

Mechanical and Thermal Properties of Poly(lactic acid)/Starch Blends with Dioctyl Maleate

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ABSTRACT: Poly(lactic acid) (PLA)/starch blends were prepared blending with dioctyl maleate (DOM). DOM acted as a compatibilizer at low concentrations (below 5%), and markedly improved tensile strength of the blend. However, DOM functioned as a plasticizer at concentrations over 5%, significantly enhancing elongation. Compatibilization and plasticization took place simultaneously according to the analysis of, for example, mechanical properties and thermal

behavior. With DOM as a polymeric plasticizer, thermal loss in the blends was not significant. Water absorption of PLA/starch blends increased with DOM concentration. DOM leaching in an aqueous environment was inhibited. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1697–1704, 2004

Key words: mechanical properties; poly(lactic acid)/starch blends; dioctyl maleate; thermal behavior

INTRODUCTION

Poly(lactic acid) (PLA) and starch are two promising candidates for biodegradable polymer blends. However, hydrophobic PLA and hydrophilic starch are thermodynamically immiscible leading to poor adhesion between the two components, resulting in poor and irreproducible performance. Two approaches are usually used to improve blend compatibilization.¹ The first approach is to introduce a third component into the polymer system, reducing the interfacial energy, improving dispersion, and consequently enhancing adhesion between binary polymer phases. A block copolymer, for instance, is often used. The second method is reactive blending. In principle, this approach promotes chemical reactions between the two polymers in a molten state, often by introducing either a reactive third component with appropriate functional groups or a catalyst. The second approach is generally more economical than the first.

Efforts have been made to improve the mechanical properties of PLA/starch blends by introducing a reactive compatibilizer or coupling agent to enhance interfacial interactions.^{2–5} Methylenediphenyl diisocyanate (MDI) is one of the most efficient coupling agents for improving mechanical properties of a PLA/starch blend by creating a strong chemical urethane linkage between the carboxyl and hydroxyl groups from PLA and starch, respectively.⁵ However, MDI is

highly toxic.^{2,3} Research has focused on finding a less toxic agent to improve mechanical properties.⁴ In a previous work,⁴ maleic anhydride (MA) was used as a nontoxic reactive compatibilizer to improve mechanical properties of PLA/starch blends in extrusion. A PLA/starch blend (55/45) with 1% MA and 10% initiator (MA basis) had a tensile strength of 52.4MPa, significantly higher than the 30.0MPa of a virgin PLA/starch (55/45) blend. However, elongation at break remained almost the same as the virgin PLA/starch (55/45) blend. Plasticizers improved the blend's elongation but also reduced tensile strength.^{6,7} The plasticizer in the blend also suppressed compatibilizer efficiency.⁷

This study is a step toward investigating the influence of a polymeric dioctyl maleate, a derivative of MA, on tensile strength and elongation of PLA/starch blends.

EXPERIMENTAL

Materials and sample preparation

PLA, supplied by Shimadzu, Inc. (Tokyo, Japan), had a weight-average molecular weight \overline{M}_w of 120 kDa and was 99% polymerized from L-lactic acid. Wheat starch was purchased from Midwest Grain Products, Inc. (Atchison, KS) with an amylose content of 23–28% and an average particle size of 18 μm . Bis (2-ethylhexyl) maleate or dioctyle maleate (DOM) with density of 0.944g/cm³ was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI).

PLA pellets were ground by a laboratory mill (Model 4 Laboratory Mill, Thomas-Wiley Co., Philadelphia, PA) into 2 mm particles before blending to make dispersion better. Wheat starch was dried in an

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oven at 135°C up to 2 h. PLA/starch at a fixed ratio of 55/45 with various DOM contents was extruded using a twin-screw extruder (TW-100, Haake, Paramus, NJ) with 19.1 mm screw diameter and 25 L/D. The processing temperature profile was set at 125, 185, and 180°C from feed inlet to the die. The pelletized extrudates were ground again using the same mill into 2 mm particles for molding. Dog-bone shaped tensile bars, following ASTM Method D 638–91, were hot compression-molded at 180°C, 5.5 MPa for 3 min by a Carver hot press (Model 3889, Carver Inc., Wabash, IN), then cooled to room temperature under ambient conditions. All molded tensile bars were preconditioned at 25°C and 50% RH for 48 h to relax internal stress prior to mechanical testing.

