

# Strengthening Blends of Poly(lactic acid) and Starch with Methylenediphenyl Diisocyanate

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**ABSTRACT:** Poly(lactic acid) (PLA) is a biodegradable polymer, but its applications are limited by its high cost. Blending granular starch with PLA reduces the cost, but the blend has poor strength properties. In this study, a 55/45 (w/w) mixture of PLA (weight-average molecular weight = 120,000 Da) and dried wheat starch was blended thermally in an intensive mixer with or without a low level of methylenediphenyl diisocyanate (MDI). Blends with MDI had enhanced mechanical properties that could be explained by the *in situ* formation of a block copolymer acting as a compatibilizer. Scanning electron micrographs showed reduced interfacial tension between the two phases. The presence of MDI also enhanced the mechanical properties of the blend at temperatures above the glass-transition temperature. Water uptakes by the PLA/starch blends with and without MDI did not differ. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1761–1767, 2001

**Key words:** biodegradable blend; poly(lactic acid)/starch; methylenediphenyl diisocyanate; coupling agent

## INTRODUCTION

Recent concerns about petroleum polymers in the environment have stimulated interest in the development of biodegradable plastics from renewable resources.<sup>1</sup> Starch is a readily available and renewable agricultural resource that is susceptible to biological and oxidative attacks. To increase the biodegradability of petroleum polymers, efforts have been made to blend starch with selected thermal plastics, such as low-density polyethylene,<sup>2</sup> poly(vinyl alcohol),<sup>3</sup> and polystyrene.<sup>4</sup> Polycaprolactone (PCL)<sup>5–7</sup> and poly(ethylene vinyl alcohol) (EVOH)<sup>8–11</sup> have been of great interest for blending with starch and starch deriva-

tives to impart full biodegradability. However, PCL and EVOH are fossil fuel-derived plastics that increase carbon dioxide in the environment<sup>1</sup> and stimulate the greenhouse effect. A thermoplastic polymer from a renewable source would be better for the development of a biodegradable plastic.

Poly(lactic acid) (PLA) is polyester made from L- or D-lactic acid. A desired stereoisomer of lactic acid can be made commercially through carbohydrate fermentation technology.<sup>12</sup> PLA can be prepared through two chemical reactions, ring-opening or direct condensation polymerization. Ring-opening polymerization<sup>13</sup> starts with lactide, a cyclic dimer of lactic acid, as a monomer, so the product is commonly called polylactide. PLA made from the direct condensation polymerization of lactic acid is called poly(lactic acid). The PLAs derived from these two pathways have similar mechanical properties.<sup>14</sup>

Pure PLA can degrade slowly to carbon dioxide, methane, and water in the environment over

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a period of several months to 2 years, compared with 500–1000 years for petroleum plastics.<sup>15</sup> It has many properties comparable to those of polyethylene, polypropylene, polystyrene, and polyethylene terephthalate, such as stiffness, tensile strength, and gas permeability.<sup>16</sup> In the past few decades, the applications of PLA as a biodegradable polymer have mainly been in the biomedical field. However, it has also been fabricated into a wide variety of consumer products, including compostable bags for waste, table utensil films, and paper coatings, and has been spun into fiber and cloth.

Natural starch exists in a tiny, rigid, granular form. The introduction of low-cost starch as a filler to PLA would result in a fully renewable biodegradable material. However, some blends have poor mechanical properties, especially at high starch concentrations, because of weak interfacial attractions between starch granules and the PLA matrix.<sup>17,18</sup> Generally, the mechanical properties of a blend can be improved by the strong interfacial tension between the filler and matrix being overcome.<sup>19–21</sup> Reducing the interfacial tension and strengthening the interaction between polymer phases can transfer the internal stresses from the filler to the matrix and, consequently, enhance the strength of the blend.<sup>22</sup> Strong interfacial adhesion can be achieved with the addition of a coupling agent to the blend system. A good coupling agent should have functional groups that react with both the matrix and filler. Methylenediphenyl diisocyanate (MDI), which is highly reactive with both hydroxyl and carboxyl groups to form urethane linkages,<sup>23</sup> could be a good coupling agent<sup>24</sup> between starch and PLA. Residues of untreated MDI are not expected in a blend because of the high reactivity of its isocyanate groups. In addition, the small amount of urethane linkages in the blend could be attacked by some fungi<sup>25</sup> and absorbed by soil.<sup>26</sup>

The objective of this study was to determine the effects of MDI on the mechanical behavior, thermal dynamic mechanical properties, crystallization, microstructure, and water absorption of a PLA/starch blend.

