

THE EFFECT OF PHYSICAL AGING, STARCH PARTICLE SIZE, AND STARCH  
OXIDATION ON THERMAL-MECHANICAL PROPERTIES OF POLY(LACTIC  
ACID)/STARCH COMPOSITES

by

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AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the requirements for the degree

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Department of Grain Science and Industry  
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## Abstract

Poly(lactic acid) (PLA), a synthetic biopolymer, is a promising substitute of some petroleum-based polymers due to its mechanical and biodegradable properties. But, because of the high cost of PLA (compared to those petroleum plastics for disposable application), starch has been incorporated into PLA to reduce cost and accelerate the biodegradability rate of the composites. But, the addition of starch as filler to PLA decreased mechanical performance of the composite. The addition of methylenediphenyl diisocyanate (MDI) into PLA/starch blends improved drastically the mechanical properties of the composite.

Results from thermal-degradation analysis showed that PLA had the highest Arrhenius activation energy and strongest thermal endurance of all samples, followed by PLA/starch/MDI and PLA/starch. Aged samples exposed to fluctuating humidity storage conditions significantly decreased their performance. But, storing the samples in plastic bags could minimize degradation of properties. PLA and its composites with starch would not significantly affect application function when they are stored in controlled environment. PLA and PLA/starch based composites sealed in plastic bags can be stored in fluctuating humidity conditions (30-90% RH) for up to 30 days.

Tensile strength, elongation, and damping increased with average particle size of starch granules (APS). But, declination of these properties was detected with APS larger than 45  $\mu\text{m}$ . Crystallinity increased as the APS decreased. Young's modulus, storage modulus, and moisture absorption were not significantly affected by the starch APS. The use of MDI as a coupling agent altered the role of starch APS on those properties of poly(lactic acid)/starch composite.

The oxidation of the primary alcohol group on C6 of starch molecules up to 10% degree of substitution did not significantly affect the mechanical properties of PLA/starch/MDI, but the composites showed a reduced inelastic deformation (tensile curve) and significant increase in storage modulus and damping. Results suggest that a substitution of hydroxyl group on C6 of starch molecules for carboxyl group (up to 10%) increased the strengthening effect of MDI enough to reduce inelastic deformation of the composites upon load, but not enough to enhance mechanical properties.

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## Table of Contents

List of Figures .....	ix
List of Tables .....	xi
Acknowledgements .....	xii
CHAPTER 1 - INTRODUCTION .....	1
Overview .....	1
Literature review .....	2
Biodegradable polymers .....	2
Poly(lactic acid) (PLA) .....	3
Starch .....	5
Filler system in plastic industry .....	5
Methylenediphenyl diisocyanate (MDI) .....	6
Physical aging .....	7
Starch oxidation .....	7
Objectives .....	8
CHAPTER 2 - THERMAL DEGRADATION AND PHYSICAL AGING OF POLY(LACTIC ACID) AND ITS BLENDS WITH STARCH .....	9
Abstract .....	9
Introduction .....	10
Material and Methods .....	11
Materials .....	11
Sample Preparation and Storage .....	12
Thermal Degradation .....	12
Differential scanning calorimetry (DSC) .....	13
Tensile testing .....	13
Dynamic mechanical analysis (DMA) .....	14
Moisture Content .....	14
Results and Discussion .....	14
Thermal degradation .....	14

Thermal properties.....	15
Mechanical properties and moisture.....	18
Dynamic mechanical properties .....	20
Conclusion .....	21
Figures and Tables.....	22
<b>CHAPTER 3 - INFLUENCE OF STARCH PARTICLE SIZE ON THERMAL-</b>	
<b>MECHANICAL PROPERTIES OF POLY(LACTIC ACID)/STARCH COMPOSITES</b> 29	
Abstract.....	29
Introduction.....	30
Material and Methods.....	31
Materials.....	31
Starch particle size distribution characterization.....	32
Starch damage and amylose content characterization .....	32
Separation of starch fractions by particle size using sieving .....	32
Sample preparation .....	33
Mechanical properties.....	34
Thermal properties.....	34
Scanning electron microscopy.....	35
Moisture content .....	35
Results and Discussion .....	35
Mechanical properties.....	35
Morphology.....	37
Thermal properties.....	38
Amylose content, starch damage, and commodity effects.....	39
Conclusion .....	40
Figures and Tables.....	41
<b>CHAPTER 4 - EFFECT OF OXIDATION OF THE PRIMARY ALCOHOL GROUP OF</b>	
<b>STARCH WITH TEMPO ON PROPERTIES OF PLA/STARCH COMPOSITES .....</b> 50	
Abstract.....	50
Introduction.....	51
Material and Methods.....	53

Materials.....	53
Oxidation procedure .....	53
Work-up of the oxidized starch .....	54
Inherent viscosity of oxidized starch .....	55
Sample preparation .....	55
Mechanical properties.....	56
Thermal properties.....	56
Morphology.....	56
Water absorption .....	57
Results and Discussions.....	57
Inherent viscosity of oxidized starch .....	57
Mechanical properties.....	58
Thermal properties.....	60
Morphology.....	60
Water absorption .....	61
Conclusion .....	62
Figures and Tables.....	63
CHAPTER 5 - Summary and Further Research .....	71
Summary.....	71
Further research.....	72
References.....	73



## List of Figures

Figure 2.1 (A) Thermalgravimetric analysis plots, TGA; and (B) the corresponding derivative plots of the data, DTG, of PLA, PLA/starch, PLA/starch/MDI composites, and starch. ....	24
Figure 2.2 Thermal endurance curves of PLA, PLA/starch, and PLA/starch/MDI composites.....	25
Figure 2.3 Excess enthalpy of relaxation as affected by aging time for: (A) unsealed PLA samples stored at constant RH (50%) and PLA samples (unsealed and sealed) stored at fluctuating RH; (B) PLA/starch samples (unsealed and sealed) stored at fluctuating RH; and (C) PLA/starch/MDI samples (unsealed and sealed) stored at fluctuating RH. ....	26
Figure 2.4 The $\tan \delta$ as a function of temperature at 1Hz for PLA samples stored at (A) 50% RH and 25°C for different periods of time; (B) unsealed PLA samples and (C) sealed PLA samples stored at fluctuating RH from 30 to 90% and 25°C for different periods of time.....	27
Figure 2.5 The $\tan \delta$ as a function of temperature at 1Hz for (A) unsealed PLA/starch composites; (B) sealed PLA/starch composites; (C) unsealed PLA/starch/MDI composites; and (D) sealed PLA/starch/MDI composites, stored at fluctuating RH from 30 to 90% and 25°C for different periods of time.....	28
Figure 3.1: Particle size distribution curve and respective average particle size of rice, corn, wheat, and potato starches.....	45
Figure 3.2: SEM micrograph of: (A) rice starch; (B) corn starch; (C) wheat starch; and (D) potato starch.....	46
Figure 3.3: Scheme of PLA/starch/MDI system with: (A) small starch particles; (B) medium starch particles; and (C) large starch particles.....	47
Figure 3.4: Damping ( $\tan \delta$ ) of PLA/starch/MDI composites of different starch particle sizes.....	48
Figure 3.5: SEM micrograph of tensile fractured surface of PLA/starch/MDI composite with starch average starch particle size of: (A) 6 $\mu\text{m}$ ; (B) 15 $\mu\text{m}$ ; (C) 26 $\mu\text{m}$ ; (D) 47 $\mu\text{m}$ ; and (E) 71 $\mu\text{m}$ .....	49

Figure 4.1 Tensile curve of: (A) PLA/starch (control), and PLA/oxidized starch at different degrees of substitution (5, 10, and 30% DS); and (B) PLA/starch/MDI (control), and PLA/oxidized starch/MDI at different degrees of substitution (5, 10, and 30% DS). ..... 65

Figure 4.2 The  $\tan \delta$  (damping) as function of temperature at 1 Hz for: (A) PLA/starch (control), and PLA/oxidized starch at different degrees of substitution (5, 10, and 30% DS); and (B) PLA/starch/MDI (control), and PLA/oxidized starch/MDI at different degrees of substitution (5, 10, and 30% DS). ..... 66

Figure 4.3 Tensile curve of: (A) PLA/starch/MDI (75:25:0.5 wt), and PLA/oxidized starch/MDI (75:25:0.5 wt); and (B) PLA/starch (55:45 wt) with added oxidized starch at 0, 1.0, 2.5, and 5.0% over the total weigh. .... 67

Figure 4.4 The  $\tan \delta$  (damping) as function of temperature at 1 Hz for: (A) PLA/starch/MDI (75:25:0.5 wt), and PLA/oxidized starch/MDI (75:25:0.5 wt); and (B) PLA/starch (55:45 wt) with added oxidized starch at 0, 1.0, 2.5, and 5.0% over the total weigh. .... 68

Figure 4.5 SEM micrographs of: (A) PLA/starch/MDI (55:45:0.5 wt); PLA/oxidized starch/MDI (55:45:0.5 wt) at (B) 5% degree of substitution, (C) 10% degree of substitution, and (D) 30% degree of substitution; (E) PLA/starch/MDI (75:25:0.5 wt); and (F) PLA/oxidized starch/MDI (75:25:0.5 wt) at 5% degree of oxidation... 69

Figure 4.6 Water absorption vs. time for PLA/starch/MDI (control), and PLA/oxidized starch/MDI at different degrees of substitution (5, 10, and 30% DS). .... 70

## List of Tables

Table 2.1 Temperature of maximum rate of mass loss ( $T_{max}$ ) and degradation extent (DE) for PLA, PLA/starch, PLA/starch/MDI composites, and starch.....	22
Table 2.2 Mechanical properties, moisture content, and crystallinity of aged PLA, PLA/starch, and PLA/starch/MDI for various periods of time at constant and fluctuating room humidity .....	23
Table 3.1 Properties of PLA/starch/MDI composites with different starch average particle sizes (APS).....	41
Table 3.2 Estimated average area, volume, and mass of single starch particles; and estimated number of particles and total surface area found in one-gram of starch sample .....	42
Table 3.3 Properties of PLA/starch/MDI composites made with not-sieved starches.....	43
Table 3.4 Properties of PLA/starch/MDI composites made with potato starch with different average particle sizes (APS) .....	44
Table 4.1 Inherent viscosities of starch and oxidized starches at 5, 10, and 30% degree of substitution (DS) dissolved in dimethyl sulfoxide solution (DMSO). .....	63
Table 4.2 Blend composition and their respective mechanical properties and crystallinity .....	64

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# CHAPTER 1 - INTRODUCTION

## Overview

Substitution of conventional petroleum plastics with biodegradable and renewable materials for disposable applications is in popularity (Narayan 1991, Krochta and Mulder-Johnston 1996, Gerngross and Slater 2000). Poly(lactic acid), PLA, is a biodegradable polyester derived from carbohydrates of renewable resources (Wang et al. 2003), and presents many properties comparable to those of polyethylene, polypropylene, polystyrene, and polyethylene terephthalate (Naitove 1998). But, depending on the circumstances, PLA is still more expensive than conventional polymers and has slow degradation rate, compared to the waste accumulation rate (Reed 1981). Starch, another biodegradable polymer that can be rapidly metabolized by a wide range of organisms (Nayak 1999), can be incorporated into PLA to reduce the cost for raw material and accelerate biodegradability rate of the composites (Jacobsen and Fritz 1996). But, due to the hydrophilic properties of starch, its incorporation into plastic may cause an increase in water sensitivity and a decrease in mechanical properties, such as tensile strength and elongation (Griffin 1974 and 1990; Evangelista 1991).

To improve the interaction between matrix and filler, it is necessary to enhance the interaction between both phases (Dick 1987). Methylenediphenyl diisocyanate (MDI) is a coupling agent that contains two highly active isocyanate groups in its molecule. Isocyanate groups react with both carboxyl and hydroxyl groups, forming urethane linkages (Dieteroch et al. 1985). The addition of 0.5% (wt) of methylenediphenyl diisocyanate (MDI) to PLA/starch composite (ratio of 55 to 45 by weight) enhanced the mechanical properties (Wang et al. 2001). Without MDI, PLA/starch composite showed a drop in tensile strength and elongation by 42% and 55%, respectively, compared to pure PLA. With addition of MDI to the blend, tensile strength increased by 7.5% and elongation decreased by 23%, compared to pure PLA.

Physical aging is a natural phenomenon that affects properties of polymers. When stored at 50% relative humidity (RH) and 25°C for one year, PLA/starch composites (with and without MDI) showed quick increase of enthalpy of relaxation (aging rate)

within the first 90 days, slowing down from that age time on. PLA/starch composites with MDI showed much slower aging rate than those without MDI. Such a difference in aging was caused by addition of MDI, which enhanced the interfacial interaction between PLA and starch, promoting stronger adhesion between molecules and reducing free volume. PLA/starch samples, with and without MDI, showed decrease in tensile strength with increase of aging time. Both physical aging and relative humidity may be factors that cause decrease in mechanical properties of these systems (Wang et al. 2003).

It has been reported that the properties of a particulate-filled composite are significantly influenced by the wetting and bonding of a coupling agent at the interface of the constituent materials (Wu 1982). Wang et al. (2003) observed that tensile strength of PLA/starch/MDI composites with wheat starch was higher than with corn starch. The larger particle size of wheat starch generated a smaller total surface area (at the same weigh ratio of PLA) and less MDI would be needed in order to wet and disperse through the system, which would result in a stronger interfacial interaction between PLA and starch.

MDI is highly reactive with both carboxyl and hydroxyl groups, forming a urethane linkage (Dieteroch et al. 1985). MDI seems to function as a coupling agent in PLA/starch blends, reacting with carboxyl and hydroxyl groups of PLA and hydroxyl groups of starch (Wang et al. 2002).

An improvement of the performance of starch in PLA/starch blends could be achieved by oxidation of the primary alcohol group of starch molecules. The addition of carboxyl groups to the C6 of starch could improve the mechanical properties of PLA/starch composites by either strengthening the adhesion force between PLA and starch phases, or improving the coupling action of MDI by increasing the number of potential binding sites in the starch molecule.

## **Literature review**

### ***Biodegradable polymers***

Biodegradation can be defined as a phenomenon carried out by living organisms (such as bacteria, fungi, yeasts, insects, etc.) or their secretion products through enzymatic and/or chemical decomposition (Albertsoon and Karlsson 1994). But,

anaerobic reactions such as chemical (oxidation and hydrolysis) and physical (photo and thermal degradation) could be considered environmental factors that alter the polymer along with biodegradation. The synergism between biodegradation and anaerobic reactions eventually results in fragmentation of the polymer by destruction of its macromolecules and its respective conversion to low-molecular-weight compounds, which later on would be involved in the natural circulation of substances (Suvorova et al. 2000). Then, biodegradation of a polymer could be strictly defined as the deterioration of its physical and chemical properties by microorganism (in both aerobic and anaerobic conditions), resulting in a decrease of its molecular mass down to the formation of CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, and other low molecular-weight sub-products (Decriaud et al. 1998). Since some carbon and residues from the polymer biodegradation could be incorporated into microbial mass, all carbons should be accounted for carbon balance and all residues should be non-toxic in environmental assessments. Both residues and microbial mass should be eventually incorporated into a natural geochemical cycle (Nayak 1999).

Biodegradable polymers can be classified in three categories: natural biodegradable polymers; synthetic biodegradable polymers; and biodegradable polymer blends. As the name suggests, natural polymers are generally produced in nature by living organisms and are renewable resources. Polysaccharides (such as cellulose and starch), proteins (such as silk), and polyhydroxyalkanoates (synthesized by bacteria) are examples of natural polymers (Roper and Koch 1990) and are considered environmentally accepted degradable polymers (Wang et al. 2003). Aliphatic polyester is a well-known synthetic biopolymer that is susceptible to biological attack (Vonrecum et al. 1995) and can be hydrolyzed by lipases and esterases (Nayak 1999). The blend of biodegradable polymers has become a common practice within the industry as an alternative to reduce the overall cost of the materials and to modify properties and degradation rates (Wang et al. 2003).

### ***Poly(lactic acid) (PLA)***

PLA is well-known biodegradable polyester that has been studied extensively for tissue engineering and drug delivery system and has been widely used in human medicine (Wang et al. 2003). Many of the PLA properties are compared to those polyethylene,

polypropylene, polystyrene, and polyethylene terephthalate (such as stiffness, tensile strength, and gas permeability), turning PLA into a potential substitute to petroleum-based products such as trash bags, table utensils, films, paper coating, fiber, and cloth (Naitove 1998).

PLA is made from lactic acid produced via fermentation of carbohydrate crops such as corn, wheat, barley, cassava, and sugar cane (Chandra and Rustgi 1998). It is made from L- or D-lactic acid through two procedures: (i) ring opening polymerization, a solvent free process where lactic acid is first transferred to a low-molecular weight polylactic acid, followed by depolymerization to lactide (fluctuating dimer), and then polymerized continuously to a controlled high-molecular weight polymer (referred as polylactide) through a catalytic ring opening process (Lunt 1998); (ii) direct condensation polymerization, a catalyzed process where the water generated during the polymerization is removed by an azeotropic dehydration process, producing a high-molecular weight polymer (referred as polylactic acid) (Ajioka et al. 1995). The products from both procedures present similar properties (Ajioka et al. 1995). The properties of PLA are driven by the forms of its monomers (L-, D-, or meso-forms). PLA from pure L-lactic acid presents a higher melting point; but, due to its high crystallinity, it shows poor processing properties. The increase of D-forms into L-PLA up to 20% results in an amorphous polymer with a glass transition temperature ( $T_g$ ) of 60°C, which is not acceptable for several packaging uses (Sinclair 1996).

PLA-based polymer is completely degraded under compost conditions. Although it has a hydrophobic characteristic (non-water soluble), microbes in marine environments can degrade it into water and carbon dioxide (Briassoulis 2004), and hydrolyzes more promptly than polyhydroxyalkanoates in anaerobic condition (Reeve et al. 1994). The first step of PLA degradation does not require microbial action and is characterized by the cleavage of the ester linkages to lactic acid by a temperature and humidity-enhanced process (Agarwal et al. 1996; Ho and Pometto 1999). Then lactic acid is biodegraded by microbes into carbon dioxide, methane, and water (Sinclair 1996). The complete degradation of PLA by hydrolysis in the environment takes from several months to two years, which is relatively fast compared to 500 to 1,000 years for petroleum-based plastics such as polystyrene and polyethylene (Datta et al. 1996). But, for some specific



applications, PLA is still more expensive than petroleum-based products, and the degradation rate is still slow compared to the accumulation rate of solid waste (Wang et al. 2003).

### ***Starch***

Starch is a highly hydrophilic natural polymer, consisting of repeating 1,4- $\alpha$ -D-glucopyranosyl units (anhydroglucose units, AGU), and generally composed by a mixture of amylose and amylopectin. Amylose, a minor component (about 25%), is a linear molecule, has a molecular weight of several hundred thousands Da, and its molecular structure presents itself in a helix shape (Nayak 1999). Amylopectin is a highly branched molecule, with a molecular weight of million Da and with an average branch-length of 20-30 glucose units (Young 1984). The branch chains in amylopectin occur at C6 of the glucopyranosyl units, are arranged in clusters, and shaped in double helix structure (Jane 1995). The branched amylopectin component contains crystalline areas, while the linear amylose presents itself mostly in an amorphous form. Starch has a form of discrete granules ranging from about 5 to 40  $\mu\text{m}$  in average particle size, depending on the source (French 1984). Due to the hydrophilic nature, the water content of starch alters with changes of relative humidity. For instance, corn starch contains 6% moisture at 0% RH and 20% moisture at 80% RH (Imam et al. 1995).

Starch is an abundant and readily available natural polymer, produced in most countries and available at low cost worldwide (Wang et al. 2003). Starch is readily metabolized by a wide array of organisms (Nayak 1999). The use of starch alone in the plastic industry is unsuitable in most cases due to its lacking of melt-processability and humidity-resistance; which limits its use in extrusion or injection molding (Wang et al. 2003). But, due to its biocompatibility, starch has been used as filler, and its blending with synthetic polymers has been widely investigated (Evangelista et al. 1991).

### ***Filler system in plastic industry***

Economic factors such as rising price for petroleum-based products and an anticipated shortage of petroleum feed stocks have driven the plastic industry to incorporate fillers into the resins. The use of fillers in composites have not provided only economic advantages by lowering raw material cost, but also brought a new range of

materials with improved properties, such as higher strength, modulus, and lower thermal expansion (Ferrigno 1987). The use of fillers has been more extensively applied in thermoplastics such as polyethylene, polypropylene, polyvinyl chloride, and nylon (Dick 1987).

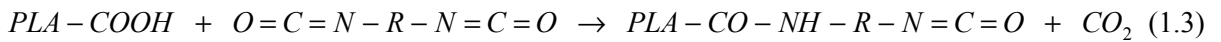
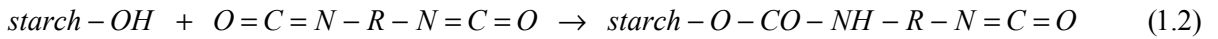
In order to be considered a good candidate, filler needs to meet some requirements, such as low cost, availability, chemical resistance, high strength, good surface wetting and bonding, and compatibility. Other factors such as density, modulus, size, shape, thermal and electrical properties, and color should be taken in consideration as well (Ferrigno 1987). Starch has been suggested as good biodegradable filler candidate due to its satisfying thermal stability and minimum interference with melt-flow properties of most materials used in the plastic industry (Griffin 1974). In cases where the interfacial interaction between the filler and the matrix is not acceptably strong enough, a coupling agent containing functional groups that interact with both filler and matrix phases can be added. The coupling agent strengthens the interfacial interaction between the phases, transmitting the internal stress from one phase to another, improving the mechanical properties of the composite (Plueddemann 1982).

