Effect of starch nanocrystals addition on the physicochemical, thermal, and optical properties of low-density polyethylene (LDPE) films

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Abstract

The aim of this study is to add rice and potato starch nanocrystals (SNCs) to a low-density polyethylene (LDPE) matrix to reinforce its structure, improve its characteristics, and broaden its applicability. The SNCs were produced by acid hydrolysis and applied to the LDPE matrix by extrusion at a concentration of 0.5% and 1%. The films were characterized in terms of physical-chemical, thermal, and structural properties. The addition of 1% SNCs produced from rice starch reduced the oxygen permeability to 1.57×10^{-4} (mlmm/MPa/min/cm^2) and increased the thermal stability of the films. The addition of potato starch SNCs in a 1% proportion increased the crystallinity of the films to 81.6%. Therefore, the incorporation of starch SNCs in the LDPE matrix showed adequate compatibility and the ability to improve the properties of the films. The mixture of LDPE with biodegradable polymers can be an alternative that can contribute to the increase in the rate of biodegradability.

1 | INTRODUCTION

The need to safeguard the well-being of consumers in different parts of the world has highlighted the industry requirement for packaging that will allow products to be

distributed with thermal insulation. Plastics are an important sector in the production of various types of packaging because they offer several advantages, such as, low cost, low density, good applicability, high quality, and versatility. [1] Nowadays, one of the most used polymers used for food packaging is polyethylene, [2] more precisely low-density polyethylene (LDPE). Its extensive industrial use is linked to its cost effectiveness, good barrier properties, ease of processing, and high transparency. [3,4] However, although the cost/benefit   of using LDPE is adequate industrially, LDPE is obtained through petrochemical processes, and its degradation can take many decades, [5] which causes accumulation in the environment, generating serious environmental pollution. [6−8] The search for polymers with higher degradability and with similar properties has been the target of studies to reduce environmental problems and keep produce quality packaging.

Starch is a biodegradable and renewable polymer that can be obtained from numerous botanical sources. [9] Moreover, starch is inexpensive, highly biologically compatible, and widely commercially applicable. [10,11] Structurally, starch is a macromolecule composed of chains of glucose units linked in a linear (amylopectin) or branched (amylopectin) structure   [12]   that   forms   amorphous   and crystalline zones. Strong acids applied in controlled hydrolysis processes can be used to hydrolyze the amorphous zones most susceptible to acid hydrolysis, resulting in the formation of starch crystals with high crystallinity and a high nanometric size called starch nanocrystals (SNCs). [13] SNCs have a contact surface that is more susceptible to crosslinking, mainly by hydrogen bonds, between the SNCs and the polymeric matrix to reinforce the structure of the materials. The incorporation of nanocrystals into polymers matrices originates the formation of threedimensional intermolecular networks that can increase thermal resistance, barrier properties, and mechanical properties of several polymers. [14,15]

Blending conventional synthetic polymers with biodegradable natural polymers is an economical and versatile approach to improve the biodegradability of petroleumbased polymers and provides more sustainable plastics with modified properties. [16] The degradation of LDPE basically occurs through two mechanisms, abiotic (oxidation and photodegradation) and biotic (micro-organisms and biooxidation). [17] Therefore, the incorporation of biodegradable materials, such as starch, favors microbiological access and making the carbons that make up the chemical structure of LDPE accessible for use as an energy source by microorganisms. [16] Blends of LDPE with starch or cellulose have been reported to be able to promote the biodegradability process of films by reducing their accumulation in the environment. [5] Therefore, objective of this study is to incorporate nanocrystals of rice and potato starches produced from chemical hydrolysis in LDPE films and evaluate the effect of these nanoparticles on the physical, chemical, thermal, and structural properties of nanocomposite films.

2 | MATERIALS AND METHODS

1 | Materials

The low-density polyethylene, LD 650 low-density polyethylene resin, was provided by ExxonMobil ^{TM} with a density of 0.914 g/cm^3 at a melting temperature of 103°C. The rice

and potato starches were acquired by Horizontes (Brazil) and other reagents used were of analytical grade.

2 | Production of nanocrystal SNCs

Starch nanocrystals were produced by acid hydrolysis, according to Zhou et al. [18] Samples of 25 g of rice and potato starch were homogenized with 250 ml of H_2SO_4 and incubated with orbital shaking at 100 rpm , at 40°C, for 5 days for rice starch and 7 days for potato starch, respectively. Afterwards, the starches were centrifuged at 1000 g for 10 min and washed several times with distilled water until a neutral pH was obtained. Finally, the starch was lyophilized and stored in glass containers refrigerated at 4°C.

3 | Production of nanocomposite LDPE/SNC pellets

For the incorporation of the SNCs in the LDPE matrix was performed in a twin screw extruder (Leistritz LSM 96/25D, Germany), at 120°C long the barrel, a screw speed of 125 rpm and a flow rate of 3 kg/h. Two different amounts (0.5 and 1wt% of rice starch nanocrystals (RSNCs) and potato starch nanocrystals (PSNCs) were used, respectively. The SNCs were fed separately downstream in open location in the barrel.

4 | Production of LDPE films

The films were produced using LDPE pellets and pellets containing SNCs in a single screw tubular extruder (Extruder O25X25D, Portugal). The temperatures applied in the extrusion were 120,140 , and 140°C; the screw speed of 50 rpm and flow rate of 2.7 kg/h. The diameter of the opening ring used, the speed applied to the rollers was 3.6 m/s; the pull ratio, 1.8 cm ; and the film width, 14 cm . The different films produced and the respective concentrations of nanomaterials used are described in Table 1.

