Film Processability and Properties of Polycaprolactone/Thermoplastic Starch Blends

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ABSTRACT: In this work, the processing and properties of blown films prepared from thermoplastic corn starch (TPS) and polycaprolactone (PCL) were studied, in particular at high TPS content. The influence of processing parameters and material moisture content on the tensile properties was also studied. The results show that final film properties are mainly controlled by the draw ratio, blow-up ratio and PCL concentration in the blends. The results also show that PCL/TPS films are less hydrophilic as PCL content increases. Finally, it was found that a very narrow processing window exists for this blend. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 179–190, 2012

Key words: blends; morphology; films; mechanical properties

INTRODUCTION

The film blowing process is widely used to produce thin polymer films used in packaging and other applications such as mulching film. However, most of these films are discarded after a single use. This results in an accumulation of material and leads to an environmental management control problem. One possible solution is the use of biodegradable polymers and their blends to produce films. However, there are some issues to be solved, such as lower mechanical properties, processing problems and higher cost of producing compared with conventional plastics.[1–22]

Starch is a low cost biodegradable polymer obtained from renewable resources, and it is considered a promising candidate for developing biodegradable materials.[1–22] However, starch has poor mechanical properties and poor melt processability.[5,7,8,13,15,16] To be processed starch has been plasticized with water, glycerol and other agents, the obtained material is widely known as thermoplastic starch (TPS).[2–4,7,8,10–12,14–16,18–20,22] A recent review on starch-based polymers processing was presented by Liu et al.[20] The techniques used to produce starch-based materials include compression molding,[3,5,9,13,19] injection molding,[4,7,8,14] extrusion,[3,4,7,8,10,14–16] and film casting[1,17,19] and blowing.[2,7,8,18–20,22] One of the most serious difficulties for production of starch-based films is poor melt strength, sticky film surface, and foaming.[18] To improve melt strength and other properties, several methods have been proposed, including blending with biodegradable polymers such as polycaprolactone (PCL),[3–8,13,14,20,21] poly(lactic acid),[5,15,20,21] or poly(vinyl alcohol).[1,20] Since starch is immiscible with these polymers, a compatibilization may be required to obtain a useful product.[5,7,9,14,15] In addition, the mechanical properties of starch-based blends evolve with time through a series of complex processes like retrogradation and plasticization from environmental moisture.[1,9,13,16,22]

There are reported some studies on TPS[1,18,19,22] and blends of TPS with other nonbiodegradable[2] and biodegradable polymers[6–8] films. The film blow processing of starch was first reported by Otey et al.[2] using different ratio of polyethylene, poly(ethylene-*co*-acrylic acid) (PEAA), and starch. Good filmability was achieved by adding low amounts of ammonia and urea to improve starch-PEAA interactions. Thunwall et al.[18] reported a processing window for the film blowing of TPS film as a function of water and glycerol content and processing temperature. Altskär et al.[19] found that residual starch granules have a negative effect on the film blowing

properties and could cause failure of the bi-axially stretched bubble. Zullo et al.[22] reported the effect of starch source and type of plasticizer and their content on the mechanical properties of blowing TPS films, the processing conditions were optimized taking into account the extensional rheological properties of the materials. Halley et al.[6] develop a biodegradable mulch film based on starch-based polymers, and reported a film blowing stability diagram. Matzinos et al.[8] studied the processing and properties of PCL/TPS blend film, and reported that starch incorporation into PCL resulted in a material with higher modulus, but lower tensile and yield strength and elongation at break. All films, even at high TPS content ($\sim$ 40–50 wt %), presented a good dispersion of TPS within PCL matrix, implying there was some compatibility between the two components.

The purpose of this work is to present an overview of the film blowing processing window of TPS/PCL blends of different TPS/PCL ratios. In addition, study the effect of films storage (moisture absorption) on tensile properties like Young's modulus, tensile strength and elongation at break is presented.

EXPERIMENTAL

Materials

Native corn starch with 5% moisture was obtained from Almidones Mexicanos S.A. (Guadalajara, Mexico). PCL CAPA 6800 was supplied by Solvay Polycaprolactones (United Kingdom). Glycerol, provided by Golden Bell Reactivos (Jalisco, Mexico), was used as a plasticizer.

Compounding

Before blend extrusion, the starch was dried in a vacuum oven for 24 h at 60°C. The native corn starch was then mixed manually with 30% wt/wt glycerol as a plasticizer. Then, the mixture was blended with 40, 50, and 60% wt/wt PCL and finally extruded in a Leistritz twin-screw extruder model Micro 27 GL/GG-36D. The nine heating zones produced a temperature profile of 80, 95, 100, 110, 120, 130, 140, 150, and 160°C from the feed hopper to the die (4 mm in diameter) with a screw speed of 100 rpm. After extrusion, the blends were pelletized.

Preparation of tubular films

A single-screw extruder Haake Rheomex 254 with a blown film device was used to prepare tubular films as described in our previous works.[23] The extruder has a L/D ratio of 25 and the temperature profile

was fixed at 45, 110, 160, and 210°C. The screw speed was maintained at 15 rpm giving a total throughput of 1.12 kg/h. A water manometer was fixed to the blowing air feed to measure the pressure inside the polymer bubble. A bypass line was used to mitigate pressure variations inside the bubble. Different draw ratio (DR), defined as the ratio of take-up roller velocity (V_f) to the extrusion velocity (V_0), were used to study the effect of this parameter on morphology and tensile properties.

$$DR = V_f/V_0 \qquad (1)$$

A schematic representation of the experimental setup is shown in Figure 1. Table I gives a list of the processing parameters and variables studied. The angular velocity of the take-up rollers, the final bubble diameter and thickness were also measured. To eliminate moisture, the blends were dried again for 24 h at 45°C before use.

Rheological measurements

A rheological analysis of the blends at different temperatures (250, 260, and 270°C) was performed via dynamic oscillatory measurements using an ARES rheometer from TA Instruments. Parallel plate geometry of 25 mm diameter and 1.5 mm gap was used. First, strain sweeps were performed to assure that the data were taken in the linear viscoelastic zone of the material. Then, frequency sweeps between 0.1 and 100 rad/s were performed at a deformation of 1%. From the experimental data, the relationship between loss modulus (G'') and storage modulus (G') are calculated to get information on the complex viscosity (η^*). Furthermore, complex viscosity data of the blends are fitted to the simple power-law to describe their behavior as:

$$\eta = K\dot{\gamma}^{n-1} \qquad (2)$$

where K is the consistency index and n is the power-law exponent.

