Physical and structural properties and thermal behaviour of starch-poly(ε-caprolactone) blend films for food packaging

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ABSTRACT

Structural and physical properties (barrier, mechanical, and optical properties) and thermal behaviour of corn starch-PCL blend films, containing glycerol as plasticizer, obtained by compression molding, at 160ºC and 130 bars, were studied. The stability on the films’ properties was also evaluated. Blend films showed phase separation of the polymers in a heterogeneous matrix with starch rich regions and PCL rich regions. Nevertheless, a small miscibility of PCL in the starch phase was detected through the shift in the glass transition temperature of the starch phase, which leads to a partial inhibition of amylose crystallization during film formation and storage. The lack of interfacial adhesion of PCL and starch phases promoted films’ fragility and reduced stretchability, although elastic modulus of the films with small PCL ratios increased. Water barrier properties of starch films were improved as the PCL increased in the blend, but oxygen permeability increased. Due to the food compatibility of this polymer blends (without any toxic compound) these could be an interesting alternative for food packaging, where some drawbacks of starch films has been overcome.

Keywords: thermoplastic starch, poly(ε-caprolactone), films, stability.

Chemical compounds studied in this article

Glycerol (PubChem CID: 753); water (PubChem CID: 952); caprolactone? (PubChem CID: 10401); Diphosphorus pentoxide (PubChem CID: 14812); Magnesium nitrate (PubChem CID: 25212)
1. INTRODUCTION

In the last decade, there has been growing interest in the development of biodegradable materials for applications in packaging technology, medicine or agriculture in order to mitigate the problems caused by non-biodegradable petroleum-derived plastics (Hubackova et al., 2013). In this sense, starch is a promising polymer because it is abundant, cheap and renewable (Lourdin, Valle, & Colonna, 1995). Although starch shows a high capacity to form homogeneous films with excellent oxygen barrier properties, they exhibit some drawbacks, such as poor mechanical properties, high water vapor sensitivity which leads to high water vapor permeability (Averous & Boquillon, 2004; Ghanbarzadeh, Almasi, & Entezami, 2011), and retrogradation. This consists of a slow recoiling of gelatinized amylose and amylopectin molecules which back into their native helical arrangements or into a new single helix conformation. The retrogradation is undesirable as it increases crystallinity and reduces film elongation over time. In order to improve the starch film properties, blends with other components, such as plasticizers, cross-linking agents or other polymers have been studied. Glycerol can be added as a plasticizer to enhance the mechanical properties of the film, increasing the flexibility (Vieira, Altenhofen, Oliveira, & Masumi, 2011).

The addition of other thermoplastic polymers to form blend starch films can modulate the films’ properties in order to improve their functionality. Of the commercially available biodegradable polymeric materials, blends based on thermoplastic starch (TPS) and hydrophobic synthetic polymers, such as aliphatic polyesters, could offer adequate solutions (Di Franco, C Cyrus, Busalmen, Ruseckaite, & Vázquez, 2004).

PCL is aliphatic polyester obtained by chemical synthesis from crude oil or from renewable resources, such as polysaccharides. PCL-based films have good water resistance. It is a thermoplastic, biodegradable, biocompatible and semi-crystalline
polymer that has a very low glass transition temperature (−60°C) (Cao, Chang, & Huneault, 2008). It also has a low melting point (58–60 °C), low viscosity, and is easily processable (Flieger, Kantorová, Prell, Řezanka, & Votruba, 2003). PCL can be blended with other polymers to improve stress crack resistance, dyeability and adhesion and has been used in combination with polymers such as cellulose propionate, cellulose acetate butyrate, polylactic acid and polylactic acid-co-glycolic acid (Woodruff & Hutmacher, 2010; Takala et al., 2013).

