Thermal and Mechanical Properties of Poly(lactic acid)/Starch/Methylenediphenyl Diisocyanate Blending with Triethyl Citrate

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Received 28 February 2002; accepted 9 September 2002

ABSTRACT: Triethyl citrate (TC) was added as a plasticizer to a blend of poly(lactic acid) (PLA) and starch in the presence of methylenediphenyl diisocyanate (MDI). As expected, TC improved the elongation at break and toughness and, at the same time, decreased the tensile strength and modulus. However, TC did not significantly affect the coupling effects of MDI on starch and PLA. The tensile strength of the blend with MDI was much greater than the tensile strength without MDI at the same TC level. The tensile properties of the blend changed dramatically as the TC concentration increased from 5 to 12.5%. At a TC concentration of 7.5%, the blend produced desirable elongation and toughness with fairly good tensile strength. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2947–2955, 2003

Key words: biodegradable plastics; mechanical properties; morphology

INTRODUCTION

Poly(lactic acid) (PLA) is a promising biodegradable polymer for use in place of petroleum-based polymers. Recently, it has been studied for applications in textiles, packaging products, and food utensils. Starch has been introduced into the PLA system to reduce the costs of the raw materials.[1–5] However, the mechanical strength of starch and PLA blends decreases dramatically, especially at high concentrations of starch because of the weak interfacial forces between starch granules and the PLA matrix.[5]

Methylenediphenyl diisocyanate (MDI) is highly reactive with both hydroxyl and carboxyl groups and forms a urethane linkage.[6] MDI was added to a starch/PLA (45/55 w/w) system to enhance the interfacial interactions between starch and PLA.[7] The mechanical properties of the blends with MDI were enhanced, and the modulus of the blends also improved at temperatures above the glass-transition temperature (T_g). The elongation of the blends ranged from 4 to 5% and was similar to that of pure PLA, which is considered too brittle and stiff for many applications.

Triethyl citrate (TC) is a small molecular weight citrate ester synthesized from naturally occurring citric acid and is commonly used as a plasticizer for many polymers.[8] It is also recommended for food applications because of its favorable physiological properties.[9] A previous study reported that citrate esters were miscible with PLA and effectively improved the elongation of PLA.[10] The objective of this study was to examine the effect of TC on the morphological, mechanical, and thermal properties of a PLA/starch/MDI blend.

EXPERIMENTAL

Materials

PLA was purchased from Shimadzu, Inc. (Tokyo, Japan). It had a molecular weight of about 120,000 Da and was polymerized mainly from L-lactic acid (according to the manufacturer's data sheet, the D stereoisomer level was less than 1%, and it was not detectable in an independent analysis). Wheat starch (Midsol 50) was obtained from Midwest Grain Prod-

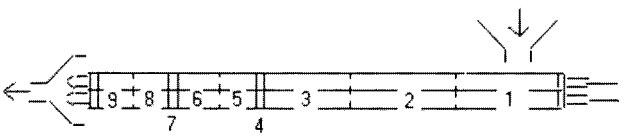

Figure 1 Schematic diagram of the screw configuration from the feeding zone to the die (American Leistriz Extruder): (1) GFF-2-30-90, (2) GFA-2-20-60, (3) GFA-2-10-90, (4) KB4-2-20-30°RE, (5) GFA-2-15-60, (6) GFA-20-10-30, (7) KB4-2-20-30°RE, (8) GFA-2-15-90, and (9) GFA-2-10-60. In 1–3, 5, 6, 8, and 9, the three numbers indicate the thread length, the pitch length, and the screw element, respectively; in 4 and 7, the four numbers stand for the kneading block, the thread number, the length of the kneading block, and the twisting angle of the kneading segments. G = corotating; F (in the second position) = conveying; A = free-meshing; F (in the third position) = freely cut; KB = kneading block; RE = conveying.

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This article is contribution 02-289-J from the Kansas Agricultural Experiment Station, Manhattan, KS 66506.

Journal of Applied Polymer Science, Vol. 88, 2947–2955 (2003)

