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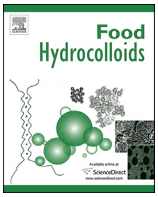

Food packaging bags based on thermoplastic corn starch reinforced with talc nanoparticles

Olivia V. López [a,b,*], Luciana A. Castillo [a], M. Alejandra García [b], Marcelo A. Villar [a], Silvia E. Barbosa [a]

[a] *Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET), Departamento de Ingeniería Química, UNS, Camino La Carrindanga km. 7, 8000 Bahía Blanca, Argentina*

[b] *Centro de Investigación y Desarrollo en Criotecnología de Alimentos, CIDCA (UNLP-CONICET), Facultad de Ciencias Exactas, UNLP, 47 y 116, 1900 La Plata, Argentina*

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ABSTRACT

Packaging bags from thermo-compressed films of thermoplastic corn starch containing talc nanoparticles (0, 1, 3 and 5% w/w) were developed. Mechanical properties of films were studied by two different techniques (tensile tests and quasi-static assays) revealing starch films reinforcement by talc addition. Strength improvement of thermoplastic starch films with talc concentration higher than 3% w/w was reflected in an increase in both Young's modulus and yield stress. Talc particles modified failure mode of thermo-seal of thermoplastic starch films giving another bags opening possibility. Usually, bags based on starch films could be only opened by tearing while those of starch-talc bionanocomposites could be torn or peeled off. Finally, in order to evaluate packaging bags tightness, films barrier properties were determined. Water vapor and oxygen permeability were reduced 54 and 26%, respectively, by talc addition (3% w/w) to thermoplastic starch.

1. Introduction

Nowadays food products market is in ongoing growth in order to supply world population's requirements. Moreover, food becoming safer, nutritious, and prolonged shelf life as well as having high quality are sued (Sorrentino, Gorrasi, & Vittoria, 2007). Thus, many efforts are focused on developing specific packages, being countless the technological progresses in this field. Packages should have tailored properties such as mechanical, optical, and barrier ones to assure integral product quality. Materials must be tough and flexible enough to guarantee their manipulation without any food product damage. In addition, other relevant issue is package tightness related to barrier properties since food organoleptic and microbial qualities depend on package's effectiveness to control gases exchange. Specific barrier requirement of a package system depends on food characteristics and intended end-use applications (Siracusa, 2012). Water vapor and oxygen are two of the main gases studied as permeants in packaging applications; they diffuse through the film modifying product quality and shelf-life. Water vapor barrier property of film packaging is important for products whose physical and chemical deteriorations are related to equilibrium moisture content (Siracusa, 2012). Concerning to oxygen impermeability, it is relevant since this gas promotes a lot of food degradation mechanisms, such as corrosive phenomena, oxidations, and organoleptic properties modifications (Russo, Simon, & Incarnato, 2006).

On the other hand, films thermo-sealable capacity and a good quality seal are indispensable requisites to develop food bags in order to assure package integrity (Chillo et al., 2008; López, Lecot, Zaritzky, & García, 2011). Bags seal quality depends on thermo-sealing conditions such as temperature, time, and pressure. Heat-sealing process consists in attaching the sides of two thermoplastic films, pressing them using a heat jaw. Thus, the bonded surface is heated up to the appropriate temperature and then it is cooled down to complete the seal (Hishinuma, 2009, p. 251). Bags seal should assure package integrity preventing microorganisms' entrance and avoiding product loss (Robertson, 2013, p. 704).

Other relevant packaging issue for market competition is related to its opening easiness, becoming gradually in an additional function. Opening packages without additional tools is the ideal way,

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[*] Corresponding author. CIDCA (UNLP-CONICET), Centro de Investigación y, Desarrollo en Criotecnología de Alimentos, Facultad de Ciencias Exactas, UNLP, 47 y 116, 1900 La Plata, Argentina. Tel.: +54 0291 4861700.
E-mail address: ovlopez75@yahoo.com.ar (O.V. López).

