12-2011

THE EFFECTS OF SOLVENT MIXTURE ON THE THERMAL AND MECHANICAL PROPERTIES OF SOLVENT CAST POLY-LACTIC ACID (PLA) FILM

Jeremy Hughes
Clemson University, jhughe3@clemson.edu

Follow this and additional works at: https://tigerprints.clemson.edu/all_theses

Part of the Engineering Science and Materials Commons

THE EFFECTS OF SOLVENT MIXTURE ON THE THERMAL AND MECHANICAL
PROPERTIES OF SOLVENT CAST POLY-LACTIC ACID (PLA) FILM

A Thesis
Presented to
The Graduate School of
Clemson University

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science
Packaging Science

By
Jeremy Duane Hughes
December 2011

Accepted by:
Ron L. Thomas, Committee Chair
Heather P. Batt
Scott W. Whiteside

DEDICATION

This thesis is dedicated to my family and professors who have helped inspire and encourage me for the past two years. This work not only represents me but you who have had such a large impact on my life. Thank you all.

ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF TABLES

List of Tables (Continued)

LIST OF FIGURES

List of Figures (Continued)

LIST OF SCHEMES

CHAPTER ONE

THE EFFECT OF SOLVENT MIXTURE ON THE PROPERTIES OF SOLVENT

CAST POLY-LACTIC ACID (PLA) FILM

ABSTRACT

The objective of this study was to investigate the effects of various solvents on the crystallinity and thermal expansion stability of PLA film. Three different PLA films were produced by the solvent casting technique; PLA in chloroform (PLA-C), PLA in methylene chloride (PLA-M), and PLA in methylene chloride: acetonitrile = 50: 50 (PLA-MA). The PLA-MA had higher % crystallinity, 46.15, than the PLA-C, 24.03, and the PLA-M, 14.25. With this increase in crystallinity, the PLA-MA had improved thermal expansion stability as shown by very low accumulated dimensional changes at 20-100 °C. Wide angle x-ray diffraction identified multiple crystalline structures for the PLA-MA. Film barrier properties were also measured. PLA-MA had the lowest oxygen permeability. However, there was no significant difference in water vapor permeability among the three PLA films. The mechanical property tests revealed that the PLA-C and PLA-M were ductile while the PLA-MA was brittle in behavior. The PLA-MA was very hazy as compared to the PLA-C and PLA-M. This work has shown that the PLA-MA had increased % crystallinity and, more importantly it had improved thermal expansion stability which can be very beneficial for the flexible packaging industry.

INTRODUCTION

Poly (lactic acid) (PLA) is a thermoplastic, compostable, and biocompatible polymer derived from renewable resources such as corn, sugar beets, potato starch, and cheese whey.[1] It has been used in the biomedical field for wound closures, prosthetic implants, bone surgery and controlled-release systems.[2] With the help of new technologies and large scale production, PLA is being used in other commodity areas such as packaging, textiles and composite materials.[3] Its application in the packaging industry, however, has certain limitations. A low deformation at break, high modulus, hydrophilic properties and low heat resistance has limited its application primarily to rigid thermoformed packaging.[4,5]

The solvent-casting technique is being widely used in biopolymer film preparation.[6] This technique involves solubilization, casting, and drying. PLA is known to be highly soluble in solvents such as methylene chloride, benzene, chloroform, and dioxane.[7,8] Each solvent influences film properties differently. For instance, chloroform induces a greater chain mobility of the polymer and dioxane causes a rough surface of the film due to its slow evaporation rate.[9,10] PLA has a low solubility in solvents such as toluene, acetone, acetonitrile, methanol, and ethyl acetate.[11] PLA films cast with toluene, acetone and ethyl acetate showed an increased hydrophobicity and a surface segregation.

Crystallinity of the film is affected by solvent induced conformational changes.[11]

Previous studies have reported that PLA solutions in chloroform and methylene chloride resulted in a random conformation of the molecules.[12] The crystallization of PLA was based on intramolecular interaction rather than intermolecular interactions.[7] Homocrystallization occurred when PLA was dissolved in chloroform due to the strong interaction between PLA and the solvent. However, stereocomplex crystallization occurred when PLA was dissolved in methanol due to the strong interaction between PLA chains.[11] In addition, there was swelling and conformational changes on the surface of the film when PLA dissolved in a poor solvent.[13] Treating PLA with a mixture of chloroform and methanol increased film crystallinity and caused hazy and milky white films.[7]

Based on previous research, it is evident that the solvent can change PLA film properties by changing its crystallinity. Few studies have been performed about the effect of solvent on the ductility and crystallinity of PLA. Also, no research has been reported about the effect of solvent on the thermal expansion stability of PLA correlated with its crystallinity. The main objective of this research was to produce PLA films with different solvents and solvent mixtures and to investigate the effect of solvents on the film properties such as film crystallinity, thermal expansion stability, and mechanical, barrier, optical and thermal properties.

MATERIALS AND METHODS

Materials

PLA resin (4032D, L-lactide/D-lactide=99/1) was donated from Nature Works, LLC (MN, USA). Polyethylene glycol 400 (PEG 400) was purchased from Sigma Aldrich (MO, USA). Chloroform was purchased from EM Science (NJ, USA). Acetonitrile was purchased from VWR International (PA, USA). Methylene chloride (DCM) was purchased from J. T. Baker (USA). All solvents used in this research were HPLC grade.

Film preparation

PLA films used in this study were prepared by the solvent-casting technique.[8] The PLA resin was preconditioned in drying oven at 40°C for 48 h to reduce the moisture content prior to use. PLA (30 g) and PEG 400 (3 g) were dissolved in 200 mL of solvent. In this study, PEG 400 was used as a plasticizer. The solution was stirred for 12 h at room temperature. The solvents and solvent mixtures used in this research were; (1) chloroform (2) methylene chloride and (3) methylene chloride: acetonitrile = 50: 50 (MA). Approximately 35 mL of the film forming solution was cast onto a BYTAC® (Norton Performance Plastics Corporation, Wayne, NJ, USA) coated 157 mm x 356 mm glass plate which was formed utilizing a customized film applicator. The cast films were

dried at room temperature and then peeled from the glass plate.

Wide angle X-ray diffraction (WAXD)

The X-ray diffraction studies were carried out using a Scintag XDS 2000 (Scintag Inc., Santa Clara, USA) with a germanium detector equipped with Scintag DMSNT Version 1.37 software. The samples were scanned from the start angle of 5 ° to the stop angle of 60 ° at step size 0.02 ° and preset time 0.5 s with a wavelength of 0.154 nm. Test was conducted at room temperature.

Thermal expansion stability

The dimensional change and the onset temperature of film were determined by a Thermomechanical Analyzer (TMA) as a function of temperature (2940, TA instruments). It represented for the thermal expansion stability of film in this study. The film samples for TMA were 0.159 cm wide and 1.27 cm long. The samples were clamped on both the ends with split aluminum balls and heated from 25 to 110 ^{o}C at the rate of 10 ^{o}C/min and 0.05 N forces with a constant nitrogen flow throughout.

Thermal properties

The glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) of the PLA films were measured using a Differential Scanning Calorimeter (Model 2920 Modulated DSC, TA instrument, USA). Specimens weighing 2 to 3 mg were heated at the rate of 10 ^{o}C/min from 0 to 200 ^{o}C with a constant nitrogen flow throughout. The percentage of crystallinity (X_c) of the PLA films was evaluated according to the following equation [14]:

$$X_c\ (\%) = (\Delta H_m - \Delta H_c)/ \Delta H^c_m \text{ x } 100$$

Where ΔH_m is the enthalpy of fusion, ΔH_c is the enthalpy of crystallization, and ΔH^c_m is the enthalpy of fusion of purely crystalline PLA (106 J/g). [14,15]

Gas barrier properties

The oxygen transmission rate (OTR) of the PLA films was measured according to ASTM standard method D 3985 using an OX-TRAN 2/20 (Mocon, Inc., Minneapolis, MN, USA). Samples were exposed to 50% relative humidity (RH) and tested at 23 $\pm$ 1 °C. Test films were conditioned in the testing cell for 10 h. Oxygen permeability (g·μm/m^2·day·Pa) was calculated by multiplying the oxygen transmission rate by the

film thickness. Tests were done in duplicate.

Water vapor transmission rate (WVTR) was measured according to ASTM F-1249 using a Permatran W 3/31 (Mocon, Inc., Minneapolis, MN, USA). Samples were exposed to 100% relative humidity (RH) and tested at 37 ± 1 °C. Test films were conditioned in the testing cell for 12 h. Water vapor permeability (g·µm/m^2·day·Pa) was calculated by multiplying the water vapor transmission rate by the film thickness. Tests were done in duplicate.

Mechanical properties

The tensile strength (TS), elongation at break (%E), and Young's modulus (ε) of the PLA films were measured using an Instron Universal Testing Machine (Model 4201, Instron Corp., Canton, MA, U.S.A.) according to the ASTM standard method D882-88. Specimen samples, 10 cm x 2.54 cm, were conditioned for 48 h at 23 ± 0.5^{o}C and 50% RH in a constant temperature and humidity chamber. Initial grip separation and cross-head speed were set at 5 cm and 25 cm/min, respectively. The values presented were the average of seven measurements.

Optical properties

Haze, lightness (L), redness (a), and yellowness (b) of films were measured using Hunterlab ColorQuest II Spectrophotometer (Hunter Associates Laboratory, Inc., Reston, VA, USA). The values presented were the average of three measurements.

Statistical analysis

Statistical significance was determined by the analysis of variance (ANOVA) using SAS (version 9.1, SAS Institute Inc., North Carolina, USA). Differences among mean values were processed by Duncan's multiple range tests. Significance was defined at a level of $p < 0.05$.

RESULTS AND DISCUSSION

Crystallinity

The X-ray diffraction profiles of the PLA films are shown in Figure 1. PLA-MA had various diffraction peaks at 17°, 19°, 22°, 28°, 32° and 35°, indicating the presence of different crystalline structures compared to PLA-C and PLA-M. PLA is much more soluble in methylene chloride than in acetonitrile. It has been reported that stereocomplex crystallization occurs when PLA is dissolved in poor solvents due to the strong interaction between PLA chains.[13] Thus, acetonitrile may have caused the production of different crystalline structures in the PLA-MA film. Comparing these results with the DSC results, PLA-MA had the highest % crystallinity, 46.15, and the highest enthalpy of fusion (ΔH_m), 48.92 J/g, which is the energy required for melting the crystals (Table 1). Casting PLA with a solvent mixture in which PLA solubility varies increased film crystallinity.[7]

PLA-C showed diffraction peaks at 17° and 19° whereas PLA-M had diffraction peaks only at 17°. PLA-C also had more % crystallinity, 24.03, than PLA-M, 14.25, due to the nature of solvent. Chloroform, which is the better solvent for PLA, interacts with the polymer chain thereby making solvent-polymer interaction stronger, leading to crystallization.[7] Crystallinty of cast films is also affected by the boiling point (bp) of the solvent.[16] Solvent with high bp takes more time to evaporate, thereby facilitating the

growth of crystals, while solvent with low bp limits the crystallization time.[17] Chloroform has a higher bp than methylene chloride and took more time to evaporate, thus leading to more crystalization in PLA-C.

PLA can crystallize in α, β, γ-forms and it depends on the processing conditions.[18-21] PLA also undergoes a conformational change in the stereocomplex formation from a 10_3 helices (α form, major 2θ: 17, 19, 22) for enantiomeric PLA chains to a 3_1 helices (β-form, major 2θ: 12, 25) in the stereocomplex.[22,23] In this research, PLA-M and PLA-C crystallized in α form and there was no conformational change from α to β-form by replacing solvent. However, the increase in peak height and width of diffraction in PLA-C suggests that chloroform might increase the crystal perfection of the polymer. In addition, PLA-MA exhibited stronger diffraction at 2θ angles of 17 and 32°. These dominant diffractions demonstrated that there were different crystalline structures in PLA-MA.

Thermal expansion stability

A key objective of this research was to increase the thermal expansion stability of PLA films prepared with various solvents. A Thermomechanical Analyzer (TMA) was used to investigate the thermal expansion stability of the PLA films by measuring the behavior of dimensional change of the film (Table 2 and Figure 2). The testing method

10

for the thermal expansion stability of PLA products has not been fully established. Our rational assumption about thermal expansion stability is that higher onset temperature and less dimensional changes represent better thermal expansion stability of the films.

The molecules in the amorphous region undergo segmental motion which leads to film expansion.[17] With the application of heat, films with high crystallinity have minimal expansion whereas films with low crystallinity or higher amorphousness have more film expansion. There was no onset temperature and less dimensional change in the PLA-MA. Therefore, the PLA-MA was the most heat stable among the three PLA films. This may due to the highest % crystallinity in the PLA-MA. The PLA-M had more dimensional changes, 340 to 548 μm, than the PLA-C, 197 to 272 μm, due to its lower % crystallinity or more amorphousness. Therefore, PLA-M was less heat stable than PLA-C.

Thermal properties

DSC thermograms of the three different PLA films are depicted in Figure 3. PLA-MA did not show T_c but showed T_g and T_m. It had the highest T_g, 58 ^{o}C, compared with the other PLA films. In other research, T_g was increased by increasing crystallinity.[24] T_g depends on the structural arrangement of the polymer and corresponds to the liquid-like motion of much longer segments of molecules during onset. This requires more free volume than the short range excursions of atoms in the glassy state.[25] PLA-MA had the

11

highest T_g thus it had less free volume space due to its dominant crystalline nature. PLA-C and PLA-M had lower T_g than PLA-MA because they had more amorphousness and free volume space. It was also observed that PLA-MA had a double melting peak at 158 and 165 ^{o}C, which may due to the presence of different crystalline structures in PLA-MA.

Barrier properties

The oxygen permeability (OP) of the PLA films is shown in Figure 4a. PLA-MA had significantly lower OP than PLA-M due to its higher % crystallinity. Polymers with higher crystallinity can lower sorption and increase the barrier for diffusion.[26] The amount of free volume size in a polymer plays a significant role in OP of the polymer as well.[27] There is a linear correlation between the OP and free volume size.[28] Amorphous regions in a film have large amount of free volume which facilitates the space for diffusion of oxygen.[17] Gas solubility also depends on the amorphous fraction in the film, and high amorphousness is directly proportional to the gas solubility. This is because the density in the amorphous region is lower than the crystalline region which increases oxygen absorption.[24]

There were no significant differences in water vapor permeability (WVP) among three PLA films (Figure 4b). Increasing % crystallinity did not improve the water vapor barrier property of PLA film. This may due to the poor water vapor barrier property of

hydrophilic PLA films in general.

Mechanical properties

      Increased crystallinity is a positive with regards to barrier properties but adds rigidity and brittleness, thus diminishing mechanical ability.[29] In this research, there were significant differences in mechanical property between PLA-MA and the other two films. PLA-MA showed the lowest tensile strength (TS), % elongation (%E), and Young's modulus (E) (Table 3). In addition, stress-strain curves determined that PLA-MA was brittle (figure not shown) while the other two films were ductile. Previous studies have shown that spherulite size increased with an increase in crystallinity and this increased spherulite size induced film brittleness.[30] In addition, E was decreased by increasing % crystallinity in this research. PLA-M had lowest % crystallinity and the highest E while PLA-MA had highest % crystallinity and the lowest E. It has been noted that fracture toughness of semi-crystalline polymers can decrease with an increase in spherulite growth due to brittleness.[30]

Optical properties

Color and haze of the three different PLA films are shown in Table 4. There were significant differences in color and haze among the films. PLA-MA had a hazy opaque color compared to the other films which is due to higher % crystallinity. In addition, PLA-C had higher haze value, 30.47, than PLA-M, 14.23, due to its higher % crystallinity. Spherulites that are larger than the wavelength of visible light scatter the light, thus making films containing large spherulites to look opaque. Most often polymer films that are opaque have high crystallinity while transparent polymer films have less crystallinity and less light diffraction due to small spherulites.[17]

CONCLUSION

Crystallization in the film was affected by different solvents or solvent mixture in this research. PLA-MA showed the highest thermal expansion stability and crystallinity. The crystalline structure of PLA-MA affected the mechanical ability due to the spherulite size induced film brittleness. However, solvent-cast PLA films with single solvent, PLA-C and PLA-M, resulted in more ductility due to more mobility from having fewer crystals. The PLA films also showed varied haziness due to the capability of the crystal structure to diffract light with different intensities. PLA-MA was milk hazy as expected due to high crystalline structure as compared to PLA-C and PLA-M, which were more transparent. In conclusion, the thermo-mechanical property of PLA films can be altered by changing the percentage of crystallinity, thereby possibly making it more suitable for a wider variety of applications.

Table 1.1

Thermal Properties of the three PLA films

	T_g	T_c	ΔH_c [a]	T_m	ΔH_m [b]	% Crystallinity
PLA-C	47	73	4.31	164	29.78	24.03
PLA-M	54	77	12.98	163	28.09	14.25
PLA-MA	58			158, 165	48.92	46.15

[a] ΔH_c is the enthalpy of crystallization
[b] ΔH_m is the enthalpy of fusion

Table 1.2

Accumulated Dimensional Changes of the three PLA films

	Onset temp. (^{o}C)	Accumulated Dimensional Change (µm)		
		20-75 ^{o}C	20-90 ^{o}C	20-100 ^{o}C
PLA-C	58	197	257	272
PLA-M	66	340	518	548
PLA-MA	-	46	49	57

Table 1.3

Mechanical Properties of the three PLA films

	TS (MPa)	%E	Young's modulus (MPa)	Polymer Type
PLA-C	40.82 ± 3.95^b	61.53 ± 10.13^a	1042.29 ± 87.95^b	Ductile
PLA-M	46.41 ± 1.67^a	67.52 ± 2.19^a	1196.43 ± 82.08^a	Ductile
PLA-MA	18.36 ± 1.95^c	2.83 ± 0.17^b	619.29 ± 49.91^c	Brittle

[a] Results are expressed as the mean ± SD (n=7).
[b] a-c: The different letters within same column differ significantly ($p < 0.05$).

