

Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

EDITORIAL

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Influence of citric acid on the properties and stability of starch-polycaprolactone based films

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ABSTRACT: The influence of citric acid (CA) on structural and physicochemical properties of blend films based on corn starch and polycaprolactone (PCL) was studied. Films were obtained by melt blending of starch and PCL and compression molding. Phase separation of polymers observed by scanning electron microscope and atomic force microscope was reduced by CA incorporation. CA affected both starch and PCL crystallization as deduced from the X-ray diffraction patterns and values of melting enthalpy. Glass transition of starch was reduced by PCL incorporation, while this occurred to a greater extent in films containing CA. Obtained results point to enhanced interactions between PCL and starch chains in films with CA, although this only quantitatively benefits the film properties at a low PCL ratio. Compounding starch with small amounts of PCL, using glycerol and CA, can supply films with better functional properties than net starch films. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42220.

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INTRODUCTION

Packaging films, made of synthetic polymers, cause serious ecological problems due to their nonbiodegradability. Increased social awareness about environmental protection has made it necessary to intensify research for the purposes of developing biodegradable packaging materials.¹ These materials must be competitive in price and should have similar properties to the petroleum-derived plastics.² In the last few years there has been a significant increase in the number of studies about biodegradable packaging materials from economically viable sources. Of these materials, starch is remarkable for its low cost, renewability and processability by means of traditional thermoplastic techniques.^{3,4}

Starch represents more than 60% of the cereal grains produced worldwide and it is relatively easy to extract.⁵ Of the so-called bioplastics, starch is of great importance because of its low cost, availability, and technical characteristics. Starch-based films are continuous, homogeneous, odorless, and colorless while exhibiting very low oxygen permeability.^{6–8} However, they have some disadvantages such as high hydrophilicity (water sensitivity) and poor mechanical properties as compared with conventional synthetic polymers.⁹ Furthermore, depending on temperature and relative humidity (RH), the starch film structure undergoes changes during storage, e.g., in crystallinity and chain aggregations, which greatly affect the films' physical properties.^{10,11} To

improve and maintain their properties it is necessary to add plasticizers, fillers, or cross-linking agents. The most common plasticizer used in starch-based films is glycerol. This polyol reduces the intermolecular attractive forces in the native starch and increases its flexibility or stretchability.¹²

On the other hand, polycaprolactone (PCL) is one of the most commercially available biodegradable polymers. It is synthetic and thermoplastic, with interesting properties such as its low water solubility and permeability and high degree of extensibility.^{1,13} Several authors have shown that blends of PCL and starch are readily biodegradable and thermoprocessable by conventional methods.^{14–17} However, starch and PCL (molecular structures shown in Figure 1) are chemically incompatible and their blends show phase separation,¹³ which implies that the obtained materials are heterogeneous with insufficiently improved properties, as occurs with other starch blends with more hydrophobic polymers of different polarity.^{18,19} This is the main limit of the starch/PCL blends, represented by the lacking of adhesion between the polysaccharide and the synthetic polymer matrices owing to their different polarity giving consequently poor final properties. In fact, starch and hydrophobic polymers (as PCL) are immiscible and simple mixing produce blends with separate phase. To improve the compatibility and the adhesion between the phases of the two immiscible polymers, different strategies, such as the incorporation of

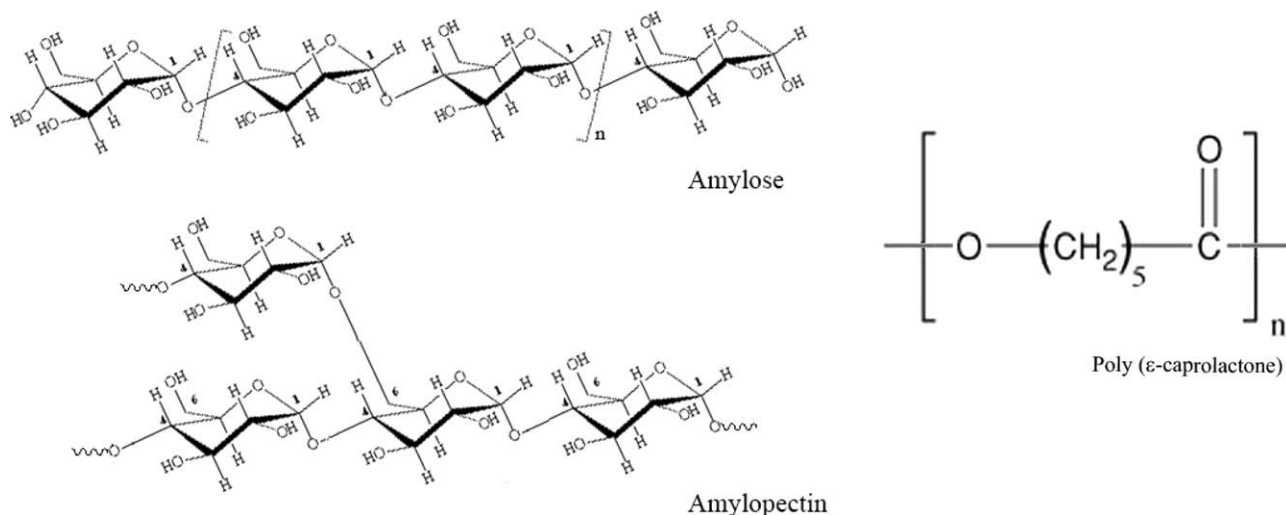


Figure 1. Chemical structure of starch: amylose and amylopectin and polycaprolactone.

compatibilizers to the starch blends, have been analyzed. Avella *et al.*²⁰ introduced a reactive functional group (pyromellitic anhydride) on a PCL phase to increase the polar nature of the matrix and so to improve the adhesion between the components of materials.

Citric acid (CA) can be an appropriate compatibilizer because it is a cheap organic acid widely used in the food industry with cross-linking capability through the reaction of its carboxyl groups.^{21,22} The three carboxyl groups in CA molecules can interact with the hydroxyl groups of the starch molecules through the formation of esters, which contributes to the decrease in the hydrophilic nature of the starch. According to other authors, esterification using polycarboxylic acids takes place with the polymer's hydroxyl groups at high temperatures (about 160°C), through the formation of anhydride groups.²³ This reaction can contribute to improve the water vapor barrier properties of the starch matrix due to the reduction of available hydroxyl groups²⁴ while decreasing the crystallization and retrogradation phenomena of the starch polymers.²⁵ CA can also act as compatibilizer, plasticizer, and depolymerization agent with different polymers depending on the processing conditions.²⁶ Likewise, CA can act as a catalyst for ϵ -CL polymerization and transesterification reactions in PCL.²⁷ The incorporation of CA to starch-PCL blends could improve the polymers' compatibility due to the enhancement of the starch hydrophobicity through the process of esterification, thus giving rise to films with more adequate properties for food packaging: with less water and time sensitivity and better mechanical response. CA has been used as compatibilizer in starch/poly(butylene adipate-co-terephthalate) films obtained by one-step reactive extrusion, notably improving of the film properties.²⁸ Likewise, properties of starch/poly(lactic acid) blend films were also improved by adding CA.^{26,29} No previous studies have been found about the effect of CA on starch-PCL blend films.

The aim of this work was to analyze the influence of CA addition on the structural, thermal, and physical properties of starch-PCL blend films obtained by compression molding, and their stability throughout the storage time.

MATERIALS AND METHODS

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). PCL (pellets ~3 mm, average M_n 80,000 Daltons, impurities <1.0% water) was provided by Fluka (Sigma-Aldrich Chemie, Steinheim, Germany). CA was provided by Fisher (Scientific Afora, Valencia, Spain). Phosphorus pentoxide (P_2O_5), magnesium nitrate-6-hydrate ($Mg(NO_3)_2$), sodium hydroxide (NaOH), and phenolphthalein were obtained from Panreac Química, S.A. (Castellar Vallés, Barcelona).

Film Preparation

Eleven formulations based on starch and PCL, with and without CA, were prepared. Starch:PCL ratios (w/w) were 100:0, 90:10, 80:20, 70:30, 60:40, and 0:100 while a starch:CA ratio of 1:0.01 (w/w) was used; 30% (wt) of glycerol with respect to the starch content was added as plasticizer. Native starch and glycerol were dispersed in distilled water (2 g of starch/g water) and, afterwards, PCL was added to the aqueous mixture. The blends were identified by the percentage of starch (S) and the presence of CA: S90, S90-CA, S80, S80-CA, S70, S70-CA, S60, S60-CA. Films with 100% starch (S), with and without CA, and PCL (PCL) were also analyzed for comparisons.

Aqueous blends were progressively melt-blended using a two-roll mill (Model LRM-M-100, Labtech Engineering, Thailand) at 160°C and 8 rpm for 30 min until a homogeneous paste sheet was obtained. The CA was added to the blends in the last 10 min of the homogenization. The paste sheet formed was conditioned at 25°C and 53% RH using $Mg(NO_3)_2$ oversaturated solutions for 48 h before compression molding.

The films were obtained by compression moulding (Model LP20, Labtech Engineering, Thailand). Four grams of the paste were put onto steel sheets and preheated on the heating unit for 5 min. The films were performed at 160°C for 2 min at 30 bars, followed by 6 min at 130 bars; thereafter, a cooling cycle (40°C/min) was applied for 3 min. The films obtained were

conditioned at 25°C and 53% RH for 1 (initial time) and 5 (final time) weeks before their characterization.

Film Characterization

Film Thickness and Extensibility. The film thickness was measured with a Palmer digital micrometer (Palmer–Comecta, Spain, ± 0.001 mm) at six random positions around the film. The extensibility during the thermo-compression step was estimated by the relationship between the surface and the weight of films with known dimensions. This parameter was expressed in cm^2/g of the film.

