Effect of the Processing Methods on the Performance of Polylactide Films: Thermocompression Versus Solvent Casting

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Received 5 May 2005; accepted 30 September 2005
DOI 10.1002/app.23403

ABSTRACT: Polylactide (PLA) films were prepared by the thermocompression and solvent-casting methods, and selected properties, such as the mechanical, water-vapor-barrier, thermal, and thermomechanical properties, were tested. The solvent-cast films contained 13.7% solvent, which functioned as a plasticizer, as evidenced by the results of the measurements of dry matter and thermogravimetric analysis as well as dynamic mechanical analysis. The PLA films prepared by the thermocompression method were strong and brittle, with maximum tensile strength (σ_{max}) and maximum elongation at break (ε_{max}) values of 44.0 ± 2.2 MPa and 3.0 ± 0.1%, respectively; however, the solvent-cast films were more ductile, with σ_{max} and ε_{max} values of 16.6 ± 1.0 MPa and 203.4 ± 20.8%, respectively. The water vapor permeability of the PLA films was lower than that of plastic films such as low-density polyethylene and high-density polyethylene but higher than that of commonly used biopolymer films. In addition, both types of tested PLA films were water-resistant and not soluble in water. The thermocompressed films showed higher thermal stability than the solvent-cast films. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3736–3742, 2006

Key words: polyactide; films

INTRODUCTION

The growth of environmental concern over nonbiodegradable, petrochemical-based plastic materials has raised interest in the use of biodegradable alternatives originating from renewable sources. Renewable-source-based biodegradable plastics can be divided into three broad categories:[1–5] (1) natural biopolymers, such as carbohydrates, proteins, and lipids, obtained from plants or animals; (2) renewable-resource-based biopolymers, such as aliphatic polyesters, including microbial polyesters such as polyhydroxyalkanoates [e.g., polyhydroxybutyrate, polyhydroxyvalerate, and their copolymers (polyhydroxybutyrate–polyhydroxyvalerate)], and chemically synthesized biopolymers such as poly(glycolic acid), poly(ε-caprolactone), poly(vinyl alcohol), and polylactides (PLA); and (3) blends or composites of these biopolymers.

The main factors determining the utilization of these biodegradable plastics are their performance, processing, and cost. Except for cellulose, which is widely used for making paper and paperboards, most natural biopolymers have limited use because of performance and processing problems. On the other hand, aliphatic polyesters generally have good performance and processability but are rather expensive for industrial use.

Among the aliphatic polyesters, PLA is one of the most promising because it is thermoplastic, biodegradable, and biocompatible and has high strength, high modulus, and good processability. PLA is synthesized from lactic acid, which is derived from renewable resources, such as corn or sugar beets.[6] In addition to its environmentally friendly nature, PLA can also be used for food contact surfaces and is generally recognized as safe. Because of high production costs, PLA has been used in limited areas, such as the preparation of medical devices (bone surgery, sutures, chemotherapy, etc.) in the early stages of development. Because the production cost has been lowered by new technologies and large-scale production, the application of PLA has been extended to other commodity areas such as packaging, textiles, and composite materials.[7]

Like other petrochemical-based plastics, PLA can be processed by various methods such as injection molding, sheet extrusion, blow molding, and thermoforming. PLA films can also be made by various methods such as extrusion, thermocompression, and solvent-

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Contract grant sponsor: Korea Science and Engineering Foundation; contract grant number: R01-2003-000-10389-0.

Journal of Applied Polymer Science, Vol. 101, 3736–3742 (2006)

casting methods. The extrusion of PLA is the preferred method for high-throughput production intended for applications such as packaging. The thermocompression method also is useful as a processing method because of its simplicity and capability of producing films without solubilization. The solvent-casting method has been commonly used for the preparation of biopolymer films,[8–10] which involves solubilization, casting, and drying steps. Because PLA is known to be soluble in a variety of solvents such as tetrahydrofuran, benzene, chloroform, and dioxane,[6] PLA films can be prepared by the solvent-casting method with any of these solvents. According to a review of existing literature, no research work regarding PLA films prepared by the solvent-casting method has been reported. Generally, properties of PLA films are expected to be affected by the processing methods used because of the different degrees of thermomechanical history involved. The main objective of this study was to prepare PLA films with two different methods, that is, the thermocompression and solvent-casting methods, and investigate the effects of processing methods on the properties of the prepared PLA films.

