# Properties of Poly(lactic acid) Blends with Various Starches as Affected by Physical Aging

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**ABSTRACT:** Poly(lactic acid) (PLA) and starch are both biodegradable and renewable polymers derived from agricultural feedstock. A previous study showed that a small amount (0.5%) of methylenediphenyl diisocyanate (MDI) could enhance the mechanical properties of starch and PLA blends by improving the interfacial interaction. In this study, blends of PLA (1/1, w/w) and starch with or without MDI were evaluated for thermal and mechanical properties as well as morphology, as affected by physical aging when stored up to 12 months at 25 °C and 50% relative humidity. The blends were prepared by thermally blending PLA with wheat starch, corn starch, and/or high amylose corn starch, with or without MDI. All samples exhibited phenomena of physical aging. The samples with MDI aged more slowly, showing a slower reduction rate of excess enthalpy relaxation, than those without MDI. The mechanical properties decreased slowly as aging proceeded. Microstructure showed a reduced interaction between starch and PLA around the interface with aging. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3683–3689, 2003

**Key words:** biodegradable; plastics; aging

## INTRODUCTION

Currently there is increasing interest in using biodegradable and renewable materials for disposable applications as an alternative to some conventional petroleum plastics.[1–4] Poly(lactic acid) (PLA) is a promising synthetic biopolymer derived from agricultural feedstock.[5] However, PLA is expensive due to complicated processing procedures. Starch is a readily available, abundant, and inexpensive natural polymer. Incorporating starch into PLA may reduce production cost. Previous research[6] shows that the mechanical properties are greatly improved in a starch/PLA (45/55, weight basis) blend containing only 0.5% wt methylenediphenyl diisocyanate (MDI). Physical aging is an inherent characteristic of the amorphous phase in glassy or partially glassy polymers and usually occurs around its glass transition temperature ($T_g$).[7,8] It involves spontaneous changes of the thermodynamic state of a material that are completely reversible. When a polymer is cooled from melt state, its molecular chain becomes frozen if the temperature is below its $T_g$. The polymer is in a nonequilibrium state, having large volume, enthalpy, and entropy.[7] At temperatures near or slightly below $T_g$, the free volume will reduce spontaneously toward an equilibrium thermodynamic state, resulting in a reduction in enthalpy. This process is referred to as physical aging, and it is time-dependent.

The concept of free volume is usually used to describe the physical aging process. Free volume controls the molecular mobility of large segments of the polymer chains, which in turn influences the physical and mechanical properties, such as shrinking, stiffness, and brittleness, and decreases its damping.[9–11] Physical aging can be monitored by differential scanning calorimetry (DSC).[10,12] The endothermic enthalpic recovery peaks around $T_g$ in DSC scans indicate a reduction in free volume. In the present study, the effects of physical aging on the thermal and mechanical properties and the morphology of PLA/starch blends with or without MDI were reported.

## EXPERIMENTAL

### Materials

PLA resin with a molecular weight of 120,000 Da and derived mainly from L-lactic acid (99%) was purchased from Shimadazu (Tokyo, Japan). Wheat starch (Midsol 50) with an amylose content of about 23–28% and a particle size of 17.95–18.09 $\mu$m was provided by Midwest Grain Products, Inc. (Atchinson, KS). Industrial corn starch (Silver Medal Pearl-1100) with an amylose content of about 25% was purchased from Cargill, Inc. (Minneapolis, MN). High-amylose corn starch (Hylon VII) with an amylose content of about 70% was provided by National Starch & Chemical (Bridgewater, NJ). All the starch samples were dried

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to about 0.5 wt % moisture content according to AACC method 44-15A[13] in a convection oven at 130 °C for 2 h before blending. Methylenediphenyl diisocyanate (MDI, Rubinate 1840) in a dark brown liquid form, a mixture of MDI and isomer containing about 45% 4,4′-MDI, was obtained from ICI Polyurethanes (Geismar, LA).