### ***Methylenediphenyl diisocyanate (MDI)***

Methylenediphenyl diisocyanate (MDI) is a coupling agent that contains two highly active isocyanate groups in its molecule. MDI is found in three stereoisomers; methylenediphenyl-4,4'-diisocyanate, methylenediphenyl-2,4'-diisocyanate, and methylenediphenyl-2,2'-diisocyanate. Usually, polymeric MDI consists of a mix of these isomers and the higher three-ring and poly-ring-containing isocyanates. Isocyanate groups react with both carboxyl and hydroxyl groups, forming urethane linkages (Dieteroch et al. 1985). Diisocyanate reacts with PLA in melt state to form urethane ester (Hiltunen et al. 1997, Zhong et al. 1999) and works as a chain extender by increasing the molecular weight of PLA (Zhong et al. 1999). The urethane linkage formed during the reaction between PLA and MDI could be attacked by some fungi (Owen et al. 1995) and absorbed by the soil (Cowen et al. 1998).

Starch molecules are rich in hydroxyl groups, which are reactive with diisocyanate groups (Narayn 1991). The addition of 0.5% (wt) MDI into PLA/starch

blends (55:45 w/w) strengthens the interfacial interaction between the phases and shows a drastic improvement of tensile strength and elongation of the blends when compared to those without MDI (Wang et al. 2001). It has been suggested that the interfacial interaction is enhanced by the chemical reaction between PLA and MDI or starch and MDI (Equations 1.1, 1.2, and 1.3).



### ***Physical aging***

Physical aging is an inherent characteristic of polymers that significantly interferes in the physical properties of the amorphous phase in glassy or partially glassy polymers, and usually occurs around its glass transition temperature ( $T_g$ ) (Struik 1978a, Chartoff 1997); which effects are evident by shrinkage of specific volume, decrease of specific enthalpy and entropy, and decrease of molecular mobility. These phenomena are associated with decrease of free volume, which controls the mobility of large segments of the polymer chains and affects the mechanical properties of polymers (shrinkage, stiffness, brittleness, and decrease in damping) (McGonigle et al. 2000, Ke and Sun 2002a, Martinez-Vega et al. 2002).

### ***Starch oxidation***

Oxidation of starch has been widely studied to develop conditions that improve its properties and spread its application (Mukprasirt et al. 2002, Adebowale and Lawal 2003, Mostafa and Morsy 2004). Sodium bromide (NaBr), gaseous chlorine, calcium hypochlorite, hydroperoxide, potassium permanganate, ammonium persulfate, and sodium hypochlorite (NaOCl) are the agents most frequently used to oxidize starch (Wing 1994). But, these agents attack the secondary alcohol group at C2, C3, and C4, and the primary alcohol group at C6 of the glucose units in a random fashion (Brouch 1985; Floor et al. 1989). This leads to hydrolysis of the glycosidic bonds, with opening and

cleavage of the monomeric rings, and, consequently, to loss of polymer properties and decrease of viscosity of the starch (Chang and Cho 1997). Moreover, these oxidation reactions are hard to control and to reach a desired degree of oxidation of the starch (Suh et al. 2002).

De Nooy et al. (1994, 1995) presented a novel methodology using a stable organic nitroxyl radical, 2,2,6,6-tetramethyl-1-piperidinyl oxoammonium ion (TEMPO), NaBr, and NaOCl, enabling the selective oxidation of the primary alcohol group in the presence of the secondary alcohol group. In a TEMPO-mediated oxidation, the primary alcohol group is oxidized to an aldehyde, which is further oxidized to a carboxylic acid, and the secondary alcohol group is oxidized to a ketone (Anelli et al. 1987). TEMPO-mediated oxidation of the primary alcohol group of wheat starch showed a selectivity of >95%, a yield of 98%, and an oxidation yield of 95% (Chang and Robyt 1996).

## **Objectives**

The aim of this work is to determine the effect that the presence of starch granules have on physical, mechanical and thermal properties of PLA/starch blends. Specific objectives are to study (1) thermal degradation and the effect of physical aging on thermal-mechanical properties of PLA/starch composites; (2) the influence of starch particle size on thermal-mechanical properties of PLA/starch composites; and (3) the effect of oxidation of the primary alcohol group of starch with TEMPO on properties of PLA/starch composites.

## **CHAPTER 2 - THERMAL DEGRADATION AND PHYSICAL AGING OF POLY(LACTIC ACID) AND ITS BLENDS WITH STARCH**

### **Abstract**

Poly(lactic acid) (PLA) and its blends with starch and methylenediphenyl diisocyanate (MDI) were extruded in a twin-screw extruder and compress-molded in a dog-bone shaped tensile bars to form test specimens. The thermalgravimetric profile and thermal endurance of these samples were characterized. The effect of physical aging on mechanical and thermal properties of these samples was evaluated. For the aging study, samples were stored at 25°C and relative humidity fluctuating between 90 and 30%, from 2 to 180 days, with or without a polyethylene bag as a moisture barrier. Physical aging of pure PLA samples stored in a controlled environment from 2 to 360 days was also evaluated. The presence of MDI in the PLA/starch composite did not affect the thermal decomposition profile. The PLA showed the highest Arrhenius activation energy and strongest thermal endurance of all samples, followed by PLA/starch/MDI and PLA/starch. The exposure of the samples to storage conditions with fluctuating humidity significantly decreased their thermal-mechanical performance. But, storing the samples in plastic bags could minimize degradation of properties. The storage of PLA and its composites with starch would not significantly affect application function when they are stored in controlled environment. The mechanical properties of PLA and PLA/starch based composites sealed in plastic bags and stored in fluctuating humidity conditions (30 to 90% RH) were significantly constant for as long as 30 days.

## Introduction

The use of biodegradable and renewable materials to replace conventional petroleum plastics for biodegradable and renewable materials for disposable applications is becoming popular (Narayan 1991, Krochta and Mulder-Johnston 1996, Gerngross and Slater 2000). Poly(lactic acid) (PLA), a synthetic biopolymer derived from agricultural feedstock, is a promising polymer due to its mechanical and biodegradable properties (Datta et al. 1995, Krochta and Mulder-Johnston 1996). But, the cost of PLA is still higher than that of petroleum plastics for disposable applications due to its complicated processing procedures. Starch, another biodegradable polymer that can be rapidly metabolized by a wide range of organisms (Nayak 1999), can be incorporated into PLA to reduce the cost for raw material and accelerate the biodegradability rate of the composites (Jacobsen and Fritz 1996). Composites of PLA/starch at ratio of 55/45 compatibilized with coupling reagents, such as methylenediphenyl diisocyanate (MDI) (Wang et al. 2001) and meliate anhydride (Zhang and Sun 2004), gave strong mechanical properties. Hydroxyl and carboxyl groups in both starch and PLA molecules are expected to interact with either isocyanate or anhydride groups of coupling reagents, improving interfacial adhesion between PLA and starch. With plasticizers, mechanical properties of the PLA/starch composites ranged from 12 to 65 MPa of tensile strength and from 4 to 180% of elongation (Ke and Sun 2001b, 2002).

Physical aging is a natural phenomenon that significantly affects the physical properties of the amorphous phase in glassy or partly glassy polymers. The effect of aging takes place around glass transition temperature ( $T_g$ ) and can be noticed by shrinkage of specific volume, decreases in specific enthalpy and entropy, and a decrease in molecular mobility. These effects are associated with decrease of free volume, which controls the mobility of large segments of the polymer chains and affects the mechanical properties of polymers (shrinkage, stiffness, brittleness, and decrease in damping) (Celi and Scandola 1992, Hay 1995, McGonigle et al. 2000, Ke and Sun 2002a).

When stored at 50% RH and 25°C, PLA/starch composites (with and without MDI) showed a quick increase of enthalpy of relaxation (aging rate) within the first 90 days, slowing down from that time on. The PLA/starch composites with MDI showed a

much slower aging rate than did those without MDI. Such a differences in aging were caused by addition of MDI, which enhanced the interfacial interaction between PLA and starch, promoting stronger adhesion between molecules and reducing free volume. The PLA/starch samples, with and without MDI, showed a decrease in tensile strength with longer aging time. Both physical aging and relative humidity may be factors that cause decreases in mechanical properties of these systems (Wang et al. 2003).

Thermalgravimetric analysis (TGA) is a helpful tool to characterize thermal degradation (amount and rate of mass loss), thermal stability, and the lifetime behavior of polymeric materials. Such characterizations provide valuable information for selection of material, prediction of product performance, and product quality. Three thermal-degradation steps can be observed on mass-loss plots of starch, PLA, and starch/PLA blends (50/50 and 30/70 wt %): (1) around 70°C, attributed to water loss; (2) between 250 and 350°C, attributed to degradation of starch components; and (3) above 350°C, attributed to pyrolysis of PLA (Mano et al. 2003). The degradation extent (DE) of PLA was almost complete (99%), whereas starch showed DE of 75%. The DE of the PLA fraction of Starch/PLA blends was similar to their nominal PLA content (57% for 50 wt/wt, and 75% for 70 wt/wt).

The aim of this present study was to characterize the thermal degradation and endurance and to report the effect of physical aging on PLA and PLA/starch composites when they are stored in fluctuating relative humidity conditions. The physical aging of pure PLA samples in constant relative humidity (50%) condition was also evaluated to complement the work reported by Wang et al. (2003).

## **Material and Methods**

### ***Materials***

A PLA resin with molecular weight of 120,000 Da, and derived mainly from L-lactic acid, was purchased from Shimadzu (Japan). Wheat starch with an amylose content of about 28% and average particle size of 20 µm was purchased from Midwest Grain Products, Inc. (Atchinson, KS). Methylenediphenyl diisocyanate (MDI, Rubinate 1840) in a dark brown liquid was obtained from ICI Polyurethanes (Geismar, LA). A commercially available 177x133-mm zipper-sealing-type polyethylene bags (Ziploc, S.C.

Johnson & Son, Inc., Racine, WI), with a film thickness of 0.05-mm, were purchase from a local grocery store.

### ***Sample Preparation and Storage***

PLA resin was ground by a laboratory mill (Model 4 Laboratory Mill, Thomas-Wiley Company, Philadelphia, PA) with a 2-mm screen. Ground PLA and starch were dried to about 5% wt moisture content, according to AACC method 44-15A, in a conventional oven at 130°C for 2 hours before sample preparation. Three compounds were evaluated: PLA, PLA/starch (55:45 w/w), and PLA/starch/MDI (55:45 w/w + 0.05% wt over total weight). Each sample was mixed in a planetary blender and passed through a co-rotating, conical, twin-screw extruder (TM-100, Haake, Paramus, NJ) at 125/185/185°C barrel temperature and 135 rpm, and ground with the same laboratory mill, and were compression-molded into a testing specimen type IV, following ASTM method D-638-91, with a hot press (Model 3890, Auto “M”, Carver Inc., Wabash, IN) at 176°C and molding pressure of 4.2 MPa for 15 minutes. The molded specimens were cooled down to 57°C, under room condition, before removal from the mold. The specimens used for thermal-degradation study were stored for 48 hours at 50% R.H. and 25°C before analysis.

Two sets of each sample were prepared for the physical aging study in fluctuating relative humidity conditions: one set was sealed in a commercially available polyethylene bags, whereas the other set was not. Both sets were initially stored at 90% RH and 25°C for a week and then at 30% RH and 25°C for another week. This cycle was repeated during storage up to 180 days. The aged samples were characterized at 2, 30, 60, 120, and 180 days of storage. Physical aging of pure PLA samples stored at 50% RH and 25°C was evaluated at 2, 30, 90, 180, and 360 days of storage.

### ***Thermal Degradation***

The thermogravimetric behavior of the composites was determined by using TGA (Perkin-Elmer TGA Pyris 7, Norwalk, CT) under a nitrogen flow. Samples weighing approximately 10 mg were heated from 50 to 600°C, at a heating rate of 10°C/minute. The Arrhenius activation energy ( $E_A$ ) was determined according to ASTM method E1641-99. For each composite, 3-mg ( $\pm 1$  mg) samples were heated from 50 to 600°C at



1, 2, 5, and 10°C/min. The temperature at 5, 10, 15, and 20% decomposition from each heating rate was used for calculation. These  $E_A$  values were used to generate a thermal endurance curve (lifetime) according to ASTM method E1877-00.

### ***Differential scanning calorimetry (DSC)***

The thermal transition of aged specimens was determined, with three replicates, by DSC (Perkin-Elmer DSC Pyris 1, Norwalk, CT). The calibration of the instrument was set by using indium as a standard material. About 8 mg ( $\pm 2$  mg) collected from the aged specimens was weighed into an aluminum DSC pan, and the thermal behavior was recorded by heating the sample from  $-20$  to  $200^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , under a nitrogen purge. The enthalpy of relaxation ( $\Delta H_{EX}$ ) of each aged specimen was determined by integrating the area under the peak around the  $T_g$ . A rough estimation of crystallinity (in percentage) of the samples for each aging period was calculated by using the formula in Equation 2.1 (Fisher 1973):

$$\text{Crystallinity} [\%] = \left[ \left( \frac{\Delta H_m - \Delta H_c}{X} \right) / \Delta H_m^0 \right] \times 100 \quad (2.1)$$

where the heat of crystallization ( $\Delta H_c$ ) and heat of fusion ( $\Delta H_m$ ) were determined by integrating the area under the DSC curve around the temperature of crystallization ( $T_c$ ), and the temperature of melt ( $T_m$ ), respectively. The variable  $\Delta H_m^0$  is a value supposing that 100% of the sample is in a crystalline form. For PLA,  $\Delta H_m^0$  is 93.6 J/g (Fisher 1973). The variable X is equal to 1 for samples containing just PLA, and is equal to 0.55 for samples containing the blend PLA/starch at a 55/45 ratio (with and without MDI). The crystallinity of the samples right after being removed from the mold was also determined to observe the effect of the initial storage time on crystal formation.

### ***Tensile testing***

Tensile strength ( $\sigma$ ), elongation ( $\epsilon$ ), and modulus at break (Young's Modulus, E) of the aged specimens were determined with the Instron testing system (Model 4465, Canton, MA), according to ASTM method D638-91, with a crosshead speed of 5 mm/min and 25-mm gauge length. Five replicates were made for each sample.

### ***Dynamic mechanical analysis (DMA)***

The dynamic mechanical characteristics of the aged samples were determined with DMA (Perkin-Elmer TGA Pyris 7, Norwalk, CT) in a three-point bending mode. A 10x4x2-mm test specimen was scanned from 20 to 160°C at a rate of 3°C/min and 1Hz under a nitrogen purge. The damping ( $\tan \delta$ ) and storage modulus ( $E'$ ) were determined.

### ***Moisture Content***

The percentage of moisture content of the aged specimens was determined by using the broken samples from the tensile test. The specimens, in three replicates, were dried at 130°C for 3 days in a conventional oven, and their moisture content was determined by difference of weight (in percentage). The percentage of moisture content of the samples just after the removal from the mold was also determined to study the effect of the initial storage time on the amount of water absorbed by the specimens.

## **Results and Discussion**

### ***Thermal degradation***

Figure 2.1.A shows the plots of weight loss (TGA) of PLA, PLA/starch, PLA/starch/MDI, and starch; and Figure 2.1.B shows their corresponding derivative (DTA) plots. The thermal decompositions that took place under 350°C were attributed to thermal degradation of the starch components, and those taking place above 350°C were related to the pyrolysis of the PLA components (Ke and Sun 2001a). The initial-mass loss in starch (around 50 to 100°C) corresponded to moisture losses. Slight moisture losses were observed in PLA/starch and PLA/starch/MDI composites, which indicate that less water was absorbed in their structures. The PLA did not show any significant moisture loss.

Table 2.1 presents the peak position of the weight loss ( $T_{\max}$ ) and the degradation extent (DE) of PLA, PLA/starch, PLA/starch/MDI composites, and starch. The PLA decomposes almost completely (98.5%) at 376°C. The PLA/starch composite, with and without MDI, showed two  $T_{\max}$  values to those for starch and PLA decomposition temperatures (320 and 378°C, respectively). For these composites, the DE above 350°C

(~56%) reflects the amount of PLA in the blend (55%wt). Similar  $T_{\max}$  and DE for starch have been reported in literature (Ke and Sun 2001a).

The thermal-endurance curve (Figure 2.2) estimates the lifetime (duration) of a material exposed at a certain temperature. The PLA showed the greatest  $E_A$  (228.1 KJ/mol). A greater value for  $E_A$  indicates that a larger amount of energy is needed to decompose the matter. Indeed, PLA showed the greatest thermal endurance of all (Figure 2.2). The effect of its greater activation energy can be noticed on TGA plots (Figure 2.1.A); PLA took longer to start decomposing than did PLA/starch composites (with or without MDI). The closeness of  $E_A$  values for PLA/starch and PLA/starch/MDI composites (183.4 and 190.9 KJ/mol, respectively) reflects the similarity of their TGA plots (Figure 2.1.A). But, this small difference becomes clearly noticeable on their thermal-endurance curves (Figure 2.2). The PLA/starch composite with MDI showed greater thermal endurance than that without MDI. This difference might be caused by the enhancing effect of MDI on the interfacial adhesion between PLA and starch molecules, which would require a larger amount of energy to decompose the matter.

### ***Thermal properties***

Free volume and internal energy of a polymer usually decrease during storage because of aging. Such physical aging often causes heat absorption at  $T_g$  transition of the polymer (Struik 1978a, Mo and Sun 2003). Therefore, the excess enthalpy of relaxation ( $\Delta H_{EX}$ ), the area under the endothermic peak at the  $T_g$ , can be used as an indicator of aging (Aref-Azar and Hay 1982). The slope,  $\alpha$ , of the respective linear regression indicates the relative aging rate. The observable linearity relationship between  $\Delta H_{EX}$  and log aging time indicates that all samples aged in an exponential fashion. Aging was fast through the first 30 days, and slowed down after 30 days.

Pure PLA generally aged more slowly than the PLA/starch composites did. The PLA/starch with MDI composites aged more slowly than the PLA/starch without MDI (Fig. 3.A-C). Samples with the same composition aged more slowly at constant 50% RH conditions than did those stored in fluctuating RH conditions. Samples sealed with polyethylene bags aged more slowly than those without sealing did.

Water plays an important role in the physical aging of these PLA and PLA/starch blend samples. In blends with a high PLA/starch ratio (7:3 and greater), the starch granules are well covered by the continuous PLA matrix and, then, are less exposed to the water molecules from the environment. By decreasing this ratio (down to 55:45, for instance), the PLA matrix becomes less continuous, and the starch granules become more exposed to the water molecules (Ke and Sun 2000, Wang et al. 2002). Due to the hydrophilic characteristic of starch, the absorption of water into the composites is mainly attributed to the starch fraction (Wang et al. 2001, Ke and Sun 2001a). Water acts as an effective plasticizer to starch (Ke et al. 2002b) and increases the molecular mobility of PLA (Wang et al. 2003), which would facilitate the aggregation of PLA chains, resulting in faster nucleation and crystallization of the PLA molecules.

The isothermal crystallization process in thermoplastic polymers occurs in two steps. The first step, known as primary crystallization (or primary growth front), is characterized by portions of the system at different steps of development. While some nucleated portions are in a growth stage, others have just started their nucleation, and some are still awaiting nucleation. The primary crystallization is usually described by the Avrami Equation (Eq. 2.2) (Avrami 1939, 1940 and 1941), showing the familiar S-shaped curve (when overall crystallinity is plotted against linear and log time). It is considered to be completed when most of the spherulite surfaces encroach on each other. The second step, known as secondary crystallization, takes place after the primary crystallization and occurs as densification of the non-crystalline matter, with no associated crystallization. The secondary crystallization is referred to as physical aging and is observed as a long-term continuation of crystallization. The secondary crystallization proceeds at a slower rate and may occur by any of the following ways: (a) crystallization of shorter or less perfect chains of the main polymer; (b) crystallization of purposely (or not purposely) added chains of different species; (c) crystallization of the main polymer in small packets formed at the previous crystallization step; (d) further growth of crystals formed during the crystallization step; or (e) continuing perfection of crystals formed during primary crystallization (Schultz 2001).

$$\Phi(t) = 1 - \exp(-Kt^m) \quad (2.2)$$

where  $\Phi$  is the crystalline volume fraction developed at time  $t$  and constant temperature,  $K$  depends on the geometry of growth, and  $m$  is a suitable parameter termed Avrami exponent.

Analysis carried out on PLA, PLA/starch, and PLA/starch/MDI samples just after their removal from the mold (non-aged samples) showed a percentage of crystallinity of 13.76, 6.98, and 9.19% and moisture content of 0.30, 0.40, and 0.37%, respectively. At day 2, all samples showed a sharp increase in crystallinity (Table 2.2) and it seemed that most of the crystalline structure was formed (matured) as a result of the completion of the primary crystallization step.

At day 2 (Table 2.2), unsealed PLA samples stored at fluctuating RH showed a slightly greater percentage of crystallinity (26.47%) and moisture content (1.13%) than did those stored at 50% R.H (24.11% and 1.06%, respectively). The greater percentage of crystallinity in 2-day-old samples stored at fluctuating RH (initial RH set at 90%) was caused by the larger amount of water absorbed by the samples, which would increase the plasticizing effect, facilitating the mobility of PLA chains and, consequently, its increasing crystallinity. At 180 days, PLA samples stored at constant 50% RH reached greater values of crystallinity than did those stored in fluctuating RH. Because of the constant variation of the relative humidity, the plasticizing effect of water probably was reduced drastically throughout the periods of low relative humidity (30%), retarding the formation of crystals.

Sealed PLA samples stored in fluctuating RH showed a smaller percentage of crystallinity (18.33%) and moisture content (0.83%) than those of unsealed samples. The polyethylene bags, as well as any other plastic films, works as a moisture barrier (Hirsch 1991, Osborn and Jenkins 1992), restricting the diffusion of moisture into the bags, consequently limiting the exposure of the samples to higher humidity and resulting in samples with less moisture content. Such smaller amounts of absorbed water diminished the plasticizing effect of water, slowing down the formation of crystals.

