oven at 105 and 155°C, respectively, for 1 h. All the tensile bars were preconditioned at 23°C and 50% relative humidity (RH) before mechanical analysis. Five tensile bars were prepared for each experiment.

Thermal Analysis

Differential scanning calorimetry (DSC) analysis was performed to measure thermal transition (DSC7, PerkinElmer, Norwalk, CT). The DSC was calibrated with the melting temperature and enthalpy of the standard material indium. The samples of dried, ground blends were weighed accurately into an aluminum pan and sealed hermetically. An empty pan was used as a reference. The DSC temperature increased from 25 to 200°C at a heating rate of 10°C/min. Peak temperatures and enthalpies at glass transition, crystallization, and melting were calculated. The sum of the enthalpy of the blends at different thermal stages was used as a rough estimation for crystallinity (X_c) according eq. (1).¹⁷

$$X_c(\%) = (\Delta H_m + \sum \Delta H_{ci}) * 100 / (93 * X_{PLA}) \quad (1)$$

where ΔH_m and ΔH_{ci} are the enthalpies (in joules/gram) of fusion and crystallization of the blends, respectively; and 93 J/g is the enthalpy of fusion of a PLA crystal of infinite size; and X_{PLA} is the PLA content.

Weight loss of the sample from decomposition was measured with a thermogravimetric analyzer (TGA-50, Shimadzu, Japan). The temperature ranged from 25 to 450°C under an N₂ atmosphere and was increased at 20°C/min.

Structural Analysis

Microstructures of the fractured samples obtained after tensile testing were observed with scanning electron microscopy (SEM; AutoScan, ETEC Corporation, Highlands, TX) at an accelerated voltage of 20 kV. Starch morphology was observed with a microscope (Olympus BH-2, Olympus Co., Toyato, Japan) at 40 × 10 amplification under phase contrast with 30 s of exposure. Samples of the starch and PLA blends were dissolved in chloroform and then filtered to separate the starch. The separated starch samples were transferred onto optical microscope slides for observation.

Crystallinity was determined with a Philips powder diffractometer (model APD3520 and XRG3100 X-ray generator, Philips Electronic Instruments Co., Houston, TX). The blends were ground into a fine powder about 0.5 mm in diameter by a mill (laboratory mill 3303, Falling Number AB, Huddinge, Sweden). The generator of the diffractometer was operated at 35 kV and 25 mA.

Nickel-filtered Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) was used. The measurement was performed with a range of 10–30° (2 θ) at ambient temperature. A spectrometer [KBr plate, ATI Mattson Research Series 1 Fourier transform infrared (FTIR), Madison, WI] was used to obtain IR spectra of selected samples.

Determination of Starch Gelatinization

Starch was separated from the blends by dissolving the PLA from ground blend samples in chloroform for 24 h and then filtering. The filtrate was washed repeatedly with chloroform to remove PLA completely. The separated starch was dried and stored in a desiccator for the DSC experiment. The degree of gelatinization was calculated according to the method described by Potente et al.:¹⁸

$$G = (1 - \Delta H_G / \Delta H_0) * 100\%$$

where G is the degree of starch gelatinization, ΔH_G is the enthalpy of the gelatinized starch extracted from the blends, and ΔH_0 is the enthalpy of native starch.

RESULTS AND DISCUSSION

Extrudate Appearance

The extrudates of the starch and PLA blends were an opaque white color, and their surface appearances were affected significantly by MC. At the fixed extrusion conditions used, the smoothness of the extrudate surface increased as MC increased up to 20% and then became rough as moisture increased up to 50%. At high MC, such as 40 or 50%, visible foaming occurred at the die because of the high water-vapor pressure formed right before the die.

The final MC of the extrudates after natural cooling to ambient temperature was less than 2% regardless of initial MC. This indicated that all of the extra water vapor produced in the extrusion barrel was removed immediately at the die because of the high temperature (~ 180°C). The final MC of the extrudates was 1.89, 1.38, 1.16, 1.54, and 1.92 wt %, corresponding to 11.9, 20, 30, 40, and 50 wt % of the initial MCs.

Thermal Properties

The DSC thermograms of the blends are presented in Figure 1. As expected, the DSC curves

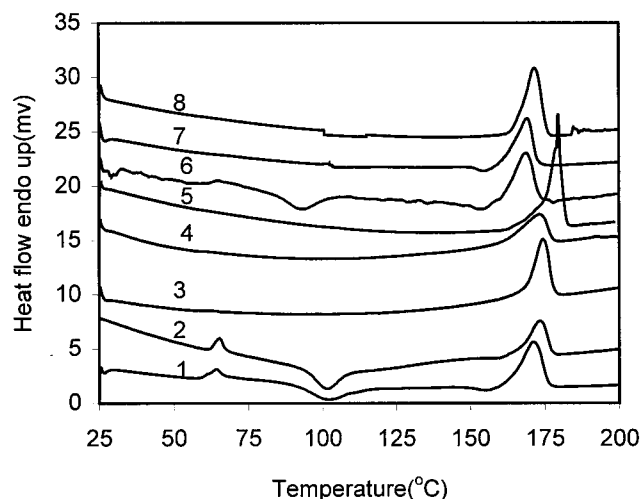


Figure 1 DSC thermograms of cornstarch and PLA blends at a 40:60 ratio: (1) extrudate with 0% MC, (2) extrudate with 40% MC, (3) compression-molded sample with 0% MC, (4) compression-molded sample with 0% MC annealed at 100°C, (5) compression-molded sample with 0% MC annealed at 155°C, (6) injection-molded sample with 0% MC, (7) injection-molded sample with 0% MC annealed at 100°C, and (8) injection-molded sample with 0% MC annealed at 155°C.

showed mainly the thermal properties of pure PLA as reported by Ke and Sun.¹⁶ The initial MC of the starch had little effect on PLA thermal transition temperatures. For example, the DSC curves 1 (0% MC) and 2 (40% MC) in Figure 1 had similar patterns. However, the thermal properties of the materials revealed different characteristics on different processing. Two exothermic peaks were observed for extrudates. One major peak was at about 100°C, which was caused by crystallization, which was in agreement with the results reported by Liu et al.¹⁹ and Matsumoto.⁹ A minor exothermic peak occurred at about 155°C. These two peaks disappeared after compression molding but were still observed after injection molding [Fig. 1(3, 6)]. However, the major peak disappeared after the annealing treatment of the injection-molded samples at 100°C [Fig. 1(7); Table I], and both peaks disappeared after annealing at 155°C [Fig. 1(8); Table I], respectively. This indicated that the minor exothermic peak at 155°C also was caused by PLA crystallization. The natural cooling rate for compression molding was slow at room conditions compared to that for the injection molding with a tap-water cooling system. Therefore, the thermal properties of the sample made with compression