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being tearing and peeling off the most suitable ones (Hishinuma, 2009 , p. 251). Several techniques can be used to study packages opening easiness through the evaluation of thermo-sealed failure mode and tear resistance.

In recent years, new bio-based materials for food packaging have been designed in order to replace their non-degradable counterparts, which are contemporaneously used (De Azeredo, 2009). It is well-known that high production costs of biodegradable materials are a stumbling block, being an important disadvantage against synthetic ones. However, eco-friendly materials development is justified since they guarantee environmental preservation. This implies to protect non-renewable sources as well as to avoid pollution problems related to the final disposition of non-degradable materials (Davis & Song, 2006). Due to its availability, biodegradability, and low cost, starch is one of the most natural polymers studied for packaging applications. Thermoplastic starch (TPS) is obtained through granular disruption by shear forces applied at high temperature in presence of a plasticizer (Corradini, Carvalho, Curvelo, Agnelli, & Mattoso, 2007). Unfortunately, TPS films have two main disadvantages in comparison to synthetic polymers: moisture absorption susceptibility and poor mechanical performance. One approach to overcome these drawbacks is the reinforcement of TPS matrix adding natural organic or mineral fillers. Among mineral fillers, talc is considered as a good candidate in order to reinforce different kind of matrixes (Castillo, Barbosa, & Capiati, 2012; Castillo et al., 2013). Talc is a phyllosilicate with a layered structure which consists of octahedral brucite [$Mg(OH)_2$] sheets sandwiched between two tetrahedral silica [Si_2O_5] sheets. Talc structure is composed of two kinds of surfaces: a weakly energetic “basal surface” with basic and hydrophobic Si—O—Si groups and a more energetic “edge surface” with acid and hydrophilic Si—OH groups and residual magnesium cations (Comard et al., 2004). Thus, both layered structure and the nanometric size thickness make talc particles suitable to be intercalated by polymer chains during composite processing (Castillo et al., 2013).

There are many works dealing with TPS based materials containing different clay minerals (Chung et al., 2010; De Melo et al., 2011; Mbey, Hoppe, & Thomas, 2012; Slavutsky, Bertuzzi, & Armada, 2012). However, there is a lack of studies related to TPS reinforcement by talc addition. Particularly, TPS films containing talc nanoparticles were obtained in a previous work and their structural properties were analyzed (Castillo et al., 2013). If the final purpose of those composite films would be their use as food packaging materials, it is required to complement previous work (Castillo et al., 2013) by the study of talc nanoparticles effect on mechanical and barrier TPS film properties.

The aim of this work was to develop packaging bags from thermo-compressed films of thermoplastic corn starch containing talc nanoparticles. Mechanical behavior, water vapor and oxygen permeability, as well as, thermo-sealing capacity of composite films were studied, analyzing talc addition effect. Besides, packaging bags opening easiness and tightness were also evaluated.

2. Materials and methods

2.1. Materials

Native corn starch was provided by Misky-Arcor (Tucumán, Argentina) with an amylose content of 23.9 ± 0.7% (López, García, & Zaritzky, 2008). Talc sample was supplied by Dolomita SAIC (Argentina). This mineral comes from an Australian ore, having a high purity (98%), median size d50 of 5.9 ± 3.8 μm (particle size at which 50% of the population resides above this point and half resides below this point) and nanometric thickness of 79 ± 16 nm (Castillo et al., 2011). Glycerol (Anedra, Argentina) was used as plasticizer.

2.2. Thermoplastic starch mixtures

Mixtures of native corn starch, glycerol (30% w/w, starch dry basis), distilled water (45% w/w, starch dry basis) and talc nanoparticles (0, 1.7, 5.2, and 8.7% w/w, starch dry basis) were prepared. Thus, talc concentrations were 0, 1, 3, and 5% w/w of talc, respect to the final starch-glycerol-water mixture. Formulations were optimized in a previous work (Castillo et al., 2013). Talc was premixed with starch to achieve good particle dispersion between both powders. Then, glycerol and distilled water were added and samples were mixed and conditioned at 25 °C during 24 h. Mixtures were processed in a Brabender Plastograph (Brabender, Germany) at 140 °C and 50 rpm for 15 min.