## EXPERIMENTAL

### Materials

PLA with a weight-average molecular weight of 120,000 Da made mainly from L-lactic acid was

purchased as chips (2.7 mm × 2.7 mm × 2 mm) from Shimadzu (Japan). Wheat starch (Midsol 50, Midwest Grain Products, Inc., Kansas City, KS) with an amylose content of 23–28% and a particle size distribution of 17.95–18.09 (95% confident limits) was used. It was dried in a convection oven at 130°C for 2 h according to AACC Method 44-15A<sup>27</sup> to about a 0.5% moisture content. Wheat starch consists of two kinds of granules: large, disc-shaped A-granules and small, spherical B-granules. The B-granules are about 30% of wheat starch by weight.<sup>28</sup> Polymeric MDI (Rubinate 1840) was obtained from ICI Polyurethanes (Geismar, LA) and contained about 45% 4,4'-methylenediphenyl diisocyanate in a dark brown, viscous, liquid form.

### Blend Preparation

The PLA chips were ground through a 2-mm screen in a laboratory mill (model 4 Laboratory Mill, Thomas–Wiley Co., Philadelphia, PA). The ratio of PLA to dried starch was 55 to 45 by weight, and MDI was added at four concentrations, 0.25, 0.5, 1, and 2 wt %, based on 100 parts of the blend. Each blend, including PLA and starch without MDI, was mixed in an intensive hot mixer (Rheomix 600, Haake, Paramus, NJ) equipped with two corotating rollers with a gap. Blends were hot-mixed at 180°C and 135 rpm for 4 min. Pure PLA also was treated under the same mixing conditions.

### Tensile Testing

Blends from the mixer were compression-molded into tensile bars (type IV) according to ASTM Method D 638-91<sup>29</sup> with a Carver hot press (model 3890, Auto “M”, Carver Inc., Wabash, IN) at 176°C and 4.2 MPa for 9–15 min. The molded specimens were cooled to 65°C before removal from the mold and then preconditioned at 50% relative humidity and 25°C for 48 h before testing. The tensile strength and elongation at break were determined with an Instron testing system (model 4465, Canton, MA) according to ASTM D 638-91<sup>29</sup> with a crosshead speed of 5 mm/min and a 25-mm gauge length. Six replicates were tested for each treatment.

### Morphology

The microstructure of a blend was observed with scanning electron microscopy (SEM; Hitachi S-3500N, Hitachi Science Systems, Ltd., Japan).

Each specimen from a tensile test was mounted on an aluminum stub, and the fractured surface was coated with a mixture of 60% gold particles and 40% palladium with a sputter coater (Desk II Sputter/Etch Unit, NJ) before observation.

#### Differential Scanning Calorimetry (DSC)

The thermal properties were determined via DSC (PerkinElmer Pyris 1, Norwalk, CT) according to ASTM Method D 3417-83.<sup>30</sup> About 5–10 mg of each sample was sealed in an aluminum pan. We erased the thermal history of a sample by heating it from 20 to 190°C at a rate of 10°C/min, holding it at 190°C for 10 min, and then cooling it to 20°C at the same rate. The thermal behavior was recorded by the reheating of the sample from 20 to 190°C at the same rate. The heats of fusion ( $\Delta H_m$ ) and crystallization ( $\Delta H_{c1}$ ) were determined. The crystallinity of PLA in the blend was calculated, where the fusion heat of 100% crystallinity of PLA ( $\Delta H_{m,PLA}$ ) was set equal to 93.6 J/g.<sup>31</sup>

#### Dynamic Mechanical Analysis (DMA)

Thermal dynamic mechanical properties were determined via DMA (PerkinElmer Pyris DMA7e, Norwalk, CT) in a three-point bending mode at a 1-Hz frequency. The test piece samples (10.00 mm  $\times$  6.36 mm  $\times$  2.00 mm) were preconditioned at 50% relative humidity and 25°C for about 48 h before analysis. The scanning temperature was 25–160°C at a heating rate of 3°C/min. The storage modulus and damping factor ( $\tan \delta$ ) were determined.