## Blends preparation

PLA resin from the manufacturer was ground using a laboratory mill (Model 4 Laboratory Mill (Thomas-Wiley Co., Philadelphia, PA)) with a 2-mm screen. The ground PLA was added to the dried starch from the various botanical sources (wheat, corn, and high-amylose corn, respectively) at a ratio of 1/1 (PLA/dried starch) by weight, and MDI was added at 0.5 wt %, on the basis of the dried starch and PLA total weight. The mixtures were then blended in an intensive compounder (Rheomix 600, Haake (Paramus, NJ)) equipped with two corotating rollers at 180 °C and 135 rpm for 4 min. The blends without MDI were prepared in the same way.

## Differential scanning calorimetry (DSC)

The thermal transitions of the blends were determined using a DSC (Perkin-Elmer Pyris 1 (Norwalk, CT)). The temperature and enthalpy of the DSC were calibrated using an indium standard. About 8 mg of each blend were weighed into an aluminum DSC pan. The thermal behavior was recorded by heating the sample from −20 to 170 °C at a rate of 10 °C/min under nitrogen purge. The excess enthalpy of relaxation caused by physical aging was characterized by integrating the area under the endothermic peak occurring around the $T_g$.

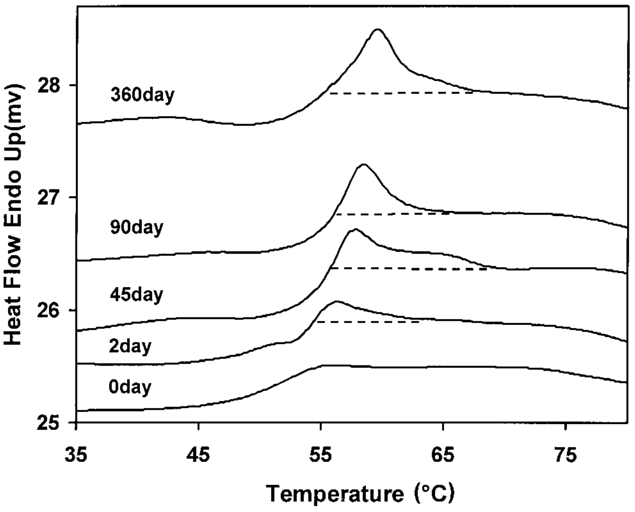

**Figure 1** DSC thermograms of the PLA/wheat starch blend (w/w, 1/1) with 0.5% MDI aged at 25 °C and 50% RH for various lengths of time (2, 45, 90, and 360 days).