Structural Properties. The surface morphology of the samples, conditioned for 5 weeks at 25°C and 53% RH, was analyzed using an atomic force microscope (AFM) (Multimode 8, Bruker AXS, Santa Barbara) with a NanoScope[®] V controller electronics. Measurements were taken using the PeakForce QNM[®] mode (Quantitative Nanomechanical Mapping). The statistical parameters: average roughness (R_a : average of the absolute value of the height deviations from a mean surface), root-mean-square roughness (R_q : root-mean-square average of height deviations taken from the mean data plane), and roughness factor (r : ratio between the three-dimensional surface and two-dimensional area projected onto the threshold plane), were calculated according to the method ASME B46.1.³⁰ The DMT Modulus map, derived from PeakForce QNM, was obtained. Three replicates for each formulation were taken to obtain these parameters.

The microstructural analysis of the cross-sections of the films was carried out by using a scanning electron microscope (SEM) (JEOL JSM-5410, Japan). The film samples were maintained in desiccators with P_2O_5 for 2 weeks at 25°C and the observations were made in duplicate for each formulation. Pieces of about 0.5 cm^2 were cut from films and mounted on copper stubs perpendicularly to their surface. Samples were gold coated and observed, using an accelerating voltage of 10 kV.

A diffractometer (XRD, Bruker AXS/D8 Advance) was used to obtain the X-ray diffraction spectra. All samples (equilibrated for 1 and 5 weeks) were analyzed at 25°C and 53% RH, between 2θ : 5° and 30° using $\text{K}\alpha$ -Cu radiation (λ : 1.542 Å), 40 kV and 40 mA with a step size of 0.05°. For this analysis, the samples were cut into 4 cm^2 . The degree of crystallinity of starch matrices was calculated as the ratio between the absorption peaks and the total diffractogram area, expressed as percentage, by using OriginPro 8.5 software. Moreover, basal spacing for starch crystallites was calculated applying the Bragg equation.

Thermal Behavior. A Differential Scanning Calorimeter DSC 1 Star[®] System (Mettler-Toledo Inc., Switzerland) was used to analyze phase transitions (PCL crystallization and starch glass transition) of the films. Weighed amounts of samples were placed into aluminium pans, sealed and drilled to favor moisture loss during the heating step. The thermograms were obtained using three scans. First, a scan from -80°C to 160°C at a rate of $50^\circ\text{C}/\text{min}$ was used to obtain the PCL melting properties, while the bonded water in the film was released. The initial and final weights of the pans were registered to assess water loss during

the first heating step. Then, the temperature was lowered to -80°C at a rate of $50^\circ\text{C}/\text{min}$. In this cooling step, the PCL crystallization temperature (T_c) and enthalpy (ΔH_c) were obtained. Finally, samples were heated to 160°C at a rate of $20^\circ\text{C}/\text{min}$ in order to analyze the starch glass transition and the melting properties of PCL.

Physicochemical Properties. The film water content was determined in samples conditioned at 53% RH and 25°C. Samples were dried for 24 h at 60°C using a convection oven (J.P. Selecta, S.A. Barcelona, Spain). Afterwards, the samples were placed in a desiccator at 25°C with P_2O_5 for 2 weeks. This was carried out in triplicate.

The film solubility in water was determined by holding the sample in bidistilled water (film:water ratio of 1:10) for 48 h. Afterwards, these 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 transferred to a desiccator with P_2O_5 at 25°C for 2 weeks to remove the residual water. Their initial and final weights were taken to calculate the amount of the film solubilized in water. These analyses were carried out in triplicate for each formulation. The bonded CA in the film was also determined in this test, by titration of the water solution. Free CA was assumed to dissolve in the aqueous phase and was determined by titration of an aliquot of the solution with NaOH (0.1N), using phenolphthalein as indicator. Analyses were carried out in triplicate for each formulation.

A universal test machine (TA.XTplus model, Stable Micro Systems, Haslemere, England) was used to determine the elastic modulus (EM) and the tensile strength (TS), and the elongation (E) at break of the films, according to the ASTM D882³¹ 2.5-cm wide and 5-cm long equilibrated samples were mounted in the film-extension grips of the testing machine and stretched at 50 mm min^{-1} until breaking. Ten replicates were performed for each formulation.

The ASTM E96-95³² gravimetric method was used to determine the Water Vapor Permeability (WVP) of the films, considering the modification proposed by McHugh *et al.*³³ 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 RH of the cabinet (53%) was held constant using $\text{Mg}(\text{NO}_3)_2$ oversaturated solutions. The cups were weighed periodically (0.0001 g) and the water vapor transmission (WVTR) was determined from the slope obtained from the regression analysis of weight loss data versus time. From WVTR data, the vapor pressure on the film's inner surface (p_2) was obtained with eq. (1), proposed by McHugh *et al.*³³ to correct the effect of the concentration gradients.

$$\text{WVTR} = \frac{P \cdot D \cdot L_n [P - p_2 / P - p_1]}{R \cdot T \cdot \Delta z} \quad (1)$$

where P , total pressure (atm); D , diffusivity of water through air at 25°C (m^2/s); R , gas law constant ($82.057 \times 10^{-3} \text{ m}^3 \text{ atm}$

Table I. Mass Fraction (X_i , g Compound/g Dried Film) of the Different Components (Starch: S, PCL, Glycerol: Gly and Citric Acid: CA) in Dried Films and Mean Values and Standard Deviation of Film Thickness and Extensibility During the Thermo-Compression Step

Films	X_S	X_{PCL}	X_{Gly}	X_{CA}	Thickness (μm)	Extensibility (cm^2/g)
S	0.7692	-	0.2308	-	268 (22) ^e	23.9 (1.1) ^a
S-CA	0.7634	-	0.2290	0.0076	217 (22) ^c	32 (4) ^{bc}
S90	0.7087	0.0787	0.2126	-	232 (17) ^{cd}	28 (2) ^{abc}
S90-CA	0.7037	0.0782	0.2111	0.0070	293 (27) ^f	23.7 (0.7) ^a
S80	0.6452	0.1613	0.1935	-	221 (9) ^{cd}	32 (2) ^c
S80-CA	0.6410	0.1603	0.1923	0.0064	239 (17) ^d	27 (2) ^{ab}
S70	0.5785	0.2479	0.1736	-	224 (9) ^{cd}	31.1 (1.1) ^{bc}
S70-CA	0.5752	0.2465	0.1726	0.0058	227 (11) ^{cd}	29.8 (0.6) ^{bc}
S60	0.5085	0.3390	0.1525	-	168 (13) ^b	45 (6) ^d
S60-CA	0.5059	0.3373	0.1518	0.0051	172 (14) ^b	41 (2) ^d
PCL	-	1.0000	-	-	149 (17) ^a	57 (9) ^e

Different superscript letters within the same column indicate significant differences among formulations ($P < 0.05$).

$\text{kmol}^{-1} \text{K}^{-1}$); T , absolute temperature (K); Δz , mean stagnant air gap height (m), considering the initial and final z value; p_1 , water vapor pressure on the solution surface (atm); and p_2 , corrected water vapor pressure on the film's inner surface (atm). Water vapor permeance was calculated using eq. (2) as a function of p_2 and p_3 (pressure on the film's outer surface in the cabinet).

$$\text{permeance} = \frac{\text{WVTR}}{p_2 - p_3} \quad (2)$$

The permeability was calculated by multiplying the permeance by film thickness. This analysis was carried out in triplicate.

The oxygen permeability (OP) of the films was determined using an OX-TRAN Model 2/21 ML (Mocon Lippke, Neuwied, Germany) according to the ASTM D3985-05.³⁴ Three samples conditioned at 53% RH and 25°C for each formulation were analyzed. The transmission values were determined every 20 min until equilibrium was reached. The film area used in the tests was 50 cm². The film thickness was considered in all cases to obtain the OP values.

The transparency of the films was determined using the Kubelka-Munk theory for multiple scattering,³⁵ as was the gloss, at 85° incidence angle, according to the ASTM D523.³⁶ The surface reflectance spectrum was determined from 400 to 700 nm with a spectrophotometer CM-3600d (Minolta Co., Tokyo, Japan) on both a white and a black background. As light passes through the film, it is partially absorbed and scattered, which is quantified by the absorption (K) and the scattering (S) coefficients. Internal transmittance (T_i) of films was determined using eq. (3).

$$T_i = \sqrt{(a - R_0)^2 - b^2} \quad (3)$$

where R_0 is the reflectance of the film on an ideal black background. The parameters a and b were calculated by eqs. (4) and (5).

$$a = \frac{1}{2} \left(R + \frac{R_0 - R + R_g}{R_0 R_g} \right) \quad (4)$$

$$b = \sqrt{a^2 - 1} \quad (5)$$

where R is the reflectance of the sample layer backed by a known reflectance R_g . Three replicates were used for each formulation. Internal transmittance (T_i) at 650 nm was used to compare samples.

The gloss was determined using a flat surface gloss meter (Multi-Gloss 268, Minolta, Germany). Three films of each formulation were analyzed, taking three measurements in each sample film. 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.

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.