Properties of PCL-starch blends have been analysed by several authors for different applications. Averous, Moro, Dole, & Fringant (2000), studied the mechanical properties, the thermal and thermomechanical behaviour and the hydrophobicity of wheat TPS-PCL materials blended by extrusion and injection moulded, containing different ratios of TPS and PCL (up to 40 wt.%). They found a phase separation of polymers due to their incompatibility, although thermal transitions of each polymer suffered minor shifts in the characteristic temperatures. The hydrophobicity of the blends considerably increased as compared with TPS. Rosa, Guedes, Pedros, & Calil (2004), also analysed the properties of PCL blends with different ratios of gelatinized and non-gelatinized corn starch. They observed that the melt flow index increased when the PCL ratio increased in the blend, while PCL reduced the water sorption capacity of the materials. A decrease in the crystallinity of PCL in the blends was also observed.

On the basis of previous studies, and despite the polymer incompatibility, PCL-starch blends could offer properties that are of interest for the development of biodegradable packaging materials for food products where some drawbacks of starch films, such as their highly hydrophilic nature, poor water barrier properties and retrogradation phenomena could be overcome, while no potentially toxic compounds are present in the film formulation, which is crucial for food packaging applications (Duquesne, Rutot,
Likewise, biodegradability of starch-PCL blends has been reported by [1]. These authors found a reduction of the PCL degradation time when it is blended with starch.

The aim of this work was to characterize the structural and physical properties (barrier, mechanical, and optical properties) and thermal behaviour of corn starch-PCL blend films, with a wide range of polymers’ ratios, obtained by compression moulding. The stability during storage time on the films’ properties was also evaluated.

2. MATERIALS AND METHODS

2.1. Materials

Corn starch was purchased from Roquette (Roquette Laisa España, Benifaió, Spain). Glycerol was obtained from Panreac Química, S.A. (Castellar del Vallès, Barcelona, Spain). Polycaprolactone (pellets ~3 mm, average Mn 80,000, impurities <1.0% water) was provided by Fluka (Sigma–Aldrich Chemie, Steinheim, Germany). P2O5 and Mg(NO3)2 were obtained from Panreac Química, S.A. (Castellar Vallés, Barcelona).

2.2. Film processing

Native starch and glycerol were dispersed in water. The starch:glycerol ratio (w/w) was 1:0.3, which was established on the basis of previous studies (Ortega-Toro, Jiménez, Talens & Chiralt, 2014) PCL was dispersed in the aqueous slurry of starch and glycerol containing 0.5 g water/g starch at different ratios to obtain four blends with 80:20, 60:40, 40:60, 20:80 starch:PCL ratios (w/w). The blends were named S80, S60, S40 and S20, respectively. Starch-glycerol (S) and pure PCL films were used as controls. The formulations were gradually mixed on a two-roll mill (Model LRM-M-100, Labtech Engineering, Thailand) at 160 °C and 8 rpm for 30 minutes until a
homogeneous paste sheet was obtained. The obtained paste sheets were conditioned at 25 °C and 53% relative humidity (RH) for 48 hours before compression molding. The films were obtained by compression molding (Model LP20, Labtech Engineering, Thailand). Four grams of the paste were put onto steel sheets and preheated on the heating unit for 5 min. Films were obtained by compressing at 160 °C for 2 minutes at 30 bars, followed by 6 minutes at 130 bars; thereafter a cooling cycle was applied for 3 minutes. The obtained films were conditioned at 25 °C and 53% RH for 1 and 5 weeks for their characterization.

2.3. Film characterization

2.3.1. Film thickness
The film thickness was measured with a Palmer digital micrometer at six random positions around the film.

2.3.2. Moisture content
The films were conditioned at 53% RH and dried for 24 h at 60 °C using a convection oven (J.P. Selecta, S.A. Barcelona, Spain) and placed in a desiccator at 25 °C with P₂O₅ for 2 weeks. This assay was performed in triplicate.