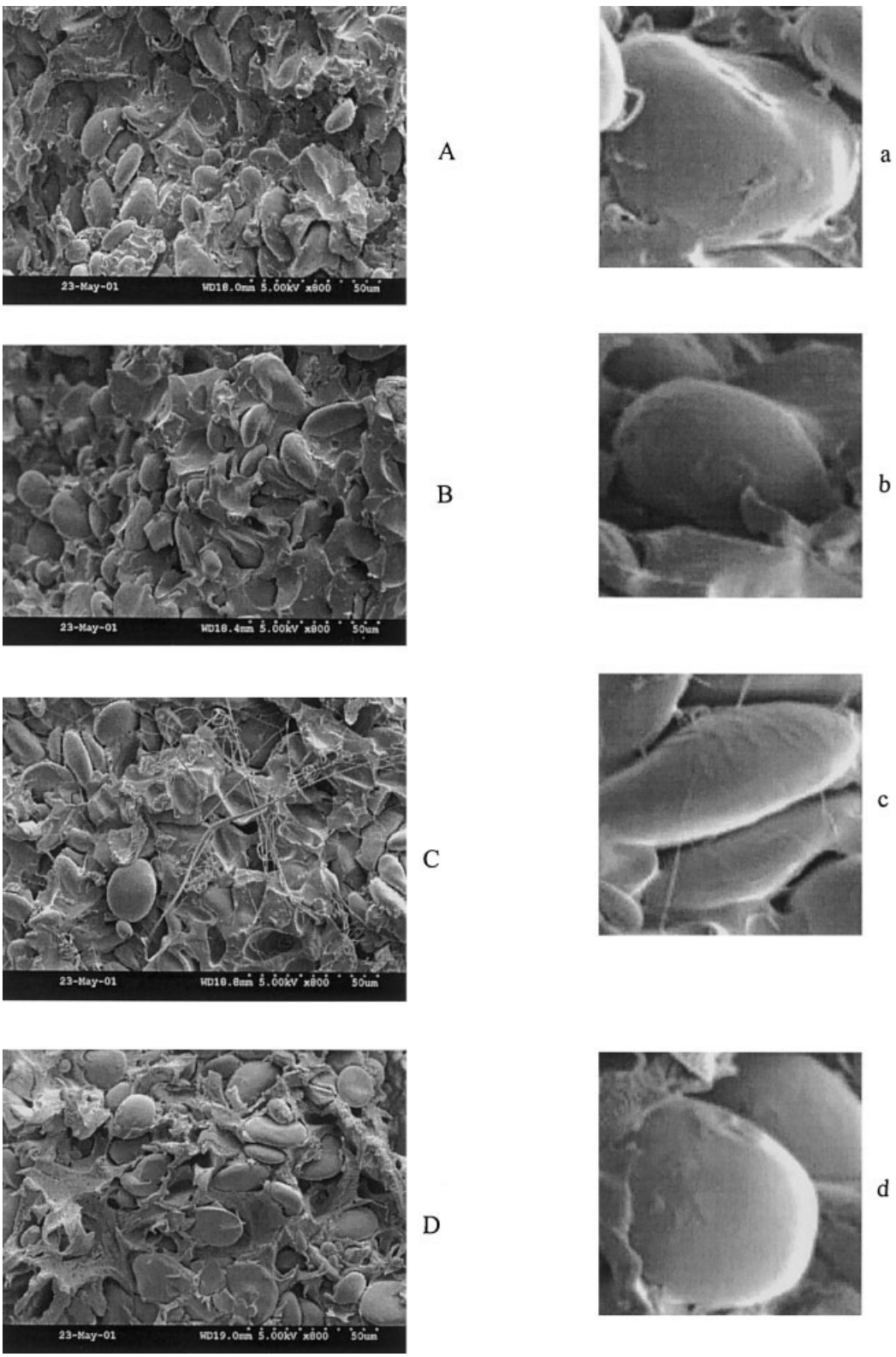


Figure 2 SEM micrographs of PLA/starch/MDI blends (55/45/0.5 w/w/w) with various TC contents: (A) 15, (B) 12.5, (C) 10, (D) 7.5, (E) 6.5, (F) 5.0, (G) 2.5, and (H) 0%. The photographs to the right (a–h) are amplified pictures of the corresponding images to the left at selected sites.

ucts, Inc. (Atchinson, KS). The granule contained approximately 75% amylopectin and 25% amylose. It was dried in a conventional oven at 130°C for 2 h according to AACC Method 44-15A (1995).11 Modified MDI was purchased from ICI Polyurethanes Group (West Deptford, NJ).