2.3. Films preparation

Thermoplastic starch films were obtained by thermo-compression using an hydraulic press, following the processing conditions reported in a previous work (Castillo et al., 2013). Mixtures were conditioned at 25 °C and 60% relative humidity (RH) and films were prepared at 140 °C and 150 kg cm^{-2} during 6 min. Before characterization, films were conditioned at 25 °C and 60 % RH. Film thickness was measured at least in ten different locations.

2.4. Films mechanical properties

Mechanical behavior of TPS films was carried out using two different devices. Tensile tests were performed in an Instron 3369 universal mechanical testing system (Instron, USA) using a crosshead speed of 2 mm/min and a load cell of 50 N. Ten test specimens (13 × 100 mm) were assayed for each film formulation and stress-strain curves were calculated from load-displacement data. Young's modulus (E), maximum tensile strength (σ_m) and elongation at break (ε_b) were calculated according to ASTM D882-00 standard method. Besides, resilience modulus (U_r) and yield strain (ε_y), as well as toughness, were also obtained.

On the other hand, quasi-static assays in uniaxial condition were performed in a dynamic-mechanical analyzer Q800 (TA Instruments, New Castle, USA) with liquid nitrogen as cooling system, using a clamp tension. At least ten specimens (60 × 30 mm) were tested for each film formulation at isothermal conditions. Assays were performed at 25 °C from 0.1 N up to specimen breakage using a constant displacement velocity of 0.3 N/min and a preload force ranged from 0.1 to 0.5 N. Stress-strain curves were recorded and analyzed using the software Universal Analysis 2000. Same mechanical properties determined by tensile tests performed in the Instron machine were also calculated from quasi-static assays. Reported results correspond to the mean value of each mechanical property.

2.5. Packaging bags based on TPS films

With the purpose of developing packaging bags based on TPS films, different complementary materials characteristics were studied.

2.5.1. Films thermo-sealing capacity

Thermo-seals were produced using an impulse-wire thermo-sealer. This sealing technique was chosen over impulse bar since the first one allows cooling the seal before the jaws are opened, enhancing thereby its strength (López et al., 2011). Besides, it is the most used technique for flexible synthetic materials and consists in heating a film sample up to its fusion temperature by a short powerful electric impulse. Thermo-sealing resistance was evaluated in an Instron 3369 universal machine (Instron, USA) by tensile assays using a constant crosshead speed of 200 mm/min and a gap between grips of 25 mm. Test samples were prepared by thermo-sealing two specimens of 25.4 mm wide obtaining a fin sealed specimens, according to ASTM F88-00 standard method. For each film formulation ten probes were used. Assays were performed after thermo-seals were cooled down and became stable. Mechanical profiles were registered and seal failure modes were determined according to ASTM F88-00 standard method. Thermo-sealing maximum tensile resistance was calculated for break, elongation, or adhesive-elongation failures. In the case of adhesive, cohesive, or delamination failures, average thermo-sealing resistance was determined considering only the 80% middle part of stress-strain curves. The involved energy, in the case of adhesive failures, was calculated as the area under the curve.

2.5.2. Film tear propagation resistance

Films tear propagation resistance was evaluated using the ASTM D-1938 standard method with some modifications. At least ten specimens of films based on TPS and TPS with 5% w/w talc particles were assayed. According to the standard test method, samples (25 × 75 mm) with a slit at 12.5 mm were prepared. Tensile tests by pulling apart the specimen were performed in an Instron 3369 universal machine (Instron, USA) using a constant crosshead speed of 250 mm/min and a gap between grips of 50 mm. Assays were carried out at room temperature. Load-time curves were recorded and average tear propagation force was determined, disregarding the initial and final portions of the curves. In order to analyze comparatively this mechanical property, tear propagation force values were normalized considering film thickness.

2.5.3. Tightness of package bags based on TPS films

In order to study TPS bags tightness, films barrier properties were determined. Moreover, a qualitatively evaluation was performed by visual analysis and a photographic register of thermo-sealed bags containing cherry tomatoes (*Lycopersicon esculentum*).