RESULTS

Thickness and Extensibility

It shows the mass fraction (X_i) of the different components in dried films, thickness of the obtained films, and their extension during the compression moulding step, expressed as the area per mass unit of the material. The PCL films were thinner than the other formulations due to their greater flowability and extensibility. In contrast, the film thickness tended to increase when the amount of starch in the matrix rose, due to the starch's reduced ability to flow. Incorporation of CA in the formulations led to an increase in the extensibility with net starch films, but had an opposite effect on starch-PCL blends with the lowest PCL ratio, and had no significant effect on films with over 30% PCL, when the influence of the greater amount of PCL in the film flowability was more notable. Chabrat *et al.*²⁶ report for blend films of wheat flour and PLA, processed at high temperature, that CA in the blends acts as compatibilizer (esterification, hydrogen bonds), as starch plasticizer and/or as depolymerization agent for both starch and PLA. Similar effects

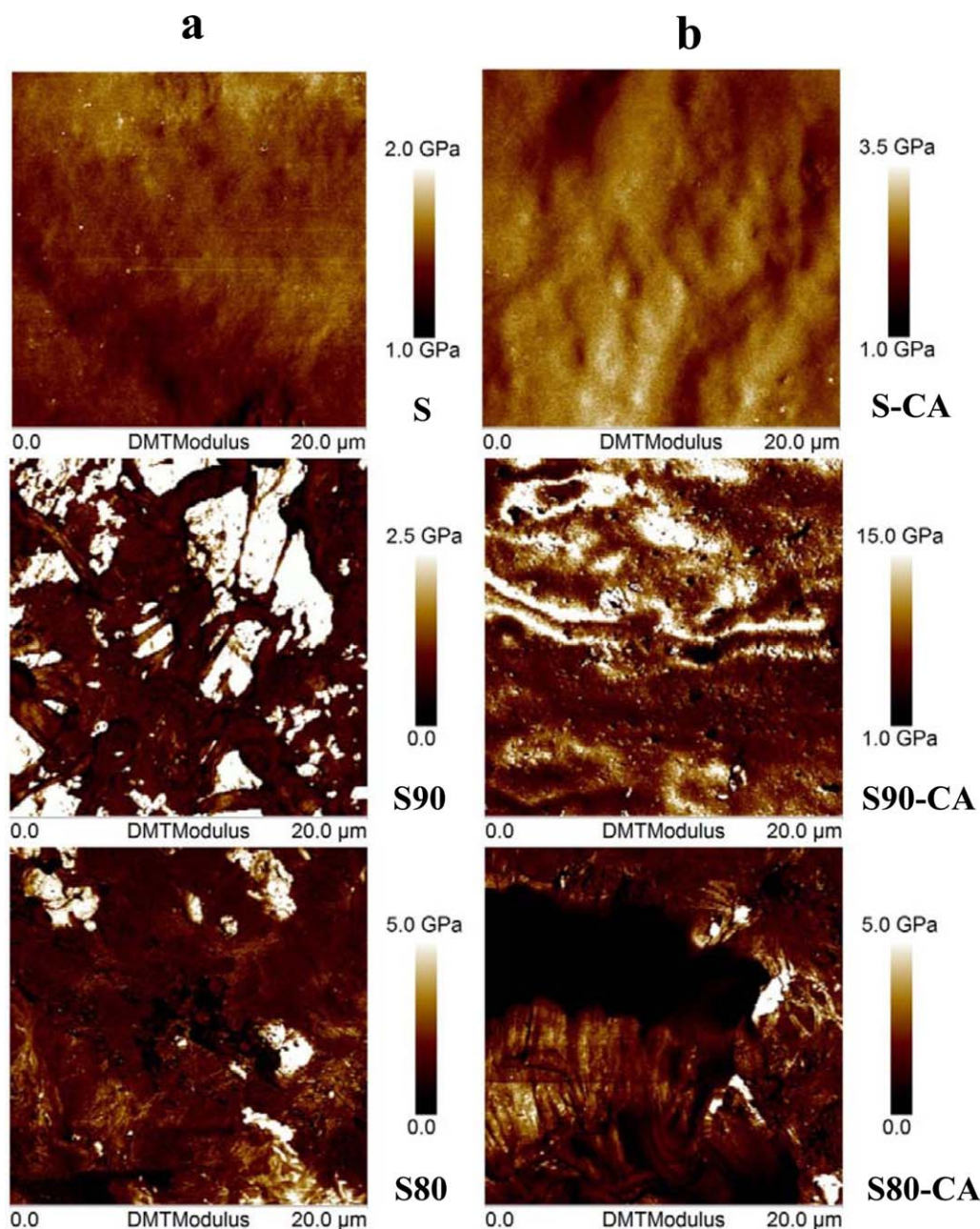


Figure 2. DMT Modulus maps obtained by AFM of starch:PCL films without (a) and with (b) citric acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

could be expected for CA in the studied S-PCL blends as concerns the starch-CA interactions. In fact, plasticization and/or depolymerization effects can be deduced from the increase in the flowability of the starch when CA was added. Its opposite effect at low PCL ratios in the film could point to the promotion of the interchain forces between both polymers promoted by CA.

Structural Analysis

Atomic Force Microscopy PeakForce QNM mode was used to acquire the images shown in Figure 2, where the DMT modulus maps for the samples' surfaces are plotted. The control formulations (S and PCL) showed more homogenous values of the sur-

face modulus than the blend films, although a great difference in their values can be observed for both control films. Net starch films had a much harder surface than net PCL films. The addition of CA to starch films did not introduce notable changes in the surface homogeneity, but in some areas, higher values of the modulus were registered, which could be due to the CA crosslinking effect. When the PCL was added to the starch matrix, the heterogeneity of the material greatly increased while the modulus reached values near to those obtained for starch films, with very soft zones, corresponding to the noncrystallized domains. In samples containing 90% starch, the incorporation of CA seemed to reduce the modulus heterogeneity

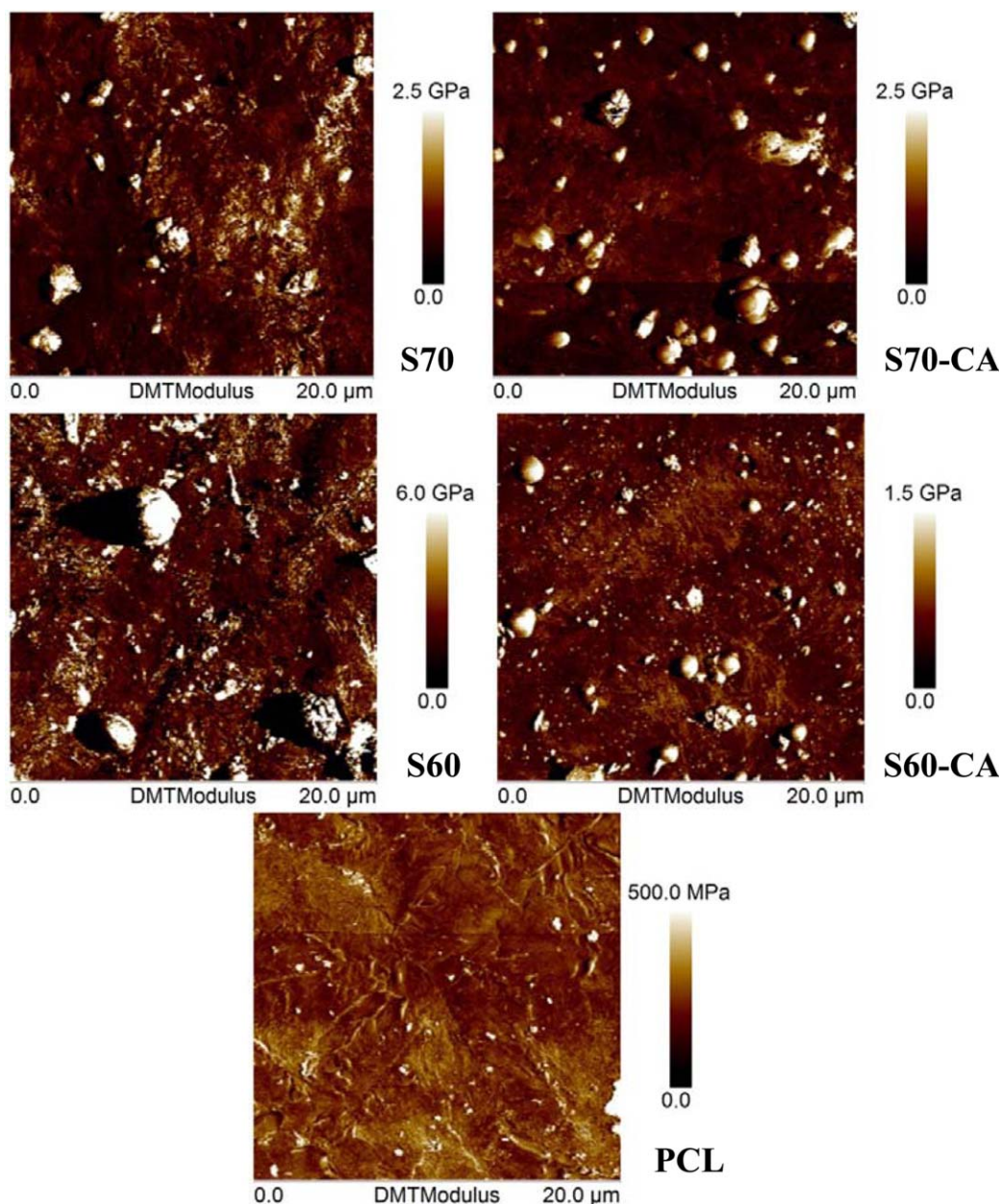


Figure 2. Continued.

level and they were harder (the surface area percentage with values of the modulus lower than 1.5 GPa was 1.2% and 67.9%, respectively for films with and without CA). This suggests that CA could be responsible for cross-linking in the starch phase²² at the same time as it contributes to enhance the polymer compatibility to some extent. This effect was not observed, or was masked, when the content of PCL was higher.