Tensile tests

Mechanical testing in tension was carried out at room temperature using an Instron Universal Testing Machine model 4411 following ASTM D882, at least five specimens shall be tested for each sample. The specimens were cut in the machine direction (Md) using the MI geometry and tested at a speed of 50 mm/min. The tests were carried out after different storage time to study the effect of normal environmental conditions (25°C and 40% HR) on the mechanical properties of the blends.
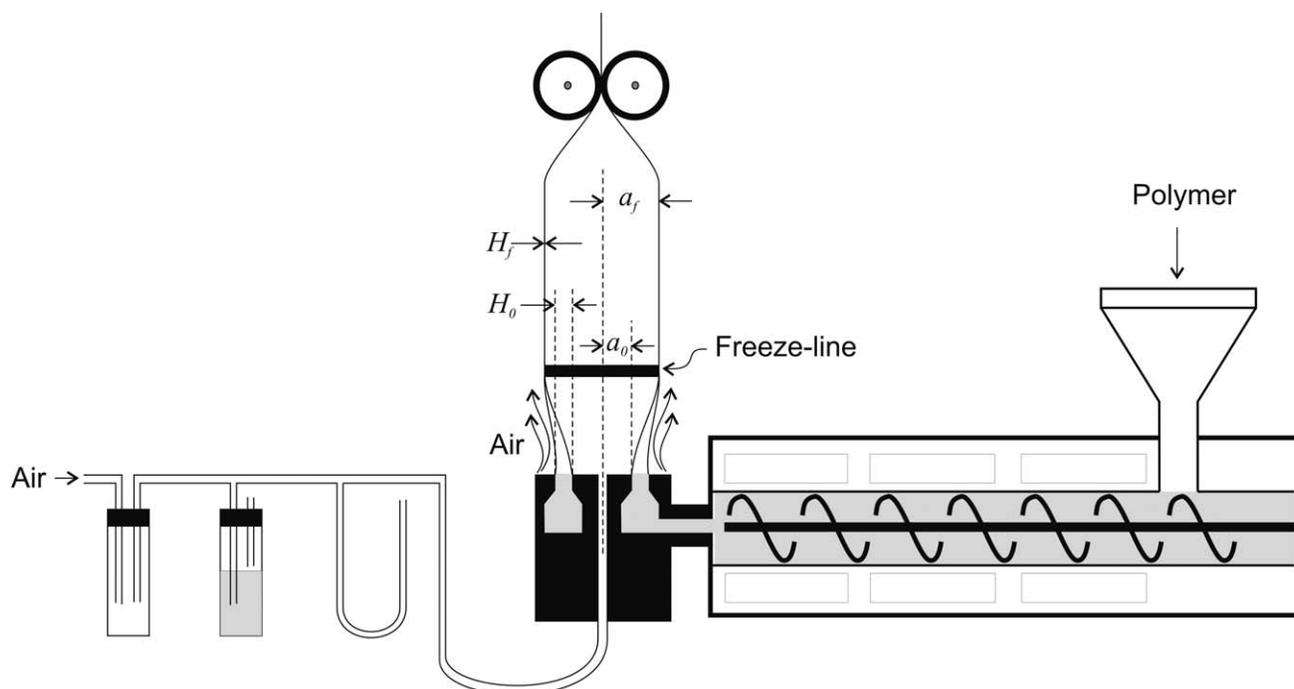
Figure 1 Schematic representation of the experimental setup used for the film blowing process.

Morphology

The samples were placed in liquid nitrogen and then fractured in both parallel and perpendicular directions to get a full three-dimensional characterization of the blend morphology. The samples were then immersed in hydrochloric acid ($1M$) to remove the TPS phase. Micrographs of the fractured and etched surfaces were obtained via scanning electron microscopy (SEM) on a Hitachi TM1000 tabletop microscope.

Moisture content and water uptake

Moisture content (MC) as a function of time was determined to measure the equilibrium content in the PCL/TPS films and the effect of this parameter

on the final mechanical properties of the films. MC was calculated as:

$$\mathrm{MC}\ (\%) = \frac{w_t - w_0}{w_0} \times 100 \qquad (3)$$

where w_t is the weight of the film for a time t and w_0 is the initial weight of the dry film ($t = 0$).

Water adsorption experiments were carried out as described in ASTM D-570. Five rectangular samples (50 mm × 10 mm) of each blend were dried at 60°C during 24 h and weighed. They were then placed into separate Petri boxes filled with distilled water (40 mL) at room temperature (20–25°C). For fixed periods of time, selected samples were removed from the water. The surface of the samples was wiped with a tissue to remove the superficial free

TABLE I
Processing Parameters for Film Blowing of PCL/TPS Blends

Processing parameter	Nomenclature	Value	Units
Die radius[a]	R_0	12.2	mm
Die gap[a]	H_0	2.9	mm
Volumetric flow[a]	Q	10.9	cm^3/min
Bubble pressure[a]	ΔP	98 – 294	Pa
Draw ratio[a]	$\mathrm{DR} = V_f/V_0$	7 – 10	–
Thickness ratio[b]	$\mathrm{TR} = H_0/H_f$	3.9 – 12.6	–
Blow-up ratio[b]	$\mathrm{BUR} = R_f/R_0$	0.5 – 1.6	–
Die temperature[a]	$\mathrm{T_d}$	210	°C
Solid density of the blend at 25°C[b]	ρ_s	1.4	g/cm^3
Melt density of the blend at 210°C[b]	ρ_m	1.2	g/cm^3

[a] Fixed parameters in the experimental design.
[b] Measured parameters.

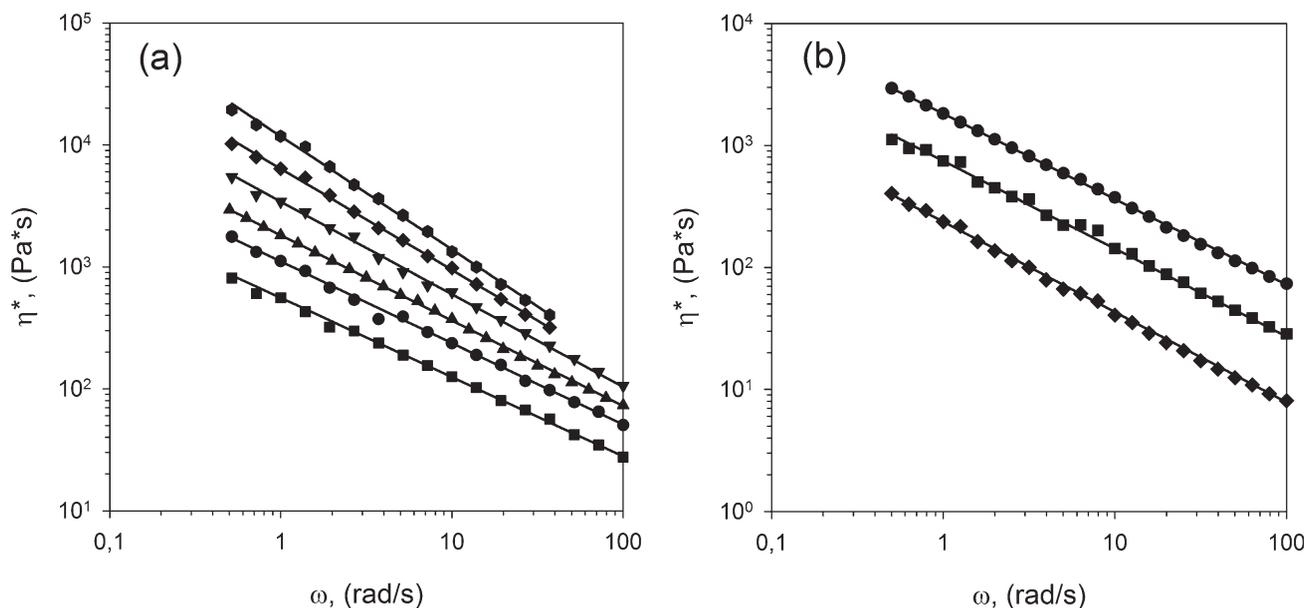**Figure 2** Complex viscosity versus frequency for PCL/TPS blends. (a) Effect of PCL content at 250°C for (hexagon): 10%, ◆: 20%, ▼: 30%, ▲: 40%, ●: 50%, and ■: 60% PCL. (b) Effect of temperature on the complex viscosity for 40% PCL blends at: ●: 250°C, ■: 260°C, and ◆: 270°C. The lines are fits to eq. (2).