Table I DSC Data of Cornstarch and PLA Blends with Varied MCs Under Annealing Treatment

Sample	Compression-Molded			Injection-Molded			
	T_{c2}^b (°C)	T_m^c (°C)	ΔH_m^d (J/g)	T_{c2} (°C)	ΔH_{c2} (J/g)	T_m (°C)	ΔH_m (J/g)
At 100°C ^a							
PLA		174.4	40.84	155.7	-0.89	173.4	40.08
0		176.2	31.3	157.7	-1.26	168.7	22.57
11.9		175.1	32.40	154.5	-0.99	169.1	23.79
20		173 and 177.7	33.7	157.7	-1.23	169.9	23.90
30		176.7	31.96	157.4	-2.05	175.1	24.73
40		176.1	34.28	155.7	-0.95	167.7	21.73
50		176.1	35.67	154.7	-1.48	169.1	24.73
At 155°C ^a							
PLA							
0		184.1	34.1			175.5	28.81
11.9		183.9	38.3			175.3	31.45
20		185.4	37.3			165.6 and 174.8	29.5
30		185.6	37.0			167.0 and 176.3	32.5
40		171.6 and 183.6	35.1			166.3 and 176.0	27.7
50		180.6	36.9			167.4 and 175.0	30.8

^a Annealing treatment at 100 and 155°C.

^b T_{c2} , crystallization temperature at about 150°C.

^c T_m , melting temperature.

^d ΔH_m , fusion enthalpy.

Table II DSC Data for Cornstarch and PLA Blends with Varied Initial MCs

Samples	First Crystallization			Second Crystallization		Melting	
	T_g (°C)	T_{c1} (°C)	ΔH_{c1} (J/g)	T_{c2} (°C)	ΔH_{c2} (°C)	T_m (°C)	ΔH_m (J/g)
MC (%) Extrudate							
Pure PLA	60.5					172.2	45.4
0	61.9	102.3	-10.29	158.4	-0.97	172.4	19.78
11.9	57.4	102.2	-9.22	155.1	-0.47	169.2	18.98
20	59.2	102.3	-13.2	156.2	-0.86	170.4	19.15
30	60.1	103.3	-13.69	159.1	-0.53	173.1	18.66
40	56.9	103.2	-13.11	156.4	-0.46	170.1	17.32
			-13.77				
50	56.8	102.8	155.6	-0.23	169.9	21.42	
Compression-molded							
Pure PLA	61.6					172.7	39.5
0						174.5	31.5
11.9						175.1	32.47
20						176.6	33.38
30						177.7	32.09
40						170.5 and 176.1	33.2
50						170.4 and 176.6	32.7
Injection-molded							
Pure PLA	61.8	98.8	-23.3	157.7	-2.67	175.1	40.37
0	62.7	92.6	-13.47	152.5	-0.82	168.9	25.45
11.9	59.8	90.5	-14.7	153.6	-1.35	170.2	26.74
20	61.4	94.0	-15.5	154.7	-1.95	169.4	24.62
30	61.3	94.8	-14.08	157.6	-1.69	175.8	26.86
40	61.8	96.0	-13.9	154.5	-1.71	168.4	22.72
50	62.4	96.5	-13.28	155.5	-1.17	169.9	22.93

T_g , glass transition temperature; T_c , crystallization temperature at about 100°C (T_{c1}) and about 150°C (T_{c2}).
 ΔH_c : crystallization enthalpy.
 ΔH_m : fusion enthalpy.

molding were similar to those made with the annealing treatment [Fig. 1(3, 4, 5, 8); Tables I and II].

The glass-transition temperature (T_g) of the blend was in the vicinity of 60°C (Table II), and the endothermal baseline shift was associated with an aging peak.²¹ The glass transition could not be clearly revealed by DSC for the compression-molded and annealed samples but was still observed by dynamic mechanical analysis (DMA; shown later in Fig. 7). Similarly, the aging peak disappeared for the compression-molded and annealed samples, which suggested that the compression molding and annealing had a deaging effect. The melting temperatures for the blends prepared by compression molding or annealing treatment were higher than those for blends prepared by injection molding or extrusion (Fig. 2; Tables I and II) because the crystallinity of the blend prepared by compression molding or an-

nealing treatment was higher than that prepared by injection molding or extrusion.

The crystallinities of the blends estimated from the DSC thermograms are presented in Figure 2. The MC of the starch had little effect on the crystallinities of the starch and the PLA blends. However, crystallinity varied significantly among the blends prepared with different processing methods and annealing temperatures. Crystallinities for the blends prepared by compression molding were similar regardless of annealing treatments and were higher than those of blends prepared by injection molding or extrusion (Fig. 2). For the blends prepared by injection molding, the crystallinity was significantly affected by annealing temperature. The effects of processing procedures on crystallinity followed the order of compression molding: annealing at 155 or 100°C \geq compression molding $>$ injection molding (an-

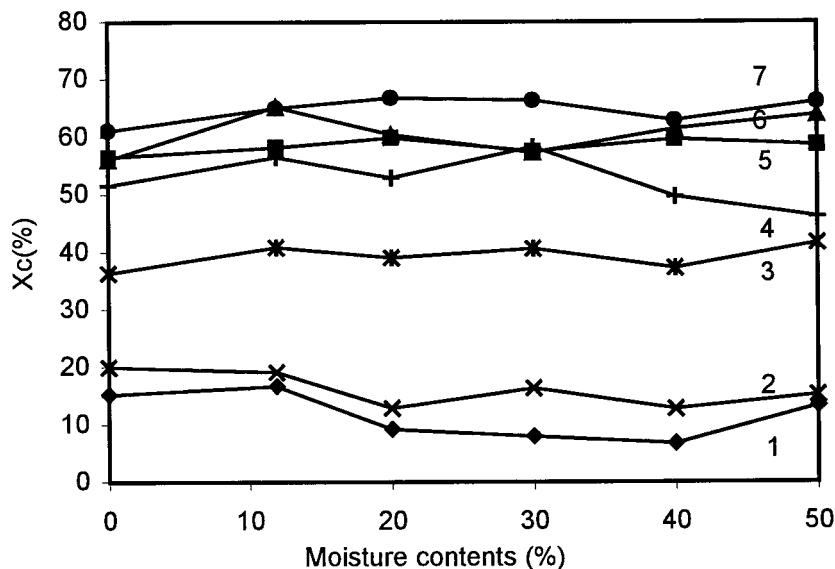


Figure 2 Crystallinity of cornstarch and PLA blends at a 40:60 ratio with varied initial MCs as estimated from DSC thermograms: (1) extrudates, (2) injection-molded sample, (3) injection-molded sample annealed at 100°C, (4) injection-molded sample annealed at 155°C, (5) compression-molded sample, (6) compression-molded sample annealed at 100°C, and (7) compression-molded sample annealed at 155°C.