2.3.3. Solubility in water
The solubility in water was determined holding the sample in bi-distilled water for 48 h, considering a film:water ratio of 1:10. Afterwards, the samples were transferred to a convection oven (J.P. Selecta, S.A., Barcelona, Spain) for 24 h at 60 °C to remove free water and then were transferred to a desiccator with P₂O₅ at 25 °C for 2 weeks till
constant weight. Solubility in water was obtained from the initial and final weights of the films. Three samples were used for each formulation.

2.3.4. Water Vapour Permeability (WVP)

The ASTM E96-95 (ASTM, 1995) gravimetric method was used for determining the WVP of the films. The modification proposed by McHugh, Avena-Bustillos, & Krochta (1993) was considered. Distilled water was placed in Payne permeability cups (3.5 cm diameter, Elcometer SPRL, Hermelle/s Argenteau, Belgium) to expose the film to 100% RH on one side. Each cup was placed in a cabinet equilibrated at 25 °C and 53% RH, with a fan placed on the top of the cup in order to reduce the resistance to water vapor transport, thus avoiding the stagnant layer effect in this exposed side of the film. The relative humidity of the cabinet (53%) was held constant using Mg(NO₃)₂ oversaturated solutions. The cups were weighed periodically (0.0001 g) and the water vapour transmission (WVTR) was determined from the slope obtained from the regression analysis of weight loss data versus time. From this data, WVP was obtained according to Jiménez, Fabra, Talens, & Chiralt (2012).

2.3.5. Oxygen Permeability (OP)

The oxygen permeation rate of the films was determined using an OX-TRAN Model 2/21 ML (Mocon Lippke, Neuwied, Germany) in samples conditioned at 53% RH and 25 °C. The transmission values were determined every 20 min until to reach the equilibrium. The exposure area during the tests was 50 cm². Three samples were studied for each formulation.

2.3.6. Tensile properties
A universal test machine (TA.XTplus model, Stable Micro Systems, Haslemere, England) was used to determine the tensile properties of films. The tensile strength (TS), the elastic modulus (EM), and the elongation (E) of the films were determined from the stress-strain curves, estimated from force-distance data obtained for different films (2.5 cm wide and 5 cm long), according to the ASTM standard method D882 (ASTM, 2001). Equilibrated samples were mounted in the film-extension grips of the testing machine and stretched at 50 mm min\(^{-1}\) until breaking. Tests were carried out at 25 ºC and 53% RH. Ten replicates were considered for each formulation.

### 2.3.7. Optical properties

The Kubelka-Munk theory for multiple scattering was applied to the reflection spectra to determine the film’s transparency (Hutchings, 1999). The surface reflectance spectrum was determined from 400 to 700 nm with a spectro-colorimeter CM-3600d (Minolta Co., Tokyo, Japan) on both a white and a black background. Internal transmittance (Ti) was obtained according to Jiménez et al. (2012).

The gloss was determined at an incidence angle of 85°, according to the ASTM standard D523 method (ASTM, 1999) using a flat surface gloss meter (Multi.Gloss 268, Minolta, Germany). Three films of each formulation were considered, taking three measurements in each sample. All results are expressed as gloss units (GU), relative to a highly polished surface of black glass standard with a value near to 100 GU.

### 2.3.8. Thermal properties

A Differential Scanning Calorimeter DSC 1 Star\(^{®}\) System (Mettler-Toledo Inc., Switzerland) was used to analyse the phase transitions in the polymer matrices. 10-15
mg of film samples were placed into aluminium pans, sealed and perforated to favour possible moisture loss during the heating run. Three scans were performed for the sample analyses. First, sample was heated from -80 °C to 160 °C at a heating rate of 20 °C/min, from which PCL melting properties ($\Delta H_m, T_m$) were obtained and in which the bonded water in the film was eliminated. In the second scan, the temperature was lowered to -80 °C at the same rate and the PCL crystallization properties ($\Delta H_c, T_c$) were obtained. Finally, samples were heated to 160 °C at a 20 °C/min to obtain the starch glass transition temperature and melting properties of PCL. The initial and final weights of the pans were registered to assess water loss during the first heating step.