water and the sample weighed. Water uptake (WU) was reported as the average of five samples as:

$$\mathrm{WU}\ (\%) = \frac{w_t - w_0}{w_0} \times 100 \qquad (4)$$

Diffusion coefficient

The environmental moisture diffusion coefficient (D) in the films was calculated according to Dufresne et al.[24] for diffusion in a thin polymer sheet at short times:

$$\frac{w_t - w_0}{w_\infty} = \frac{4}{h}\left(\frac{D}{\pi}\right)^{0.5} t^{0.5} \qquad (5)$$

where w_0 is the mass of dry film, w_∞ is the mass at equilibrium, w_t is the mass at a time t and h is the film thickness. All the measurements were performed on a Sartorius balance model BA110S with a precision of 0.0001 g.

RESULTS AND DISCUSSION

Rheology

From the experimental viscosity data [Fig. 2(a)], it can be seen that the blends are highly shear-thinning and the simple power-law of Equation (2) can be used to describe their behavior in the available range of data. Table II presents the values of the parameters at 250°C. Since PCL is practically a Newtonian

fluid,[10] the parameter n increases (slope decreases) with PCL content which controls the variation of viscosity with the rate of deformation. On the other hand, the consistency index (K) decreases with PCL content meaning lower viscosities. A rheological study of this blend was also reported by Shin et al.,[10] the complex viscosity of the blends containing concentration of TPS higher than 40 wt % exhibited strong shear-thinning characteristics. Li and Favis[25] also analyzed the rheological properties of the neat PCL and TPS as a function of frequency and found that TPS with high glycerol concentration exhibit typical gel behavior, while PCL has a broad Newtonian plateau. In general, blends with high PCL content are easy to process. The parameters are also highly function of temperature. For example, the complex viscosities of 40% PCL blend decrease strongly when temperature increased [see Fig. 2(b) and Table II], as expected.

TABLE II
Power-Law Parameters [eq. (2)] for PCL/TPS Blends

PCL content (%)	Temperature (°C)	K (Pa s^n)	n (−)
10	250	11176	0.08
20	250	6378	0.17
30	250	3426	0.24
40	250	1818	0.30
50	250	1109	0.33
60	250	557	0.35
40	260	746	0.28
40	270	236	0.26

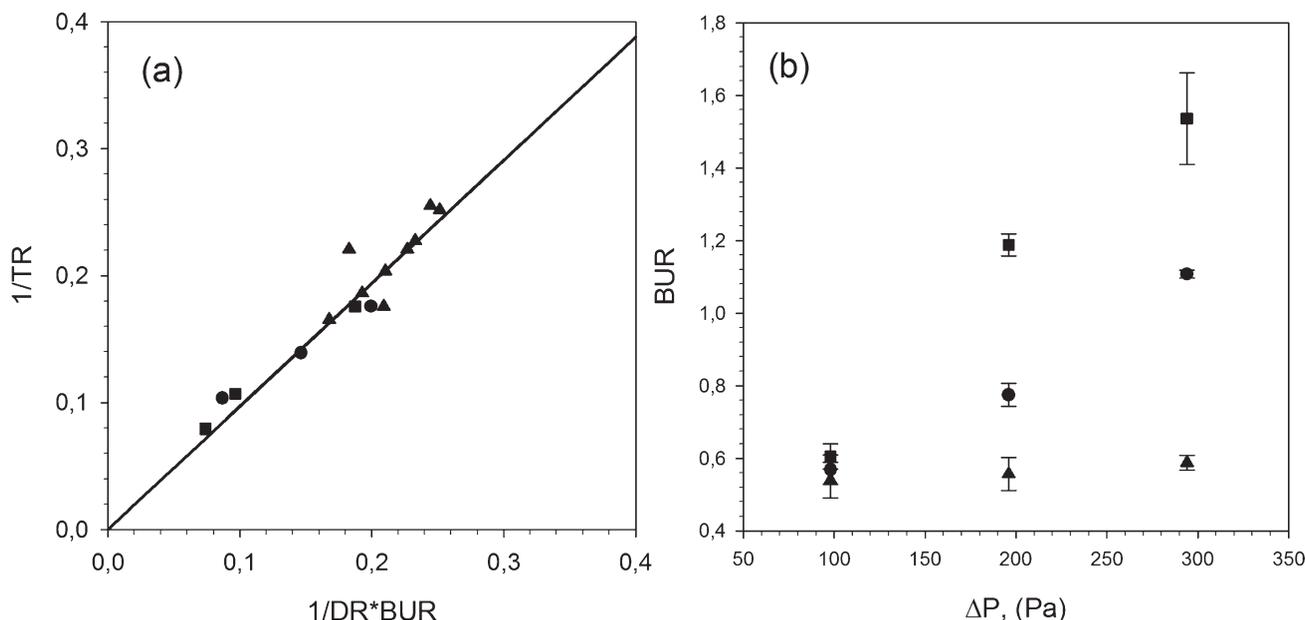**Figure 3** Filmability of PCL/TPS blends under different processing conditions. (a) Validation of eq. (7) for ▲: 40%, ●: 50%, and ■: 60% PCL in TPS. (b) BUR as a function of bubble pressure for ▲: 40%, ●: 50%, and ■: 60% PCL in TPS at DR = 8.5.

Filmability

Previous studies described possible instabilities during the blown film process.[26,27] These instabilities vary from the most common, such as draw resonance to helicoidal instability. Figure 3 shows the regions where it was possible to collect experimental data; i.e., stable bubble operation. Considering mass conservation, it is possible to calculate the mass flow (w) as:

$$w = \pi\left[(R_0 + H_0)^2 - R_0{}^2\right]V_0\rho_m = 2\pi R_f H_f V_f \rho_s \quad (6)$$

where ρ_m and ρ_s are the melt and solid polymer densities, respectively. Using the dimensionless parameters defined in Table I, eq. (6) can be written as:

$$\frac{1}{\text{TR}} = \frac{(R_0 + H_0)^2 - R_0{}^2}{2R_0 H_0}\left(\frac{\rho_m}{\rho_s}\right)\frac{1}{\text{DR}\cdot\text{BUR}} \quad (7)$$

From eq. (7), a linear relationship exists between TR^{-1} and $(\text{DR}\cdot\text{BUR})^{-1}$. Figure 3(a) shows that eq. (7) holds true for the majority of the films produced. From these data, a slope of 0.97 ± 0.03 was obtained by linear regression for stable processing conditions, which is in agreement with the theoretical value of 0.97 calculated from eq. (7) using geometrical and physical properties of the system. Nevertheless, some experimental data deviated from the theoretical relationship and can be explained by bubble instabilities at high and low DRs or at very low bubble pressure. Under our processing conditions, stable bubble occurred only for DR values between 7 and

10, which represents a very narrow processing window for these blends. However, at higher bubble pressure (BUR > 1.5), processing was easier.

