

Mechanical Properties of Poly(lactic Acid) and Wheat Starch Blends with Methylenediphenyl Diisocyanate

HUA WANG, XIUZHI SUN, PAUL SEIB

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

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ABSTRACT: Poly(lactic acid) (PLA) and wheat starch are biodegradable polymers derived from renewable sources. A previous study showed that thermally blending starch and PLA in the presence of methylenediphenyl diisocyanate (MDI) enhanced the mechanical properties of the blends. In this work, blends of PLA with various levels of wheat starch and MDI were hot mixed at 180°C then hot-pressure molded at 175°C to form test specimens. The blends were characterized for mechanical properties, fracture microstructure, and water absorption. Pure PLA had a tensile strength of 62.7 MPa and elongation of 6.5%. The blend with 45% wheat starch and 0.5 wt % MDI gave the highest tensile strength of about 68 MPa with about 5.1% elongation. The blend with 20% starch and 0.5 wt % MDI had the lowest tensile strength of about 58 MPa with about 5.6% elongation. Dynamic mechanical analysis showed that storage modulus increased and $\tan \delta$ decreased as starch level increased, but almost leveled off when starch level reached 45% or higher. Water absorption of the blends increased significantly with starch content. Yet the blend, if water proofed on its surface, has potential for short-term disposable applications. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1257–1262, 2002; DOI 10.1002/app.10457

Key words: biodegradable; biopolymers; blends; starch; polylactic acid

INTRODUCTION

In the past decades there has been a growing interest in developing plastics from biodegradable and renewable agricultural feedstock. Poly(lactic acid) (PLA) is a promising synthetic polymer derived from agricultural resources through bioconversion and polymerization. It has stiffness, tensile strength, and gas permeability comparable to those of synthetic polymers from fossil-oil¹ such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET).²

Applications of PLA are somewhat limited due to its high cost. Starch is a cheap polysaccharide derived from agricultural plants, and is susceptible to biological and oxidative attack. Natural starch exists in granular form, and it has been used as a filler in plastics to increase biodegradability.^{3–7} To prepare a fully biodegradable material from renewable resources, efforts have been made to blend starch with PLA.^{8–11} PLA degrades slowly in the environment over a period of several months to 2 years,¹² but the biodegradation rate of starch is rapid.¹³ Therefore, incorporating starch with PLA should accelerate the biodegradation rate of the blend.

Properties and processibility of a polymer blend containing starch are adversely affected by starch content. In particular, the mechanical properties of blends worsen,^{9,11} although biode-

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

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gradability increases. Previous work¹⁴ showed that the mechanical properties of a blend of PLA and wheat starch at the ratio of 55/45 (w/w) with 0.5 wt % methylenediphenyl diisocyanate (MDI) were significantly improved compared to a blend without MDI. MDI appears to function as a coupling agent, improving the interfacial interaction, and consequently, enhancing the mechanical properties of the starch and PLA blend. The objective of this article was to study the effects of various starch levels on tensile properties, microstructure, dynamic mechanical properties, and water absorption of the PLA/starch blend in the presence of 0.5 wt % MDI.

EXPERIMENTAL

Materials

PLA with molecule weight of 120,000 Da and mainly polymerized from L-lactic acid was purchased from Shimadzu, Japan. Wheat starch Midsol 50 with an amylose content about 23–28% and a particle size of 17.95–18.09 μm (about the 95% confidence interval) (Midwest Grain Products, Inc., Atchinson, KS) was dried to about 0.5% moisture content (mc), as determined by AACC method 44-15A,¹⁵ in a convection oven at 130°C for 2 h before use. Methylenediphenyl diisocyanate (MDI, Rubinate 1840), supplied as a dark brown liquid, was obtained from ICI Polyurethanes (Geismar, LA). The reagent contained about 45% 4,4'-methylenediphenyl diisocyanate apparently mixed with oligmer.

Blends Preparation

PLA chips from the manufacturer were ground into powder on a laboratory mill fitted with a 2-mm screen (Model 4 Laboratory Mill, Thomas-Wiley Company, Philadelphia, PA). PLA, starch, and 0.5 wt % MDI (based on the total weight of PLA and starch) were blended at 180°C and 135 rpm for 4 min in an intensive compounder (Rheomix 600, Haake, Paramus, NJ) equipped with two corotating rollers. The starch level in each blend was 20, 30, 45, 50, and 60%, based on the total weight of PLA and starch. Pure PLA also was treated under the same mixing conditions. After hot mixing, the blends were cooled and ground into powder using the same laboratory mill.