As expected, PLA/starch samples with MDI showed a slightly greater percentage of crystallinity than did those without MDI. By adding MDI to PLA/starch composite, the urethane linkage formed between PLA and starch molecules restricts the interface slippage, which promotes fragmentation of PLA molecules by mechanical shearing,

allowing faster reorganization of PLA fragments and increasing crystallinity (Wang et al. 2001). Smaller values of crystallinity were observed in sealed samples. As described earlier, the plastic bags limited the amount of water absorbed by the samples and, consequently, minimize the formation of crystals.

### ***Mechanical properties and moisture***

Physical aging causes the degradation of mechanical properties of a material. As mentioned before, water is an important factor, causing a reduction in mechanical properties. Both PLA samples (Table 2.2) and PLA/starch composites (Wang et al. 2003) stored at 50% RH showed a consistent stability with aging. Unsealed samples stored in fluctuating humidity had similar reductions in tensile strength and elongation (Table 2.2). As expected, PLA alone had the least reduction and PLA/starch without MDI had the greatest reduction in mechanical properties.

Un-aged PLA samples had moisture content of 0.30%. Table 2.1 shows that the moisture content of 2-day-old unsealed PLA samples stored at 50 and 90% was about 1.06 and 1.13%, respectively, and the moisture content of sealed PLA samples stored at 90% RH was about 0.80%. Even though PLA is a hydrophobic polymer with great water resistance, differences in relative humidity affect the moisture content of the samples. Because the relative humidity levels varied drastically and frequently between 90 and 30% RH along aging, such frequent hydration and dehydration (swelling and shrinking) of the samples during storage might have progressively weakened the interaction within PLA fragments. The swelling/shrinking cycles would have caused some ruptures into the PLA matrix, resulting in a system with poorer response to mechanical stress.

As mentioned before, the absorption of water by PLA/starch composites is attributed mainly to the starch. The frequent hydration and dehydration (swelling and shrinking) of starch molecules caused by the variation of relative humidity would progressively weaken the interfacial interaction between PLA and starch, resulting in deterioration of mechanical properties as aging progressed.

The values of tensile strength and elongation of PLA/starch with and without MDI (Table 2.2) show that physical aging was less intense in PLA/starch composites with MDI. The strengthening effect of MDI on the interfacial interaction between PLA

and starch molecules would enhance the resistance of the composite against the swelling/shrinking cycles. Such resistance minimized the prejudicial effect of the variation of relative humidity on the mechanical properties of the composite.

Sealed PLA samples showed tensile-strength values similar to those stored at constant 50% RH, and PLA/starch (with and without MDI) composites presented a significant decrease of deterioration of their tensile-strength values (Table 2.2). The use of polyethylene bags seemed to preserve or, at least, to decrease the deterioration of mechanical properties of the composites. The moisture barrier characteristic of the plastic bags not only restrict the diffusion of moisture into the bags, but also seems to decrease the amplitude of its variation throughout the humidity cycles. Such narrower variation in moisture content would result in less-intense swelling/shrinking cycles, preserving the integrity of the PLA matrix and the interfacial interaction between PLA and starch molecules.

The moisture content of unsealed samples reached the highest level at day 30, and leveled off (Table 2.2). On the other hand, with the use of plastic bags, the moisture content of the samples kept increasing until the sixtieth day, leveling off then. Such slowness in water absorption resulted in a gradual increase of the plasticizing effect of the water in the samples with aging, reflected in a gradual increase of elongation of the samples. The stabilization of elongation coincided with the leveling off of the moisture content of the samples.

At day 180, unsealed PLA/starch composites, with and without MDI, had a sharp drop in moisture content (Table 2.2). The reduction of the capacity for water absorption cannot be explained by the retrogradation of the starch granules because the samples were not exposed to enough water or to temperatures high enough to promote retrogradation (Colonna et al. 1987). It is possible that the water absorbed during the swelling stages of the starch granules was in large enough amounts to act as a plasticizer, promoting either growth or perfection of already existing crystallites, decreasing the capacity of the starch granules to absorb water (Jacobs and Delcour 1998).

### *Dynamic mechanical properties*

Free volume reduces with aging, reducing molecular mobility and consequently decreasing mechanical properties (Wang et al. 2003). The dynamic mechanical properties of PLA samples, as expected (Vert 1989), showed a reduction in  $\tan \delta$  as aging increased (Figures 2.4.A-C). But the decrease of  $\tan \delta$  (free volume) of PLA samples stored at constant 50% RH (Figure 2.4.A) was not abrupt. Because free volume reduced slowly, the molecular mobility reduced slowly as well; in consequence, slower reduction of their mechanical properties was observed as aging progressed. The slight reduction in  $\tan \delta$  of the unsealed PLA samples stored in fluctuating RH (Figure 2.4.B) reflects the significant deterioration of their mechanical properties during aging.

The PLA samples sealed in polyethylene bags and stored in fluctuating RH (Figure 2.4.C) showed a higher  $\tan \delta$  peak (larger free volume) than did the unsealed PLA samples (Figures 2.4.A,B). The lower percentage of crystallinity of these samples (Table 2.2) reflects a less sealed crystalline structure (density), allowing more mobility of the PLA molecules (free volume) (Hay 1995, Hutchinson 1995).

Unsealed PLA/starch and PLA/starch/MDI samples showed a more drastic decrease of  $\tan \delta$  during the first 60 days (Figures 2.5.A,C). At day 120, however,  $\tan \delta$  increased sharply for both PLA/starch composites (with and without MDI), decreasing again at day 180. The increase of  $\tan \delta$  during aging of PLA/starch samples (with and without MDI, at 50% RH) has been reported (Wang et al. 2003). The author attributed the increase of  $\tan \delta$  to the increase of moisture in the composites. Indeed, the increase of  $\tan \delta$  in this study coincided with the peak of moisture content of both PLA/starch samples (8.22% for the composite with MDI and 8.51% for the composite without MDI). With accumulation of absorbed moisture by the starch granules, the water acted as a plasticizer, resulting in the rise of  $\tan \delta$ .

With the use of polyethylene bags, PLA/starch and PLA/starch/MDI samples showed a stable  $\tan \delta$  throughout aging (Figures 2.5.B,D), with a significant drop at day 180. The peak rises from day 2 to day 60. The slow and continuous increase of moisture content through the first 60 days would have increased the plasticizing effect of the water, resulting in a continuous rise of  $\tan \delta$ . The small variation of  $\tan \delta$  reflects the



reduced effect of physical aging on the PLA/starch samples sealed in polyethylene bags, compared with those unsealed samples.

## **Conclusion**

PLA/starch composites (with and without MDI) showed similar thermal decomposition profiles. But, PLA/starch composite with MDI showed greater thermal endurance than that without MDI, having long thermal endurance for the temperature range between 50 and 100°C.

Relative humidity played an important role in physical aging. Results show that PLA and PLA/starch composites suffered significant decay of their thermal-mechanical properties when stored at fluctuating relative humidity, due to absorption and desorption of water. Such degradation can be minimized by storing the samples in plastic bags, which work as a water barrier, protecting the samples from drastic variations of relative humidity during storage.

The thermal and mechanical degradation of PLA and its composites with starch would not significantly affect application function when they are stored in a controlled environment. With polyethylene bags, these PLA and PLA/starch based composites can be stored in fluctuating humidity conditions (30 to 90% RH) for as long as 30 days. Without water-barrier sealing, storage in fluctuating humidity (30 to 90% RH) is not recommended for products based on PLA or PLA/starch.

## Figures and Tables

**Table 2.1 Temperature of maximum rate of mass loss ( $T_{\max}$ ) and degradation extent (DE) for PLA, PLA/starch, PLA/starch/MDI composites, and starch**

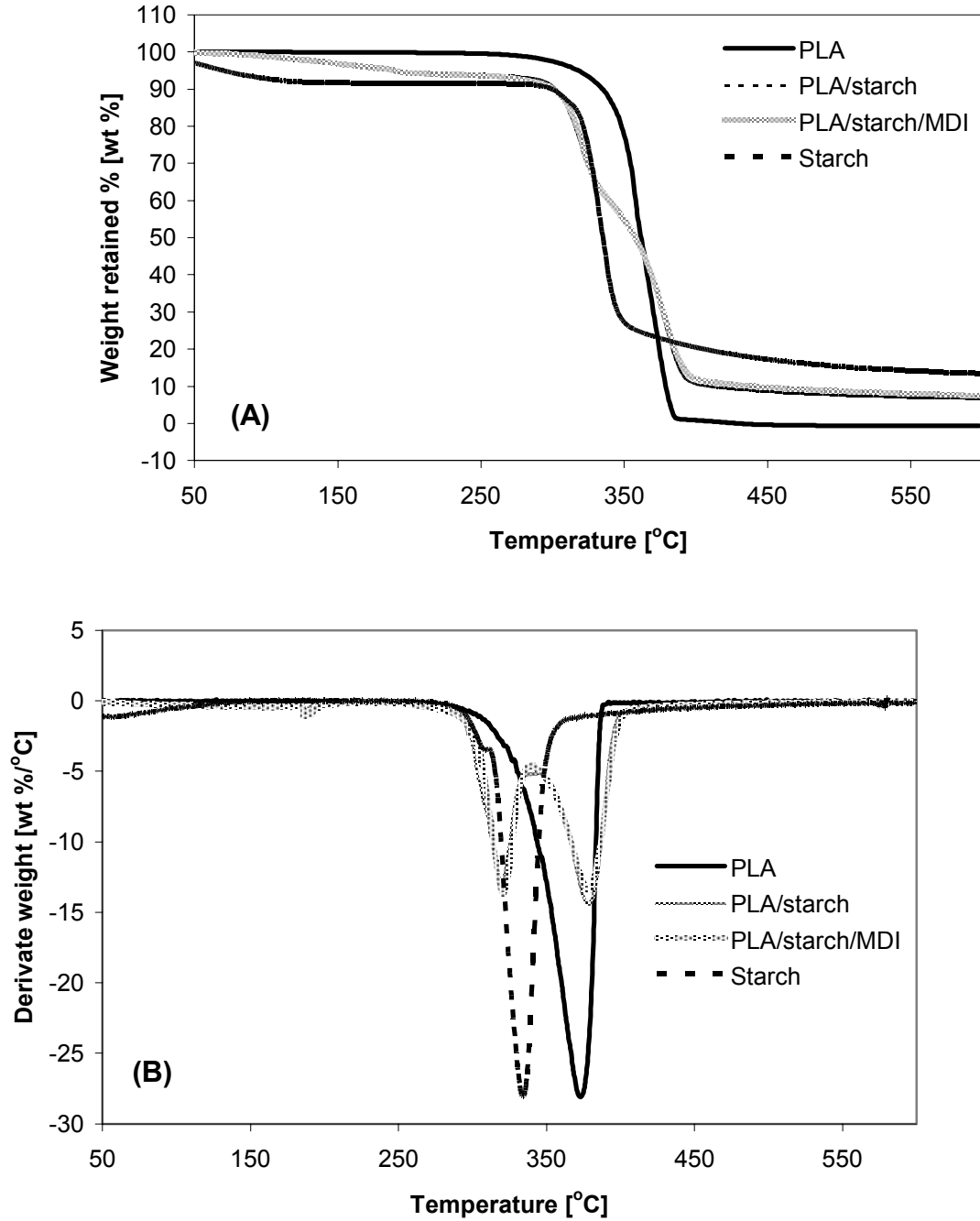
	< 350°C		> 350°C	
	$T_{\max}$ /°C	DE %	$T_{\max}$ /°C	DE %
PLA	–	–	373	98.4
PLA/starch	320	36.0	378	51.4
PLA/starch/MDI	320	34.6	378	51.9
Starch	334	77.7	–	–

**Table 2.2 Mechanical properties, moisture content, and crystallinity of aged PLA, PLA/starch, and PLA/starch/MDI for various periods of time at constant and fluctuating room humidity**

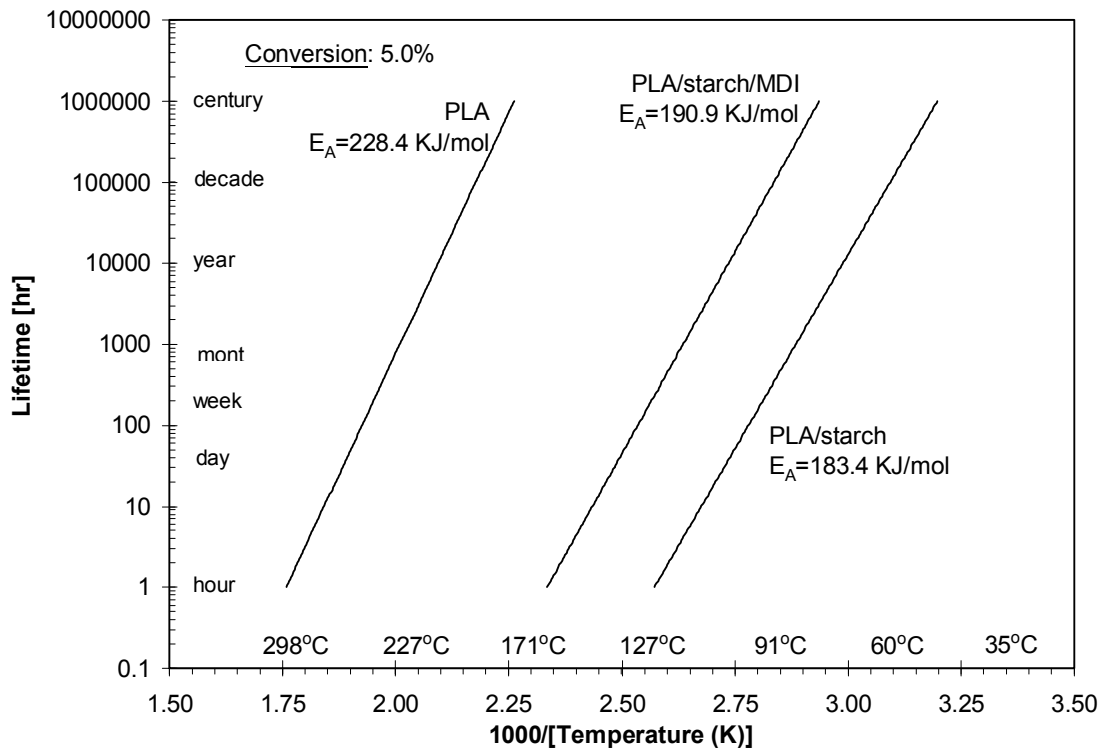
Condition	Age [days]	Tensile Strength [MPa]	Elongation [%]	Young's Modulus [GPa]	Storage Modulus [ $10^8$ MPa]	Moisture [%]	Crystallinity [%]	
PLA 50% RH Unsealed	2	58.79 <sup>a,b</sup>	4.03 <sup>a,b</sup>	1.55 <sup>a,b</sup>	7.13 <sup>a</sup>	1.06 <sup>a</sup>	24.11 <sup>d</sup>	
	30	59.49 <sup>a</sup>	3.75 <sup>b</sup>	1.60 <sup>a</sup>	8.80 <sup>a</sup>	0.49 <sup>b,c</sup>	27.95 <sup>c</sup>	
	90	59.02 <sup>a</sup>	4.46 <sup>a</sup>	1.33 <sup>b</sup>	8.86 <sup>a</sup>	0.35 <sup>c</sup>	42.09 <sup>a</sup>	
	180	55.63 <sup>b</sup>	4.44 <sup>a</sup>	1.66 <sup>a</sup>	7.63 <sup>a</sup>	0.75 <sup>a,b</sup>	40.50 <sup>a,b</sup>	
	360	58.17 <sup>a,b</sup>	4.69 <sup>a</sup>	1.65 <sup>a</sup>	9.41 <sup>a</sup>	0.75 <sup>a,b</sup>	40.65 <sup>b</sup>	
PLA 90-30% RH	Unsealed	2	55.06 <sup>a</sup>	3.77 <sup>a,b</sup>	1.89 <sup>a,b</sup>	7.74 <sup>a</sup>	1.13 <sup>a</sup>	26.47 <sup>b</sup>
		30	52.68 <sup>a,b</sup>	3.48 <sup>a</sup>	1.98 <sup>a,b</sup>	5.40 <sup>a,b</sup>	0.91 <sup>a</sup>	28.67 <sup>b</sup>
		60	48.40 <sup>b,c</sup>	3.39 <sup>a,b</sup>	1.89 <sup>b</sup>	5.78 <sup>a,b</sup>	0.96 <sup>a</sup>	34.94 <sup>a</sup>
		120	50.85 <sup>a,b,c</sup>	3.39 <sup>a,b</sup>	2.04 <sup>a,b</sup>	7.18 <sup>a</sup>	1.09 <sup>a</sup>	34.69 <sup>a</sup>
		180	45.69 <sup>c</sup>	3.19 <sup>b</sup>	2.11 <sup>a</sup>	2.98 <sup>b</sup>	0.91 <sup>a</sup>	35.19 <sup>a</sup>
	Sealed	2	58.91 <sup>b</sup>	4.33 <sup>b</sup>	1.83 <sup>b</sup>	5.18 <sup>a</sup>	0.83 <sup>a</sup>	18.33 <sup>a</sup>
		30	58.09 <sup>b</sup>	4.78 <sup>a,b</sup>	2.08 <sup>a</sup>	4.93 <sup>b</sup>	0.73 <sup>a</sup>	21.80 <sup>a</sup>
		60	55.80 <sup>b</sup>	4.92 <sup>a,b</sup>	1.93 <sup>a,b</sup>	5.87 <sup>a</sup>	1.11 <sup>a</sup>	18.48 <sup>a</sup>
		120	64.24 <sup>a</sup>	5.12 <sup>a</sup>	2.03 <sup>a,b</sup>	6.59 <sup>a</sup>	0.79 <sup>a</sup>	18.58 <sup>a</sup>
		180	57.56 <sup>b</sup>	5.11 <sup>a</sup>	2.11 <sup>a</sup>	5.69 <sup>a</sup>	1.02 <sup>a</sup>	18.49 <sup>a</sup>
PLA/starch 90-30% RH	Unsealed	2	31.52 <sup>a</sup>	2.73 <sup>a</sup>	2.39 <sup>a</sup>	4.41 <sup>a</sup>	4.30 <sup>c</sup>	31.38 <sup>a</sup>
		30	8.90 <sup>b</sup>	2.07 <sup>a,b</sup>	1.49 <sup>b</sup>	2.23 <sup>b</sup>	8.29 <sup>a</sup>	33.11 <sup>a</sup>
		60	7.22 <sup>b,c</sup>	2.00 <sup>a,b</sup>	1.42 <sup>b</sup>	2.44 <sup>b</sup>	8.14 <sup>a</sup>	34.31 <sup>a</sup>
		120	5.04 <sup>c,d</sup>	1.74 <sup>b</sup>	1.24 <sup>b</sup>	2.65 <sup>b</sup>	8.51 <sup>a</sup>	30.20 <sup>a</sup>
		180	8.67 <sup>d</sup>	0.91 <sup>c</sup>	0.55 <sup>c</sup>	2.13 <sup>b</sup>	5.73 <sup>b</sup>	31.73 <sup>a</sup>
	Sealed	2	45.89 <sup>a</sup>	3.07 <sup>b</sup>	2.38 <sup>a</sup>	7.79 <sup>a</sup>	1.88 <sup>c</sup>	10.20 <sup>b</sup>
		30	39.92 <sup>b</sup>	3.19 <sup>a,b</sup>	2.21 <sup>c</sup>	7.27 <sup>a</sup>	4.98 <sup>b</sup>	11.95 <sup>a,b</sup>
		60	38.88 <sup>b</sup>	3.56 <sup>a</sup>	2.14 <sup>c</sup>	7.02 <sup>a</sup>	6.12 <sup>a</sup>	2.41 <sup>a,b</sup>
		120	39.73 <sup>b</sup>	3.51 <sup>a</sup>	2.26 <sup>b,c</sup>	5.77 <sup>a</sup>	6.40 <sup>a</sup>	15.10 <sup>a</sup>
		180	33.05 <sup>c</sup>	3.38 <sup>a,b</sup>	2.33 <sup>a,b</sup>	5.77 <sup>a</sup>	6.21 <sup>a</sup>	14.47 <sup>a</sup>
PLA/starch/MDI 90-30% RH	Unsealed	2	54.26 <sup>a</sup>	4.20 <sup>a</sup>	2.33 <sup>a</sup>	4.18 <sup>a</sup>	4.62 <sup>c</sup>	34.08 <sup>b,c</sup>
		30	24.87 <sup>b</sup>	2.84 <sup>b</sup>	2.01 <sup>b</sup>	2.53 <sup>b,c</sup>	8.10 <sup>a</sup>	35.23 <sup>a,b</sup>
		60	15.72 <sup>c</sup>	2.47 <sup>c</sup>	1.80 <sup>c</sup>	1.53 <sup>c</sup>	8.02 <sup>a</sup>	34.29 <sup>b,c</sup>
		120	11.21 <sup>d</sup>	2.17 <sup>d</sup>	1.57 <sup>d</sup>	3.50 <sup>a,b</sup>	8.22 <sup>a</sup>	32.78 <sup>c</sup>
		180	12.91 <sup>c,d</sup>	2.19 <sup>d</sup>	1.62 <sup>d</sup>	4.12 <sup>a,b</sup>	6.28 <sup>b</sup>	36.00 <sup>a</sup>
	Sealed	2	63.40 <sup>a</sup>	4.09 <sup>a</sup>	2.50 <sup>a</sup>	5.42 <sup>a</sup>	1.68 <sup>c</sup>	11.21 <sup>a</sup>
		30	52.70 <sup>b</sup>	4.27 <sup>a</sup>	2.18 <sup>b,c</sup>	7.29 <sup>a</sup>	4.58 <sup>b</sup>	11.45 <sup>a</sup>
		60	41.50 <sup>c</sup>	3.79 <sup>a</sup>	2.31 <sup>b</sup>	5.61 <sup>a</sup>	5.88 <sup>a</sup>	12.23 <sup>a</sup>
		120	42.28 <sup>c</sup>	3.82 <sup>a</sup>	2.14 <sup>c</sup>	6.06 <sup>a</sup>	6.18 <sup>a</sup>	13.98 <sup>a</sup>
		180	41.06 <sup>c</sup>	4.03 <sup>a</sup>	2.16 <sup>b,c</sup>	6.55 <sup>a</sup>	6.10 <sup>a</sup>	12.20 <sup>a</sup>