5 | Characterization of LDPE films and nanocomposites

1 | Optical properties

Opacity and color were analyzed using a colorimeter (Minolta, CR-400, Japan). The color was expressed as a total color difference (ΔE^*) obtained using Commission Internationale de l'Éclairage (CIE) standard illuminant D65. The ΔE * was calculated from Equation (1), and the opacity was calculated using Equation (2).

$$\Delta E *= \sqrt{(L*-L_s^*)^2 + (a*-a_s^*)^2 + (b*-b_s^*)^2} \qquad (1)$$

$$O_P = \frac{Y_b}{Y_w} \times 100 \qquad (2)$$

where O_P is expressed as a %, Y_b represents the black standard, and Y_w represents the white standard for each evaluated film.

TABLE 1 Films composition

Polymer	Nanoparticle	Code
Low-density polyethylene (LDPE)	-	LDPE
	1% rice starch nanocrystals	LDPE/RSNCs 1%
	0.5% potato starch nanocrystals	LDPE/PSNCs 0.5%
	1% potato starch nanocrystals	LDPE/PSNCs 1%

2 | Mechanical properties

The mechanical properties of the films were evaluated in Extenciometer (ZwickRoell Z005, Germany) according to ASTM Standard Method D882-02. [19] The films were cut up into 10 strips 10×1.5 cm in the transversal and longitudinal direction. The applied traction speed was 200 mm/s, the post-test speed was 500 mm/s, and the separation distance of the claws was 50 mm . The films were characterized for tensile strength (TS), elongation at break (E), and Young modulus (M).

3 | Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was applied to the films using a DMA (Tryton T101423D TTDMA, United Kingdom). The films were cut into strips of 30×5 mm. The test was carried out in a temperature range from 30 to 100°C, heating rate of 5°C/min, frequency of 1 MHz and dynamic force of 1 N .

4 | Contact angle assessment

The contact angle of the films was evaluated using a microscope in static mode (Contact Angle System OCA 20, Germany). The contact angle was evaluated using a drop of $3\mu l$ of water with a speed of $2\mu l/s$. At the same moment that the drop was deposited on the surface of the film, the image was recorded by the SCA 20 software to calculate the contact angle. Measurements were performed in triplicate using the average of five drops for each replicate.

5 | Water vapor permeability (PVA) and oxygen permeability (PO)

PVA was obtained by gravimetric means according to the standard method E96-00. [20] PVA was measured by weighing permeation cells for 7 days every 24 h . The permeation cells contained dry silica inside (0% relative humidity) and were hermetically closed so that the only form of water

vapor permeation was through the film exposed on the surface (5 cm in diameter). The permeation cell was placed in a desiccator containing a saturated solution of calcium chloride with a relative humidity of 75%. PVA was calculated using Equation (3).

$$PVA = \frac{W \cdot L}{A \cdot t \cdot \Delta P} \tag{3}$$

where PVA was in gmm/m^2; kilopascal (kPa); W(g) was the body of water gained; L (mm) was the thickness of the film; A (m^2) was the area of film exposed for permeation; t (day) was the time of mass gain; and ΔP (kPa) was the variation in water vapor pressure through the film.

The PO of the films was meditated using a gas diffusion permeabilimeter (Gas Permeameter DP-100A, United States). The films were fractionated in circles 5 cm in diameter and evaluated in duplicate. The equipment has a permeation area where the films are exposed individually and checks the amount of oxygen capable of permeating the films during 3 h .

6 | Thermogravimetric analysis

The films were characterized in terms of thermal properties by thermogravimetric analysis (TGA) (TA instruments TGAQ500, USA). The samples were fractionated in quantities between 2 and 5 mg . The sweeping temperature applied was 30 to 600°C with a variation rate of 10°C/min and nitrogen flow rate of 40ml/min.

7 | X-ray diffraction

The films were characterized according to the crystallinity pattern using an X-ray diffractometer (Bruker, D8 Advance, United States). The evaluation was carried out in 2θ in the regions from 3 to 40° with a voltage of 40 kV and a current of 40 mA . The relative crystallinity (CR) was calculated through the relationship between the amorphous area and the crystalline area expressed as a percentage of crystallinity.

8 | Scanning electron microscopy

The films were evaluated for cross-sectional microscopy using a scanning electron microscope (SEM) (NOVA

200 NanoSEM, USA). The films were fractionated with the aid of liquid nitrogen and covered with a gold bed to increase conductivity. During the test, electron acceleration voltages of 5 and 10 kV and an approximation of 3000 × were used.

9 | Statistical analysis

The tests were performed in triplicate; the averages and the standard deviations were mentioned throughout the results. Analysis of variance (ANOVA), followed by the Tukey test, was applied using Statistic 5.0 software to determine significant differences between means at the 95% significance level.

3 | RESULTS AND DISCUSSION

The SNCs produced and incorporated in the films were previously characterized (data not shown) and are shown in the study conducted by Martins, Latorres, and Martins. [21] The sizes of the nanoparticles obtained were 300 nm for the nanocrystals from rice starch and 548 nm for the nanocrystals from potato starch. Figure 1 presents images of the films prepared with the different concentration of nanocrystals. It is possible to verify that the addition of the SNCs changed the film homogeneity and particles can be easily observed.