Mechanical and thermal properties measurement

Tensile tests were carried out with an Instron universal testing machine (Model 4465, Canton, MA) at room temperature using a crosshead rate of 5 mm/min.

Thermal characteristics of PLA/starch/DOM blends were determined by differential scanning calorimetry (DSC) (Perkin–Elmer Pyris 1, Norwalk, CT) from 0 to 200°C at a scanning rate of 10°C/min under protection of nitrogen flow. All results were obtained from the second DSC scan to eliminate different thermal history effects. Crystallinity was estimated according to the following equation⁸:

$$\chi_c = \frac{\Delta H_m / \phi_{PLA}}{\Delta H_m^0} \times 100\% \quad (1)$$

where ΔH_m and ΔH_m^0 are enthalpies (J/g) of fusion of blend and PLA crystal of infinite size with a value of 93.6 J/g, respectively; ϕ_{PLA} PLA fraction in the blend.

A dynamic mechanical analyzer (DMA) (Perkin–Elmer Pyris DMA7e (Norwalk, CT)) was used for a three-point bending test at a frequency of 1Hz. Scanning temperature was set from 0 to 160°C at a heating ramp of 3°C/min.

TABLE I
Effect of Dioctyl Maleate (DOM) on Mechanical Properties of Poly(lactic acid)/Starch (55/45) Blends

Blends	Tensile strength (MPa)	Elongation (%)
PLA/starch (55/45)	30.0 ± 2.6	2.68 ± 0.05
PLA/starch/DOM (55/45/0.5)	40.0 ± 3.2	2.37 ± 0.27
PLA/starch/DOM (55/45/1.0)	41.2 ± 4.1	2.21 ± 0.17
PLA/starch/DOM (55/45/2)	43.6 ± 3.7	2.38 ± 0.34
PLA/starch/DOM (55/45/5)	26.7 ± 1.8	2.71 ± 0.71
PLA/starch/DOM (55/45/8)	24.9 ± 2.0	3.30 ± 0.46
PLA/starch/DOM (55/45/10)	19.9 ± 2.7	24.3 ± 7.8
PLA/starch/DOM (55/45/15)	16.2 ± 0.9	36.0 ± 4.4

TABLE II
Effect of Adding Initiator L101 on Mechanical Properties of Poly(lactic acid) (PLA)/Starch (55/45) Blend with Dioctyl Maleate (DOM)

Blends	Tensile strength (MPa)	Elongation (%)
PLA/starch/DOM/L101 (55/45/1/0.1)	41.2 ± 3.1	2.79 ± 0.21
PLA/starch/DOM/L101 (55/45/2/0.1)	43.4 ± 2.9	2.40 ± 0.17
PLA/starch/DOM/L101 (55/45/5/0.1)	32.8 ± 2.0	2.17 ± 0.22
PLA/starch/DOM/L101 (55/45/8/0.1)	27.8 ± 3.1	2.49 ± 0.40
PLA/starch/DOM/L101 (55/45/10/0.1)	24.1 ± 2.4	29.8 ± 4.6
PLA/starch/DOM/L101 (55/45/15/0.1)	19.0 ± 1.2	44.2 ± 2.1

RESULTS AND DISCUSSION

Mechanical properties

As reported by Zhang and Sun,⁴ MA reacted with free radicals of PLA induced by an initiator, forming stable chemical bonds, as shown by improved mechanical properties. DOM, a derivative of MA with a chemical structure similar to MA, contained the same carboxyl groups as PLA, making it miscible with PLA. A virgin blend of PLA/starch (55/45) showed a typical brittle characteristic with a tensile strength of 30.0 MPa and elongation of 2.68%. By adding liquid DOM to a PLA/starch (55/45) blend, the tensile strength of the blend increased to a remarkable 40.0 MPa at 0.5% DOM (Table I) and reached a maximum value of 43.6 MPa at 2% DOM. Elongation of the blend remains almost the same in the range from 0 to 8% DOM. On further increasing DOM, the corresponding elongation was dramatically extended to 24.3% at 10% DOM, almost 7 times the elongation at 8% DOM, while tensile strength decreased to 19.9 MPa. The elongation then increased to 36.0% and tensile strength reduced to 16.2 MPa at 15% DOM. There is probably a critical percentage of DOM between 8 and 10% that forms a continuous plasticizer phase. From Table I, it appears that the varying function of DOM in the blend depends on its concentration: at lower concentration, DOM acted as a compatibilizer, while it acted as a plasticizer when the concentration was 10% or higher. This is a newly identified function of DOM. Either compatibilizer or plasticizer is closely related to its chemical structure, particularly its surface chemical end groups. A compatibilizer should have functional groups that can react with matrix or a substance to reduce the interfacial tension of two polymers. A plasticizer is often in a liquid dispersion form or dispersed in a matrix. DOM has a similar structure to MA and acts as a compatibilizer at lower concentrations; while at higher concentrations, DOM is in liquid droplet form, appearing