2.3.9. X-ray diffraction

A diffractometer (XRD, Bruker AXS/D8 Advance) was used to obtain X-ray diffraction patterns. All samples (equilibrated for 1 and 5 weeks) were analyzed at 25 °C and 53% RH, between 2$\theta$: 5° and 30° using K$\alpha$ Cu radiation ($\lambda$: 1.542 Å), 40 kV and 40 mA with a step size of 0.05°. For this analysis, 4 cm$^2$ samples were used.

2.3.10. Scanning Electron Microscopy (SEM)

The microstructural analysis of cross-sections of films was carried out by using a Scanning Electron Microscope (JEOL JSM-5410, Japan). Film samples were maintained in desiccators with P$\text{$_2$}$O$_5$ for two weeks at 25 °C and observations were carried out in at least two samples per formulation. Pieces of about 0.5 cm$^2$ were immersed in liquid nitrogen and then cryo-fractured to observe the revealed surface. They were mounted on copper stubs and gold-coated for observation, using an accelerating voltage of 10 kV.
2.3.11. Atomic Force Microscopy (AFM)

Samples conditioned for 5 weeks at 25 °C and 53% RH using P₂O₅ were observed by AFM to analyze their surface morphology using an Atomic Force Microscope (Multimode 8, Bruker AXS, Santa Barbara, USA) with a NanoScope® V controller electronics. Measurements were taken from several areas of film surface (20 µm²) using PeakForce QNM® mode (Quantitative Nanomechanical Mapping). The DMT Modulus mode derived from PeakForce QNM was plotted in the 2-D plane of the sample. Three samples were analyzed for each formulation.

2.3.12. Statistical analysis

Statgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, MD) was used to carry out statistical analyses of data through analysis of variance (ANOVA). Fisher’s least significant difference (LSD) was used at the 95% confidence level. Homogenous group samples were indicated in tables with the same letter or number superscripts. Letters when film formulation was compared and numbers when the same sample at different storage time was compared.

3. RESULTS

3.1. Physical properties of films

3.1.1. Thickness, extensibility, water solubility and moisture content.

Table 1 shows the thickness and the extensibility (film surface per mass unit during the compression molding) of the starch-PCL based films equilibrated at 25 °C and 53% RH for 1 week. A significant decrease in thickness and an increase in extensibility (p < 0.05) were observed when the content of PCL rose in the films, indicating greater
flowability. Films without PCL were the thickest as a result of the greater resistance to flow of the material during compression. These results show the promotion of the flowability of polymer blends by the addition of PCL, as observed by Rosa et al. (2004), thus favouring their thermo-processing.

Table 1 also shows the solubility in water and the moisture content of the films. The moisture content showed significant changes (p < 0.05) with the storage time for formulations S, S80 and S60. As expected, the higher the starch content in the films, the greater the water sorption capacity (Averous et al., 2000; López, Zaritzky, Grossmann, & García, 2013). The hydrophobic character of PCL reduces the water adsorption capacity of the blend films and their equilibrium moisture content. Likewise, when the ratio of PCL in the films increased, their water solubility decreased, as shown in table 1, without significant (p < 0.05) changes during storage. The results confirm the expected changes in the water affinity of the films when the ratio of PCL increased, which supposes an advantage with respect to starch materials.

3.1.2. Barrier properties

Table 2 shows the values of Water Vapour Permeability (WVP) at a RH gradient of 53-100 % and at 25 °C, after 1 and 5 storage weeks. The WVP values fell significantly (p < 0.05) when the PCL ratio increased in the films, without significant changes during storage. Nevertheless, the obtained values for starch-PCL blends were not in the established range of WVTR for food systems’ requirements (Schmid et al. 2012) and additional reduction would be necessary. In this sense the bilayer films composed by an PCL layer and starch-PCL blend layer could be an alternative since perpendicular resistance of both layers to water vapour transfer would be much more effective. The
WVP values of the PCL layer are in the range of the WVTR requirements for meat and MAP products (Schmid et al. 2012).