The total difference in color and opacity of the films were characterized as optical properties, which are presented in Table 2. Opacity is an important property in food packaging, because as opacity increases, light penetration decreases. [22] The reduction in light transmission slows oxidative processes in foods enhanced by the absorption of light. [23] LDPE is a polymer widely used industrially because it has high transparency. [24] However, the addition of 1% of SNCs, both for rice and potato, significantly increased ($p < .05$) the opacity of the films. Orr et al. [15] also observed that the addition of higher concentrations of cellulose nanocrystals in a LDPE and polypropylene matrix increased the opacity of the films. According to Mukurubira et al., [25] the addition of nanocrystals to the polymeric matrix can occupy previously empty spaces of the polymer molecules complementing the structure, reducing light transmission and making the films opaquer.

The total color difference considers changes caused in all measurement parameters, L* (brightness), a* (red to green variations), and b^* (yellow to blue variations). Therefore, the addition of the SNCs changed the color spectrum, and these were accentuated as the concentration of SNCs increased. Dong et al. [26] observed a significant increase in the total color difference with the addition of different concentrations of garlic essential oil in an LDPE matrix. According to Goudarzi et al., [27] color changes can be caused by caramelization reactions between mono-, di-, and oligosaccharides present in nanocrystals. When they are subjected to the presence of heat during the extrusion process, they can cause a color change. Among the SNCs evaluated, those produced from potato starch caused greater variation in the total color difference. The botanical differences between the starches cause different behaviors between the materials [28]; in addition, the larger size of the rice potato nanocrystals may have influenced the formation of agglomerations in the films, [22] thus enabling caramelization reactions to increase.

Films hydrophobicity was measure by contact angle, higher contact angles indicate that the polymer is more hydrophobic. [5] Films with a contact angle lower than 90° are considered hydrophilic, while contact angles with angle higher than 90° are considered hydrophobic. [24] The addition of rice starch and potato starch nanocrystals increased the contact angle between the drop and the film, indicating the increased hydrophobicity of the films and characterizing them as hydrophobic (Table 2). Datta et al. [1] observed that the addition of nanosilica in LDPE and starch blends increased the contact angle from 38° to 97° using the same method as described in this study. According to the authors, the increase in the contact angle indicates homogeneity between the nanomaterial and the LDPE matrix. Leite et al. [29] evaluated the contact angle in gelatin films with nanocrystals added and verified an increase in the contact angle with the addition of 2.5% nanocrystals. The authors attributed this effect to the formation of hydrogen bonds between the nanocrystals and the film matrix, thus reducing the hydroxyls available for bonding with the molecules and water.

The mechanical properties, evaluated in the transversal and longitudinal directions because their production in a bioriented extruder promoted greater stretching of the films in the longitudinal direction, of the LDPE and nanocomposite films are depicted in Table 3. The oriented extrusion process can generate stretching in one direction (one-dimensional orientation) and in two directions (bioriented). The orientation process improves film properties, such as, strength, rigidity, and optical properties, among others. [30] The characteristics of the films may differ according to the production method, conditions, equipment, and polymers, among others. A major challenge in the extrusion of natural polymers is due to the great limitations of processing temperature, which can result in its degradability. [15]

The modulus of elasticity of the LDPE and nanocomposite films in the transversal and longitudinal orientations is shown in Table 3. In both orientations, the
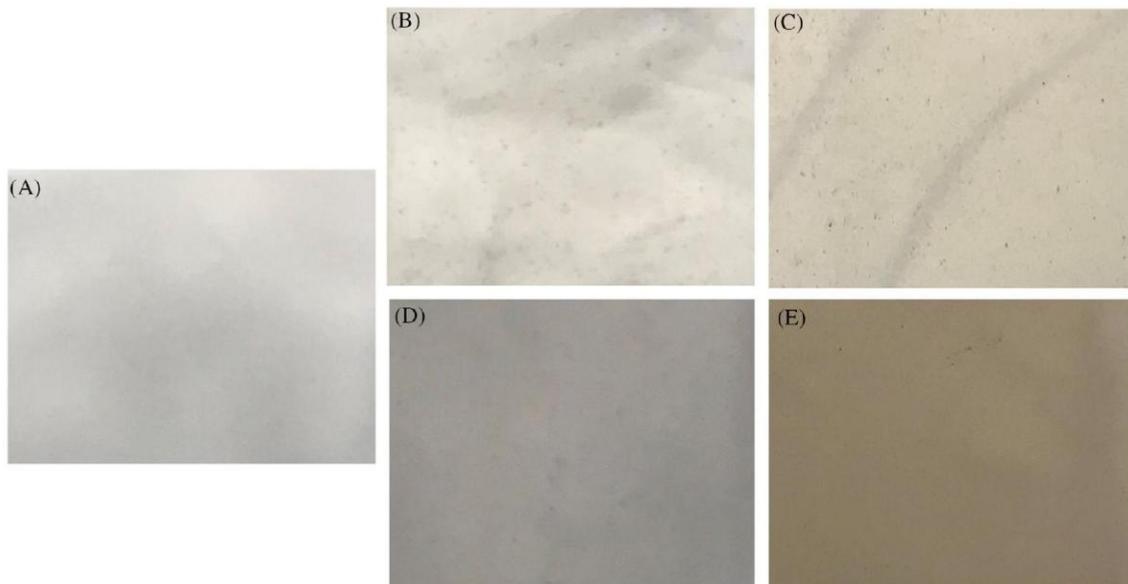

FIGURE 1 Images of the nanocomposite LDPE and LDPE/SNCs films. (A) LDPE, (B) LDPE/RSNCs 0.5%, (C) LDPE/PSNCs 0.5%, (D) LDPE/RSNCs 1%, and (E) LDPE/PSNCs 1%