EXPERIMENTAL

Materials

Poly(L-lactate) (Biomer L9000; weight-average molecular weight = 200 kDa, weight-average molecular weight/number-average molecular weight = 1.98) was obtained from Biomer, Inc. (Krailling, Germany). PLA resins were dried in a vacuum oven at 60°C for 24 h before use. Chloroform was purchased from J.T. Baker (Mallinkrodt Baker, Inc., Phillipsbury, NJ).

Preparation of the films

PLA films were prepared with two different methods, that is, thermocompression and solvent-casting methods. For the preparation of the thermocompressed films, PLA was thermally compacted with a Carver laboratory press (hydraulic unit, model 3925, Carver, Inc., Wabash, IN). About 2 g of PLA was placed between two stainless steel plates (1 mm thick, 25.4 cm wide, and 25.4 cm long) lined with aluminum foil and then inserted them between the platens of the press heated to 190°C. A pressure of about 10,000 psi (68.9 MPa) was applied for 3 min, and this was followed by the removal of the aluminum foil liners, which were still attached to the compacted PLA film from the stainless steel plates. The PLA film layer was easily peeled from the aluminum foil layers after cooling in the air to room temperature.

For the preparation of the solvent-cast films, 5 g of PLA was dissolved in 100 mL of chloroform with vigorous mixing at room temperature (≈ 23°C). The dissolved solution was poured onto a leveled Teflon protective overlay (Cole–Parmer Instrument Co., Chicago, IL) mounted on a glass plate (24 × 30 cm) framed on four sides, spread evenly with a bent glass rod, and then allowed to dry for about 24 h at room temperature. The resultant film was peeled intact from the casting surface.

All the PLA films were cut into 7 × 7, 2 × 2, and 2.54 × 10 cm^2 pieces for the measurement of the water vapor permeability (WVP), water solubility (WS), and tensile properties, respectively.

Film thickness

The film thickness was measured with a micrometer (Dial Thickness gauge 7301, Mitutoyo, Tokyo, Japan) with a 0.01-mm accuracy.

Conditioning

All film samples were preconditioned in a constant-temperature humidity chamber set at 25°C and 50% relative humidity (RH) for at least 48 h.

Transparency

The transparency of the PLA films was determined by the measurement of the transmittance percentage at 660 nm with a UV–vis spectrometer (Lamda 25, PerkinElmer Instruments, Norwalk, CT).

Tensile properties

The tensile properties, such as the maximum tensile strength (σ_{max}), maximum elongation at break (ε_{max}), and modulus of elasticity (E), of each film were evaluated with a Instron model 5565 universal testing machine (Instron Engineering Corp., Canton, MA). The initial grip separation was set at 50 mm, and the crosshead speed was set at 50 mm/min.

WVP

WVP ($g \cdot m/m^2 \cdot s \cdot Pa$) was calculated as follows:

$$\mathrm{WVP} = (\mathrm{WVTR} \times L)/\Delta p$$

where WVTR is the water vapor transmission rate ($g/m^2 \cdot s$) measured through a film, L is the mean film thickness (m), and Δp is the partial water vapor pressure difference (Pa) across the two sides of the film. WVTR was determined gravimetrically with a modification of ASTM Method E 96-95. In calculating WVP, the effect of the resistance of the stagnant air layer between the film undersides and the surface of the water in the cups was corrected.[11]

WS

WS of each film was measured according to the method of Rhim et al.[12] Three randomly selected samples of each type of film were first dried at 105°C for 24 h to determine the initial dry matter (DM). Three more pieces of film were placed in a 50-mL beaker containing 30 mL of distilled water. The beakers were covered with parafilm (American National Can, Greenwich, CT) and stored in an environmental chamber at 25°C for 24 h with occasional, gentle stirring. Undissolved DM was determined by the removal of the film pieces from the beakers, gentle rinsing with distilled water, and then oven drying (105°C, 24 h). WS was expressed as the percentage of dissolved DM.