On the other hand, Figure 3(b) shows how bubble radius changes with PCL content for similar processing conditions. It is clear that increasing the amount of PCL increases substantially the radius. This behavior is attributed to lower blend viscosity as PCL content increases as presented in Figure 2(a); i.e., lower viscosity promotes film deformation in the radial direction at constant bubble pressure. Rodriguez-Gonzalez et al.[28] in a rheological study of TPS with high content of glycerol indicated that TPS exhibits a larger storage modulus (G') than its loss modulus (G''). Furthermore, increasing the glycerol content in TPS resulted in a reduction of both G' and G'' (plasticizing effect).

Moisture uptake

Figure 4(a) shows the MC at 25°C and 40% HR for 40% PCL blends under various processing conditions. The equilibrium was reached in approximately 7 days and the equilibrium MC was between 1.8 and 2.2% depending on the processing conditions. These values are lower than the 10% reported in the literature for montmorillonite/TPS nanocomposites which clearly indicates that the addition of 40% PCL improves substantially the water resistance of starch blends.[29,30] Other study also reported lower water absorption by blending starch with PCL.[31] The origin of this phenomenon can be the formation of a
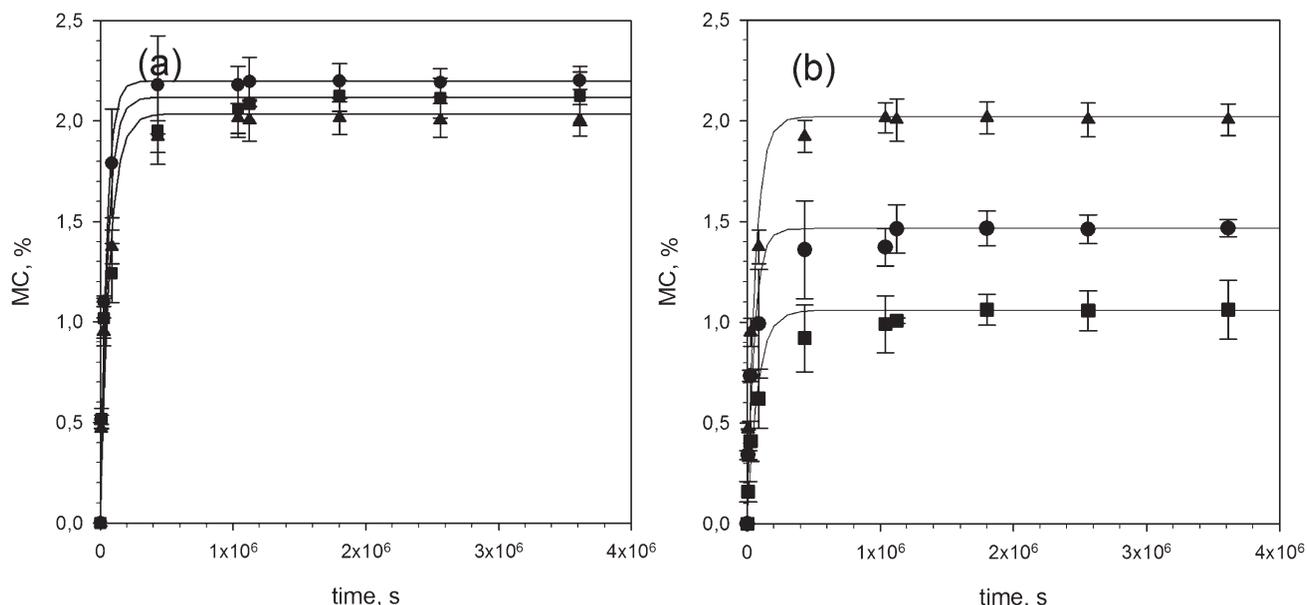
Figure 4 (a) Moisture content (MC) as a function of time for 40% PCL films produced at DR = 7 and bubble pressure of ●: 98 Pa, ■: 196 Pa, and ▲: 294 Pa. (b) Moisture content (MC) as a function of time for films produced at DR = 8.5 and a bubble pressure of 294 Pa for PCL content of ▲: 40%, ●: 50%, and ■: 60%. The lines are fits to eq. (5).

PCL skin on the film surface attributed to the difference in melt viscosities between TPS and PCL. Since TPS has a much higher viscosity than PCL (about one order of magnitude), when the bubble is stretched via bi-axial deformation, TPS segregate the PCL at the film surface. This morphology can reduce the possibility of water molecules entering the material as shown in Figure 5. The PCL skin formation in the films is important to control the moisture uptake.

Figure 4(b) presents the effect of PCL content on moisture absorption of the blends at DR = 8.5. The results show that MC decreases as PCL content increases. For example, the equilibrium MC decreased by 50% (from 2 to 1%) by increasing PCL content from 40 to 60%. This confirms the water resistance improvement generated by PCL addition.

Figure 6 shows the WU of the blends as a function of time. In this case, an equilibrium content of 25% for 40% PCL was reached in approximately 4 h. Once again, it is clear that PCL addition improves the water resistance of starch-based films.
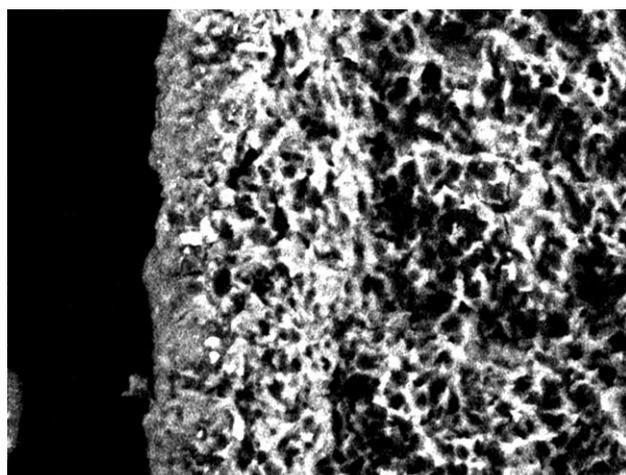

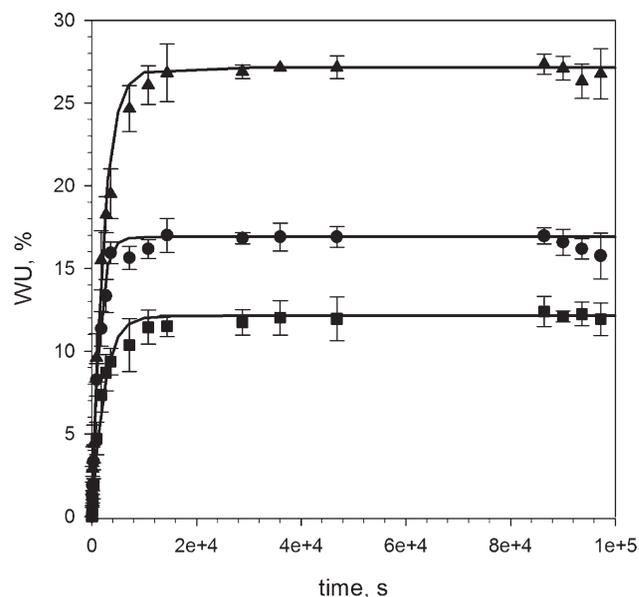**Figure 5** Micrograph of 40% PCL/TPS film in the machine direction with DR=7.