Films	Optical properties		Contact angle (°)
	ΔE^*	Opacity (%)	
LDPE	$0.45^e \pm 0.01$	$10.9^b \pm 0.10$	$94.6^d \pm 0.60$
LDPE/RSNCs 0.5%	$1.62^d \pm 0.06$	$10.6^b \pm 0.10$	$99.3^c \pm 0.10$
LDPE/RSNCs 1%	$3.31^b \pm 0.21$	$11.7^a \pm 0.10$	$99.3^c \pm 0.90$
LDPE/PSNCs 0.5%	$1.87^c \pm 0.03$	$10.8^b \pm 0.30$	$102.4^a \pm 0.40$
LDPE/PSNCs 1%	$6.10^a \pm 0.14$	$11.7^a \pm 0.10$	$100.5^b \pm 0.40$

Note: Mean ± standard deviation. Different letters in the same column indicate significant differences ($p < .05$); ΔE*, total color difference. Abbreviations: LDPE, low-density polyethylene films; LDPE/PSNC 0.5%, low-density polyethylene films containing potato SNCs at 0.5% concentration; LDPE/PSNC 1%, low-density polyethylene films containing potato SNCs at 1% concentration; LDPE/RSNC 1%, low-density polyethylene films containing rice SNCs at 1% concentration; LDPE/RSNCs 0.5%, low-density polyethylene films containing rice SNCs at 0.5% concentration.

TABLE 2 Optical properties and contact angle of LDPE and LDPE/SNCs nanocomposite films

addition of potato starch nanocrystals in a concentration of 1% (LDPE/PSNC 1%) showed higher elasticity modulus of greater than for LDPE. While in the transversal direction, the addition of 1% nanocrystals increased around 50% the modulus when compared to standard LDPE, in the longitudinal direction, the same amount increased only around 16%. Gray et al. [16] obtained an increase in modulus with the addition of cellulose nanocrystals in an LDPE matrix. The increase in modulus indicates compatibility between the nanocrystals and the LDPE matrix due to the formation of hydrogen bonds between the hydroxyls present in the nanocrystals and the LDPE, promoting the structural reinforcement of the films. Moreover, according to Butron et al., [31] nanocrystals act as connecting agents that increase tension transfer through the film. Sabet et al. [32] detected an increase in modulus of elasticity with the addition of graphene in the LDPE matrix and concluded that nanomaterials in the LDPE matrix increase the structural reinforcement when the materials are compatible and capable of forming crosslinking.

The tensile strength data for LDPE and LDPE/ nanocomposite films are also presented in Table 3. In the cross-sectional direction, the addition of the SNCs reduced the TS for all nanocomposite films. However, in

TABLE 3 Mechanical properties of LDPE and nanocomposite films

Films	Transverse			Longitudinal		
	Young modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Young modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
LDPE	184.84[c] ± 4.7	14.31[a] ± 0.7	606.7[a] ± 3.7	202.62[b] ± 4.6	18.24 [a] +0.9	162.3 [d] ± 3.7
LDPE/RSNC 0.5%	184.84 [c] ± 4.2	7.67 [d] ± 0.3	10.1[b] ± 0.8	129.53 [d] + 2.6	11.75 [b] + 0.7	173.9[c] ± 3.8
LDPE/RSNC 1%	195.77 [b] ± 2.5	8.58[c] ± 0.4	12.0[b] ± 0.6	122.08[e] ± 4.0	11.52 [b] +1.1	241.0[b] ± 2.0
LDPE/PSNC 0.5%	180.29[d] ± 4.3	8.23 [c] ± 0.3	11.4 [c] ± 0.5	134.80[c] ± 2.5	12.81 [b] + 0.6	257.2 [a] ± 2.1
LDPE/PSNC 1%	277.29 [a] ± 5.2	13.04 [b] ± 0.5	12.0[c] ± 0.9	244.15 [a] ± 1.1	18.30[a] ± 0.9	257.6[a] ± 2.1

Note: Mean ± standard deviation. Different letters in the same column indicate significant differences ($p < .05$).
Abbreviations: GPa, gigapascal; LDPE, low-density polyethylene films; LDPE/PSNC 0.5%, low-density polyethylene films containing potato SNCs at 0.5% concentration; LDPE/PSNC 1%, low-density polyethylene films containing potato SNCs at 1% concentration; LDPE/RSNC 1%, low-density polyethylene films containing rice SNCs at 1% concentration; LDPE/RSNCs 0.5%, low-density polyethylene films containing rice SNCs at 0.5% concentration; Mpa, megapascals.
the longitudinal, the addition of 1% potato starch nanocrystals kept the TS statistically equivalent to the LDPE control around, 18 MPa . Several authors report an increase in TS with the addition of starch, cellulose, and nanoparticle nanocrystals in LDPE matrices. [3,16,24,31−33] Some studies report that the increase in the concentration of the SNCs further increases the TS. [16,31] Therefore, it is believed that the reduction in TS may have occurred due to the small amount of SNCs added to the films; thus, it did not show the effect of structural reinforcement. The highest concentration of potato SNCs (LDPE/PSNCs 1%) showed TS very close to the TS of the control film indicating that higher concentrations of nanocrystals would probably increase the structural reinforcement and consequently, the TS.

The elongation of LDPE films decreases in the transverse direction with the addition of the SNCs. The reduction of the elongation at break was also verified by Rojas et al., [2] who evaluated the addition of zinc oxide nanoparticles in an LDPE matrix. The authors attributed this reduction to the decrease in the mobility of the polymer chain, which became more rigid and compact with the addition of nanomaterials. The addition of the SNCs made the film matrix more rigid, reducing its elasticity. Wang et al. [34] evaluated the same effect of cellulose nanocrystals in a polylactic acid and polyamide matrix. The authors associated this reduction to the formation of crosslinking between the nanocrystals and the film matrix. The connections reinforce the structure of the materials and consequently reduce its flexibility. Garg et al. [35] evaluated the addition of starch in the LDPE matrix and also verified a reduction in the film elongation. The authors believe that this reduction occurred due to intermolecular bonds between the starch and the polymer made the matrix more rigid. Different effect was noticed in the longitudinal directions, where an increase of the elongation at break was detected for all concentrations.