TABLE III
Effect of Combined Dioctyl Maleate (DOM) with Coupling Agent Maleic Anhydride (MA) on Mechanical Properties of Poly(lactic acid)/Starch Blend

Blends	Tensile Strength (MPa)	Elongation (%)
PLA/starch/MA/L101/DOM (55/45/1/0.1/10)	26.4 (1.0)	21.1 (7.2)
PLA/starch/MA/L101/DOM (55/45/1/0.1/15)	23.8 (1.4)	36.2 (6.1)

as a plasticizer while its compatibilizer ability is suppressed by the enhanced mobility of its chains.

The initiator plays a key role in improving compatibility and mechanical properties of PLA/starch blends compatibilized by MA. Mechanical properties of PLA/starch blends with up to 2% DOM in the presence of initiator L101 were not improved (Table II). However, at higher DOM concentrations, the addition of an initiator improved tensile strength and elongation of the blends. Though DOM has no potential to form stable chemical bonds with PLA or starch, in the presence of L101, the improved mechanical properties suggested that DOM might physically absorb free PLA chain radicals.

The PLA/starch blend with 10% or higher DOM coupled with MA/L101 had significantly higher tensile strength (Table III) than blends without MA/L101 (Table I), while the elongation remained almost the same. This indicates that the combination of DOM and MA takes advantage of the merits of each, that DOM gives the blend a fair elongation, and MA significantly improves tensile strength.

Thermal properties

DSC thermal behavior of PLA/starch blends with various DOM contents is shown in Figure 1. The control PLA/starch blend without DOM had a glass transition temperature (T_g) of 57.3°C, a cold-crystallization temperature of 101.8°C, and a single melting peak; and its melting temperature is 167.6°C (Table IV). Adding 1% DOM slightly decreased T_g to 54°C, and increased cold-crystallization temperature to 107.3°C. The T_g s of the samples shifted toward lower temperatures when DOM content was further increased (Fig. 1), while the T_g at each DOM concentration was still lower than the acetyl triethyl citrate (ATC) plasticized PLA/starch blend at the same ATC concentration.⁹ The crystallization temperature of the blend increased at lower DOM concentrations, and the temperature reached its highest point, 112.4°C, at 2% DOM. After that, the temperature decreased to 90°C at 15% DOM. Two melting endothermic peaks were observed for the sample with 1% DOM, and the low-temperature shoulder endothermic peak gradually disappeared when the DOM concentration increased up to 10%. The melting peak of the blend with 10% DOM was 9.2°C lower than for the PLA/starch without DOM. At low DOM concentrations, 1–8%, cold crystallization temperature increased crystallization behavior over control. The left shoulder melting endothermic peak probably is explained by the cold-crystallization induced, imperfect spherulites and melting before PLA spherulites melted. DOM slightly depressed melting temperature of the blends (Table IV), as well as recrystallization temperature, which is as not prominent as low molecular weight plasticizer ATC plasticized blends.⁹ The reduction in crystallinity as DOM con-