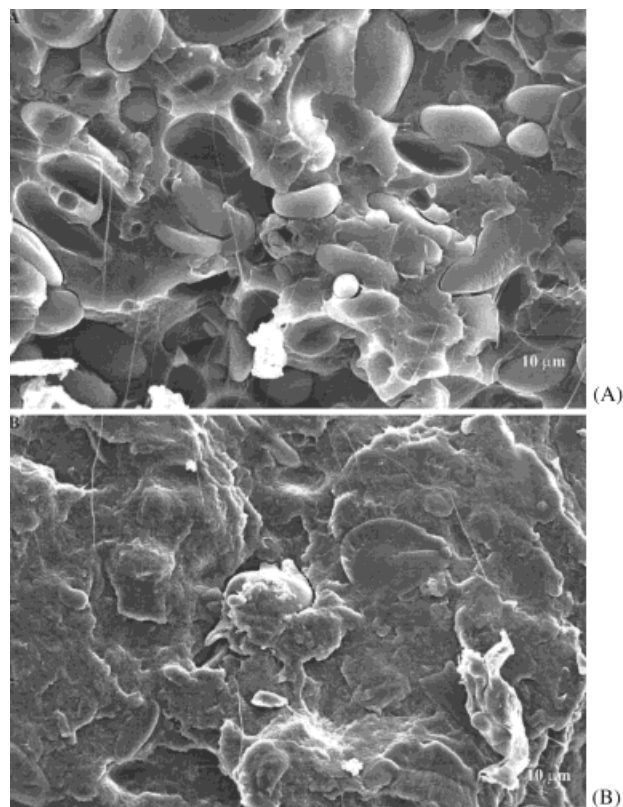
#### Water Absorption

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

## RESULTS AND DISCUSSION

#### Morphology

Figure 1(A) shows the SEM micrograph of the tensile fracture surface of the 55/45 (w/w) PLA/



**Figure 1** SEM micrographs of the tensile fracture surface of PLA/starch blends (55/45 weight ratio) (A) without MDI and (B) with 0.5% MDI.

starch blend without MDI. Two phases can be seen clearly, and in the fracture process, many starch granules were pulled out from the matrix, with large voids thereby being created. Also, gaps between remaining starch granules and the PLA matrix are visible. These results indicate poor interfacial adhesion between PLA and granular starch. Figure 1(B) shows the micrograph of a blend after compounding with 0.5 wt % MDI. Few individual starch granules can be observed, and those that are distinguishable appear to be coated with matrix PLA. Moreover, fracturing of the blend occurred through the starch granules rather than at their interface.

The SEM results are consistent with the formation of a block or graft copolymer of starch/PLA joined by urethane bonds formed during reactive compounding with MDI. The same SEM evidence was found when 3% starch-*graft*-PCL increased interfacial adhesion in a 70/30(w/w) starch/PCL blend.<sup>7</sup> Starch-*graft*-PLA coupled by ester bonds probably formed during the reactive extrusion of a 30/70 (w/w) blend of starch/lightly maleated

**Table I Mechanical Properties of Raw PLA and PLA/Starch Blends at 55/45 Weight Ratio with Various MDI Levels (Weight)**

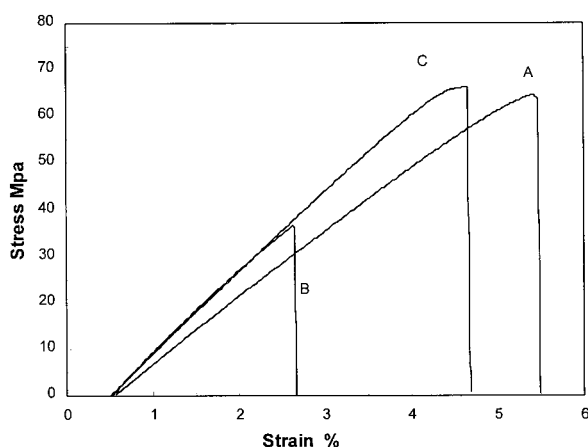
Samples	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (GPa)
Raw PLA	62.1bc	5.69a	1.41a
PLA/starch without MDI	36.0d	2.58c	1.73c
PLA/starch with 0.25% MDI	62.3c	4.37b	1.89b
PLA/starch with 0.5% MDI	66.7a	4.40b	1.94b
PLA/starch with 1% MDI	64.9abc	4.77b	1.94b
PLA/starch with 2% MDI	65.3ab	4.50b	1.92b

Levels of MDI are weight percentages based on blend. Values in the same column followed by the same letter are not significantly different ( $p < .05$ ).