Tensile Testing

Powdered blends were then compression-molded into tensile bars (type IV) following ASTM test

method D-638-91¹⁶ using a hot press (Model 3890, Auto "M," Carver Inc., Wabash, IN) at a set temperature of 176°C and molding pressure of 4.2 MPa. Molding time was defined as the time required for the sample to reach the set temperature from the starting point of the molding. Molded specimens were then cooled to 57°C before removal from the mold and then preconditioned at 50% relative humidity and 25°C for 48 h before testing. Tensile strength and elongation at break were determined using an Instron testing system (Model 4465, Canton, MA) according to ASTM D-638-91¹⁶ with a crosshead speed of 5 mm/min and 25-mm gauge length. Six replicates were tested for each treatment.

Morphology

The microstructure of a blend was observed using a scanning electron microscope (SEM) (Hitachi S-3500N, Hitachi Science Systems, Ltd., Japan). A specimen from a tensile test was mounted on an aluminum stub, and the fractured surface was coated with a mixture of 60% gold and 40% palladium particles by a sputter coater (Desk II Sputter/Etch Unit, Moorestown, NJ) prior to the observation.

Dynamic Mechanical Analysis (DMA)

Thermal dynamic mechanical properties were determined by DMA (Perkin-Elmer Pyris DMA7e, Norwalk, CT) in a three-point bending mode at 1 Hz frequency. The samples (10.00 \times 6.36 \times 2.00 mm) were preconditioned at 50% relative humidity and 25°C for about 48 h before analysis. Scanning temperature was from 25 to 160°C at a heating rate of 3°C/min. Storage modulus and $\tan \delta$ were also determined.

Water Absorption

The broken specimens (30 \times 15 \times 2 mm) from tensile strength testing were dried at 50°C for 24 h and then used for a water absorption test. The dried specimens were immersed in distilled water at 25°C for specific intervals, removed from water and blotted with tissue paper to remove the excess surface water, and then weighed. Three replicates were tested for each treatment. Water absorption was calculated based on the dry weight.

Table I Mechanical Properties of Pure PLA and PLA/Starch Blends at Various Starch Levels with 0.5 wt % MDI

Sample	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (GPa)
Pure PLA	62.70 bc	6.1 a	1.41 b
20% starch	58.25 d	5.6 ab	1.52 b
30% starch	62.46 bc	6.1 a	1.63 a
45% starch	68.06 a	5.1 bc	1.81 a
50% starch	63.70 b	5.2 bc	1.75 a
60% starch	60.59 cd	4.9 c	1.78 a

Values in the same column followed by the same letter are not significantly different ($p < 0.05$).

RESULTS AND DISCUSSION

Mechanical Properties

Table I shows the tensile strength and elongation of pure PLA and the blends with various starch levels made in the presence of 0.5 wt % MDI. Tensile strength of the blends at all starch levels was similar to that of pure PLA. The blend with 45% starch had the highest tensile strength while the one with 20% starch had the lowest strength. There was no significant change in elongation for starch blends compared to pure PLA until the starch level reached 30%. Between 30–60%, elongation leveled off remaining near 5.0%. Young's modulus for blends increased as starch content increased up to 45%. Beyond 45% starch content, Young's modulus remained the same (1.75–1.81 GPa).

In a binary system of PLA and starch, as reported by Ke and Sun,¹¹ the tensile strength and elongation of blends decreased significantly as wheat starch content increased. In their study, at 20% starch in a blend, the tensile strength decreased to 44.7 MPa from 62 MPa for pure PLA, and elongation decreased from 6.1 to 4%. At 60% starch content, the tensile strength was about 30 MPa with 2% elongation.¹¹

The present work showed that the addition of MDI improved the mechanical properties of the PLA/starch blend. Adhesion at the interface between PLA and starch might exist, as suggested by Wang et al.¹³ For the PLA/starch blend without MDI, gaps were observed in scanning electron microscopy between the PLA matrix and the starch granules, with the starch granules acting as a filler.^{13,16} Without MDI, the starch granules and the gaps acted as stress concentrators in a blend, which induced cracks upon tensile testing that resulted in lower strength and elongation.