The storage module (E′) of the LDPE films containing 1% rice starch nanocrystals (LDPE/RSNCs 1%) (Figure 2) exhibited lower value than LDPE, presenting an initial resistance value of 30 MPa and breaking at around 65°C with E'close to 2 MPa . By contrast, LDPE films containing 1% potato starch nanocrystals (LDPE/PSNCs 1%) started with a lower E′(30MPa) compared to LDPE; however, but higher temperatures kept the value around 10 MPa , higher than LDPE. Sabet et al. [32] noticed an increase of E' with the addition of nanomaterials, such as graphene in the LDPE matrix. The authors believe that this increase is due to the structural reinforcement caused by nanomaterials linked to LDPE. The addition of graphene to the structure makes it more compact, consequently boosting the E'. According to Dufresne, [36] the addition of nanocrystals to films can increase the storage module and materials resistance. The SNCs form crosslinks with the polymer structure and provides structural reinforcement. In some cases, the addition of the SNCs can reduce the storage module, often due to the agglomeration of these materials and their poor dispersion.

Figure 2A also presents tan delta obtained from DMA data, which measures the molecular movement of polymers and can be defined as the relationship between the loss of module E'' and storage module E' (tan delta = E'' / E'). Through tan delta, glass transition temperatures (Tg) due to the increased mobility of the material with temperature variations can be determined [37]. LDPE films containing 1% potato starch nanocrystals present a peak around 58°C. Martins et al. [38] determined in their study the gelatinization temperature of potato starch which was around 60°C. Thus, it is believed that the tan delta observed is the increase in the mobility of nanocrystals of potato starches due to the temperature increase. According to Common et al. [39], the Tg of the polyethylene is around −100°C; therefore, with the
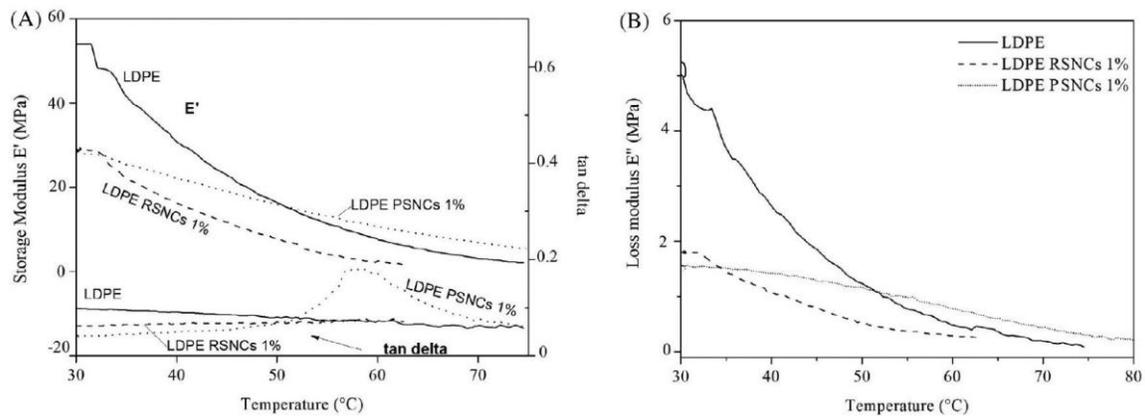
FIGURE 2 Spectrum of dynamic material analysis (DMA) of low-density polyethylene (LDPE) control and containing nanocomposites (LDPE/SNCs) (A) storage module (E') and tan delta and (B) loss of the module (E''). LDPE, low-density polyethylene films; LDPE/RSNC 1%, low-density polyethylene films containing rice SNCs at 1% concentration; LDPE/PSNC; LDPE/PSNC 1%, low-density polyethylene films containing potato SNCs at 1% concentration temperature range applied, it would not be possible to observe the tan delta.

The thermal properties of polymers are characteristics that direct the process conditions that can be applied in the production of films and the different final applications. [32] The LDPE and LDPE/SNCs nanocomposite films were characterized by thermogravimetry, and the results are shown in Figure 3.

The films displayed only one decomposition peak and loss of weight of 99% for all the materials, demonstrating the great homogeneity of the films. The LDPE control film showed an average degradation temperature of 468°C, while LDPE/SNCs films containing 1% nanocrystals of potato starch and rice starch exhibited temperatures of 471.3 and 470°C, respectively. When nanocrystals were added in a concentration of 0.5%, the temperature remained the same as that of the control film. The addition of the SNCs caused a small increase in the temperature degradation of the LDPE films/ nanocomposite SNCs in comparison with the LDPE control films. Other authors perceived an increase in degradation temperature with the addition of nanomaterials, such as montmorillonite, [40] zinc oxide, [2] graphene, [32] and copper. [3] According to Rojas et al., [2] the connections established between the polymer and nanomaterials form more compact network that keeps radicals connected and increase stability. Moreover, the reduction of

heat diffusivity due to the insertion of nanomaterials can cause an increase in degradation temperatures.