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

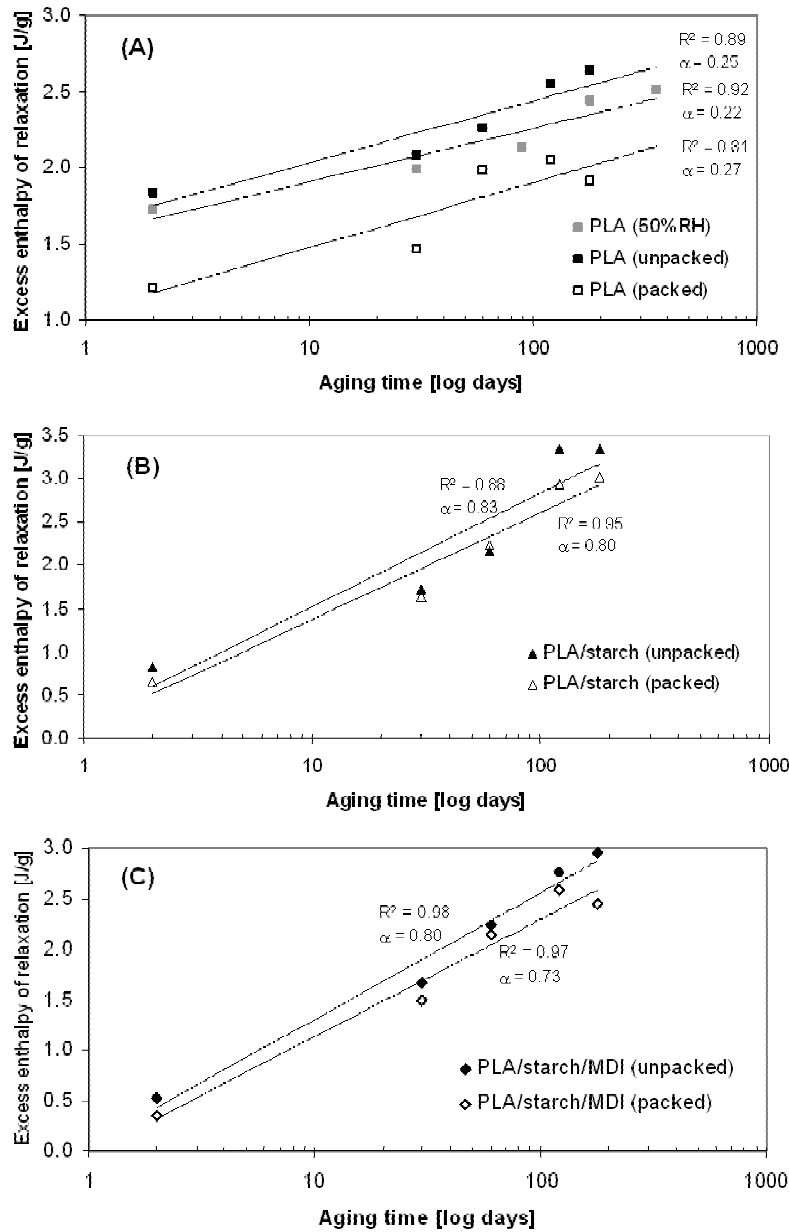
Figure 2.1 (A) Thermalgravimetric analysis plots, TGA; and (B) the corresponding derivative plots of the data, DTG, of PLA, PLA/starch, PLA/starch/MDI composites, and starch.



**Figure 2.2 Thermal endurance curves of PLA, PLA/starch, and PLA/starch/MDI composites.**



**Figure 2.3 Excess enthalpy of relaxation as affected by aging time for: (A) unsealed PLA samples stored at constant RH (50%) and PLA samples (unsealed and sealed) stored at fluctuating RH; (B) PLA/starch samples (unsealed and sealed) stored at fluctuating RH; and (C) PLA/starch/MDI samples (unsealed and sealed) stored at fluctuating RH.**



**Figure 2.4** The  $\tan \delta$  as a function of temperature at 1Hz for PLA samples stored at (A) 50% RH and 25°C for different periods of time; (B) unsealed PLA samples and (C) sealed PLA samples stored at fluctuating RH from 30 to 90% and 25°C for different periods of time.

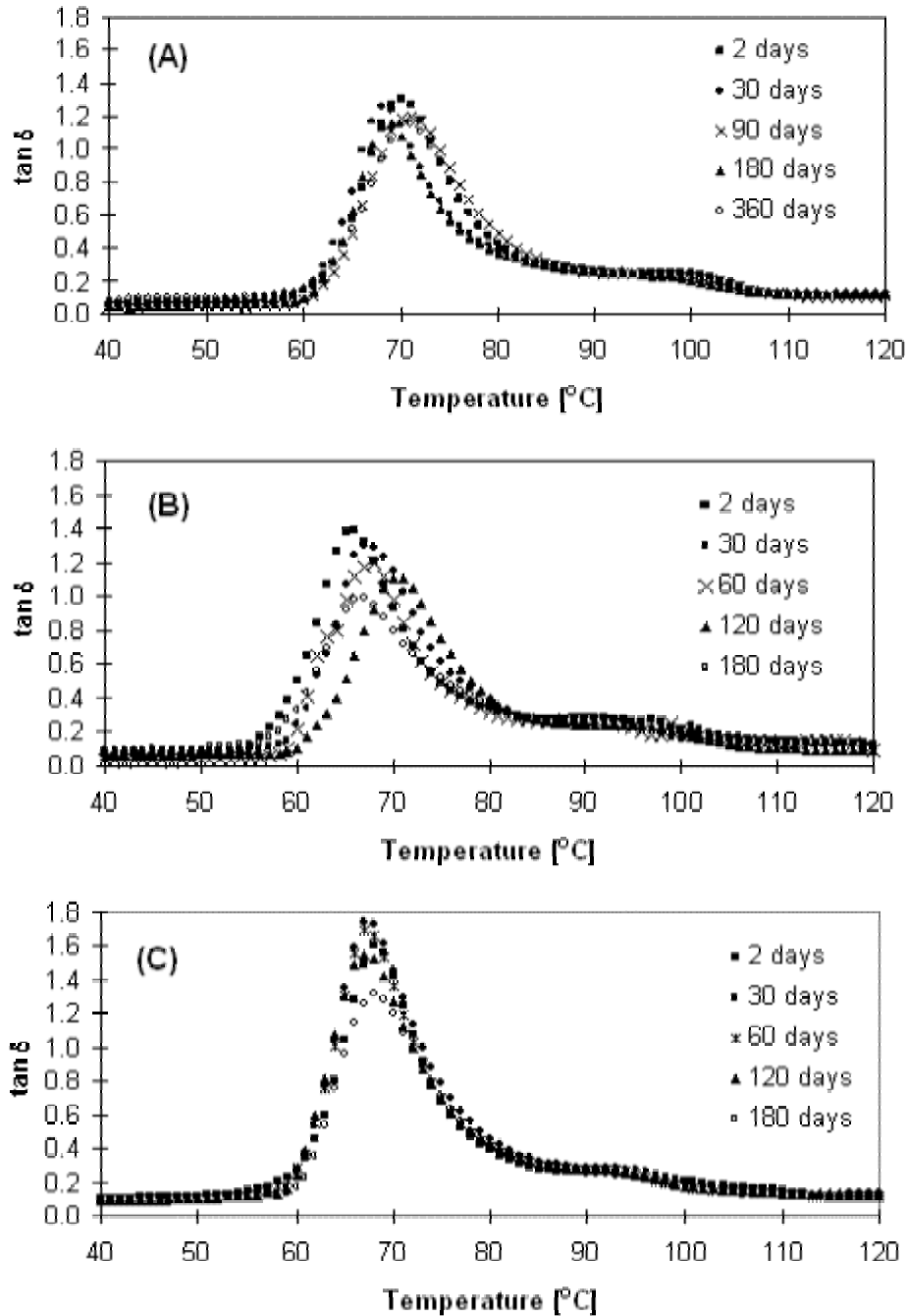
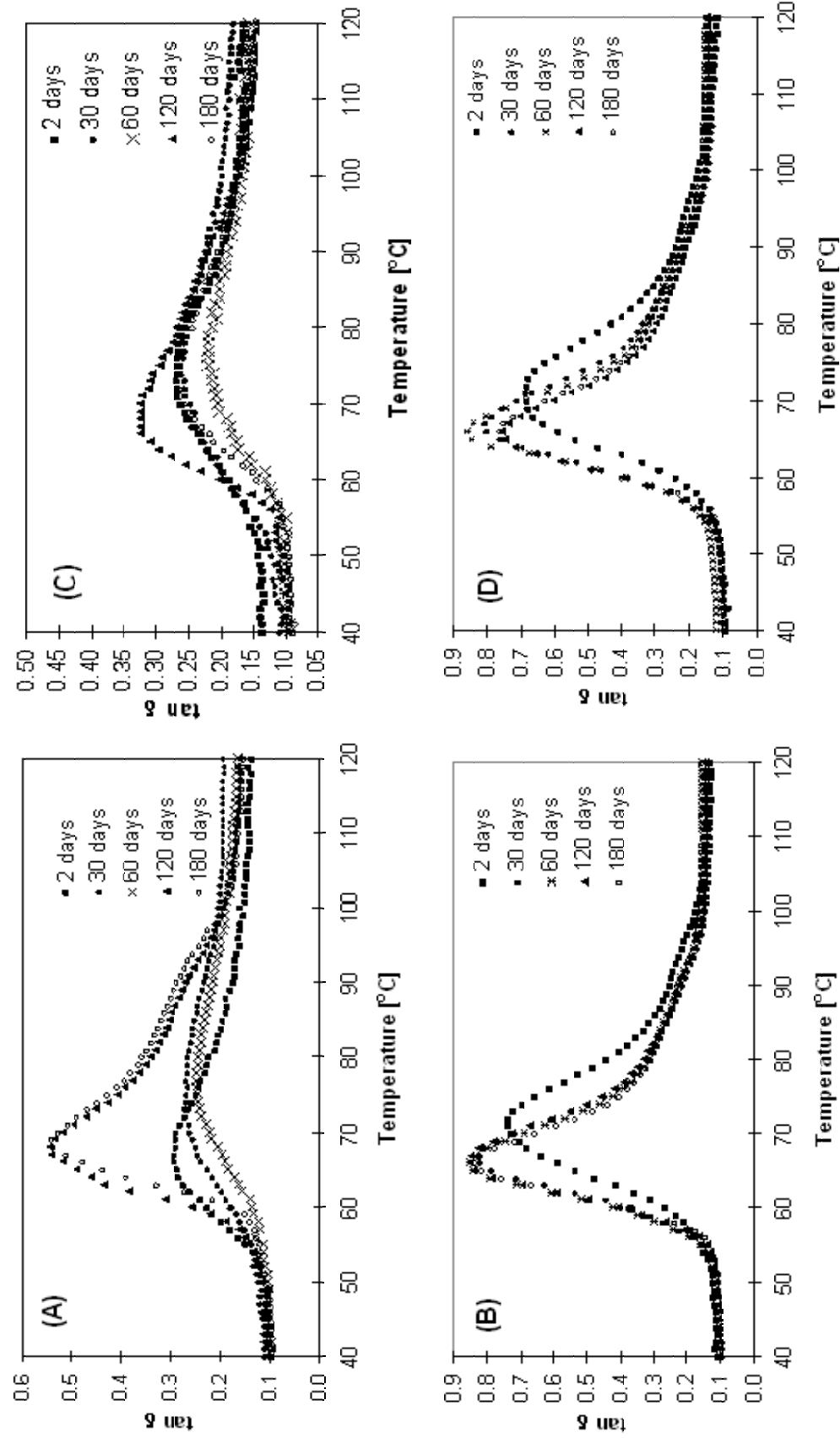


Figure 2.5 The  $\tan \delta$  as a function of temperature at 1Hz for (A) unsealed PLA/starch composites; (B) sealed PLA/starch composites; (C) unsealed PLA/starch/MDI composites; and (D) sealed PLA/starch/MDI composites, stored at fluctuating RH from 30 to 90% and 25°C for different periods of time.





# **CHAPTER 3 - INFLUENCE OF STARCH PARTICLE SIZE ON THERMAL-MECHANICAL PROPERTIES OF POLY(LACTIC ACID)/STARCH COMPOSITES**

## **Abstract**

This work reports the effect of starch average particle size (APS) on mechanical and thermal properties of poly(lactic acid)/starch composites with methylenediphenyl diisocyanate (MDI) as a coupling agent. The samples were blended in a hot-mixer equipped with two co-rotating rollers with a gap, and press-molded into bone-shaped specimens (Type IV). Results show that tensile strength, elongation, and damping increased with APS. But, declination of these properties was detected with APS larger than 45  $\mu\text{m}$ . Crystallinity of the blends increased as the APS decreased. Young's modulus, storage modulus, and moisture absorption of the composites were not significantly affected by the starch APS. The use of MDI as a coupling agent altered the influence of the starch APS on mechanical properties of poly(lactic acid)/starch composite. The amount of MDI used seems to be not enough to wet all starch granules of composites made with small starch APS.

## **Introduction**

Poly(lactic acid) is a biodegradable polyester derived from carbohydrates of renewable resources (for instance, corn) (Wang et al. 2003), and exhibits many of its properties comparable to those of polyethylene, polypropylene, polystyrene, and polyethylene terephthalate (Naitove 1998). But, depending on the circumstances, PLA is still more expensive than conventional polymers and has a relatively slow degradation rate when compared to the waste accumulation rate (Reed 1981).

Starch is a naturally available biodegradable polymer that exhibits satisfying thermal stability and minimal interface with the melt-flow properties of most materials utilized in the plastic industry (Griffin 1974). Starch may be added to a PLA matrix as a filler to decrease its cost, improve its biodegradation rate, and produce a completely renewable biodegradable plastic (Wang et al. 2003). But, due to the hydrophilic properties of starch, its incorporation into plastic may cause an increase in water sensitivity and a decrease in mechanical properties, such as tensile strength and elongation (Griffin 1977a,b; Evangelista 1991).

A negative effect of starch on the mechanical properties of films has been reported (Griffin 1977a,b; Gage 1990; Evangelista 1991). In starch-filled polyethylene films, tensile strength and elongation exhibits an inverse relationship to APS (Lim et al. 1992). Filler with larger particle size is associated with a non-uniform distribution of internal stress and strain when compared to filler with smaller particle size (Wang et al. 2003).

A recent study (Ke and Sun 2000) reported that PLA thermal behavior is not affected by the presence of starch. But, the tensile strength and elongation of the composite decrease as starch content increases, which was believed due to weak adhesion forces between the PLA and starch phases. The adhesion forces could be formed by polar interactions due to hydrogen bonding between carboxyl groups in PLA and hydroxyl groups in starch.

To improve the interaction between matrix and filler, it is necessary to enhance the interfacial adhesion between both phases (Dick 1987). Methylenediphenyl diisocyanate (MDI) is a coupling agent that contains two highly active isocyanate groups

in its molecule. Isocyanate groups react with both carboxyl and hydroxyl groups, forming urethane linkages (Dieteroch et al. 1985). The addition of 0.5% (wt) of MDI to PLA/starch composite (ratio of 55 to 45 by weight) enhanced the mechanical properties (Wang et al. 2001). Without MDI, PLA/starch composite showed a drop in tensile strength and elongation by 42% and 55%, respectively, compared to pure PLA. With the addition of MDI to the blend, tensile strength increased by 7.5% and elongation decreased by 23%.

Wang et al. (2003) observed that tensile strength of PLA/starch/MDI composites with wheat starch was higher than with corn starch. The larger particle size of wheat starch generated a smaller total surface area (at the same weight ratio of PLA), and less MDI would be needed in order to wet and disperse through the system, which would result in a stronger interfacial interaction between PLA and starch.

It has been reported that the properties of a particulate-filled composite is significantly influenced by the wetting and bonding of a coupling agent at the interface of the constituent materials (Wu 1982). The aim of this study was to verify the influence of starch granule size on mechanical and thermal properties of PLA/starch composites in the presence of MDI as a coupling agent.

## **Material and Methods**

### ***Materials***

A PLA resin, with molecular weight of 120,000 Da and derived mainly from L-lactic acid, was purchased from Shimadzu (Tokyo, Japan). Rice starch was purchased from Sigma-Aldrich, Co. (Saint Louis, MO); industrial corn starch (Silver Medal Pearl-100) was provided by Cargill, Inc. (Minneapolis, MN); commercial wheat starch (Midsol 50) was purchased from Midwest Grain Products, Inc. (Atchinson, KS); and potato starch (Superior Potato Starch) was provided by KMC (Denmark). Methylenediphenyl diisocyanate (MDI, Rubinate 1840) in a dark brown liquid was purchased from ICI Polyurethanes (Geismar, LA).

### ***Starch particle size distribution characterization***

Particle size distribution and average particle size (APS) of starches were determined accordingly to the AACC Method 50-11 with the Lecotrac particle size analyzer (model LTS-150 Leco Corp., St. Joseph, MI). Figure 3.1 shows the particle size distribution curves of all starches used in this work.

Rice starch was characterized by its tiny polyhedral-shaped form (Figure 3.2.A, detail magnified by 4,000 times). Rice starch had narrow particle size distribution and the smallest average particle size of all starches (6.0  $\mu\text{m}$ ). Corn starch was a mixture of spherical and polyhedral-shaped granules (Figure 3.2.B), while wheat starch had disc-shaped granules (Figure 3.2.C). Even though corn and wheat starches showed distinct values of APS (15 and 20  $\mu\text{m}$ , respectively), their particle size distributions overlapped. The values of APS for corn and wheat starches are similar to values found in literature (Wang et al. 2001, 2003). Potato starch granules have an oval-shaped form (Figure 3.2.D) and showed a wide particle size distribution range and the largest MV of all starches (48.8  $\mu\text{m}$ ).

### ***Starch damage and amylose content characterization***

Starch damage in the starches was determined following the AACC Method 76-30A using a Chopin SD4 (Chopin Instruments, France). Amylose content of the starches was determined using Megazyme amylose/amylopectin assay kit for the measurement of the amylose and amylopectin contents of starches (Megazyme International Ireland, Ireland). Amylose and damage starch contents are given in Table 3.1.

### ***Separation of starch fractions by particle size using sieving***

Starches were sieved following a modified procedure by Bathgate and Palmer (1972) and Lim et al. (1992). Starch slurry solutions (25g in 400mL of water) were transferred into stainless-steel test sieves and stirred with a plastic scrapper to allow starch granules to flow through the mesh. The retained fraction (A) of starch granules was repeatedly washed with distilled water until flowing filtered solution was clear, and collected. The filtrate fraction was centrifuged at 5875g for 6 minutes, and the

precipitated fraction (B) was collected. Both fractions, (A) and (B), were dried in conventional oven at 45°C for 24 hours.

In order to minimize undesirable effect of particle size on the results, corn and wheat starches were sieved to slightly shift their particle size curves apart and to narrow their particle size range. Corn starch was sieved through 20 µm sieve aperture (No. 635) and only the sieved fraction (filtrated) was preserved for study. Wheat starch was sieved consecutively through 32 and 20 µm sieves aperture (No. 450 and 635, respectively), and only the retained fraction (on the 20 µm sieve aperture) was preserved for study.

Due to the broad particle size range of potato starch, two different fractions were obtained by sieving it consecutively through 63 and 32 µm sieve apertures (No. 230 and 450, respectively). Both retained fractions, on 63 and 32 µm sieve apertures, were preserved for study. Rice starch was spared from sieving because its particle size distribution was clearly distinguished from the other starch samples.

To avoid the effects of starch sources on mechanical and thermal properties, another experiment was conducted using potato starch with four distinct particle size distribution ranges. These four particle size ranges included (1) larger than 63 µm (No. 230); (2) between 63 and 45 µm (No. 230 and 325, respectively); (3) between 45 and 25 µm (No. 325 and 500, respectively); and (4) smaller than 25 µm (500 mesh). Table 3.1 shows the average particle size of all starches used in this work.

### ***Sample preparation***

PLA resin was ground by a laboratory mill (Model 4 Laboratory Mill, Thomas-Wiley Company, Philadelphia, PA) with a 2-mm screen. Ground PLA and starches were dried to about 5% wt moisture content, according to AACC method 44-15A, in a conventional oven at 130°C for 2 hours before sample preparation. PLA was blended with starch at a ratio of 55 to 45 (w/w) and MDI (0.5% wt over the total weight), and transferred to an intensive hot mixer (Rheomix 600, Haake, Paramus, NJ) equipped with two co-rotating rollers with a gap. The blends were hot-mixed for 4 minutes at 185°C and 135 rpm. After mixing, all samples were ground using the same laboratory mill described above. The ground samples were compression-molded into a type IV testing specimen, following ASTM method D-638-91, using a hot press (Model 3890, Auto “M”, Carver

Inc., Wabash, IN) at 176°C and molding pressure of 4.2 MPa for about 15 minutes. The molded specimens were cooled at room temperature to 57°C before removal from the mold and were stored in environmental chamber at 50% relative humidity (RH) and 25°C for 48 hours.

