

Enhancing Compatibilizer Function by Controlled Distribution in Hydrophobic Polylactic Acid/Hydrophilic Starch Blends

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ABSTRACT: Various polylactic acid (PLA)/cornstarch blends, with and without the compatibilizer methylenediphenyl diisocyanate (MDI), were prepared by melt processing using a twin-screw extruder. In the blends where it was included, MDI was distributed in either the PLA or starch phase through controlling processes conditions. The effects of MDI inclusion and its distribution on the resultant microstructures, mechanical properties, and thermal and rheological behaviors of the blends were studied via scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis, mechanical testing, and Haake rheometer. The

results showed that when the MDI was distributed in the starch phase before blending with PLA, the highly reactive isocyanate groups in the MDI were most probably consumed by water, resulting in an overall weakening of its compatibilizing effect. However, when the MDI was distributed in the PLA phase before blending with starch, modulus, yield strength, and impact strength were all increased. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2189–2195, 2011

Key words: PLA; starch; blend; compatibilizer; distribution; microstructure

INTRODUCTION

The development of biodegradable materials, especially for short-term applications, has become increasingly important due to environmental concerns and because of the depletions of global oil reserves. Blending techniques are particularly important in the development of new biodegradable materials, as most raw materials are either of poor quality or very expensive. Polylactic acid (PLA) and starch are two promising candidates for biodegradable polymer blends, because both materials are commercially available and are derived from renewable resources.^{1–27} However, hydrophobic aliphatic polyester PLA and hydrophilic starches are thermodynamically immiscible, which generally leads to poor adhesion between the two components and thus poor performance. Various compatibilizers and addi-

tives to improve the interfaces between PLA and starch have been evaluated, such as polyvinyl alcohol,⁸ acetyl triethyl citrate,^{9,10} maleic anhydride,^{11–14} and lactide.^{15,16}

Chemicals containing isocyanate groups have attracted much attention as possible compatibilizers or coupling agents for PLA and starch,^{17–25} and methylenediphenyl diisocyanate (MDI), in particular, has been widely investigated.^{21–25} Blends incorporating MDI have exhibited enhanced mechanical properties that could be explained by the *in situ* formation of a block copolymer that acts as a compatibilizer. Starch is a highly hydrophilic material that contains anhydro-glucose units linked by α -D-1,4-glycosidic bonds. Native and gelatinized starch normally contains moisture. Previous research has shown that reactive functional groups, such as the isocyanate groups in MDI, could be consumed by the water absorbed in starch granules, which would weaken the coupling function at the interfaces between the starch and polyester phases.^{24,28,29}

In this work, we have been trying to develop a processing technique to enhance the function of compatibilizer MDI. In this article, we reported different methods of MDI distribution in PLA/starch blends, and their effectiveness in reducing the reactions between the isocyanate groups in MDI and the water in starch, and thus enhancing compatibilizer

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function. The effects of the inclusion of MDI, and in particular its distribution, on the microstructural, mechanical, and rheological properties of various blends of hydrophobic PLA and hydrophilic starch were systematically studied via scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), mechanical testing, and Haake rheometry.

EXPERIMENTAL

Materials and Compounding

A commercially available PLA (PLA 7000D from NatureWorks) and a high-amylose cornstarch with a moisture content of 13.1% (supplied by Penford, Australia) were used in the experimental work. Starch was first gelatinized with water at a ratio of 75/25 using a twin-screw extruder (Thyson Ø30, L/D 40) with screw configuration of two mixing zones. The 10 temperature zones from feeder to die were set to 70, 90, 120, 150, 170, 160, 140, 120, 115, and 110°C, respectively. The low die temperature was set up to avoid foaming during gelatinization extrusion. RPM was 120. Pellets of gelatinized starch were then premixed with PLA, at various ratios, before compounding in the extruder set to a maximum temperature of 180°C.