nealing at 155°C) > injection molding (annealing at 100°C) > injection molding = extrusion (Fig. 2). For compression molding, the sample was cooled in the mold at room conditions, which were slow enough for crystal formation. For injection molding, the sample was cooled in the mold with tap water, which was quenching and resulted in

less crystal formation. Similarly, for extrusion, the sample temperature was about 185°C before the die and then was suddenly dropped to room temperature, which was fast cooling and also caused low crystallinity. The annealing treatment enhanced the crystallinity of the blends. However, the crystallinity of the blends prepared by

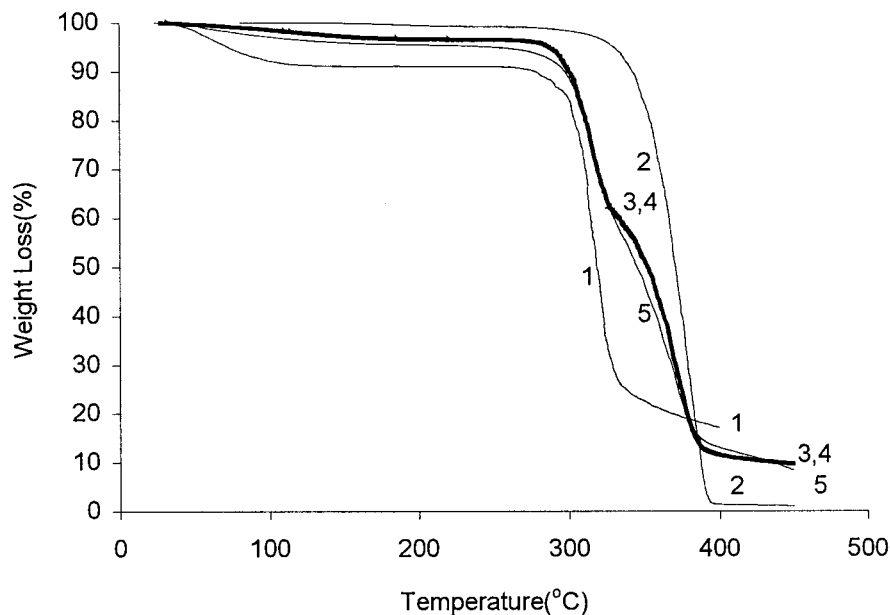


Figure 3 TGA thermograms of (1) native cornstarch, (2) pure PLA, and blends of cornstarch and PLA at a 40:60 ratio with (3) 11.9, (4) 30, and (5) 50% MC.

Table III Decomposition Temperatures and Weight Loss of Corn Starch and PLA (40 : 60) Blends (Extrudate) as Measured by a Thermogravimetric Analyzer

Sample	Starch in Blend			PLA in Blend		
	Onset (°C)	Endset (°C)	Maximum (°C) ^a	Onset (°C)	Endset (°C)	Maximum (°C) ^a
Cornstarch	299.8	331.7	317.5			
Pure PLA				351.3	389.8	370.7
Blend with 10% MC	301.8	322.5	314.3	347.5	384.8	367.7
Blend with 30% MC	299.6	325	314.1	348.1	384.9	367.2
Blend with 50% MC	297.8	327.2	313.6	341	382.7	362

^a Maximum rate of decomposition.

injection molding and then annealing was even lower than that of blends prepared by compression molding. Crystal formation might have been

easier from slow cooling directly from the melt than that from annealing of a solid stable structure formed by fast cooling.