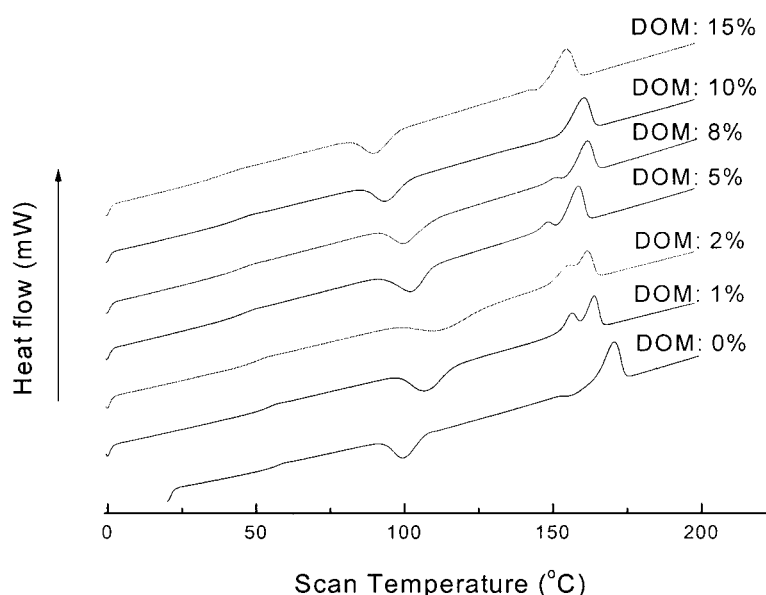


Figure 1 Effect of dioctyl maleate (DOM) on thermal behavior of poly(lactic acid)/starch (55/45) blends as determined by differential scanning calorimetry (DSC).

TABLE IV
Effect of Dioctyl Maleate (DOM) on Glass Transition Temperature (T_g), Re-crystallization Temperature (T_c), Melting Temperature (T_m), and Crystallinity for Cold-Crystallization (χ_c) and Melting Crystallization (χ_m) of Poly(lactic acid)/Starch (55/45) Blends

DOM content (wt %)	T_g (°C)	T_c (°C)	T_m (°C)	χ_c (%)	χ_m (%)
0	57.3	101.8	167.6	-20.7	40.2
1	54.0	107.3	163.8	-19.3	37.9
2	50.2	112.4	161.5	-18.3	36.3
5	45.2	102.5	158.5	-17.9	36.6
8	43.4	100.2	161.5	-14.1	29.8
10	44.7	93.9	160.3	-12.6	27.2
15	39.2	90.0	154.5	-13.8	31.5

centration increased is due to the inability of polymer chains to fully incorporate into the growing crystalline lamella, implying that there were some defects in the crystals. Hence, DOM is less efficient in lowering thermal transition temperatures than ATC because of DOM's polymeric characteristics.

DMA analysis was performed to track the temperature dependence of storage modulus (E') and loss factor $\tan \delta$ behaviors of the blends. The temperature dependence of E' of all blends followed similar patterns (Fig. 2A). The E' remains almost the same below T_g but then drops suddenly where the region is characterized as glass transition. An abrupt increase of E' after glass transition is attributed to the crystallization