Table 1.4

Optical Properties of the three PLA films

	L	a	b	Haze
PLA-C	98.69 ± 0.17^a	0.16 ± 0.06^b	0.01 ± 0.23^b	30.47 ± 5.32^b
PLA-M	97.97 ± 0.09^a	0.07 ± 0.01^b	0.08 ± 0.01^b	14.23 ± 1.38^c
PLA-MA	86.48 ± 3.70^b	1.94 ± 0.22^a	5.41 ± 0.31^a	85.32 ± 3.75^a

[a] Results are expressed as the mean ± SD (n=3).
[b] a-d: The different letters within same column differ significantly ($p < 0.05$).
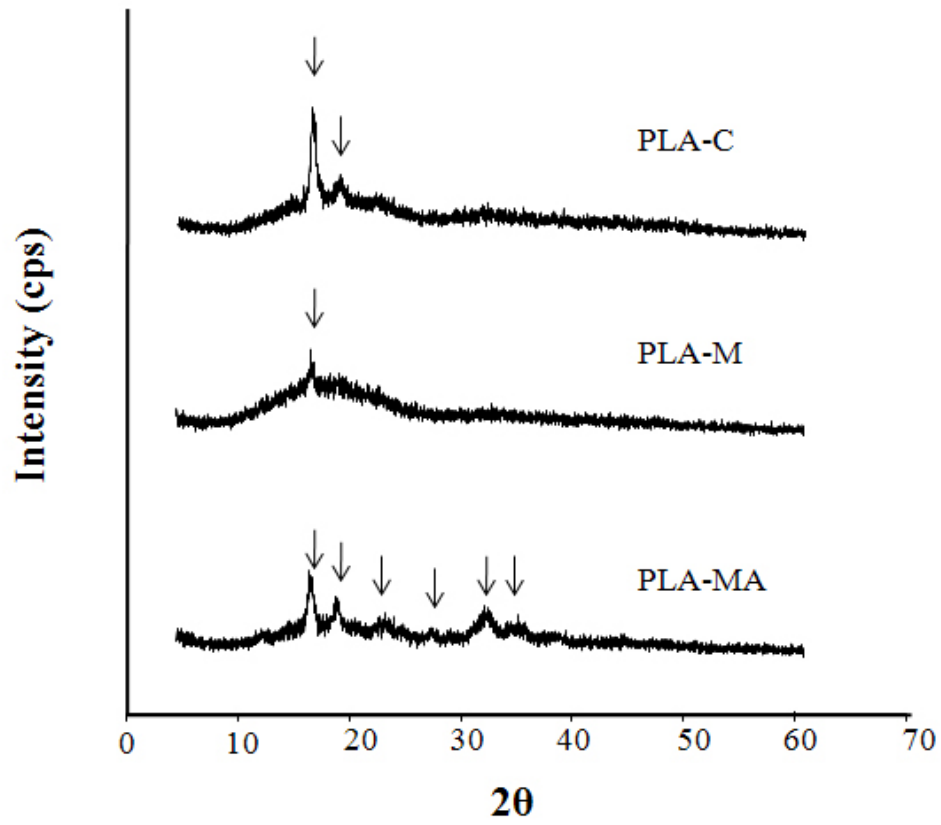
Figure 1.1 Wide-angle X Ray diffraction patterns of the three PLA films.
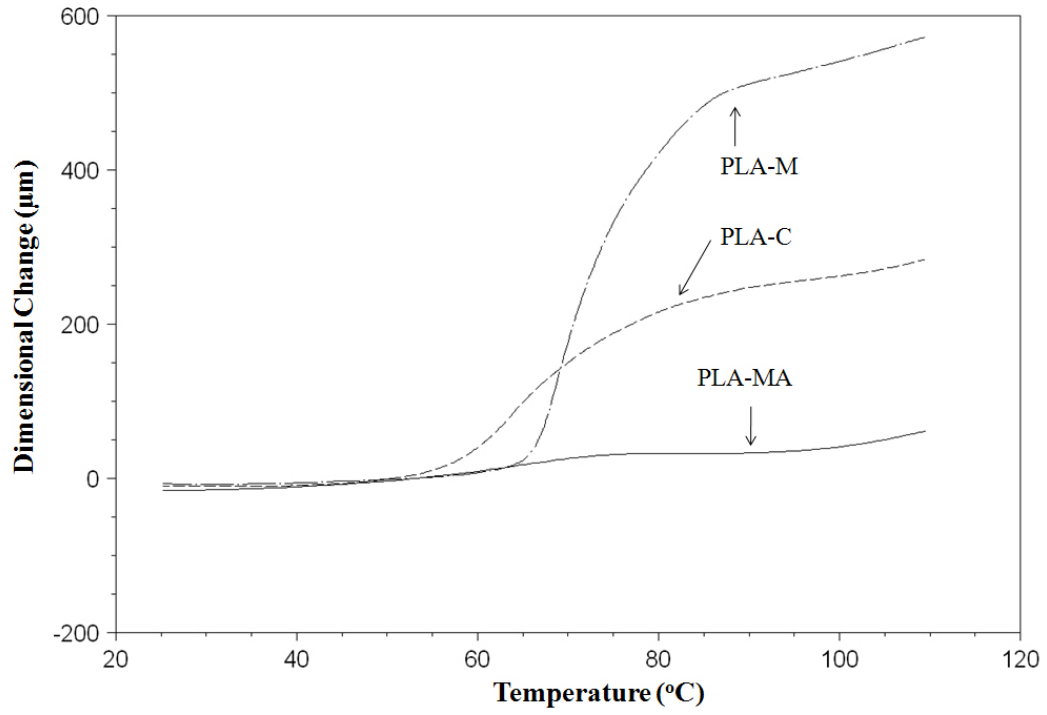
Figure 1.2 TMA thermograms of the three PLA films.
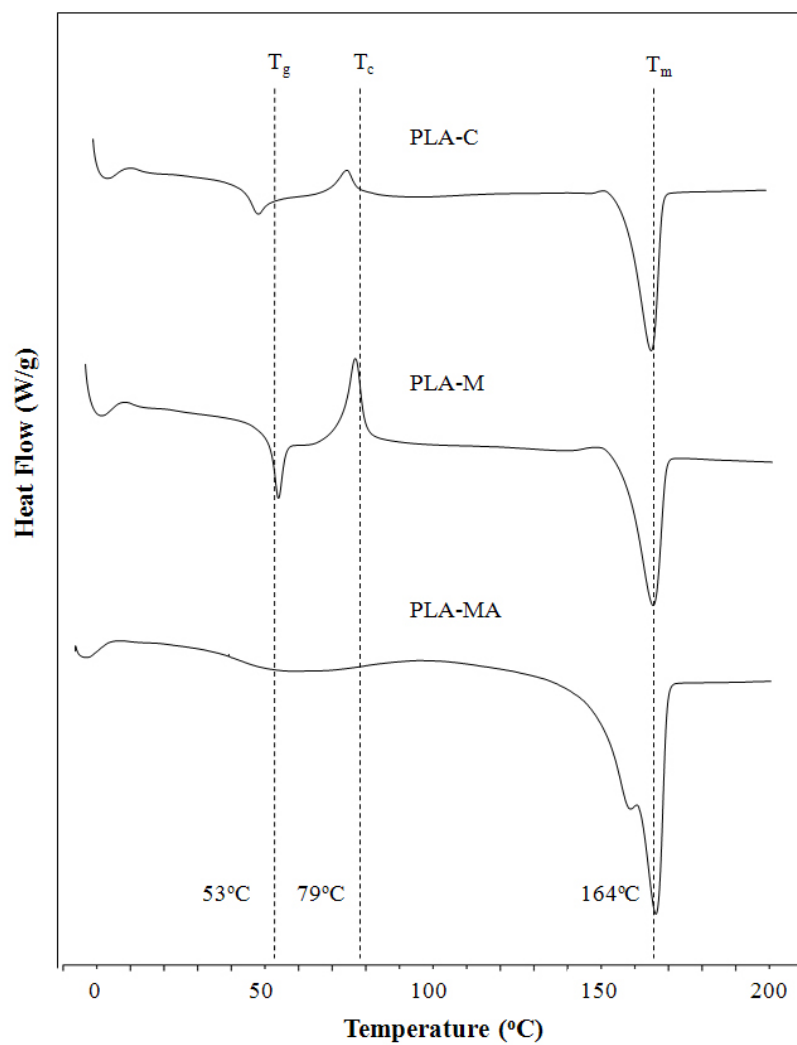
Figure 1.3 DSC thermograms of the three PLA films.
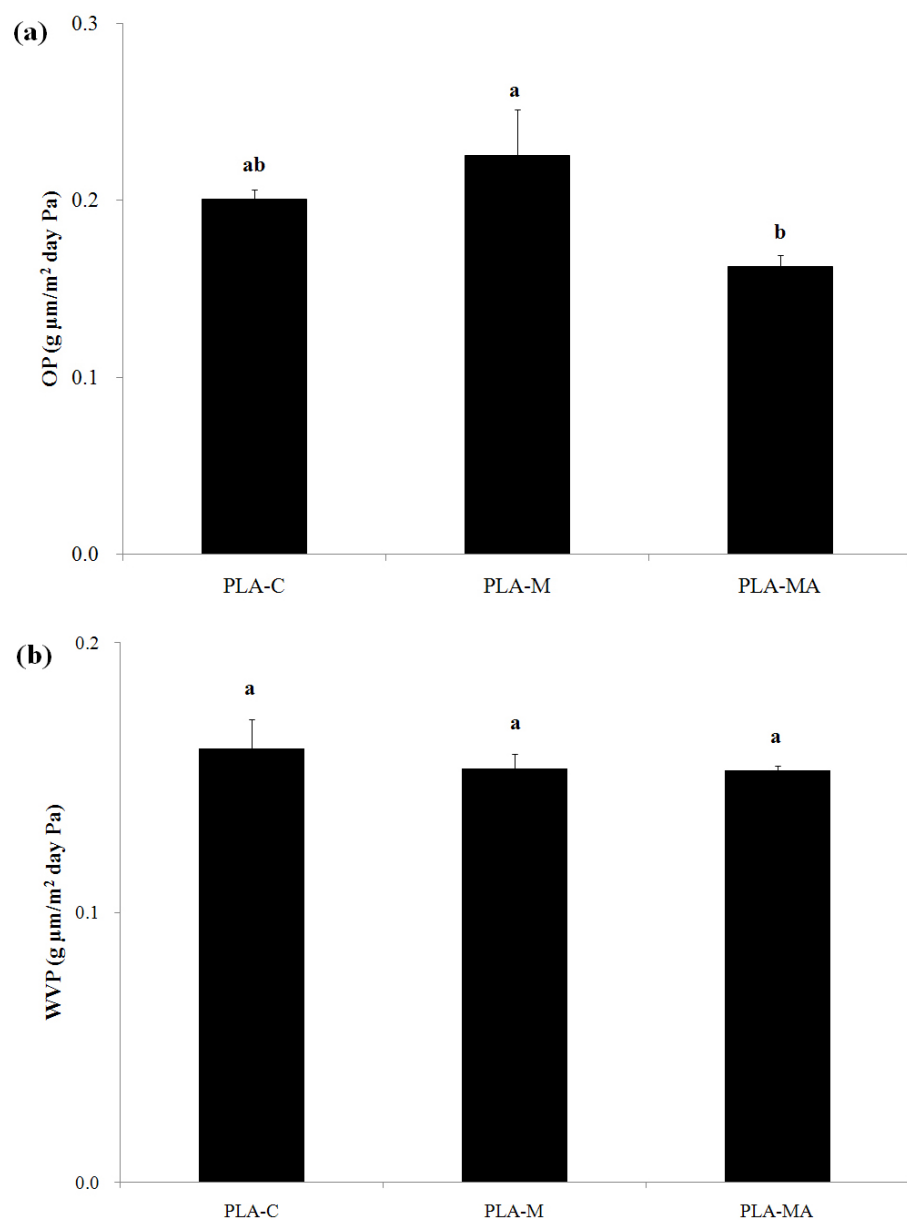
Figure 1.4 Barrier properties of the three PLA films (a) oxygen permeability (OP) (b) water vapor permeability (WVP). Different letters differ significantly *(n=2, P < 0.05)*.

REFERENCES CITED

1. Garlotta, D. J Polym Environ 2001, 9, 63.

2. Mano, J.; Gomez-Ribelles, J.; Alves, N.; Salmeron-Sanchez, M. Polym 2005, 46, 8258.

3. Drumright, R.; Gruber, P.; Henton, D. Adv Mater 2000, 12, 1841.

4. Pillin, I.; Monterelay, N.; Grohens, Y. Polym 2006, 47, 4676.

5. Okamoto, K.; Ichikawa, T.; Yokohara, T.; Yamaguchi, M. Eur Polym J 2009, 45, 2304.

6. Pezzin, A.; Alberda, G.; Zavaglia, C.; Ten Brinke, G.; Duek E. J Appl Polym Sci 2003, 88, 2744.

7. Furuhashi, Y.; Wakuda, H.; Yoshie, N. Seisan-kenkyu 2006; 58(3), 353.

8. Byun, Y.; Kim, Y.T.; Whiteside, S. J Food Eng 2010, 100, 239.

9. Bistac, S.; Schultz, J. Prog Org Coat 1997, 31(4), 347.

10. Haidong, L.; Wei, N.; Chao, D.; Xuesi, C.; Xiangling, J. Eur Polym J 2009, 45, 123.

11. Paragkumar, T.; Edith, D.; Jean-Luc, S. Appl Surf Sci 2006, 253, 2758.

12. Huda, M.; Yasui, M.; Mohri, N.; Fujimura, T.; Kimura, Y. Mater Sci Eng A. 2002, 333(1-2), 98.

13. Sodergard, A.; Stolt, M. Prog Polym Sci 2002, 27, 1123.

14. Sarasua, J.R.; Arraiza, A.L.; Balerdi, P.; Maiza, I. Polym Eng Sci 2005, 45, 745.

15. Masirek, R.; Kulinski, Z.; Chionna, D.; Piorkowska, E.; Pracella, M. J Appl Polym Sci 2007, 105, 255.

16. Chang, J.; Sun, B.; Breiby, D.; Nielsen, M.; Sölling, T.; Giles, M.; McCulloch, I.; Sirringhaus H. Chem Mater 2004, 16, 4772.

17. Selke, S.; Culter, J.; Hernandez, R. In Plastics Packaging (2nd ed), Selke, S.; Culter, J.; Hernandez, R., Ed; Hanser Publications: Cincinnati, 2004, Chap. 3.

18. Xiao, H.; Liu, F.; Yeh, J. J. Applied Poly Sci 2010, 117, 2980.

19. De Santis, P.; Kovacs, J. Biopolymers 1968, 6, 299.

20. Hoogsteen, W.; Postema, A. R.; Pennings, A. J.; Ten Brinke, G.; Zugenmaier, P. Macromolecules 1990, 23, 634.

21. Cartier, L.; Okihara, T.; Ikada, Y.; Tsuji, H.; Puiggali, J.; Lotz, B. Polymer 2000, 41, 8909.

22. Brizzolara, D.; Cantow, H. J.; Diederichs, K.; Keller, E.; Domb, A. J. Macromolecules 1996, 29, 191.

23. Slager, J.; Brizzolara, D.; Cantow, H.; Domb, A. Polym Adv Technol 2005, 16, 667.

24. Drieskens, M.; Peeters, R.; Mullens, J.; Franco, D.; Lemstra, P.; Hristova-Bogaerds, D. J Polym Sci, Part B: Polym Phys 2009, 47, 2247.

25. Ahmed, J.; Varshney, S.; Zhang, J.; Ramaswamy, H. J Food Eng 2009, 93, 308.

26. Escobal, A.; Iriondo, C.; Katime, I. Polym Test 1999, 18(4), 249.

27. Andersson, A.; Zhai, W.; Yu, J.; He, J.; Maurer, F. Polym 2010, 51(1), 146.

28. Byun, Y.; Hong, S.; Kim, K.; Jeon, D.; Kim, J.; Whiteside, S.; Park, H. Radiat Phys Chem 2007, 76, 974.

29. Sanchez-Garcia, M.; Gimenez, E.; Lagaron, J. Carbohydr Polym 2008, 71, 235.

30. Park, S.; Todo, M.; Arakawa, K.; Koganemaru, M. Polym 2006, 47, 1357.

31. Kim, Y.; Lee, Y.; Han, J.; Han, S.; Han, M. J Electrochem Soc 2007, 154(12), H995.

CHAPTER TWO

THE EFFECTS OF SOLVENT MIXTURE ON THE MECHANICAL AND THERMAL

PROPERTIES OF SOLVENT CAST POLY-LACTIC ACID (PLA) FILM

ABSTRACT

The objective of this research was to determine the optimum solvent mixture to improve flexibility while maintaining the thermal stability of PLA solvent-cast films. PLA films were produced from mixed solvent solutions of (M: methylene chloride) and (A: acetonitrile) using the solvent-casting technique. The ratio of solvents used were 70% methylene chloride with 30% acetonitrile (73MA), 60% methylene chloride with 40% acetonitrile (64MA) and 50% methylene chloride with 50% acetonitrile (55MA). The single solvent solution was 100% methylene chloride (100M). Differential Scanning Calorimetry (DSC) showed films with increased amounts of acetonitrile had higher amounts of % crystallinity due to the full formation of crystals during the casting process and no enthalpy of crystallization. Thermomechanical Analysis (TMA) revealed the addition of acetonitrile increases the thermal stability of the PLA films. Stress strain curves showed that high crystalline films were brittle while less crystalline films were ductile. Both Wide Angle X-ray Diffraction (WAXD) and Transmission Electron Microscopy (TEM) showed 55MA and 64MA had the highest % crystallinity, more developed crystal structure and more pronounced lattice images. Film 73MA was the

only film that exhibited both flexibility and good thermal stability. The 30%

concentration of acetonitrile developed crystals that stopped growing due to solvent

evaporation, but upon heating in TMA, the crystals began to grow fully thus improving

thermal stability. This work shows that PLA film produced by solvent casting from

solvent mixture compared to a traditional single solvent will have better thermal and

mechanical performance.

INTRODUCTION

Poly (lactic acid) (PLA) is an aliphatic thermoplastic, compostable, biocompatible polymer derived from starch contained in products like corn, sugar cane and sugar beets.[1] For the past several years PLA has been used in the biomedical field for implant applications and wound dressing.[2] With the advance of new technologies and processes, PLA is being used in areas of packaging, textiles and composite materials.[3] With respect to packaging PLA has certain limitations. Low deformation at break, low heat resistance and brittle behavior are factors that limit PLA from being more widely used in the packaging industry.[3-5]

The use of PLA in packaging has primarily been for rigid packaging due to its poor mechanical properties as a thin material.[7] The solvent-casting technique is a widely used technique in research used to produce thin biopolymer films.[6] Previous research involving solvent-casting focused on increasing the crystallinity of thin PLA film to improve thermal stability using various solvent mixtures, but this, in turn, diminished its mechanical ability.[14] The lack of ductility limits the practical use of PLA as a thin film. Solvent-casting involves dissolving a resin polymer into a solvent such as methylene chloride, chloroform and benzene and then casting it into a thin, wet film to dry.[8,9] The mobility of solvent molecules in a polymer solution plays a large role in the properties of the polymer.[10] The solvent induced conformational changes affect the crystallinity of

the polymer.[37] PLA has low solubility in solvents like toluene, acetone, acetonitrile and ethyl acetate.[37] Casting using a solvent like methylene chloride showed more of a polymer solvent interaction and led to good solubility.[14] Huda, et al. (2002) discovered that PLA solutions in methylene chloride and chloroform resulted in a random conformation of molecules. Byun, et al. (2011) used PLA solutions of methylene chloride and acetonitrile and saw an intramolecular interaction of molecules leading to a polymer-polymer interaction. Preliminary studies have proven that solvents like methylene chloride and chloroform produce clear films that have good mechanical properties but poor thermal stability. The mixture of methylene chloride and acetonitrile together altered the crystalline structure of PLA thin films, enhancing thermal stability but the material remained brittle.[14] The purpose of this research was to find the optimum ratio of solvent mixtures to produce a PLA film that is both thermally stable yet ductile in behavior.

