Effect of Surfactant on the Formation of Chitosan/ε-Polycaprolactone Blend Films for Food Packaging Applications

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Abstract

The objective of this study was to develop and characterize chitosan-ε-polycaprolactone (CHI/PCL) polymer blends with Tween 80 as a compatibilizer for application in packaging. The blends were produced by casting, with up to 10% (w/w) PCL in the CHI matrix. These blends were characterized in terms of their microstructure, chemical interactions, mechanical and thermal properties, solubility and water vapor permeability (WVP). The micrographs showed microsphere-like structures from the PCL in the continuous phase of CHI. Fourier transform infrared spectroscopy (FTIR) indicated a high interaction between CHI amino groups and PCL carbonyls, resulting in blends with greater ductility than the pure CHI film, thus providing greater flexibility. In the crystallinity analyses, the presence of PCL favored an increase in crystalline regions, limiting the passage of light. Given the results, blends are an alternative for application in multilayer systems and can be considered for use as a biodegradable fraction in food packaging.

1 Introduction

Plastic packaging plays an important role in the conservation and preservation of product quality, and for the most part, it is composed of nonbiodegradable synthetic raw materials [1, 2]. After use, most of these packages are indiscriminately disposed of, and this scenario, together with the slow kinetics of plastic degradation, leads to the accumulation of solid waste in the environment [3]. Such issues drive research on biodegradable polymers because such polymers not only have renewable sources and are nontoxic but also allow the use of composting for the recycling of packaging at the end of its useful life[4].

One of the most studied biopolymers is chitosan (CHI), a polysaccharide derived from the partial deacetylation of chitin [5]. Its biodegradable nature, film-forming capacity with low ethylene permeability and antimicrobial activity have aroused interest in its use for food packaging[6]. However, CHI films are hydrophilic and have low extensibility, which restricts their application in functional films [7]. Aiming to improve these properties, most current studies investigate the blending of CHI with biodegradable polyesters for biomedical applications, as well as for applications in the packaging market [1, 7].

From this perspective, ε-polycaprolactone (PCL) is a strong candidate, and its use in blends has been investigated for several biopolymer matrices, such as starch [4], polylactic acid (PLA)[8], poly-3-hydroxybutyrate (PHB)[9] and CHI[7]. The hydrophobic characteristics of PCL may promote a reduction in water affinity in hydrophilic films. Furthermore, its low melting point (58–60°C) and low glass transition temperature provide superior rheological and ductile properties with easy conformability [4]. However, thermal analyses have revealed the formation of two phases, in which the antagonistic properties of CHI and PCL make blending difficult at the molecular level, thus requiring the use of compatibilizers in the system[1].

Therefore, the use of surfactants can be seen as an alternative because their amphiphilic characteristics allow a greater association of the hydrophobic fraction with the hydrophilic matrix [7]. The hydrophilic
fraction reduces the number of sites that interact with water, while the hydrophobic fraction can act as a barrier to water vapor [10, 11]. A promising alternative is Tween 80, a nonionic surfactant and emulsifier widely used as an additive in food applications[12].

In view of the arguments presented, the present study aimed to develop polymer blends with CHI and PCL compatibilized with Tween 80. The blends formed were characterized in terms of their morphology, chemical interactions, mechanical and thermal properties, resistance to moisture and water vapor permeability (WVP) for potential application as food packaging.

1 Materials And Methods

1.1 Materials

CHI (molar mass = 71,300 g.mol⁻¹) with a degree of deacetylation of 85.9% was provided by Polymar Ciência e Nutrição S/A (Brazil); acetic acid PA was obtained from Sigma Aldrich (USA); PCL (molar mass ~ 50,000 g.mol⁻¹) was provided by Capa™ Perstorp (Sweden); trichloromethane (or chloroform) (molar mass = 119.38 g.mol⁻¹) was obtained from Panreac (Spain); and polysorbate 80 surfactant (Tween 80) was obtained from Sigma Aldrich (USA).

1.2 Production of films

The film-forming CHI solution was prepared by adapting the methodology of Dias et al. (2014) by dissolving 2% (w/v) in 0.5% acetic acid (v/v) solution. Then, the solution was placed in an ultrasonic shaker (Sonifer Cell Disruptor Branson 450D, Manchester, UK) with 400 W power for 10 min and 80% amplitude. After homogenization, the solution was filtered through a gauze membrane. PCL was solubilized in chloroform to prepare the film-forming solution at a concentration of 5% (w/v)[13].