Figure 6 Water uptake (WU) following water immersion as a function of time for films produced at DR = 7 and a bubble pressure of 294 Pa for ▲: 40%, ●: 50%, and ■: 60% PCL in TPS. The lines are fits to eq. (5) with D (10^{-11} m$^{2/s}$) of ▲: 10, ●: 5, and ■: 2.

TABLE III
Water Diffusion Coefficient in PCL/TPS Films

DR (−)	PCL content (%)	Film thickness (µm)	D (10^{-12} m²/s)
7	40	73 ± 3	5.0
7	40	70 ± 4	4.0
7	40	66 ± 6	3.0
8.5	40	54 ± 3	2.0
8.5	50	30 ± 3	0.9
8.5	60	23 ± 2	0.4
10	40	48 ± 3	2.0

Moisture uptake increase with TPS content in the blends; because the more polar part (TPS) increased in the blend. After 72 h of water immersion, the samples were dried for 24 h in a vacuum oven at 50°C. The results showed that less than 2% of the blend was dissolved by this operation, thus indicating some long term stability of the films.

The values for the diffusion coefficient D are reported in Table III. The results show that the diffusion coefficient decreases when the amount of PCL increase. It is also clear that D decreases when film
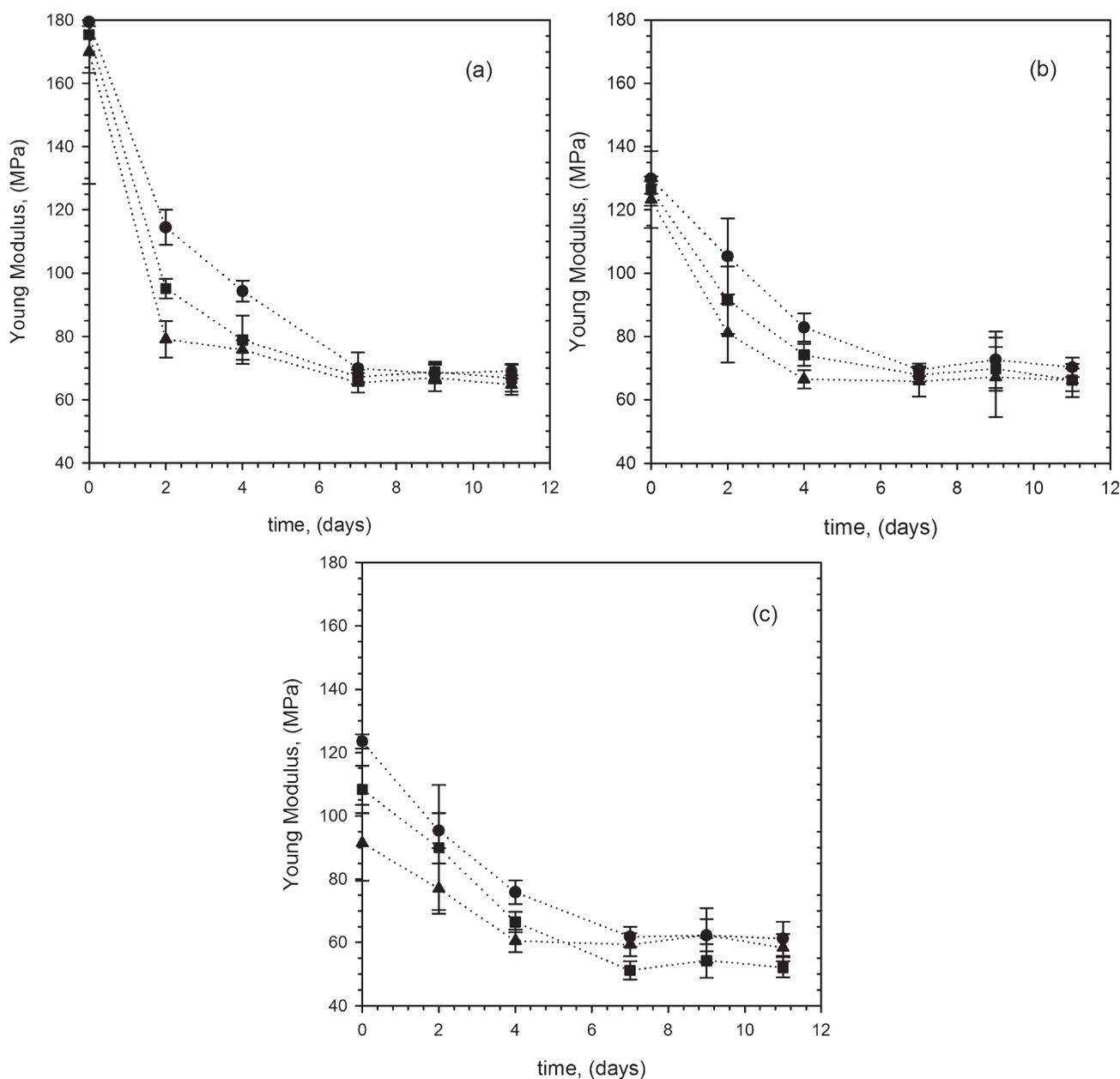