MATERIALS AND METHODS

Material

The PLA resin (4032D) used for this research was donated by Nature Works, LLC (MN, USA). PLA resin constituted a 99:1 ratio of L to D oligomer PLA (Scheme 1.). Methylene chloride was purchased from JT Baker (UA). Acetonitrile was purchased from VWR International (PA, USA) and Polyethylene glycol 400 (PEG 400) used was purchased from Sigma Aldrich (MO, USA). All solvents used were HPLC grade.

Film Preparation

Preparing the film was done by using the solvent casting technique. Before casting, the PLA resin was placed into a drying oven at 35°C for 48hrs to remove any moisture. 30g of PLA and 3g of PEG400 were dissolved into 200mL of solvent. The mixtures were stirred for 12hrs before casting. The solvents used for this study were methylene chloride (M) and acetonitrile (A). The plasticizer used was polyethylene glycol with a molecular weight of 400. The amount of plasticizer used ranged from 10% to 20%, increasing in 2% increments. The ratios of solvents used were 100% methylene chloride (100M), 50:50 methylene chloride: acetonitrile (55MA10), 60:40 methylene chloride: acetonitrile (64MA) and 70:30 methylene chloride: acetonitrile (73MA). 35mL of dope solution was

cast onto a BYTAC® (Norton Performance Plastics Corporation, Wayne, NJ, USA) coated 157 mm x 356 mm glass plate which was formed utilizing a customized film applicator. The cast films were then air dried at 23°C for 12hrs. The films then peeled off the plates and dried in an oven at 35°C for 8hrs to evaporate any residual solvent left in the film. Only film 55MA had a plasticizer content of 20% as films 64MA and 73MA produced pin holes during casting with 20% plasticizer.

X-Ray Diffraction

Wide angle X-Ray Diffraction patterns were recorded using a copper anode X-Ray tube (Cu-K$_\alpha$ radiation, $\lambda = 1.5418$ Å) (Rigaku Ultima IV Tokyo, Japan). The scanning region of the diffraction angle (2θ) was 10° to 30° with continuous scan mode at a scan speed of 0.200 deg. /min. D spacing from TEM was confirmed using Bragg's Law:

$$n\lambda = 2d \sin(\theta)$$

(DSC) Differential Scanning Calorimetry

Differential scanning calorimetry DSC) of PLA solvent cast films were performed on a Model 2920 Modulated DSC (TA instrument, USA). The glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) of the PLA films were measured using DSC. Specimens weighing 6 to 7mg were heated at a rate of

10°C/min. from 20° to 180°C with a constant nitrogen flow throughout. The percentage of crystalinity (X_c) of the PLA films was calculated according to the following equation:

$$X_c (\%) = (\Delta H_m - \Delta H_c)/ \Delta H^c_m \bullet 100$$

Where ΔH^c_m is the enthalpy of fusion of pure crystalline PLA (93.1 J/g).[12, 21, 24]

Thermal Stability

Thermal stability was analyzed by a Thermomechanical Analyzer (TMA) (2940, TA instruments).The film samples for TMA were cut into strips 0.159 cm wide and 1.27 cm long.   The samples were clamped on both the ends with split aluminum balls and heated from 25 to 110°C at the rate of 10°C/min with a constant nitrogen flow throughout.

Mechanical Properties

The tensile strength (TS), elongation at break (%E), and Young's modulus (ε) of the PLA films were measured using an Instron Universal Testing Machine (Model 4201, Instron Corp., Canton, MA, U.S.A.) according to the ASTM standard method D882-88. Specimen samples, 10 cm x 2.54 cm, were cut from film samples. Samples were conditioned for 48 h at 23° ± 0.5°C and 50% RH at a constant temperature and humidity before the measurement. Initial grip separation and cross-head speed were set at 5 cm and 25 cm/min, respectively. The values presented were the average of seven

measurements. Stress strain curves were generated at a grip separation of 5cm and a cross-head speed of 12.5 mm/min.

(POM) Polarized Optical Micrographs

Spherulite images were obtained using a Nikon Optiphot Microscope (Japan) equipped with an NEC (NC-8CCD) color camera. DSC samples used to study thermal transition were cooled slowly from melt to obtain spherulite images.

TEM Images

All TEM images were captured using a High Resolution Transmission Electron Microscope (Hitachi H-9500) equipped with a LaB6 filament. Operation at 200kV was used for optimum, high resolution imaging. The microscopes software calculated the d-spacing of crystal lattice seen in the images.

Optical Properties

Haze, transparency and clarity of the PLA film were collected using a BYK Gardner Haze Gard Plus (Model 4725, Germany).

Statistical Analysis

Statistical significance was determined by analysis of variance (ANOVA) using SAS

(version 9.1, SAS Institute Inc., NC). Significance was defined at a level of $P < 0.05$.

RESULTS AND DISCUSSION

Crystallinity and X-Ray Diffraction

X-Ray diffraction profiles of the cast PLA films were taken only of films with 10% plasticizer since the increase in plasticizer did not change the crystalline structure. PLA films 55MA and 64MA showed multiple diffraction peaks at 2θ angle 12°, 15°, 17°, 19° and 23°, indicating the presence of new crystalline structures as compared to 73MA and 100M (Fig. 1). PLA was dissolved more easily in methylene chloride than in acetonitrile. Previous reports showed that the formation of stereocomplex crystallization occurs when PLA is dissolved in a poor solvent due, in part, to the strong interaction in polymer chains[13]. Byun, et al. (2010) discovered that acetonitrile mixed with methylene chloride may induce the production of multiple crystalline structures in PLA film[14]. Comparing those results with DSC data (Table 1-3) showed there was a correlation with the number of peaks and percent crystallinity. Mixing solvents with varying PLA solubility can increase the crystallinity of the film[15]. 55MA and 64MA, having larger amounts of acetonitrile, had the highest % crystallinity and highest enthalpy of fusion for melting crystals.

Unlike 55MA and 64MA, PLA film 73MA and 100M showed diffraction peaks at only 17° and 19° and a small spike at 23° for 100M (Fig. 1). Their % crystallinity

differed with 73MA having 31.01 and 100M having 25.99 % (Table 3). However, the enthalpy of fusion for melting (ΔH_m) for 100M and 73MA were more similar with 100M having an enthalpy of 38.95 J/g and 73MA with 40.12 J/g. The larger melting enthalpy for 73MA10 compared to 100M could mean that during casting the addition of acetonitrile resulted in fewer crystals not completely formed. When subjected to DSC analysis more crystals started to form before melt as indicated by the amount of energy to melt the crystal. PLA dissolved in poor solvents like acetonitrile promote more polymer-polymer interactions and leads to more crystalinity[15]. As for the enthalpy of crystallization (ΔH_c), only solvent mixtures of 100M and 73MA showed any energy levels (14.75J/g and 11.25 J/g, respectively) (Table 3). The release of energy during this exothermic transition proves more crystalline arrangement was taking place. A larger crystallization enthalpy seen with 100M (14.75J/g) indicated more crystals were being arranged during heating. A lesser value or the absence of a crystallization enthalpy was confirmation that crystals had already formed during casting of the film. The crystallinity of solvent cast film was also effected by solvent properties. Solvents that have high boiling points (bp) have lower rates of vaporization which leads to more time to facilitate the growth of crystals. In contrast, solvents with low boiling points have a higher rate of vaporization and a reduced time for crystal growth[15,16].

Poly ($_L$– lactic acid) (PLLA) and poly ($_D$– lactic acid) (PDLA) are isotactic and can crystallize into α, $β$ and γ-forms[17-21]. Previous research showed that PLA undergoes a conformational change. The lowest energy conformation of a single PLLA chain is either helical 10_3 (α-form, major 2θ: 17, 19, 22) or 3_1 helices ($β$-form, major 2θ: 12, 25)[21-23, 40]. Jianming et al. (2005) stated that PLLA crystal structures with loose 10_3 helical chain packing is less thermally stable than the standard α form.[43] This research also proved that 73MA and 100M crystallized in the α-form due to their peak angle at 2θ 17°. However, PLA 55MA10 and 64MA10 showed small peaks at 2θ 12°, indicating a conformational change to $β$-form. The increase in peak width and height of 55MA and 64MA at 2θ 17° suggests that acetonitrile may increase the crystal perfection of the polymer. The more intense peaks in 55MA and 64MA showed that there were more crystalline structures than with 100M and 73MA.

The x-ray diffraction peaks indicated the main crystalline features of 100M and 73MA by the diffraction peaks at 17° (d=0.2636nm), which is an indication of α-form crystals. 55MA10 and 64MA10 saw multiple diffraction peaks, including 12° (d=0.3708nm), 15° (d=0.2978nm) and 19° (d=0.2367) with a more intense peak at 17°. The additional peaks at angles 12°, 15° and 19° and the increase in peak intensity at 2θ 17° revealed a predominant growth of α-form polymorph and the addition of $β$-form crystals.[11] TEM images confirmed the spacing of the lattice (Fig's 2-4). Overall

crystallinity may have been limited due to the 99:1 ratio of L to D PLA. Previous studies have shown that adding the D form into PLLA significantly increased the crystallization of PLLA forming stereocomplex crystallites in PLLA's matrix.[41, 42]

Appearance

The appearance of the films differed from very opaque to transparent (Fig 5). Values for haze, transmittance and clarity of the 10% plasticizer PLA films with 10% plasticizer were measured (Table 2). Not shown are films with plasticizer % ranging from 12 to 20%. 55MA and 64MA had 100% haze due to its large spherulite size. 100M was transparent in appearance and had the lowest haze value. Polymers with higher crystallinity are more opaque than films with less crystallinity. This is due to larger spherulite size in high crystalline polymers scattering light from the different crystal phase changes.[26] Polymers with smaller sized spherulites are more transparent and therefore have less light scattering. As expected, the less crystalline 73MA and 100M had the highest clarity. Because these crystals are so small, less light is scattered and the film appears clear.

Thermal Properties

Films 55MA and 64MA did not show any noticeable T_c but did show a T_g and T_m (Table's. 1-3 & Fig's. 6-8). The T_g of the film is dependent on the polymer's structural arrangement and corresponds to the torsional oscillation of carbon backbone and side groups resulting in long range segmental motion above the T_g.[25, 26] The T_g's varied in curve shape and broadness (Fig's. 6-8). The presence of crystalline structures in semi-crystalline polymers has been known to effect the glass transition resulting in a more broad transition area as compared to more amorphous polymers.[27] Films 55MA and 64MA showed a low sloped glass transition point versus the sharp angled peaks of the more amorphous 73MA and 100M (Fig's. 6-8). The lack of a crystalline peak for 55MA and 64MA indicated that the polymer reached its maximum crystallinity early in the casting process. It is assumed that a double melting peak for 55MA and 64MA is attributed to the melting of multiple crystalline structures. Previous research noted that lower temperature melting peak was attributed to the melting of subsidiary, thinner lamella while the higher temperature and more predominant melting peak was due to the melting of dominant thicker lamellae.[28-30] It is assumed that the addition of acetonitrile promotes crystal growth which was confirmed by X-ray diffraction (Fig. 1).

Thermal Stability

The thermal stability of each PLA film was determined by measuring the amount of dimensional change with respect to temperature (Table's 5-6 & Fig's 9-11). Although testing methods for the thermal stability of PLA material is not fully understood, it was assumed that higher onset temperatures and low linear thermal expansion is representative of less dimensional change and better thermally stability. Increasing the crystal structure and crystallinity of a polymer can lead to more thermal stability at higher temperatures.[31] When molecules in more amorphous regions are subjected to heat they begin to undergo segmental motion which in turn leads to expansion of the material.[26] Films 55MA and 64MA had the least dimensional change compared to 100M as also observed by Byun et al. (2010). Film 55MA and 64MA also had lower thermal expansion coefficients throughout the whole plasticizer range (Table 5&6). Film 100M saw the most change of all four solvent mixtures with a thermal expansion coefficient of 15.63 µm/°C, dimensional change of 1546µm and an onset temperature of 62.54°C (Table 5). These findings were similar to Byun et al. (2010), where the single solvent cast film performed poorly when compared to solvent mixtures that included acetonitrile. 73MA had similar melting enthalpies and mechanical properties with 100M but, very different dimensional stability (73MA16 0.00 µm/°C vs. 100M10 15.63 µm/°C), respectively. The inclusion of acetonitrile in smaller concentrations gave films just

enough crystal structure to perform thermally like a crystalline polymer yet they were ductile enough to have viscoelastic behavior. Therefore, PLA 55MA, 64MA and 73MA were more heat stable than single solvent 100M.

Mechanical Properties

The thermal studies showed that when crystallinity is increased thermal properties are enhanced. Increased crystallinity however adds rigidity and brittleness which leads to poor mechanical ability.[32] Polymer chain strength depends on the strength of –C–C– bonds. The theoretical strength of these –C–C– bonds can be estimated on the dissociation energy of unstressed –C–C– bonds on the basis of a two atom molecule.[33] Films 55MA and 64MA showed the lowest tensile strength, young's modulus and % elongation (Table's 8&9). Poly ethylene glycol 400 (PEG 400) was used as the plasticizer to help enhance the mechanical properties of the PLA film and decrease T_g.[39] Pillin et al. (2006) showed that adding more plasticizer (PEG 400) to the film, decreased T_g. PEG 400 was chosen for its ability to increase mobility of PLA macromolecules, which is a large factor aiding the crystallization kinetics of a polymer.[39] Stress strain curves showed that PLA 73MA and 100MA with 10% plasticizer behaved ductile while 55MA and 64MA were brittle (Fig 12). This study also showed that increasing the plasticizer concentration didn't always result in a stronger film, with the exception of

55MA which saw a significant increase in tensile strain (Table 8). Comparing the 10%

mixtures only, film 55MA and 64MA showed the lowest values for TS of 9.13 and

13.02MPa, respectively. They also had the lowest % elongation and % elongation

(Table's 9 & 10). The less crystalline 100M and 73MA had better mechanical

performance (Table 10). 100M had higher TS and modulus values of 52.19 and

12.02Mpa, whereas 73MA10 had a TS value of 37.65Mpa and a modulus of 9.87Mpa.

The % elongation however was significantly higher for 73MA10 than any of the films

tested at 49.36% (Table 10). Previous papers have shown that spherulite size increased

with increasing crystallinity making the material brittle.[34] The crystallinity could be the

key factor in why 55MA and 64MA ruptured before 100M and 73MA. Crazing is an

important deformation mechanism observed in amorphous polymers and appears as

horizontal lines from a tension source during tensile strain (Fig's 13 & 14).[35] These

cracks are an energy absorbing mechanism and increased fracture energy is accelerated

by these cracks.[36] At this point the tie molecules have been stretched to their limit,

hydrogen bonds have broken and covalent bonds are beginning to yield and were seen

only in 100M and 73MA. The effect of increased flexibility can be seen by stress strain

curves (Fig 12). Films 55MA and 64MA having more crystallinity had very little tensile

stress and rupture at the yield point. Films 100M and 73MA showed significant stress

yield with a plastic region indicated by the increase in tensile strain before rupture.

Although film 100M saw the highest tensile stress, 73MA was much more flexible. Developing films with good flexibility along with good thermal stability was the main objectives of this research. Stress strain curves with plasticizer concentrations above 10% where not shown as they did not show any difference in the shape of the curve.

HR-TEM and POM

Most of the cast films showed well defined crystalline lattice plane packing (Fig's. 2-4). 55MA10 shows lattice fringes with a d-spacing of 0.2353nm (Fig. 2). Each dark region indicates a single crystalline structure with a lattice appearance. Film 64MA10 (Fig. 3) showed clear lattice fringes with d-spacing's of 0.2532 and 0.2003nm. Areas with tightly packed planes indicated more phase changes took place. Hoogsten et al. (1990) suggested this phase for PLLA as an orthombic unit cell that includes six helices with three fold helical conformation (Fig. 15).[44] Clear, light colored areas beyond the extent of the lattice fringe are the amorphous regions of the polymer. 73MA10 (Fig. 4) also showed a crystal lattice with a d-spacing of 0.2859nm butt were not as visible as 55MA and 64MA. Graphs from x-ray diffraction (Fig. 1) show that 73MA10 has only one predominant peak at 2θ angle 17°. Film 100M did not show a crystalline lattice under high resolution TEM. This was expected as the 100M film showed the least crystalinity and poor thermal stability. Seok, et al. (2009) noticed that as the d-spacing

increased in polyethylene by use of clay fillers, the mechanical properties increased. Likewise, the more closely packed the spacing the higher the melting temperature and heat of fusion.[45] Spherulite images were obtained by heating the film in DSC and quenching the polymer upon cooling from melt to obtain spherulites (Fig. 16). The samples were taken out of the DSC pans and placed under the microscope for viewing. The horizontal lines seen across the images are from the DSC pans. PLA is such a slow crystallizing polymer that precise cooling control was needed to produce spherulites, thus the use of DSC samples. The two vertical lines are a .01nm separation distance. All spherulite images are similar in size indicating that the effect the solvents had on the polymer may be temporary. These same samples where then taken back to x-ray diffraction to identify any structural change. Diffraction peaks of the PLA material after subjected to DSC can also be seen (Fig. 17). The uniformity of diffraction peaks indicated that the effect the solvent had on the polymer during casting was a temporary phenomenon.

CONCLUSION

Film crystallinity was affected by the mixture of different solvents. The increase of crystallinity in film 55MA and 64MA gave the film more thermal stability and less linear expansion. 100M had the least crystallinity; therefore it had the most thermal dimensional change. The films also had a different appearance. The films with higher % crystallinity (55MA and 64MA) had more haze than the less crystalline films due to larger crystal formation. The less crystalline films (73MA10 and 100M) had smaller crystal formation resulting in more clarity and transparency. However, 73MA with nearly the same amount of crystallinity as 100M showed similar thermal stability as 55MA and 64MA. This may be due to the introduction of acetonitrile in small quantities to aid in the formation of crystalline structures that did not fully grow until heating. Increasing the crystallinity had an effect on the mechanical ability of the film. Increasing the crystallinity made the film more brittle (55MA and 64MA), whereas lower crystallinity (100M and 73MA) showed ductile performance having more chain mobility. The difference in crystallinity could be seen in the clarity of the film. The film changed from a transparent to white film as crystallinity increased. X-ray diffraction confirmed the presence of crystalline structures. 55MA and 64MA had the most crystal peaks as compared to 100M and 73MA. Lattice images of the films seen by high resolution TEM showed that the presence of acetonitrile promoted different phase changes. The effect of

solvents on the structure of PLA was temporary. X-ray diffraction showed this to be the case when film samples crystallized from melt were scanned. Spherulite size was also similar after melting the film by DSC. The objective of this study was to produce a flexible, thermally stable PLA film from solvent mixtures using the solvent casting technique. Film 73MA with 31% crystallinity proved to be the best film for these two performance parameters. Films with crystallinity higher than 31% had low tensile strength and elongation. Films that had crystallinity below 31% showed lower onset temperatures and higher dimensional change. 31% crystallinity appeared to be the optimum crystallinity for films to have good thermal stability and flexibility.