### ***Mechanical properties***

Tensile strength ( $\sigma$ ), elongation ( $\epsilon$ ), and modulus at break (E, Young's Modulus) of samples were determined, using five replicates, by Instron testing system (Model 4465, Canton, MA), following ASTM method D638-91 with a crosshead speed of 5-mm/min and 25-mm gauge length. The dynamic mechanical characteristics of samples were determined by DMA (Perkin-Elmer Pyris 7, Norwalk, CT) in a three-point bending mode. Sample dimensions were 10x4x2-mm. Sample was scanned from 20 to 160°C under a nitrogen purge at a rate of 3°C/min and 1Hz. The damping ( $\tan \delta$ ) and storage modulus were determined. Five replications were made.

### ***Thermal properties***

The thermal transition of the specimens was determined, with five replicates, by DSC (Perkin-Elmer DSC Pyris 1, Norwalk, CT). The calibration of the instrument was set by using indium as a standard material. About 8 mg ( $\pm 2$  mg) collected from the specimens was weighed into an aluminum DSC pan, and the thermal behavior was recorded by heating the sample from -20 to 200°C at a rate of 10°C/min, under a nitrogen purge. A rough estimation of crystallinity (in percentage) of the samples for each specimen was calculated by using the formula in Equation 3.1 (Fisher 1973):

$$Crystallinity [\%] = \left[ \left( \frac{\Delta H_m - \Delta H_c}{X} \right) / \Delta H_m^0 \right] \times 100 \quad (3.1)$$

where the heat of crystallization ( $\Delta H_c$ ) and heat of fusion ( $\Delta H_m$ ) were determined by integrating the area under the DSC curve around the temperature of crystallization ( $T_c$ ), and the temperature of melt ( $T_m$ ), respectively. The variable  $\Delta H_m^0$  is a value supposing that 100% of the sample is in a crystalline form. For PLA,  $\Delta H_m^0$  is equal to 93.6 J/g (Fisher 1973). For this study, the variable X is equal to 0.55; which corresponds to the fraction of PLA in the blend.

### ***Scanning electron microscopy***

The microstructure of starch granules and fractured specimens were observed using a Hitachi S-35000N scanning electron microscope (SEM) (Hitachi Science Systems, Ltd., Ibaraki, Japan) at an accelerated voltage of 20KV. The samples were mounted on an aluminum stub and its fractured surface was coated with a gold/palladium (60:40 %) mixture with a sputter coater (Desk II Sputter/Etch Unit, NJ). The micrograph of starch granules and fractured specimens had standardized magnification of 500 and 200 times, respectively.

### ***Moisture content***

The percentage of moisture content of specimens was determined using the broken samples from the mechanical analysis. The specimens, in three replicates, were dried at 130°C for 3 days in a conventional oven and their moisture content was determined by difference of weigh (in percentage).

## **Results and Discussion**

### ***Mechanical properties***

Table 3.1 shows the properties of PLA/starch/MDI composites made with rice and sieved corn, wheat, and potato starches. Tensile strength and elongation tended to increase with increasing starch average particle size. But, at APS of 71  $\mu\text{m}$ , values of both properties dropped significantly.

The average density of starch granules is 1.5g/cm<sup>3</sup> (Gausman et al 1952, Biss and Cogan 1988, Steinke and Johson 1991). Supposing that all starch particles in a sample has the same respective average particle size and a spherical shape; it is possible to estimate the area (Equation 3.2), volume (Equation 3.3), and mass (Equation 3.4) of a single starch particle (values are shown in Table 3.2).

$$A_{sphere} = 4\pi r^2 \quad (Eq.3.2)$$

$$V_{sphere} = \frac{4}{3}\pi r^3 \quad (Eq.3.3)$$

$$\rho = \frac{m}{V_{sphere}} \quad (Eq.3.4)$$

where:  $A_{sphere}$  = area of the sphere,  $\text{cm}^2$ ;  $r$  = ray,  $\text{cm}$ ;  $V_{sphere}$  = volume of the sphere,  $\text{cm}^3$ ;  $\rho$  = density,  $\text{g}/\text{cm}^3$ ; and  $m$  = mass.

As mentioned earlier, Wang et al. (2003) suggested that, at the same weight ratio, the difference in tensile strength of PLA/starch/MDI composites made with wheat and corn starches was due to differences in total surface area of the starch granules. But, Table 3.2 shows that the estimated total surface area in 1-g of corn starch is only about 1.7 times larger than in 1-g of wheat starch. However, the difference in tensile strength can be better explained by the difference in the numbers of starch granules. It is estimated in Table 3.2 that 1-g of starch with an APS of 6  $\mu\text{m}$  has about 10 times more starch particles than 1-g of starch with an APS of 15  $\mu\text{m}$ ; about 50 times more particles than starch with an APS of 26  $\mu\text{m}$ ; about 302 times more particles than starch with an APS of 47  $\mu\text{m}$ ; and about 1,000 times more particles than a starch with an APS of 71  $\mu\text{m}$ . At the same weight ratio of PLA, starch, and MDI, composites made with smaller starch granules had more starch particles than those made with larger starch granules, as illustrated in Figure 3.3. Because of the fixed amount of all components, the amount of MDI present in the blend would not be enough to disperse and react with a larger number of small starch particles (Figure 3.3.A). Hence, the strengthening effect of MDI on PLA-starch interfacial interaction would be limited, resulting in a system with poorer resistance to mechanical stress. In this case, MDI seems to be a limiting factor.

As starch particle size increases, the total number of starch particles present in the blend decreases. At a certain starch particle size (Figure 3.3.B), the amount of MDI would be enough to uniformly wet and disperse throughout the starch particles, increasing the number of regions with strengthened PLA-starch interfacial interaction and, consequently, resulting in enhanced mechanical properties.

But, when starch particle size becomes too large (Figure 3.3.C), the total number of starch granules decreases even further. At this point, MDI would not disperse homogeneously throughout the starch granules, resulting in a system with unequal distribution of strengthened PLA-starch loci. Different regions of the composite would respond differently to mechanical stress. Then, the weaker regions would rupture earlier than the stronger ones, diminishing the overall mechanical performance of the composite.



Damping ( $\tan \delta$ ) is a measurement widely used in engineering for manufacturing products that will be exposed to noise or vibration (Sperling 2001). When the material presents high damping, its system is more capable of dissipating energy. The PLA/starch composite containing larger starch particle size showed higher damping (potato starch) (Figure 3.4). The capacity of the system to dissipate energy increased with increase of average particle size. This capacity decreased in composites with average particle size larger than 47  $\mu\text{m}$ , though. As described earlier, at 71  $\mu\text{m}$  the strengthened PLA-starch interaction points would not be as homogeneously dispersed as at 47  $\mu\text{m}$ . Then, internal stress and strain would be less uniformly distributed throughout the system, reducing its capacity of dissipating energy.

The Young's Modulus of a material indicates its stiffness (Sperling 2001), and the storage modulus measures the amount of stored energy during deformation (Cowie 1974). Results (Table 3.1) show that both properties are not significantly influenced by the starch particle size.

### ***Morphology***

Figure 3.5.A shows micrograph of composite containing the smallest average particle size (rice starch, APS = 6  $\mu\text{m}$ ). The right side of Figure 3.5.A (magnified by 1,000 times) shows the discontinuity (roughness) of the PLA matrix. As discussed above, rice starch in the composite possesses greater number of starch particles in the blend and the amount of MDI is not enough to disperse and react with all starch granules. The heterogeneous phases (PLA and starch) of the cross-sectional area and the voids created by the starch granules pulled out of the matrix during fracture process clearly indicate the poor interfacial interaction between PLA and starch, and consequently, the poor mechanical properties.

With increase in particle size, Figures 3.5.B-C (15 and 26  $\mu\text{m}$ , respectively), PLA matrix shows less discontinuity. The moderate roughness means larger number of regions with stronger interfacial interaction between PLA and starch particles, which reflects the better response of the composites to mechanical stress.

At an average particle size of 47  $\mu\text{m}$  (highest values of tensile strength), PLA matrix presented smoother and more continuous surface (Figure 3.5.D). At this point,

MDI was well dispersed within starch particles and strengthened PLA-starch interfacial interactions were more uniformly distributed through the composite. The presence of broken starch granule (white arrow) indicates that when load was applied to the specimen, PLA/starch interaction was so strong that the starch granule was broken apart.

The fractured surface of composite containing the largest average particle size (71  $\mu\text{m}$ ), Figure 3.5.E, showed signs of roughness. As described earlier, the less uniform distribution of strengthened PLA-starch interaction cause a less homogeneous distribution of internal stress and strain throughout the system, diminishing the overall mechanical performance of the composite. But, the composite still presented a more continuous matrix and properties than those with smaller average particle size (Figure 3.5.A-C).

### ***Thermal properties***

It has been reported that starch increases the crystallization rate of PLA in PLA/starch composites (Ke and Sun 2003a). The half-time crystallization ( $t_{1/2}$ , or the time needed to form 50% of the final crystallinity) decreased slightly with increase of starch content, resulting in a slight increase of the crystallization rate of PLA. The authors concluded that starch could be considered as a nucleating agent in PLA crystallization.

In this study, crystallinity in PLA/starch/MDI composites decreased as starch average particle size increased (Table 3.3). As explained earlier, at the same weigh basis, samples containing starch with smaller particle size had greater number of starch granules than samples containing starch with larger particle size. A greater number of starch particles results in a greater number of nuclei in the system. Hence, it was expected that composites made of starch with smaller particle size have higher crystallinity.

The shape and orientation of filler particles significantly affect the melt rheology of the filled thermoplastics (Khan 1987). Griffin (1990) demonstrated that wheat starch granules have advantages as filler in plastic films. The disk-shaped large wheat granules oriented with the long axis in the extruder direction, leading both small and large wheat granules to rapidly accommodate inside the film. Composites made with starch average particle size of 26  $\mu\text{m}$  (wheat starch) had a greater crystallinity than those made with 15  $\mu\text{m}$  (corn starch). The oriented disposition of wheat granules in the composite during

press-molding would facilitate the motion of PLA molecules in the matrix, increasing the crystallinity.

The smallest average particle size (6  $\mu\text{m}$ ) of rice starch resulted in the largest total surface area of all samples. The drastic raise in crystallinity of composites made with this starch would be caused by mechanical degradation of PLA chains during mixing. Mechanical shearing between PLA and tiny rice starch molecules might generate enough energy to break PLA chains into smaller fragments. The shorter length of PLA fragments would acquire more mobility into the system, increasing drastically the crystallization of the PLA.

### ***Amylose content, starch damage, and commodity effects***

Amylose and damage starch content do not seem to directly affect properties of PLA/starch/MDI composite made with not-sieved starches (Table 3.3). But, further studies may be conducted to determine possible synergetic effect. There was no significant difference in the amylose content of the different fractions of potato starch (Table 3.4). On the other hand, starch damage has a clear inverse relation to average particle size. But, starch damage does not seem to directly affect mechanical properties, since mechanical properties do not respond strictly to starch damage variation.

A slight relationship between average particle size and properties of the different fraction of potato starch was found (Table 3.4). The four distinct particle size distribution ranges of potato starch were very narrow and extremely close to one another. Tensile strength and elongation showed slight changes with variation of average particle size. Tensile strength and elongation were essentially constant from 19 to 39  $\mu\text{m}$ , dropping slightly from 53 to 63  $\mu\text{m}$  (Table 3.3). A drop in both properties was expected, since particle sizes were located between 47  $\mu\text{m}$  (best performance) and 71  $\mu\text{m}$  (decay of performance). The higher values of properties found with potato starch fractions (compared to those found in Table 1) reflect their narrower particle size range, which provides a more homogeneous particle size distribution. There was no significant difference in Young's modulus and a fairly constant storage modulus (Table 3.4). But, a well-defined effect of average particle size on crystallinity was detected. Moisture

content of specimens did not show any significant difference with increasing average particle size.

### **Conclusion**

Tensile strength, elongation, and damping of PLA/starch/MDI composite increase with increase of starch average particle size (from 6 to 47  $\mu\text{m}$ ). But, properties of the composites declined significantly when the starch particle size was 71  $\mu\text{m}$ . Young's and storage modules kept fairly constant with variation in starch average particle size.

Crystallinity of the composites decreased with increase of average particle size. The absorption of moisture of PLA/starch/MDI composite was not significantly affected by starch average particle size. The properties of the composites seemed to not be significantly affected by amylose content, starch damaged and commodity.

MDI might be a limiting factor in composites with small starch average particle size, and its use as a coupling agent altered the role of average particle size of the filler (starch) on properties of starch-filled composites (PLA/starch).

## Figures and Tables

**Table 3.1 Properties of PLA/starch/MDI composites with different starch average particle sizes (APS)**

Starch type	APS [ $\mu\text{m}$ ]	$\sigma$ [MPa]	$\varepsilon$ [%]	E [GPa]	E' [ $10^8\text{MPa}$ ]	Cryst. [%]	MC [%]
Rice	6.0	58.26 <sup>c</sup>	4.01 <sup>c</sup>	2.75 <sup>a</sup>	4.66 <sup>a,b</sup>	20.70 <sup>a</sup>	1.32 <sup>a</sup>
Corn	15.0	62.46 <sup>b</sup>	4.26 <sup>b,c</sup>	2.67 <sup>a,b</sup>	5.98 <sup>a</sup>	7.70 <sup>b,c</sup>	1.23 <sup>a</sup>
Wheat	26.0	63.38 <sup>b</sup>	4.52 <sup>b,c</sup>	2.59 <sup>b</sup>	5.73 <sup>a</sup>	9.55 <sup>b</sup>	1.04 <sup>a</sup>
Potato	47.0	69.65 <sup>a</sup>	5.18 <sup>a</sup>	2.64 <sup>b</sup>	3.22 <sup>b</sup>	6.64 <sup>b,c</sup>	1.34 <sup>a</sup>
Potato	71.0	65.57 <sup>b</sup>	4.73 <sup>a,b</sup>	2.63 <sup>b</sup>	5.38 <sup>a,b</sup>	3.74 <sup>b,c</sup>	1.40 <sup>a</sup>

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

Where: APS = average particle size;  $\sigma$  = tensile strength;  $\varepsilon$  = elongation; E = Young's Modulus; E' = storage modulus; Cryst. = crystallinity; and MC = moisture content.

**Table 3.2 Estimated average area, volume, and mass of single starch particles; and estimated number of particles and total surface area found in one-gram of starch sample**

Starch type	APS [ $\mu\text{m}$ ]	r [ $10^{-4}\text{cm}$ ]	Area [ $10^{-6}\text{cm}^2$ ]	Volume [ $10^{-10}\text{cm}^3$ ]	Mass [ $10^{-10}\text{g}$ ]	Particles in 1g of starch [ $10^6$ ]	TSA in 1g of starch [ $\text{cm}^2$ ]
Rice	6.0	3.0	1.1	1.1	1.7	3708.0	4078.8
Corn	15.0	7.5	7.1	17.7	26.5	377.2	2658.1
Wheat	26.0	13.0	21.2	92.0	138.1	72.4	1534.9
Potato	47.0	23.5	69.4	543.6	815.4	12.3	853.6
Potato	71.0	35.5	158.4	1874.0	2811.0	3.6	570.2

Where: APS = average particle size; r = ray of starch particle; TSA = total surface area.

**Table 3.3 Properties of PLA/starch/MDI composites made with not-sieved starches**

Starch type	APS [μm]	AC [%]	SD [1/UCD]	σ [MPa]	ε [%]	E [GPa]	E' [10 <sup>8</sup> MPa]	Cryst. [%]
Rice	6.0	19.13 <sup>c</sup>	0.25 <sup>b</sup>	55.07 <sup>c</sup>	3.61 <sup>c</sup>	2.66 <sup>a</sup>	3.51 <sup>a</sup>	20.08 <sup>a</sup>
Corn	14.9	23.03 <sup>b</sup>	0.23 <sup>c,b</sup>	62.03 <sup>b</sup>	4.23 <sup>b,c</sup>	2.65 <sup>a</sup>	5.39 <sup>a</sup>	10.02 <sup>b,c</sup>
Wheat	20.0	28.28 <sup>a</sup>	0.31 <sup>a</sup>	63.85 <sup>a,b</sup>	4.54 <sup>a,b</sup>	2.65 <sup>a</sup>	6.45 <sup>a</sup>	12.62 <sup>b</sup>
Potato	48.8	17.63 <sup>d</sup>	0.29 <sup>c</sup>	67.40 <sup>a</sup>	4.99 <sup>a</sup>	2.53 <sup>a</sup>	6.02 <sup>a</sup>	7.19 <sup>c</sup>

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

Where: APS = average particle size; AC= amylose content; SD= starch damage; σ = tensile strength; ε = elongation; E = Young's Modulus; E' = storage modulus; Cryst. = crystallinity; and MC = moisture content.

**Table 3.4 Properties of PLA/starch/MDI composites made with potato starch with different average particle sizes (APS)**

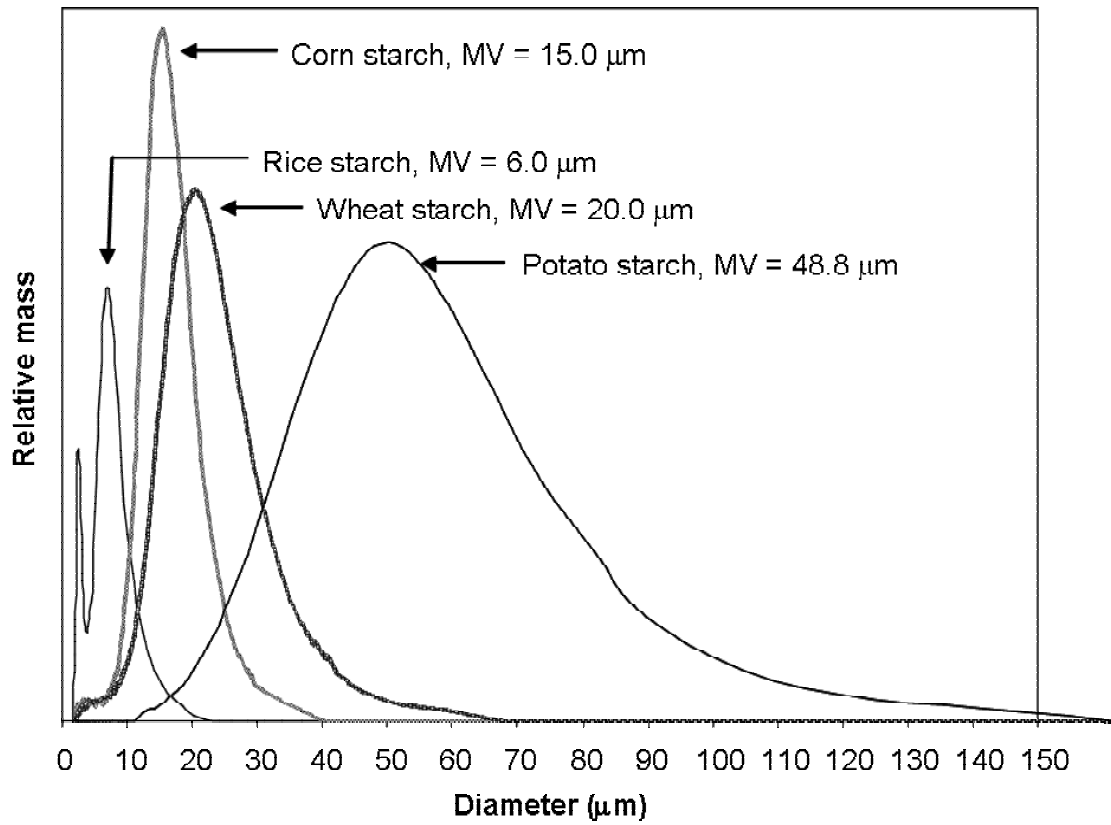
Starch type	APS [μm]	AC [%]	SD [1/UCD]	σ [MPa]	ε [%]	E [GPa]	E' [10 <sup>8</sup> MPa]	Cryst. [%]	MC [%]
Potato	19.0	16.86 <sup>a</sup>	0.46 <sup>a</sup>	69.28 <sup>a</sup>	5.82 <sup>a</sup>	2.67 <sup>a</sup>	5.37 <sup>a,b</sup>	8.04 <sup>a</sup>	1.67 <sup>a</sup>
Potato	39.0	17.72 <sup>a</sup>	0.32 <sup>c</sup>	68.77 <sup>a</sup>	5.23 <sup>a,b</sup>	2.64 <sup>a</sup>	5.84 <sup>a</sup>	3.92 <sup>b</sup>	2.47 <sup>a</sup>
Potato	53.0	19.81 <sup>a</sup>	0.21 <sup>b</sup>	66.80 <sup>a,b</sup>	5.09 <sup>b</sup>	2.64 <sup>a</sup>	4.74 <sup>a,b</sup>	2.61 <sup>c</sup>	2.59 <sup>a</sup>
Potato	63.0	19.71 <sup>a</sup>	0.15 <sup>a</sup>	65.30 <sup>b</sup>	5.00 <sup>b</sup>	2.74 <sup>a</sup>	3.98 <sup>b</sup>	0.47 <sup>d</sup>	1.45 <sup>a</sup>

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

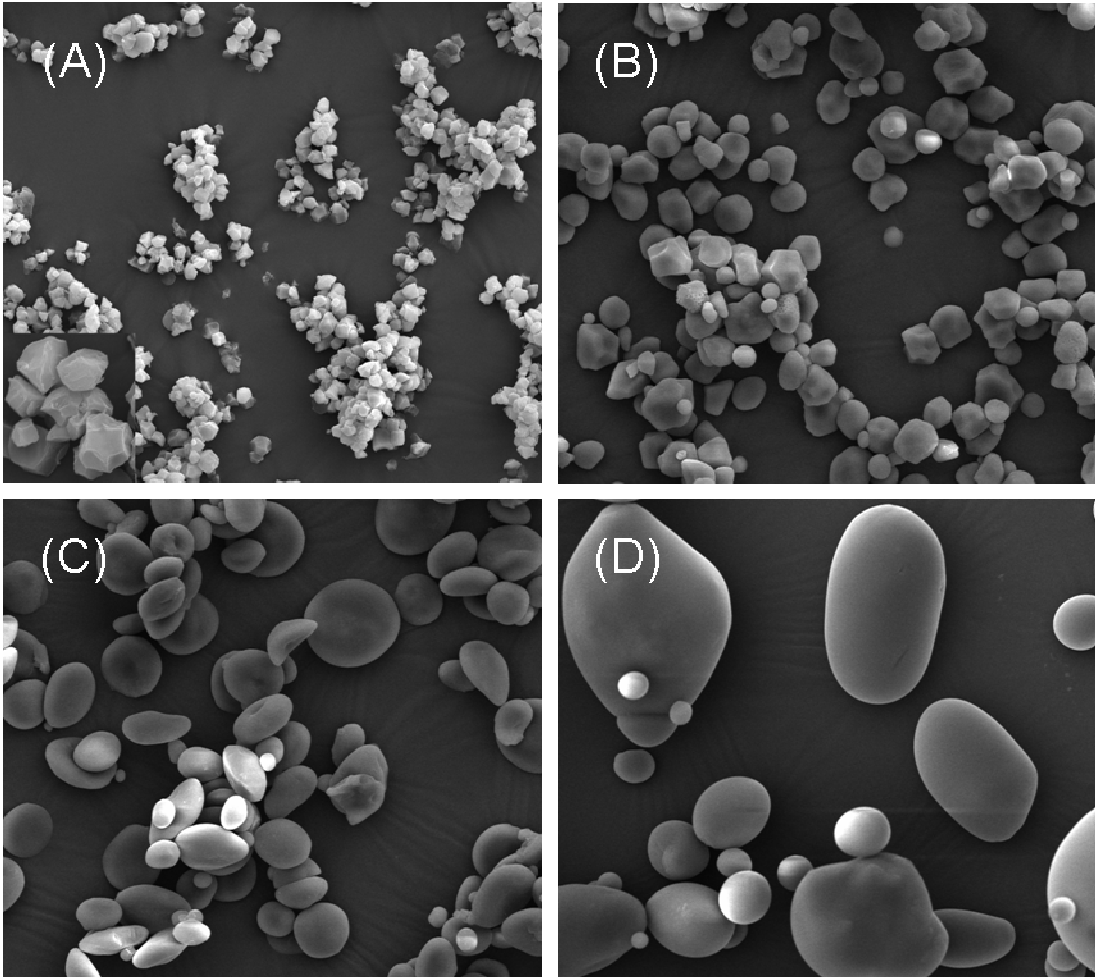
Where: APS = average particle size; AC= amylose content; SD= starch damage; σ = tensile strength; ε = elongation; E = Young's Modulus; E' = storage modulus; Cryst. = crystallinity; and MC = moisture content.