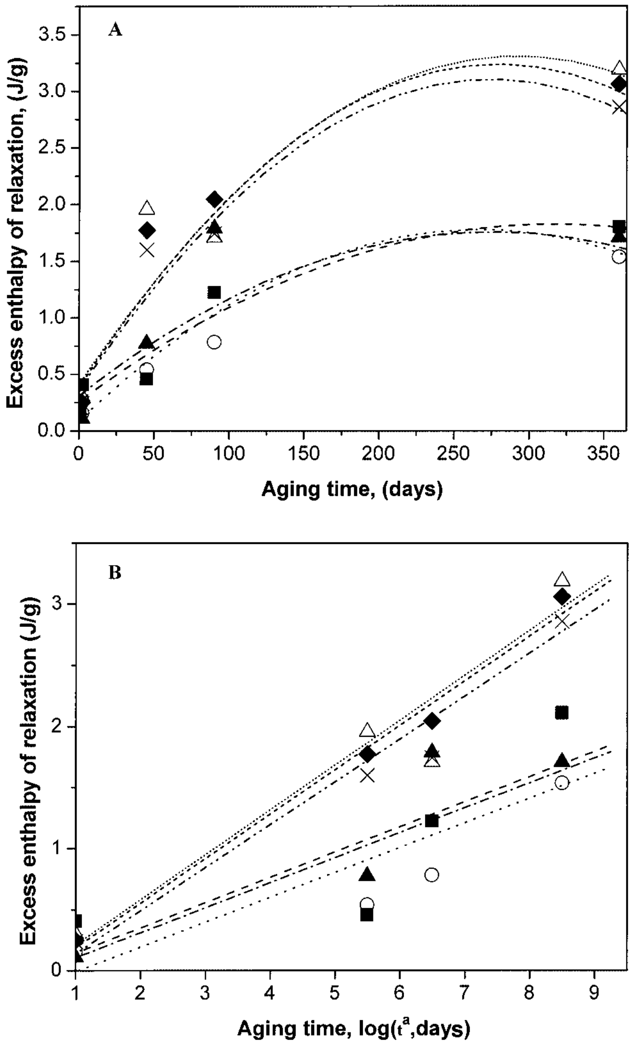

**Figure 2** Excess enthalpy relaxation (A) and log aging time (B) as affected by aging time for the blend with equal weight of PLA and starch without or with 0.5 wt % MDI aged at 25 °C and 50% RH for various days: wheat starch and 0.5% MDI (– – ■ – –), corn starch with 0.5% MDI (· · · ○ · · ·, high-amylose corn starch with 0.5% MDI (– ● –▲– ● –), wheat starch without MDI (–··–×–··–), corn starch without MDI (– – ◆ – –), and high-amylose starch without MDI (· · · Δ · · ·).

## Tensile testing

The blends from the hot mixer were ground by a laboratory mill (Model 4 Laboratory Mill, Thomas-Wiley (Philadelphia, PA)) with about a 2-mm particle size and then compression-molded into a testing specimen (type IV) following ASTM method D 638-91[14] using a hot press (Model 3890, Auto "M", Carver Inc. (Wabash, IN)) at 176 °C and a molding pressure of 4.2 MPa for about 15 min for the blend with MDI and 8

**TABLE I**
**Mechanical Properties of Blends of Equal Weight of PLA and Various Starches without MDI**

| | Wheat | | | Native corn | | | High-amylose corn | | |
|---|---|---|---|---|---|---|---|---|---|
| Days | $\sigma$ (MPa) | $\varepsilon$ (%) | E (GPa) | $\sigma$ (MPa) | $\varepsilon$ (%) | E (GPa) | $\sigma$ (MPa) | $\varepsilon$ (%) | E (GPa) |
| 2 | 31.79a | 2.7a | 1.67b | 34.58a | 2.6a | 1.68a | 34.74a | 2.7a | 1.62a |
| 45 | 32.74a | 2.5a | 1.77a | 32.24a | 2.4ab | 1.73a | 29.31bc | 2.4b | 1.62a |
| 90 | 32.96a | 2.6a | 1.66b | 32.97a | 2.4b | 1.72a | 31.11b | 2.5ab | 1.58a |
| 360 | 28.49b | 2.5a | 1.55c | 27.56b | 2.5ab | 1.48b | 27.34c | 2.4b | 1.49b |

Blends aged at 25 °C and 50% RH for various days.

[a] Values in the same column followed by the same letter are not significantly different ($P < 0.05$).

**TABLE II**
**Mechanical Properties of Blends of Equal Weight of PLA and Various Starches with 0.5 wt.% MDI**

| | Wheat | | | Native corn | | | High amylose corn | | |
|---|---|---|---|---|---|---|---|---|---|
| Days | $\sigma$ (MPa) | $\varepsilon$ (%) | E (GPa) | $\sigma$ (MPa) | $\varepsilon$ (%) | E (GPa) | $\sigma$ (MPa) | $\varepsilon$ (%) | E (GPa) |
| 2 | 63.70a | 5.2a | 1.75a | 58.79ab | 5.3a | 1.72a | 60.80a | 5.3a | 1.64ab |
| 45 | 61.12a | 4.4bc | 1.80a | 60.64a | 4.8bc | 1.71a | 58.97ab | 4.4bc | 1.73a |
| 90 | 54.62b | 4.7ab | 1.55b | 57.82b | 5.0ab | 1.64b | 57.28b | 4.8b | 1.57bc |
| 360 | 51.32b | 4.0c | 1.58b | 53.12c | 4.4cd | 1.50c | 52.43c | 4.2cd | 1.54cd |

Blends aged at 25 °C and 50% RH for various days.

[a] Values in the same column followed by the same letter are not significantly different ($P < 0.05$).

min for the blend without MDI. The molded specimens were then cooled to 57 °C before being removed from the mold and were stored at 50% relative humidity (RH) and 25 °C. Samples were tested following 2, 45, 90, and 360 days of storage. Tensile strength, elongation, and modulus at break of the aged specimens were determined using an Instron testing system (Model 4465 (Canton, MA)) according to ASTM method D 638-91[14] with a crosshead speed of 5 mm/min and a 25-mm gauge length. Five replicates were molded for each treatment at each storage period.