CHI/PCL blends were prepared at different percent concentrations (w/w): 97/3, 95/5, 93/7 and 90/10 (Fig. 1). In preliminary tests, values higher than 10% PCL promoted visual phase separation of the blends. The surfactant polysorbate 80 (Tween 80) was added at 18% (w/w) relative to the total polymer mass. The solutions were homogenized in an Ultra-Turrax (IKA T18 basic, Wilmington, USA) at 1400 rpm at 55°C for 5 min.

Subsequently, the solutions were poured into glass plates (20 x 10 cm) for drying under ambient conditions for 48 hours. Before analysis, the films were placed in a BOD incubator (NT 705 - BOD Incubator, Nova técnica, Piracicaba, Brazil) at 23 ± 2°C with a relative humidity of 50 ± 5% for 48 hours, according to method D618-13 [14]. The experiment was conducted using a completely randomized design with 3 replicates.

1.3 Characterization of the films

The microstructure of the polymer blends was analyzed using scanning electron microscopy (SEM, LEO EVO 40 XVP – Zeiss, Cambridge, England). The micrographs were generated using an acceleration voltage
of 20 kV. All samples were coated with a gold layer to avoid charging of the sample surface under the electron beam and affixed to the metal surface with double-sided adhesive carbon tape.

The interaction between the components of the blends was determined by spectral analysis in the infrared region obtained by a spectrophotometer (Shimadzu FTIR-8300) in attenuated total reflectance (ATR) mode. The spectra of the samples were obtained by the accumulation of 32 scans in the range of 400 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) in an environment with controlled temperature and humidity.

The physical form of the natural polymer and the changes in the structure of the crystalline lattice of the blends were studied using X-ray diffraction (XRD). The spectrograms were obtained using a Shimadzu LabX XRD-6100 diffractometer with a CuK\(_\alpha\) radiation source (\(\lambda = 0.154056 \text{ Å}\)) with 30 kV voltage and 30 mA. The samples were scanned in a 2\(\theta\) angular range of 4\(^{\circ}\) to 40\(^{\circ}\) with a step size of 0.02\(^{\circ}\) min\(^{-1}\). Finally, the curves were prepared using Origin 8.0 software. The relative crystallinity index (CI) values of the polymer blends were calculated according to Eq. 1 [15]:

\[
CI(%) = \left( \frac{H_c}{H_c + H_a} \right) \times 100 \quad (\text{Eq. 1})
\]

where CI is the crystallinity index (%); \(H_c\) is the intensity of the crystalline peak; and \(H_a\) is the intensity of the amorphous phase after subtracting the baseline intensity.

The thermal profiles of the films were evaluated by thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTGA) and differential scanning calorimetry (DSC). The thermogravimetric curves were obtained by a TA Q500 analyzer (TA Instruments, New Castle, DE, USA). Approximately 10 mg of sample was subjected to heating from 25 to 800°C under a heating rate of 10°C.min\(^{-1}\) in an inert nitrogen atmosphere (flow rate of 50 mL.min\(^{-1}\)). The maximum degradation temperature of the analyzed samples was determined from the derivative thermogravimetric (DTG) curve.

DSC analysis was performed in a Q100 device (TA Instruments, New Castle, DE, USA). The samples (approximately 7 mg) were subjected to heating from −70°C to 150°C at a heating rate of 10°C.min\(^{-1}\) under an inert nitrogen atmosphere. A first heating ramp (25 to 150°C) was performed to eliminate the thermal history. Then, the samples were cooled to -70°C. The second heating ramp from −70°C to 150°C was applied to determine the glass transition temperature (Tg) and melting temperature (Tm) of the samples.

The thickness of the films was analyzed using a digital micrometer (Digimes) with a scale of 0 to 25 mm and a resolution of 0.001 mm. The thickness measurements were performed at 5 different locations in the film samples, and the mean thickness of the samples was calculated. The mechanical properties of the samples were measured in a texture analyzer (Stable Microsystems, model TATX2i, Surrey, 158, England) was used to classify the material properties...
and assess the structural integrity of the blends. The samples were prepared in strips (100 mm x 10 mm), fixed by the ends to the probe holder, and tested using a separation speed of 2 mm.s⁻¹ until breaking. In the tensile tests, tensile strength (TS), Young's modulus (YM) and elongation at break (E) values were obtained. The tests were performed under constant ambient temperature.

