Film Processability and Properties of Thermoplastic Starch and Polycaprolactone Blends

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1. Abstract

The processing and mechancial properties of blown films prepared from thermoplastic corn starch (TPS) and polycaprolactone (PCL) has been studied. The aim was to determinate the filmability window of film blowing polycaprolactone/thermoplastic starch blends with a high TPS ratio. Also the influence of processing parameters on mechanical properties was studied in order to seek some effects on the blown films yield behaviour. Moreover, the effect of moisture content on mechanical properties during the first days of storage was also studied. The results shows that final film dimensions can be controlled mainly by variations of draw ratio and bubble pressure exhibiting a narrow filmability window, also variations on PCL concentration of the blend affects the final dimensions of the film due to rheological properties of the blends. The effect of moisture uptaking during storage in the mechanical properties is substantial in order to obtain films with good development.

2. Introduction

The film blowing process is widely used to produce polymer films which are used in packaging and other applications such as agricultural coating. However, most of these films are discarded after a single use, resulting in accumulation of material which becomes an environmental management control problem. One possible solution to solve this problem is the development of biodegradable materials that has been recently carried out. However, many of the actual substitution candidates have serious limitations related to properties and costs (1).

Starch is a material that can be used to produce biodegradable film, because of its large natural abundance and low cost. However, starch based materials have poor mechanical properties and processing problems (2). One of the most serious limitations for film production is poor melt strength. This property is defined as the ability of the melt to deform without rupture (3). A study of starch and glycerol films was published recently (4). The authors found that film blowing of material based on natural starch was significantly more difficult than processing modified starch or starch based blends. Similarly, a recent work (5) found that residual starch granules have a negative effect on the film-blowing properties and could cause failure of the bi-axially stretched bubble, thus restricting the extent of stretching. In order to improve melt strength and other properties, several methods including blending with biodegradable polyesters such as polycaprolactone (PCL), poly(lactic acid) (PLLA) or poly(vinyl alcohol) have been proposed (6-13).

Finally, the time evolution of mechanical properties of starch based blends involves a series of complex processes like retrogradation and plasticization with environmental moisture that has not been deeply studied. In this paper, high TPS content were used in the blown film process to study the effect of environmental exposition of starch based films along the first days of storage. Also, the importance of the processing conditions on mechanical properties like Young modulus and strain at break was studied.

3. Experimental

Corn native starch with 5% moisture was obtained from Almidones Mexicanos S.A. (Guadalajara, México). Polycaprolactone CAPA 6800 was supplied by Solvay Polycaprolactones (United Kingdom). Glycerol from Golden Bell Reactivos (México) was utilized as a plasticizer. 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% glycerol as a plasticizer. Then, the mixture was blended with 40, 50 and 60% PCL in a Leistritz twin-screw extruder model Micro 27 GL/GG-36D, and finally pelletized. The extruder temperature profile was 80, 95, 100, 110, 120, 130, 140, 150 and 160°C from the feed hopper to the die. The screw speed

was fixed at 100 rpm. A single-screw extruder Haake Rheomix 254 with a blown film device was used to prepare tubular films. In order to eliminate moisture, the blends were dried again for 24 h at 45°C. The extruder has a L/D of 25 and a temperature profile of 45, 110, 160 and 210°C. The screw speed was maintained at 15 rpm giving a total throughput of 1.12 kg/h. The schematic set-up is presented in Figure 1. Tensile experiments were carried out at room temperature using an Instron Universal Testing Machine model 4411 following ASTM D882-02.

4. Results and Discussion

Figure 1 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:

$$\dot{w} = \pi \left[\left(R_0 + H_0 \right)^2 - R_0^{\,2} \right] V_0 \rho_m = 2\pi R_f H_f V_f \rho_s \qquad (1)$$

where ρ_m and ρ_s are the melted and solid polymer densities, respectively. Equation (1) can be written as:

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

From Equation (2), a linear relationship exists between TR^{-1} and $(DR \cdot BUR)^{-1}$. Figure 1 shows that Equation (2) holds true for majority of the films produced. From the data presented in Figure 2, a slope of 0.97±0.03 was obtained by linear regression for conditions that effectively the film is stable. This is in agreement with the theoretical value of 0.97 calculated from Equation (2) using the geometry and physical properties of the polymers. Nevertheless, some experimental data are not in agreement with the theoretical linear relationship with dimensions and processing film conditions. This disagreement can be explained easily by the instabilities in bubble when the DR value is high or low and when the pressure into the bubble film is very low. In general under our processing conditions at DR higher than 10 and under than 7 is very difficult to perform the stable film bubble, this is a very close filmability window, however if the bubble pressure is high, (the enough to produce a BUR approximately of 1.5 or higher) the processing is easier.