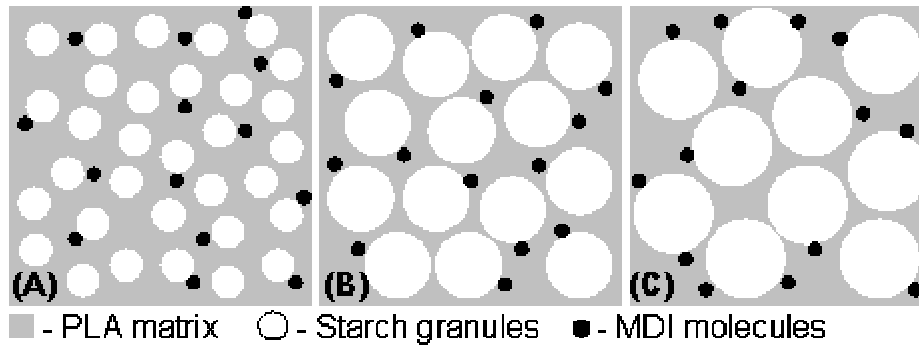
**Figure 3.1: Particle size distribution curve and respective average particle size of rice, corn, wheat, and potato starches**



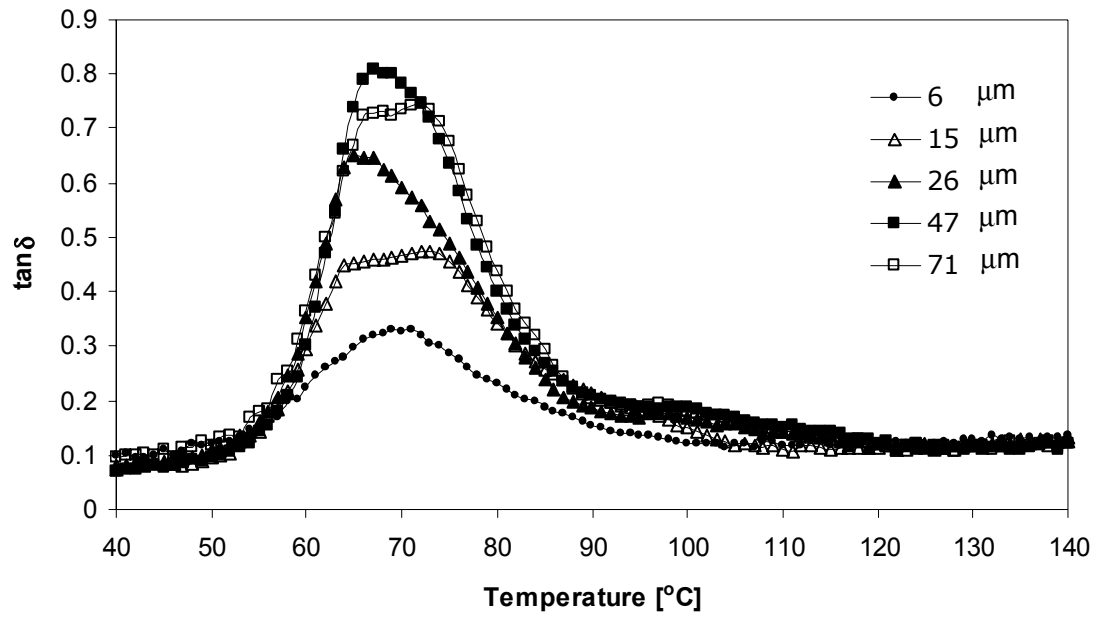
**Figure 3.2: SEM micrograph of: (A) rice starch; (B) corn starch; (C) wheat starch; and (D) potato starch**



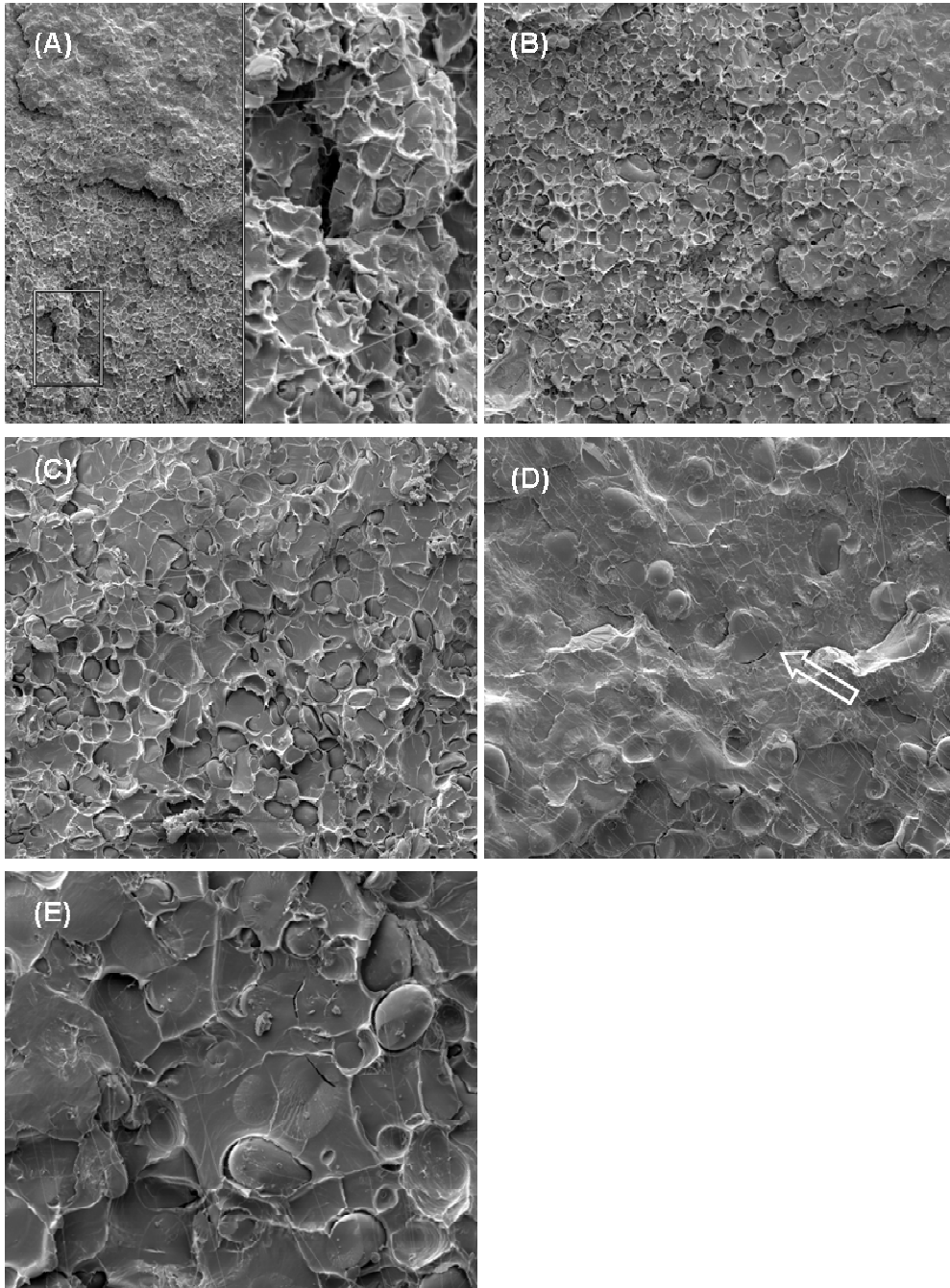
**Figure 3.3: Scheme of PLA/starch/MDI system with: (A) small starch particles; (B) medium starch particles; and (C) large starch particles**



**Figure 3.4: Damping ( $\tan \delta$ ) of PLA/starch/MDI composites of different starch particle sizes**



**Figure 3.5: SEM micrograph of tensile fractured surface of PLA/starch/MDI composite with starch average starch particle size of: (A) 6  $\mu\text{m}$ ; (B) 15  $\mu\text{m}$ ; (C) 26  $\mu\text{m}$ ; (D) 47  $\mu\text{m}$ ; and (E) 71  $\mu\text{m}$**



## **CHAPTER 4 - EFFECT OF OXIDATION OF THE PRIMARY ALCOHOL GROUP OF STARCH WITH TEMPO ON PROPERTIES OF PLA/STARCH COMPOSITES**

### **Abstract**

The effect of the oxidation of the primary alcohol group of starch on mechanical and thermal properties of poly(lactic acid)/starch composites is reported. The samples were extruded in a twin-screw extruder and compress-molded in a dog-bone shaped tensile bars (Type IV). Results showed that the oxidation of the primary alcohol group up to 10% degree of substitution did not significantly affect mechanical properties of PLA/starch blends with methylenediphenyl diisocyanate (MDI) as the coupling agent, but composites showed a tensile curve with a reduced inelastic deformation and significantly increased storage modulus and damping. Results suggest that the substitution of hydroxyl group on C6 of starch molecules for carboxyl group increased the strengthening effect of MDI enough to reduce inelastic deformation of the composites upon load, but not enough to enhance mechanical properties.

## **Introduction**

Poly(lactic acid) (PLA), a synthetic biopolymer derived from agricultural feedstock, is a promising substitute for some petroleum-based polymers due to its mechanical and biodegradable properties (Datta et al. 1995, Krochta and Mulder-Johnston 1996). But, the cost of PLA is still higher than that of petroleum plastics for disposable applications due to its complicated processing procedures. Starch, another biodegradable polymer that can be rapidly metabolized by a wide range of organisms (Nayak 1999), can be incorporated into PLA to reduce cost for raw material and accelerate biodegradability rate of the composites (Jacobsen and Fritz 1996).

The addition of starch as filler to PLA does not affect PLA thermal properties. But, as the starch content increased, the PLA matrix become less continuous, resulting in a reduced effective cross-section area and, consequently, decreasing its mechanical performance. Tensile strength and elongation of PLA/starch blend at a 55/45 weigh ratio decreases by about 42 and 55%, respectively, compared with pure PLA (Ke and Sun 2000). The use of a geometric model for tensile strength as a function of filler concentration for a particulate-filled two-phase polymer composite developed by Nicolais and Narkis (1971) indicates that some adhesion forces probably existed between PLA and starch phases. These forces may be caused by polar interaction between the two phases, and hydrogen bonding force between the carbonyl group in the PLA and the hydroxyl group in the starch (Ke and Sun 2000).

Several approaches have been tried to improve the performance of the starch in composites made with PLA and starch blends. An increase in the moisture content of the starch showed some effect on the structure of compression-molded PLA/starch composites. SEM micrographs of blends with low moisture content showed a typical starch-filling system where two heterogeneous phases, PLA and starch, were distinctly noticeable. As moisture content increased, the degree of gelatinized starch increased, and a more uniform structure could be seen. But, the increase in moisture content did not show any significant improvement in the mechanical properties (Ke and Sun 2001). An increase above 50% of the amylose content in PLA/starch composites showed an improvement of water resistance without affecting mechanical properties. PLA/starch

blends containing 50% of amylose showed slightly higher tensile strength, and blends containing 50 and 70% amylose corn starch had lower water absorption than those containing 0 and 28% amylose corn starch (Ke et al. 2003a).

MDI is highly reactive with both carboxyl and hydroxyl groups, forming a urethane linkage (Dieteroch et al. 1985). MDI seems to function as a coupling agent in PLA/starch blends, reacting with carboxyl and hydroxyl groups of PLA and hydroxyl groups of starch (Wang et al. 2002). A successful attempt to reduce the interfacial tension and to strengthen the interaction between PLA and starch molecules was achieved by the addition of 0.5% of methylenediphenyl diisocyanate (MDI) to PLA/starch blend (55:45 w/w), improving drastically the strength and elongation by about 85 and 70%, respectively, compared to PLA/starch blend without MDI (Wang et al. 2001).

Alternatively, the performance of starch in PLA/starch blends could be enhanced by oxidation of the primary alcohol group of starch molecules. The addition of carboxyl groups to the C6 of starch could improve the mechanical properties of PLA/starch composites by either strengthening the adhesion force between PLA and starch phases, or improving the coupling action of MDI by increasing the number of potential binding sites in the starch molecule.

From a vast list of common agents that oxidize starch such as sodium bromide (NaBr), gaseous chlorine, calcium hypochlorite, hydroperoxide, potassium permanganate, and ammonium persulfate, sodium hypochlorite (NaOCl) is the most frequently used oxidizer due to the higher proportion of hydrophilic carboxyl groups added to the oxidized starch (Wing 1994). A drawback is that all of these agents attack the secondary alcohol groups at C2, C3, and C4, and the primary alcohol group at C6 of the glucose units in a random fashion (Boruch 1985; Floor et al. 1989). The oxidation of the secondary alcohol group is followed by the hydrolysis of the glycosidic bonds, with opening and cleavage of the monomeric rings, resulting in loss of polymer properties and a decrease in the viscosity of the starch (Chang and Cho 1997). Besides, oxidation reactions using these agents are difficult to control and thus to reach a desired degree of oxidation (Suh et al. 2002).

De Nooy et al. (1994, 1995) presented a novel methodology using a stable organic nitroxyl radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), NaBr,



and NaOCl, which enabled the selective oxidation of the primary alcohol group in the presence of secondary alcohol groups. Sodium hypochlorite and NaBr were used as regenerating oxidants and water as the solvent (Suh et al. 2002). In a TEMPO-mediated oxidation, the primary alcohol group is oxidized to aldehydes, which is further oxidized to carboxylic acids, and the secondary alcohol group is oxidized to ketones (Anelli et al. 1987). TEMPO-mediated oxidation of the primary alcohol group of wheat starch showed a selectivity of >95%, a yield of 98%, and an oxidation yield of 95% (Chang and Robyt 1996).

The aim of this work was to strengthen the thermal-mechanical properties of PLA/starch composites by a TEMPO-mediated oxidation of the primary alcohol group of starch at different degrees of substitution.

## **Material and Methods**

### ***Materials***

A PLA resin, with molecular weight of 120,000 Da and derived mainly from L-lactic acid, was purchased from Shimadzu (Japan). Wheat starch with amylose content about 28% and average particle size of 20  $\mu\text{m}$  was purchased from Midwest Grain Products, Inc. (Atchinson, KS). 2,2,6,6-tetramethyl-1-piperidine oxoammonium salt/sodium (TEMPO) was purchased from Wako Chemicals (Japan). Methylenediphenyl diisocyanate (MDI, Rubinate 1840) in a dark brown liquid was obtained from ICI Polyurethanes (Geismar, LA). Sodium bromide, sodium hypochlorite solution (5%, w/v), and ethanol were laboratory grade and purchased from Fisher Scientific Co. (New Jersey, NJ) without further purification.

### ***Oxidation procedure***

Wheat starch (100 g) was suspended in 2,000 mL of water (5% starch solution), stirred, and held at a temperature below 4°C using an ice bath. One-gram of 2,2,6,6-tetramethyl-1-piperidine oxoammonium salt/sodium (TEMPO) and 32 g of sodium bromide were dissolved in 100 mL of water, stirred until TEMPO was completely dissolved, and then added to the starch solution. The pH of the starch solution was adjusted to 10.80 by adding 0.5 M of sodium hydroxide. A previously determined amount

of sodium hypochlorite solution (5% w/v) to oxidize the starch at 5%, 10%, and 30% degree of substitution was added to the solution by constant dripping (~2 drops/sec) using a burette, and the pH of the solution was maintained at 10.80 (using an Accumet AB 15 pH Meter, Fisher Scientific Co., U.S.A.) by addition of 0.5 M sodium hydroxide using a burette.

The volume of sodium hypochlorite necessary to reach the desired degree of substitution of the primary alcohol group of the starch was determined by: (A) the determination of the amount of sodium hypochlorite required to completely oxidize the primary alcohol group; which was continuously added to the starch solution until the total volume of sodium hydroxide required to maintain the pH at 10.80 reached a plateau level; and (B) the calculation of the amount of sodium hypochlorite required to oxidize the starch at 5%, 10%, and 30% degree of substitution based on the amount determined in (A).

NaOCl was slowly added to the solution to make sure that a selective reaction took place at the surface of the starch granule, which would preserve the integrity of the starch molecule against tearing the starch molecules off for deeper oxidation.

### ***Work-up of the oxidized starch***

The partially oxidized starch was precipitated by adding 2 volumes of ethanol and washing 5 times with water by centrifugation (20 minutes at 2,000 x g). The washed oxidized starch was continuously stirred in a 0.1N hypochloric acid solution (for 30 min, at 4°C) to exchange the Na<sup>+</sup> located at C6 of oxidized starch (as a result of the oxidation reaction) for the H<sup>+</sup> from the solution. Preliminary tests showed that exposure of the oxidized starch to 0.1N HCl solution for an amount of time either shorter or longer than 30 min produced composites with poorer mechanical properties than those exposed for 30 min. It was not determined if oxidized starch still had any remaining sodium ion at C6 after 30 min of ion exchange reaction. But, longer exposure to the acidic solution could lead to some depolymerization of the starch granules by acidic hydrolysis (Chung and Seib 1991, Manelius et al. 2000), resulting in loss of polymer properties. Finally, the oxidized starch was washed 3 times with water/ethanol (3:7 by volume) and one time with ethanol by centrifugation, and dried in a vacuum oven at 45°C for 24 hours.

### ***Inherent viscosity of oxidized starch***

The inherent viscosity of starch (control) and oxidized starches at 5, 10, and 30% degree of substitution was determined using the modified methodology described by Myers and Smith (1964). Dry starch oxidized at 0 (control), 5, 10, and 30% degree of substitution ( $0.3000 \pm 0.0002$  g) was dispersed in 100 mL of DMSO at 25°C. The starch was dissolved by continuously stirring the solution for 30 min at 30°C. The solution was gravity-filtered using a medium porosity fritted glass funnel; the filtrate was transferred into a Cannon-Ubbelohde capillary viscometer. The viscometer was placed in a temperature bath preheated at 30°C, it was allowed 15 min for the temperature of the solution in the viscometer to reach equilibrium, and the flow time was determined in three replicates. The inherent viscosity (dL/g) was calculated using the Equation 4.1.

$$\eta_{inh}^{30^\circ C}_{0.3\%} = \frac{\ln t/t_0}{C} \quad (4.1)$$

where:  $\eta_{inh}^{30^\circ C}_{0.3\%}$  = inherent viscosity at 30°C and solution concentration of 0.3g/dL;  $t$  = average solution flow time, s;  $t_0$  = average solvent flow time, s; and  $C$  = solution concentration, dL/g.

### ***Sample preparation***

PLA resin was ground by a laboratory mill (Model 4 Laboratory Mill, Thomas-Wiley Company, Philadelphia, PA) with a 2-mm screen. Ground PLA and starch (used for control sample) were dried to about 5% wt moisture content, according to AACC method 44-15A, in a convection oven at 130°C for 2 hours before sample preparation. Samples were blended in a planetary blender following formulation described in Table 4.2, and passed through a co-rotating conical, twin-screw extruder (TM-100, Haake, Paramus, NJ) at 125/185/185°C barrel temperature and 200 rpm. After extrusion, all samples were ground using the same laboratory mill described above, and compression-molded into a testing specimen type IV, following ASTM method D-638-91, using a hot press (Model 3890, Auto “M”, Carver Inc., Wabash, IN) at 176°C and molding pressure of 4.2 MPa for about 15 minutes. The molded specimens were cooled at room temperature to 57°C before removal from the mold and stored in environmental chamber at 50% relative humidity (RH) and 25°C for 48 hours before analysis.