PLA because SEM showed increased interfacial adhesion with respect to a blank of starch/PLA.<sup>32</sup>

### Mechanical Properties

The tensile strength and elongation of the PLA/starch blend without MDI under ambient conditions decreased by about 42 and 55%, respectively, compared with those of pure PLA (Table I). For the blend with 0.5% MDI, the tensile strength increased by about 7.5% and elongation decreased by about 23% with respect to pure PLA. The mechanical properties of the blends were not significantly affected by MDI concentrations above 0.5%. The blend without MDI appeared more brittle, and no yield point was observed (Fig. 2). For the blend with 0.5 wt % MDI, the material showed properties similar to those of pure PLA, except for Young's modulus (Fig. 2).

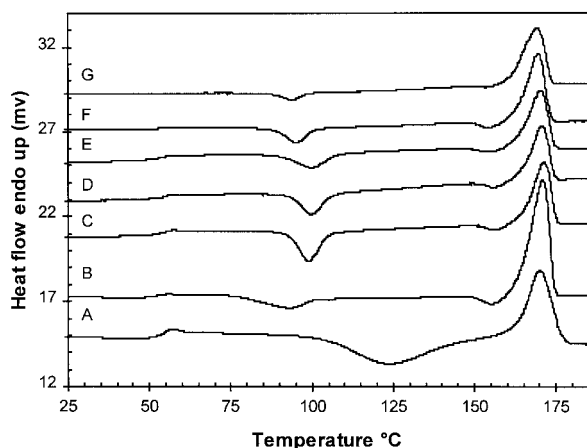


**Figure 2** Stress-strain curves of PLA and PLA/starch blends (55/45 weight ratio): (A) raw PLA, (B) blend without MDI, and (C) blend with 0.5 wt % MDI.

As expected, the starch granules in the PLA matrix without MDI acted as stress concentrators, often inducing cracks and resulting in low strength and elongation. However, strong adhesion existed between starch and the PLA matrix in the presence of MDI, so the mechanical property of the blend was improved greatly. With MDI, a covalent linkage likely was formed at the PLA/starch interface so that the interfacial adhesion was enhanced and, consequently, improved the tensile strength. Meanwhile, such adhesion might not cause severe restriction of elongation by forming a proper entanglement, which was capable of being stretched along the matrix. Both MDI and starch had a positive effect on Young's modulus, but the effect from starch was more significant (Table I). In the blend, the molecular mobility of PLA was restricted by rigid starch granules, which had a high modulus, and covalent MDI bonding at the interface. The fact that the PLA molecules were less free to stretch resulted in a high Young's modulus.

### Crystallization

The DSC thermograms of the blends are presented in Figure 3, and the DSC results are summarized in Table II. The raw PLA [Fig. 3(A)] had a melting temperature of about 170°C and a broad crystallization peak starting at about 100°C and ending at about 150°C. The thermally treated PLA [Fig. 3(B)] had a lower crystallization temperature than the raw PLA but a much greater crystalline melting peak. The PLA molecules might undergo some degradation shearing, hydrolysis, or backbiting when mixed at high temperatures. The increased proportion of short chains would shift the crystallization tempera-



**Figure 3** DSC thermograms of PLA and PLA/starch blends (55/45 weight ratio): (A) raw PLA, (B) thermally treated PLA, (C) blend without MDI, (D) blend with 0.25 wt % MDI, (E) blend with 0.5 wt % MDI, (F) blend with 1 wt % MDI, and (G) blend with 2 wt % MDI.

ture to low values and make the crystallization easier, thereby increasing crystallinity.<sup>33</sup>