Table 4 shows the barrier properties for LDPE and LDPE/LDPE/nanocomposite SNC films. LDPE is reported in the literature as a polymer widely used in
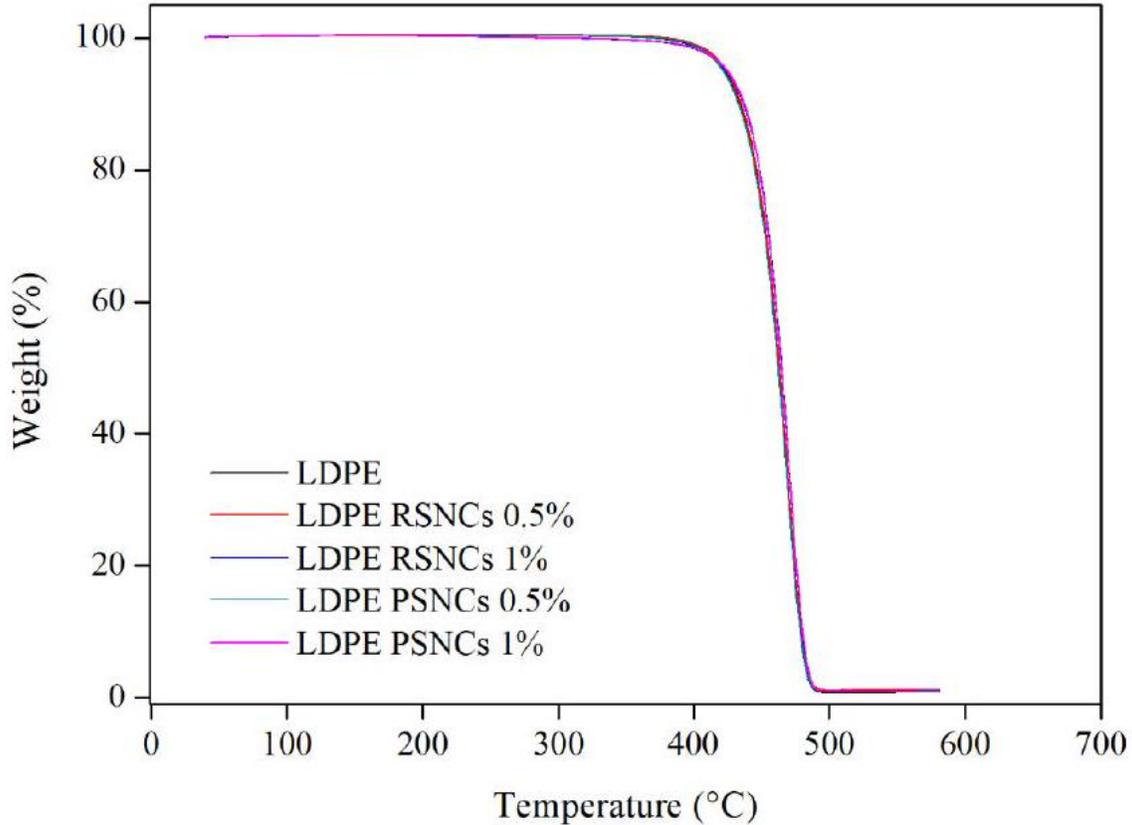

FIGURE 3 TGA of LDPE and LDPE/SNCs nanocomposite films. LDPE/PSNC 0.5%, low-density polyethylene films containing potato SNCs at 0.5% concentration; LDPE/PSNC 1%, low-density polyethylene films containing potato SNCs at 1% concentration; LDPE/RSNC 1%, low-density polyethylene films containing rice SNCs at 1% concentration; LDPE/RSNCs 0.5%, low-density polyethylene films containing rice SNCs at 0.5% concentration

industry due to its low gas permeation in thin matrices. [24] The application of nanomaterials has been assessed as promising to reduce the permeation of gases and water. [41] The addition of nanocrystals to LDPE films did not show significant changes in terms of PVA. However, regarding OP, the addition of 1% rice and potato starch nanocrystals (LDPE/RSNC 1% and LDPE/PSNCs 1%) significantly reduced the oxygen permeation of the LDPE matrix. Luo et al. [41] detected a reduction in

TABLE 4 Water vapor and oxygen permeability of LDPE and LDPE/SNCs nanocomposite films

Films	Oxygen permeability (ml mm/MPa/ min/cm^2)	Water vapor and oxygen permeability (g.mm/d.m².KPa)
LDPE	$1.89E - 04^b \pm 4E - 06$	$0.10^a \pm 0.04$
LDPE/RSNC 0.5%	-	$0.12^a \pm 0.02$
LDPE/RSNC 1%	$1.57E - 04^c \pm 2E - 06$	$0.09^a \pm 0.01$
LDPE/PSNC 0.5%	-	$0.09^a \pm 0.01$
LDPE/PSNC 1%	$1.86E - 04^a \pm 9E - 07$	$0.11^a \pm 0.02$

Note: Mean $\pm$ standard deviation. Different letters in the same column indicate significant differences ($p < .05$).
Abbreviations: LDPE, low-density polyethylene films; LDPE/PSNC 0.5%, low-density polyethylene films containing potato SNCs at 0.5% concentration; LDPE/PSNC 1%, low-density polyethylene films containing potato SNCs at 1% concentration; LDPE/RSNC 1%, low-density polyethylene films containing rice SNCs at 1% concentration; LDPE/RSNCs 0.5%, lowdensity polyethylene films containing rice SNCs at 0.5% concentration. oxygen permeation in an LDPE film containing nanometric calcium carbonate. Lomate et al. [3] also noticed a reduction in the PVA of LDPE films containing copper nanoparticles. According to the authors, nanometric materials are inserted into pores present in the films and delay the passage of water vapor. Furthermore, Gray et al. [16] reported that the reduction in water vapor permeation can be attributed to the good adhesion of nanocrystals to the polymer matrix through the formation of hydrogen bonds to form a denser 3D network that makes it difficult for gases to pass through the matrix. Palai et al. [42] remarked that the addition of nanocrystals forms tortuous paths in the film matrix that restrict the passage and/or propagation of water/gas molecules through the polymer matrix. Besides difficult paths, other parameters, such as the length of molecules, size of nanocrystals, concentration of nanomaterial, state of agglomeration, and conductivity can be related to the permeation of gases/water.