Thermal analysis

The thermal analysis of the PLA films was performed on a DSC Q100 differential scanning calorimeter (TA Instruments, New Castle, DE). About 5 mg of a sample was sealed in an aluminum pan and heated from -15 to 200°C at a 10°C/min scanning rate. A nitrogen flow (60 mL/min) was maintained throughout the test. For each sample, the glass-transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) were determined from the thermogram. T_m and T_c were taken as the peak values of the respective endotherms, and T_g was taken as the midpoint of the heat capacity changes. The transition temperatures as well as the enthalpy of crystallization (ΔH_c) and enthalpy of fusion (ΔH_m) were calibrated with indium as the standard. The degree of crystallinity (x_c) of the PLA films was evaluated according to the following equation:

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

where ΔH_m^c is the enthalpy of fusion of purely crystalline PLA (i.e., 106 J/g).[13]

The thermal stability of each film was tested with thermogravimetric analysis (TGA; Hi-Res TGA 2950 thermogravimetric analyzer, TA Instruments). About 5 mg of each sample was heated from room temperature to 600°C at a heating rate of 20°C/min under a nitrogen flow rate of 70 cm^3/min. The thermomechanical properties of the PLA films were tested with dynamic mechanical analysis (DMA; DMA Q800, TA Instruments) with the procedure of Ogale et al.[14] Each PLA sample (ca. 6×40 mm^2) was tested in the tensile mode at a frequency of 1 Hz and a deformation amplitude of 20 μm. The temperature was programmed to increase from room temperature to 100°C at a rate of 2°C/min.

Statistical analysis

The measurements of $\sigma_{\max}$, $\varepsilon_{\max}$, E, WVP, and WS were triplicated with individually prepared films as the replicated experimental units. Statistics on a completely randomized design were determined with the General Linear Models procedure in the statistical analysis system (SAS) program. The significance of each mean property value was determined ($P < 0.05$) with a t test.

TABLE I
Apparent Properties of the Thermocompressed and Solvent-Cast PLA Films

PLA film	Thickness (μm)	DM (%)	T (%)[a]
Thermocompressed	$120.0 \pm 3.5_b$	$99.8 \pm 0.1_b$	$93.2 \pm 0.1_a$
Solvent-cast	$91.4 \pm 1.2_a$	$87.3 \pm 0.1_a$	$95.2 \pm 0.1_b$

The means of three replicates plus or minus the standard deviation are shown. Any two means in the same column followed by the same letter were not significantly different by t testing ($P > 0.05$).

[a] Transmittance of the film determined at 660 nm.

RESULTS AND DISCUSSION

Apparent film properties

Freestanding PLA films were prepared with the thermocompression and solvent-casting methods. The apparent properties of the PLA films are shown in Table I. The thickness of the PLA films prepared by the thermocompression method was significantly higher than that of the solvent-cast films. Although the thickness of the films was not consistent with the film preparation methods, it was not expected to affect the determination of the other film properties. However, the film thickness could be controlled as desired by changes in the sample amount, compression temperature, and pressure for the preparation of the thermocompression films or by changes in the PLA concentration or casting area for the solvent-cast films. The PLA films prepared by the solvent-casting method were as transparent as polystyrene films. The transmittance of the PLA films prepared by the solvent-casting method was 95.2%. On the other hand, the PLA films prepared by thermocompression were semitransparent. In general, the clarity of films is known to be affected by additives such as plasticizers and the processing temperature.[15] The clarity of the thermocompressed PLA films could be increased by an increase in the processing temperature within the range of degradation temperatures of the polymer.