### Moisture content

The moisture content of the aged specimens was determined using the fractured specimens from the tensile test. The fractured specimens were dried at 130 °C in a conventional oven for three days. Three replicates were tested for each blend/storage blend treatment.

### Morphology

The microstructure of a blend was observed using a scanning electron microscope (SEM) (Hitachi S-3500N (Hitachi Science Systems, Ltd., Ibaraki, 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 by a sputter coater (Desk II Sputter/Etch Unit, Denton Vacuum, Moorestown, NJ) prior to the observation.

## RESULTS AND DISCUSSION

### Thermal properties

PLA is a semicrystalline polymer, and dried starch exists in a granular form in the blend. The thermal behavior of the blend characterized by DSC is a description of the PLA matrix.[10,12] Figure 1 shows the DSC thermograms of PLA/wheat starch blends with MDI aged at 25 °C and 50% relative humidity for

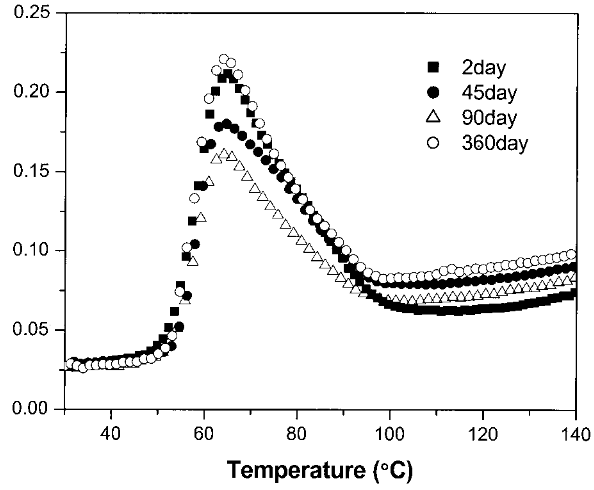

**Figure 3** Tan $\delta$ as a function of temperature at 1 Hz for the blends of PLA and wheat starch (w/w, 1/1) with 0.5 wt % MDI at 25 °C and 50% RH for various lengths of storage time (2, 45, 90, 180, and 360 days).

**TABLE III**
**Percent Moisture Content of Blends of Equal Weight of PLA and Various Starches with 0.5 wt% MDI**

| Sample | Days | | | |
|---|---|---|---|---|
| | 2 | 45 | 90 | 360 |
| Native corn starch with MDI | 2.99 | 3.51 | 3.00 | 3.99 |
| Native corn starch without MDI | 3.27 | 3.55 | 3.17 | 4.70 |
| Wheat starch with MDI | 3.21 | 3.60 | 3.15 | 4.13 |
| Wheat starch without MDI | 3.10 | 3.47 | 3.80 | 4.19 |
| High-amylose corn starch with MDI | 2.73 | 3.52 | 3.20 | 3.97 |
| High-amylose corn starch without MDI | 2.84 | 3.35 | 3.24 | 4.08 |

Blends aged at 25 °C and 50% RH for various days.