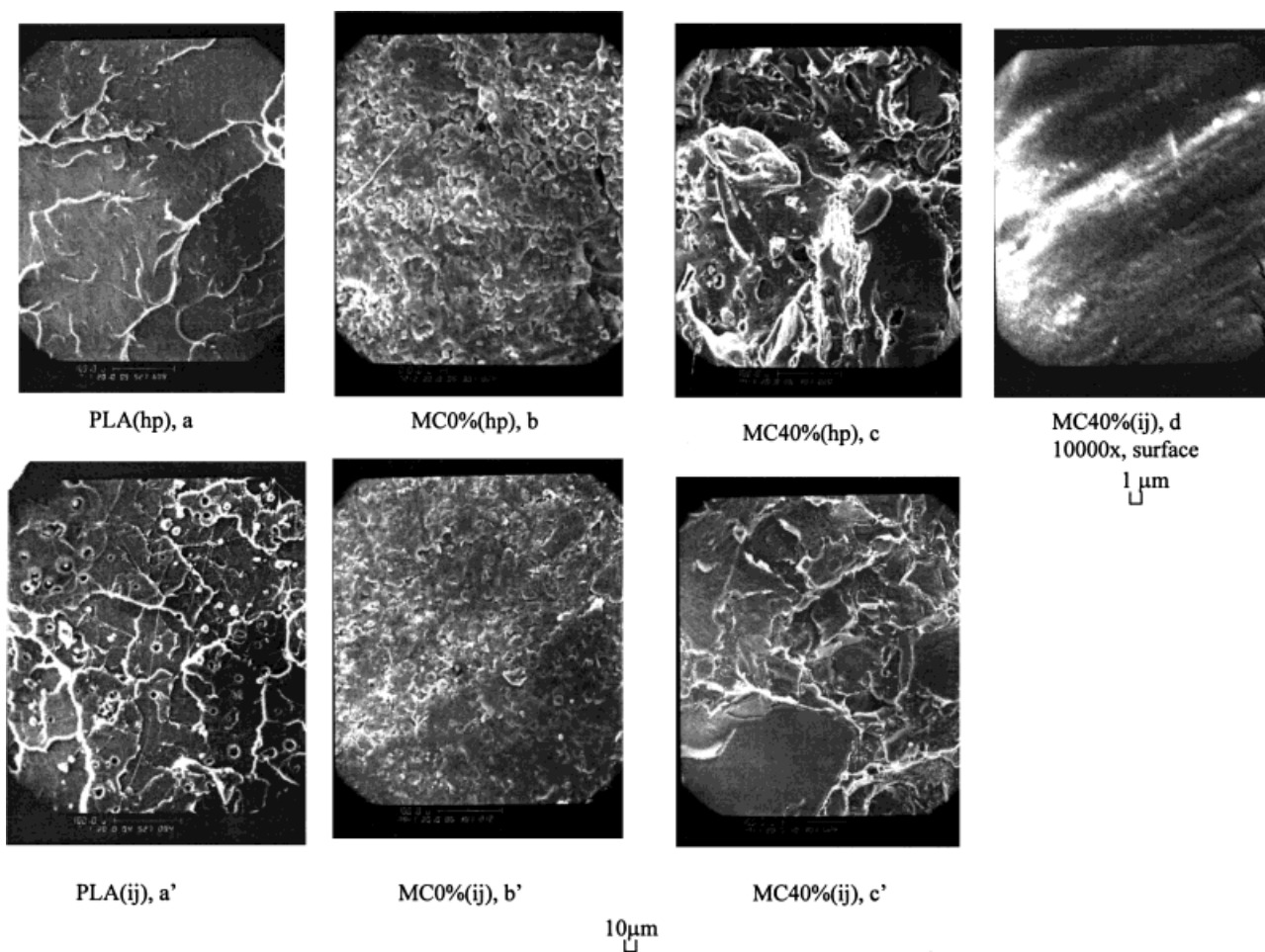


Figure 4 SEM micrographs of pure PLA and blends of cornstarch and PLA at a 40:60 ratio: (a) compression-molded pure PLA, (a') injection-molded pure PLA; (b) compression-molded sample with 0% MC, (b') injection-molded sample with 0%MC, (c) compression-molded sample with 40% MC, (c') injection-molded sample with 40% MC, and (d) injection-molded sample with 40%MC (surface, 10,000×).

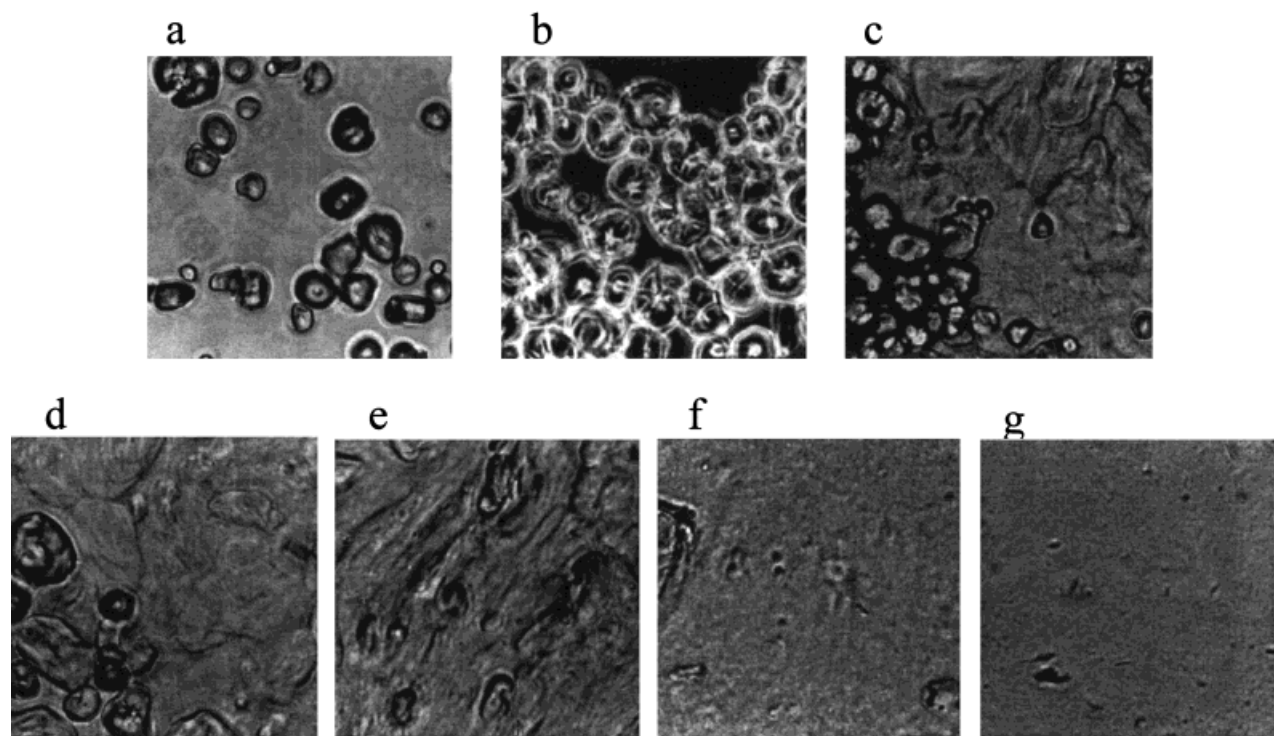


Figure 5 Photographs of (a) native cornstarch and starches extracted from the starch and PLA blends at a 40:60 ratio with (b) 0, (c) 11.9, (d) 20, (e) 30, (f) 40, and (g) 50% MC.

The thermogravimetric analysis (TGA) thermograms of selected samples are presented in Figure 3, and the thermogravimetric data are shown in Table III. For pure PLA, the thermal decomposition started at 351.3°C and ended at 389.8°C with a decomposition temperature of 370.7°C. For native starch, the corresponding decomposition temperatures were 299.8, 331.7, and 317.5°C. As expected, the decomposition curves of the starch and PLA blends were in between those of native starch and pure PLA (Fig. 3). For the PLA extracted from the blends with 10% MC (Table III), the decomposition temperature was about 3–5°C lower than that of pure PLA, indicating that PLA became slightly degraded in the presence of water during processing. The PLA degradation remained the same as the MC increased up to 30% but increased slightly as the MC increased

to 50% (Table III). A similar trend was observed for the starch extracted from the blends. Starch chains would be cut short at a high shear rate in the presence of high moisture and then could be decomposed easily.