Figure 3 shows SEM micrographs of the cross-section of the studied films, with or without CA, conditioned at 25°C and 53% RH for 1 week. S and PCL samples have a continuous and homogeneous structure. The PCL sample showed its typical cryofracture behavior in liquid nitrogen, where elongation of the amorphous zones (very ductile, $T_g = -67^\circ\text{C}$)²⁰ can be observed

despite the low temperature. When PCL was added to the starch matrix, the films were heterogeneous, in agreement with the noncompatibility of the polymers. In the formulations with low PCL ratio (S90), an effective distribution of PCL in the starch matrix can be observed. Nevertheless, when the proportion of PCL increased (S70 and S60) large domains of interpenetrated PCL-rich and starch-rich phases were observed.

The addition of CA caused changes in the films' microstructure. The S-CA films showed a continuous matrix with some cracks, which suggests the formation of a more brittle matrix. Likewise, S-CA films were more homogeneous than the S films, which indicates that CA contributes to the fragmentation and dissolution of the native starch granules (acid gelatinization), as observed by other authors.^{37,38} Likewise, in the formulations with less PCL

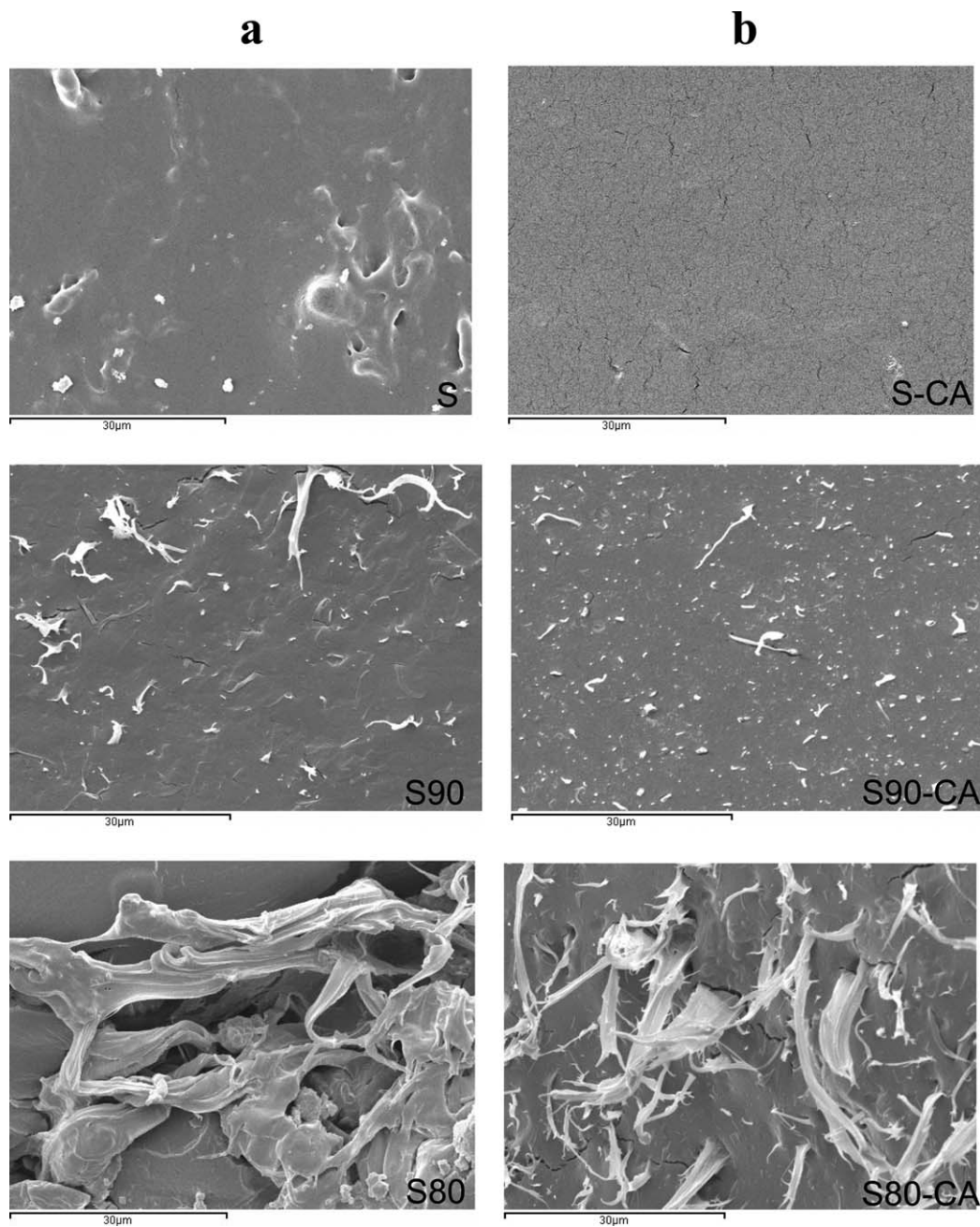


Figure 3. SEM micrographs of starch: PCL films without (a) and with (b) citric acid.

(S80-CA and S90-CA), the CA promotes changes in the dispersion of PCL in the starch matrix; PCL particles are finer and better dispersed in the starch continuous phase. Similar results were reported by Chabrat *et al.*²⁶ for blend films of wheat flour-PLA-glycerol (75:25:15) with different ratios of CA. In the formulations S70-CA and S60-CA, the changes were not evident probably due to the fact that the ratio of PCL is too high to be compatible with the starch. The increase in polymer compatibility of PCL may be due to the partial esterification of starch hydroxyl groups with CA, and its depolymerization effects on both polymers which can induce a greater affinity between them.^{23,26}

Figure 4 shows the X-ray diffraction patterns of the films stored for 1 and 5 weeks under controlled conditions. Spec-

trum of S films presented low intensity, broad diffraction peaks, and a large amorphous scattering halo. These characteristics correspond to a semicrystalline polymer with low crystallinity. In all formulations containing starch, the typical crystalline forms of amylose were V type, with peaks at 2θ of about 13° and 20° . This V type crystalline structure is formed by crystallization of amylose in single helices involving glycerol or lipids. Nevertheless, this V-type crystalline structure can be divided into two subtypes, namely V_a (anhydrous) with peaks at 13.2° and 20.6° and V_h (hydrated) with peaks at 12.6° and 19.4° (Castillo *et al.*³⁹). These two subtypes could be observed in the different films, depending on their composition and storage time. Starch-glycerol films showed V_a

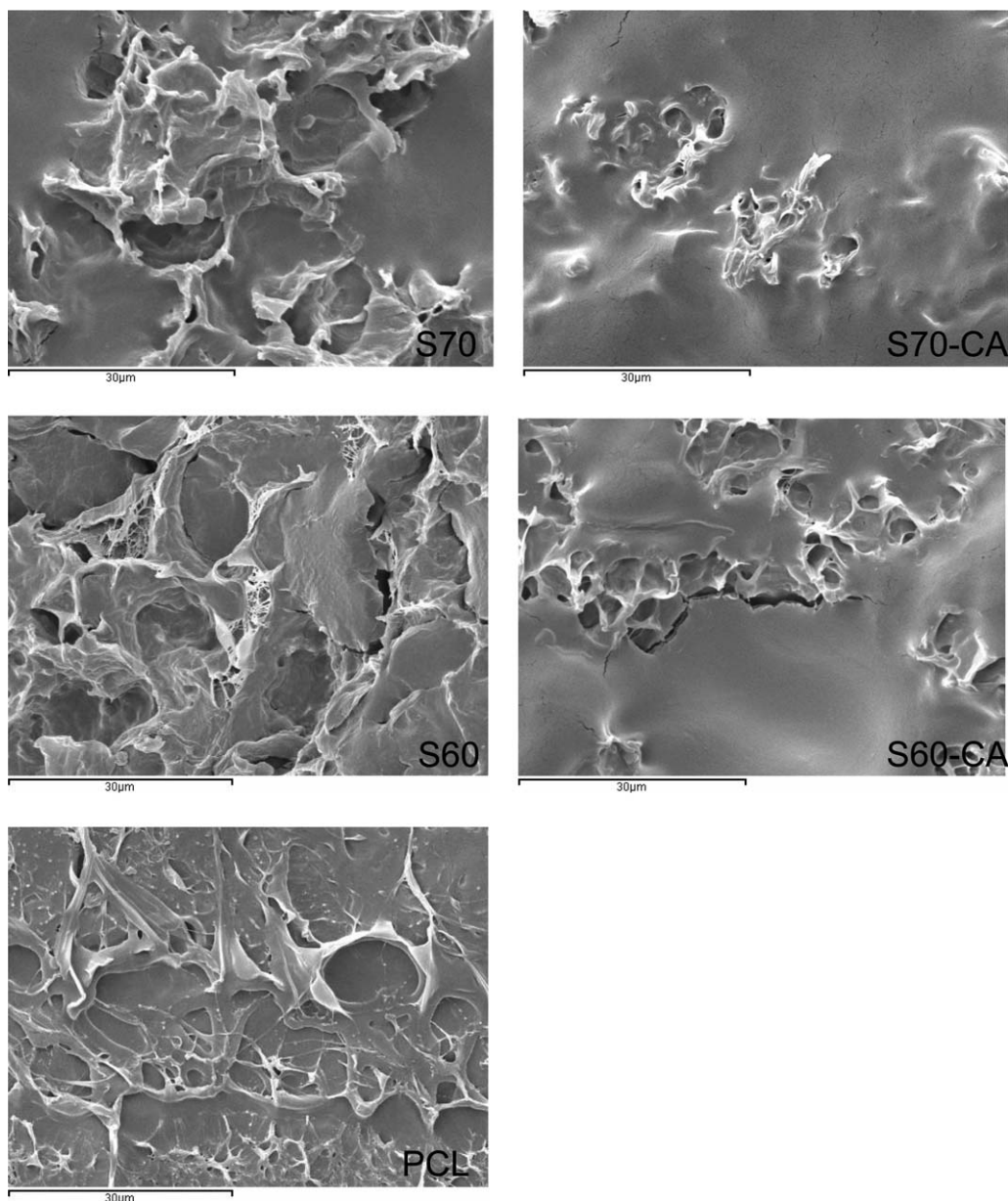


Figure 3. Continued.

subtype at both storage times, whereas when they contained CA, both V_a and V_h subtypes were initially formed and predominantly developed into the V_a subtype during storage. So, CA addition promoted the simultaneous formation of V_a and V_h crystalline subtypes, while the crystallinity degree increased at both 1 and 5 storage weeks. This could be due to the hydrolysis effect which, upon reducing the mean molecular weight, promotes molecular mobility, thus favoring the crystalline arrangement. At 5 storage weeks, there were no differences between the observed peaks for S and S-CA samples, although the increase in the crystallinity degree was higher in S-CA. Some authors⁴⁰ reported that the citrate substituent altered chain packing and generated more amorphous structures in starch. Nevertheless, probably due to the hydrolysis

effect, CA promoted starch crystallization under the conditions used for film preparation.