The DM contents of the PLA films were significantly different ($P < 0.05$) according to the preparation methods. The DM content means the PLA content. A PLA film prepared by thermocompression was more than 99.8% PLA; however, the DM content of the solvent-cast films was 87.3%. The DM content of the solvent-cast films was significantly lower than that of the thermocompressed PLA films. This may have been

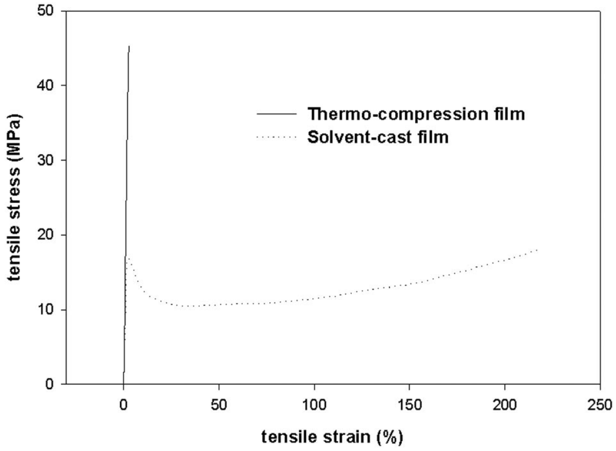

Figure 1 Tensile property curves of the thermocompressed and solvent-cast PLA films.

due to the fact that some portion of the solvent used for dissolving PLA was retained to make a polymer matrix in the solvent-cast films. This was further evidenced in the TGA results (shown later in Fig. 3). The solvent retained in the film was expected to affect other film properties.

Tensile properties

The tensile properties of films are very important in selecting diverse applications for polymer films. As important mechanical properties of packaging films, σ_{max}, ε_{max}, and E indicate the ability of films to maintain integrity under the stress occurring during the processing, handling, and storage of the packaged materials. Figure 1 shows a typical pattern of the stress–strain relationship of PLA films. The PLA films prepared by the thermocompression method had higher modulus and strength (higher σ_{max}) but lower toughness (less energy required to break) than the PLA films prepared by the solvent-casting method. The tensile testing results for the PLA films are shown in Table II. σ_{max}, ε_{max}, and E of PLA films prepared by thermocompression were 44.0 ± 2.2 MPa, 3.0 ± 0.1%, and 2070.6 ± 18.8 MPa, respectively. These results are comparable to the previously reported values of unoriented PLA films[6] (47.6–53.1 MPa for σ_{max}, 3.1–5.8% for ε_{max}, and 3447–4000 MPa for E). PLA is known to possess good mechanical properties and clarity in addition to good processability; however, its brittleness has been pointed out as its major drawback for many applications.[6,7,16] Moreover, the solvent-cast PLA films had mechanical properties significantly different from those of the thermocompressed films. σ_{max}, ε_{max}, and E of the solvent-cast PLA films were 16.6 ± 1.0 MPa, 203.4 ± 20.8%, and 927.1 ± 59.1 MPa, respectively. The ε_{max} values of the PLA films prepared by the solvent-casting method were almost 70 times higher than those from the thermocompressed films.

In contrast to ε_{max}, σ_{max} of the solvent-cast films was reduced to less than 40% of that of the thermocompressed films. Although σ_{max} of the solvent-cast PLA films was much lower than that of the PLA films prepared by the thermocompression method, its value was still comparable to those of widely used plastic films such as low-density polyethylene (LDPE) and high-density polyethylene (HDPE), of which the tensile strength values are known to be 13 and 26 MPa, respectively.[17]

The differences in the mechanical properties of the thermocompressed and solvent-cast PLA films were mainly due to the film preparation method. Generally, film properties such as flexibility and gas-barrier properties depend on the polymer structure, manufacturing process, physicochemical conditions (i.e., temperature, pressure, solvent composition, and concentration), and presence of plasticizers and other additives.[15,18–23] Differences in the processing parameters, such as the temperature, pressure, and existence of the solvent, may determine the extent of conformational changes, aggregation, and chemical crosslinking that occur during the preparation of films. A higher chain order induced in heat-cured films may favor film cohesion and, therefore, a decrease in the flexibility and an increase in the brittleness of the films; this phenomenon is apparent with protein-based films such as wheat gluten,[24] soy protein,[25] and whey protein.[26] The thermal treatment of protein films is known to promote the formation of intra- and intermolecular crosslinks. However, no such evidence for crosslinking was found for the PLA films.