TABLE 2.1

Thermal Properties of Solvent Cast PLA Films 55MA

PLA film	T_g	T_C	T_m	$\Delta H_c\,(J/g)^a$	$\Delta H_m\,(J/g)^b$	% Crystalinity
100M10	57	80	165	14.75	38.95	25.95
55MA10	55	-	167	-	53.01	56.94
55MA12	52	-	165	-	50.72	54.48
55MA14	53	-	165	-	53.53	57.49
55MA16	54	-	164	-	51.92	55.76
55MA18	53	-	164	-	51.65	55.47
55MA20	54	-	164	-	49.57	53.24

[a] ΔH_c : enthalpy of crystallization.
[b] ΔH_m : enthalpy of fusion.

TABLE 2.2

Thermal Properties of Solvent Cast PLA Films 64MA

PLA film	T_g	T_C	T_m	$\Delta H_c\,(J/g)^a$	$\Delta H_m\,(J/g)^b$	% Crystalinity
100M10	57	80	165	14.75	38.95	25.95
64MA10	53	-	167	-	48.59	52.19
64MA12	54	-	166	-	50.63	54.38
64MA14	53	-	166	-	46.46	49.90
64MA16	54	-	165	-	48.62	52.22
64MA18	54	-	165	-	46.44	49.88

[a] ΔH_c : enthalpy of crystallization.
[b] ΔH_m : enthalpy of fusion.

Table 2.3

Thermal Properties of Solvent Cast PLA Films 73MA

PLA film	T_g	T_C	T_m	$\Delta H_c\,(J/g)^a$	$\Delta H_m\,(J/g)^b$	% Crystalinity
100M10	57	80	165	14.75	38.95	25.95
73MA10	58	83	165	11.25	40.12	31.01
73MA12	54	81	163	14.25	37.44	24.91
73MA14	49	78	163	12.99	38.28	27.16
73MA16	55	80	162	15.01	37.10	23.73
73MA18	54	79	162	13.52	36.40	24.57

[a] ΔH_c : enthalpy of crystallization.
[b] ΔH_m : enthalpy of fusion.

Table 2.4

Haze Measurements of the four PLA films

PLA film	Haze (%)	Transmittance (%)	Clarity (%)
55MA10	99.96 ± 0.10^a	22.8 ± 0.96^c	0.18 ± 0.34^c
64MA10	100.0 ± 0.00^a	42.88 ± 2.22^b	2.5 ± 0.89^c
73MA10	62.52 ± 16.31^b	93.6 ± 1.49^a	49.91 ± 18.34^b
100M10	6.71 ± 2.05^c	94.4 ± 0.39^a	98.66 ± 0.27^a

[a] Different letters within the same column are significantly different $(P < 0.05)$
[b] Results are expressed as the mean $\pm$ SD $(n = 9)$.

Table2.5

Dimensional Change of the 55MA PLA Cast films

PLA film	Thermal Expansion Coefficient (μm/°C)	Onset (°C)	Dimensional Change (μm)
100M10	15.63	62.54	1546
55MA10	.6219	148.86	214.6
55MA12	.5676	148.47	179.9
55MA14	0	159.04	80.8
55MA16	.1161	158.22	140
55MA18	.7936	155.18	171.6
55MA20	.4437	152.66	150.7

Table 2.6

Dimensional Change of the 64MA PLA Cast films

PLA film	Thermal Expansion Coefficient (μm/°C)	Onset (°C)	Dimensional Change (μm)
100M10	15.63	62.54	1546
64MA10	.6812	148.06	172
64MA12	.2213	150.49	162.2
64MA14	2.765	-	239.3
64AM16	.9785	106.28	92.94
64MA18	1.148	127.35	224.2

Table 2.7

Dimensional Change of the 73MA PLA Cast films

PLA film	Thermal Expansion Coefficient ($\mu m/°C$)	Onset (°C)	Dimensional Change (μm)
100M10	15.63	62.54	1546
73MA10	.8194	149.41	217.9
73MA12	1.209	150.04	283.7
73MA14	.9413	156.6	237.1
73MA16	0	156.37	153.8
73MA18	.1702	154.21	224

Table 2.8

Mechanical Properties of 55MA PLA Cast films

PLA film	Tensile Strain (MPa)	Young's Modulus (MPa)	% Elongation
100M10	$52.19 \pm 7.52^{a}_{1}$	$12.02 \pm 1.97^{a}_{1}$	$14.24 \pm 10.37^{a}_{2}$
55MA10	$9.13 \pm 1.03^{d}_{3}$	$2.96 \pm 0.40^{d}_{3}$	$3.20 \pm 0.67^{b}_{2}$
55MA12	9.70 ± 0.67^{d}	2.87 ± 0.42^{d}	3.61 ± 0.67^{b}
55MA14	18.13 ± 2.78^{b}	7.32 ± 1.29^{b}	2.50 ± 0.29^{b}
55MA16	$12.17 \pm 3.83^{c,d}$	5.29 ± 1.06^{c}	2.25 ± 0.41^{b}
55MA18	$15.86 \pm 3.71^{b,c}$	$6.21 \pm 1.14^{b,c}$	2.55 ± 0.30^{b}
55MA20	14.05 ± 0.72^{c}	1.24 ± 0.22^{e}	2.82 ± 0.25^{b}

[a] Different letters   and subscript numbers within the same column are significantly different (P < 0.05).

[b] Results are expressed as the mean ± SD (n = 7).

[c] Subscript numbers are differences among 10% plasticizer only.

Table 2.9

Mechanical Properties of 64MA PLA Cast films

PLA film	Tensile Strain (MPa)	Young's Modulus (MPa)	% Elongation
100M10	52.19 ± 7.52^a	12.02 ± 1.97^a	14.24 ± 10.37^a
64MA10	$13.02 \pm 1.64^b{}_3$	$3.93 \pm 0.80^b{}_3$	$3.51 \pm 0.81^b{}_2$
64MA12	7.74 ± 2.53^c	2.89 ± 1.12^b	2.78 ± 0.61^b
64MA14	$4.67 \pm 0.79^{c,d}$	1.68 ± 0.35^c	2.75 ± 0.33^b
64MA16	2.26 ± 0.47^d	1.07 ± 0.29^c	2.01 ± 0.37^b
64MA18	$4.57 \pm 1.10^{c,d}$	1.72 ± 0.35^c	2.66 ± 0.36^b

[a] Different letters and subscript numbers within the same column are significantly different ($P < 0.05$).
[b] Results are expressed as the mean $\pm$ SD ($n = 7$).
[c] Subscript numbers are differences among 10% plasticizer only.

Table 2.10

Mechanical Properties of 73MA PLA Cast films

PLA film	Tensile Strain (MPa)	Young's Modulus (MPa)	% Elongation
100M10	52.19 ± 7.52^a	12.02 ± 1.97^a	14.24 ± 10.37^a
73MA10	$37.65 \pm 2.70^b{}_2$	$9.87 \pm 0.60^b{}_2$	$49.36 \pm 22.89^b{}_1$
73MA12	37.02 ± 1.90^b	9.81 ± 0.68^b	27.41 ± 26.27^b
73MA14	31.89 ± 2.38^d	7.79 ± 0.82^c	21.20 ± 18.69^b
73MA16	$35.53 \pm 2.24^{b,d}$	9.55 ± 0.59^b	27.23 ± 22.18^b
73MA18	33.29 ± 3.07^d	8.98 ± 0.78^b	12.70 ± 9.45^b

[a] Different letters and subscript numbers within the same column are significantly different ($P < 0.05$).
[b] Results are expressed as the mean $\pm$ SD ($n = 7$).
[c] Subscript numbers are differences among 10% plasticizer only.
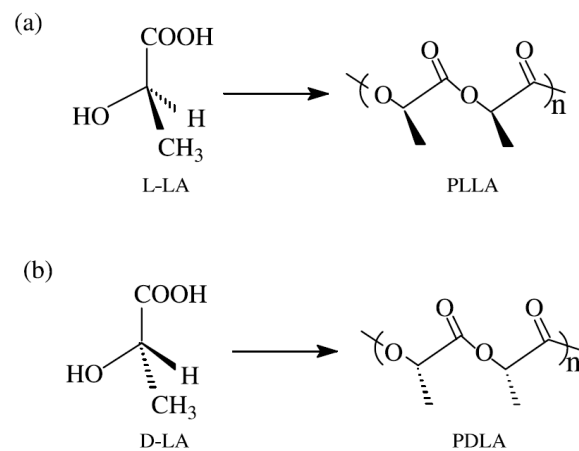
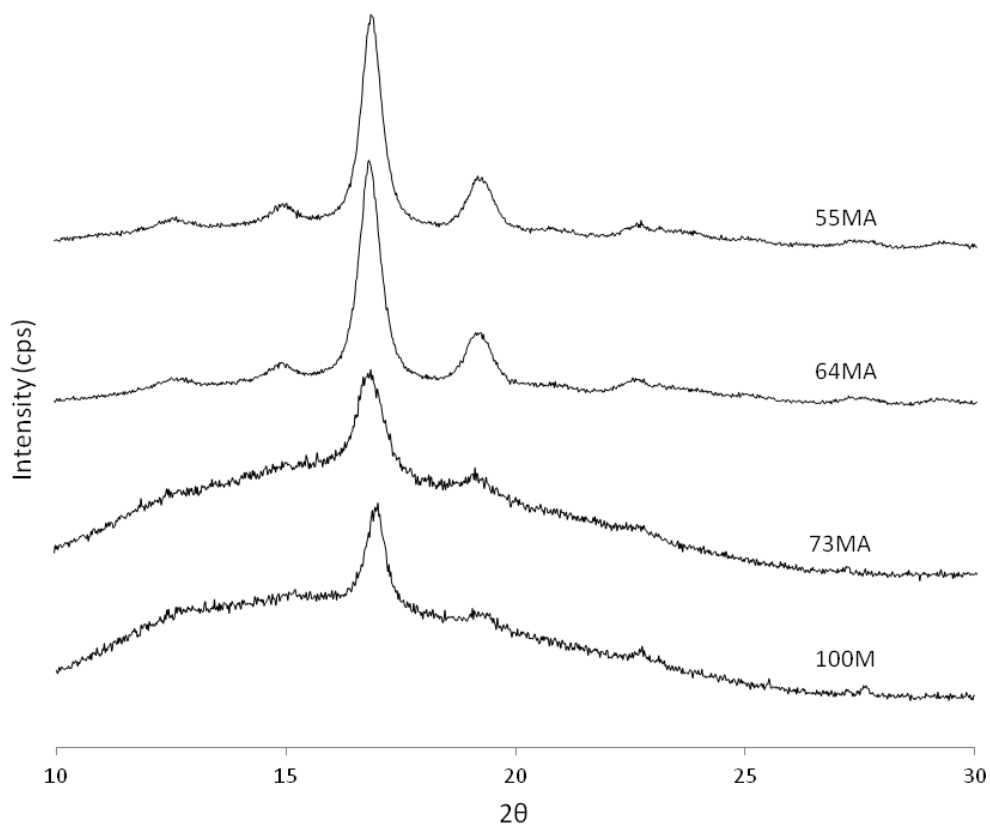Scheme 2.1 Molecular structure of (a) PLLA and (b) PDLA.

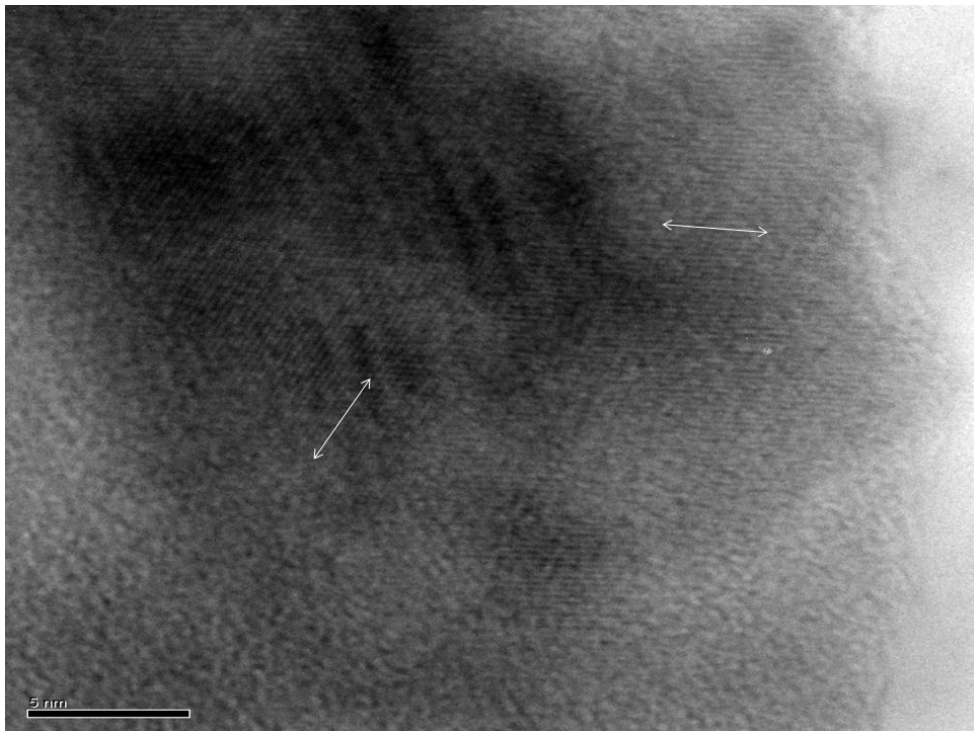Figure 2.1 Wide-angle X-ray diffraction patterns of the four different PLA films.
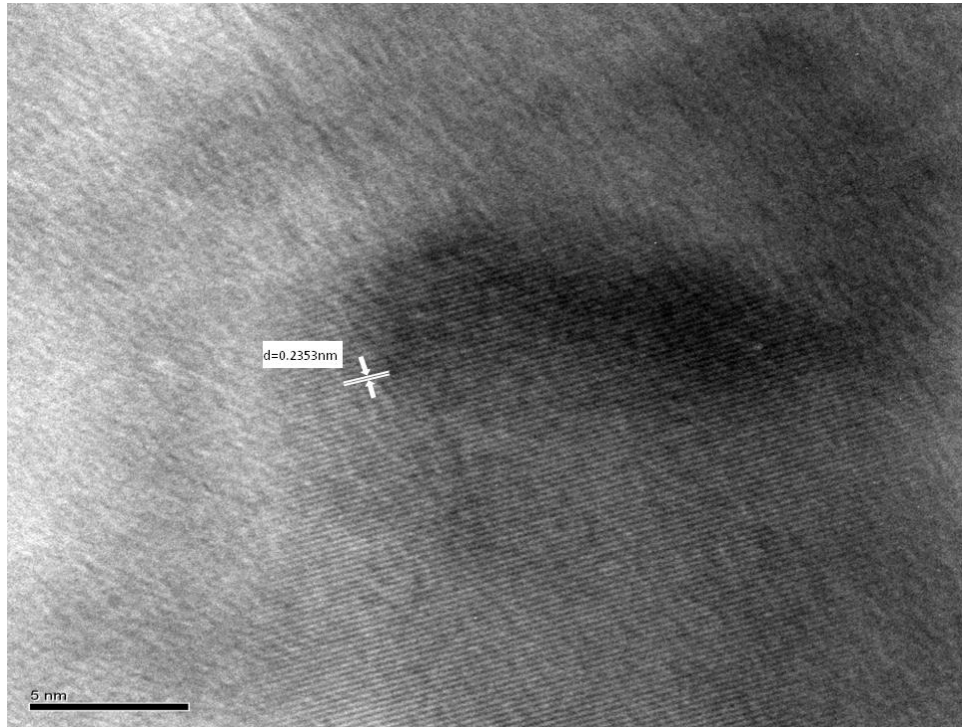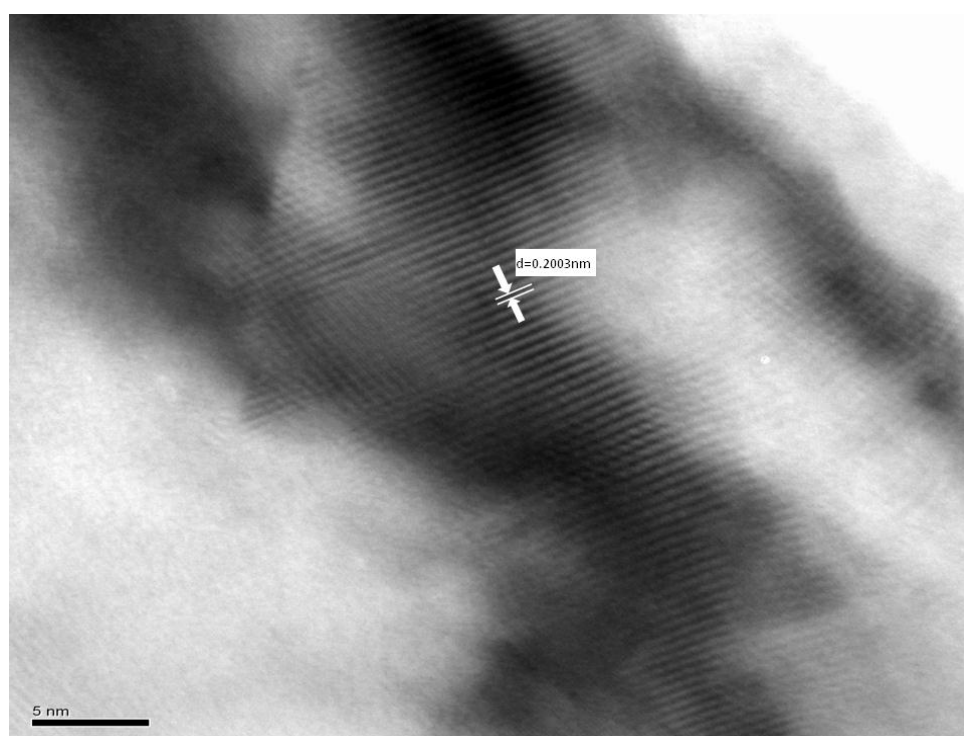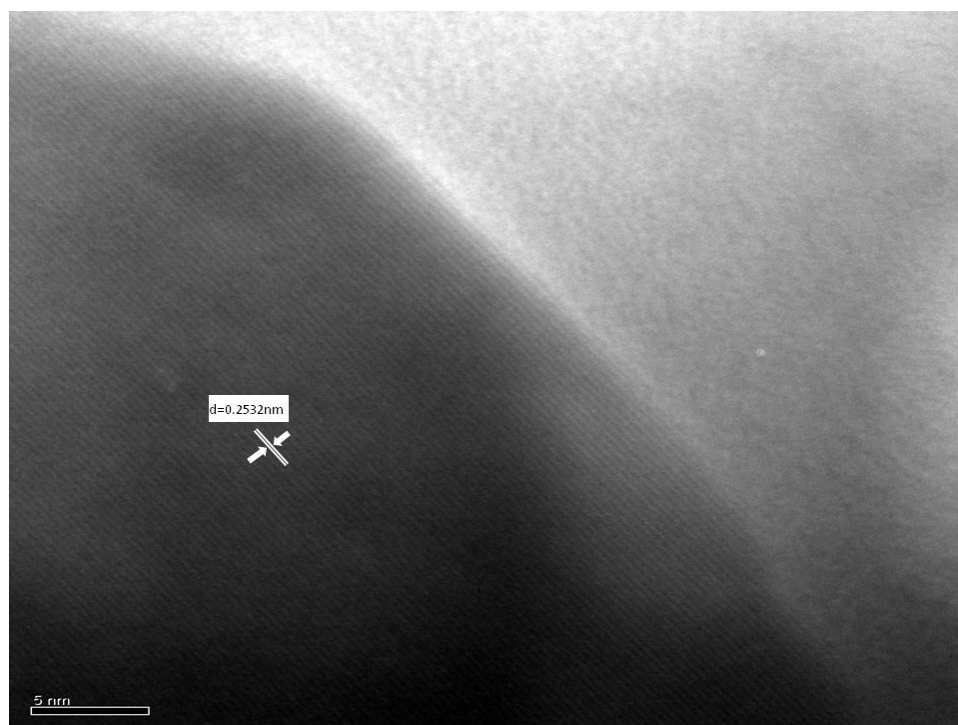
Figure 2.2 TEM images of PLA 55MA
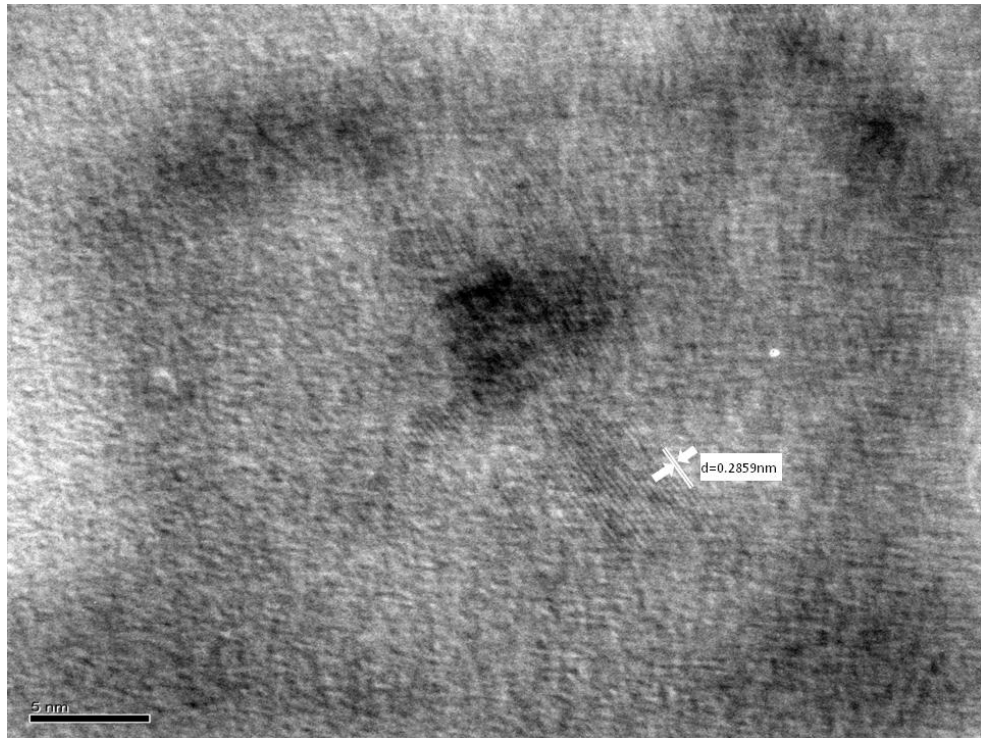
Figure 2.3 TEM images of PLA 64MA
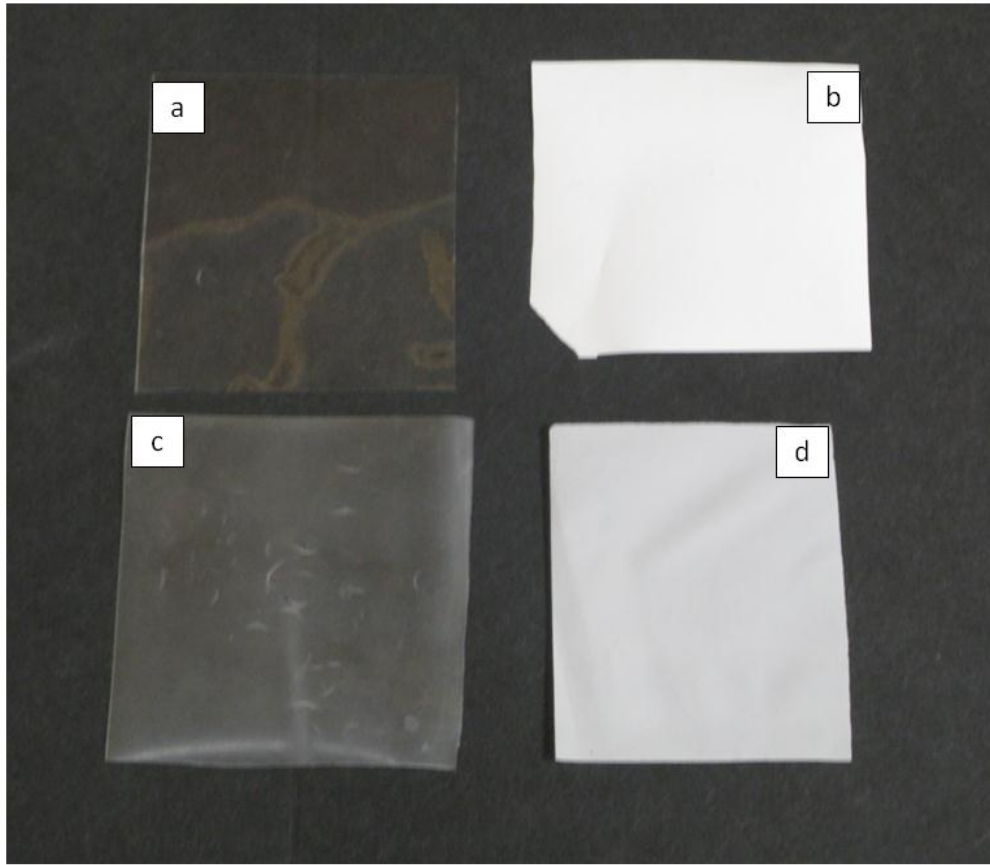
Figure 2.4 TEM images of PLA 73MA