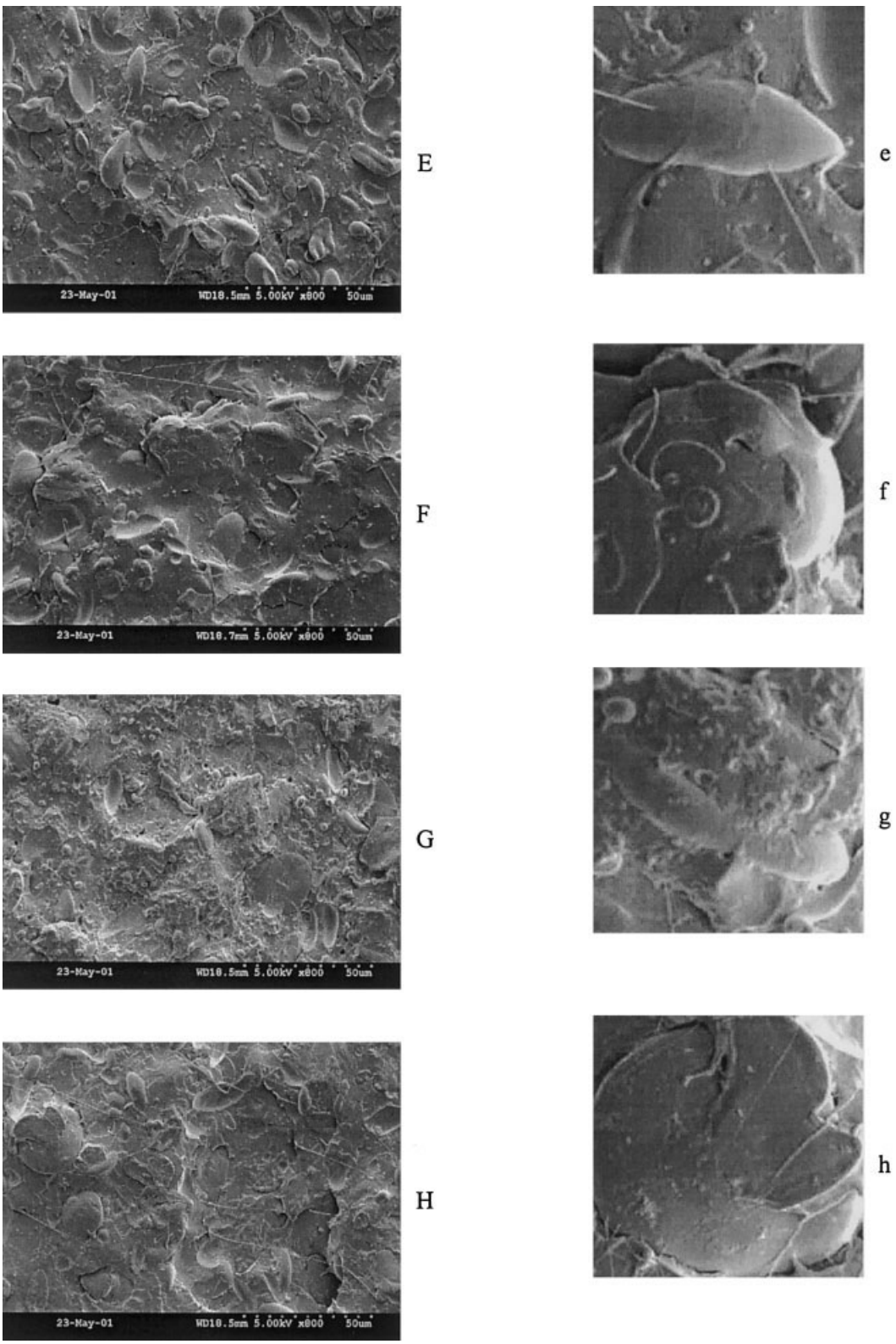


Figure 2 (*Continued from the previous page*)

Blend preparation

It is desirable to maximize the starch content in starch/PLA blends as long as an acceptable level of performance is maintained. It was found that the maximum utilization of starch and the best mechanical properties would be obtained when the content of starch was 45% in the presence of MDI.[7] The optimized amount of MDI was 0.5%. Therefore, a fixed ratio of starch, PLA, and MDI (45/55/0.5 w/w/w) was used in the experiments, and the MDI was calcu-

TABLE I
Transition Temperatures (°C) of the Blends with Various Plasticizer Contents

TC (%)	T_g	T_{c1}	T_{c2}	T_m
15	19.1 (16.1)	64 (76.7)	137.6 (—)	161.6 (162)
12.5	22.5	71.6	139.2	162.1
10	27.6 (27.3)	75.1 (83.5)	140.1 (144.5)	163.9 (166.3)
7.5	33.1	80.1	143.4	165.7
6.5	34.9	83.4	144.1	166.4
5	40.9 (38.8)	84 (90.8)	144 (149.8)	167.2 (169.6)
2.5	47.2	86.4	148	169.5
0	54.2	96.2	156	172

The data in parentheses are for blends without MDI.

lated from the total amount of PLA and wheat starch. The PLA was ground into small particles of about 2 mm. It was then premixed with the MDI so that the MDI would be uniformly distributed over the surface of the PLA powder. The PLA/MDI blend was mixed with wheat starch in a stand mixer (Ultra Power Kitchen Aid, St. Joseph, MI). The mixture was stored in a polyethylene plastic bag. The blends studied had a 45/55/0.5 (w/w/w) ratio of starch to PLA to MDI mixed with TC. Eight TC contents were formulated with starch/PLA/MDI (2.5, 5, 6.5, 7.5, 10, 12.5, and 15%), and the thermal, morphological and mechanical properties of these blends were measured as described in subsequent sections.