The melting temperatures of PLA were not affected by the addition of either starch or MDI, but the extent of crystallization of PLA was affected (Fig. 3, Table II). The crystalline melting peak of about 170°C for the PLA/starch blend without MDI [Fig. 3(C)] was lower than that of thermally treated PLA [Fig. 3(B)]. Starch granules might restrict the molecular motion of the PLA matrix and result in a decreased crystallinity (Table II). However, the crystallinity of the blend with 0.25% MDI [Fig. 3(D)] was greatly reduced but was restored at 0.5% MDI and then leveled off at 0.5–1% MDI. At a 0.25% MDI concentration, the interfa-

cial interaction between starch and the PLA matrix restricted the PLA chain orientation, resulting in a low crystallinity compared with that of the blend without MDI. However, at MDI concentrations above 0.5%, the urethane linkage between starch and PLA restricted the interface slippage and resulted in an increase in PLA molecular fragmentation during mechanical shearing, which would accelerate the crystallization and increase the crystallinity. In this blending system, the formation of urethane linkages and PLA chain fragmentation both contributed to the crystallization in a complicated fashion.

### Dynamic Mechanical Properties

Storage modulus and  $\tan \delta$  values of selected samples as a function of temperature at 1 Hz are plotted in Figure 4, and the corresponding storage modulus data are summarized in Table III. The blend with 0.5% MDI had the highest storage modulus, whereas the raw PLA had the lowest. The storage modulus of all three samples suddenly dropped at about 55–70°C because of glass-transition effects, but raw PLA had the largest drop, and the blend with MDI had the smallest. Both raw PLA and the PLA/starch blend without MDI showed an increased storage modulus between 85 and 105°C due to crystallization. Such crystallization behavior was not observed for the starch/PLA blend with MDI. The storage modulus of the PLA/starch blend with MDI at high temperatures was high enough for the blend to be rigid and almost the same as that of the blend without MDI at room temperature (Table III).

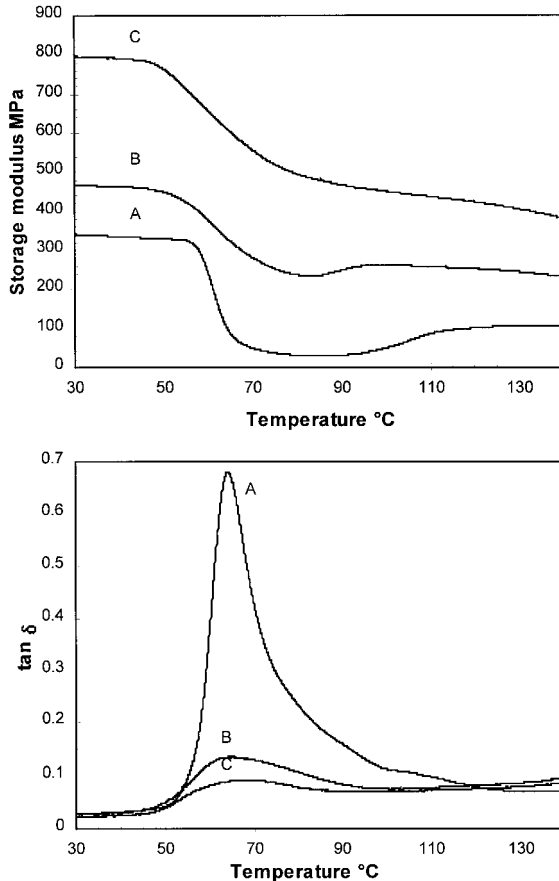
The mechanical damping factor  $\tan \delta$  usually is associated with inelastic manifestation in the ther-

**Table II** Melting and Crystallization Properties of PLA and PLA/Starch Blends at 55/45 Weight Ratio with Various MDI Levels

Sample	Heating		Crystallinity <sup>a</sup> (%)
	$\Delta H_m$ (J/g)	$\Delta H_c$ (J/g)	
Raw PLA	44.7	40.6	47.7
Thermally treated PLA	54.1	9.8	57.8
PLA/starch without MDI	48.5	28.8	51.8
PLA/starch with 0.25% MDI	43.3	22.0	46.3
PLA/starch with 0.5% MDI	48.7	16.9	52.1
PLA/starch with 1% MDI	52.9	12.3	56.5
PLA/starch with 2% MDI	51.9	5.5	55.4

Levels of MDI are weight percentages based on blend.

<sup>a</sup> Crystallinity based on PLA matrix.