Above all, the presence of a solvent in the solvent-cast films may be considered a decisive factor for the observed decrease in σ_{max} and E with an increase in ε_{max}. As mentioned previously, about 13% of the solvent was retained in the solvent-cast films (Table I) and functioned as a plasticizer of the films. Plasticizers are usually used to overcome film brittleness caused by extensive intermolecular forces. Plasticizers reduce these forces and increase the mobility of polymer chains, resulting in more flexible films. Various types

TABLE II
σ_{max}, ε_{max}, and E Values of the Thermocompressed and Solvent-Cast PLA Films

PLA film	σ_{max} (MPa)	ε_{max} (%)	E (MPa)
Thermocompressed	$44.0 \pm 2.2_b$	$3.0 \pm 0.1_a$	$2170.6 \pm 18.8_b$
Solvent-cast	$16.6 \pm 1.0_a$	$203.4 \pm 20.8_b$	$927.1 \pm 59.1_a$

The means of three replicates plus or minus the standard deviation are shown. Any two means in the same column followed by the same letter were not significantly different by t testing ($P > 0.05$).

TABLE III
WVP and WS Values of the Thermocompressed and Solvent-Cast PLA Films

PLA film	WVP ($\times 10^{-14}$ kg m/m^2 s Pa)	RH inside cup (%)[a]	WS (%)
Thermocompressed	$2.61 \pm 0.07_a$	$99.5 \pm 0.1_b$	$0.0 \pm 0.0_a$
Solvent-cast	$4.66 \pm 0.25_b$	$98.7 \pm 0.1_a$	$0.0 \pm 0.0_a$

The means of three replicates plus or minus the standard deviation are shown. Any two means in the same column followed by the same letter were not significantly different by *t* testing ($P > 0.05$).

[a] Actual RH values underneath the film of the WVP measuring cup

of plasticizers, such as citrate esters,[27] poly(ethylene glycol), glucose monoesters,[16,28] and oligomeric lactic acid,[13] have been used to improve the flexibility and resilience of PLA. The resulting plasticized PLA materials showed an increase in $\varepsilon_{\max}$ with a decrease in $\sigma_{\max}$. For example, Labrecque et al.[27] reported that extruded PLA films increased in their elongation from 7 up to 610%, while decreasing in $\sigma_{\max}$ from 51.7 to 7.2 MPa, with the addition of 30% triethyl citrate as a plasticizer. This result of an increase in the resiliency with a reduction of the strength by the addition of a plasticizer well agrees with the results in this study.

WVP and WS

The WVP values, along with actual RH conditions at the undersides of films during testing, of the thermocompressed and solvent-cast PLA films are shown in Table III. The WVP values, 2.61×10^{-14} and 4.66×10^{-14} kg m/m^2 s Pa for the thermocompressed and solvent-cast films, respectively, agreed well with the results for extruded PLA films reported by Auras et al.[29] They reported that WVP of PLA films, determined by Permatran W3/31 (Mocon, Inc., Minneapolis, MN), ranged from 1.48 to 2.20×10^{-14} kg m/m^2 s Pa, depending on the temperature and PLA resin type used. Although the WVP values of the PLA films were 50–100 times higher than those of LDPE and HDPE (9.26 and 2.31×10^{-16} kg m/m^2 s Pa, respectively),[30] they were 2 orders of magnitude lower than those of carbohydrate- or protein-based biopolymer films.[31] A difference in WVP between the thermocompressed and solvent-cast PLA films was evidenced. This difference in WVP can be mainly attributed to the plasticizing effect of the solvent in the solvent-cast films. The fact that plasticizers increase film permeability is well documented in the literature.[32,33]

It was also noticed in this study that the actual RH values at the inner film surface were close to 100% for both PLA films. This indicated that the water vapor pressure underneath the film was the same as that right above the water surface; therefore, it was not necessary for PLA films to account for the resistance of a stagnant air layer between the film and water surface in the WVTR measuring cups.[12]