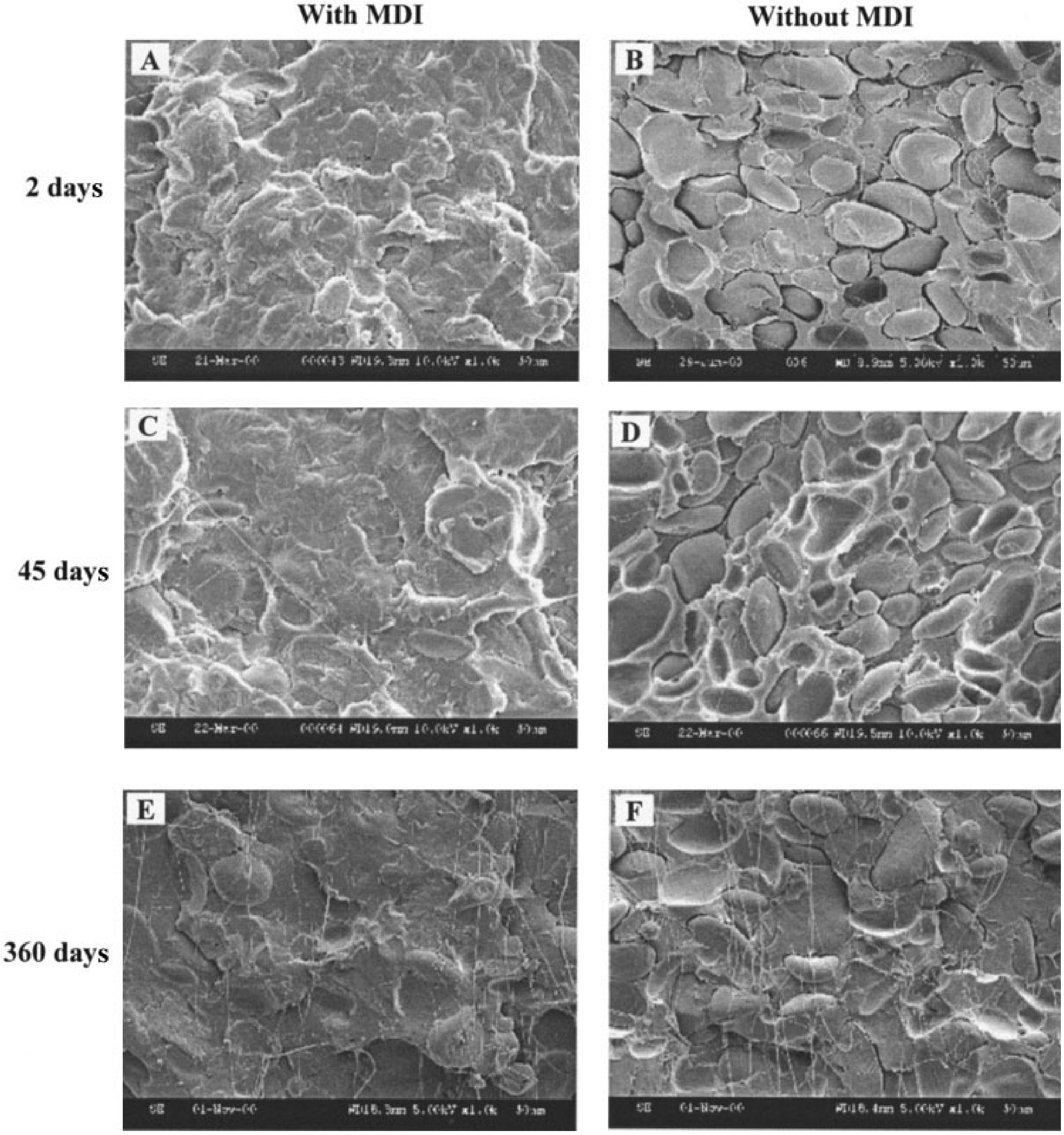

**Figure 4** Scanning electron micrographs of the tensile fracture surface of PLA and wheat starch (w/w, 1/1) blends with MDI aged for two days (A), 45 days (C), and 360 days (E); and without MDI aged for two days (B), 45 days (D), and 360 days (F).