The compatibilizer, MDI (purity 99.9% wt), was added into the blends at different stages to control its distribution (either 0.5 or 1.0% wt):

- MDI was added to the starch phase during starch gelatinization—specimens-labeled PLA/(Starch+MDI).
- MDI was first compounded with the PLA phase before blending with gelatinized starch—specimens-labeled (PLA+MDI)/Starch.

To obviate the effects of PLA decomposition during extrusion, all the PLA in this work were subject to the same extrusion times.

An additional set of samples was produced, whereby, premixed PLA and MDI were delivered to the extruder through the main hopper, whereas gelatinized starch was added via a side-feeder attachment. The results from this set of samples were used to support those blends prepared with MDI distributed in the PLA phase before blending with starch.

Torques during compounding was recorded to analyze the processing properties of the blends.

Specimen preparation and mechanical testing

All mechanical test specimens were prepared using a Battenfeld injection molder at an injection temperature of 180°C. Tensile properties were evaluated in accordance with American Society for Testing and

Materials (ASTM) D5938 on an Instron tensile testing apparatus (5565) at a crosshead speed of 10 mm/min. Impact testing was carried out in accordance with ASTM 256 on a Radmana IRT 2000 instrumented impact tester in Izod mode at an impact strain rate of 3.5 m/s. All the specimens were kept in the same conditions (23°C and 64% RH) for 48 h before testing.

Microstructure characterization

An FEI Quanta 200 ESEM was used to examine the morphologies of both impact-fracture and freeze-fracture surfaces of the various blends, with imaging performed in high-vacuum mode at an accelerating voltage of 10 kV. All fracture surfaces were coated with iridium before examination. Freeze-fracture surfaces were obtained by immersing specimens in liquid nitrogen for 3 min and then manually fracturing them. These specimens were then immersed in an ultrasonic water bath for 1 h at ~ 50°C to dissolve and remove any starch phase on the surfaces. Surfaces were examined by SEM before and after surface starch removal.

Thermal analysis

A Pyris-1 DSC was used to study the effects of MDI on the thermal properties of samples cut from impact specimens. The specimens were first heated to 220°C and kept at that temperature for 1 min to remove all previous thermal history, then quenched to produce amorphous PLA. A heating rate 5°C/min was used to evaluate the thermal behaviors of the materials heated from 40 to 200°C. A Pyris-1 TGA apparatus was used to study the thermal stability of samples heated to 650°C at a rate of 20°C/min in the N₂ atmosphere.

RESULTS AND DISCUSSION

Figure 1 shows the mechanical properties of the various blends as a function of MDI inclusion and distribution, and PLA/starch ratio. For the blends without MDI, modulus initially increased slightly with the addition of starch, reaching a maximum at a PLA/starch ratio of approximately 80/20. Any further increase in starch content resulted in a reduction in the modulus value. A similar pattern was observed for impact strength; however, maximum values were attained at ~ 40% starch content. Tensile strength decreased slightly with increasing starch content. Similar results for blends without the inclusion of a compatibilizer are reported elsewhere.^{5–19}

Figure 1 also shows that the addition of MDI resulted in high modulus, tensile strength, and impact strength and that increasing the MDI content