A counter-rotating, twin-screw laboratory extruder (Leistritz Micro 18, American Leistriz Extruder Corp., Sommerville, NJ) was used that had a screw diameter of 18 mm, a center distance of 15 mm, a screw operating length of 30D, one feeding zone, and five heating zones. The screw configuration from the feeding zone to the die is shown in Figure 1. Workable extrusion parameters were obtained from a preliminary experiment with various screw speeds, temperature profiles, and die sizes. In this work, the temperature profile was 150°C (feeding zone) and 185°C (five heating zones and the die), the die size was 7 mm, and the screw speed was 150 rpm.

Molding

An injection-molding machine (Boy 22S, Boy Machines, Postfach, Germany) was used for the preparation of the tensile bars. The three temperature zones were 150 (near the inlet), 175, and 175°C, and the molding injection pressure was 150 psi. The injection time was 5 s, and the cooling time was 20 s.

Scanning electron microscopy (SEM)

The fractured microstructure of the blend was observed with 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 with a sputter coater (Desk II sputter/etch unit, Denton Vacuum, Moorestown, NJ) before observation.

Mechanical analysis

Tensile tests were performed with an Instron testing machine (Model 4466, Canton, MA) according to ASTM Standard D 638-92 with a crosshead speed of 5 mm/min and a gauge length of 30 mm. All samples were preconditioned at 23°C and 50% relative humidity for 48 h before the mechanical analysis, and tests were also performed under the same conditions. The dynamic mechanical properties were determined with dynamic mechanical analysis (DMA; DMA-7e, PerkinElmer,

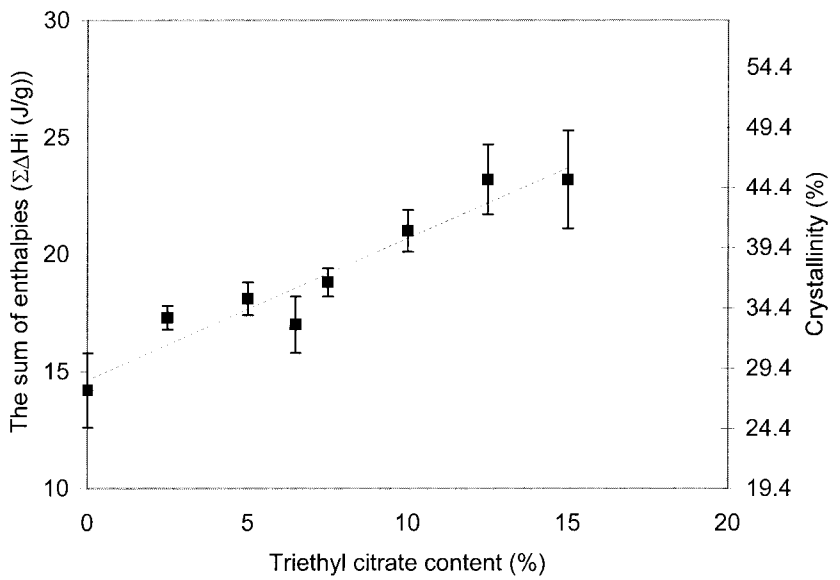


Figure 3 Crystallinity of PLA/starch/MDI blends (55/45/0.5 w/w/w) with various plasticizer contents.