The water vapor barrier properties of the films were evaluated according to ASTM E96-16 [17]. In the gravimetric method, the samples were cut in a circular shape 8 cm in diameter and fixed in permeation cells containing silica gel in their central part. Next, the capsules were placed in a desiccator containing saline solution to ensure a water gradient in the system at a temperature of 25°C with a relative humidity of 50 ± 3%. Cell weight was monitored for 8 days at 24-h intervals to monitor the weight variation during that period. The flow was determined by linear regression between the weight gain points, according to Eq. 2 [18].

\[
WVP = \frac{g}{t \cdot A} \cdot \frac{x}{\Delta P} \quad \text{(Eq. 2)}
\]

where \( g \) is the weight gain (g); \( t \) is the total time in (s); \( A \) is the permeation area (m²); \( x \) is the mean thickness (m); and \( \Delta P \) is the difference in ambient pressure between silica and pure water (kPa). The tests were performed in triplicate for all samples.

The water solubility of the films was determined in triplicate, according to the method proposed by Gontard et al. [19], with modifications. Film samples measuring 4 x 4 cm² were dried in an oven at 50°C until constant dry weight (\( W_i \)) to remove moisture. Subsequently, each sample was immersed in 50 mL of distilled water in a Falcon tube under slow stirring for 24 hours. Subsequently, the samples were dried in an oven at 50°C until constant weight to obtain the final dry weight of the samples (\( W_f \)). Solubility was expressed according to Eq. 3 in terms of the weight of dry matter solubilized in water (\( W_s \))[20].

\[
\% W_s = \frac{(W_i - W_f)}{W_i} \quad \text{(Eq. 3)}
\]

where \( W_i \) is the initial mass; \( W_f \) is the final mass; and \( W_s \) is the weight of dry matter solubilized in water.

1.4 Statistical analysis of the results

The data from the mechanical tests, the WVP data and the solubility data were subjected to analysis of variance, and the means were grouped together by the Scott-Knott test at 5% probability (\( p < 0.05 \)) using SISVAR® software. The SEM, FTIR, XRD, and DSC results were subjected to qualitative analysis.

2 Results And Discussion

2.1 Scanning electron microscopy (SEM)

Fig. 2 shows micrographs of the surfaces of the control films (CHI and PCL) and CHI/PCL blends.
The CHI (Fig. 2A) and PCL (Fig. 2B) control films showed a homogeneous, compact surface without the formation of voids or fissures and a microstructured surface with spherulites, indicating a crystalline phase in the PCL film. Regarding the micrographs of the blends (Fig. 2C, 2D, 2E and 2F), it is possible to note the presence of spherical structures dispersed in the CHI biopolymer matrix originating from PCL.

When analyzing the micrographs of the cross-sections of the samples (Fig. 3), the same pattern is observed with the formation of PCL microspheres in the CHI matrix. In the interfacial region, indicated by the arrows in Fig. 3, the microspheres show regions of interconnection with the CHI matrix, suggesting interaction between the polymers due to the presence of the surfactant. However, the polymer-polymer interactions were not strong enough to ensure the molecular miscibility of the phases [21].

2.2 X-ray diffraction (XRD)

XRD is a nondestructive technique for characterizing crystalline materials, such as polymeric films. It provides information on structures, phases, preferred crystal orientations (texture) and other structural parameters, such as the average grain size, crystallinity, stress and crystal defects[22].