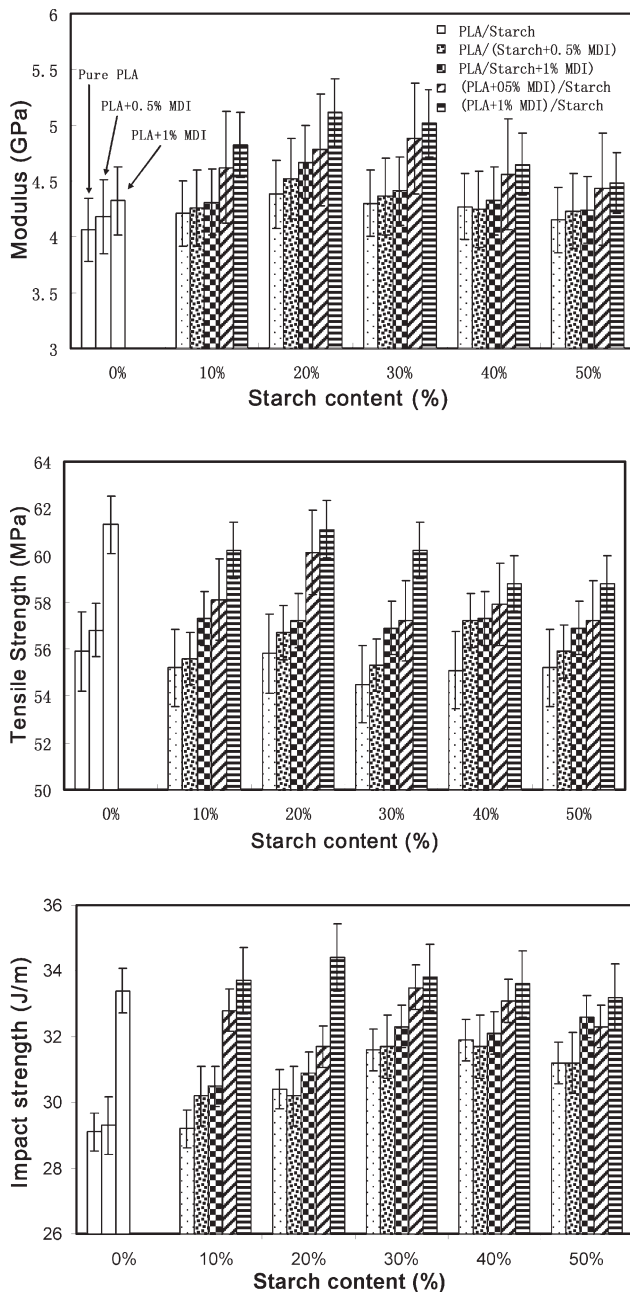


Figure 1 Mechanical properties of blends as a function of MDI distribution and PLA/starch ratio.

from 0.5 to 1.0% resulted in further improvement in mechanical properties. Similar trends as a result of compatibilizer inclusion have been reported previously,^{20–23} and have been explained by the *in situ* formation of a compatibilizing block copolymer between the isocyanate groups in MDI and the hydroxy groups associated with the starch and polyester.

It is important to note that the distribution of MDI had a clear effect on the mechanical properties of blends, with the highest values recorded for blends where MDI was distributed in the PLA phase before blending with starch. This phenomenon can be

explained by the tendency of the highly reactive isocyanate groups in MDI to react with the water absorbed in starch.

If MDI is initially compounded with starch and 25% water, the dominant interaction would be expected to be between the MDI and water, due to the high free-water content. In the current work, the gelatinized starch not only had a lower concentration of water (~ 16%) but also the water molecules may have had reduced mobility if they were bound (via hydrogen bonding) to the numerous hydroxyl groups present in the starch. A small amount of bubbles due to NCO/H₂O reaction were observed in the compounded pellets; however, these were removed in the injection molding process.

The most pronounced improvements to mechanical properties occurred in the blends where MDI was incorporated in the PLA phase before blending with gelatinized starch, which could be explained by a number of different mechanisms. For example, during the pre-blend extrusion, the MDI may have reacted with the hydroxy groups present at the end of the PLA polyester chains, producing a MDI-grafted polyester that extended the chain lengths,^{30,31} or it may have remained unreacted but well dispersed within the polyester matrix (based on the calculation of PLA mole 1: MDI mole 2.4 for MDI 0.5% formulation). In the first scenario, the isocyanate groups in the MDI-grafted polyester could have then reacted with the hydroxyl groups in the starch during the second extrusion to produce a compatibilizing starch/polyester block copolymer. In the second scenario, the freely dispersed isocyanate groups in the MDI could have reacted with the hydroxyl groups in the starch and PLA during the second extrusion. In addition, the extrusion of PLA + MDI with gelatinized starch may have resulted in further hydrolysis of the ester groups in the PLA via the water bound in the gelatinized starch, producing more hydroxyl end groups for the isocyanate to react with.