Table 2 also shows the Oxygen Permeability (OP) values of the films. The control film (S) had such low oxygen permeability that this value could not be measured with the equipment used. The very low OP of starch films has been reported by other authors (López et al., 2013). However, PCL films and those containing a high ratio of this component (S40, S20) exhibited such high OP values that they were beyond the measurement range of the equipment. Samples S80 and S60 showed a significant increase (p < 0.05) in the OP values with respect to the pure starch films as a result of the PCL addition. No significant changes in the OP of the films occurred during the storage. The hydrophobic character of PCL promoted the increase in the oxygen permeability due to their chemical affinity which favours the gas solubility in the polymer matrix (Park, Testin, Vergano, Park, & Weller, 1996). So, the incorporation of PCL into starch matrices modifies their barrier properties, improving the water vapour barrier properties, but reducing the barrier to oxygen.

Oxygen barrier properties of net starch films cover the whole range of food packaging requirements, but when the PCL ratio increased in the blend films, different food products fall outside of their OTR range (Schmid et al. 2012). As commented on above, and according with the barrier properties of each film, the formation of PCL-starch bilayer films would be an adequate option to obtain materials appropriate for food packaging, particularly meat and MAP products or nuts and snacks.

3.1.3. Tensile properties

Figure 1 shows the typical stress-strain curves of the starch:PCL films stored at 53% RH for 1 week. The pure PCL films showed a high plastic deformation after the yield
point as shown in Figure 1a. Values of the strength and deformation in the yield point were $18.17 \pm 1.06$ MPa and $13 \pm 4\%$, respectively. PCL is a ductile polymer which can be deformed until $1100\%$ in agreement with Ishiaku, Pang, Lee, & Mohd Ishak (2002). Films containing low ratio of starch (S20 and S40 samples) exhibited an initial rupture followed by subsequent partial breaks (Figure 1b), while blends with less PCL content exhibited only one clear break point (Figure 1b). This indicates that PCL tend to be the continuous phase as its ratio increase in the matrix, but the interruptions provoked by the starch phase promote the film failure, thus losing the ductile properties of PCL, as reported by Averous et al. (2000).

Table 3 shows the tensile properties of the films conditioned at $53\%$ RH and $25$ °C for 1 and 5 weeks of storage. Significant changes ($p < 0.05$) were observed in all tensile parameters when PCL was added to starch films. Despite the fact that the elastic modulus of pure PCL and pure S films did not show significant differences, their blends exhibited higher values. Nevertheless, the resistance to break (TS) and extensibility (E) of the films significantly ($p < 0.05$) decreased when PCL was incorporated. No significant differences in any tensile parameter were observed for the different blends. The obtained results were similar to those reported by Corradini, Mattoso, Guedes, & Rosa (2004) for blends of PCL and zein, and by Ishiaku et al. (2002) for PCL and sago starch blends. In both cases, the incompatibility of polymers was observed. The effect of storage time on the mechanical properties of the blend films reveals different behaviour depending on the PCL ratio. Films with higher ratios of starch (up to $60\%$) exhibit a marked increase (nearly two times) in the elastic modulus over the storage time, whereas no significant changes were observed for films whose starch content was under $40\%$. This suggests that retrogradation phenomena occurred in the
continuous starch matrix, giving rise to recrystallization and chain aggregation which makes the cohesion forces in the polymer network more intense (Mali, Grossmann, Garcia, Martino, & Zaritzky, 2006). This effect was not observed for films with the greatest proportions of PCL, where EM did not change during storage time. Blend films did not show changes in the resistance at break (TS values), although this increased in pure starch films in line with the retrogradation effects. Deformation at break decreased in all the films over storage time, except for the one that contained the greatest ratio of PCL. This reduction is especially marked in pure starch films. The incorporation of PCL into starch matrices seems to reduce the changes in the mechanical properties of starch films throughout time, but the polymer incompatibility makes its efficiency limited due to the phase separation of polymers and the increase in the interface area where adhesion forces are not intense enough.