Structure

The fracture structures of cross sections of selected samples are presented in Figure 4. Pure PLA had a smooth fracture structure [Fig. 4(a, a')], and the blends of starch and PLA had a typical two-phase polymer blending structure [Fig. 4(b, b', c, c')]. At 0% MC, the starch was embedded in the continuous PLA matrix as a filler and remained as granules because of its poor gelatinization [Fig. 4(b, b')]. As the MC increased, for example at 40% [Fig. 4(c, c')], starch became

Table IV Gelatinization Degree of Cornstarch in Blends (Cornstarch/PLA-40 : 60) with Varied MCs

Sample (MC)	Native cornstarch	0%	11.9%	20%	30%	40%	50%
ΔH_G (J/g)	14.13	6.58	3.52	2.1	1.34	~ 0	~ 0
Gelatinization (%)	0	43.4	75.1	85.2	90.5	~ 100	~ 100

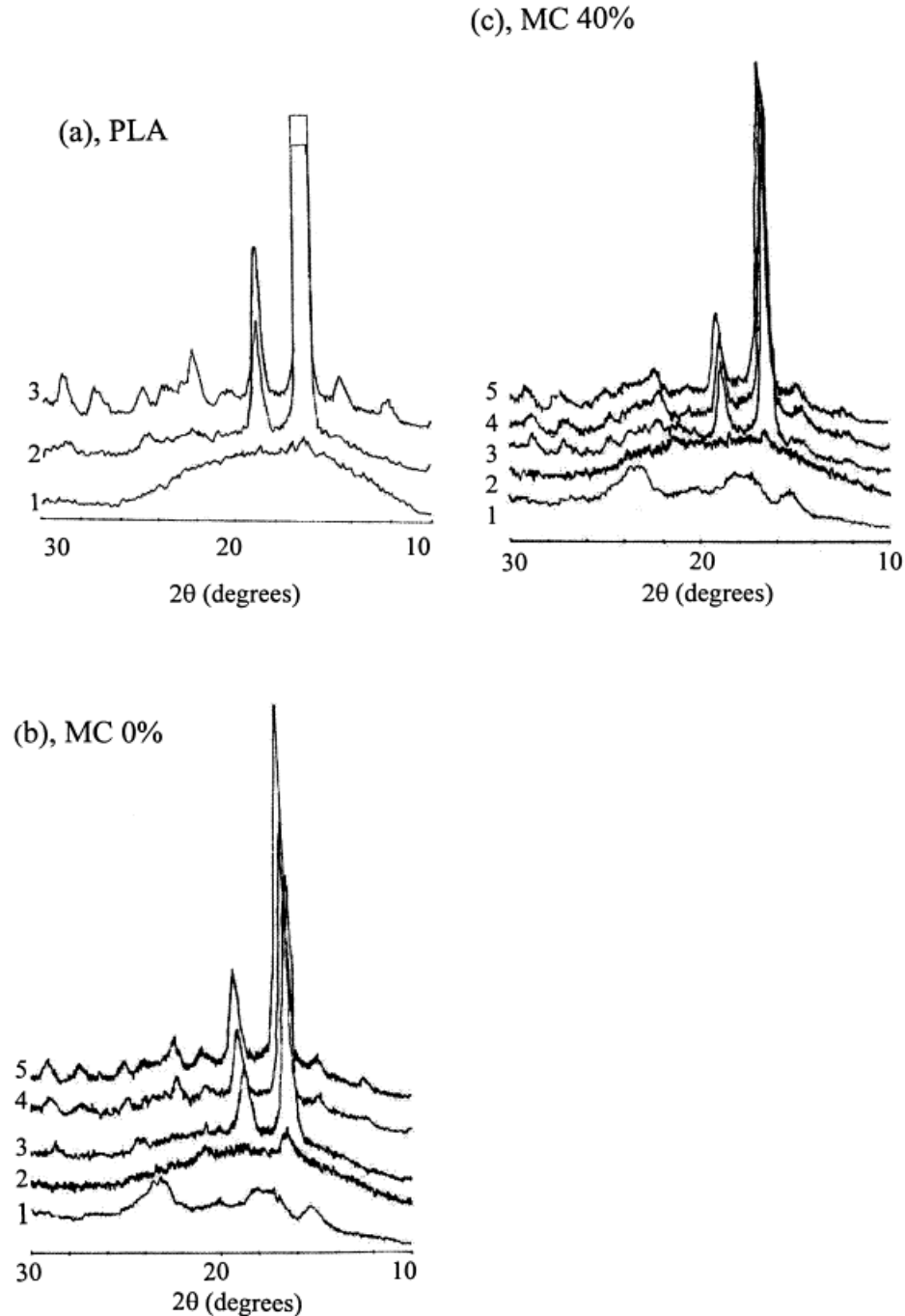


Figure 6 X-ray diffraction scattering graphs of (a) pure PLA blends of starch and PLA at a 40:60 ratio with (b) 0 and (c) 40% MC. For graph (a), the pure PLA was (1) injection molded and (2) then annealed at 100 and (3) 155°C. For graphs (b) and (c), the curve numbers corresponded to (1) native cornstarch, (2) injection-molded sample, (3) injection-molded sample annealed at 100°C, (4) compression-molded sample, and (5) compression-molded sample annealed at 100°C.

more gelatinized, fewer starch granules were observed, blends became uniform, and the state of starch in the blends could not be observed clearly

because of the uniformity. In this case, larger magnified SEM pictures (10,000 \times) of a sample surface with 40% MC were performed to the ob-

Table V FTIR C=O Stretching Vibrating Absorption of Pure PLA, Isolated PLA from the Starch/PLA Blend, and the Starch/PLA Blend at 0 and 40% MCs

Sample	PLA	Isolate PLA ^a	mc00hp ^b	mc00ij ^c	mc40hp ^d	mc40ij ^e
γ_{CO} ^f (cm ⁻¹)	1758.8	1759.1	1763.8	1765.8	1764.4	1763.1

^a PLA was separated from the starch/PLA blend with 0% MC.

^b Compression-molded sample blended from 0% MC starch and PLA.

^c Injection-molded sample blended from 0% MC starch and PLA.

^d Compression-molded sample blended from 40% MC starch and PLA.

^e Injection-molded sample blended from 40% MC starch and PLA.