Figure 2 shows SEMs of the impact-fracture surfaces of different PLA/starch blends (ratio 70/30) after mechanical testing in which PLA appears as a continuous phase with starch distributed as spherical particles (maximum diameter ~ 15 μm). For the blend without MDI [Fig. 2(a)], the interfaces between the starch and PLA phases are poor, and thus, the phase separation between starch and PLA can be clearly observed. There are clear gaps between starch particles and PLA matrix. This is expected, as hydrophilic starches and hydrophobic aliphatic polyesters are thermodynamically immiscible. Figure 2(b) shows the fracture surface of the blend with MDI distributed in the starch phase, starch particles can be clearly identified, indicating that little reaction had occurred between the isocyanate in the MDI

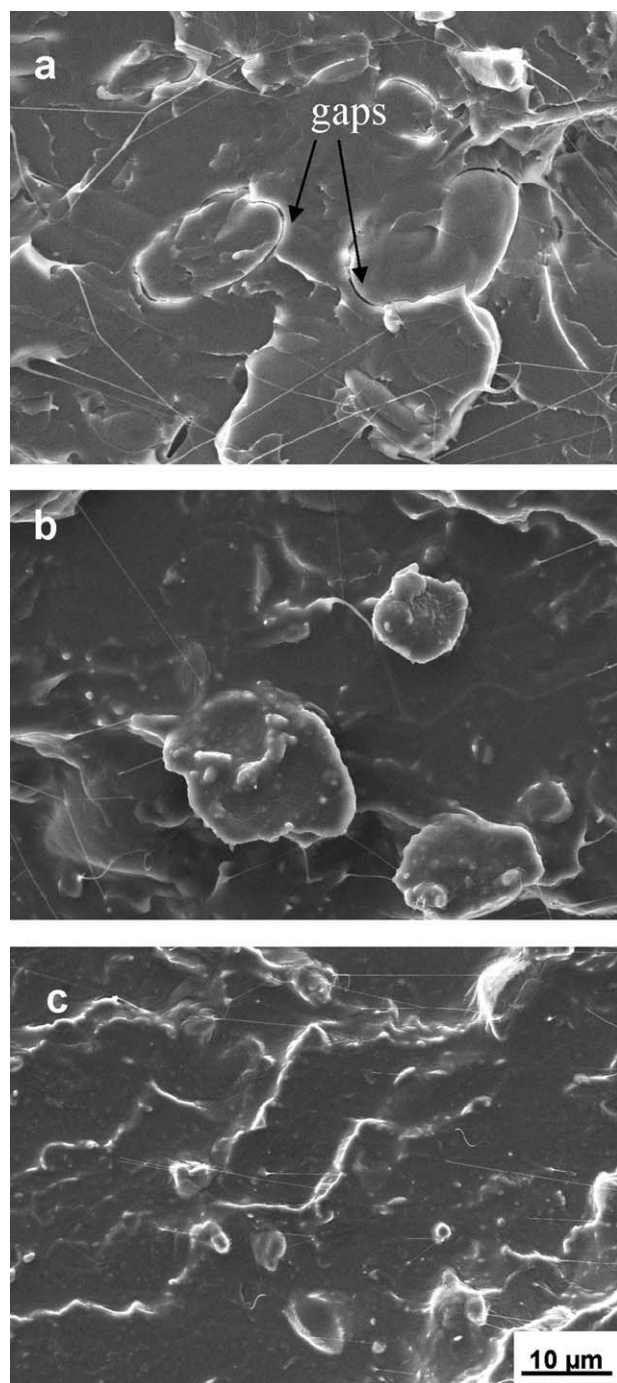


Figure 2 SEMs of impact-fracture surfaces of PLA/starch blends (ratio 70/30) containing 1% MDI distributed in different phases: (a) reference PLA/starch blend without MDI; (b) PLA/(Starch+MDI); and (c) (PLA+MDI)/Starch.

and the hydroxyl groups in starch and PLA, with the isocyanate have more likely been consumed by the water in the starch. On the other hand, the fracture surface of the blend, where MDI was distributed in the PLA phase revealed significant improvement in phase compatibility, as shown in Figure 2(c) in which spherical starch particles and the interfaces between the phases are indistinct. This improved

compatibility correlates with the observed improvements to mechanical properties and can be explained by the formation of a compatibilizing block copolymer between the isocyanate groups in MDI and the hydroxy groups in the starch and PLA.