Table 1 shows the diffractograms of the CHI and PCL films and CHI/PCL blends. The diffractogram of the CHI film showed poorly defined peaks at 2θ = 9° and 11°, with a wide peak starting at 13° and ending at 36°, suggesting a predominantly amorphous nature without defined crystallinity peaks. Amorphization of CHI occurs when diluted in acetic acid solutions. This occurs due to the total destruction of the crystalline region during the dissolution process (MA et al., 2013). In the case of the PCL control film, two sharp peaks are observed at 2θ = 21° and 23°, indicating the crystalline properties of PCL [23, 24]. It is worth mentioning that the addition of PCL to the matrix favored the presence of crystalline zones, which is convenient for application in packaging, since an increase in crystallinity decreases the passage of light and consequently reduces the degradation of products with high fat content[3, 25].

| Treatment | 2θ    | Degree of crystallinity |
|-----------|-------|-------------------------|
| CHI       | -     | -                       |
| A3        | 21.4° | 27%                     |
| A5        | 21.5° | 13%                     |
| A7        | 21.5° | 30%                     |
| A10       | 21.9° | 33%                     |
| PCL       | 21.4° | 76%                     |

It was also observed that in the films of the CHI/PCL blends, the presence of the characteristic peaks of CHI (9° and 11°) and PCL (21° and 23°) in the polymer blends indicated that there were interactions between the polymers in the blend.
as in samples A3 and A5, reduced the intensity of the PCL peaks and the degree of crystallinity (Table 1). CHI indirectly interferes with the growth of PCL crystals and may even change the structure from crystalline to amorphous during the production of blends, thus decreasing the degree of crystallinity [26].

### 2.3 Fourier transform infrared spectroscopy (FTIR)

To evaluate possible chemical modifications during film formation with the addition of compatibilizer, FTIR-ATR analysis was performed of the 4 formulations tested. The samples were not evaluated in the range of 2000 to 4000 cm$^{-1}$ since the presence of significant stretching was not observed in the analyzed treatments [27, 28]. In Fig. 5, the CHI film spectrum showed characteristic peaks at 1641 cm$^{-1}$ (C = O stretching, amide I), 1545 cm$^{-1}$ (N-H stretching), 1149 cm$^{-1}$ (C-O-C asymmetric stretching) and 892 cm$^{-1}$, characteristic of the saccharide structure of CHI [29–32]. Bands associated with pure PCL (Fig. 5) were found at 1720 cm$^{-1}$ (ester C = O stretching) and 1240 cm$^{-1}$ (C-O-C asymmetric stretching) [4, 27, 31].

The carbonyl groups of PCL interact with the hydroxyl and amine groups present in CHI and form ester and amide bonds [33]. In the spectra, shifts in three bands were observed: the first shift from 1720 cm$^{-1}$ to 1735 cm$^{-1}$ was associated with the C = O vibration present in the pure PCL spectrum, the second shift from 1641 cm$^{-1}$ to 1648 cm$^{-1}$ was associated with amide I, and the third shift from 1545 cm$^{-1}$ to 1554 cm$^{-1}$ corresponded to amide II. Such shifts to a higher frequency may be related to electrostatic interactions between CHI amino groups and PCL ester groups [34].

The region close to 1560 cm$^{-1}$ shows characteristic vibrations of amino groups protonated with acetic acid, forming chitosan acetate (-NH$^+$.Ac-)[35]. Therefore, the presence of -NH$^+$.Ac- was attributed to the formation of an amorphous CHI film structure, as shown in the XRD analysis. The characteristic band of the chloroform solvent (785 cm$^{-1}$) was not detected in any of the samples studied [13].

### 2.4 Mechanical tests

According to the analysis of variance, the factor treatment was significant (p < 0.05) for all variables of the mechanical tests. The YM, TS and E values are shown in Table 2.
Table 2
Mechanical test results for the CHI and PCL films and CHI/PCL blends.

| Treatments | TS (MPa)     | E (%)     | YM (MPa)   |
|------------|--------------|-----------|------------|
| CHI        | 20.03 ± 0.21c | 2.47 ± 0.07a | 2035.63 ± 6.79e |
| A3         | 13.03 ± 0.31b | 8.45 ± 0.23d | 1302.50 ± 3.84c |
| A5         | 10.69 ± 0.20a | 10.75 ± 0.24f | 1069.43 ± 7.95b |
| A7         | 12.65 ± 0.66b | 6.47 ± 0.02b | 1374.63 ± 0.58d |
| A10        | 10.59 ± 0.13a | 7.44 ± 0.58c | 1058.93 ± 8.16b |
| PCL        | 19.27 ± 1.05c | 9.59 ± 0.55e | 377.50 ± 8.5a  |

\[a, b, c, d, e, f\] Means in columns with the same letter do not differ statistically by the Scott-Knott test (p < 0.05). TS = Tensile strength; E = Elongation; YM = Young’s modulus.