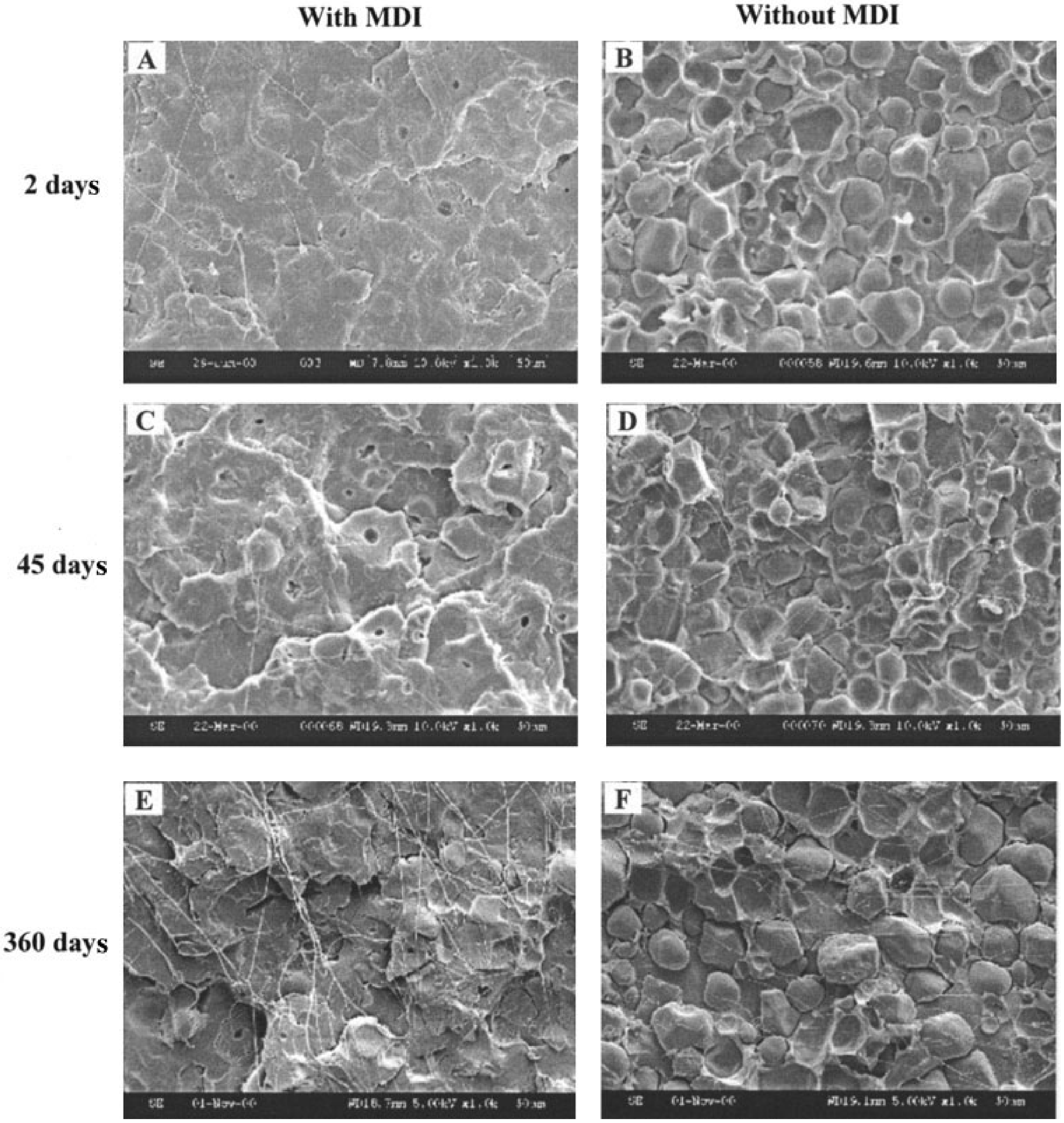

**Figure 5** Scanning electron micrographs of the tensile fracture surface of PLA and corn starch (w/w, 1/1) blends with MDI aged for two days (A), 45 days (C), and 360 days (E); and without MDI aged for two days (B), 45 days (D), and 360 days (F).

different periods of time. The excess enthalpy of relaxation ($\Delta H_{EX}$) of the blend at its $T_g$ increased as aging proceeded. All the blends had similar DSC characteristics. The aging was initially rapid and then slowed as storage time increased, as shown in Figure 2(A). The apparent linear relationship of $\Delta H_{EX}$ vs log $t_a$ storage time, shown in Figure 2(B), indicates an exponential relationship.

The aging rate of the blends was independent of the starch source but was influenced by the addition of MDI. The blends with MDI showed a much slower aging rate compared with those of the blends without MDI. Previous work[6] has proven that a stronger interfacial interaction exists between PLA and starch with addition of MDI and that the PLA matrix is constrained by starch granules. The excess enthalpy of relaxation is correlated to the free volume, which reduced slowly for the blend with MDI because of the stronger interfacial adhesion.