Figure 3 shows SEMs of freeze-fracture surfaces of PLA/starch blends (ratio 70/30), both before and after the ultrasonic bath treatment to remove surface starch. In this figure, the images are of prebath surfaces (left), postbath surfaces (center), and higher magnification of postbath starch holes. As with the impact-fracture surfaces, the PLA appears as a continuous phase, whereas the starch phase appears in spherical form or as dark holes (maximum diameter $\sim 10 \mu\text{m}$) following surface starch removal. Figure 3(a) shows the PLA/starch blend without MDI. It is seen that removed starch appears as spherical holes with smooth edges. Similar microstructure was also observed when MDI was distributed in the starch phase [Fig. 3(b)]. When the MDI was distributed in the PLA phase, the shape of the holes became irregular [Fig. 3(c)]. The spherical holes became random and the edges became rough and unclear. Figure 3(a1, b1, and c1) shows the enlarged holes from SEM images on the left. It can be observed that the surface and edge of the holes are very smooth when the MDI was distributed in starch phase or without MDI [Fig. 3(a,b)]. The surface of the holes became rough and some broken pieces appear on the surface when MDI was distributed in PLA phase, giving a clear indication that the interface between starch and PLA has been improved through addition of MDI into the PLA phase.

The effects of MDI distribution were also evaluated by DSC and TGA. Figure 4 shows DSC thermograms of pure PLA, gelatinized starch, and PLA/starch blends with and without MDI. There are no discernible changes of the thermograms for the gelatinized starch ($\sim 12\%$ moisture content) with and without MDI (see “Starch and PLA” in Fig. 4), which is expected as the thermal signals of gelatinized starch (glass transition and recrystallization) are much weaker than conventional polymers.^{32,33} The glass transition temperature T_g ($\sim 60^\circ\text{C}$), cold crystallization temperature T_c ($110\text{--}130^\circ\text{C}$), and melting temperature T_m ($140\text{--}160^\circ\text{C}$) of PLA were detected for all blends. The addition of MDI to pure PLA had no discernable effect on its T_g , T_c , or T_m (see “Starch and PLA” in Fig. 4).

The T_g of PLA was relatively unaffected by blending with starch, either with or without MDI, due to the phase separation. MDI appeared to enhance the cold crystallization of PLA, and for the blends where MDI was distributed in the PLA phase (see “(PLA+MDI)/Starch” in Fig. 4), which exhibited improved interfaces between the PLA and starch, the starch may have acted as a nucleation agent for PLA, resulting in lower T_c values. For the T_m of