The addition of surfactant (Tween 80) and PCL to the CHI matrix caused a plasticizer effect and matrix discontinuity, respectively. Both effects caused the weakening of intermolecular bonds between CHI, PCL and surfactant and consequently decreased YM and TS, although the E of the film increased compared to those of the CHI and PCL control films.

The CHI and PCL control films showed TS values that did not differ significantly (p < 0.05). However, the addition of 10% PCL to the CHI matrix caused a reduction in this parameter from 20.03 MPa to 10.59 MPa. This decrease may be related to the changes caused by PCL in the structure of CHI chains, since the network structures of the CHI films with PCL and surfactant were less resistant. This characteristic is due to the greater flexibility of PCL chains that have a -C-O- bond, which are responsible for the greater difficulty of regular/ordered packaging of the film network, thus dominating among the characteristics of the amorphous phase[36].

This same behavior was observed in blends of starch and poly(butylene adipate-co-terephthalate) (PBAT) with Tween 80, where the hydrophobic groups of the surfactant (high molar mass) aggregated between the biopolymer chains, hindering the structural formation of the film [10]. In the blends, PCL, which has an ester functional group, could form hydrogen bonds with CHI, as seen in the FTIR results, ensuring higher TS values than those observed for extruded low-density polyethylene (LDPE)/CHI films without compatibilizers.

Regarding E, the blends had significantly greater (p > 0.05) values than the CHI film, forming a more ductile material. These results indicate that both PCL and the surfactant acted as plasticizers, facilitating mobility between CHI chains [37]. Regarding YM, which describes the stiffness of a material, the blends
had significantly lower (p < 0.05) values than the CHI control film, exhibiting more flexibility, which favors the absorption and recovery of energy in the elastic deformation of packaging [7]. These results corroborate previous theories of the plasticizing action of added PCL and surfactant.

2.5 Thermogravimetric analysis (TGA)

Figure 6 (a-f) shows the TGA mass loss and DTG curves generated for the PCL and CHI films and blends A3, A5, A7 and A10. The PCL film (Fig. 6a) showed a single stage of mass loss in the temperature range between 30°C and 800°C. The maximum degradation temperature (T\text{max}) was 410°C, which corresponds to the rupture of the polyester chain through the ester pyrolysis reaction with the release of CO\textsubscript{2}, H\textsubscript{2}O and hexanoic acid [4, 38]. The residual percentage was 0.79%.

The CHI film (Fig. 6b) showed three stages of mass loss in the temperature range between 30°C and 600°C. The first stage (52–220°C) with a T\text{max} of 150°C is attributed to water loss and acetic acid residues through the breakdown of hydrogen bonds between CHI amino and hydroxyl groups [39]. The second stage (220–382°C) with T\text{max} at 270°C is related to the degradation of the CHI saccharide rings, resulting in the decomposition of acetylated and deacetylated units by the breaking of glycosidic bonds [5]. The last stage of the CHI film, which occurred between 382°C and 600°C, corresponds to carbonization, with a residual percentage of approximately 35.87%.

For samples A3 and A5 (Fig. 6c and 6d), there were five stages of mass loss, while in samples A7 and A10 (Fig. 6e and 6f), there were four stages. In the blends, the initial degradation peak observed for all treatments was close for all samples, ranging from 23°C to 62°C, and the second maximum degradation peak was found to vary between 123°C and 136°C; both peaks represented the loss of water bound to CHI amino groups, in addition to the elimination of some traces of acetic acid [40]. The third stage had a maximum degradation peak between 268°C and 275°C, which is related to the degradation of the CHI main chain from the breakdown of glycosidic bonds. The fourth stage had maximum degradation peaks between 393°C and 397°C, related to the pyrolysis of the ester group of the PCL chain [26].

The fifth and final stage in samples A3 and A5, with a maximum degradation peak between 412°C and 413°C, corresponds to the carbonization of the last polymer chains. This behavior indicates that the polymer-polymer interactions in the samples with lower concentrations of PCL were stronger than those in the samples with higher concentrations of PCL, corresponding to a higher energy and maximum degradation rate for the decomposition of samples A3 and A5 [40]. Therefore, the addition of PCL was able to increase the thermal stability of the material relative to the pure CHI film, but this behavior was not maintained with increasing PCL concentration.

