

The Effect of Solvent Mixture on the Properties of Solvent Cast Polylactic Acid (PLA) Film

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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 to 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 with 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. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3577–3582, 2012

Key words: polylactic acid (PLA); solvent; crystallinity; thermal expansion stability; TMA

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

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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). Polyethylene glycol 400 (PEG 400) was purchased from Sigma Aldrich (MO). Chloroform was purchased from EM Science (NJ). Acetonitrile was purchased from VWR International (PA). Methylene chloride (DCM) was purchased from J. T. Baker. 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 pre-conditioned 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 Corp., Wayne, NJ) coated 157 mm × 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) 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°C at the rate of 10°C/min and 0.05N 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). Specimens weighing 2 to 3 mg were heated at the rate of 10°C/min from 0 to 200°C with a constant nitrogen flow throughout. The percentage of crystallinity (X_c) of the PLA films was evaluated according to the following equation¹⁴:

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

where ΔH_m is the enthalpy of fusion, ΔH_c is the enthalpy of crystallization, and ΔH_m^c 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). Samples were exposed to 50% relative humidity (RH) and tested at $23 \pm 1^\circ\text{C}$. Test films were conditioned in the testing cell for 10 h. Oxygen permeability ($\text{g}\cdot\mu\text{m}/\text{m}^2\cdot\text{day Pa}$) 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). Samples were exposed to 100% relative humidity (RH) and tested at $37 \pm 1^\circ\text{C}$. Test films were conditioned in the testing cell for 12 h. Water vapor permeability ($\text{g}\cdot\mu\text{m}/\text{m}^2\cdot\text{day Pa}$) 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 (E) of the PLA films were measured using an Instron Universal Testing

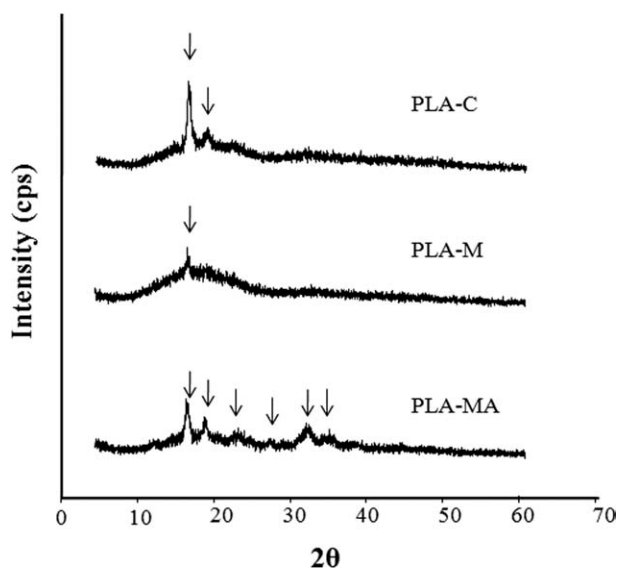


Figure 1 Wide-angle X-ray diffraction patterns of the three different PLA films.

Machine (Model 4201, Instron Corp., Canton, MA) according to the ASTM standard method D882-88. Specimen samples, 10 cm × 2.54 cm, were conditioned for 48 h at $23 \pm 0.5^\circ\text{C}$ 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). 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., NC). 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 I). 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 Crystallinity 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 crystallization 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

TABLE I
Thermal Properties of the Three Different 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 II
Accumulated Dimensional Changes of the Three Different PLA Films

	Onset temperature (°C)	Accumulated dimensional change (μm)		
		20–75°C	20–90°C	20–100°C
PLA-C	58	197	257	272
PLA-M	66	340	518	548
PLA-MA	–	46	49	57

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 II and Fig. 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.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 tempera-

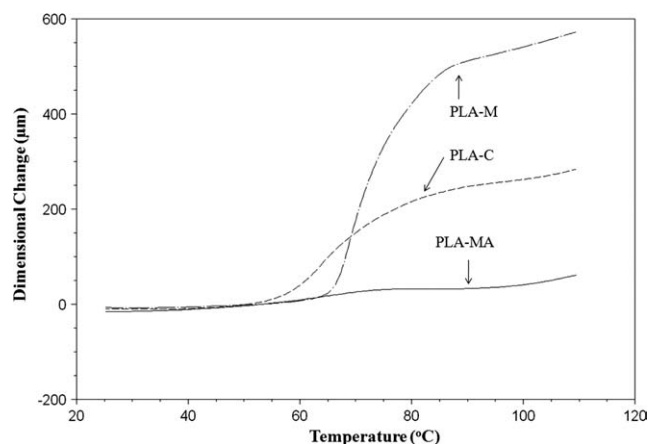


Figure 2 TMA thermograms of the three different PLA films.