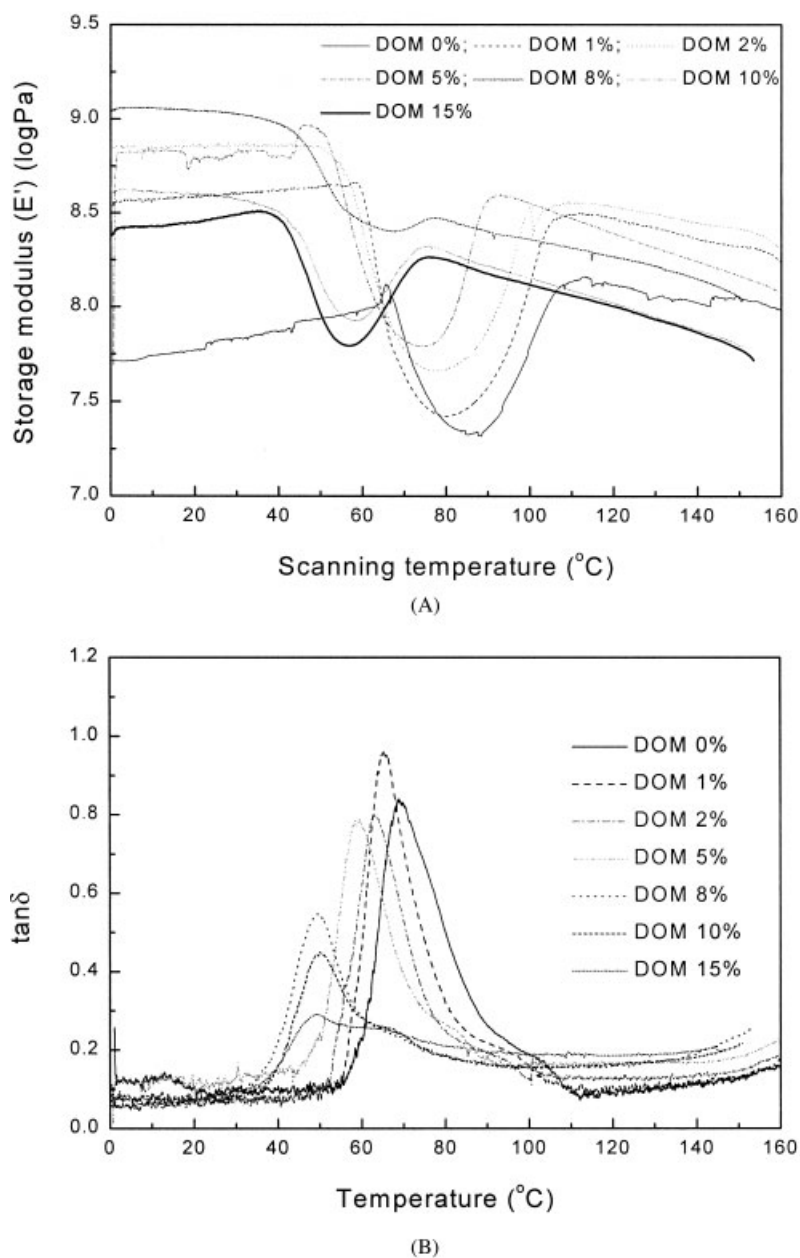


Figure 2 Effect of dioctyl maleate (DOM) concentration on dynamic mechanical properties of poly(lactic acid)/starch (55/45) blends: (A) storage modulus (E'), (B) loss factor ($\tan \delta$).

TABLE V
Dynamic Mechanical Properties of Poly (lactic acid) (PLA)/Starch (55/45) Blends with Different Dioctyl Maleate (DOM) Concentration

DOM (%)	Storage modulus (MPa)			tan δ height	tan δ width ΔT ($^{\circ}C$)	tan δ peak ($^{\circ}C$)	Temp of lowest E' at transition ($^{\circ}C$)
	20 $^{\circ}C$	Lowest at transition	150 $^{\circ}C$				
0	58.8	21.2	110.5	0.840	49.6	69.0	85.0
1	389.9	26.4	208.1	0.961	49.6	65.3	80.1
2	722.9	46.0	260.0	0.803	53.2	63.0	77.3
5	622.1	61.7	146.2	0.789	53.9	59.7	74.5
8	1109.9	251.5	112.6	0.547	52.1	49.6	67.6
10	395.7	84.5	62.5	0.451	59.2	50.1	58.6
15	282.1	62.1	59.8	0.290	71.7	49.6	56.9

of PLA upon heating.¹⁰ The value of E' increased over control when DOM was added at any concentration. This further confirms that DOM acted as a compatibilizer to enhance the E' of the blend. The maximum value of E' below T_g was achieved at 8% DOM. A decrease in E' below T_g was observed when DOM content was increased from 8 to 10%, but decreased at 15% DOM, where the plasticizer function of DOM starts to play a role in the blend. A continuous DOM phase was generated above the threshold of DOM concentration, after which the plasticizer characteristic of DOM predominated. When DOM was added, the glass transition, where the E' dramatically dropped, shifted towards a lower temperature, and exhibited the plasticizer function. According to the DMA analysis, the compatibilization and plasticization took place simultaneously; compatibilization predominated at DOM concentrations below 8%, while plasticization predominated at DOM concentrations above 10%. The tensile test results also exhibited a similar tendency. Tensile strength improved at DOM concen-

trations below 8%, but elongation was dramatically enhanced at DOM concentrations above 10%. Tensile tests are in agreement with DMA modulus analysis.