In PCL starch blends, the characteristic peaks of crystalline PCL appeared, but starch peaks can also be distinguished, since overlapping only occurs at 2θ near 21° . In all these blends, starch showed the V_a subtype crystallization at initial time but it became the V_h subtype after the 5 storage weeks, regardless of the presence of CA. This tendency was only observed when PCL was present in the film, which suggests that PCL induced the formation of this crystalline subtype. The interplanar basal spacing deduced from 2θ values was greater for the V_h form than for V_a , these being 6.7 and 4.3 Å and 7.0 and 4.6 Å, respectively for V_a and V_h .

When the amount of PCL increased, sharper and more intense peaks were observed in the diffractograms, due to the PCL

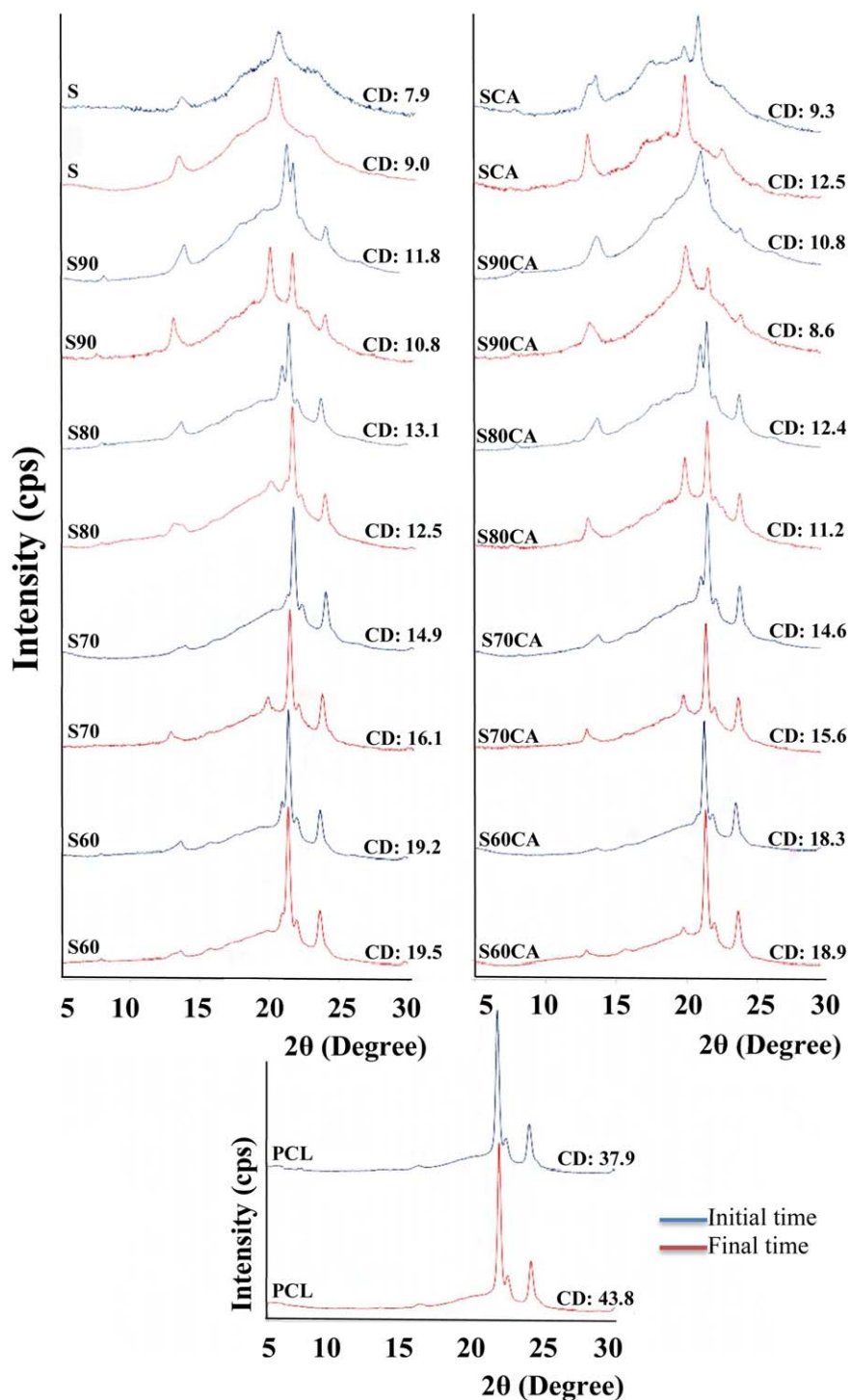


Figure 4. X-ray diffraction patterns of starch:PCL films without (a) and with (b) citric acid at initial and final time of storage at 53% relative humidity and 25°C. Crystallinity degree (CD, %) of each sample is shown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crystallinity, with the main peaks at 2θ : 22° and 24°, as reported by Mark.⁴¹ According to the theory of kinematical scattering, peak sharpening is caused by either greater crystal size or the absence of lattice defects. The degree of crystallinity in the films increased when the PCL ratio rose, due to the predominantly crystalline structure of this polymer. In general, CA addition to

starch PCL blends gave rise to a slightly lower ratio of crystallinity in the films at both 1 and 5 storage weeks, contrary to what was observed for net starch films. No clear effect of storage time could be observed in blend films, since small increases or decreases in the percentage of crystallinity could be observed, depending on the formulation.

Therefore, CA or PCL slightly modified the starch crystallization pattern. CA promoted the crystalline forms in glycerol plasticized starch films, whereas it reduced the total degree of crystallinity in the films when they contain PCL, which could indicate that CA affected the PCL crystallinity degree. In general, a slight progress of crystallization occurred during storage time, but this was not appreciable for blend films with a lower ratio of PCL. CA promoted the formation of V_h subtype crystalline forms in starch films, as well as PCL at long storage times.

Thermal Analysis

It shows the thermal properties of the studied films conditioned for 1 and 5 weeks. Two heating scans and one cooling scan were performed. In the first heating scan, the melting temperature (T_m) of PCL was determined as the peak temperature of the endotherm as well as the melting enthalpy (ΔH_m). This has been analyzed for samples stored for different times (1 and 5 weeks, initial and final) in order to detect changes in the PCL crystalline structure, as could be deduced from X-ray diffraction patterns. During the cooling step, the crystallization temperature (T_c peak) and enthalpy (ΔH_c) of PCL were obtained from the crystallization exotherm. Finally, during the second heating scan, the melting temperature, and enthalpy of the newly crystallized PCL (during the cooling step) and the glass transition temperature (T_g) of starch (midpoint) were determined.

The T_g of the starch phase significantly decreased ($P < 0.05$) when PCL was incorporated into the starch matrix. This decrease was constant (about 12°C), regardless of the PCL ratio in the blend. This indicates that PCL partially solubilizes in the starch phase, thus decreasing the mean molecular weight of the amorphous blend and the molecular mobility, which reduces the T_g value. The amount of PCL that the starch phase can incorporate at a molecular level was less than 10%, since this sample also shows two phases, as revealed by the microstructural analyses.

The incorporation of CA also led to a decrease in the T_g values of starch (ΔT about 13°C) and this effect was maintained for starch-PCL blend films. This decrease in the T_g can be attributed to a depolymerisation effect in starch, which implies a reduction in the polymer molecular weight leading to an increase in the molecular mobility, but also to a better solubilization of PCL in the starch phase with a similar impact in the mean molecular weight of this amorphous phase or to a combination of these two phenomena, as reported by Chabrat *et al.*²⁶ for wheat flour-PLA blend films.

The T_c values of the PCL in the different films were 12°C and there were no significant differences between the different formulations or net PCL films. The crystallization enthalpy (ΔH_c) was about 52 J/g PCL for samples without CA and slightly decreased (49–50 J/g PCL) when CA was present in the film, the difference being statistically significant. This suggests that changes in the ability of PCL to crystallize were induced by CA, in agreement with that deduced from the X-ray diffraction data.