## Mechanical properties

For the blend with native corn and high-amylose corn starch without MDI, the tensile strength of the blends

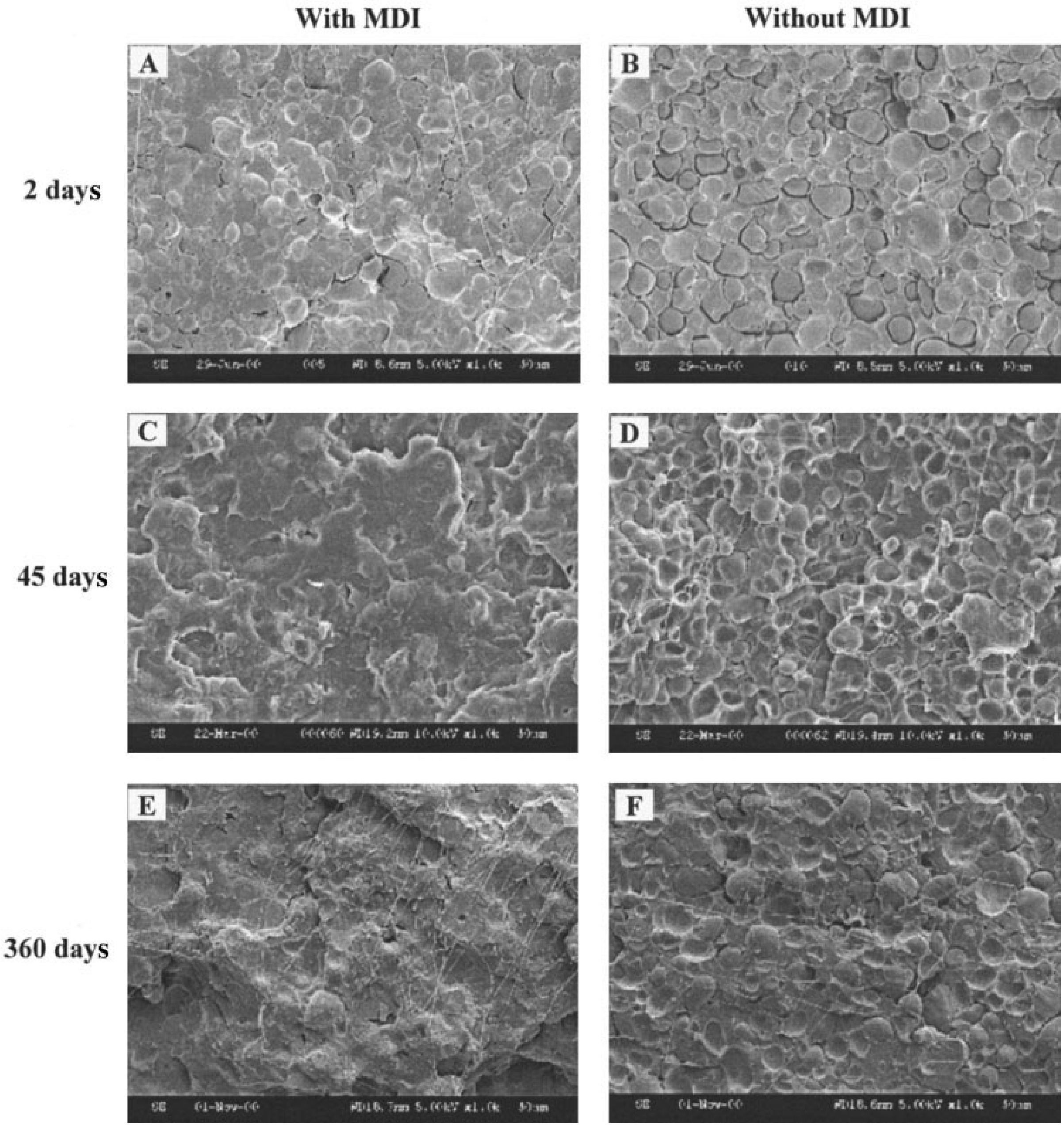

**Figure 6** Scanning electron micrographs of the tensile fracture surface of PLA and high amylose starch (w/w, 1/1) blends with MDI aged for two days (A), 45 days (C), and 360 days (E); and without MDI aged for two days (B), 45 days (D), and 360 days (F).