According to the fracture theory developed by Griffith,¹⁷ fracture toughness is usually associated with fracture energy. For high toughness, the fracture energy must be at least equal to or larger than the surface energy at the interface of cracking, which can be described by the area under the stress–strain curve. The blends with MDI had higher fracture energy than that without MDI, as noted by Ke and Sun.¹¹ MDI has two highly reactive isocyanate groups that might react¹⁸ with both carboxyl and hydroxyl groups on PLA and with the hydroxyl groups on starch simultaneously during mixing at 180°C. Some of these reactions probably resulted in primary chemical bonds between the surface of starch granules and PLA, leading to high interface adhesion, and consequently high fracture energy.

Microstructure

Generally, the tensile properties of a blend are associated with its microstructure. The fracture surface of pure PLA was smooth [Fig. 1(A)], where the surface of starch/PLA blends with 0.5 wt % MDI [Fig. 1(B)–(F)] were rough, which is typical of a compatible structure. For the 45% starch blend, most of the starch granules were well enveloped by the PLA matrix and fractures occurred through the PLA matrix. At starch levels below 45%, only a few starch granules were observed clearly in the matrix and the fracture occurred at some of the interfaces between the PLA matrix and starch granules, suggesting that the starch granules were not well wetted by the PLA matrix. At 50% starch content, starch granule aggregations were observed clearly, and the split starch granules were probably a result of the fracture. At starch content of 60%, the fracture occurred though the interface at some locations probably due to the high concentration of starch.

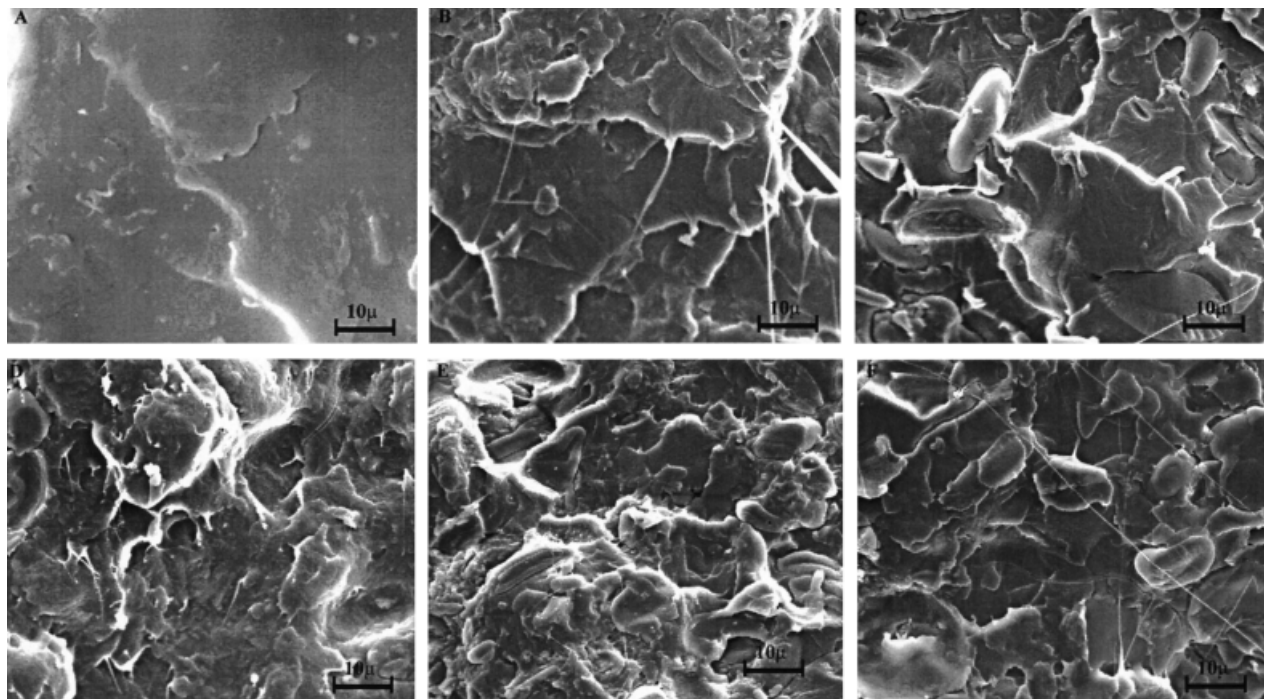


Figure 1 Scanning electron micrographs of tensile fracture surface of pure PLA (A) and PLA/starch blends with 0.5 wt % MDI at starch level of 20% (B), 30% (C), 45% (D), 50% (E), and 60% (F).