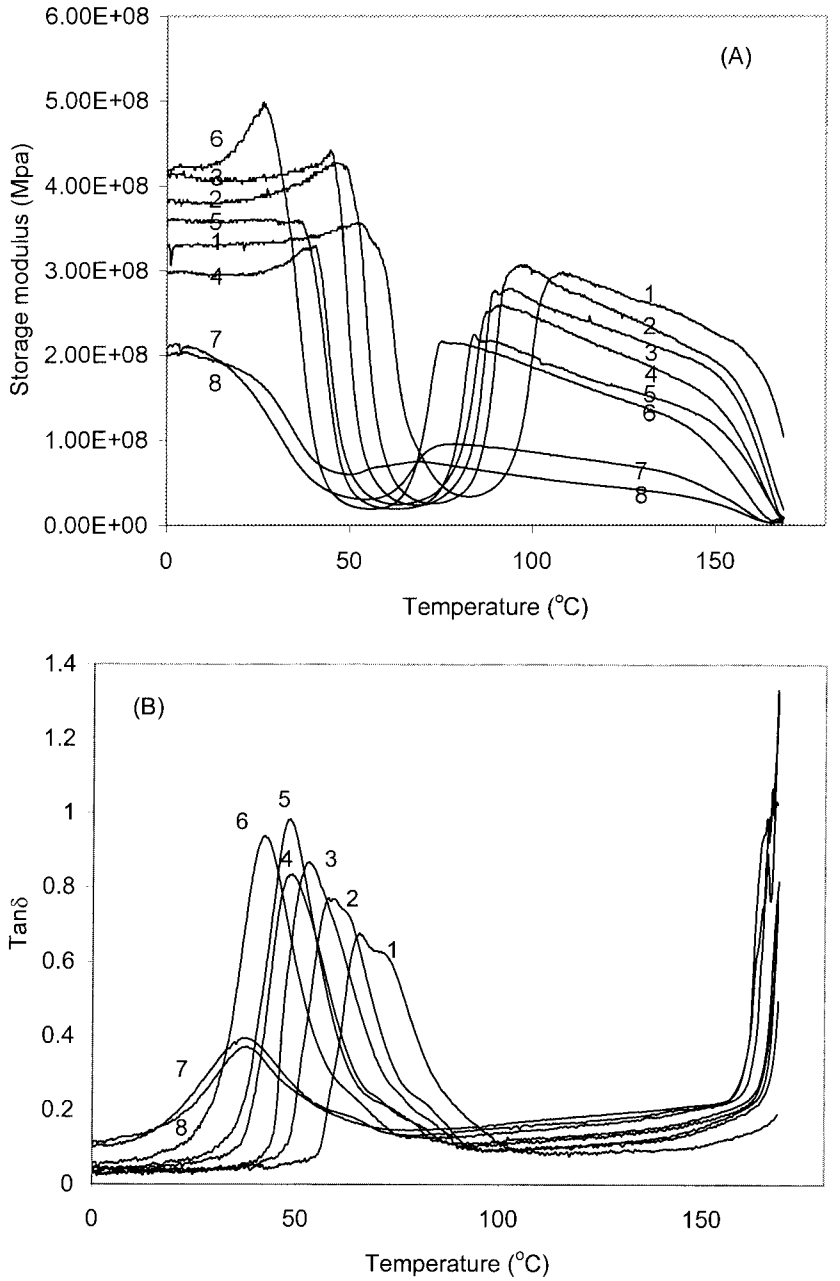


Figure 4 DMA of PLA/starch/MDI blends (55/45/0.5 w/w/w) with various plasticizer contents [(1) 0, (2) 2.5, (3) 5.0, (4) 6.5, (5) 7.5, (6) 10, (7) 12.5, and (8) 15%]: (A) storage modulus and (B) tan δ.

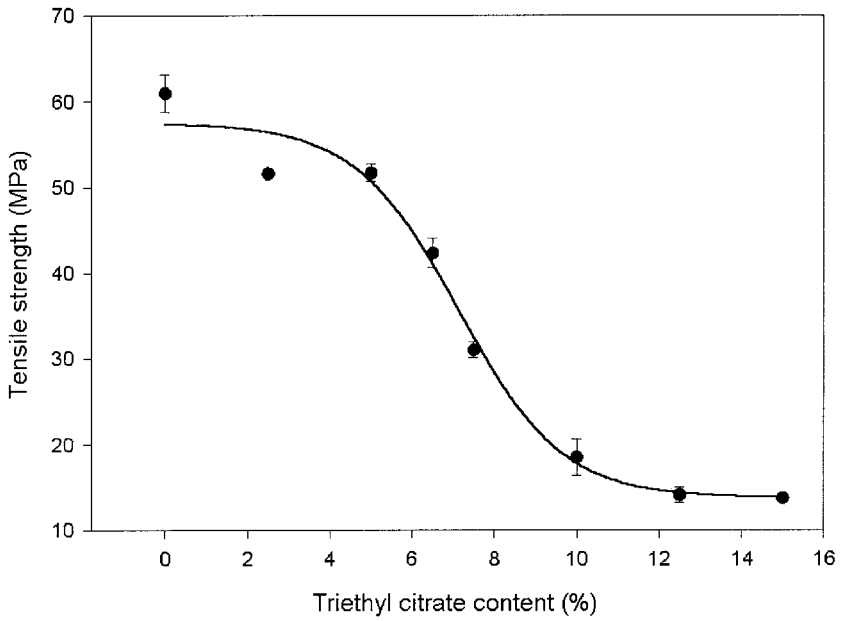
Norwalk, CT) with a three-point bending rectangle method at 1 Hz and 25–180°C at 5°C/min. The storage modulus, loss modulus, and tan δ were analyzed. Seven tensile bars were prepared for each blend.