3.1.4. Thermal properties

Table 4 shows the thermal properties of the studied films obtained from DSC analysis. The Tg value of starch (obtained from the second heating scan) was about 126 ºC, similar to that reported by other authors (Ortega-Toro et al., 2014). In S20 formulation, the Tg value of starch was not observed because of the very weak signal associated with the low starch ratio in the sample. The Tg value of PCL was not detected due to the operation temperature range of the equipment, although its value (-60 ºC) was reported by other authors (Averous et al., 2000).

When PCL was incorporated, the Tg of starch decreased significantly (ΔTg~12ºC), regardless of the ratio of PCL. This suggests a partial miscibility of PCL in the starch phase. The decrease in Tg, as well as the higher values of ΔCp, is coherent with the lower molecular weight of PCL, which reduced the mean molecular weight of the
starch-rich phase. This favours the plasticization of the starch phase, thus increasing its flowability during thermo-processing, as previously commented on, while favouring its thermo-processing.

The melting behaviour of PCL, characterized in the first heating scan, was similar for every film, regardless of the PCL ratio, even for 100 % PCL films. The $T_m$ value for films stored for 1 week was 63°C and the $\Delta H_m$ was 72 J/g of PCL, similar to those reported by other authors (Averous et al., 2000; Matzinos, Tserki, Kontoyiannis, & Panayiotou, 2002; Kweon, Kawasaki, Nakayama, & Aiba, 2003). For samples stored for 5 weeks, although the same $T_m$ values were obtained, $\Delta H_m$ slightly increased (about 82 J/g of PCL) which indicates that the degree of crystallinity of PCL in the films increased throughout storage in both pure and blend films. No effect of starch on the PCL crystallinity was observed in the films.

The crystallization behaviour of PCL during the cooling step was also constant for all the samples, regardless of the film composition. The $T_c$ value (peak) was about 12 °C and the $\Delta H_c$ was close to 52 J/g of PCL. As compared with melting constants, the values of $T_c$ and $\Delta H_c$ were lower, revealing the supercoiling effect during the cooling step after the previous melting. As expected, the $\Delta H_m$ values of the second heating step reproduced those obtained for $\Delta H_c$, since all crystallized PCL melts during heating.

The results reveal that, for the obtained films, starch did not affect the melting behaviour of PCL, which, in turn, suggests a very low, or null, miscibility of starch in the PCL-rich phase. Likewise, the crystallization of the PCL progress during storage time and supercoiling occurred in fast cooling processes, as given by the DSC analysis.

This is in contrast to that described by other authors (Averous et al., 2000; Matzinos et al., 2002; Wang, Rodriguez-Perez, Reis & Mano, 2005) who report a small inhibition of PCL crystallization in PCL-starch blend films obtained by different techniques.
3.1.5. Optical properties

Table 5 shows the gloss at an 85° incidence angle and the internal transmittance at 650 nm of the films conditioned for 1 and 5 weeks. Films of pure components (PCL and S) presented the highest gloss values, while blend films were less glossy with no marked differences. The decrease in the gloss of blends can be attributed to changes in the surface roughness caused by the immiscibility of the polymers, which gives rise to the formation of a heterogeneous matrix with greater surface roughness (Jiménez et al., 2012). No formulation exhibited significant changes in the film gloss over storage time.

The internal transmittance values decreased when the ratio of PCL in the matrix rose, in line with the greater opacity of this polymer. The PCL formulation had the lowest transmittance and in no case did any significant changes in internal transmittance occur during the storage time.