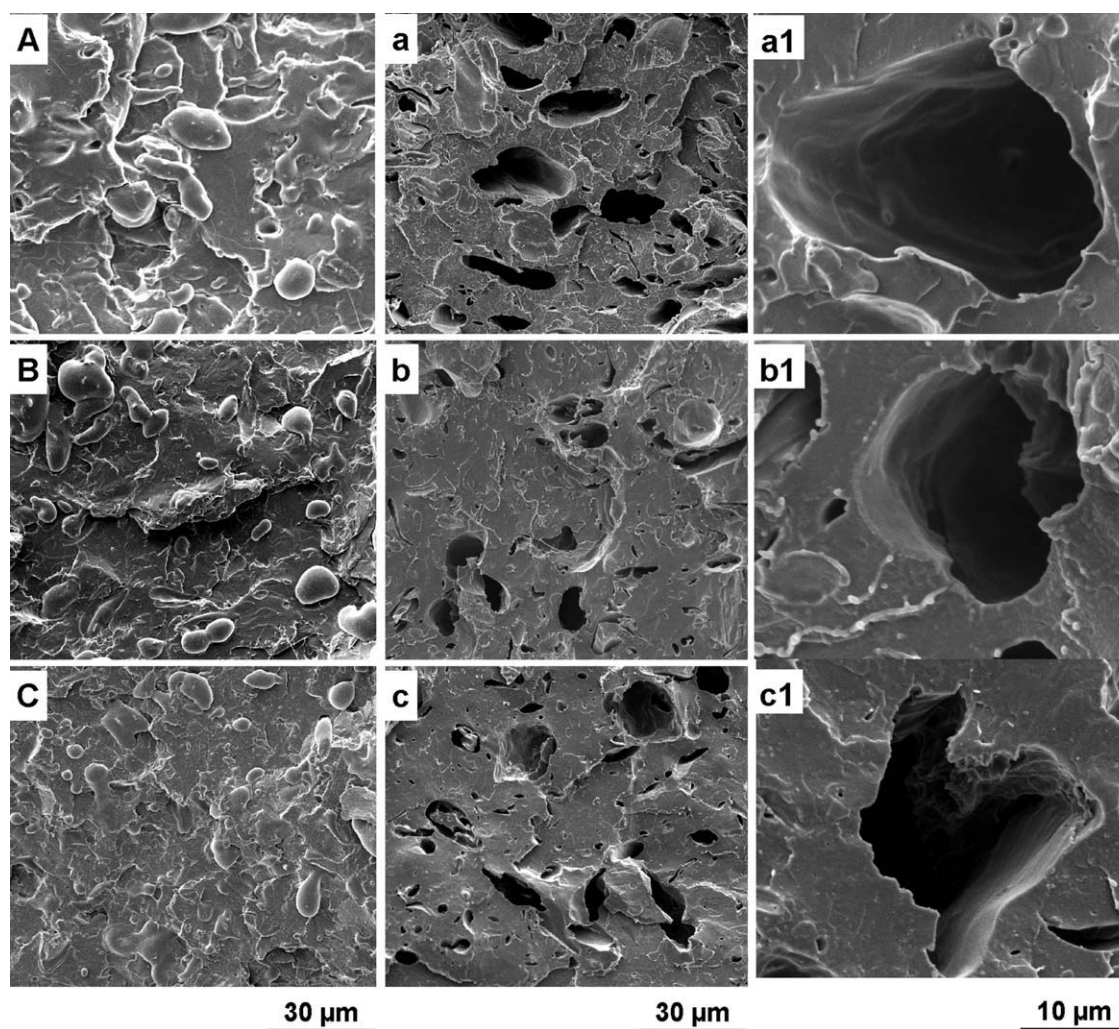


Figure 3 SEMs of freeze-fracture surfaces of PLA/starch blends (ratio 70/30) containing 1% MDI distributed in different phase. (A), (a), and (a1) reference PLA/starch blend without MDI; (B), (b) and (b1) PLA/(Starch+MDI); and (C), (c) and (c1) (PLA+MDI)/Starch.

PLA, it is interesting to note that the major discernible difference in the thermograms is the appearance of double melting peaks for the blends with MDI distributed in the PLA phase (see "(PLA + MDI)/Starch" in Fig. 4). Similar double melting peaks have been observed previously and were attributed to melting–recrystallization.³⁴ Again, the interfacial improvement between the PLA and starch may have enhanced nucleation, which would promote melting–recrystallization. The results of a detailed study of the thermal behavior of these blends will be published in a separate article.

Figure 5 shows the TGA results of the effects of MDI and its distribution on the decomposition temperatures of starch, PLA, and their blends. It can be seen that the decomposition peak of the pure starch was at $\sim 350^{\circ}\text{C}$ and that of PLA was $\sim 390^{\circ}\text{C}$. Although the decomposition peak of starch remained constant after the addition of MDI, that of PLA increased by $\sim 5^{\circ}\text{C}$. The two decomposition peaks observed for the PLA/

starch blends are attributed to the decomposition of starch and PLA, respectively. It is interesting to note that the second decomposition peak for the blend where MDI was distributed in the PLA phase was at a slightly higher temperature, which confirms the benefits of PLA-phase distribution of MDI.