2.6 Differential scanning calorimetry (DSC)

The DSC curves show information on the miscibility of the components of the blend through the analysis of changes in Tm and Tg as a function of composition [24]. The thermograms of CHI, PCL and the blends are shown in Fig. 7. CHI underwent thermal degradation at approximately 270°C before melting, while...
pure PCL undergoes thermal degradation at approximately 60°C; thus, the degradation process was monitored to determine the miscibility of the two polymers [41, 42]. In this analysis, the CHI control film showed no endothermic peak associated with the melting process. These parameters indicate the amorphous characteristics of the CHI film, as also observed in the XRD analysis results. In the case of the pure PCL control film, a single endothermic peak was observed, which corresponds to crystalline melting at 54°C.

When compared to the results for pure PCL, the blends showed a small reduction in Tm (Table 3). This drop in temperature can be attributed to the interactions between the carbonyl groups of PCL and the hydroxyl (-OH) and amino (-NH₂) groups of chitosan, causing a reduction in the crystallinity of the blends relative to that of the PCL film [1]. Similar conclusions were made for the CHI/PCL blends, where the reduction in Tm was attributed to the interference of CHI in the growth of the PCL crystals, limiting the organization of the PCL molecules in the CHI matrix [42].

Regarding Tg, the CHI film showed a deviation at a baseline of approximately 18°C, and there was no thermal record for Tg in the PCL sample. Although studies indicate the Tg of PCL films is at -60°C [4], a value was not detected in the present study due to a possible shift in the Tg range and the limitations of the equipment.

One of the miscibility classifications in polymer blends is related to Tg. When a blend is miscible, it has only one Tg, intermediate to that of the pure components, while immiscible systems exhibit the Tg values of the pure polymers because the interactions between the polymer chains of the system components are so weak that separate domains are formed between the components [43]. Other blends have systems where a small amount of the chains of each polymer interact, causing a change in the temperature and speed with which the chains acquire mobility, leading to a small shift from the Tg values of the pure components; such systems are classified as partially miscible [44].

The CHI/PCL blends had two Tg values, the first in the range of -24 ° to -21°C and the other at approximately 17°C, which can be attributed to PCL and CHI, respectively (Table 3). A partial interaction between polymer chains generates a change in Tg, so this small shift observed in the Tg of the blends suggests that CHI and PCL are partially miscible [25, 45]. The results are shown in Fig. 3, where the presence of a continuous phase and a dispersed phase in the blends can be observed.

The incorporation of PCL into the CHI matrix resulted in an increased Tg relative to that of the pure PCL film. This increase in Tg is a result of the decrease in the space available for molecular motion [46, 47]. Therefore, the addition of Tween 80 helped with the bonding of the phases, favoring intermolecular interactions between hydroxyls in the Tween 80 chains and the functional groups of CHI and PCL, which was also observed in the FTIR analysis results. These interactions among the three components are responsible for the increase in Tg for PCL, but there was no large change in the Tg for CHI [42], as observed in Table 3.
Table 3  
Phase transition temperatures of the CHI film, CHI/PCL blends and PCL film.

| Treatment | $T_g$ 1 ($^\circ$C) | $T_g$ 2 ($^\circ$C) | $T_m$ ($^\circ$C) |
|-----------|---------------------|----------------------|------------------|
| CHI       | 18                  | -                    | -                |
| A3        | 17                  | -24                  | 52               |
| A5        | 17                  | -22                  | 52               |
| A7        | 17                  | -22                  | 53               |
| A10       | 17                  | -21                  | 53               |
| PCL       | -                   | -                    | 54               |

2.7 Solubility and water vapor permeability (WVP)

The mean WVP values for CHI and PCL films and blends are shown in Table 4. The hydrophobic properties of PCL provided a reduction in solubility of almost 34% when incorporated into the CHI matrix.