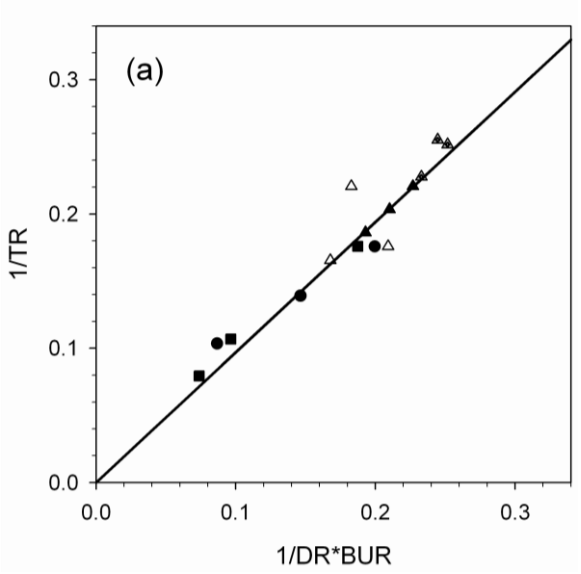

Figure 1. Filmability of PCL/TPS blends under different processing conditions for 40 (▲), 50 (●) and 60 (■) % of PCL

The Young modulus of 40% PCL blends as a function of time is presented in Figure 2 for different processing conditions. Since starch is a hygroscopic material, it is expected that conditioning at a given environment for different period of time will affect the resulting moisture content and also the mechanical properties of the films. The results of Figure 2 show that dry samples gave significantly higher Young modulus than the conditioned ones. In the first 2 days, the samples have larger modulus decreases. Similar behavior has been reported by Chaléat et al. (15) and it was attributed to water acting as a plasticizer. Moisture content variation has an effect analogous to temperature variation. The effect of MC has been reported that have a direct influences on Tg and this affects several mechanical properties on the blends (16,17). It can be seen that when DR increases, the Young modulus decreases from 180 MPa to 130 MPa and then 120 MPa for a ΔP=98 Pa (BUR= 0.6, 0.5 and 0.45, respectively). A similar behavior was observed for all cases of pressure change in the bubble. However, as BUR increases at constant DR, this promotes an additional decrease of the Young modulus in dried films, while no effect was observed for samples containing the equilibrium moisture. This would be a contradictory result since deformation generally promotes crystallization in semi-crystalline polymers and increased crystallinity tends to increase the values of Young modulus. But when the Young modulus was measured in samples containing the equilibrium moisture.

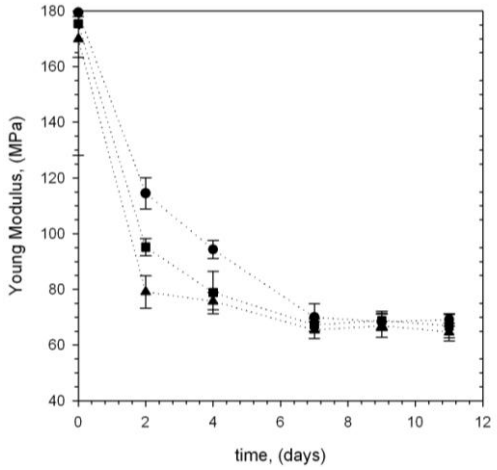

Figure 3. Young modulus of PCL/TPS blend films as a function of storage time at DR=7 (a), 8.5 (b) and 10 (c) with different pressure drops: 98 (●), 196 (■) and 294 Pa (▲).

The strain at break of the samples is shown in Figure 3 as a function of storage time for different processing conditions. The figure shows a large increase with storage time of the strain at break: from less than 10% in dry films to near to 140% after 7 days for samples extruded at BUR= 0.6 and DR=7. This behavior is attributed to an increase in mobility of starch chains due to plasticization due to moisture variation (15). It is possible that previous film deformation promotes a failure point degrading the polymeric matrix structure. As a result, the samples exhibit a progressive decrease in elongation at break as DR increases (18).

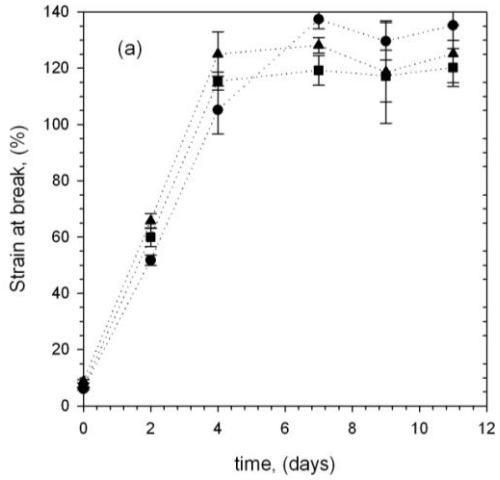

Figure 4. Strain at break of PCL/TPS blend films as a function of storage time at DR=7 (a) and 10 (b) with different pressure drops: 98 (●), 196 (■) and 294 Pa (▲).

5. Conclusions

Filmability and mechanical properties of PCL/PTS blends blown films were determinate. The films shows a very narrow filmability window with some instabilities when DR and pressure drop were low. The blends exhibited a remarkable improvement in the mechanical properties such as Young modulus and strain at break by the addition of PCL to the starch. Also the moisture content on the blends plays an important role in blends with a PCL concentration below 60%.

6. References

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