Figure 6 shows the effects of MDI and its distribution on the torque of various blends during compounding at 180°C and 120 rpm. It is seen that addition of MDI increased the torque of pure PLA, which could be due to molecular weight increase through the reaction of isocyanate groups in MDI with the hydroxy groups at the end of PLA chain. Similar results for other polyesters such as Polycaprolactone (PCL) and Poly(butylene succinate adipate) (PBSB) have also been observed.²⁹ As shown in Figure 6, the highest torque values were recorded for the blends where MDI was distributed in the PLA phase, which further confirms the benefits of PLA-phase distribution of MDI. The results of a detailed

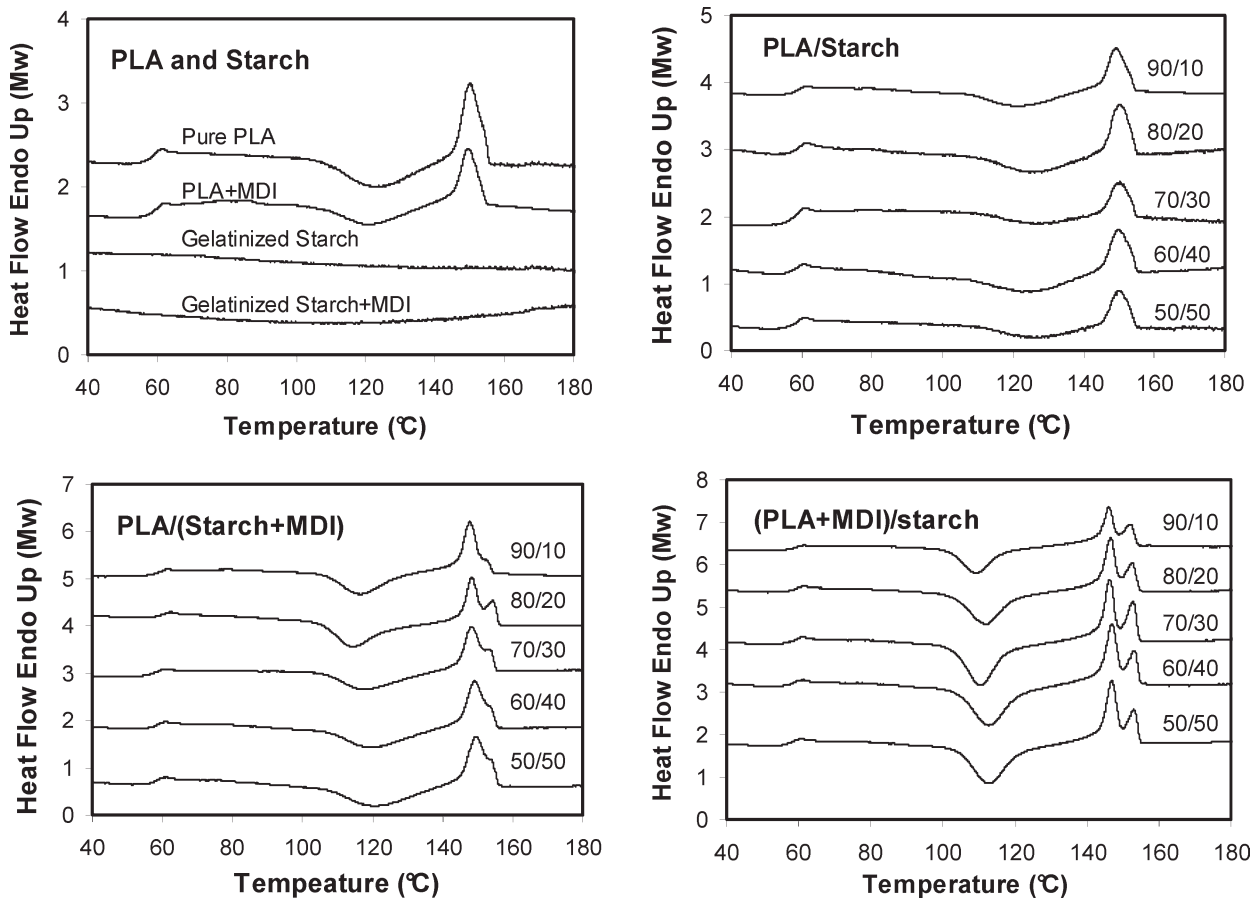


Figure 4 DSC thermograms of the effects of MDI distribution in PLA/starch blends on the thermal properties of PLA.

study of the rheological properties of the various blends will be reported in a separate article.

CONCLUSIONS

The function of compatibilizer MDI has been enhanced through controlling its distribution. Vari-

ous blends of biodegradable polyester PLA and gelatinized cornstarch, with and without the compatibilizer MDI, were prepared via melt blending using a twin-screw extruder. The distribution of MDI was controlled in either the PLA or starch phase through pre-blend processing. The results of DSC and TGA analyses showed that the blends revealed improved