A detailed comparison of the dynamic mechanical properties of PLA/starch blends with different DOM concentrations is presented in Table V. The specific E' was compared at three different temperatures. At room temperature (20 $^{\circ}C$), PLA/starch blend had the lowest E' , while the blend with 8% DOM had the highest E' . While in the glass transition range, PLA/starch processed the lowest E' value of 21.2 MPa, causing the softest materials. The blend with 8% DOM gave the blend its highest E' value within the transition area. E' of the blends with DOM dropped by more than 10 times, while E' at room temperature for the blends without DOM dropped by 1/3. The compatibilization of DOM was apparently reflected in this transition range. At higher temperatures, for instance 150 $^{\circ}C$, the E' for PLA/starch blend was even higher than the E' at room temperature. For the DOM loaded samples, the E' s at this temperature were lower than

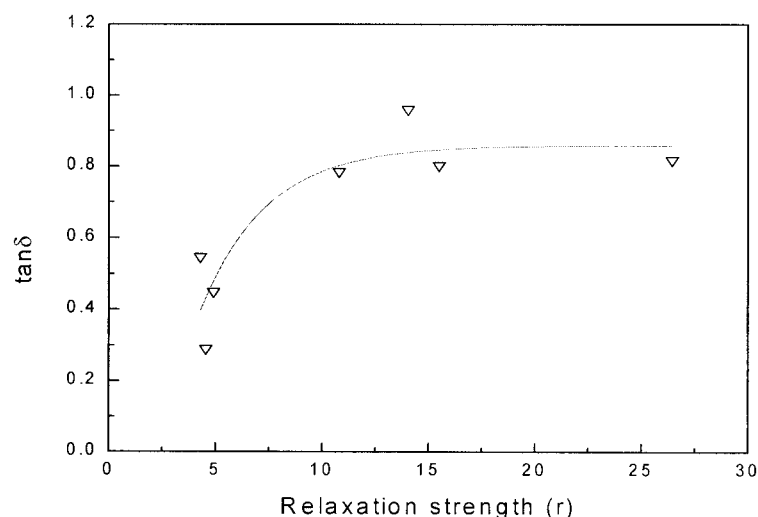


Figure 3 Height of the loss factor (tan δ) peak as a function of relaxation strength for poly(lactic acid) (PLA)/starch/dioctyle maleate (DOM) blends.

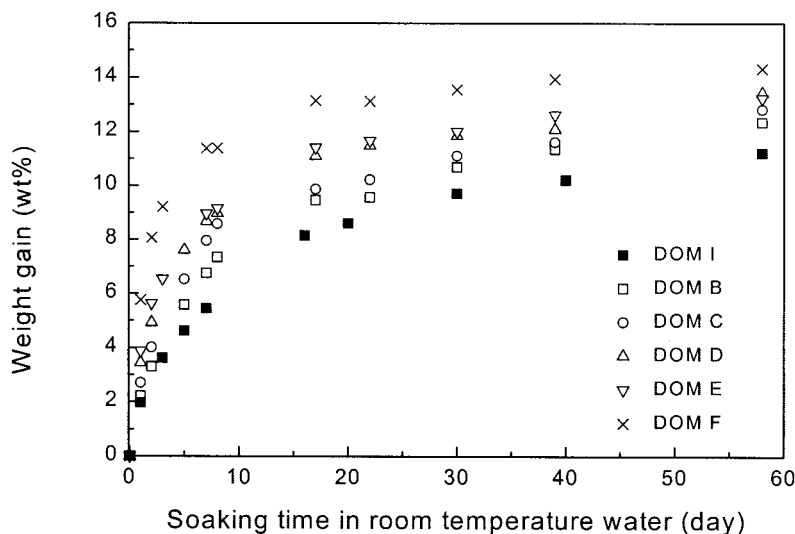


Figure 4 Weight gains of poly(lactic acid) (PLA)/starch/dioctyl maleate (DOM) specimen in distilled water at room temperature.

for those at room temperature. The E' of the samples with 10 and 15% DOM were even lower than the unplasticized PLA/starch blend, and the plasticization effect predominated at this concentration. The plasticization of DOM was also reflected in the decreased transition temperature where the lowest E' was achieved with DOM concentrations.