Thermal analysis

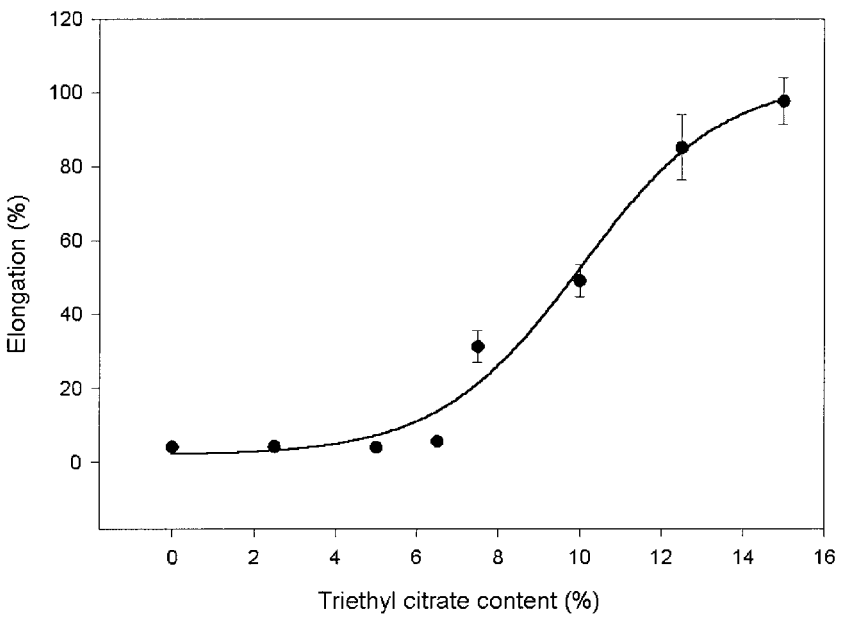
Differential scanning calorimetry (DSC; DSC7, PerkinElmer) was used to measure the thermal transitions. DSC was calibrated with the melting temperature (T_m) and enthalpy of the standard material indium. Dried and ground samples of the blends were weighed into an aluminum pan and hermetically sealed. An empty pan was used as a reference. The DSC temperature increased from 25 to 200°C at a heating rate of 10°C/min. The peak temperatures and enthalpies at the glass transition, crystallization, and melting were recorded. The sum of the enthalpy of the blends at different thermal stages was used as a rough estimation for the crystallinity (X_c):

$$Xc(\%) = (\Delta H_m + \Sigma \Delta H_{ci})*100/(93.6*X_{PLA}) \quad (1)$$

where ΔH_m and ΔH_{ci} are the enthalpies (J/g) of fusion and crystallization of the blends, respectively, and 93.6 J/g is the enthalpy of fusion of a PLA crystal of infinite size.[12] X_{PLA} is the percentage of the PLA content.



(a)



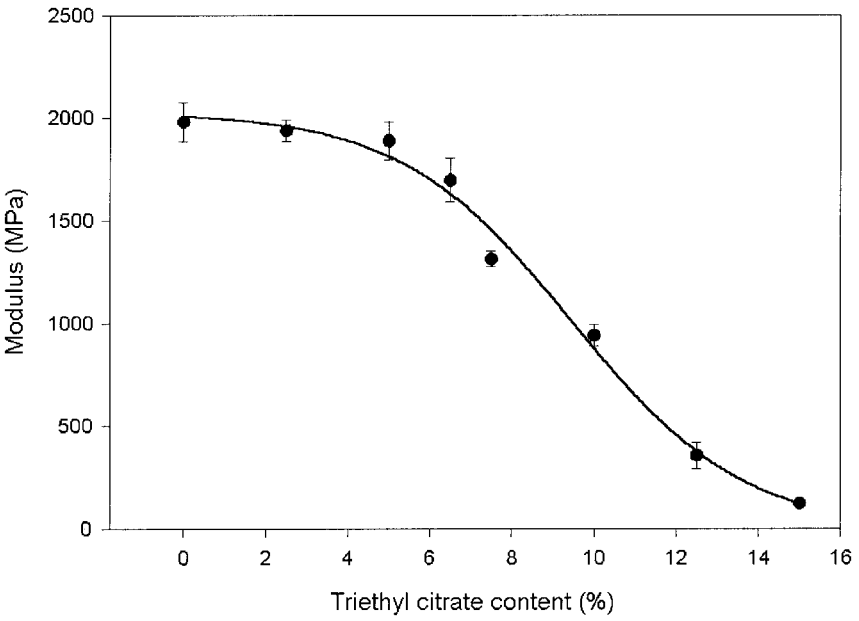
(b)

Figure 5 Tensile properties of PLA/starch/MDI blends (55/45/0.5 w/w/w) with various plasticizer contents: (a) tensile strength, (b) elongation, (c) modulus, and (d) toughness.