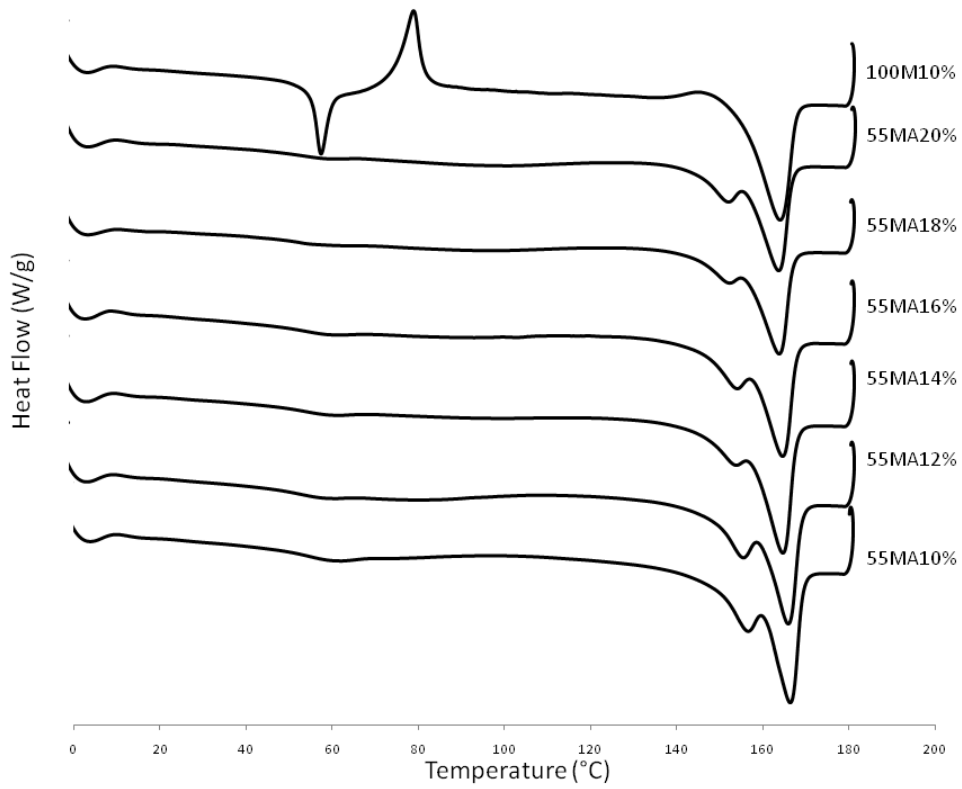Figure 2.5 Photographic images of PLA (a) 100M; (b) 55MA; (c) 73MA; (d) 64MA.

Figure 2.6 DSC thermograms of the 55MA PLA films initial heating.
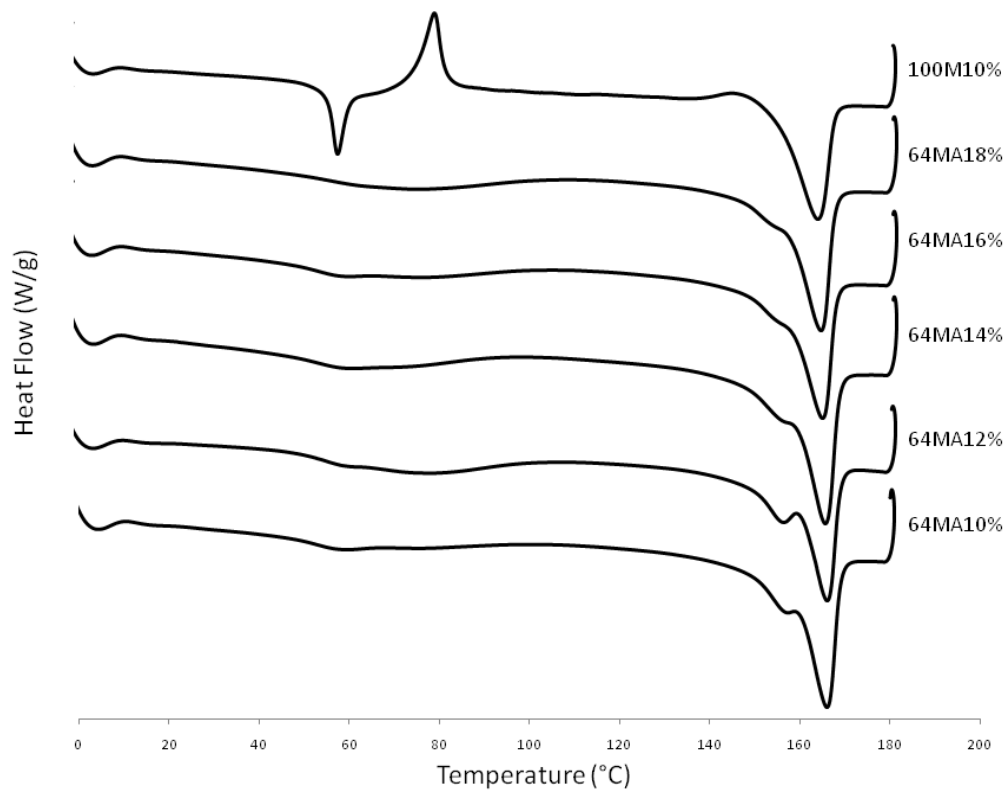The amount of plasticizer is shown as 10 to 20%.

Figure 2.7 DSC thermograms of the 64MA PLA films initial heating. The amount of plasticizer is shown as 10 to 18%.