^f γ_{CO} : wave number.

serve the morphology of the starch in the blends. Some small particles (about or less than 1 μm) were observed [Fig. 4(d)], indicating that the starch was completely gelatinized in the blends with 40% MC. However, the gelatinized starch in the blends was still packed as fine particles but was dispersed more uniformly.

Starch granule structures at varied MCs as measured by microscopic examination are presented in Figure 5, and their corresponding gelatinization degrees as measured by DSC are shown in Table IV. At 0% MC, most starch still remained as granules, although some granules were ruptured during extrusion by heat and shear force [Fig. 5(b)] as compared to the native starch [Fig. 5(a)]. As the MC increased, starch became more gelatinized, and intact starch granules were reduced and became swollen [Fig. 5(c, d, e)]. As moisture continued increasing to 40 or 50%, starch became fully gelatinized (Table IV), and no granular structure was observed [Fig. 5(f, g)].

X-ray scattering patterns of pure PLA and starch and PLA blends with 0 and 40% MC prepared by compression and injection molding before and after annealing treatment are presented in Figure 6. For pure PLA extrudates [Fig. 6(a-1)], two small peaks were observed, one was at about 18–20°C and the other at about 16–18°C, indicating low crystallinity because of the fast cooling rate after extrusion. After annealing at 100°C, two large peaks appeared [Fig. 6(a-2)] because of the increase in crystallinity during the annealing treatment; one was at about 18.8°C, and the other was at about 16.2°C. These two peaks became larger after annealing at 155°C, and many small peaks appeared between 20 and 30°C and 12 and 14°C [Fig. 6(a-3)]. Native cornstarch showed an A-type X-ray pattern [Fig. 6(b-1)], which was in agreement with the results reported by Whistler et al.²⁰ The X-ray patterns for the blends were similar to those for pure PLA, indicating that

starch had little effect on crystallinity [Fig. 6(b)]. The blends prepared by compression molding [Fig. 6(b-4)] had larger peaks (higher crystallinity) than those prepared by injection molding [Fig. 6(b-2)]. The blends prepared by compression molding and then annealing [Fig. 6(b-5)] had larger peaks than that those prepared by injection molding and then annealing [Fig. 6(b-3)]. The X-ray patterns of the blends with 40% MC [Fig. 6(c)] were similar to those with 0% MC [Fig. 6(b)], indicating that starch gelatinization did not significantly affect the crystallization of the blend. The X-ray results confirmed those from the DSC measurements.

FTIR was performed to investigate possible interactions between PLA and starch (Table V). No peak shift was observed at the carbonyl stretching vibrating absorption as compared with pure PLA that was injection-molded and the PLA extracted from an injection-molded blend. Also, no peak shift was observed between samples with 0 and 40% MC or those prepared by compression and injection molding, indicating that starch gelatinization and molding methods had no effect on chemical reactions or structural changes of the starch and the PLA blending system. However, about a 5 cm⁻¹ shift was observed between the peak for pure PLA and those for the starch and PLA blends (Table V), which was caused by the carbonyl stretching vibration. This indicated that a weak interaction, possibly some hydrogen bonding, might have existed between starch and PLA because of the carbonyl groups in the PLA and hydroxyl groups in the starch.

Mechanical Properties

The samples prepared by injection molding had higher tensile strengths and elongation but lower moduli and lower crystallinities compared to those prepared by compression molding (Table

Table VI Mechanical Properties of Starch and PLA Blends (40/60) at Varied MCs

Sample	Compression-Molded			Injection-Molded		
	Tensile Strength (MPa)	Elongation Break (%)	Modulus (GPa)	Tensile Strength (MPa)	Elongation Break (%)	Modulus (GPa)
Pure PLA	61 ^a	6.33 ^a	1.20 ^a	64.0 ^a	7.40 ^a	1.12 ^a
Blends with MC						
0	29.6 ^b	2.10 ^b	1.6 ^b	35.8 ^b	4.39 ^b	1.06 ^b
11.9	27.1 ^c	1.71 ^c	1.8 ^c	36.6 ^{b,c}	4.38 ^b	1.03 ^b
20	25.7 ^{c,d}	1.89 ^d	1.68 ^b	38.3 ^{c,d}	4.76 ^b	1.00 ^b
30	25.5 ^{c,d}	1.64 ^{c,e}	1.76 ^d	37.3 ^{c,d}	4.40 ^b	1.00 ^b
40	24.7 ^{d,e}	1.67 ^{c,e}	1.76 ^d	37.9 ^{c,d}	4.30 ^b	0.99 ^b
50	23.4 ^{e,f}	1.81 ^{c,d}	1.57 ^b	32.9 ^e	4.87 ^b	0.81 ^c

Results are based on least significant difference (LSD) procedure at the $\alpha = 0.05$ level; means with the same letter in the same row are not significantly different.

VI). Under the processing conditions used in this study, the blends made by injection molding had fewer voids and fewer cracks than those prepared by compression molding. Besides, the heating history of these two molding methods was different, which might be the reason for the difference in properties. Starch gelatinization had slight effects on the tensile strength of the blends prepared by compression molding (Table VI). The morphology of the gelatinized starch in the blends would affect the effective cross-section area of the continuous phase, and the voids in the blends would concentrate stress and act as crack initiators. As MC increased, the degree of starch gelatinization increased, and starch became more dispersible, which produced more voids and resulted in a reduction in tensile strength. For injection-molded samples, MC had almost no effect on the mechanical properties of the blend because of fewer voids and fewer cracks. However, as MC increased to 50%, the tensile strength reached the lowest value because the PLA degradation at 50% MC was larger than that at lower MCs, based on the decomposition results (Table III).