The crystallinity of the LDPE and LDPE/SNC nanocomposite films was evaluated using X-ray diffraction (XRD) and is shown in Figure 4. The presence of short and sharp peaks in the region of 2° − 20° and the presence of a short peak in the region of 34° represent the crystallinity spectrum of materials such as LDPE. [3] The addition of smaller SNCs (0.5%) did not modify the crystallinity. However, the additions of 1% of the SNCs caused an increase in peak intensity and a consequent increase in relative crystallinity. While LDPE/PSNCs 1% present a relative crystallinity of 81.6%, LDPE standard has a crystallinity of 75.7%. Sabet et al. [32] observed an increase in crystallinity of LDPE films attenuated from
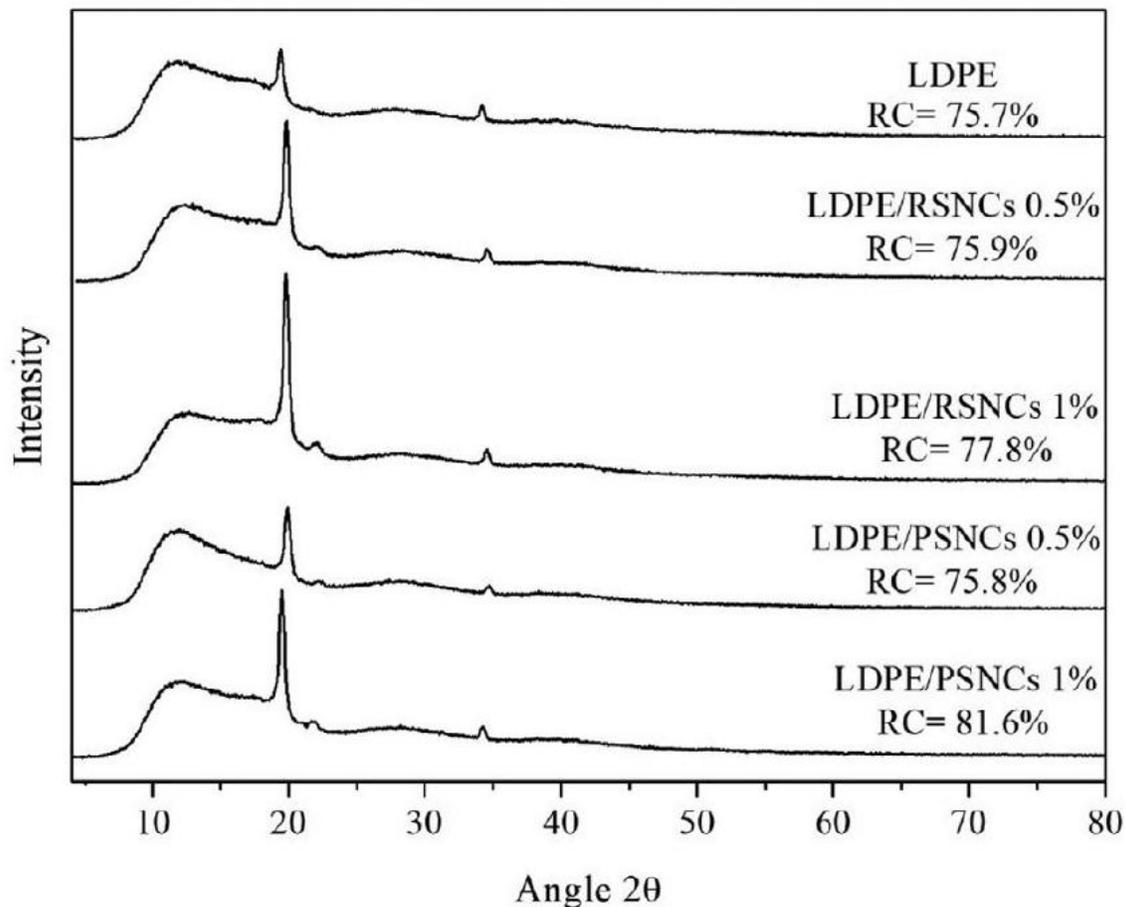
FIGURE 4 Diffractogram and relative crystallinity (CR) of LDPE and LDPE/SNC nanocomposite films. LDPE/PSNC 0.5%, low-density polyethylene films containing potato SNCs at 0.5% concentration; LDPE/PSNC 1%, low-density polyethylene films containing potato SNCs at 1% concentration; LDPE/RSNC 1%, low-density polyethylene films containing rice SNCs at 1% concentration; LDPE/RSNCs 0.5%, low-density polyethylene films containing rice SNCs at 0.5% concentration graphene. The authors comment that the addition of nanomaterials contributed to the intensification of the peaks; in addition, they mention that an increase in the concentration of the nanomaterial caused an increase in crystallinity. According to Dufresne [36] the addition of nanocrystals in different polymeric matrices promotes the structural reinforcement of the material due to the formation of hydrogen bonds between the nanocrystals and the polymer. The increase in structural density offers an increase in the crystallinity of the materials.