The melting behavior of PCL in the first heating scan, where no fusion was previously provoked, gave T_m values of 63°C and ΔH_m values of about 72 J/g of PCL for samples stored for 1

Table II. Mean Values and Standard Deviation of Thermal Properties of the Starch:PCL Films Stored for 1 Week (Initial) and 5 Weeks (Final)

Films	Glass transition			Crystallization Initial			Fusion in the first heating scan			Fusion in the second heating scan		
	T_g (midpoint)	ΔC_p	T_c peak	ΔH_c (J/g PCL)	T_m peak	ΔH_m (J/g PCL)	ΔH_m (J/g PCL)	T_m peak	ΔH_m (J/g PCL)	T_m peak	ΔH_m (J/g PCL)	
S	126.0 (0.3) ^d	0.112 (0.002) ^b	-	-	-	-	-	-	-	-	-	
S-CA	113.0 (0.7) ^b	0.054 (0.009) ^a	-	-	-	-	-	-	-	-	-	
S90	114.5 (0.7) ^c	0.17 (0.02) ^d	12.0 (0.2) ^a	51.4 (0.9) ^{bc}	62.4 (0.7) ^{bc}	72.4 (0.4) ^a	81.9 (1.0) ^{ab}	55.18 (0.05) ^{bcd}	51.8 (1.3) ^a	54.9 (0.2) ^{bc}	50 (2) ^a	
S90-CA	101.6 (0.2) ^a	0.112 (0.008) ^b	12.10 (0.14) ^a	49.2 (0.9) ^a	61.1 (0.9) ^a	72.1 (0.5) ^a	79.7 (0.5) ^a	54.0 (0.2) ^a	50 (2) ^a	54.0 (0.2) ^a	50 (2) ^a	
S80	114.31 (0.05) ^c	0.1280 (0.0014) ^{bc}	12.5 (0.6) ^{ab}	52.3 (0.3) ^c	62.9 (0.6) ^c	72.3 (1.3) ^a	82.3 (0.7) ^b	55.4 (0.3) ^d	51.2 (1.3) ^a	55.4 (0.3) ^d	51.2 (1.3) ^a	
S80-CA	101.2 (0.2) ^a	0.131 (0.010) ^{bc}	12.6 (0.4) ^{ab}	49.3 (0.9) ^a	60.97 (0.12) ^a	72.2 (0.4) ^a	81.0 (1.5) ^{ab}	54.11 (0.05) ^a	50.5 (0.9) ^a	54.11 (0.05) ^a	50.5 (0.9) ^a	
S70	114.35 (0.13) ^c	0.139 (0.013) ^c	12.3 (0.3) ^{ab}	52.0 (0.6) ^c	62.32 (0.62) ^{bc}	72.1 (0.3) ^a	81.7 (0.9) ^{ab}	54.9 (0.2) ^{bc}	51.4 (1.4) ^a	54.9 (0.2) ^{bc}	51.4 (1.4) ^a	
S70-CA	101.53 (0.13) ^a	0.052 (0.014) ^a	12.95 (0.07) ^b	50.7 (1.1) ^{abc}	61.55 (0.03) ^{ab}	72.4 (0.4) ^a	79.9 (0.6) ^a	54.8 (0.4) ^b	49.9 (1.1) ^a	54.8 (0.4) ^b	49.9 (1.1) ^a	
S60	114.8 (0.2) ^c	0.126 (0.004) ^{bc}	12.33 (0.07) ^{ab}	52.2 (0.8) ^c	63.0 (0.2) ^c	72.5 (0.6) ^a	81.9 (1.0) ^{ab}	55.13 (0.04) ^{bcd}	51.0 (1.3) ^a	55.13 (0.04) ^{bcd}	51.0 (1.3) ^a	
S60-CA	100.9 (0.5) ^a	0.041 (0.004) ^a	12.3 (0.3) ^{ab}	50.3 (0.2) ^{ab}	61.51 (0.02) ^{ab}	72.2 (0.4) ^a	79.8 (0.4) ^a	54.88 (0.14) ^b	49.7 (1.0) ^a	54.88 (0.14) ^b	49.7 (1.0) ^a	
PCL	-	-	12.6 (0.6) ^{ab}	52.4 (0.3) ^c	63.5 (0.6) ^a	72.8 (1.4) ^a	82.2 (1.5) ^b	55.4 (0.4) ^{cd}	51.0 (1.2) ^a	55.4 (0.4) ^{cd}	51.0 (1.2) ^a	

Different superscript letters within the same column indicate significant differences among formulations ($P < 0.05$).

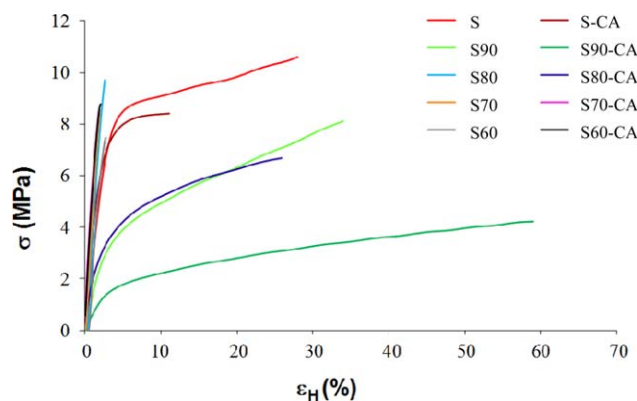


Figure 5. Typical stress–strain curves of the different films after 1 week of storage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

week, regardless of the film formulation; this indicates that, at this storage time, PCL is crystallized to the same extent in every case. Similar results have been reported by other authors for films of wheat thermoplastic starch/PCL blends,¹³ LDPE/starch/PCL blends,¹⁴ or chlorinated starch–PCL blends.⁴² Nevertheless, after 5 storage weeks, a slight increase was observed in the melting peak, T_m , and ΔH_m , which indicates that the crystallization of PCL progresses slightly during storage. This occurred to a slightly lesser extent when CA was incorporated to the formulation (lower values of ΔH_m).

Likewise, the T_m and ΔH_m obtained in the second scan were lower than the values obtained in the first scan, as observed by other authors for pure PCL.⁴³ The ΔH_m values of the second scan were very close to the ΔH_c values, in line with the melting of the crystallized polymer during the thermal scanning.¹⁷ From the ΔH_m values obtained in the first and second scans, supercooling effects during the cooling step in DSC analyses can be deduced, while CA slightly reduces the ability of PCL to crystallize. This suggests that there are molecular changes in the polymer either brought about by depolymerisation or by the occurrence of stronger interactions with the starch chains promoted by CA reactions.

Physicochemical Properties

Figure 5 shows typical tensile curves of the different films stored for 1 week under controlled conditions. The incorporation of CA to the net starch film provoked a decrease in the film stretchability, while the resistance to break and elastic modulus were hardly affected. This has previously been reported and attributed to the crosslinking of starch chains, which reduced their possibilities of slipping during the tensile test.²² Nevertheless, in blend films with a low ratio of PCL (S90 and S80), CA greatly increased the film stretchability, although the elastic modulus and resistance to break were reduced. This suggests that the polymer compatibility increased and that the films gain extension ability associated with the presence of a very stretchable polymer, such as PCL. This is particularly effective in films containing the lowest PCL ratio. Blend films with a higher ratio of PCL, both with and without CA, exhibited a very low deformation capacity and break at low deformation levels probably due to the low adhesion forces between the phases in the

matrix, where both polymers are arranged in large domains of separated phases with scarce union forces between them.

Figure 6 shows the tensile parameter values at 1 and 5 storage weeks for the different formulations. When the starch is blended with PCL, EM was greater than in the control formulations (S and PCL), except for sample S90 where EM was significantly lower ($P < 0.05$). Likewise, EM values significantly increased during storage in almost every case, which indicates that starch chain aggregations progressively increased in the continuous phase, thus hardening the matrix. The increase in EM for PCL concentrations over 20% suggests that the conformation of the starch chains in the starch domains changed in the presence of the hydrophobic PCL chains in the matrix, thus promoting stronger intermolecular bonds, while the forces in the union zones are weak. The latter was reflected in the significant decrease in the film's resistance to break and stretchability when the PCL ratio increased in the matrix. Only the S90 sample gains extensibility, as compared with the S control, especially when it contains CA (S90-CA), although it loses resistance to break. These results indicate that, at this PCL ratio, a better integration of both polymers occurred, as deduced from thermal behavior and microstructural analyses. This integration was enhanced when CA was added to the film, which led to a significant gain in the film stretchability, probably through the role of PCL chains in the matrix. Net PCL films exhibited very ductile behavior with yield point (not break) at 18.17 ± 1.06 MPa and 13 ± 4 percentage deformation. Other authors reported that the PCL films' break occurs at 1100%.⁴⁴

The incorporation of CA to the films caused a reduction in the EM and the resistance (TS) at break of the blend films, except for the S60 sample where both parameters slightly increased. As concerns elongation, CA greatly promotes the extensibility of S90 and S80 samples, whereas it did not affect the very low values of the S70 and S80 samples. These results are coherent with a combined effect of CA, previously reported by other authors for starch blend films: cross linking between starch chains, or even with the end hydroxyl groups of PCL (loss of stretchability), partial hydrolysis of the starch and PCL chains and plasticizing effect of the nonbonded CA molecules (decrease in the elastic modulus and resistance to break).^{4,22,26} The differentiated behavior of S90 and S80 samples with a relatively low ratio of PCL indicates that the interactions between starch and PCL chains promoted by CA predominate over the overall behavior of non-well-adhered separate phases of PCL and starch in blend films.

As concerns the development of the mechanical behavior of the films during storage time, two trends were observed. When the proportion of PCL was low (S90 and S80 samples with and without CA), the EM and TS parameters increased and the elongation decreased. The changes were not marked when the amount of PCL was high (S70, S70-CA, S60, and S60-CA). As previously commented on, this suggests that starch chain aggregation progressed during storage (retrogradation phenomenon), even when CA or PCL was added, this being more notable when the starch dominated in the matrix. Nevertheless, films with 10% PCL and CA maintained a good mechanical response after 5 weeks' storage time.