### ***Mechanical properties***

Tensile strength ( $\sigma$ ), elongation ( $\epsilon$ ), and Young's modulus (E) of samples were determined, using five replicates, by Instron testing system (Model 4465, Canton, MA), following ASTM method D638-91 with a crosshead speed of 5-mm/min and 25-mm gauge length. The dynamic mechanical characteristics of samples were determined by DMA (Perkin-Elmer Pyris 7, Norwalk, CT) in a three-point bending mode. Sample dimensions were 10x4x2-mm. Sample was scanned from 20 to 160°C at a rate of 3°C/min and 1Hz under nitrogen purge. The storage modulus ( $E'$ ) at 25°C and damping ( $\tan \delta$ ) were determined. Five replications were made.

### ***Thermal properties***

The thermal transition of the specimens was determined, with five replicates, by DSC (Perkin-Elmer DSC Pyris 1, Norwalk, CT). The calibration of the instrument was set by using indium as a standard material. About 8 mg ( $\pm 2$  mg) collected from the specimens was weighed into an aluminum DSC pan, and the thermal behavior was recorded by heating the sample from  $-20$  to  $200^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , under a nitrogen purge. A rough estimation of crystallinity (in percentage) of the samples for each specimen was calculated by using the formula in Equation 4.2 (Fisher 1973):

$$\text{Crystallinity} [\%] = \left[ \left( \frac{\Delta H_m - \Delta H_c}{X} \right) / \Delta H_m^0 \right] \times 100 \quad (4.2)$$

where the heat of crystallization ( $\Delta H_c$ ) and heat of fusion ( $\Delta H_m$ ) were determined by integrating the area under the DSC curve around the temperature of crystallization ( $T_c$ ), and the temperature of melt ( $T_m$ ), respectively. The variable  $\Delta H_m^0$  is a value supposing that 100% of the sample is in a crystalline form. For PLA,  $\Delta H_m^0$  is equal to 93.6 J/g (Fisher 1973). For this study, the variable X is equal to 0.55; which corresponds to the fraction of PLA in the blend.

### ***Morphology***

The microstructure of fractured specimens was observed using a Hitachi S-35000N scanning electron microscopy (SEM) (Hitachi Science Systems, Ltd., Ibaraki, Japan) at an accelerated voltage of 20KV. The samples were mounted on an aluminum

stub and its fractured surface was coated with gold/palladium (60:40 %) mixture with a sputter coater (Desk II Sputter/Etch Unit, NJ). The micrograph of fractured specimens had standardized magnification of 200 times.

### ***Water absorption***

The percentage of moisture content in specimens was determined using the broken samples from the mechanical analysis. The specimens, in three replicates, were dried at 130°C for 72 hours in a conventional oven and their moisture content was determined by difference of weigh (in percentage).

For the water absorption test, broken specimens (30x15x4-mm) from tensile testing were dried at 50°C for 24 hours, cooled to room temperature, weighed, and immersed in distilled water at 25°C for specific intervals of time. Specimens were removed from water, blotted with tissue paper to remove the excess water, and weighed. The water absorption was determined by the average of three replicates per treatment and expressed as percentage on dried basis.

## **Results and Discussions**

### ***Inherent viscosity of oxidized starch***

Inherent viscosity significantly decreases with increase in the level of oxidation of starch (Table 4.1), indicating that some depolymerization of the starch granules has occurred. Suh et al. (2002) showed that the selectivity of oxidation of the primary alcohol group in a TEMPO-mediated oxidation was affected by change in temperature. The temperature of the solution during the oxidation of the starch at 5 and 10% degree of substitution were easily maintained below 4°C due to the smaller volume of NaOCl and NaOH solutions (kept at room temperature) required throughout the reaction. The temperature of the solution to oxidize the starch at 30% degree of substitution fluctuated between 4 and 6°C due to the larger volume of the added chemicals throughout the reaction. The rise in temperature could have reduced the selectivity of the oxidizing agent, causing some cleavage of the monomeric ring of the glucose unit and consequently decreasing its viscosity (Suh and el 2002). Some oxidation must have occurred inside the starch granules. Wheat starch granules present an average pore diameter of  $57.0 \times 10^{-10}$  m

(Fortuna et al. 2000); which are wide enough to allow the penetration of the small-molecular-weight molecules involved in the oxidation reaction. In addition to that, all samples must have suffered some depolymerization by acidic hydrolysis during ion exchange reaction (Chung and Seib 1991, Manelius et al. 2000).

### ***Mechanical properties***

The mechanical properties of all blends are summarized in Table 4.3. Results showed that, in the absence of MDI as a coupling agent (samples 1 thru 4), an increase to 10% degree of substitution of the hydroxyl group in C6 for carboxyl did not show any significant effect on tensile strength, elongation, and Young's Modulus of the composites. A significant decay of mechanical properties was observed at a degree of substitution of 30% (sample 4). The decay could be caused by an extensive hydrolysis of the glycosidic bonds of the starch granules, decreasing its polymer properties, and consequently the mechanical performance of the composite.

Under mechanical stress (load), a material goes through deformation of its shape and size. The deformation is characterized as elastic if the material returns to its original form upon removal of the mechanical force. On the other hand, if the stress (load) applied exceeds the capacity of the material to respond elastically to the deformation (elastic limit), the material undergoes inelastic deformation and its structure will be permanently deformed (Haward 1973, Vincent 1974). Figure 4.1.A shows that samples containing added carboxyl groups to C6 up to 10% had similar tensile curves, with the samples being elastically stretched (elastic deformation) until the point of rupture; while sample 4 (30% degree of substitution) was weaker and showed a small inelastic deformation (leveling of the curve) before the point of rupture.

In the presence of MDI (samples 5 thru 8), the composites did not show any significant difference of mechanical properties up to a degree of substitution of 10% (Table 4.2). But, samples 5 thru 7 showed distinct tensile curves (Figure 4.1.B). All three samples were similarly elastically stretched (elastic deformation). But, sample 5 (control) showed a longer inelastic deformation than samples 6 and 7; which characterized a longer permanent deformation (inelastic deformation) of the molecular structure prior to rupture. The shorter inelastic deformation of samples 6 and 7 (5 and 10% degree of substitution,

respectively) could be an indication that there were more available binding sites on the starch granules to react with MDI, increasing the capacity of the composites to elastically respond to stress (load). It would not be enough to significantly improve the mechanical performance, but enough to maintain its molecular structure upon stress, minimizing its inelastic deformation prior to rupture. Once again, composites made with starch at 30% degree of substitution (sample 8) showed a significant decay of mechanical properties.

Storage modulus measures the amount of stored energy during deformation (Cowie 1974); while damping ( $\tan \delta$ ) measures the capacity of the material to dissipate energy (Sperling 2001). In the absence of MDI (samples 1 thru 4), storage modulus at 25°C (Table 4.2) and damping (Figure 4.2.A) did not change with increase of degree of substitution up to 10% (Table 4.2). But, in the presence of MDI (samples 5 thru 8), a significant increase of storage modulus at 25°C was observed at a degree of substitution of 5% (Table 4.2), and damping increased with increase of degree of substitution (Figure 4.2.B). An increase of storage modulus and damping suggest that composites made with starch oxidized at 5 and 10% degree of oxidation (samples 6 and 7, respectively) had more capacity to elastically respond to the energy input (stress) than the control (sample 5).

At a weigh ratio of PLA/starch/MDI of 75:25:0.5; samples 9 (control) and 10 (oxidized starch at 5% degree of oxidation) did not show any significant difference in tensile strength, elongation, and Young's Modulus (Table 4.2). Tensile curve of sample 10 did not show the inelastic deformation observed in sample 9 (Figure 4.3.A). But, samples 9 and 10 did not show any significant difference of storage modulus (Table 4.2) and no clear difference of damping (Figure 4.4.A).

Oxidized starch at 5% degree of substitution was added to PLA/starch blends at different concentrations of 0 (control), 1, 2.5, and 5% over the total weight (samples 11 thru 14; respectively) to determine if oxidized starch would have any coupling effect between starch and PLA molecules. Results from Table 4.2 showed that the addition of oxidized starch into PLA/starch blends did not improve mechanical properties. Tensile strength had a significant decrease in composites with 2.5 and 5% of oxidized starch. No significant difference was observed on tensile curves (Figure 4.3.B) and storage modulus

(Table 4.2), and decay on damping was detected with the addition of oxidized starch (Figure 4.4.B).

### ***Thermal properties***

Starch increases the crystallization rate of PLA in PLA/starch composites by decreasing the half-time crystallization ( $t_{1/2}$ , or the time needed to form 50% of the final crystallinity), resulting in a slight increase of the crystallization rate of PLA. Then, starch can be considered as a nucleating agent in PLA crystallization (Ke and Sun 2003b).

In the absence of MDI (samples 1 thru 4), the crystallinity did not show any significant increase with increase of degree of substitution of oxidized starch up to 10%. But, a significant increase could be noticed in a sample containing oxidized starch at 30% degree of oxidation. The drastic decay in inherent viscosity of oxidized starch at 30% degree of substitution (Table 4.1) suggests that the sample suffered an extensive hydrolysis of the glycosidic bonds during the process of oxidation; which would result in a weakened internal molecular structure. The internal damage of the structure would facilitate some mechanical degradation by shearing between molecules during extrusion. Such friction could generate enough energy to break the weakened starch granules into smaller particles. Then, composites containing oxidized starch at 30% degree of substitution would have a larger number of nuclei in the system, resulting in composites with higher crystallinity. Even though some hydrolysis and mechanical degradation have probably occurred with oxidized starches at 5 and 10% degree of substitution, the extent of the damage was not enough to significantly increase crystallinity. Samples containing MDI (samples 5 thru 10) showed similar behavior. Only sample 8 (30% degree of substitution) showed a significantly higher crystallinity, which could be explained by the same reasons cited above. Samples containing oxidized starch as the coupling agent (samples 11 thru 14) did not show any significant difference in crystallinity.

### ***Morphology***

Figure 4.5 shows the SEM micrograph of the tensile fractured surface of PLA/starch/MDI at a weight ratio of 55:45:0.5 (A thru D) and at a weight ratio of 75:25:0.5 (E and F). For the composites with non-oxidized starch (A and E), a typical micrograph could be observed, with most of the starch particles enclosed by the PLA



matrix, the fractures mainly taken place through the PLA matrix and some eventual fractures taken place through the starch granule (indicated by the white arrow).

A similar surface structure could be observed as starch was oxidized at 5% degree of substitution (B and F), with a few split starch granules showing irregular internal ruptures (indicated by the white arrow and amplified in detail). The internal rupture could be caused by either: (i) an increase of internal stress due to a stronger interfacial interaction between starch surface and PLA; (ii) a result of a weakened internal starch structure due to the breakage of the glycosidic bond in the starch during oxidation; or (iii) a combined effect of both. A larger number of starch granules presenting greater internal ruptures were observed as starch was oxidized at 10% degree of oxidation (C).

As oxidation of starch increased up to 30% degree of substitution (D), a drastically increased number of ruptured starch granules were exposed on the fractured surface. The ruptures suggest that the interfacial interaction between PLA and starch was intact, but the internal molecular structure of the starch granules were extensively damaged during oxidation, resulting in a granule with low tolerance to stress, and consequently in a composite with poor mechanical performance.

### ***Water absorption***

PLA is a hydrophobic polymer. On the other hand, starch is hydrophilic due to its abundance of hydroxyl groups (Shogren 1997) and it can absorb up to about 50% of its mass in water at 25°C (French 1984). Because of the hydrophilic characteristic of starch, the absorption of water into the composites is mainly attributed to the starch fraction (Wang et al. 2001, Ke and Sun 2001). The substitution of the hydroxyl group at the C6 for carboxyl group increases the solubility of the starch in water (Chang and Robyt 1996, Suh et al. 2002). Then, it was expected that the greater the degree of substitution, the greater the water absorption of the composites.

Samples 5, 6, and 7 (control, 5% and 10% degree of oxidation; respectively) did not show any significant difference in water absorption. Water absorption increased to a great extent during the first 15 days and leveled off to about 12% (Figure 4.6). On the other hand, in sample 8 (30% degree of substitution), water absorption sharply increased up to about 20% during the first 9 days. Then it dropped because some starch leached out

from the composite; which was visually detected as a white-cloudy material in the water. Wang et al (2002) reported the precipitation of starchy material leached out of PLA/starch composites soaked in water. No significant increase of solubility of the starch was achieved up to a 10% degree of substitution.

### **Conclusion**

The substitution of hydroxyl group at C6 for carboxyl group up to 10% did not show any significant effect on mechanical properties of PLA/starch/MDI composites. But, PLA/starch/MDI composites with starch oxidized up to 10% degree of substitution showed a reduced inelastic deformation (tensile curve) and significantly increased storage modulus and damping. Results suggest that the substitution of the hydroxyl group on C6 of starch molecules to carboxyl group increased the strengthening effect of MDI enough to reduce inelastic deformation of the composites upon load, but not enough to enhance mechanical properties.

The drastic decay in inherent viscosity of starches oxidized at 30% degree of substitution suggests that the poor mechanical properties of PLA/oxidized starch/MDI at 30% degree of substitution were caused by an extensive hydrolysis of the glycosidic bonds of the starch molecules during the oxidation procedure. The weakened molecular structure of the starch could have compromised the overall mechanical performance of the composites.

In the absence of MDI, the oxidation of starch did not show any improvement of the interfacial interaction between PLA and starch molecules. The addition of oxidized starch as the coupling agent to PLA/starch blends did not improve mechanical properties.

## Figures and Tables

**Table 4.1 Inherent viscosities of starch and oxidized starches at 5, 10, and 30% degree of substitution (DS) dissolved in dimethyl sulfoxide solution (DMSO).**

	Inherent viscosity in DMSO [dL/g]
Starch	4.88 <sup>a</sup>
Oxidized starch at 5% degree of substitution	4.21 <sup>b</sup>
Oxidized starch at 10% degree of substitution	4.02 <sup>c</sup>
Oxidized starch at 30% degree of substitution	2.47 <sup>d</sup>

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

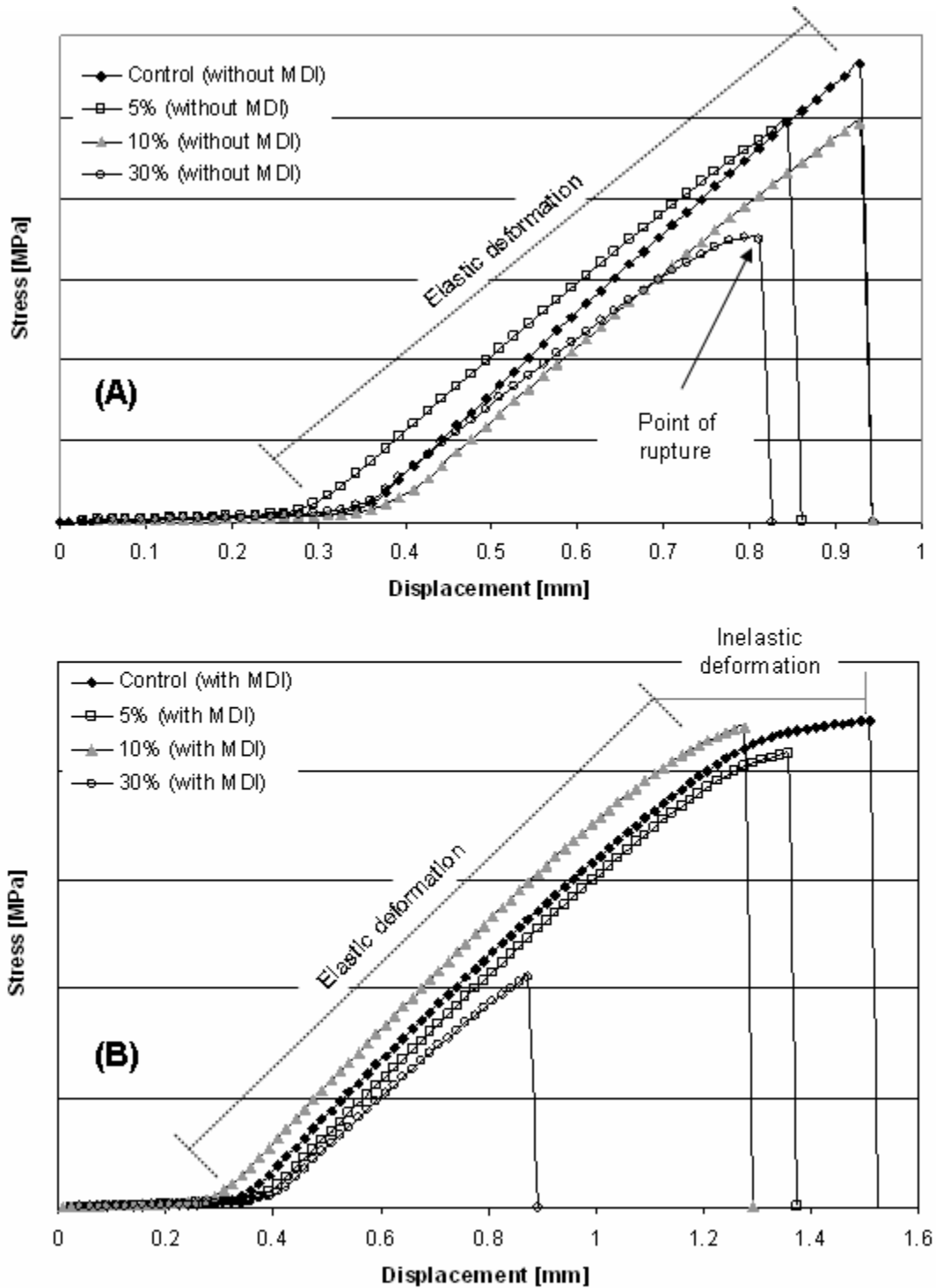
**Table 4.2 Blend composition and their respective mechanical properties and crystallinity**

Sample code	Blend composition (wt)	$\sigma$ [MPa]	$\varepsilon$ [%]	E [GPa]	$E'$ [ $10^8$ MPa]	Cryst. [%]
1	PLA/starch (55:45 wt) (control)	42.11 <sup>a</sup>	3.09 <sup>a</sup>	2.39 <sup>a</sup>	6.37 <sup>b</sup>	9.13 <sup>b</sup>
2	PLA/oxidized starch at 5% DS (55:45 wt)	40.68 <sup>a</sup>	2.94 <sup>ab</sup>	2.19 <sup>a</sup>	8.44 <sup>ab</sup>	9.58 <sup>b</sup>
3	PLA/oxidized starch at 10% DS (55:45 wt)	38.99 <sup>a</sup>	2.96 <sup>ab</sup>	2.26 <sup>a</sup>	7.34 <sup>ab</sup>	9.84 <sup>b</sup>
4	PLA/ oxidized starch at 30% DS (55:45 wt)	27.54 <sup>b</sup>	2.73 <sup>b</sup>	1.92 <sup>b</sup>	9.16 <sup>a</sup>	11.81 <sup>a</sup>
5	PLA/starch (55:45 wt) + 0.5% MDI (wt) (control)	62.67 <sup>a</sup>	4.22 <sup>a</sup>	2.38 <sup>a</sup>	6.56 <sup>b</sup>	10.22 <sup>b</sup>
6	PLA/modified starch at 5% DS (55:45 wt) + 0.5% MDI (wt)	60.83 <sup>a</sup>	4.34 <sup>a</sup>	2.31 <sup>b</sup>	8.73 <sup>a</sup>	9.63 <sup>b</sup>
7	PLA/modified starch at 10% DS (55:45 wt) + 0.5% MDI (wt)	61.66 <sup>a</sup>	4.20 <sup>a</sup>	2.43 <sup>ab</sup>	7.52 <sup>ab</sup>	10.21 <sup>b</sup>
8	PLA/modified starch at 30% DS (55:45 wt) + 0.5% MDI (wt)	29.70 <sup>b</sup>	2.92 <sup>b</sup>	2.09 <sup>c</sup>	6.60 <sup>b</sup>	11.95 <sup>a</sup>
9	PLA/starch (75:25 wt) + 0.5% MDI (wt) (control)	61.77 <sup>a</sup>	4.52 <sup>a</sup>	2.34 <sup>a</sup>	4.66 <sup>a</sup>	14.32 <sup>a</sup>
10	PLA/modified starch at 5% DS (75:25 wt) + 0.5% MDI (wt)	56.06 <sup>a</sup>	4.45 <sup>a</sup>	2.39 <sup>a</sup>	4.81 <sup>a</sup>	13.38 <sup>a</sup>
11	PLA/starch (55:45 wt) (control)	42.29 <sup>a</sup>	3.12 <sup>a</sup>	2.40 <sup>a</sup>	6.14 <sup>a</sup>	8.98 <sup>a</sup>
12	PLA/starch (55:45 wt) + 1.0% modified starch at 5% DS (wt)	39.05 <sup>ab</sup>	3.03 <sup>a</sup>	2.64 <sup>a</sup>	5.96 <sup>a</sup>	7.17 <sup>a</sup>
13	PLA/starch (55:45 wt) + 2.5% modified starch at 5% DS (wt)	37.55 <sup>b</sup>	3.21 <sup>a</sup>	2.58 <sup>a</sup>	4.80 <sup>a</sup>	7.28 <sup>a</sup>
14	PLA/starch (55:45 wt) + 5.0% modified starch at 5% DS (wt)	37.16 <sup>b</sup>	3.05 <sup>a</sup>	2.40 <sup>a</sup>	6.79 <sup>a</sup>	7.43 <sup>a</sup>

<sup>a</sup> Values in the same column followed by the same letter are not significantly different (P<0.05).

Where: DS = degree of substitution  $\sigma$  = tensile strength;  $\varepsilon$  = elongation; E = Young's Modulus;  $E'$  = storage modulus; and Cryst. = crystallinity.