The evaluation of the morphological structure of the cross-section of the LDPE and LDPE/LDPE/SNC nanocomposite films was performed by SEM, Figure 5. LDPE films containing rice starch nanocrystals in concentrations of 0.5% and 1% (Figure 5B,C) do not show apparent crystals inserted in the polymer matrix. However, they showed great porosity and apparent fibers. Dufresne [36] comments that the SNCs connect to the most varied polymeric matrices through crosslinking, forming a 3D network capable of making films more compact and highly resistant. The apparent homogeneity of the rice starch nanocrystals in the LDPE matrix can be correlated with decreased oxygen permeability, where the addition of 1% rice SNCs significantly reduced O_2 permeation.

LDPE films with potato starch nanocrystals incorporated in both concentrations (Figure 5D,E), it was possible to observe large crystals inserted in the structure of
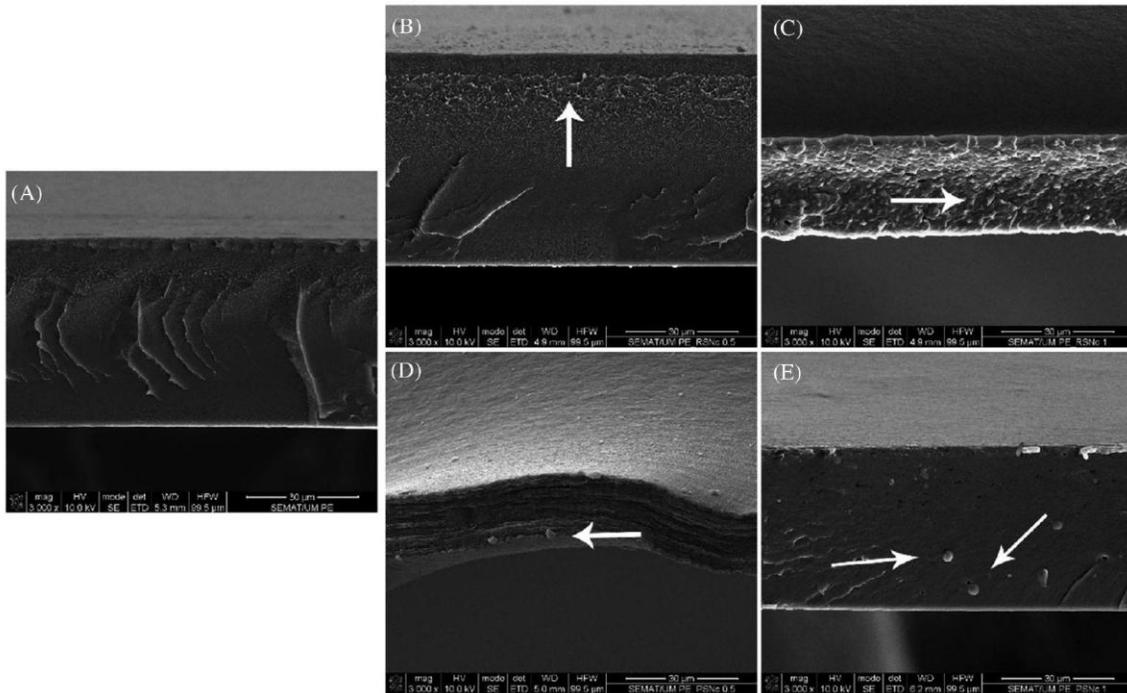

FIGURE 5 Micrograph of the films (A) LDPE, (B) LDPE containing 0.5% rice SNCs (C) LDPE containing 1% rice SNCs, (D) LDPE containing 0.5% potato SNCs, (E) LDPE containing 1% potato SNCs. LDPE/PSNC 0.5%, low-density polyethylene films containing potato SNCs at 0.5% concentration; LDPE/PSNC 1%, low-density polyethylene films containing potato SNCs at 1% concentration; LDPE/RSNC 1%, low-density polyethylene films containing rice SNCs at 1% concentration; LDPE/RSNCs 0.5%, low-density polyethylene films containing rice SNCs at 0.5% concentration

the film. The presence of these crystals may be associated with agglomeration of potato nanocrystals. Since the potato SNCs have larger sizes (548 nm) than the SNCs produced from rice starch (300 nm), they have a greater agglomeration potential as evidenced by the polydispersity index of 0.77 (data not shown). Gray et al. [16] observed a similar effect when trying to add starch to the LDPE matrix. The authors detected granules inside the transverse fractures of the films and attributed this to reduced homogenization of the starch with LDPE forming clusters not linked to the matrix.

4 | CONCLUSIONS

The addition of nanocrystals to the low-density polyethylene (LDPE) matrix modified the films and promoted improvements in some of the properties. As for the mechanical properties, the addition of 1% potato SNCs to the film matrix caused an increase in the transversal elastic modulus by approximately 50% and an increase in elongation at break to 257%, when compared with the standard LDPE film. Moreover, they provided an increase in the thermal stability of the polymer and a reduction of oxygen permeability with 1% of the

SNCs, and the nanocrystals from rice reduced the oxygen permeability by 17% compared with the standard. As for the structural evaluation, the crystallinity of the films increased with the addition of nanocrystals at a concentration of 1%. For the LDPE/ PSNCs treatment, the highest relative crystallinity of 81.6% was obtained compared with the LDPE standard, which presented 75.6% crystallinity. Therefore, the addition of nanocrystals to LDPE matrix, in general, proved to be efficient as a means of structural reinforcement, improving mechanical and barrier properties of LDPE films. Taking these conclusions with account, the incorporation of these nanomaterials in a biodegradable matrix could be a solution to replace synthetic packing film with single use.

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