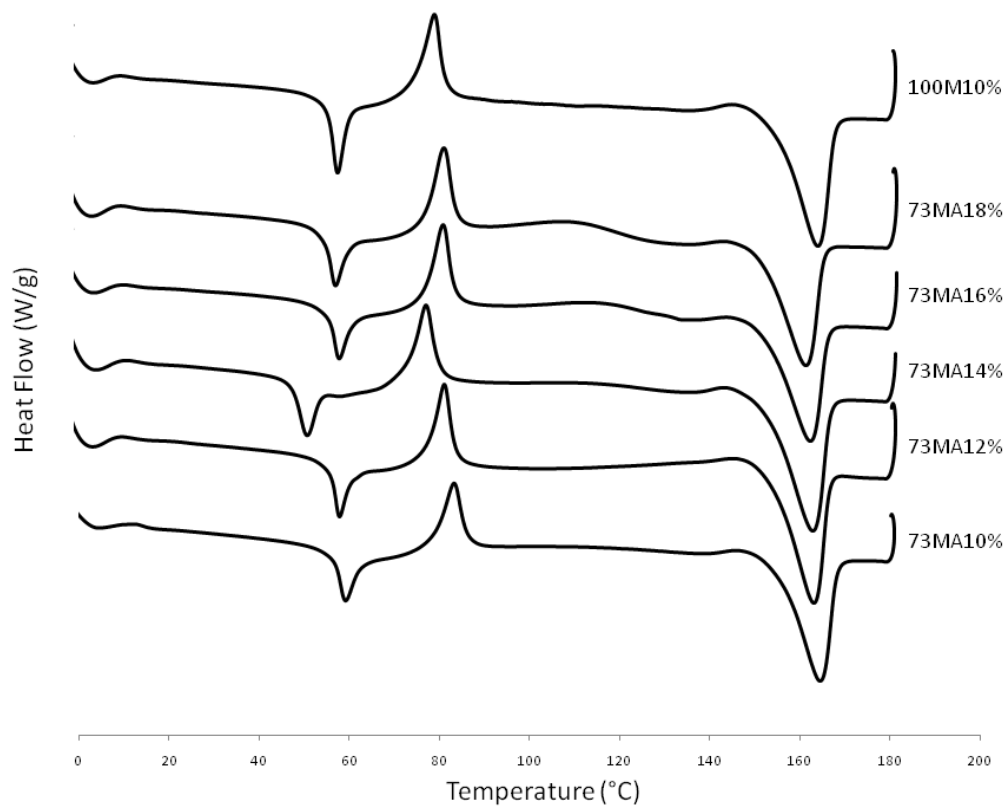Figure 2.8 DSC thermograms of the 73MA PLA films initial heating.
The amount of plasticizer is shown as 10 to 18%.
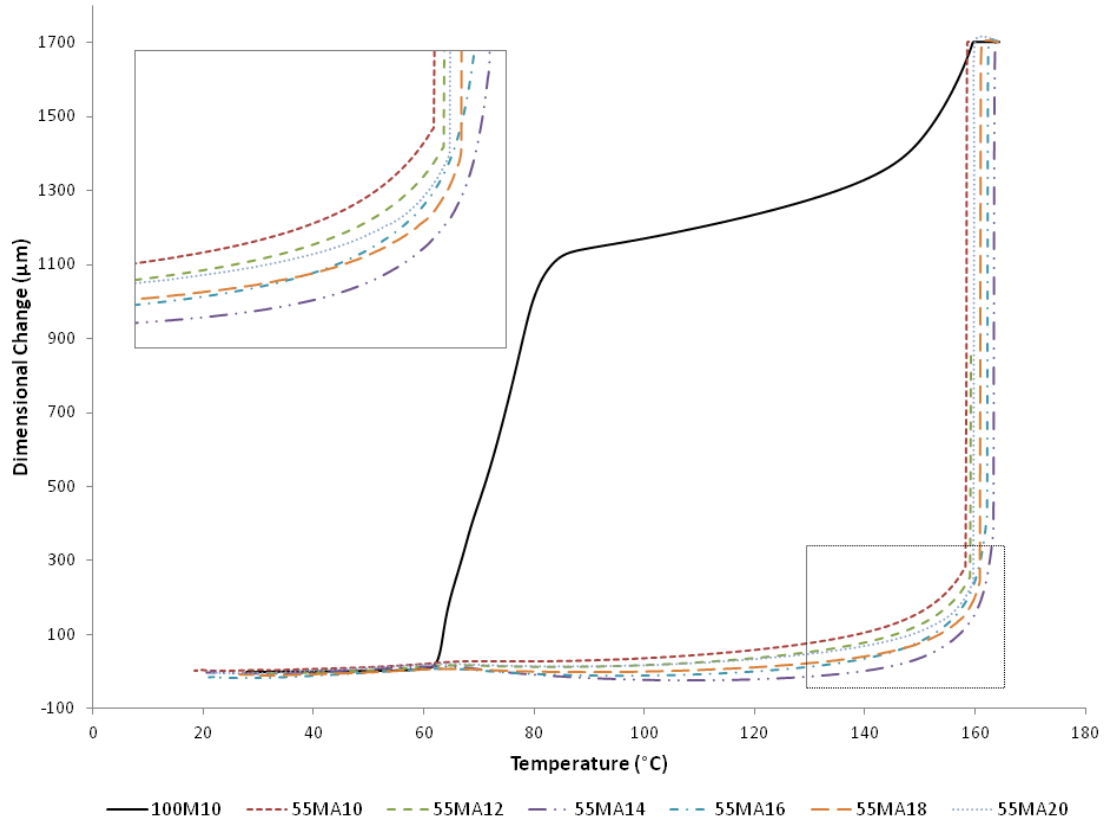
Figure 2.9 TMA thermograms of 55MA PLA.
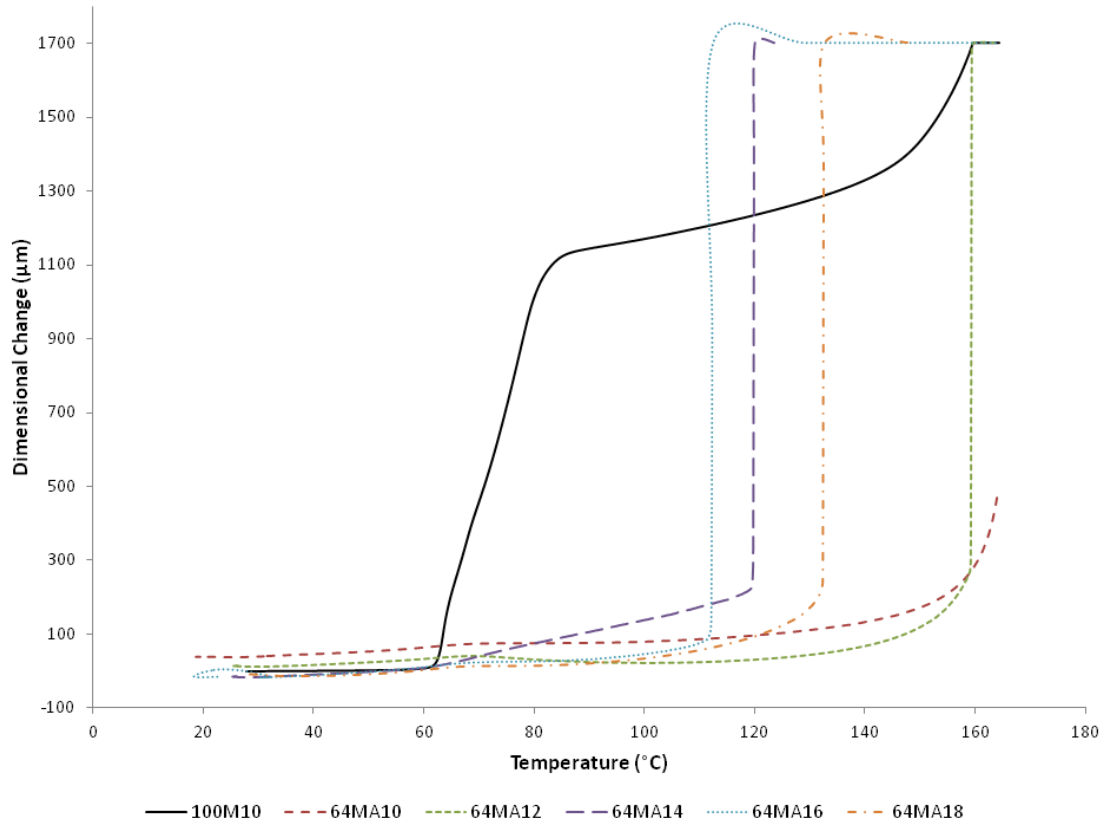
Figure 2.10 TMA thermograms of 64MA PLA.
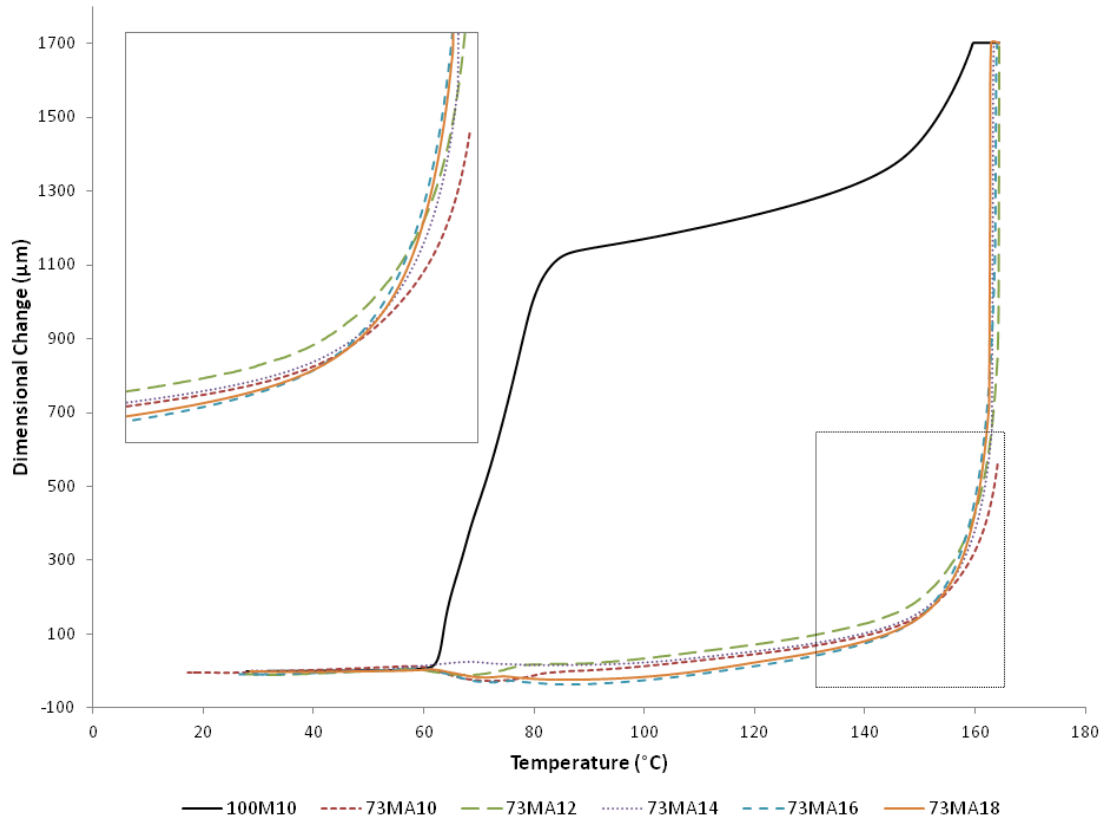
Figure 2.11 TMA thermograms of 73MA PLA.
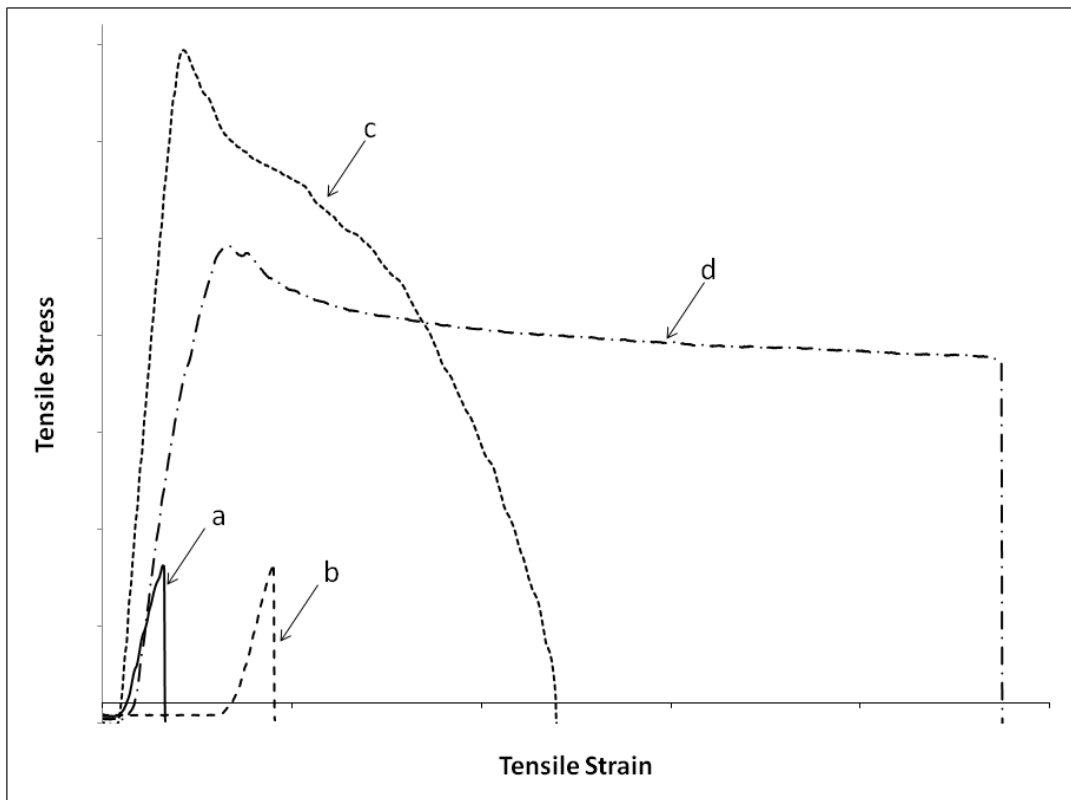
Figure 2.12 Stress Strain curves of PLA film (a) 55MA; (b) 64MA; (c) 100M; (d) 73MA.
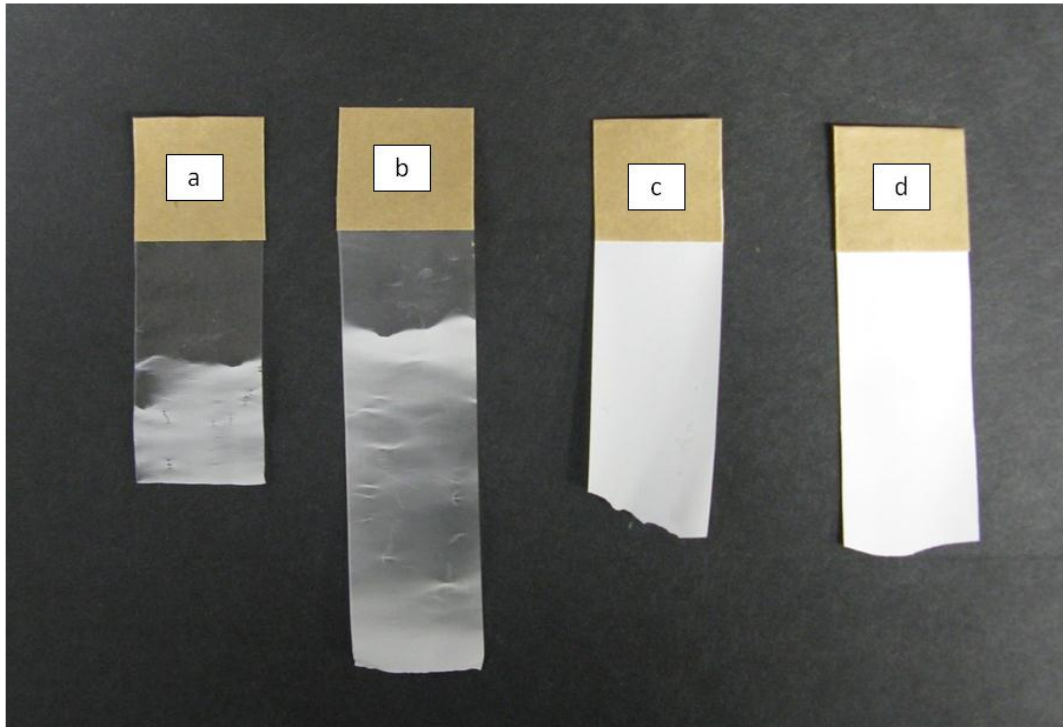
Figure 2.13 Tensile specimens after testing (a) 100M; (b) 73MA; (c) 64MA; (d) 55MA.
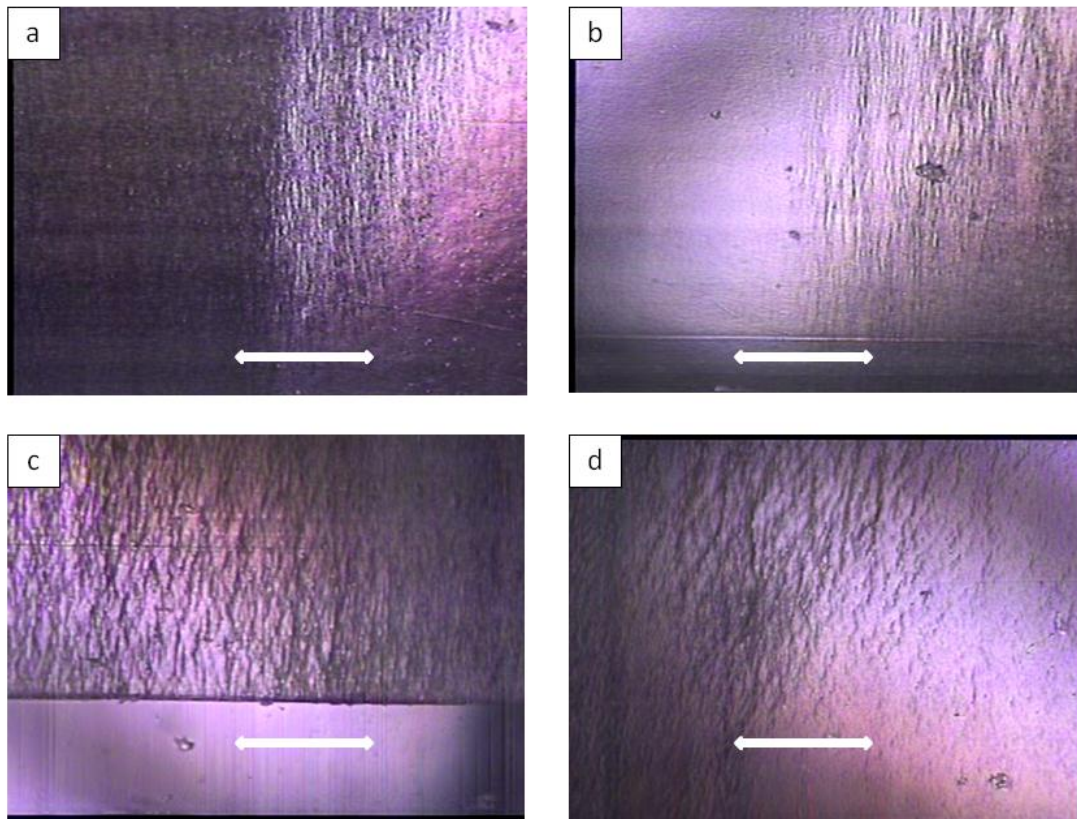
Figure 2.14 POM images of crazing at 40x magnification, (a), (c) 73MA; (b), (d) 100M. Arrows indicate direction film sample was pulled during tensile tests.
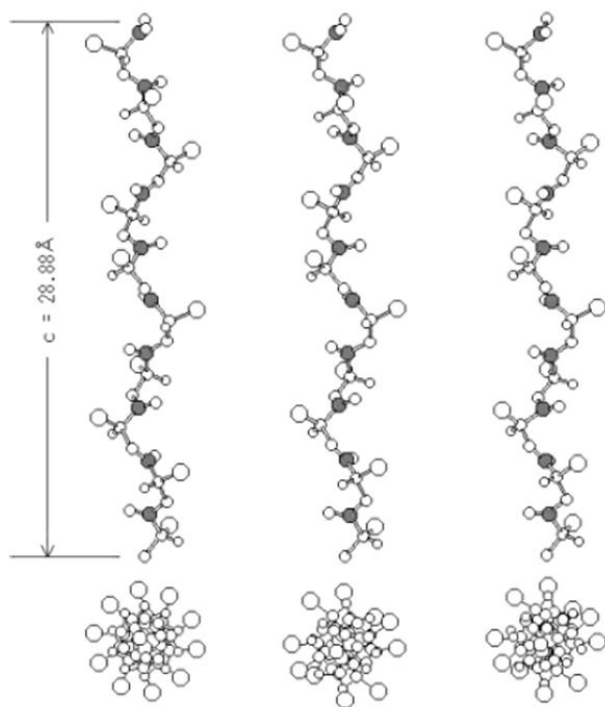
Figure 2.15 Helical model structures. Shaded circles denote carbonyl carbon atoms and the outer large circles denote methyl groups.
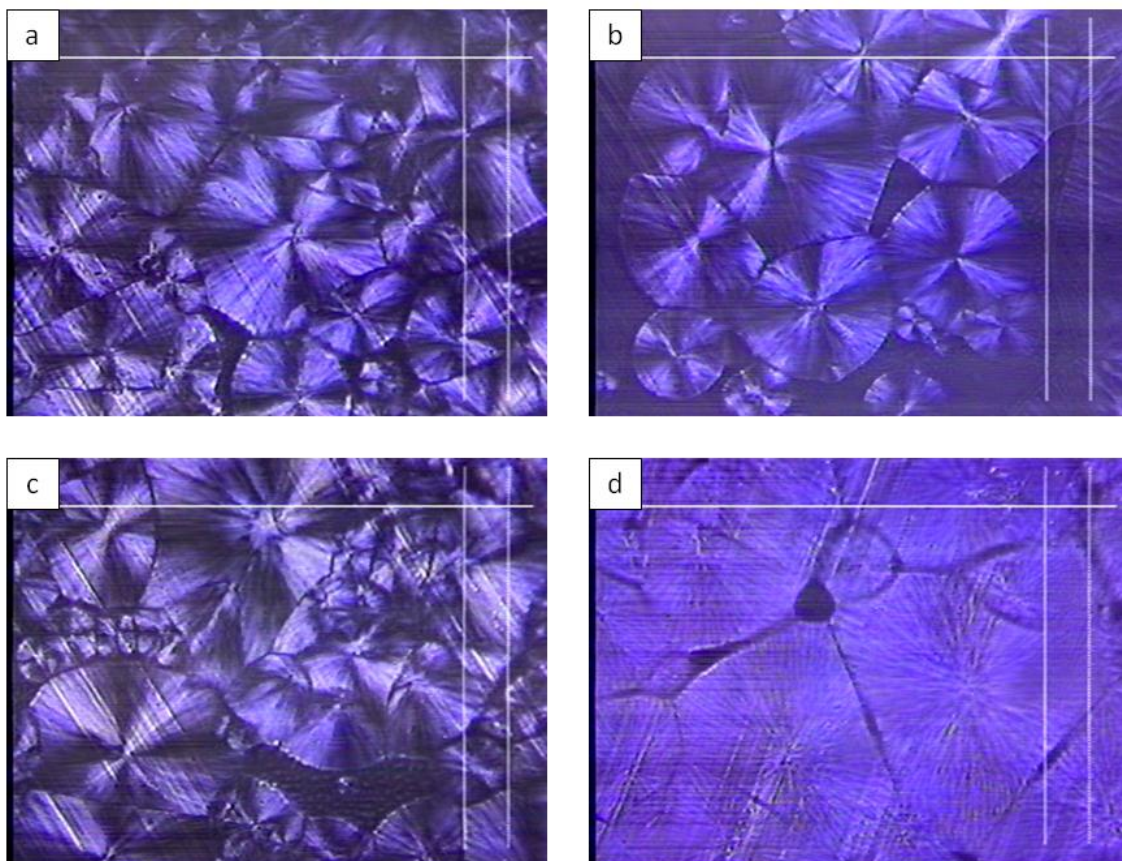
Figure 2.16 Spherulite images obtained by POM from DSC slow cooled samples (a) 100M10; (b) 73MA10; (c) 64MA10; (d) 55MA10.
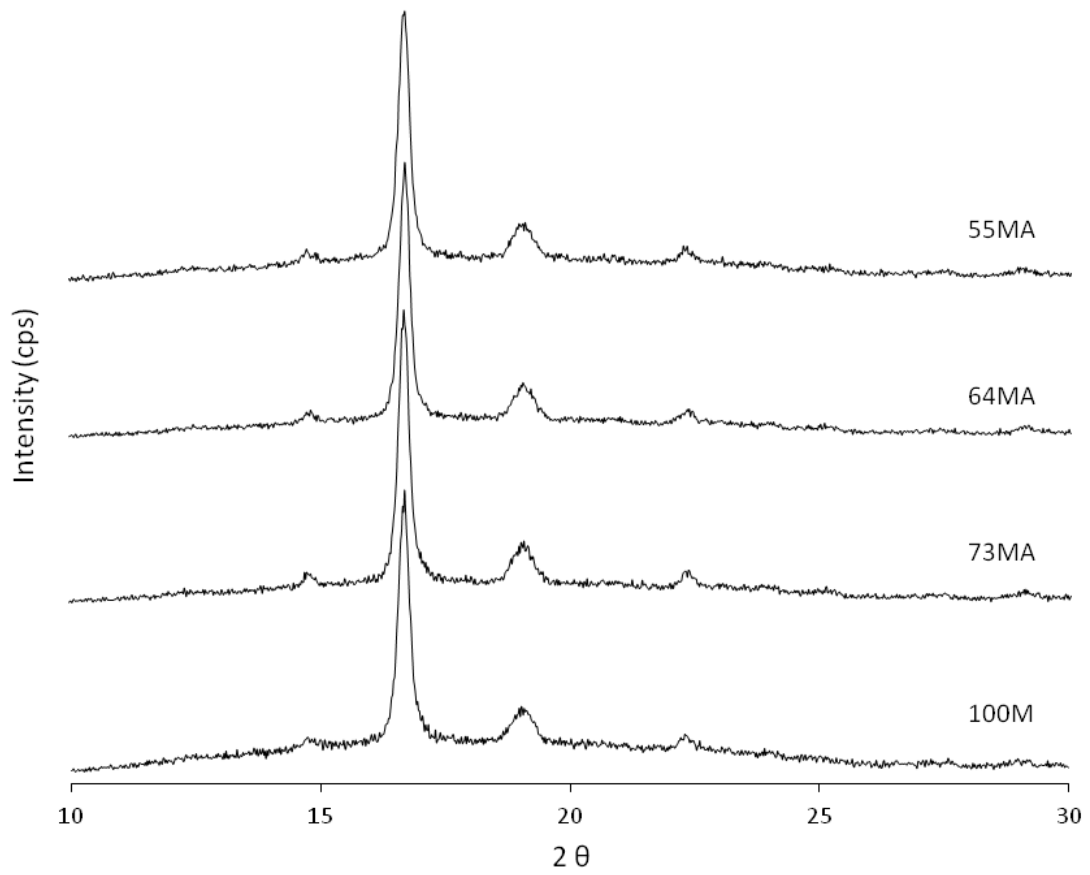
Figure 2.17 Wide-angle X-Ray diffraction patterns of film after heating to melt.