at day two was slightly higher than that with wheat starch (Table I). This result is in agreement with that reported by Lim and Jane.[16] Wheat starch in this work had an average particle size of 18 $\mu$m, while corn and high-amylose corn starch had a similar size of about 10.3–11.5 $\mu$m.[15,16] For a filling system, the internal stress and strain are less uniformly distributed for larger particle size filler than for smaller particle size filler, resulting in poor tensile properties.[17] However, for the blends with MDI, the tensile strength is higher for the blend with wheat starch than for the blend with native corn or high-amylose corn starch (Table II). Wheat starch, because of its larger particle size, has smaller total surface area than corn or high-amylose corn starch at the same weight ratio to PLA. Therefore, less MDI would be needed to wet and disperse, and this would lead to a stronger interfacial adhesion.

The tensile properties of the samples decreased as the aging time increased in the first 90 days. Dynamic mechanical analysis also showed that tan $\delta$ decreased with aging time during the first 90 days (Fig. 3). As discussed, the free volume reduced as the aging proceeded, resulting in a reduced molecular mobility and, hence, decreased mechanical properties. It was a typical characteristic of aging that tan δ decreased,[7] which is in agreement with the DSC data on excess enthalpy of relaxation presented in Figure 2(A). However, the tan δ for the sample stored 360 days increased tremendously. The moisture content of the sample increased from about 3.0% at day two and leveled off at 3.5% during the first 90 days. Then the moisture content increased to 4.2% at day 360 (Table III) for this sample as shown in Figure 3. The accumulated moisture absorbed by the starch acted as a plasticizer, resulting in a significant rise in tan δ.

### Microstructure

Morphological studies, with the aid of scanning electron microscopy (SEM), provide the source of the fracture and the relationship of the microstructure and mechanical properties. All blends, regardless of starch types, had a similar microstructure. Figures 4–6 show the microstructures of the blends from wheat, corn, and high-amylose starch, respectively. Wheat starches (Fig. 4) show a larger particle size than corn (Fig. 5) and high-amylose corn (Fig. 6). The samples with MDI at day two (Figs. 4(A), 5(A), and 6(A)) express a typical compatible structure, which was well wetted and bound at the interface, while the structure of the blend without MDI (Fig. 4(B)) is typically noncompatible. For samples with MDI at day 360 (Figs. 4(E), 5(E), and 6(E)), there are minor gaps observed around the interface at some locations, which probably were caused by the reduced interfacial interaction from both physical aging and the rise in RH. Many starch granules were split into two halves, indicating that the starch granules were not as rigid as those at day two. These results are in agreement with the changes in thermal and mechanical properties.

Moreover, many threads derived from the interface were observed in blends containing MDI as aging proceeded. This phenomenon was also observed on the fracture surface of the blend without MDI (Figs. 4(F), 5(F), and 6(F)), but less than on the surface of those with MDI (Figs. 4(E), 5(E), and 6(E)). The ability of the starch granules in the blend to be wetted and bound was enhanced because of MDI, which meant a decrease in surface energy. This, in turn, increased the amorphous region at the interface of the PLA matrix.[17,18] Crystalline regions are more rigid, restrained, and less extensible than amorphous regions. As mentioned earlier, when the aging proceeded, the PLA matrix shrank, resulting in a gap around the interface, where some molecular chains were less restricted by the interfacial interaction. Hence, during tensile stretching, the less crystallized PLA molecular chains around the interface were more stretchable as compared with those away from the interface.

## CONCLUSIONS

The enthalpy of relaxation (aging rate) of the blend decreased quickly in the first 90 days of aging and then slowed down. The blends with MDI had a slower aging rate than those without MDI. Both physical aging and an increase in moisture level due to relative humidity are two possible factors leading to a decrease in mechanical properties of the starch/PLA blends during storage. Physical aging and moisture level may have an interactive effect. Combined, they could interfere with the interfacial interaction between starch and PLA.

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