Figure 4.1 Tensile curve of: (A) PLA/starch (control), and PLA/oxidized starch at different degrees of substitution (5, 10, and 30% DS); and (B) PLA/starch/MDI (control), and PLA/oxidized starch/MDI at different degrees of substitution (5, 10, and 30% DS).



**Figure 4.2** The  $\tan \delta$  (damping) as function of temperature at 1 Hz for: (A) PLA/starch (control), and PLA/oxidized starch at different degrees of substitution (5, 10, and 30% DS); and (B) PLA/starch/MDI (control), and PLA/oxidized starch/MDI at different degrees of substitution (5, 10, and 30% DS).

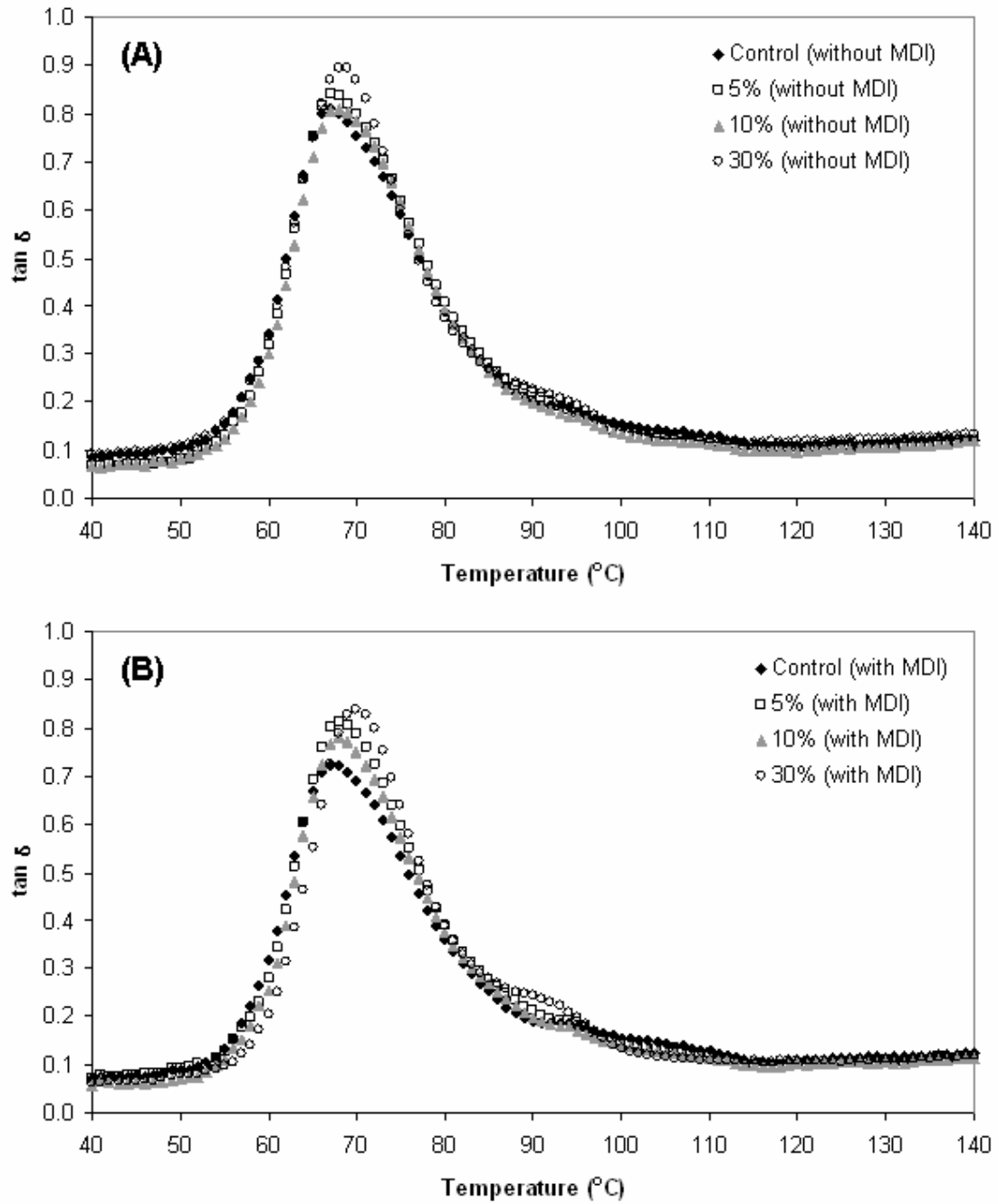
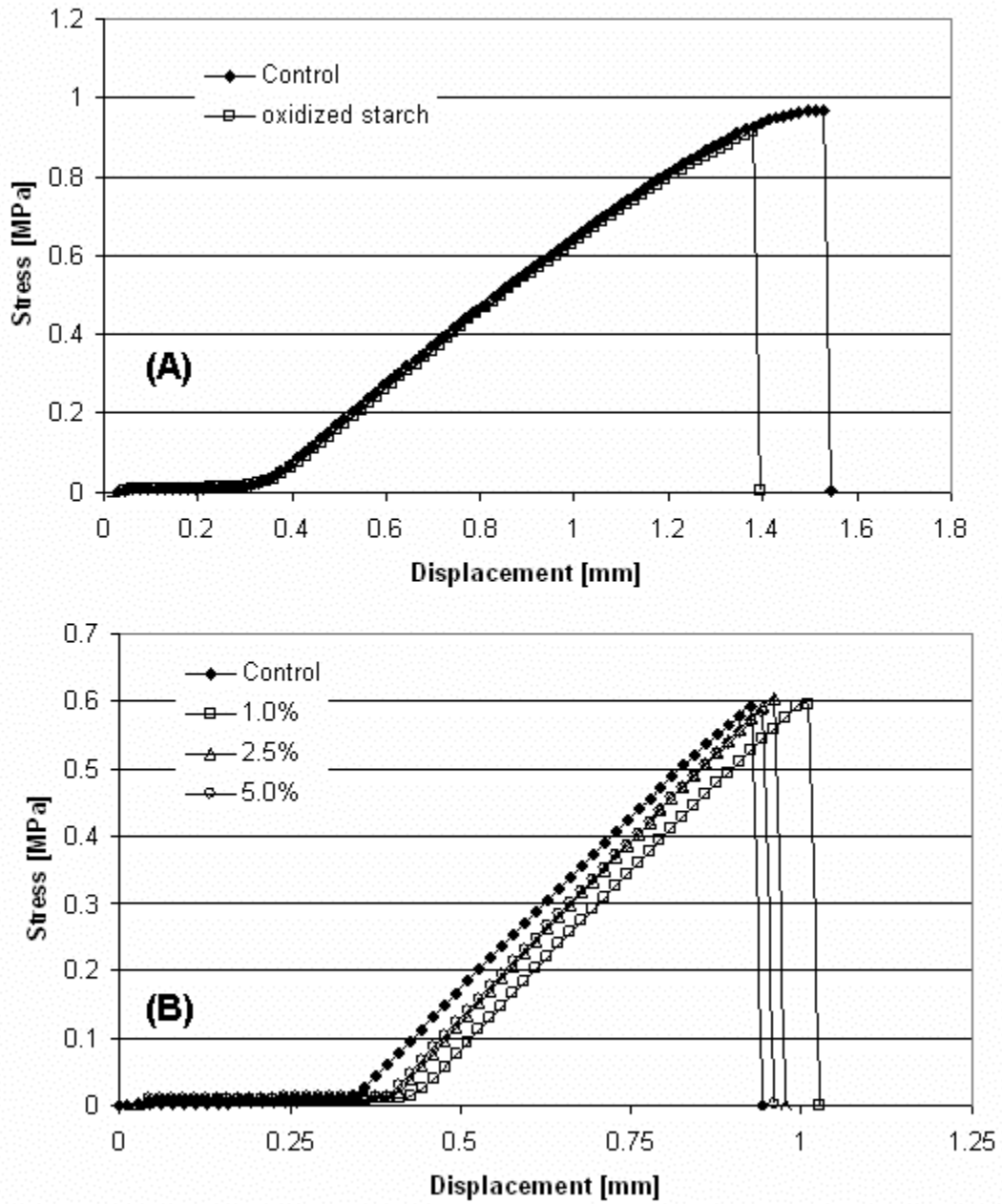
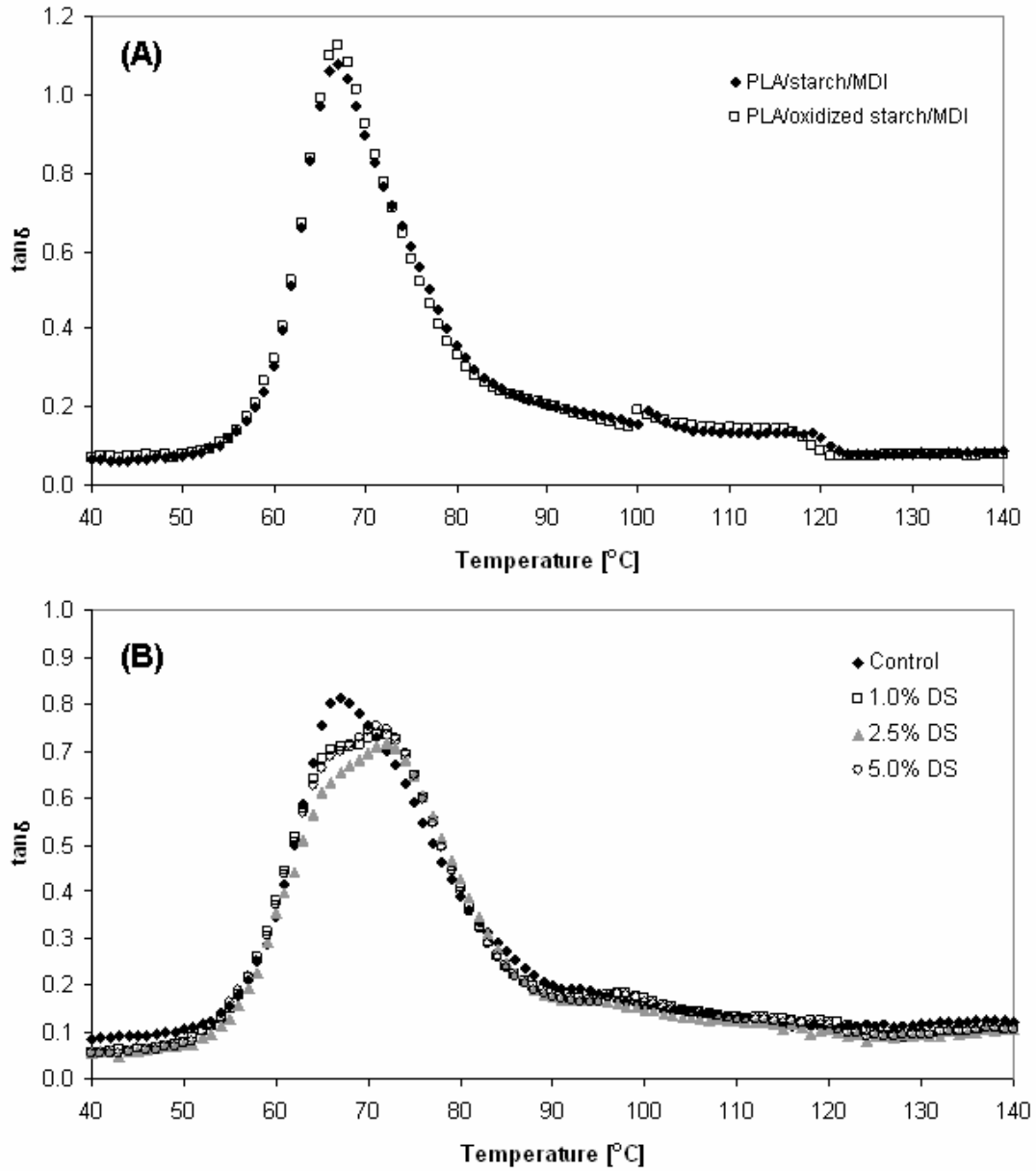


Figure 4.3 Tensile curve of: (A) PLA/starch/MDI (75:25:0.5 wt), and PLA/oxidized starch/MDI (75:25:0.5 wt); and (B) PLA/starch (55:45 wt) with added oxidized starch at 0, 1.0, 2.5, and 5.0% over the total weigh.

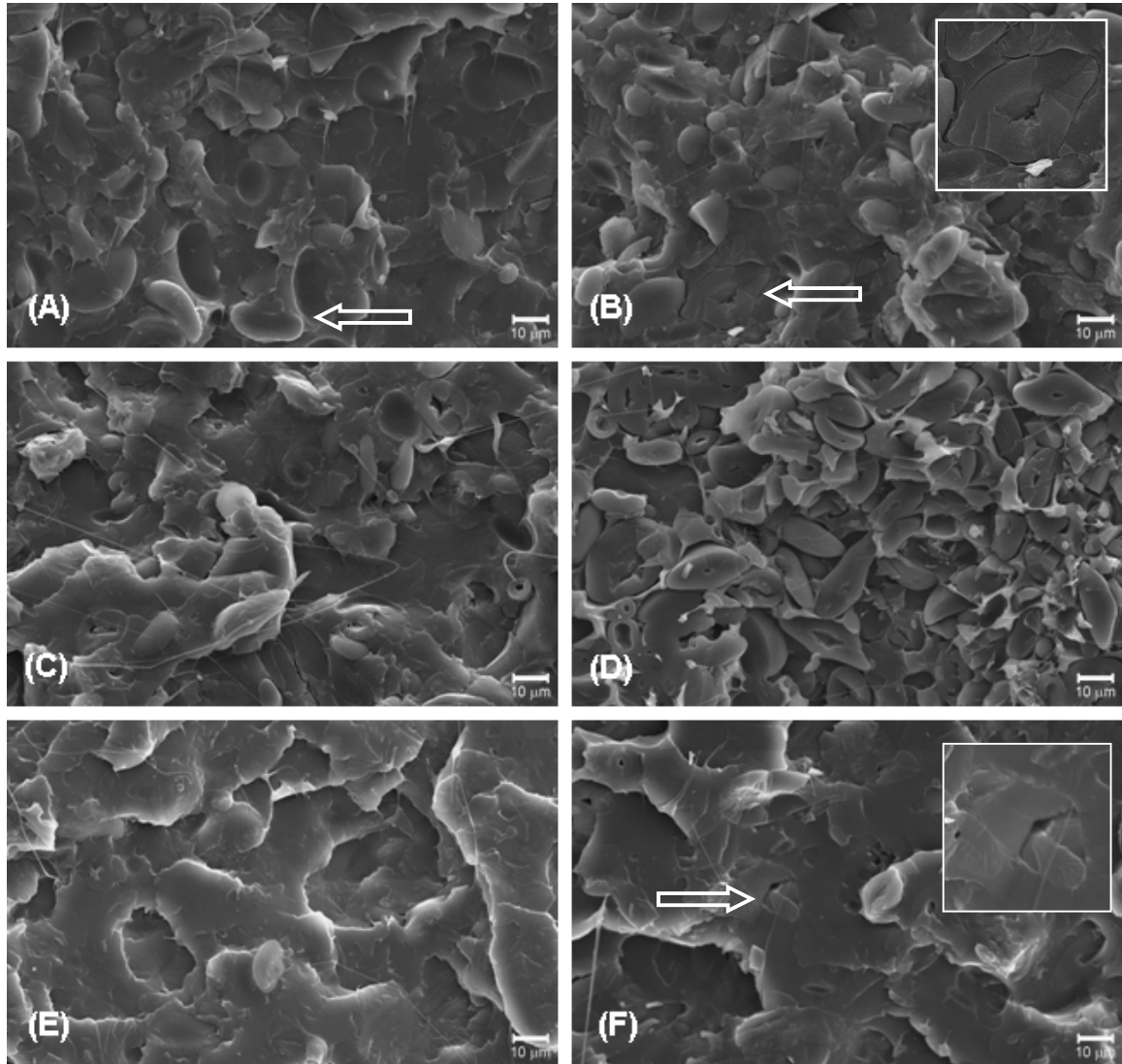


**Figure 4.4** The  $\tan \delta$  (damping) as function of temperature at 1 Hz for: (A) PLA/starch/MDI (75:25:0.5 wt), and PLA/oxidized starch/MDI (75:25:0.5 wt); and (B) PLA/starch (55:45 wt) with added oxidized starch at 0, 1.0, 2.5, and 5.0% over the total weigh.

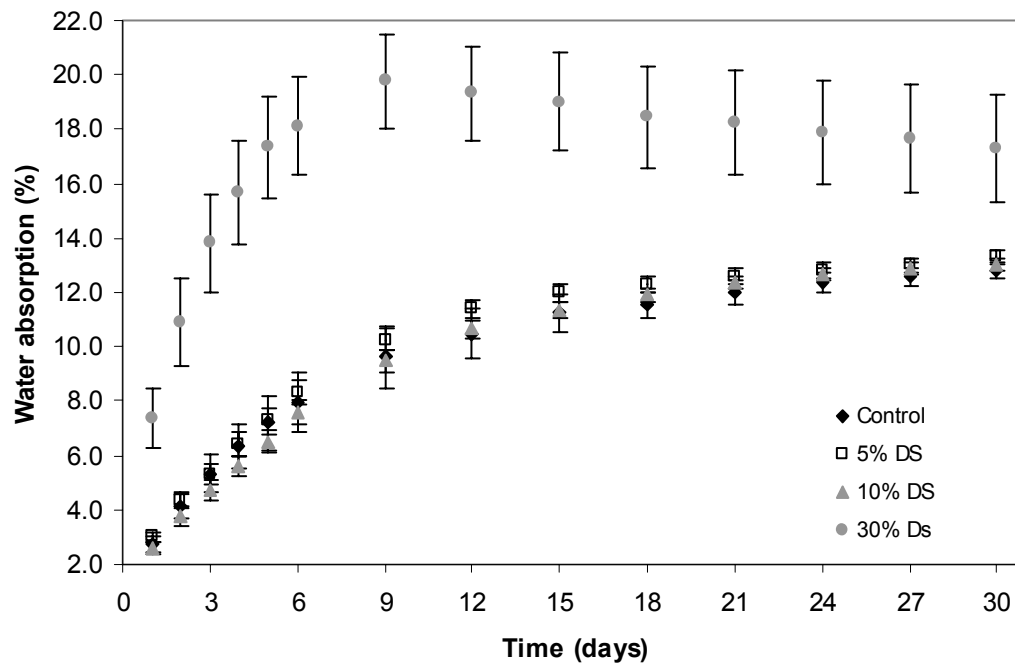




**Figure 4.5 SEM micrographs of: (A) PLA/starch/MDI (55:45:0.5 wt); PLA/oxidized starch/MDI (55:45:0.5 wt) at (B) 5% degree of substitution, (C) 10% degree of substitution, and (D) 30% degree of substitution; (E) PLA/starch/MDI (75:25:0.5 wt); and (F) PLA/oxidized starch/MDI (75:25:0.5 wt) at 5% degree of oxidation.**



**Figure 4.6 Water absorption vs. time for PLA/starch/MDI (control), and PLA/oxidized starch/MDI at different degrees of substitution (5, 10, and 30% DS).**



## CHAPTER 5 - Summary and Further Research

### Summary

PLA/starch composite with MDI showed higher thermal endurance than that without MDI, having long thermal endurance for temperature range between 50 and 100°C. Relative humidity played an important role on physical aging. Results show that PLA and PLA/starch composites suffered significant decay of their thermal-mechanical properties when stored at fluctuating relative humidity due to absorption and desorption of water. Such degradation can be minimized by storing the samples in plastic bags, which work as a water barrier, protecting the samples from drastic variations of relative humidity levels during storage.

Tensile strength, elongation, and damping of PLA/starch/MDI composite increase with increase of starch average particle size (from 6 to 47  $\mu\text{m}$ ). But, properties of the composites declined significantly when the starch particle size was 71 $\mu\text{m}$ . Crystallinity of the composites decreased with increase in average particle size. The absorption of moisture of PLA/starch/MDI composite was not significantly affected by starch average particle size. MDI might be a limiting factor in composites with small starch average particle size, and its use as a coupling agent altered the role of average particle size of the filler (starch) on properties of starch-filled composites.

The substitution of hydroxyl group at C6 for carboxyl group up to 10% did not show any significant effect on mechanical properties of PLA/starch/MDI composites. But, composites showed a reduced inelastic deformation (tensile curve) and significantly increased storage modulus and damping. Results suggest that the substitution of the hydroxyl group on C6 of starch molecules to carboxyl group increased the strengthening effect of MDI enough to reduce inelastic deformation of the composites upon load, but not enough to enhance mechanical properties. The poor mechanical properties of PLA/oxidized starch/MDI at 30% degree of substitution seemed to be caused by an extensive hydrolysis of the glycosidic bonds of the starch molecules during the oxidation

reaction; weakening molecular structure of the starch, and consequently compromising the overall mechanical performance of the composites.

### **Further research**

The effect of starch retrogradation and crystallization on thermal-mechanical properties of aged PLA/starch pellets (stored at constant and fluctuating relative humidity conditions) should be investigated. It has been shown that during aging, retrogradation and crystallization of both amylose and amylopectin occurs (van Soest 1996). The retrogradation of starch in starch-based plastics results in a product with inferior mechanical properties, affecting stiffness, strength and elongation (van Soest 1994).

The influence of the starch granule shape on thermal-mechanical properties and rheology of PLA/starch blends should be investigated. Khan and Prud'homme (1987) observed that shape and orientation of filler particles showed significant effects on the rheology of filled thermoplastics. Plastic films made with wheat starch (filler) would present some inherent advantages because of the fact that the disc-shaped large granules of wheat starch oriented with the long axis in the machine direction of the extruded film; which would allow both small and large wheat starch granules to readily accommodate inside a thin film (Griffin 1990).

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