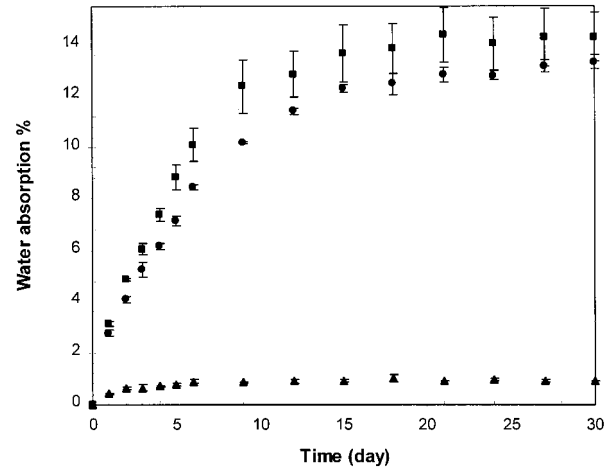


**Figure 4** Storage modulus (top) and  $\tan \delta$  (bottom) versus temperature at 1 Hz for PLA and PLA/starch blends (55/45 weight ratio): (A) raw PLA, (B) blend without MDI, and (C) blend with 0.5 wt % MDI.

mal phase-transition zone. Pure PLA had a sharp and high damping peak [Fig. 4(A), bottom], whereas the damping of the blend with MDI was low and broad, which means that the blend was rigid. The damping properties of a starch-reinforced blend usually are affected by the starch content; the

**Table III** Storage Moduli of Raw PLA and PLA/Starch Blends at 55/45 Weight Ratio with 0.5% MDI at Different Temperatures

Sample	Storage Modulus (MPa)			
	30°C	80°C	100°C	120°C
Raw PLA	340	31	50	102
PLA/starch without MDI	468	238	262	253
PLA/starch with 0.5% MDI	796	495	451	423



**Figure 5** Water absorption versus time for PLA and PLA/starch blends (55/45 weight ratio): (▲) raw PLA, (■) blend without MDI, and (●) blend with 0.5 wt % MDI.

higher the starch content is, the lower the value of the damping factor is.<sup>34</sup> In a blend system with filler particles, the filler would limit the mobility of the matrix molecular chain, thereby affecting the relaxation of the matrix chains and causing a lower damping in the transition zone compared with that of the pure polymer matrix. The new damping mechanisms for a filler system suggested by Nielson and Landel<sup>35</sup> can explain these results well. These damping mechanisms include (1) particle-particle friction, (2) particle-polymer motion with no adhesion at the filler interface, and (3) changes in the properties of the polymer near the interface. In the blend with MDI, the specific interaction between the filler and polymer matrix from the existence of MDI enhanced the interfacial adhesion and tended to create an adsorbed layer of polymer surrounding the filler surface, which restricted the molecular motion and resulted in a lower damping.

### Water Absorption

Starch is hydrophilic because it contains an abundance of hydroxyl groups, but PLA is a hydrophobic polymer.<sup>36</sup> When starch is soaked in excess water at 25°C, it can take up to about 50% water<sup>37</sup> on a dry basis. Therefore, the theoretical maximum water content absorbed by the blend containing a 45% starch phase is about 23% when submerged in excess water at 25°C. The water absorption for both blends with or without MDI increased greatly during the first 15 days and then leveled off at about 14% (Fig. 5). No significant difference in water absorption occurred be-

tween the blends with and without MDI. The water absorption for raw PLA also had the same tendency as that of the blend with starch but leveled off at about 1%. These results indicated that starch content was the major factor affecting the water absorption of the PLA/starch blends.

## CONCLUSIONS

A low concentration (0.25–0.5 wt %) of MDI during the hot mixing of approximately equal weights of dry granular starch and PLA dramatically improved the strength and elongation properties of the blend. With this one-step method, the ingredients PLA, starch, and MDI could be added into an injection-molding machine or extruder to produce shaped pieces. The blends slowly absorbed liquid water, making them suitable for molding into degradable single-use items. The higher water absorption after a long time would probably lead to better biodegradability. The completeness of the reaction of MDI in the blend should be determined, as well as the fate of the methylenediphenyl urethane linkage groups during biodegradation. Further study on extrusion and injection molding should be conducted.

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