Figure 7 Young modulus of 40% PCL/TPS blend films as a function of storage time at different DR values: (a) 7, (b) 8.5, and (c) 10 with different bubble pressure ●: 98 Pa, ■: 196 Pa, and ▲: 294 Pa.
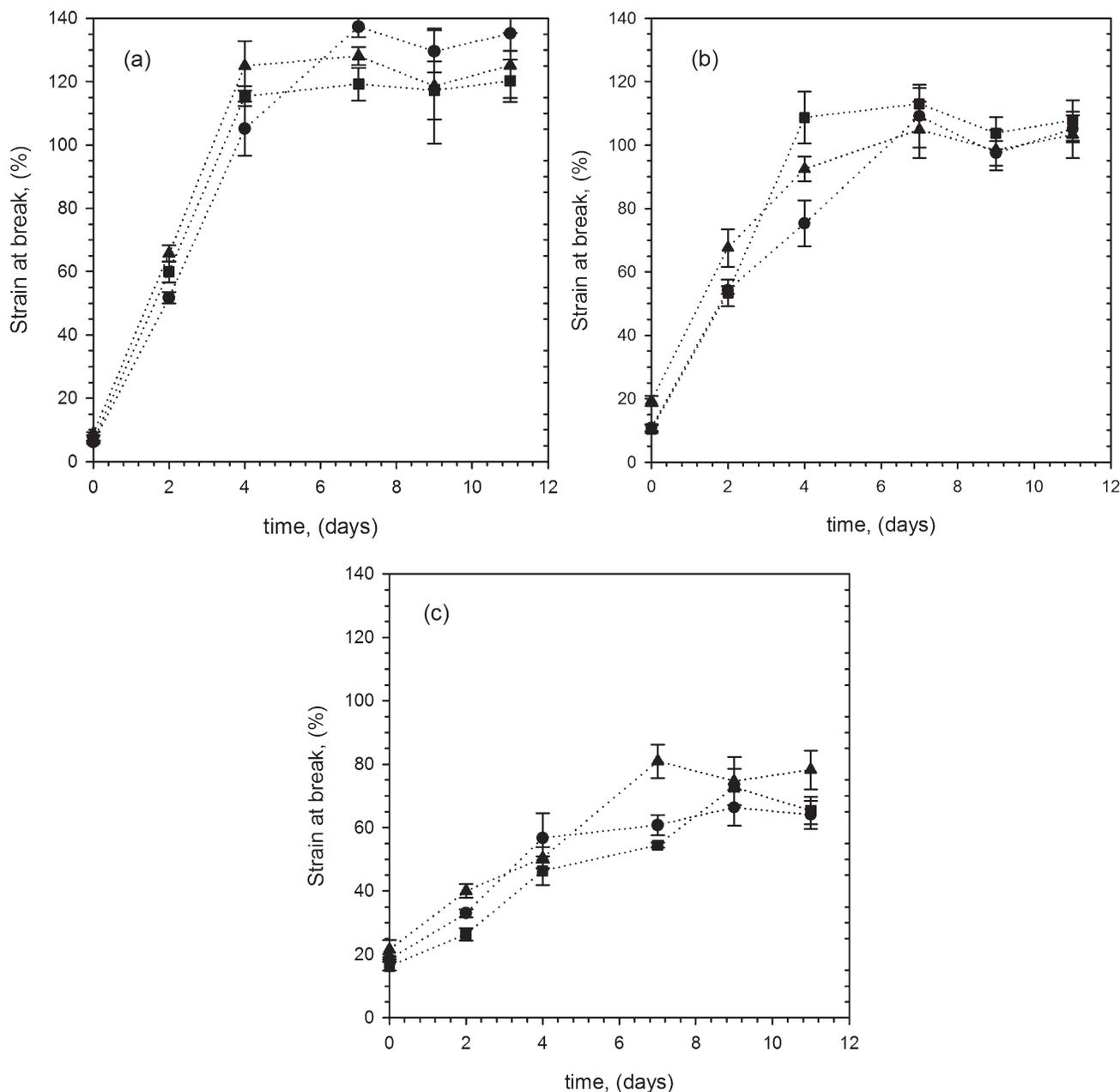
Figure 8 Strain at break of 40% PCL/TPS blend films as a function of storage time at different DR values: (a) 7, (b) 8.5, and (c) 10 with different bubble pressure ●: 98 Pa, ■: 196 Pa, and ▲: 294 Pa.

deformation increases. It is obvious that higher PCL content in the blend gives less possibility for the water vapor to diffuse from the environment to the TPS hygroscopic region of the films; i.e., the environmental moisture must follow a more tortuous trajectory, thus decreasing the diffusion rate and therefore the diffusion coefficient is lower. Furthermore, lower diffusion coefficients at constant composition were obtained by increasing film deformation (higher BUR values). This phenomenon is directly related to the morphology of the films. As presented in Figure 5, a skin is observed on the film surface. As film deformation increases, the amount of distributed starch

particles in the PCL skin is smaller, which restricts the amount of humidity that can diffuse through this skin.

Mechanical properties

Effect of MC and processing conditions

Young modulus of 40% PCL blends as a function of time is presented in Figure 7 for different processing conditions. Since starch is hygroscopic, it is expected that storage under different environmental condition will influence humidity uptake and MC will have a
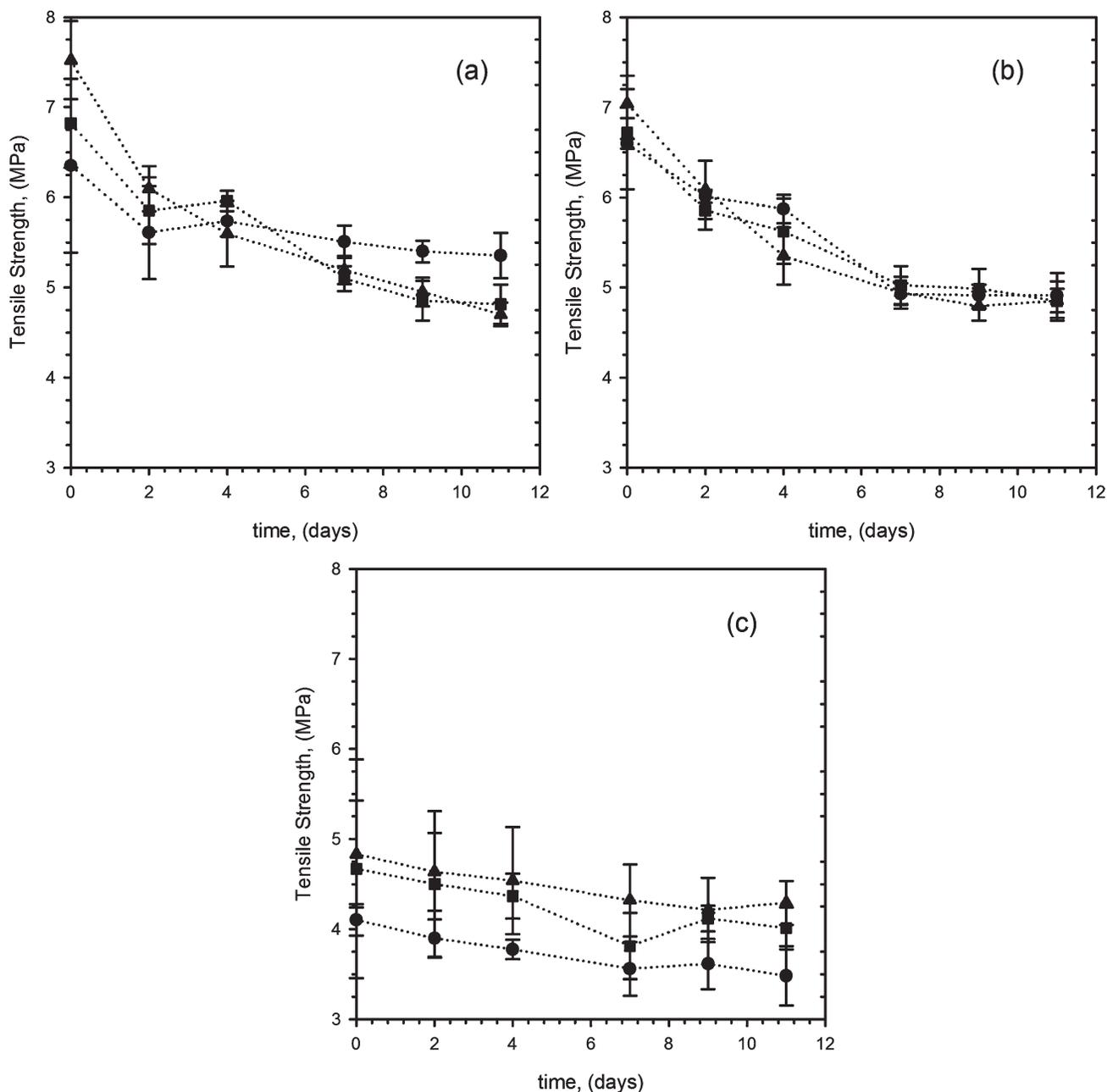
Figure 9 Tensile strength of 40% PCL/TPS blend films as a function of storage time at different DR values: (a) 7, (b) 8.5, and (c) 10 with different bubble pressure ●: 98 Pa, ■: 196 Pa, and ▲: 294 Pa.