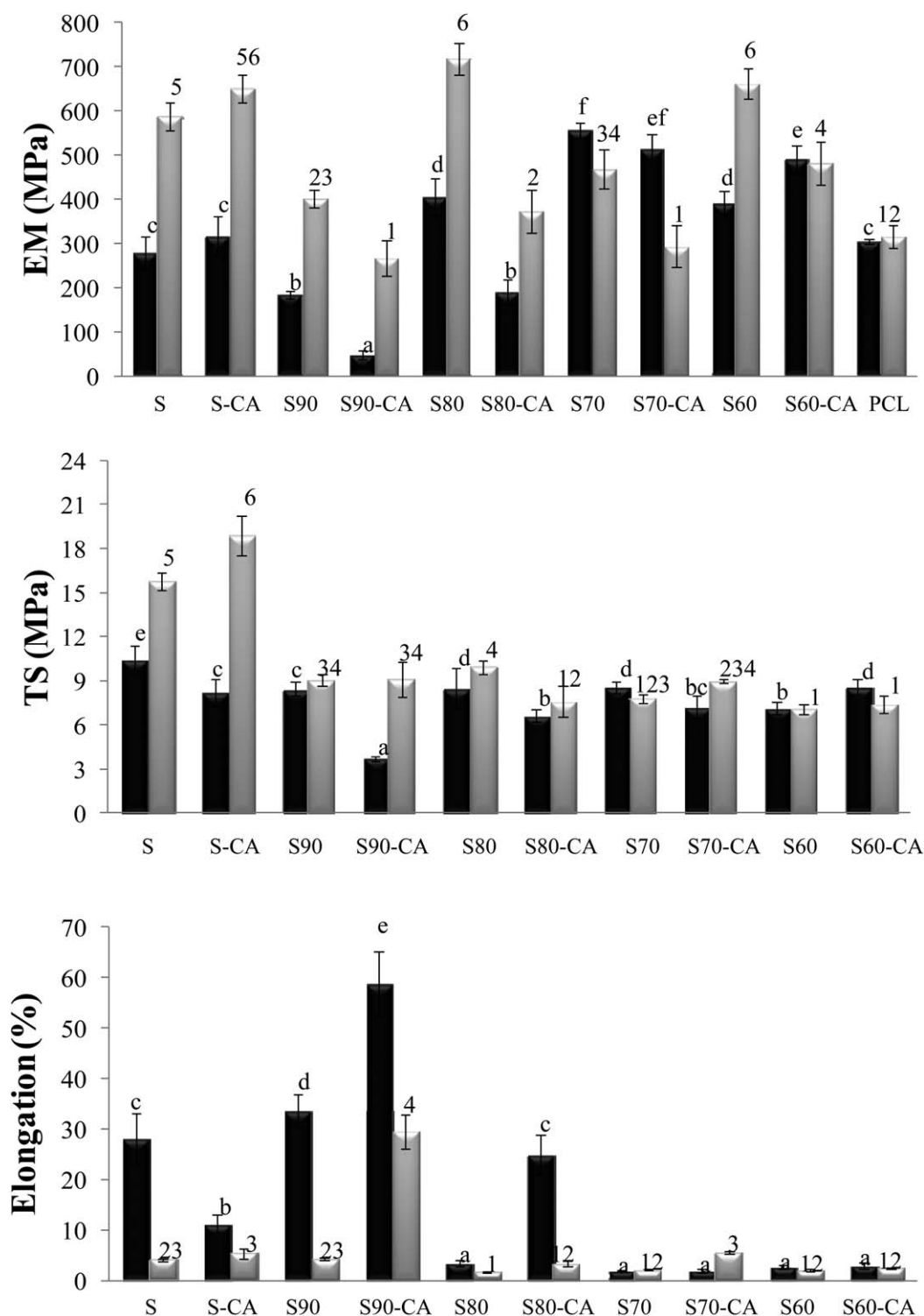


Figure 6. Mean values of elastic modulus and stress and strain at break for the different films stored for 1 (black bars) and 5 (gray bars) weeks at 53% relative humidity and 25°C. LSD intervals (95% confidence level) for each mean value are shown. Different letters or numbers on the columns indicate significant differences among formulations after 1 or 5 storage weeks, respectively.

III shows the values and standard deviation of the equilibrium water content, water solubility and bonded CA of the studied films at the initial and final storage times. The water content (X_w) decreased when the amount of PCL rose in the blend due to its hydrophobic character. In general, at 1 week of storage,

formulations with CA exhibited a significantly lower ($P < 0.05$) water content than the CA-free films. This indicates that a certain extent of esterification of the starch hydroxyl groups could occur during the film's thermoprocessing (blend in roll mills and compression molding) at the high temperature used

Table III. Mean Values and Standard Deviation of Water Content (g Water/g Dried Film), Film Solubility (g Solubilized Film/g initial Dried Film) and Bonded Citric Acid (Ratio with Respect to the Amount in the Film) of the Different Films Stored at 53% Relative Humidity and 25°C

Films	X_w		Film solubility		Bonded citric acid
	Initial	Final	Initial	Final	
S	0.0613 (0.0006) ^{h1}	0.079 (0.004) ^{g2}	0.19 (0.07) ^{d1}	0.24 (0.05) ^{d1}	-
S-CA	0.059 (0.002) ^{gh1}	0.076 (0.002) ^{fg2}	0.35 (0.03) ^{f1}	0.371 (0.012) ^{f1}	0.80 (0.03) ^a
S90	0.0664 (0.0004) ^{j1}	0.074 (0.003) ^{ef2}	0.120 (0.009) ^{bc1}	0.138 (0.002) ^{b2}	-
S90-CA	0.0543 (0.0007) ^{ef1}	0.0713 (0.0005) ^{e2}	0.328 (0.005) ^{f1}	0.331 (0.005) ^{e1}	0.84(0.03) ^a
S80	0.0535 (0.0008) ^{e1}	0.061 (0.002) ^{d2}	0.132 (0.003) ^{bc1}	0.137 (0.013) ^{b1}	-
S80-CA	0.056 (0.003) ^{ef1}	0.061 (0.015) ^{d2}	0.362 (0.013) ^{f1}	0.32 (0.02) ^{e2}	0.86(0.03) ^a
S70	0.057 (0.003) ^{fg1}	0.063 (0.004) ^{d1}	0.099 (0.003) ^{b1}	0.106 (0.006) ^{b1}	-
S70-CA	0.047 (0.003) ^{d1}	0.0578 (0.005) ^{c2}	0.24 (0.02) ^{e1}	0.30 (0.02) ^{e2}	0.81(0.04) ^a
S60	0.0409 (0.0006) ^{c1}	0.046 (0.002) ^{b2}	0.13 (0.03) ^{bc1}	0.13 (0.02) ^{b1}	-
S60-CA	0.03331 (0.00014) ^{b1}	0.0458 (0.0014) ^{b2}	0.16 (0.02) ^{cd1}	0.19 (0.02) ^{c1}	0.83(0.04) ^a
PCL	0.003 (0.002) ^{a1}	0.0021 (0.0005) ^{a1}	0.00022 (0.00011) ^{a1}	0.0004 (0.0002) ^{a1}	-

Different superscript letters within the same column indicate significant differences among formulations ($P < 0.05$). Different superscript numbers within the same row indicate significant differences due to storage time ($P < 0.05$).

(160°C) and in the absence of water, since these are adequate conditions for CA esterification reactions with chain hydroxyls.²³ The fall in the number of hydroxyls will reduce the water affinity of the polymer, while cross-linking between different starch chains will reinforce the intermolecular binding, by introducing covalent bonds thus improving the water uptake resistance.^{4,37,45} Nevertheless, a significant increase ($P < 0.05$) in the films' water content during the storage time was observed in every case, except in the pure PCL film, thus indicating that the equilibrium was not reached at 1 week of storage. At this time, the effect of CA on the films' moisture content was not significant, which suggests that there was no notable reduction of active points for water adsorption.

As concerns the water solubility of films, the values were lower than the glycerol mass fraction in the films except in the case of those films containing CA (Table I), which indicates that in no case is this component completely released to the water medium. Compared with the S formulation, films without CA experienced a significant ($P < 0.05$) decrease in water solubility when PCL was present in the film, regardless of its ratio; this is coherent with their increased hydrophobic character and the subsequent inhibition of the mass transport rate of polar water soluble compounds. On the other hand, the film solubility increased when CA was added, although this was slightly reduced for higher PCL ratios. The increase in this parameter suggests the partial hydrolysis of macromolecules caused by CA, resulting in a greater quantity of linear, smaller fragments of starch which are more water soluble.^{28,46} Yoon *et al.*³ reported an increase in the solubility of starch-polyvinyl alcohol (PVA) blend films when the CA concentration increased. Likewise, a similar effect was reported for modified starch-polyvinyl alcohol blends.^{47,48} Shi *et al.*²⁵ reported a decrease in the polymer molecular weight when CA was added to thermoplastic corn starch as co-plasticizer with glycerol. The lower values of the CA induced water solubility, when PCL ratio increased in the

blends, suggest that no notable hydrolysis of this polymer occurred.

The values of the ratio of bonded CA with respect to the amounts added to the films did not differ significantly from formulation to formulation. This suggests that CA reacts with starch chains or with glycerol, taking into account that the CA-glycerol-starch ratios were constant in every formulation and that the CA-PCL ratio decreased as PCL rose in the blend. So, neither are there any notable CA-PCL reactions (such as possible transesterification) nor does the PCL presence affect the starch or glycerol reactions with CA. Esterification reactions of CA with glycerol have previously been described in starch-glycerol-CA films.⁴⁹ Nevertheless, this reaction could not be confirmed from the obtained data, since for films with CA solubility values were always greater than the mass fraction of glycerol in the films, even when the PCL ratio was at its highest and the solubility value at its lowest.