REFERENCES CITED

1. Garlotta, D. J Polymer Environ 2001, 9, 63.

2. Mano, J.; Gomez-Ribelles, J.; Alves, N.; Salmeron-Sanchez, M. Polymer 2005, 46, 8258.

3. Drmright, R.; Gruber, P.; Henton, D. Adv Mater 2000, 12, 1841.

4. Sin-Lin Yang.; Zhi-Hua, W.; Yang, W.; Yang, M. Polymer Test 2008, 27, 957-963.

5. Jong-Whan Rhim; Seok-In Hong; Chang-Sik Ha Food Sci. & Tech. 2009, 42, 612-617.

6. Pezzin, A.; Alberda, G.;Zavaglia, C.; Ten brinke, G.; Duek, E. J Appl Polym Sci 2003, 88, 2744.

7. Pillin, I.; Monterelay, N.; Grohens, Y. Polymer 2006, 47, 4676.

8. Furuhashi, Y.; Wakuda, H.; Yoshie, N.; Seisan-kenkyu 2006, 58, 353.

9. Byun, Y.; Kim, Y. T.; Whiteside, S. J Food Eng 2010, 100, 239.

10. Jyh-Ping H.; Sung-Hwa, L. Euro Polym J 2005, 41, 1036-1042.

11. Shujin, W.; Jinglin, Y.; Jiungau, Y. Carbohydr Polym 2008, 74, 731-739.

12. Lim, L.T.; Auras, R.; Rubino, M.; Prog Polym Sci 2008, 33, 820-852.

13. Sodergard, A.;Stolt, M. Prog Polym Sci 2002, 27, 1123.

14. Byun, Y.; Whiteside, S.; Thomas, R.; Dharman, M.; Hughes, J.; Kim, Y.T. J   Appl Polym Sci.

15. Furuhashi, Y.; Wakuda, H.; Yoshie, N.; Seisan-kenkyu 3006, 58, 353.

16. JT Baker.com

17. Xiao, H.; Liu, F.; Yeh, J. J Appl Polym Sci 2010, 117, 2980.

18. De Santis, P.; Kovacs, J. Biopolymers 1968, 6, 299.

19. Hoogsteen, W.; Postema, A. R.;Pennings, A. J.; Ten Brinke, G.; Zugenmaier, P. Macromolecules 1990, 23, 634.

20. Cartier, L.; Okihara, T.; Ikada, Y.; Tsuji, H.; Puiggali, J.; Lotz, B. Polymer 2000, 41, 8909.

21. Ting, Ting, L.; Xiang, Yang, L.; Chaobin, H. Polymer 2010, 51, 2779-2785.

22. Brizzolara, D.; Cantow, H. J.; Diederichs, K.; Keller, E.; Domb, A. J. Macromolecules 1996, 29, 191.

23. Slager, J.; Brizzolara, D.; Cantow, H.; Domb, A. Polymer Adv Technol 2005, 16, 667.

24. Fischer, E. W.; Sterzel, H. J.; Wegner, G.; Kolloid-Z u Z. Polymer 1973, 251, 980.

25. Ahmed, J.; Varshney, S.; Zhang, J.; Ramaswamy, H. J Food Eng 2009, 93, 308.

26. Selke, S.; Culter, J. D.; Hernandez, R. Plastics Packaging 2nd ed.; Hanser Publications: Cincinnati, 2004; Chapter 3.

27. Stuik LCE. Physical ageing in amorphous polymers and other materials. New York: Elsevier, 1978.

28. Alfonso, G. C.; Pedemonte, E.; Pontzetti, L. Polymer 1979, 20, 104.

29. Carpento, L.; Marsano, E.; Valeti, B.; Zanardi, G. Polymer 1992, 33, 3865-3872.

30. Tan, S.S.; Su, A.U.; Luo, J.;Zhou, E.L. Polymer 1999, 40, 1223.

31. Hao, T.; Pintauro, P.N. 1999, 35, 1023-1035.

32. Sanchez-Garcia, M.; Gimenez, E.; Lagaron, J. Carb Polymer 2008, 71, 235.

33. Galeski, A. Prog Polymer Sci 2003, 28, 1643-1699.

34. Park, S.; Todo, M.; Arakawa, K.; Koganemaru, M. Polymer 2006, 47, 1357.

35. Michler, G.; Baltá-Calleja, F. Mech Prop of Polymers Based on Nanostructure and Morphology. T&F Group: Boca Raton, 2005; Chapter 5.

36. Miller, E. Introduction to Plastics and Composites. Marcel Dekker Inc: New York, 1996; Chapter 7.

37. Paragkumar, T.; Edith, D.; Jean-luc, S. Appl Surf Sci 2006, 253, 2758.

38. Huda, M.; Yasui, M.; Mohri, N.; Fujimura, T.; Kimura, Y. Mater Sci Eng A 2002, 333, 98.

39. Pillin, I.; Montrelay, N.; Grohens, Y. Polymer 2006, 47, 4676-4682.

40. Bor-Kuan, C.; Hia-Hsu, S.; Shu-Chuan, C.; Antonia, F. C. Polymer 2010, 51, 4667-4672.

41. Yamane H.; Sasai, K. Polymer 2003, 44, 2569-2575.

42. Hong, X.; Cuiqing, T.; Muhuo, Y.; Polymer 2006, 47, 3922-3928.

43. Jianming, Z.; Yongxin, D.; Harumi S.; Hideto, T.; Isao, N.; Shouke, Y.; Yukihiro, O. Macromolecules 2005, 38, 8012-8021.

44. Hoogsten, W.; Postema, A.R.; Pennings, A.J.; tenBrinke, G.; Zugenmaier, P. Macromolecules 1990, 23, 634.

45. Seok, Kim.; Soo-Jin Park. Journal of Colloid and Interface Science 2009, 332, 145-150.

CHAPTER THREE

THE EFFECTS OF CHLOROFORM AND ACETONITRILE SOLVENT MIXTURE

ON THE PROPERTIES OF SOLVENT CAST POLY-LACTIC ACID (PLA) FILM

ABSTRACT

The objective of this study was to investigate the effects of various solvents on the crystallinity and thermal expansion stability of PLA film. Four different PLA films were produced by the solvent casting technique; PLA in chloroform (100C), 70% chloroform: 30% acetonitrile (73CA), 60% chloroform: 40% acetonitrile (64CA) and 50:50 chloroform acetonitrile (55CA). 64CA had the highest % crystallinity at 48.1%. 73CA showed the least amount of % crystallinity. With this increase in crystallinity, 64CA had improved thermal expansion stability with no accumulated dimensional changes. 73CA with low % crystallinity showed improvements as well. Wide angle x-ray diffraction identified multiple crystalline structures for all films with acetonitrile. The mechanical property tests revealed that 100C and 73CA were ductile while 55CA and 64CA were brittle. More haze was seen in the more crystalline 55CA and 64CA compared to 73CA and single solvent 100C. 73CA had increased thermal expansion stability with the addition of acetonitrile to increase crystallinity, yet behaved like an amorphous film with improved flexibility.

INTRODUCTION

Poly (lactic acid) (PLA) is a thermoplastic, compostable, and biocompatible polymer derived from renewable resources such as corn, sugar beets, potato starch, and cheese whey.[1] It has been used in the biomedical field for wound closures, prosthetic implants, bone surgery and controlled-release systems.[2] With the help of new technologies and large scale production, PLA is being used in other commodity areas such as packaging, textiles and composite materials.[3] Its application in the packaging industry, however, has certain limitations. A low deformation at break, high modulus, hydrophilic properties and low heat resistance has limited its application primarily to rigid thermoformed packaging.[4,5]

The solvent-casting technique is being widely used in biopolymer film preparation.[6] This technique involves solubilization, casting, and drying. PLA is known to be highly soluble in solvents such as methylene chloride, benzene, chloroform, and dioxane.[7,8] Each solvent influences film properties differently. For instance, chloroform induces a greater chain mobility of the polymer and dioxane causes a rough surface of the film due to its slow evaporation rate.[9,10] PLA has low solubility in solvents such as toluene, acetone, acetonitrile, methanol, and ethyl acetate.[11] PLA films cast with toluene, acetone and ethyl acetate showed an increased hydrophobicity and a surface segregation.

Crystallinity of the film is affected by solvent induced conformational changes.[11]

Previous studies have reported that PLA solutions in chloroform and methylene chloride resulted in a random conformation of the molecules.[12] The crystallization of PLA was based on intramolecular interaction rather than intermolecular interactions.[7] Homocrystallization occurred when PLA was dissolved in chloroform due to the strong interaction between PLA and the solvent. However, stereocomplex crystallization occurred when PLA was dissolved in methanol due to the strong interaction between PLA chains.[11] In addition, there was swelling and conformational changes on the surface of the film when PLA was dissolved in a poor solvent.[13] Treating PLA with a mixture of chloroform and methanol increased film crystallinity and caused hazy, milky white films.[7]

Based on previous research, it is evident that the solvent can change PLA film properties by changing its crystallinity. Few studies have been performed about the effect of solvent on the ductility and crystallinity of PLA. Also, no research has been reported about the effect of solvent on the thermal expansion stability of PLA correlated with its crystallinity. The main objective of this research was to produce PLA films with different solvent mixtures that had both good thermal expansion stability and flexibility. Other aspects such as film crystallinity, optical and thermal properties were also examined.

MATERIALS AND METHODS

Materials

PLA resin (4032D, L-lactide/D-lactide=99/1) was donated from Nature Works, LLC (MN, USA). Polyethylene glycol 400 (PEG 400) was purchased from Sigma Aldrich (MO, USA). Chloroform was purchased from EM Science (NJ, USA). Acetonitrile was purchased from VWR International (PA, USA). Chloroform was purchased from J. T. Baker (USA). All solvents used in this research were HPLC grade.

Film preparation

PLA films used in this study were prepared by the solvent-casting technique.[8] The PLA resin was preconditioned in a drying oven at 40°C for 48 h to reduce the moisture content prior to use. PLA (30 g) and PEG 400 (3 g) were dissolved in 200 mL of solvent. In this study, PEG 400 was used as a plasticizer. The solution was stirred for 12 h at room temperature. The solvents and solvent mixtures used in this research were: (1) chloroform (100C) (2) chloroform: acetonitrile = 50:50 (55CA) (3) chloroform: acetonitrile = 60:40 (64CA) (4) chloroform: acetonitrile = 70:30 (73CA). Approximately 35 mL of each film forming solution was cast onto a BYTAC® (Norton Performance Plastics Corporation, Wayne, NJ, USA) coated 157 mm x 356 mm glass plate, which was formed utilizing a customized film applicator. The cast films were dried at room

temperature and then peeled from the glass plate.

Wide angle X-ray diffraction (WAXD)

X-ray diffraction scans were recorded using a copper anode X-ray tube (Cu-K$_\alpha$ radiation, λ = 1.5418Å) (Rigaku Ultima IV Tokyo, Japan). The samples were scanned from the start angle of 10° to the stop angle of 30° with a continuous scan mode at a scan speed of 0.200 deg./min.

Thermal expansion stability

The dimensional change and the onset temperature of the films were determined by a Thermomechanical Analyzer (TMA) as a function of temperature (Model 2940, TA instruments). Data from TMA determined the thermal expansion stability of the films. The film samples for TMA were 0.159 cm wide and 1.27 cm long. The samples were clamped on both the ends with split aluminum balls and heated from 25 to 165 ^{o}C at the rate of 10 ^{o}C/min and 0.05 N forces with a constant nitrogen flow throughout.

Thermal properties

The glass transition temperature (T$_g$), crystallization temperature (T$_c$), and melting temperature (T$_m$) of the PLA films were measured using a Differential Scanning

Calorimeter (Model 2920 Modulated DSC, TA instrument, USA). Specimens weighing 2 to 3 mg were heated at the rate of 10 ^{o}C/min from 20 to 180 ^{o}C with a constant nitrogen flow throughout. The percentage of crystallinity (X_c) of the PLA films was evaluated according to the following equation [14]:

$$X_c\ (\%) = (\Delta H_m - \Delta H_c)/\ \Delta H^c_m \times 100$$

Where ΔH_m is the enthalpy of fusion, ΔH_c is the enthalpy of crystallization, and ΔH^c_m is the enthalpy of fusion of purely crystalline PLA (93.1 J/g). [14-16]

Mechanical properties

The tensile strength (TS), elongation at break (%E), and Young's modulus (ε) of the PLA films were measured using an Instron Universal Testing Machine (Model 4201, Instron Corp., Canton, MA, U.S.A.) according to the ASTM standard method D882-88. Specimen samples, 10 cm x 2.54 cm, were conditioned for 48 h at 23 ± 0.5^{o}C and 50% RH in a constant temperature and humidity chamber. Initial grip separation and cross-head speed were set at 5 cm and 25 cm/min, respectively. The values presented were the average of seven measurements.

Optical properties

Haze, transparency and clarity of the PLA films were collected using a BYK Gardner Haze Gard Plus (Model 4725, Germany)

Statistical analysis

Statistical significance was determined by analysis of variance (ANOVA) using SAS (version 9.1, SAS Institute Inc., NC). Significance was defined at a level of $p < 0.05$.

RESULTS AND DISCUSSION

Crystallinity

The X-ray diffraction profiles of the PLA films are shown in Figure 1. PLA-MA had various diffraction peaks at 13°, 15°, 17°, 19° and 23°, indicating the presence of different crystalline structures compared to 100C with noticeable peaks at $17°$ and $19°$. PLA is much more soluble in chloroform than in acetonitrile. It has been reported that stereocomplex crystallization occurs when PLA is dissolved in poor solvents due to the strong interaction between PLA chains.[13] Thus, acetonitrile may have caused the production of different crystalline structures in the mixed solvent films. Comparing these results with the DSC results, 64CA had the highest % crystallinity, 48.1, and the second highest enthalpy of fusion (ΔH_m), which is the energy required for melting the crystals (Table 1). Casting PLA with a solvent mixture in which PLA solubility varies increased film crystallinity.[7]

100C showed diffraction peaks at 17° and 19° with a % crystallinity of 17.1. Comparing 100C with the solvent mixtures, it is obvious that the presence of acetonitrile promotes more formation of crystalline structures. Acetonitrile is a poor solubilizing solvent for PLA, but when added to a good solvent like chloroform it interacts with the polymer chain thereby making solvent-polymer interaction stronger, leading to crystallization.[7] Crystallinity of cast films is also affected by the boiling point (bp) of the

solvent.[17] Solvents with high bp take more time to evaporate, thereby facilitating the growth of crystals, while solvent with low bp limits the crystallization time.[18] Acetonitrile has a higher bp than chloroform and took more time to evaporate, thus leading to more crystallization in 55CA and 64CA.

PLA can crystallize in α, β, γ-forms depending on the processing conditions.[19-22] PLA also undergoes a conformational change in the stereocomplex formation from a 10_3 helices (α form, major 2θ: 17, 19, 22) for enantiomeric PLA chains to a 3_1 helices (β-form, major 2θ: 12, 25) in the stereocomplex.[23,24] In this research, 100C crystallized in α form and there was no conformational change from α to β-form by replacing solvent. Film's 55CA and 64CA however showed small diffraction peaks at 13°, 23° and 28° indicating a possible conformational change to β-form (Figure 1). The increase in peak height at 2θ 17° and 19° for 73CA indicates that acetonitrile might increase the crystal perfection of the polymer. These dominant diffractions demonstrated that there were different crystalline structures for the solvent mixtures.

Thermal expansion stability

A key objective of this research was to increase the thermal expansion stability of PLA films prepared with various solvents. A Thermomechanical Analyzer (TMA) was used to investigate the thermal expansion stability of the PLA films by measuring the

behavior of dimensional change of the film (Table 2 and Figure 2). The testing method

for the thermal expansion stability of PLA products has not been fully established. Our

rational assumption about thermal expansion stability is that higher onset temperature

and less dimensional changes represent better thermal expansion stability of the films.

The molecules in the amorphous region undergo segmental motion which leads to

film expansion.[18] With the application of heat, films with high crystallinity have minimal

expansion whereas films with low crystallinity or higher amorphousness have more film

expansion. There was late onset temperature and small dimensional change in the 55CA

and 64CA compared to 100C. Films that included small amounts of acetonitrile, (73CA)

also had lower linear thermal expansion. 64CA did not see an expansion coefficient

whereas 100C was at 19.7. Therefore, the solvent mixtures with higher amounts of

acetonitrile were the most heat stable films. This may due to their having the highest %

crystallinity. Although 100C and 73CA have similar % crystallinity, it is assumed that a

network of crystals was made during casting for 73CA.