definite effect on mechanical properties. As expected, the results in Figure 7 show that dry samples (tested just after processing) gave significantly higher Young modulus than conditioned ones. In the first 2 days, the results are highly dependent on the processing conditions. For example, samples extruded at BUR = 0.6 and DR = 7 have a 36% reduction in Young modulus (from 180 to 115 MPa) after 2 days of storage, but the decrease is only 11% over the following 2 days with a final 14% loss in the last 3 days before stabilizing at 70 MPa (39% of its original value). Similar behavior was reported by

Chaléat et al.[29] The lower Young modulus is attributed to water molecules acting as plasticizers. It is easy to see that modulus stabilization after 7 days is directly related to the equilibrium MC also obtained after a week (see Fig. 4).[29] MC has been reported to influence directly the glass transition temperature (T_g) and several mechanical properties of the blends.[28,32] In all cases, the Young moduli stabilized between 50 and 70 MPa after 7 days, the value being function of the processing conditions.

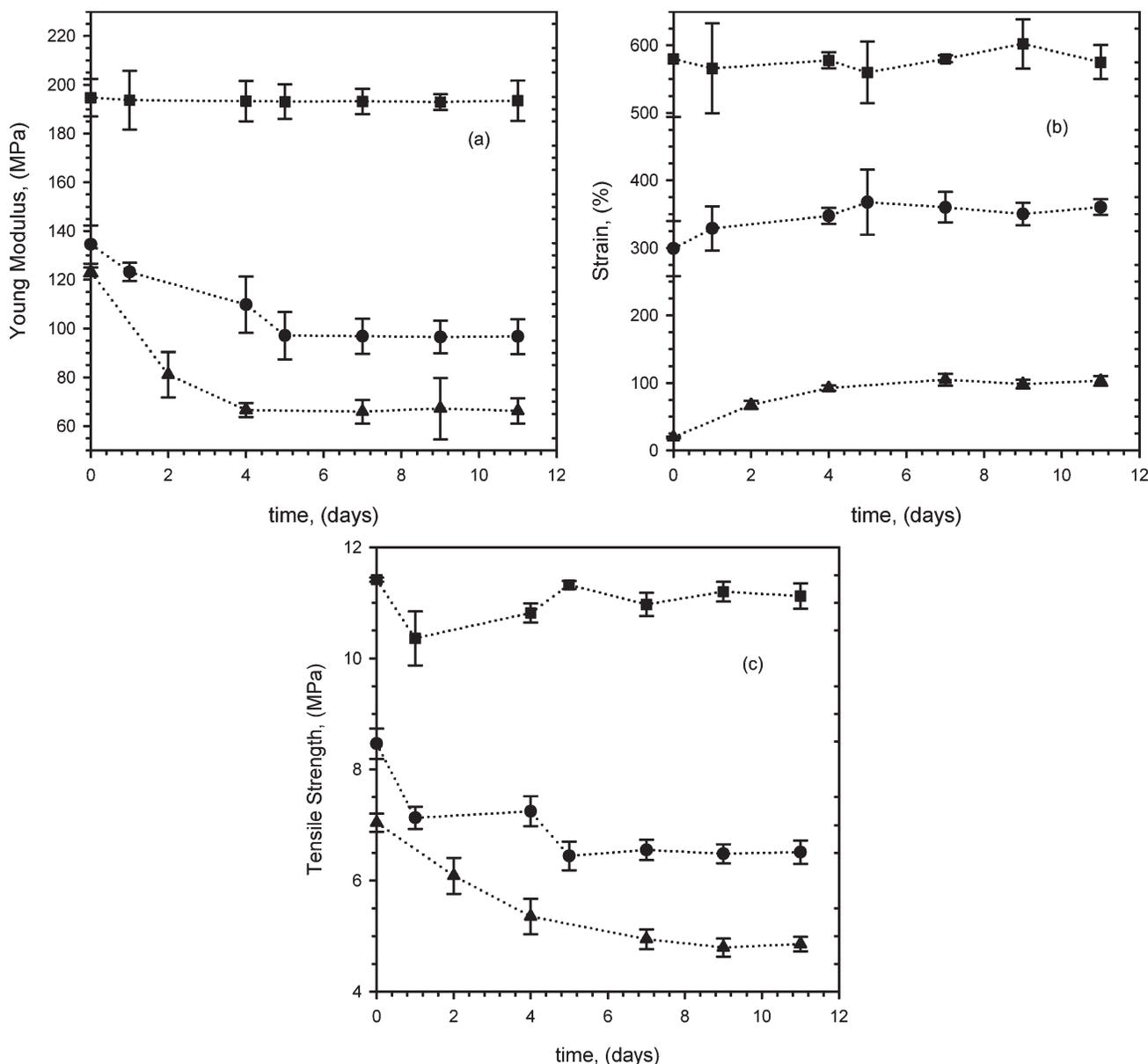In the past, the effect of processing conditions on blend film properties has been studied.[33–35] In such

Figure 10 Tensile properties of the films as a function of storage time for films produced at DR = 8.5 and _P = 294 Pa. (a) Young modulus, (b) strain at break, and (c) and tensile strength for ▲: 40%, ●: 50%, and ■: 60% PCL in TPS.

cases, polymer molecular chain orientation was shown to have a substantial influence on the final mechanical properties of the films.[36] Unfortunately, there is no information in the literature about the influence of processing conditions on the mechanical properties of starch-based materials. In our case, the deformation in the melt state plays an important role. It can be seen that the Young modulus decreases from 180 to 130 MPa and then to 120 MPa for $\Delta P = 98$ Pa at DR = 7 and films thickness of 0.75, 0.70, and 0.60 mm, respectively. Similar trends were observed for all cases of bubble pressure variations. However, the effect of deformation rate on the Young modulus is noticeable only for samples tested shortly after being extruded and negligible effect is

observed when the equilibrium moisture is reached. This would be a contradictory result since deformation generally promotes crystallinity in semicrystalline polymers and crystallinity tends to increase the values of Young modulus. But for the equilibrium Young modulus, it is clear that the effect is only on the TPS phase (amorphous phase). This behavior should be related to the DR promoting a toughness reduction in starch-based materials.