Dynamic Mechanical Properties

Two transitions were observed on the DMA curves (Fig. 7), one associated with the glass transition at about 60°C and the other with melting at about 150°C. The samples prepared by compression molding [Fig. 7(a-3)] demonstrated very different thermal viscoelastic behaviors than those prepared by injection molding [Fig. 7(a-1)]. For the compression-molded sample, the storage modulus decreased sharply at its T_g and then leveled

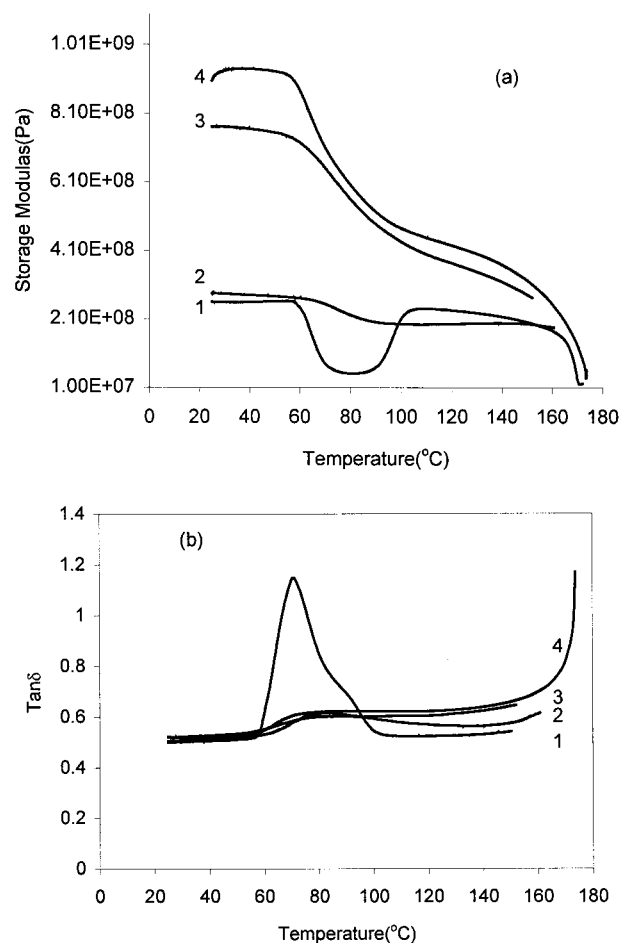


Figure 7 (a) DMA storage modules and (b) tan δ of blends of cornstarch and PLA at a 40:60 ratio. Curve numbers in (a) and (b) corresponded to (1) injection-molded sample, (2) injection-molded sample annealed at 100°C, (3) compression-molded sample, and (4) compression-molded sample annealed at 100°C.

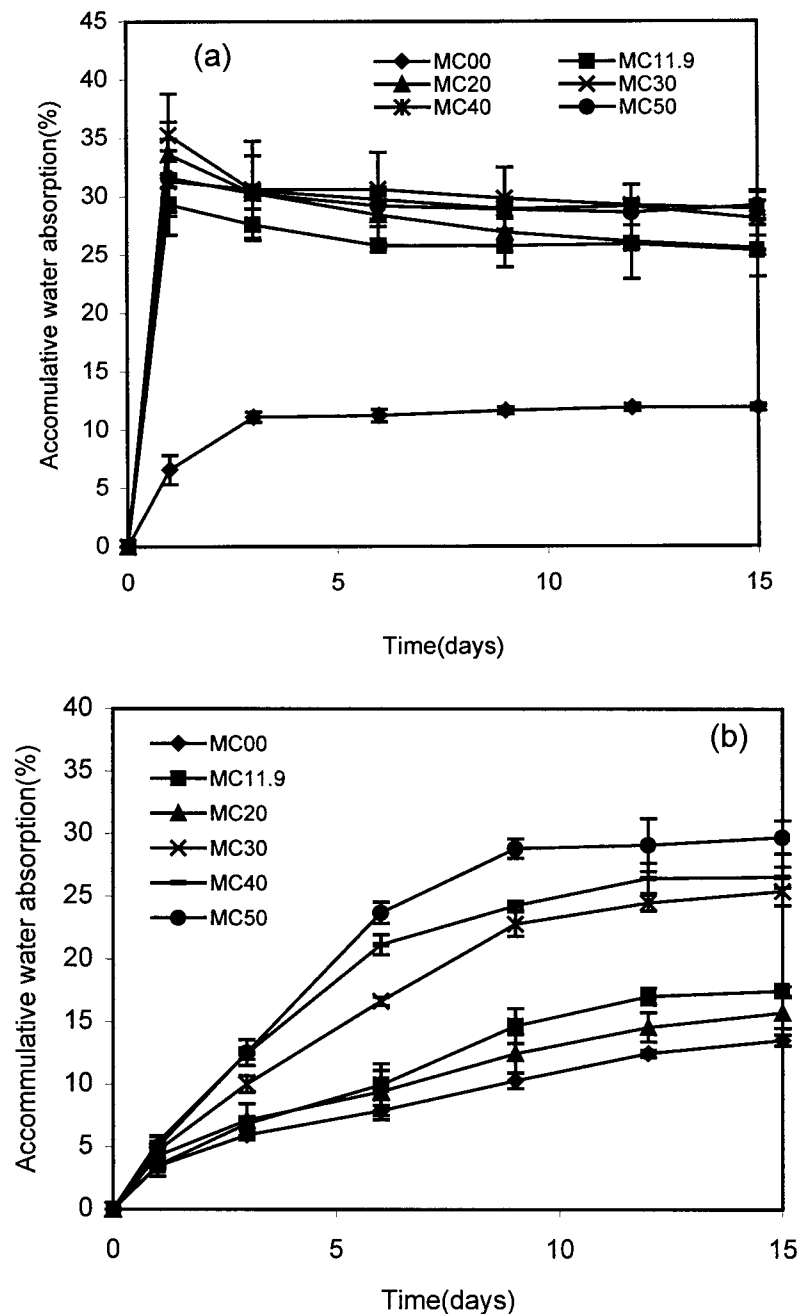


Figure 8 Water absorption of cornstarch and PLA blends at a 40:60 ratio with varied initial MC levels in room conditions for 15 days: (a) compression-molded and (b) injection-molded samples.

off until melting. For the injection-molded sample, the storage modulus dropped suddenly at its T_g , leveled off at about 95°C, increased fast stopping at about 105°C, and then leveled off until its melting. These were typical thermal viscoelastic behaviors of semicrystalline polymers. At T_g , the molecular mobility of the blends increased because of their amorphous component, causing a decrease in modulus.

Because the crystallinity of the injection-molded sample was low, further cold crystallization occurred in the temperature range from 95 to 105°C, resulting in an increase in modulus [Fig. 7(a-1)].