According to Wu,¹⁹ for a particulate-filled composite made with a coupling agent, the wetting and bonding at the interface significantly influenced the properties of the composite. To form an adhesive bond, the first step requires an interfacial molecular contact by wetting. Because of the wetting, the molecules diffuse across the interface and react chemically to establish covalent bonds across the interface. The diffusion is usually accelerated by low surface tension, which enhances wetting and increases the adhesive bond strength and, consequently, the fracture energy. Any interfacial defects may result in poor wetting and poor adhesive bond strength.

As discussed above, molecular diffusion and absorption are two critical factors to the wetting property. In a well-wetted blend, there are few voids and entrapped air bubbles due to the reduced surface tension of the filler. MDI has a boiling temperature of about 208°C²⁰ and the isocyanate groups are highly polar. It seems possible that the surface tension of starch could be reduced in the presence of MDI during mixing.

The thermal properties of the starch and PLA during blending also might play an important role in the wetting of the starch granules' surface. At

low starch levels in a blend with MDI, it was observed that the time needed to reach the set temperature during hot mixing was shorter (15 to 30 s) because PLA has a higher thermal conductivity than the dried starch. PLA undergoes depolymerization during the hot mixing step (mixing time was fixed at 4 min). An increased portion of PLA short chains would increase the levels of hydroxyl and carboxyl groups in the matrix, which would compete with starch hydroxyls for MDI. In addition, even if the bonding layer at the interface between PLA and starch was achieved, it might be degraded to some degree because of the larger shearing at the set mixing temperature. At higher starch levels, 1 to 2 min of additional mixing time was required for the blend to reach the set temperature. In this situation, less PLA was degraded and more MDI was available for starch. However, the amount of MDI was fixed at 0.5 wt %, which probably was insufficient to wet all the starch. It seems that 45% starch and 0.5 wt % MDI was an optimum combination, which gives a calculated mole ratio of PLA to MDI of about 1/40. This data suggests that each starch level may have an optimum MDI content.

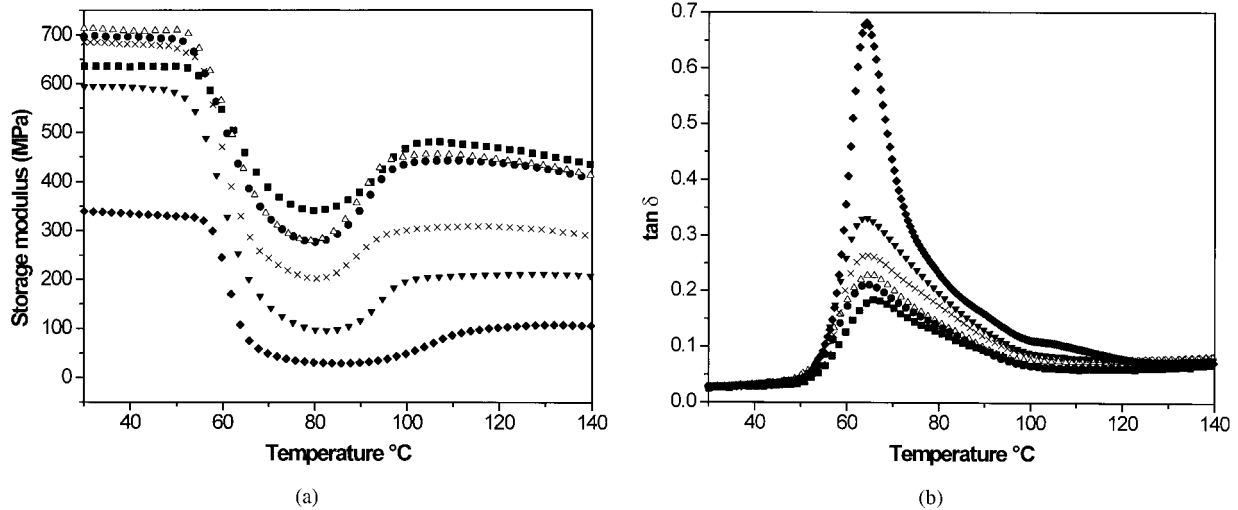


Figure 2 Pure PLA (◆), PLA/starch blends with 0.5 wt % MDI at starch level of 20% (▼), 30% (×), 45% (●), 50% (△), and 60% (■) (wt) of starch fillers. (A) Dynamical mechanical properties of storage modulus vs. temperature at 1 Hz; (B) $\tan \delta$ vs. temperature.