The strain at break of the samples is shown in Figure 8 as a function of storage time for different processing conditions. The figure shows an important increase of strain at break with storage time. The value increased from less than 10% for dry films to nearly 140% after 7 days for films of 60 μm
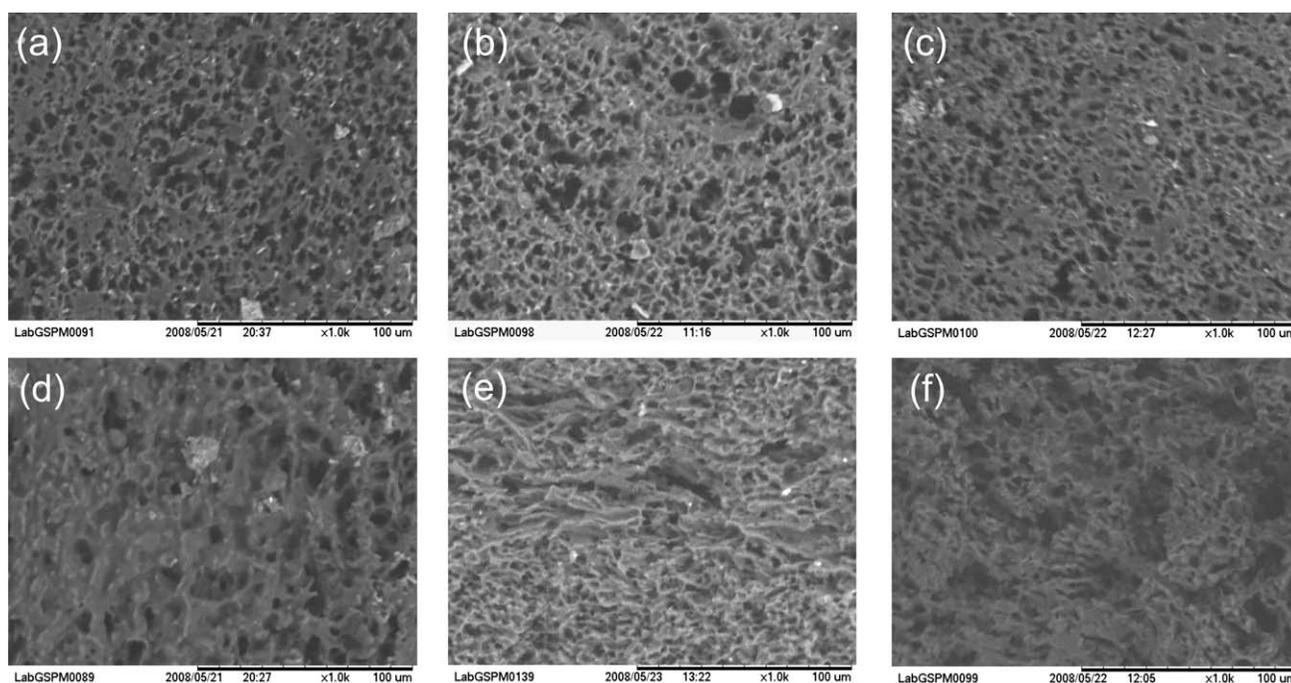
Figure 11 Morphology of 40% PCL in TPS in the machine direction (top row) and in the transverse direction (bottom row) for DR = 7 and different films thickness: 75 μm (first column), 70 μm (second column), and 60 μm (third column).

extruded at DR = 7. This important increase is attributed to an improved mobility of starch molecules due to plasticization from higher MC.[29] Also, it can be observed that the breaking behavior changes from a brittle to a more ductile rupture. Around the fourth day of storage, stress whitening occurred around the failure zone revealing some plastic deformation and the value of strain at break increased substantially from this point onwards. Figure 8 also shows the importance of DR on the strain at break. Substantial changes are observed from DR = 7 to 10 as a result of stretching in the Md. The Md samples experienced a rapid drop in elongation from 140 to 70% in dry samples. Elongation at break is considered highly indicative of the residual potential for the stretching of the amorphous tie chain molecules. Therefore, the Md samples processed at the highest DRs may contain highly oriented molecules with small possibility for additional stretching. As a result, the films exhibit a progressive decrease of the elongation at break as DR increases.[37]

The tensile strength is also one of the most important parameters in polymer films because it represents the maximum stress that the material can withstand. Figure 9 presents this property as a function of storage time for all of the processing conditions studied. It is clear that MC has the most important influence. Lower tensile strength is associated with a significant decrease in Young modulus giving a much weaker material.

Effect of PCL content

Figure 10 presents the Young modulus, elongation at break and tensile strength of the PCL/TPS blends as a function of storage time (DR = 8.5 and ΔP = 294 Pa). The Young modulus of the blends is surprisingly higher for samples having the highest amount of PCL. In a previous study, Matzinos et al.[8] showed that the Young modulus increased from 241 to 308 MPa by increasing the starch content from 0 to 50%. This was related to the higher modulus of the starch. However, their glycerol content (plasticizer) was only 20%. In our case, 30% glycerol was used which resulted in TPS with lower Young modulus than the neat PCL (≈320 MPa).

The effect of *MC* was also evaluated. From Figure 10, it can be seen that the effect of MC is more important than TPS addition. For example, *MC* does not have a significant effect on the Young modulus for samples with 60% PCL. This is attributed to the very low amount of moisture absorbed (<0.4%). The stress is mainly supported by the PCL matrix. But for samples with 50 and 40% PCL, the effect of MC is more important. The Young modulus decreases from 135 to 97 MPa (22% reduction) for films with 50% PCL, while it decreased from 125 to 65 MPa (50% of the original value) at 40% PCL. Since TPS has lower mechanical resistance than PCL, elongation at break and tensile strength also decreased with increasing starch content. For example, samples with 40% PCL have elongations at break increasing

from 20 to 100% with storage time. The value increases up to 600% for samples with 60% PCL, independent of storage time.

Morphology

Finally, Figure 11 presents some micrographs of 40% PCL film taken in the longitudinal and transversal direction. As presented in the experimental part, the TPS phase was extracted using $1M$ HCl to improve the phase contrast in the morphology. From these images, it is possible to see that the matrix is the PCL phase although it is the phase having the lowest viscosity. Furthermore, there is almost no dispersed phase deformation (mainly spherical particles). This indicates that stress transfer imposed by the processing condition (DR and BUR) is not occurring at the interface. This can also be concluded from the fact that both longitudinal and transversal morphologies are similar.

Based on the results obtained, it is clear that careful control of processing conditions can be done for blown films prepared from TPS and PCL blends. Because production of biodegradable polymers films is highly important for packaging applications, further work is under way to investigate these properties.

CONCLUSIONS

The stable processing window for PCL/TPS blends produced by extrusion film blowing was determined by applying different DRs and bubble pressures for PCL content between 40 and 60% using glycerol as a plasticizer. From the films produced, MC, WU, and tensile properties were determined as a function of time (storage). From the results obtained, several conclusions can be drawn.

Under our processing conditions, the filmability window of the blends is very narrow. It was found that films can be produced under stable condition only for DR between 7 and 10 giving film thicknesses between 75 and 23 μm. The resulting blends showed a lower hydrophilic character when the PCL content increased from 40 to 60%. It was observed that the maximum of WU, as well as the rate of water absorption, was reduced by increasing the amount of PCL. In all cases, equilibrium was reached within 7 days. The films also exhibited a remarkable improvement in the mechanical properties such as Young modulus, when the blend reached 60% PCL and the storage time had negligible influence on the mechanical properties of the films. The strain at break was improved by the addition of PCL to the starch from less than 100% with 40% of PCL to almost 600% for 60% PCL blends.

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