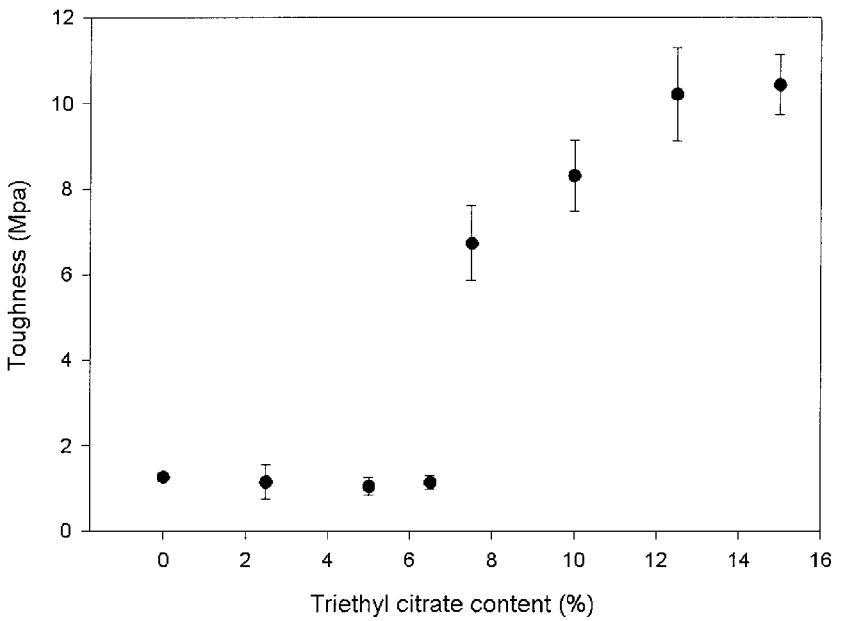
RESULTS AND DISCUSSION

Morphology

Two phases can clearly be observed in the SEM pictures of the blends shown in Figure 2. Gaps between the two phases are obvious for the samples with more than 7.5% TC [Fig. 2(A–D)], but gaps between the two phases were small for the samples with less than 6.5% TC [Fig. 2(E–H)]. As a plasticizer, TC molecules were uniformly distributed in the PLA matrix and starch granules, and this increased the distance between molecules and reduced interactions between PLA and starch. The blend containing MDI in the presence of TC [Fig. 2(A)] appeared more solid with fewer gaps than a similar blend without MDI, as seen in our previous work.[13] Starch granules coated with PLA were found in all the samples [Fig. 2(a–e)]. However, the amount of PLA adhering to starch granules in the samples with TC contents of less than 6.5% [Fig. 1(e–h)] was more than for those with TC contents greater than 7.5%. These results suggested that MDI



(c)



(d)

Figure 5 (*Continued from the previous page*)

still improved the adhesion between starch and PLA in the presence of TC. However, as the TC content increased, the coupling effects of MDI decreased, and this resulted in obvious phase separation between the starch and PLA.

Thermal properties and crystallization

PLA is a semicrystalline polymer, and dried starch existed in a granular form in the blends. The thermal behavior of the blends was mainly influenced by PLA, and this agreed with the results reported by Ke and Sun.[13,14] The DSC results for the transition temperatures of the blends with various plasticizer contents are summarized in Table I. The second DSC scan results were used so that any heat history effect would be avoided. All the transition temperatures of the blends, including the T_g, cold crystallization temperatures (T_{c1} and T_{c2}), and T_m, decreased as the TC content increased. The effect of TC on reducing T_g was more than its effects on T_m, and the rubbery-state range between T_g and T_m broadened as TC increased. The T_g of the blends reached room temperature as the TC content reached 10%. All the transition temperatures (T_g, T_{c1}, T_{c2}, and T_m) of the