Both PLA films maintained their integrity without swelling even after 24 h of incubation in water at room temperature with gentle stirring; that is, they were not soluble in water, as indicated by the WS results. Such high water resistance of PLA can be used in many applications, including packaging, paper coating, and blending with other biopolymers such as chitosan[34] and starch.[28]

Thermal properties of the PLA films

The thermal-transition properties of the PLA films were investigated with differential scanning calorimetry (DSC) and are shown in Figure 2 and Table IV. The thermal-transition temperatures, such as T_g and T_c, of the thermocompressed films were higher than those of the solvent-cast films; however, T_m was not affected by the film preparation method. T_g of the PLA films prepared by the thermocompression method was 62.5°C, which was comparable to the previously reported values of 57–60°C.[6] However, T_g of the PLA films prepared by the solvent-casting method decreased dramatically down to 37.6°C. The decrease in T_g of the solvent-cast PLA films could be primarily attributed to the plasticizing effect of the solvent retained in the films. It is well known that plasticizers added during film preparation cause a decrease in T_g

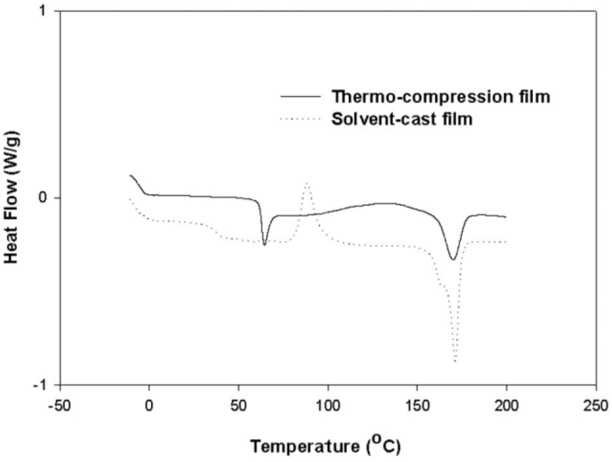

Figure 2 DSC thermographs of the thermocompressed and solvent-cast PLA films.

TABLE IV
Thermal-Transition and Onset-of-Degradation Temperatures of the Thermocompressed and Solvent-Cast PLA Films

PLA film	T_g (°C)	T_c (°C)	T_m (°C)	T_D (°C)[a]	ΔH_c (J/g)	ΔH_m (J/g)	x_c (%)
Thermocompressed	62.5	135.1	170.2	395.5	1.2	15.1	13.1
Solvent-cast	37.6	88.4	171.1	389.7	18.3	29.6	10.7

[a] Onset-of-degradation temperature.

of polymeric films.[35] Such a decrease in T_g partially explains the change in the mechanical and barrier properties of the PLA films prepared by the solvent-casting method. Generally, mechanical and barrier properties of polymers at any particular temperature are affected by T_g.[36] Above T_g, polymers exist in a rubbery state in which chain mobility reduces barrier properties. At temperatures below T_g, polymers exist in a glassy state in a brittle form. Therefore, the solvent-cast PLA films with lower T_g resulted in a higher water vapor barrier and lower mechanical strength than those of the counterpart thermocompressed PLA films. In addition, differences in the barrier and mechanical properties of the PLA films could also be expected from differences in x_c. x_c of the thermocompressed PLA films was higher than that of the solvent-cast films, as shown in Table IV. Although the difference was not large, a higher crystallinity would explain the lower permeability, higher tensile strength, higher storage modulus, and semitransparency observed in the thermocompressed PLA films in comparison with the solvent-cast films.

Thermal stability test results for the PLA films examined by TGA are also shown in Table IV. The weight-loss curves as a function of the temperature are shown in Figure 3. The solvent-cast PLA films decreased about 10% with respect to their initial weight during heating between 80 and 150°C because of the removal of the solvent captured in the films. This fact coincided with the DM results (Table I). The higher onset temperature of the thermocompressed films, that is, 395.50°C versus 389.74°C for the solvent-cast films, indicated higher thermal stability.