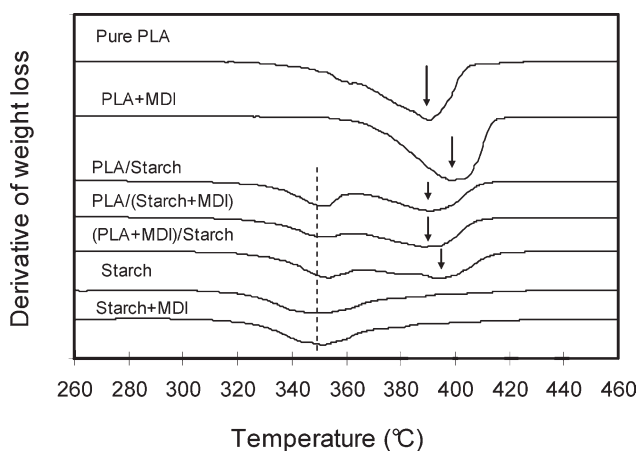


Figure 5 TGA results of the effects of MDI and its distribution on the thermal decomposition of PLA/starch blends.

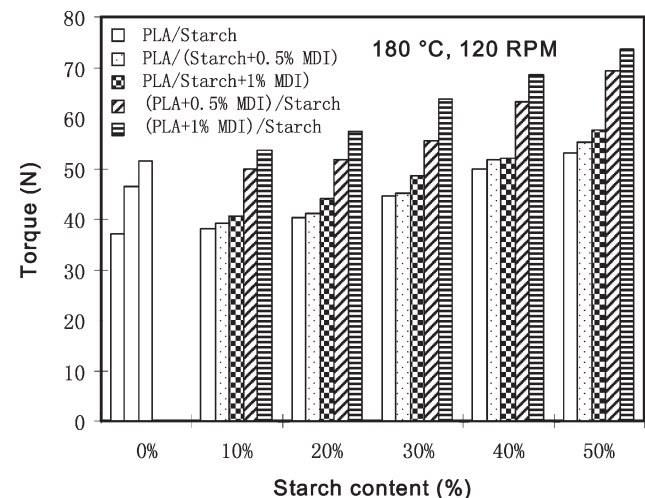


Figure 6 Effects of MDI and its distribution on the torque of PLA/starch blends during compounding.

thermal properties where MDI was distributed in the PLA phase recorded. The results of mechanical testing showed that modulus, yield strength, and impact strength were all increased when MDI was distributed in the PLA phase. SEM observations revealed that the interfaces between the starch and PLA phases were improved when MDI was distributed in the PLA phase. These improvements in mechanical and interfacial properties were possibly due to the formation of a compatibilizing block copolymer between the isocyanate groups in MDI and the hydroxy groups associated with the starch and polyester. The concept of enhancing the function of a compatibilizer through controlling distribution could be applied across a wide range of hydrophilic/hydrophobic blends.

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