The relaxation processes associated with the glass transition of the amorphous phase of PLA could be clearly discussed in the DMA. The relaxation temperatures can be taken at the maximum of the respective $\tan\delta$ peak (Fig. 2B). The temperatures of the peaks shifted toward lower temperatures with DOM (Fig. 2B and Table V), indicating that the DOM in the blends smooths the chain mobility of the PLA/starch and acts as a plasticizer. The $\tan\delta$ peak height reached its maximum at 1% DOM and then declined with DOM concentration. With DOM concentration, the $\tan\delta$ peak temperature shifted toward lower temperatures while the width of the $\tan\delta$ peak widened. $\tan\delta$ is defined by the ratio of loss modulus (E'') to E' . E'' is related to the plasticizer continuous phase, which remains during dynamic deformation, and E' to the breakdown and reformation of the phase. In other words, $\tan\delta$ reflects the ratio between the phase portion that is capable of being broken down and reconstituted and the portion that remains unchanged during dynamic deformation. Consequently, $\tan\delta$ is sensitive to DOM structure in the blend. The greater the continuous phase portion withstanding dynamic deformation and the smaller the portion being broken down and reformed, the lower the value of $\tan\delta$. This suggests that the development of the plasticizer continuous phase has major effects on $\tan\delta$.

It was reported that for polymer-diluent systems,^{11,12} the drop in E' curves accompanying the relaxation transition is proportional to the height of

the corresponding mechanical loss peak expressed in terms of $\tan\delta$. The relaxation strength (r) can be expressed as follows¹³:

$$r = \frac{E'_g - E'_r}{E'_r} \quad (2)$$

where E'_g is glassy modulus at 5°C, and E'_r is rubbery modulus at the lowest peak prior to re-crystallization. As seen in Figure 3, a lower $\tan\delta$ peak at its glass transition doesn't affect the relaxation strength (around 5). The $\tan\delta$ in this range corresponds to the specimen with higher DOM concentration (>10%). A higher DOM concentration corresponds to a lower $\tan\delta$ peak, but does not mean a stiff specimen because the E' below T_g is still low. At lower DOM concentration, the relaxation strength vertically increased against $\tan\delta$ when $\tan\delta$ was around 0.9, which means relaxation strength is sensitive to the addition of DOM at its low concentrations. Wu¹³ reported a linear increase between relaxation strength and the height of $\tan\delta$ peak in a chlorinated polyethylene (CPE)/chlorinated paraffin (CP) system. The difference may result because the PLA/starch/DOM system exhibits a crystallization behavior following the glass transition before melting further retarded the relaxation. The apparent E' value after T_g could be much lower if there was no cold-crystallization, which differs from the E' in the rubbery CPE/CP system.

In comparing Figures 2A and 2B, the dynamic mechanical properties of the PLA/starch blends are strongly affected by adding DOM. The large shift to a lower relaxation temperature of the PLA/starch/DOM blends clearly indicates the dilution of DOM and enhanced chain mobility. It should be again noted that the compatibility and optimum DOM concentra-

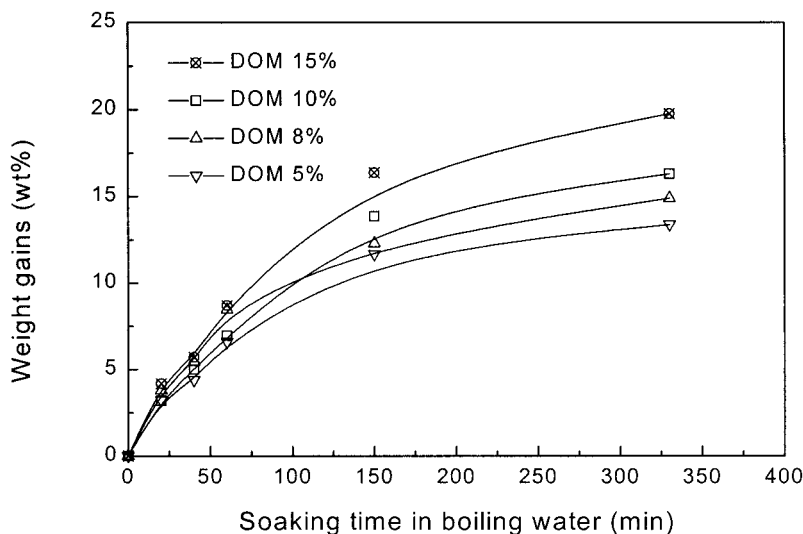


Figure 5 Weight loss of poly(lactic acid) (PLA)/starch/dioctyl maleate (DOM) specimen in boiling water.

tion were crucial to property improvement as well as to the formation of ductile biodegradable polymeric materials. In a previous work,⁹ ATC reduced the thermal transition temperature while enhancing crystallinity. In this work, the reduced thermal transition temperature was not consistent with enhanced crystallinity. Hence, the improved E' below T_g of DOM blends compared to PLA/starch blend is not ascribed to the enhanced crystallinity described by Ke and Sun⁶ but to compatibilization.