Water vapor permeability (WVP) was performed using two different standard methods. According to ASTM E96-00 standard method, WVP was determined gravimetrically. Films with an exposure area of 38.48 cm^2 were fixed on test cells containing a desiccant (calcium chloride). Test cells were placed in chamber with controlled temperature (25 °C) and RH (50%). After steady-state conditions were reached, weight of test cells was measured every 1 h over 1 day. Water vapor transmission rate (WVTR) was determined using equation (1).

$$\mathrm{WVTR} = \frac{\left(\frac{\Delta m}{t}\right)}{A} \quad [1]$$

where Δm is the mass change (g), t is the time (s) and A corresponds to the exposure area (m^2).

On the other hand, a PERMATRAN-W® Model 3/33 (Mocon Inc., USA) was used to measure films water vapor transmission, according to ASTM F 1249-89 standard method. Film sample was placed in a test cell which is divided into two chambers separated by the specimen. The inner chamber is filled with nitrogen (carrier gas) and the outer chamber with water vapor (test gas). Water molecules diffuse through the film to the inside chamber and WVTR is registered. Measurements were carried out at 25 °C and films were subjected to a partial water vapor pressure gradient. Masking specimens with precut aluminum foil were used to avoid saturation leaving an uncovered film area of only 5 cm^2.

From WVTR values obtained by both standard methods, WVP was calculated using equation (2).

$$\mathrm{WVP} = \frac{l\ \mathrm{WVTR}}{\Delta p} \quad [2]$$

where l corresponds to film thickness (m) and Δp is the partial pressure difference across the films (Pa).

Oxygen mass transfer rates were analyzed at 25 °C using a Mocon OX-Tran2/20 (Mocon Inc., USA) based on the ASTM 3985 standard method. Test cell was composed by two chambers separated by the sample (10 cm^2). On one side of the film 100% oxygen gas was flowing, and on the other side there is a flow of nitrogen gas (98% N_2 and 2% H_2). The RH of both gases was controlled at 75% by a humidifier. All barrier properties were determined at least by triplicate.

2.6. Statistical analysis

Analysis of variance (ANOVA) was used to compare mean differences on samples properties. Besides, comparison of mean values was performed by Fisher's least significant difference test conducted at a significance level $p = 0.05$.

3. Results and discussion

Mechanical behavior of TPS films was characterized by two independent and complementary techniques (tensile tests and quasi-static assays). It is well known that fillers incorporation to TPS matrixes allows improving mechanical properties of composite materials. Fig. 1 shows stress-strain curves corresponding to TPS and its bionanocomposites containing talc particles determined by both techniques. As it is observed in the curves obtained by tensile and quasi-static assays, filler addition did not modify stress-strain behavior of TPS, showing a characteristic curve of ductile materials. Table 1 presents mechanical properties of developed materials. Despite different values were obtained by both techniques, talc addition influence on TPS mechanical performance was similar. Tensile and quasi-static experiments revealed that the lowest used talc concentration did not affect ($p > 0.05$) film stiffness. Considering results from quasi-static assays, a stiffness increment of around 15% was observed for samples with 3% w/w talc concentration. A 5% w/w of talc addition increased Young's modulus around 68 and 81%, determined by tensile and quasi-static experiments, respectively. Incorporation of 1% w/w talc particles to TPS formulations increased 1.2 times the maximum tensile stress, determined by tensile tests. Both techniques demonstrated that 3 and 5% w/w talc incorporation increased significantly ($p < 0.05$) TPS yield stress. Well dispersion and distribution of nanoparticles within the matrix, attributed to good starch-talc compatibility, allow TPS materials reinforcement (Lim, Lee, & Tay, 2009). Particle-matrix interfacial adhesion could be associated to the edge surfaces which have hydrophilic groups such as -Si—OH and -Mg—OH (Chabrol et al., 2010). In addition, Ferrage et al. (2002) reported the presence of electronegative sites on talc tetrahedral sheets propitious to form hydrogen bonds with polypropylene methyl groups. Similar interaction could be expected for composites based on TPS and talc nanoparticles.