IV shows the water vapor permeability (WVP) and OP of the studied films after 1 and 5 storage weeks. The addition of PCL promoted a significant decrease ($P < 0.05$) in the WVP of the studied films; the higher the PCL content, the greater the reduction for films stored for both 1 and 5 weeks. The hydrophobic phase in the starch matrix can explain this behavior, since the material presents a greater tortuosity factor for the transport of water molecules. The incorporation of CA to the starch matrix did not imply a significant reduction in WVP values in films equilibrated for 5 weeks, when they gained moisture content. It is likely that the crosslinking and hydrolysis phenomena effects on mass transport properties of the material were balanced. In blend films, CA did not improve water vapor barrier properties.

The OP values for S and PCL formulations were not shown because their values were outside the sensitivity range of the equipment used: those of the S formulation were too low and those of the net PCL films too high. The OP values of blend

Table IV. Mean Values and Standard Deviation of Water Vapor Permeability (WVP) and Oxygen Permeability (OP) of the Different Films After 1 (Initial) and 5 (Final) Weeks of Storage at 53% Relative Humidity and 25°C

Films	WVP (g mm kPa ⁻¹ h ⁻¹ m ⁻²)		OP 10 ¹⁵ (cm ³ m ⁻¹ s ⁻¹ Pa ⁻¹)	
	Initial	Final	Initial	Final
S	18.1 (1.4) ^{h1}	16 (2) ^{e1}	<D.L.	<D.L.
S-CA	12 (2) ^{de1}	15.6 (1.2) ^{e1}	0.26 (0.05) ^{a1}	0.281 (0.004) ^{a1}
S90	14.5 (0.7) ^{f1}	15.8 (1.2) ^{e1}	0.22 (0.09) ^{a1}	0.23 (0.15) ^{a1}
S90-CA	13.0 (1.4) ^{ef1}	15 (2) ^{e1}	0.4 (0.2) ^{a1}	0.54 (0.06) ^{a1}
S80	11 (2) ^{de1}	9.3 (0.6) ^{cd1}	6.5 (0.3) ^{ab1}	6 (3) ^{b1}
S80-CA	10.0 (0.6) ^{d1}	10.8 (1.0) ^{d1}	2.4 (0.3) ^{a1}	3.9 (0.2) ^{ab2}
S70	7.5 (0.7) ^{c1}	10.4 (0.7) ^{cd2}	17.1 (0.9) ^{cd1}	14.6 (1.1) ^{c1}
S70-CA	6.3 (0.7) ^{c1}	8.5 (0.3) ^{c1}	11.6 (1.2) ^{bc1}	12 (2) ^{c1}
S60	8 (2) ^{c1}	5.4 (0.4) ^{b1}	33 (12) ^{e1}	26 (3) ^{d1}
S60-CA	2.9 (0.8) ^{b1}	3.55 (0.11) ^{b1}	24 (2) ^{d1}	27.1 (0.8) ^{d1}
PCL	0.120 (0.04) ^{a1}	0.117 (0.011) ^{a1}	> D.L.	> D.L.

D.L.: 0.1–200 mL/(m² d). Different superscript letters within the same column indicate significant differences among formulations ($P < 0.05$). Different superscript numbers within the same row indicate significant differences due to storage time ($P < 0.05$).

films significantly ($P < 0.05$) increased in line with the PCL ratio in the film, while the addition of CA did not present a notable effect. No notable changes in the OP values of the films were observed after 5 storage weeks. So, the barrier properties of starch films were positively affected by PCL blending for water vapor but negatively affected for oxygen, in agreement with the different chemical affinity of PCL with both molecules. Even in samples with 10% PCL, where CA acts as a compatibilizer, there was no observed impact of this compound on film barrier properties.

V presents the values and standard deviation of roughness parameters, internal transmittance at 650 nm, and gloss at 85° of the studied films conditioned under controlled conditions for

1 and 5 weeks. In general, the roughness parameters did not show marked differences while they did exhibit a slight tendency to decrease when the PCL ratio increased, the net PCL films were not as rough as net starch films. Likewise, the roughness tended to decrease after the addition of CA in line with the promotion of the fragmentation and gelatinization of starch granules caused by the acid.^{26,37,50} In the analysis of this parameter, it is necessary to take into account that the compression molding could affect the surface roughness and mask the effect caused by the components of the polymeric matrix.

The gloss of the films was related with their surface roughness⁵¹ and, therefore, the process by which it is obtained can also affect it. In general, the films showed low gloss, their values

Table V. Mean Values and Standard Deviation of Surface Roughness Parameters and Optical Properties of the Different Films After 1 (Initial Time) and 5 (Final Time) Weeks of Storage at 53% Relative Humidity and 25°C

Films	Roughness parameters			Gloss (85°)		Ti (650 nm)	
	<i>r</i> (%)	<i>R_a</i> (nm)	<i>R_q</i> (nm)	Initial	Final	Initial	Final
S	6.1 (0.9) ^{abc}	215 (61) ^a	263 (63) ^a	40 (5) ^{c1}	37.2 (1.5) ^{bcd1}	85.1 (0.3) ^{h1}	84.2 (0.2) ^{fg2}
S-CA	2.5 (0.2) ^a	165 (59) ^a	206 (72) ^a	39 (5) ^{c1}	32 (2) ^{b1}	85.5 (0.6) ^{h1}	85.9 (0.8) ^{g1}
S90	13 (5) ^d	198 (60) ^a	247 (65) ^a	37 (9) ^{bc1}	35 (6) ^{bc1}	77.3 (0.6) ^{bc1}	79.8 (0.6) ^{cd2}
S90-CA	3.2 (1.2) ^a	148 (30) ^a	200 (38) ^a	52 (3) ^{d1}	43 (17) ^{de2}	79.4 (0.3) ^{def1}	81 (0.4) ^{de2}
S80	8 (3) ^{bc}	202 (26) ^a	255 (26) ^a	29 (9) ^{c1}	31 (9) ^{b1}	82.4 (0.6) ^{g1}	82.5 (1.1) ^{ef1}
S80-CA	14 (4) ^d	390 (216) ^b	497 (35) ^b	20 (13) ^{a1}	14 (2) ^{a1}	73.6 (0.6) ^{a1}	76 (0.7) ^{a1}
S70	8 (3) ^{bc}	220 (57) ^a	271 (68) ^a	34 (10) ^{bc1}	46 (4) ^{e2}	80.9 (0.14) ^{efg1}	80.9 (0.4) ^{de1}
S70-CA	11 (3) ^{cd}	199 (58) ^a	265 (72) ^a	31(9) ^{bc1}	35 (10) ^{bcd1}	76.2 (0.7) ^{b1}	77.1 (0.6) ^{ab1}
S60	5.6 (1.4) ^{ab}	163 (60) ^a	210 (79) ^a	38 (6) ^{c1}	37 (4) ^{bcd1}	81.2 (1.3) ^{fg1}	81.6 (0.7) ^{de1}
S60-CA	9.2 (1.3) ^{bcd}	163 (26) ^a	214 (26) ^a	50 (7) ^{d1}	41 (10) ^{cde2}	78.8 (0.8) ^{cde1}	79.4 (0.8) ^{cd1}
PCL	6.0 (0.9) ^{ab}	154 (16) ^a	195 (25) ^a	59 (16) ^{e1}	57 (9) ^{f1}	78 (2) ^{cd1}	78 (2) ^{bc1}

Different superscript letters within the same column indicate significant differences among formulations ($P < 0.05$). Different superscript numbers within the same row indicate significant differences due to storage time ($P < 0.05$).

ranging between 20 and 59 GU, with high variability, and without clear tendencies as a function of their composition. The net PCL films exhibited the highest gloss values according to their lowest roughness parameters obtained by AFM.

The internal transmittance (T_i), as a measure of film transparency, tended to decrease in line with the PCL ratio, according to the greater heterogeneity of the matrix with two non-miscible phases and a different refractive index. The incorporation of CA improved the film transparency of the S90 sample, but increased the film's opacity in the other blend films. No notable changes in this parameter occurred while the film was stored for 5 weeks. The different effect of CA in the S90 films is coherent with the improvement in the polymer compatibility deduced from the thermal and mechanical behavior of these films.

CONCLUSIONS

CA improves the properties of corn starch-PCL blend films with a low PCL ratio (S:PCL ratio of 90:10), while it was not effective at compatibilizing blends with higher amounts of PCL. This was observed in the microstructural analyses and deduced from the film's physicochemical properties. The incorporation of CA in the films affected both starch and PCL crystallization as deduced from the X-ray diffraction patterns of starch and PCL melting enthalpy values. The glass transition of starch was reduced by the incorporation of PCL in line with its partial solubilization in the starch phase, but lower than 10% with respect to starch. This decrease was greater in the presence of CA. So, CA promoted stronger interactions between PCL and starch chains, although this only quantitatively benefited the film properties at a low PCL ratio. In fact, blend films with a 90:10 starch-PCL ratio with CA exhibited the highest stretchability, with good mechanical resistance. The water solubility of the films increased when they contained CA, due to the acid hydrolysis of starch, although the water transfer rate was limited in blend films. CA did not affect the barrier properties of the blend films which showed intermediate values, between those of net starch and PCL films, according to their ratio in the film. So, compounding starch with small amounts of PCL, using glycerol and CA, can supply films with better functional properties than net starch films.

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