The thermomechanical properties of the PLA films were investigated by DMA, and the storage modulus and loss tangent curves as a function of the temperature are shown in Figure 4. The storage modulus values had magnitudes of approximately 3.7 and 2.6 GPa for the thermocompressed and solvent-cast PLA films, respectively, at the starting temperature of 30°C. They began to drop steadily as the temperature increased and reached minimum plateau values at about 70°C. The tan δ values of the thermocompressed PLA films showed one distinctive peak, whereas those of the solvent-cast films showed a broad band for a peak. This broad peak of the solvent-cast films could be attributed to the solvent in the films. T_g of the thermocompressed PLA films indicated that the temperature at which tan δ peaked (ca. 70°C) was somewhat higher than that determined by the DSC measurement (62.5°C), whereas that of the solvent-cast film could not be determined distinctively in the DMA curve because of the broad dispersion of the curve affected by the solvent in the films.

CONCLUSIONS

Two different types of PLA films were prepared with the thermocompression and solvent-casting methods.

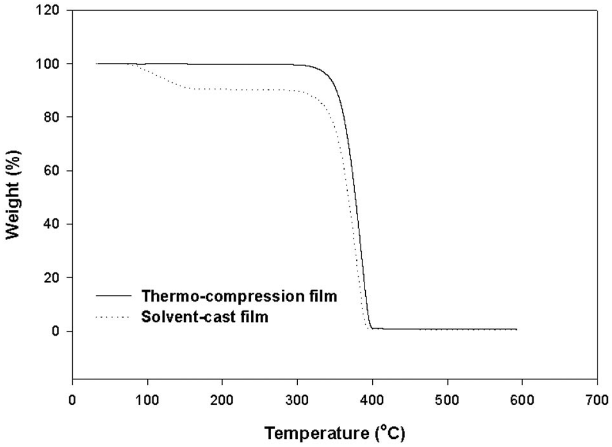

Figure 3 TGA curves of the thermocompressed and solvent-cast PLA films.

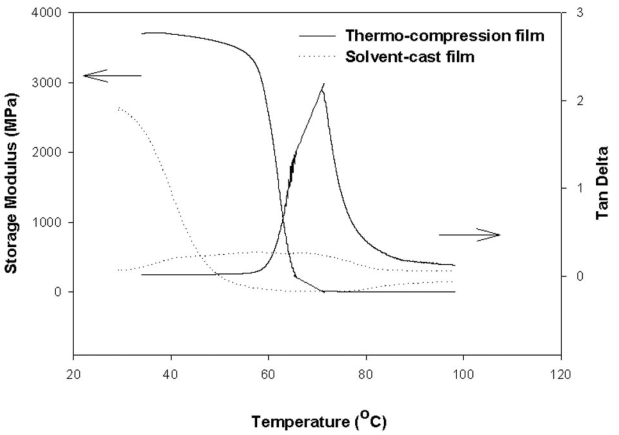

Figure 4 Storage modulus and tan δ curves of the thermocompressed and solvent-cast PLA films.

The PLA films prepared by the solvent-casting method were transparent, whereas those prepared by the thermocompression method were semitransparent. DM and TGA measurements indicated that more than 10% of the solvent was retained in the solvent-cast PLA films and functioned as a plasticizer, affecting the film properties. The ductility of the solvent-cast films increased dramatically in comparison with those of the thermocompressed films, but with the sacrifice of the tensile strength. WVP of the PLA films was also affected by the film preparation method. TGA results indicated that the thermal stability of the thermocompressed films was higher than that of the solvent-cast films. Generally, the mechanical properties of the PLA films were comparable to those of LDPE or HDPE, and they were also completely water-resistant. Higher WVP values and lower mechanical properties of the solvent-cast PLA films compared with those of the thermocompressed films were mainly caused by the plasticizing effect of the solvent retained in the films and partly caused by the lower x_c value of the solvent-cast films. This indicates that PLA films with desirable mechanical and barrier properties can be prepared by the adjustment of the amount of an appropriate type of plasticizer according to the desired application area.

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