Water absorption and DOM migration

The PLA/starch blend exhibited improved water absorption because of the incorporation of hydrophilic starch; the equilibrium absorption was approximately

10% after two months of soaking in room temperature water. Further weight gains of the PLA/starch blends with DOM were observed. The weight gain was similar to the weight gains of the PLA/starch blend, increasing rapidly in the first 20 days and then leveling off. Weight gains increased proportionally with DOM content in the blends (Fig. 4). Similar water uptake with a more rapid increase in weight gains and a larger equilibrium weight gain was observed when samples were immersed in boiling water (Fig. 5). Water absorption by starch has been investigated extensively.^{2,3,14-16} The low molecular weight plasticizer ATC leached out of PLA/starch blends into water and reduced mechanical properties, as discussed in Zhang and Sun.⁹ Unlike low molecular weight plasticizer, however, the polymeric plasticizer DOM has different

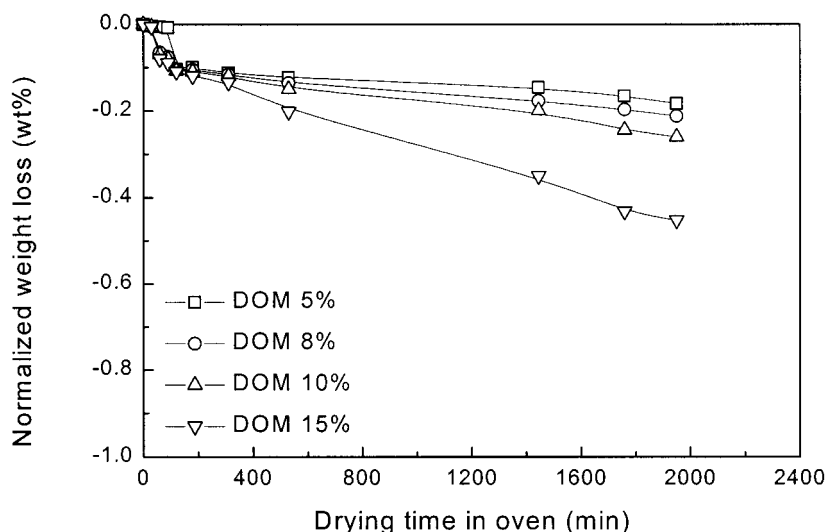


Figure 6 Thermally induced weight loss of poly(lactic acid) (PLA)/starch/dioctyl maleate (DOM) specimen in conventional oven at 135°C.

characteristics. Weight gains were proportional to DOM concentration in the blends. It seems that the additional weight gain compared to weight gains with PLA/starch blend can be ascribed to water absorption by DOM. DOM, with its high molecular weight, should leach little to the water, thus overcoming the resin hardening.¹⁷

Thermal treatment conditions for PLA/starch blends with different concentrations of DOM should induce minimal thermal weight loss (Fig. 6) at 135°C, though the minor loss of DOM was still proportional to DOM concentrations in the blend. This suggests that DOM is a thermally stable plasticizer, a favored property for PLA/starch plastics. In thermally induced low molecular weight plasticizer, for instance ATC, migration and loss from the bulk specimen were high, and the mechanical properties were thereby dramatically reduced.⁹

CONCLUSION

DOM acted as a compatibilizer for PLA/starch systems at concentrations below 8%. Further increasing DOM concentrations reduced tensile strength but markedly increased elongation, where DOM acted as a polymeric plasticizer. The combination of MA and DOM gave a higher tensile strength and elongation than the blend including either MA or DOM. Thermal transitions of the blends decreased with DOM concentration. As a polymeric plasticizer, DOM thermal migration was minimal at 135°C. Wa-

ter absorption of the blends increased with DOM concentration. The characteristics of DOM are useful in producing soft polymeric materials with acceptable mechanical properties without thermal loss in thermal processing or leaching in an aqueous environment application.

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