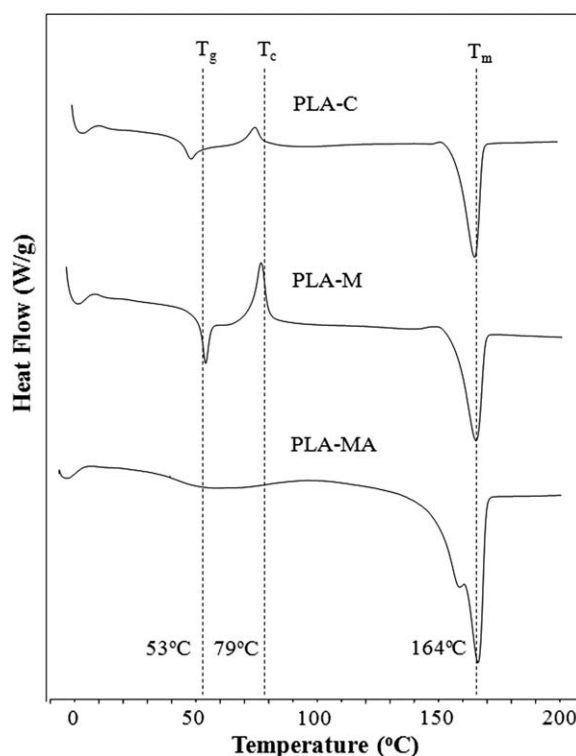


Figure 3 DSC thermograms of the three different PLA films.

ture and less dimensional change in the PLA-MA. Therefore, the PLA-MA was the most heat stable among the three PLA films. This may be 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°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 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°C, which may be due to the presence of different crystalline structures in PLA-MA.

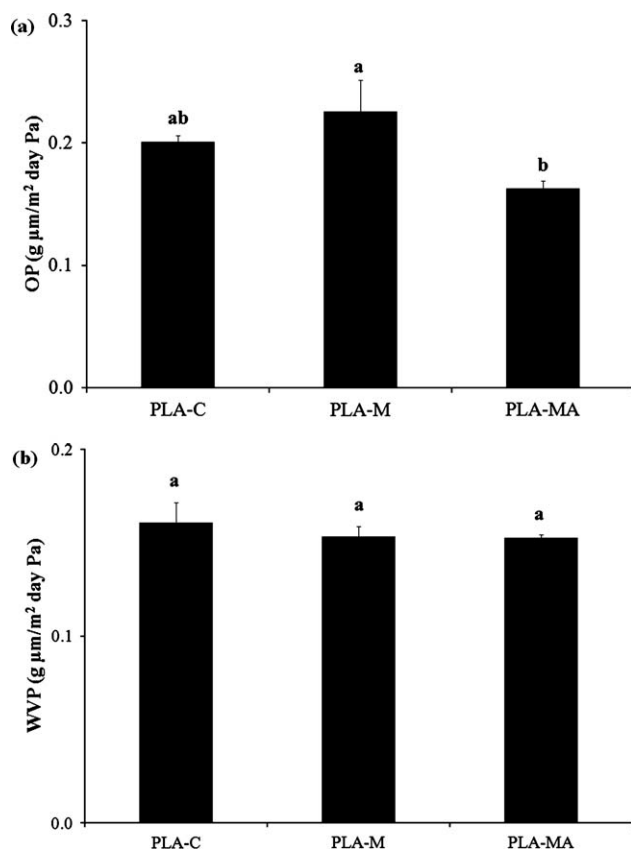


Figure 4 Barrier properties of the three different PLA films (a) oxygen permeability (OP) (b) water vapor permeability (WVP). The different letters differ significantly ($n = 2$, $P < 0.05$).

Barrier properties

The oxygen permeability (OP) of the PLA films is shown in Figure 4(a). 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 [Fig. 4(b)]. 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 improves 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 III). 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

TABLE III
Mechanical Properties of the Three Different PLA Films

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

^a b and c: The different letters within same column differ significantly ($P < 0.05$).

^b Results are expressed as the mean ± SD ($n = 7$).

TABLE IV
Optical Properties of the Three Different 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 and c: The different letters within same column differ significantly ($P < 0.05$).

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 IV. There were significant differences in color and haze among the films. PLA-MA had a hazy opaque color compared with 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

CONCLUSIONS

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 with PLA-C and PLA-M, which were more transparent. In conclusion, the thermomechanical 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.

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