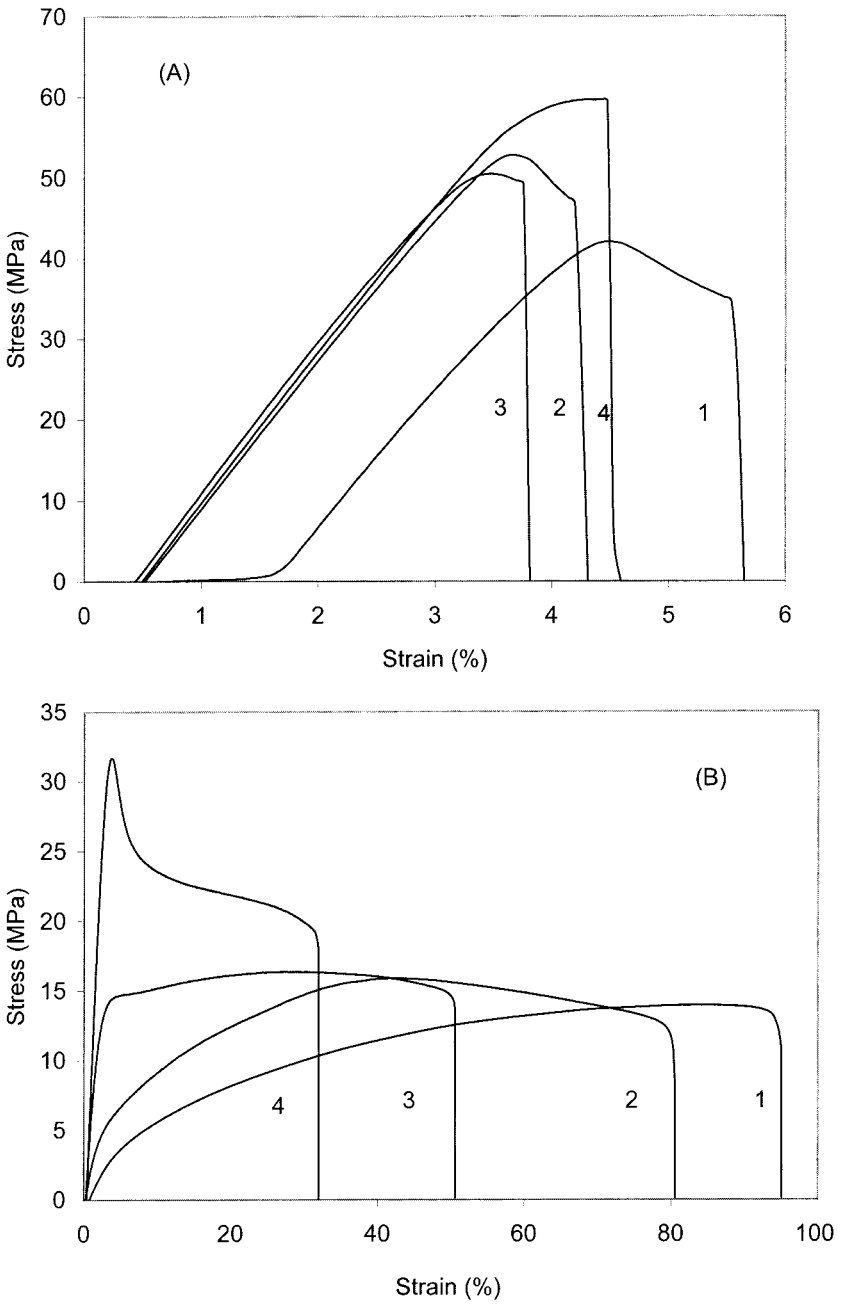


Figure 6 Tensile graphics of PLA/starch/MDI blends (55/45/0.5 w/w/w) with various plasticizer contents: (A-1) 0, (A-2) 2.5, (A-3) 5.0, (A-4) 6.5, (B-1) 7.5, (B-2) 10, (B-3) 12.5, and (B-4) 15%.

blends with MDI were slightly less than those of the corresponding blends without MDI.

The crystallinity of the blends, obtained in blending and molding, increased as the TC content increased (Fig. 3). TC reduced the viscosity of the blends, made the crystallization easier, and increased the crystallinity.

Mechanical properties

Dynamic mechanical properties

The DMA results for the blends with various TC contents are presented in Figure 4. The storage modulus of the blends had similar patterns as the temperature increased: a hump followed by a sharp decrease around T_g, then a rapid increase, leveling off, and melting [Fig. 4(A)]. The hump could be caused by the rearrangement of the molecules, relieving the stress generated in processing.[15] The modulus decreased as the TC content increased because the mobility of the blends increased and the viscosity decreased as the TC content increased. However, such a trend was not completely consistent at $T < T_g$ over the range of TC contents studied because the crystallinity of the blend increased as the TC content increased at the same time, and this

resulted in an increase in the modulus. The blends with high TC contents, such as 12.5 and 15%, had the lowest modulus. The valley caused by the sharp decrease in the storage modulus at a temperature above T_g is known as the rubbery plateau. At this point, cold crystallization occurred, causing a rapid increase in the modulus afterward. The modulus of cold crystallization of the blends decreased as the TC content increased. Tan δ increased as the TC content increased up to 10%, and then tan δ values dropped to their lowest points at high TC contents, such as 12.5 and 15%.

Tensile properties

The major function of a plasticizer is to improve the elongation at break and increase the toughness of a polymeric material. The tradeoffs include reduced tensile strength and modulus. The tensile strength, elongation at break, modulus, and toughness are shown in Figure 5. As expected, the tensile strength of the blends decreased as the TC content increased [Fig. 5(A)]. The tensile strength [Fig. 5(A)] and modulus [Fig. 5(C)] decreased slowly at TC contents of less than 5% but decreased dramatically at TC contents ranging from 5% to 12.5%, nearly leveling off at TC contents above 12.5%. The toughness also significantly improved with the inclusion of small percentages of TC [Fig. 5(D)]. A sharp increase in the toughness at about 6.5–7.5% TC contents was observed. The mechanical properties of the blends containing MDI in the presence of TC was improved, compared with the properties for those without MDI with the same TC content, as reported by Ke and Sun.[13] The typical curves of the tensile test are presented in Figure 6(A,B). The curves indicate that the blends were brittle at less than 6.5% TC contents and were ductile at greater than 6.5% TC contents.

CONCLUSIONS

The thermal transition temperatures (T_g, T_c, and T_m) of starch/PLA/MDI blends with TC decreased as the TC content increased. The crystallinity of the blends increased as the TC content increased within the concentration range tested. The elongation at break and toughness of the blends significantly improved in the TC range of 5–10%. The blend with a TC content of 7.5% resulted in desirable elongation, toughness, and strength for fast food utensil applications. The blends with more rigid or flexible properties could be used for toys and packing containers.

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