The thermal viscoelastic behaviors of the annealed samples prepared by either compression [Fig. 7(a-4)] or injection molding [Fig. 7(a-2)] were similar to that of compression-molded samples

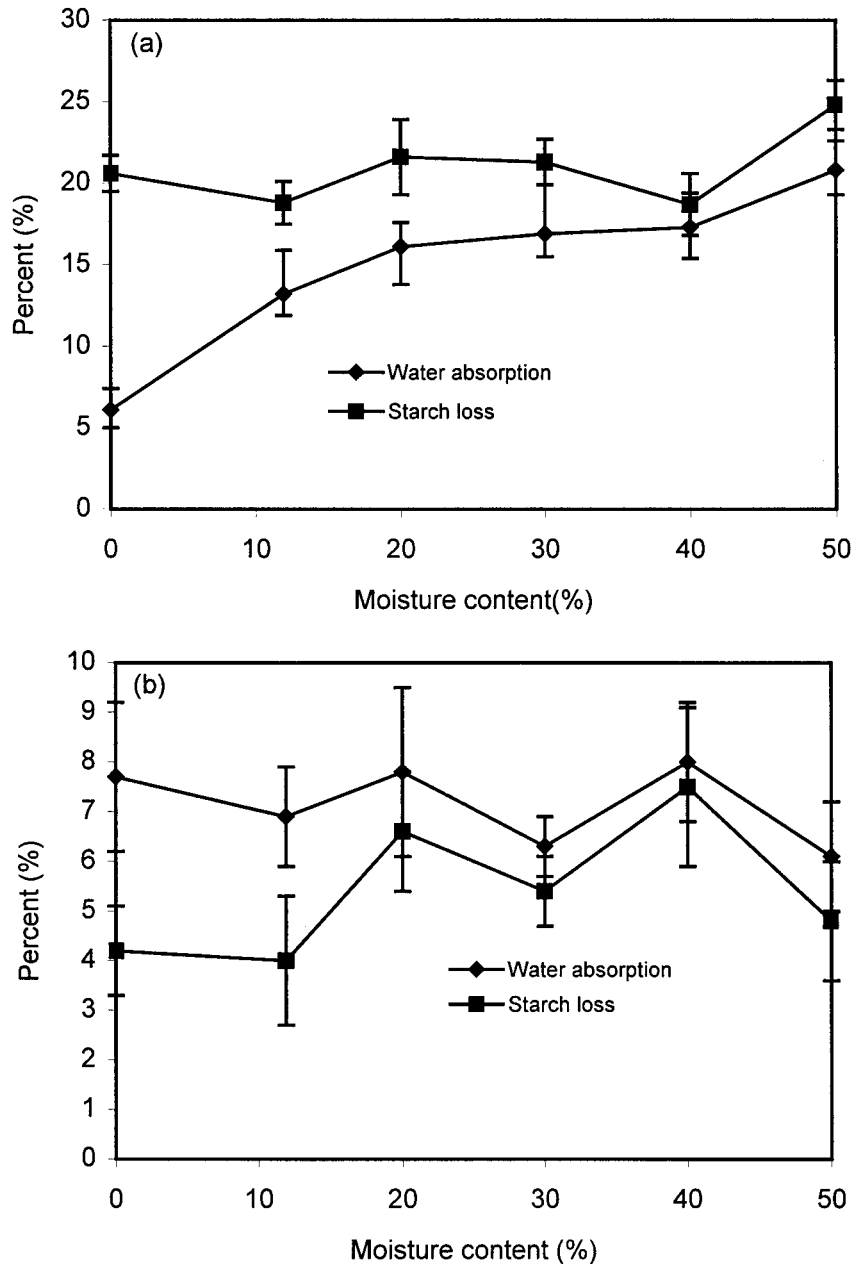


Figure 9 Water absorption of cornstarch and PLA blends at a 40:60 ratio with varied initial MC levels in boiling water for 1 h: (a) compression-molded and (b) injection-molded samples.

[Fig. 7(a-3)], except that the initial modulus of the annealed samples (at 25°C) prepared by compression molding was higher than for the samples before annealing treatment or samples prepared by injection molding. This was caused by the difference in their crystallinities (Fig. 2). The corresponding DMA curves of $\tan \delta$ are presented in Figure 7(b). The sample prepared by injection molding gave the largest $\tan \delta$ value, indicating that the

injection-molded sample contained more amorphous components than the samples prepared by compression molding or by annealing treatment. This was in agreement with the crystallinity analysis done by the DSC and X-ray scattering methods.

Water Absorption

The water absorption of the blends was affected by MC (Fig. 8). For compression molding [Fig.

8(a)] with 0% MC, it took about 3 days for the blends to be saturated, and then the water absorption leveled off at about 11% during 15 days of water soaking. In the presence of moisture regardless of MC levels, it took about only 1 day for the blends to be saturated, and then the water absorption leveled off; it increased slightly but not significantly as MC increased. This was mainly caused by the voids and cracks in the blends where water could penetrate more easily and contact with starch. For compression-molded samples in this study, the existence of voids in the blends was the main factor affecting water absorption. For injection molding [Fig. 8(b)], the sorption rates of all blends were slow, and water absorption increased as MC increased. As MC increased, starch became more gelatinized and more uniformly dispersed in the PLA matrix, resulting in an increase in the contact surface area of the starch phase at the interface. Similarly, it increased the contact area of the starch with water on the surface of the sample.

Water absorption by the samples prepared by compression molding in boiling water for 1 h increased as MC increased and was higher than that of injection-molded samples (Fig. 9). The amount of starch leached into water was not affected by the MC for either compression-molded or injection-molded samples but was higher for the samples prepared by compression molding. For the injection-molded samples, water absorption was not affected significantly by MC.

CONCLUSION

MC had few effects on PLA thermal and crystallization properties or on interactions between starch and PLA.

The crystallinity of the blends was affected significantly by processing conditions. Blends prepared by compression molding had higher crystallinity than those prepared by injection molding. Blends annealed at the second crystallization temperature (155°C) gave higher crystallinity than those annealed at the first crystallization temperature or those without annealing treatment. Blends prepared by compression molding had similar crystallinity to the annealed blends because of the slow cooling rate. Blends prepared with injection molding had the lowest crystallinity.

The starch gelatinization degree increased as MC increased. Blends with low MC had a typical particle-filling structure where starch granules were embedded in the PLA matrix. As MC in-

creased, starch became more gelatinized, and blends became uniform, but some smaller particles (about or less than 1 μm) still existed in the blends. The samples prepared by injection molding had higher tensile strengths and elongation but lower moduli and lower crystallinities compared to those prepared by compression molding. Starch gelatinization did not have a significant effect on the mechanical properties.

Water absorption of the blends increased as MC increased but was affected more strongly by the voids in the blends. Samples made by injection molding had lower water absorption than those made by compression molding.

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