Dynamic Mechanical Properties

The DMA results of pure PLA and the blends with various starch levels and 0.5 wt % MDI are presented in Figure 2. Pure PLA showed a typical thermoplastic behavior, and it had the lowest storage modulus [Fig. 2(A)]. At starch levels between 20–45%, the storage modulus was increased as the starch content increased, but at starch levels between 45–60%, the storage modulus remained approximately constant as starch levels increased. Starch levels in the blend had no effect on glass transition temperature (T_g); all the blends had the same T_g as pure PLA at about 56°C. Pure PLA had a sharp and high damping peak [Fig. 2(B)], but the $\tan \delta$ value in the blends decreased as starch level increased.

Water Absorption

Starch is a hydrophilic natural polymer, and can absorb up to about 50% water²¹ on a dry weight basis when soaked in excess water at 25°C. PLA is a hydrophobic polymer, and it absorbs water to an equilibrium level of approximately 0.8% after 2 days of water soaking at 25°C (Fig. 3). The water absorption of all PLA/starch blends increased gradually during the first 15 days then leveled off (Fig. 3). As expected, the water absorbed by the blends could be mainly attributed to the starch. Interestingly, the water absorption calculated on the starch level (Table II) was independent of

starch content in the range from 20 to 30%, and then increased slowly as the starch content increased. There may exist an optimum ratio of PLA and starch in the range from 7/3 to 6/4. When the ratio was higher than the optimum ratio, the starch granules were well covered by the continuous PLA matrix, and the possibility of exposure to water was independent of starch content. When the ratio was lower than the optimum value, the possibility of exposure to water in-

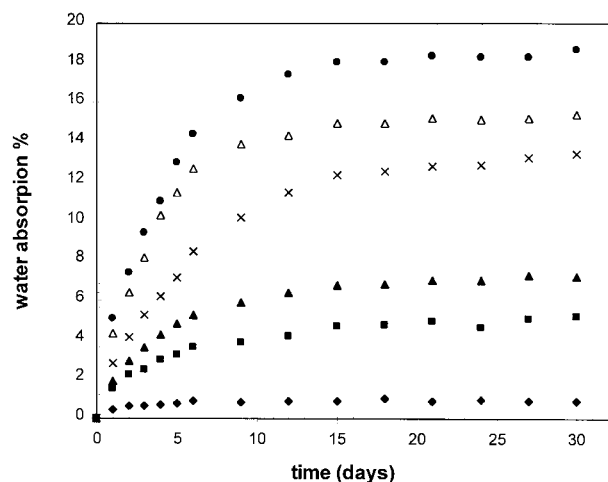


Figure 3 Water absorption of pure PLA (◆), PLA/starch blends with 0.5 wt % MDI at starch level of 20% (■), 30% (▲), 45% (×), 50% (△), and 60% (●) (wt) of starch fillers.

Table II Water Absorption of PLA/Starch Blends at Various Starch Levels and 0.5 wt % MDI after 15 Days of Soaking in Water at 25°C

Starch Content	20%	30%	45%	50%	60%
Water absorption (based on blend)	4%	6%	10%	14%	18%
Water absorption (based on starch)	20%	20%	27%	28%	30%

creased as starch level increased because of the increase in discontinuity of the PLA matrix.¹¹

CONCLUSIONS

With 0.5 wt % MDI, starch content had a slight influence on the mechanical properties of the starch/PLA blend. Statistically, the blend with 45% starch had a smooth microstructure, and gave the highest tensile strength (about 68 MPa), with elongation of about 5.1%. The blend with lower or higher starch content than 45% had a rough microstructure at the fracture surface, with a lower tensile strength (58–63 MPa) and elongation in the range of 4.9–5.6%. At starch content of 20–30%, water absorption of the starch in the blend was independent of starch content. At higher starch content, water absorption of the PLA/starch blend increased as starch content increased.

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