Thermal properties

DSC thermograms of the four PLA films are depicted in Figure 3. The only films

to not show any T_c were 64CA and 55CA. The lack of a crystalline peak for 55CA and

64CA indicates that the polymer reached its maximum crystallinity early in the casting

process and was not enhanced by the presence of heat. It is assumed that a double melting peak for 55CA and 64CA is attributed to the melting of multiple crystalline structures. Previous research noted that the lower temperature melting peak was attributed to the melting of subsidiary, thinner lamella while the higher temperature and more predominant melting peak was due to the melting of dominant thicker lamellae.[25-27] It is assumed that the addition of acetonitrile promotes crystal growth which is confirmed by X-ray scattering. This can be confirmed by the fact that 55CA having the most amount of acetonitrile, no enthalpy of crystallization and a % crystallinity of 46 (table 1). Although the heats of fusion and crystallization temps differed, T_g showed little change. Tg depends on the structural arrangement of the polymer and corresponds to the liquid-like motion of much longer segments of molecules during onset. This requires more free volume than the short range excursions of atoms in the glassy state.[28]

Mechanical properties

Increased crystallinity is a positive with regards to thermal properties but it adds rigidity and brittleness, thus diminishing mechanical ability.[29] In this research, there were significant differences in mechanical properties of the films. Films 64CA and 55CA showed the lowest tensile strength (TS), % elongation (%E), and Young's modulus (E) (Table 3). Previous studies have shown that spherulite size increased with an increase in

crystallinity and this increased spherulite size induced film brittleness.[30] In addition, %E was decreased by increasing % crystallinity in this research. 73CA had lowest % crystallinity (14.7%) and the highest %E (16.46%) while 55CA had the second highest % crystallinity (46%) and the lowest %E (3.36%). It has been noted that fracture toughness of semi-crystalline polymers can decrease with an increase in spherulite growth due to brittleness.[30]

Optical properties

Haze, transmittance and clarity of the four films are shown in Table 4. Significant differences were observed in the films. 64CA and 55CA had the highest amount of haze of 100% and 43.2 %, respectively. These two films also had the highest amount of crystallinity and was the contributing factor in higher haze due to larger spherulite size. Spherulites that are larger than the wavelength of visible light scatter light, thus making films containing large spherulites to look opaque. Transmittance of all the films was very similar with exception of 64CA at 44.56%. Clarity was high for 100C and 73CA as expected due to their clear appearance and low crystallinity. 55CA, however, had the highest clarity value at 97.89%. This could only be explained as the spherulites forming smaller crystals. Most often polymer films that are opaque have high crystallinity while

transparent polymer films have less crystallinity and less light diffraction due to small

spherulites.[17]

CONCLUSIONS

Crystallization in the film was affected by solvent and solvent mixture. 64CA showed the highest thermal expansion stability and the least dimensional change. The crystalline structure of 55CA and 64CA affected the mechanical ability of the films due to the spherulite size induced film brittleness. However, solvent-cast 100C and 73CA resulted in more ductility due to more tie molecule mobility and amorphousness from having fewer crystals. The films also showed varied haze due to the capability of the crystal structure to diffract light with different intensities. Film 64CA and 55CA showed the most amount of haze due to larger spherulite size as compared to 100C and 73CA. The results of this study show that at a ratio of 70:30, chloroform to acetonitrile with 10% plasticizer (73CA) one can produce a film that has the thermal properties of a high crystalline film and have the elongation and ductility of an amorphous film. The purpose of this research was to produce a film from solvent mixture that exhibited good thermal stability and flexibility.

Table 3.1

Thermal Properties of Solvent Cast PLA films

PLA film	T_g	T_C	T_m	$\Delta H_c (J/g)^a$	$\Delta H_m (J/g)^b$	% Crystallinity
73CA	43	95	164	26.58	40.3	14.7
64CA	46	-	164	-	44.82	48.1
55CA	53	-	164	-	42.67	46
100C	47	91	164	24.98	40.86	17.1

[a] ΔH_c : enthalpy of crystallization
[b] ΔH_m : enthalpy of fusion

Table 3.2

Dimensional Change of the four PLA films

PLA film	Thermal Expansion Coefficient (µm/°C)	Onset (°C)	Dimensional Change (µm)
73CA	3.709	152.81	447.3
64CA	0	159.2	23.18
55CA	0.133	150.46	77.91
100C	19.7	56.48	1707

Table 3.3

Mechanical Properties of the four PLA films

PLA film	Tensile Strain (MPa)	Young's Modulus (MPa)	% Elongation
73CA	50.77 ± 1.55^b	11.61 ± 3.47^a	16.46 ± 11.36^a
64CA	24.77 ± 1.01^d	6.30 ± 1.04^c	6.56 ± 11.36^{bc}
55CA	29.81 ± 2.31^c	9.3 ± 1.04^b	3.36 ± 0.45^c
100C	56.13 ± 2.18^a	10.06 ± 0.91^{ab}	12.94 ± 12.94^{ab}

[a] Different letters within the same column are significantly different $(P < 0.05)$
[b] Results are expressed as the mean ± SD $(n=7)$

Table 3.4

Haze Measurements of the four PLA films

PLA film	Haze (%)	Transmittance (%)	Clarity (%)
73CA	18.11 ± 6.05^c	94.33 ± 0.5^a	87.78 ± 0.83^c
64CA	100 ± 0.0^a	44.56 ± 2.3^c	2.09 ± 1.21^d
55CA	43.22 ± 5.63^b	91.56 ± 1.51^b	97.89 ± 0.33^a
100C	8.44 ± 1.33^d	94.56 ± 0.53^a	93.33 ± 1.58^b

[a] Different letters within the same column are significantly different $(P < 0.05)$

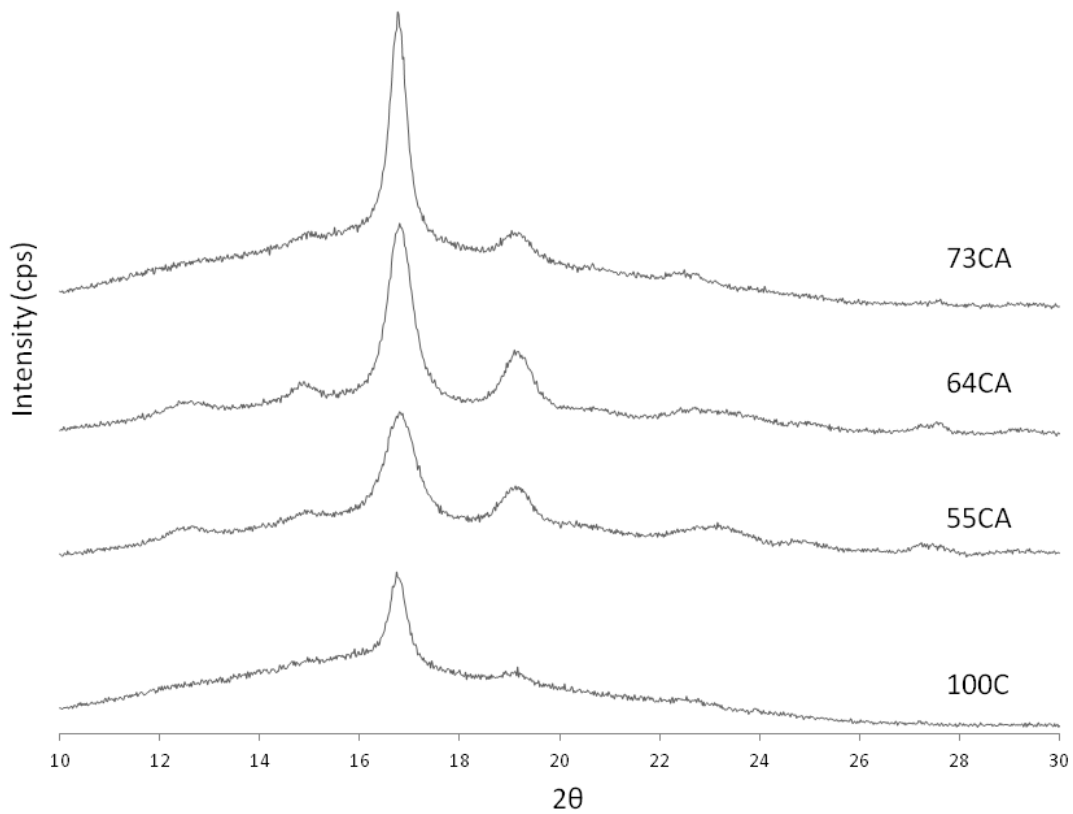[b] Results are expressed as the mean $\pm$ SD $(n=9)$

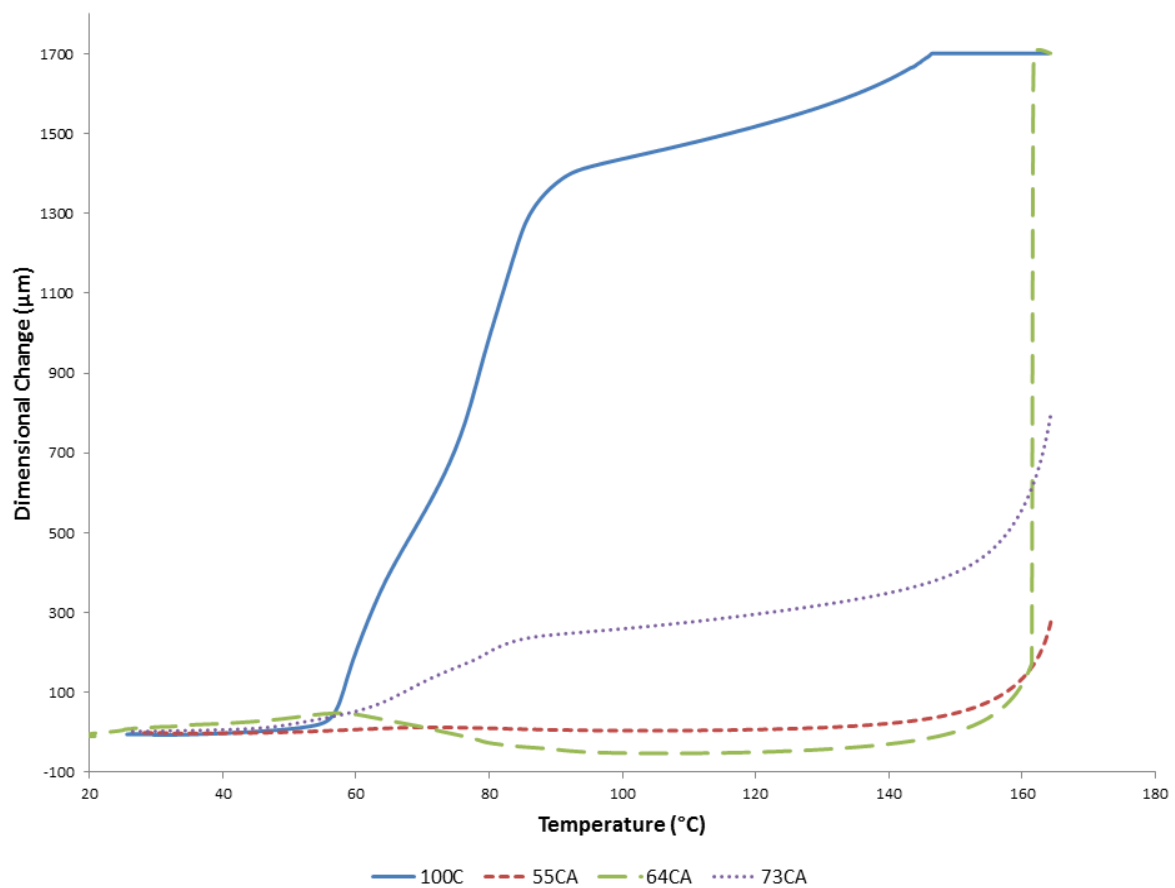Figure 3.1 Wide-angle X ray diffraction patterns of the four PLA films.

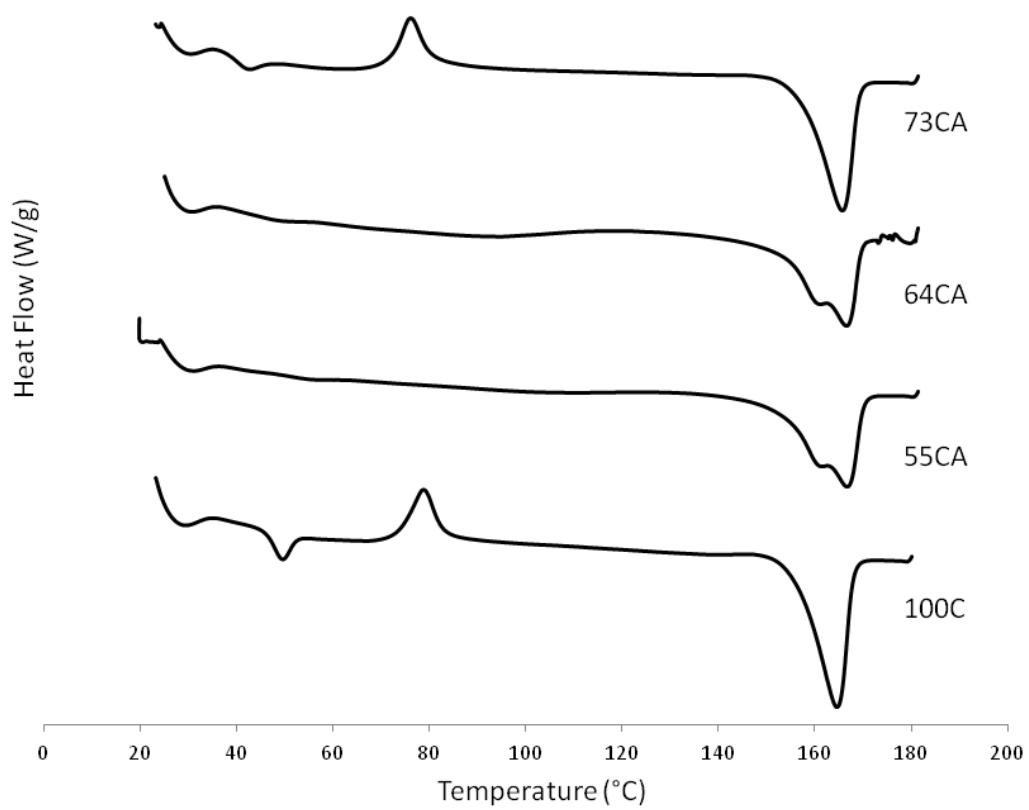Figure 3.2 TMA thermograms of the four PLA films.

Figure 3.3 DSC thermograms of the four PLA films initial heating.

REFERENCES CITED

1. Garlotta, D. J Polym Environ 2001, 9, 63.

2. Mano, J.; Gomez-Ribelles, J.; Alves, N.; Salmeron-Sanchez, M. Polym 2005, 46, 8258.

3. Drumright, R.; Gruber, P.; Henton, D. Adv Mater 2000, 12, 1841.

4. Pillin, I.; Monterelay, N.; Grohens, Y. Polym 2006, 47, 4676.

5. Okamoto, K.; Ichikawa, T.; Yokohara, T.; Yamaguchi, M. Eur Polym J 2009, 45, 2304.

6. Pezzin, A.; Alberda, G.; Zavaglia, C.; Ten Brinke, G.; Duek E. J Appl Polym Sci 2003, 88, 2744.

7. Furuhashi, Y.; Wakuda, H.; Yoshie, N. Seisan-kenkyu 2006; 58(3), 353.

8. Byun, Y.; Kim, Y.T.; Whiteside, S. J Food Eng 2010, 100, 239.

9. Bistac, S.; Schultz, J. Prog Org Coat 1997, 31(4), 347.

10. Haidong, L.; Wei, N.; Chao, D.; Xuesi, C.; Xiangling, J. Eur Polym J 2009, 45, 123.

11. Paragkumar, T.; Edith, D.; Jean-Luc, S. Appl Surf Sci 2006, 253, 2758.

12. Huda, M.; Yasui, M.; Mohri, N.; Fujimura, T.; Kimura, Y. Mater Sci Eng A. 2002, 333(1-2), 98.

13. Sodergard, A.; Stolt, M. Prog Polym Sci 2002, 27, 1123.

14. Lim, L.T.; Auras, R.; Rubino, M.; Prog Polym Sci 2008, 33, 820-852.

15. Ting, Ting, L.; Xiang, Yang, L.; Chaobin, H. Polymer 2010, 51, 2779-2785.

16. Fischer, E. W.; Sterzel, H. J.; Wegner, G.; Kolloid-Z u Z. Polymer 1973, 251, 980.

17. Chang, J.; Sun, B.; Breiby, D.; Nielsen, M.; Sölling, T.; Giles, M.; McCulloch, I.; Sirringhaus H. Chem Mater 2004, 16, 4772.

18. Selke, S.; Culter, J.; Hernandez, R. In Plastics Packaging (2nd ed), Selke, S.; Culter, J.; Hernandez, R., Ed; Hanser Publications: Cincinnati, 2004, Chap. 3.

19. Xiao, H.; Liu, F.; Yeh, J. J. Applied Poly Sci 2010, 117, 2980.

20. De Santis, P.; Kovacs, J. Biopolymers 1968, 6, 299.

21. Hoogsteen, W.; Postema, A. R.; Pennings, A. J.; Ten Brinke, G.; Zugenmaier, P. Macromolecules 1990, 23, 634.

22. Cartier, L.; Okihara, T.; Ikada, Y.; Tsuji, H.; Puiggali, J.; Lotz, B. Polymer 2000, 41, 8909.

23. Brizzolara, D.; Cantow, H. J.; Diederichs, K.; Keller, E.; Domb, A. J. Macromolecules 1996, 29, 191.

24. Slager, J.; Brizzolara, D.; Cantow, H.; Domb, A. Polym Adv Technol 2005, 16, 667.

25. Alfonso, G. C.; Pedemonte, E.; Pontzetti, L. Polymer 1979, 20, 104.

26. Carpento, L.; Marsano, E.; Valeti, B.; Zanardi, G. Polymer 1992, 33, 3865-3872.

27. Tan, S.S.; Su, A.U.; Luo, J.;Zhou, E.L. Polymer 1999, 40, 1223.

28. Ahmed, J.; Varshney, S.; Zhang, J.; Ramaswamy, H. J Food Eng 2009, 93, 308.

29. Sanchez-Garcia, M.; Gimenez, E.; Lagaron, J. Carbohydr Polym 2008, 71, 235.

30. Park, S.; Todo, M.; Arakawa, K.; Koganemaru, M. Polym 2006, 47, 1357.