3.2. Nano and microstructure of the films

Figure 2 shows the micrographs of the cross sections of films obtained by SEM. The heterogeneity of the blends was observed, evidencing the lack of miscibility of both polymers while the S and PCL films presented a homogeneous structure. No granules of native starch were observed in any case, which indicates that starch was effectively melted in the process used, giving rise to thermoplastic starch. Random-order conglomerates of starch and PCL were observed in the blend films. Likewise, blends exhibited poor interfacial adhesion, due to the different polymer polarities (Rosa, Rodrigues, Guedes, & Calil, 2003; Corradini et al., 2004). The PCL phase can be clearly distinguished due to its ductile behaviour, which defines a particular cryofracture pattern, promoting stretched filamentous formations.
The spontaneous detachment of both phases caused a loss in cohesion of the blend matrix and the lack of stretchability of the blend films (Ishiaku et al., 2002; Corradini et al., 2004).

Figure 3 shows the DMT modulus maps of the films obtained from the PeakForce QNM AFM analyses. The polymer matrices with pure components (S or PCL) show quite a homogeneous structure in terms of the surface mechanical response in line with the homogeneity of the material. The S surface was harder than the PCL, in agreement with the higher value of the elastic modulus of starch films after 5 storage weeks. Blend films had a more heterogeneous surface modulus, exhibiting light and dark areas, according to the distribution of harder (starch phase) and softer (PCL) regions at surface level. The film with formulation S20 shows the structure which bears the most similarity to pure PCL films, due to the small ratio of starch which interrupts the continuity of the PCL matrix.

The X-ray diffraction patterns of the films stored for 1 and 5 weeks are shown in Figure 4. The diffraction spectra of S films showed peaks at 13.5° 2θ and 24° 2θ angle, characteristic of the helical amylose-lipid complexes in the V-type crystallization form (Matzinos et al., 2002; Gelders, Vanderstukken, Goesaert, & Delcour, 2004). The intensity of the peaks increased in films stored for 5 weeks, which indicates the progress of amylose crystallization during storage.

PCL films show the characteristics peaks of the crystalline polymer at 21°, 22° and 24° 2θ angle. No notable changes in diffraction pattern were observed for these films during storage. For the blend films with the highest ratio of PCL, S20 and S40, the diffraction spectra were similar to those of the PCL film, which indicates that starch crystalline forms were not present after 1 or 5 storage weeks. Nevertheless, samples with higher ratios of starch, S60 and, especially S80, showed the starch typical peak at 13.5° and an
overlapping of the characteristic peaks of PCL and some of the starch in the 2θ angle range of 20-24°. In these films, the relative intensity of the starch peaks is lower than in pure starch films. This suggests that starch crystallization is partially inhibited by blending with PCL, mainly when the PCL ratio increased in the blend.

4. CONCLUSIONS

Corn starch and PCL blend films, containing 30 % glycerol with respect to starch, could be obtained by compression molding at 160°C and 130 bars. The films showed phase separation of the polymers, exhibiting a heterogeneous blend matrix where starch- rich regions and PCL- rich regions could be observed. Nevertheless, a small degree of PCL miscibility in the starch phase was detected through the shift in the glass transition temperature of the starch phase, which leads to the partial inhibition of amylose retrogradation during film formation and storage. The lack of interfacial adhesion of the PCL and starch phases promoted the films’ fragility and reduced their elongation, although small PCL ratios increased the elastic modulus of the films, indicating its adequate properties as reinforcing filler in starch matrices. Water barrier properties of starch films were improved as the PCL increased in the blend but worsening of the oxygen barrier properties was obtained. Bilayer films with both PCL and starch blend layers could meet the requirements for packaging of some foods such as meat and MAP products. Nevertheless, the overall migration in different food simulants must be assessed, according to migration limits stablished by regulation for plastic materials in contact with food.

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