The addition of a polymer with nonpolar groups such as PCL is a way to reduce the solubility of CHI films. In a study involving CHI and LDPE, there was a decrease in solubility of 13% with the incorporation of *Satureja hortensis* extract [48]. Thus, based on the values shown in Table 4, this reduction in solubility is linked to the reduction of the hydrophilic nature of CHI in the blends, with an increase in hydrophobic groups from PCL, which may hinder the ability of polar groups of CHI to interact with water, consequently leading to greater water resistance. The addition of higher concentrations of PCL could be tested because the solubility values found were low and the impermeability of PCL was shown [37]. This hydrophobicity may be related to the high degree of crystallinity (Table 1) and the presence of polar groups in the structure.
Table 4
WVP and solubility values for the CHI film, PCL film and CHI/PCL blends.

| Treatment | WVPx10^{-9} (gm^{-1}.s^{-1}.kPa^{-1}) | Solubility (%) |
|-----------|--------------------------------------|----------------|
| CHI       | 2.61 ± 0.11^b                        | 18.63 ± 2.15^c |
| A3        | 2.73 ± 0.34^b                        | 13.69 ± 2.44^b |
| A5        | 2.64 ± 0.13^b                        | 14.82 ± 2.62^b |
| A7        | 2.80 ± 0.33^b                        | 12.19 ± 3.51^b |
| A10       | 2.88 ± 0.30^b                        | 14.10 ± 0.90^b |
| PCL       | 0.83 ± 0.07^a                        | 0.40 ± 1.91^a  |

^a,^b,^c Means observed in columns with the same letter do not differ statistically by the Scott-Knott test (p < 0.05).

In the present study, the WVP values of the blends did not differ significantly (p < 0.05) from that of the CHI film. The WVP is defined by solubility and diffusivity parameters [10]. Therefore, the presence of PCL microspheres (hydrophobic part), observed in Figs. 2 and 3, may have limited the passage of water vapor, but the spaces between these microspheres favored the passage of the vapor due to interchain spacing of the biopolymer [37].

A similar increase in WVP value in polymer blends using CHI and synthetic polymers was also reported in CHI films with the addition of poly(N-vinyl-2-pyrrolidone) (PVP) and poly(ethylene oxide) (PEO) [49]. In that study, it was observed that the fragile intermolecular interactions between the CHI molecules and the synthetic polymers resulted from greater distances between the molecules of the polymers, favoring an increase in the WVP of the films, as inferred from SEM and DSC analyses. The addition of the surfactant did not reduce the WVP of the films, and its amphiphilic character increased the number of hydroxyl groups, which interacted with both the CHI and PCL chains.

3 Conclusion

The surfactant acted as a stabilizer in the formulation by reducing the interfacial energy between the polymers, thus allowing intermolecular interactions between the PCL and CHI chains. However, these interactions were not strong enough to establish miscibility, since the presence of microspheres suggests a discontinuity of the matrix, or to increase the water vapor barrier properties, indicating that the surfactant increased the free volume between the chains. However, the addition of PCL at small concentrations to the CHI matrix resulted in more ductile and less rigid films than pure CHI films, in addition to reducing water solubility by up to 34% and increasing thermal stability (higher degradation temperature) [49].

Thus, CHI/PCL biopolymer blends in the packaging market...
is in a multilayer system, with the blend representing a biodegradable fraction placed between two polymers with properties of interest in packaging applications.

**Declarations**

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**Figures**

**Figure 1** - Graphic summary of the preparation of films with CHI, PCL and surfactant.

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**Figure 1**

Graphic summary of the preparation of films with CHI, PCL and surfactant.
**Figure 2** - Micrographs of the surfaces of the CHI, PCL and CHI/PCL films. A) CHI; B) PCL; C) A3; D) A5; E) A7; F) A10.

**Figure 3** - Micrographs of cross sections of the CHI/PCL blends. a) A3; b) A5; c) A7; d) A10.
Figure 3

Micrographs of cross sections of the CHI/PCL blends. a) A3; b) A5; c) A7; d) A10.

Figure 4 - FTIR spectra of CHI, PCL and CHI/PCL blends (A3, A5, A7, A10).

Figure 4

FTIR spectra of CHI, PCL and CHI/PCL blends (A3, A5, A7, A10).
Figure 5 - TGA and DTG curves of the films a) PCL, b) CHI, c) A3, d) A5, e) A7 and f) A10.

Figure 6 - DSC curves of CHI, PCL and the CHI/PCL blends.
Figure 6

DSC curves of CHI, PCL and the CHI/PCL blends.