Elongations at break values obtained by tensile tests were significantly different ($p < 0.05$) to those determined by quasi-static assays, being around 60 and 17%, respectively (Table 1). Elongation at break values corresponding to the different studied formulations, were not significantly different ($p > 0.05$) among them (Table 1). The fact that film ductility is kept almost constant despite talc incorporation could be mainly associated to different contributions related to talc surfaces and particle orientation. On one side, few accessible hydroxyl groups on talc edge surface lead

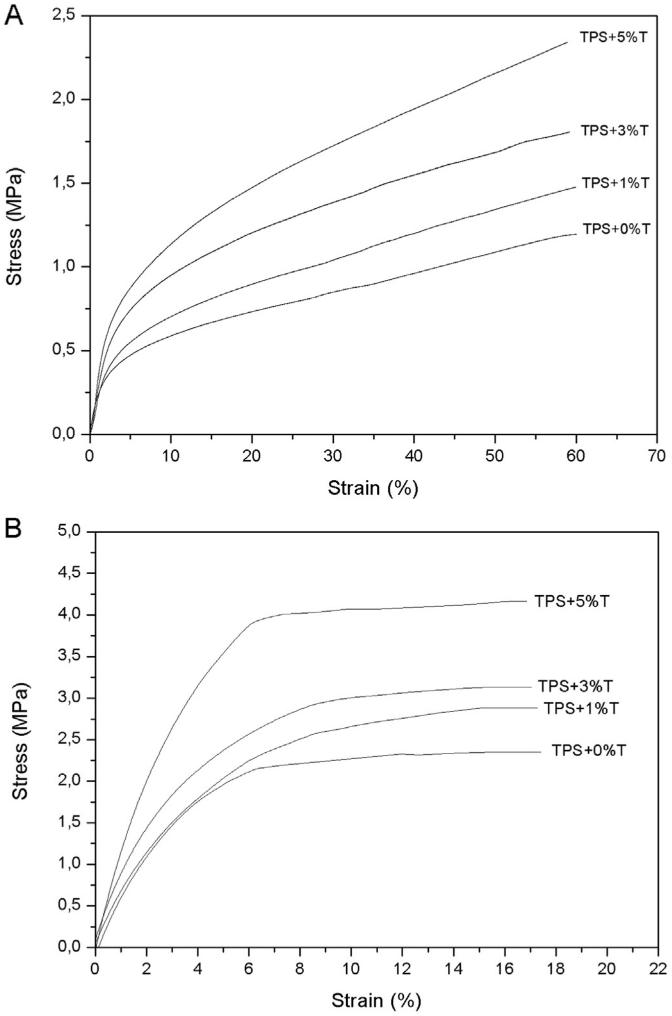

Fig. 1. Stress-strain curves of films based on thermoplastic corn starch (TPS) with talc nanoparticles (T) at different concentrations (0, 1, 3 and 5% w/w). A) Tensile tests and B) quasi-static assays.

to strong (hydrogen bonding) but localized talc-TPS interfacial adhesion. On the other hand, weak interaction between talc basal surface and starch matrix is attributed to the organophilic nature of this surface. Both aspects along with particle basal orientation, reported in a previous work (Castillo et al., 2013), could allow starch chains sliding despite talc incorporation. It is important to note that ductility is a relevant mechanical issue for film applications since it determines the degree of allowable material deformation up to fracture.

Mechanical properties values from tensile tests of TPS-talc bionanocomposites had the same order of magnitude than those reported by Carvalho, Avérous, and Tadini (2011) for TPS films containing native and organo-modified clays. However, those authors observed a different effect of filler incorporation on TPS film mechanical properties. They stressed that the addition of 3% w/w montmorillonite to a matrix based on starch with 23% w/w glycerol, reduced tensile strength and elongation at break around 40 and 60%, respectively. In this sense, talc nanoparticles improved notably TPS mechanical performance by increasing film stiffness and tensile strength without affecting their ductility. Table 1 also presents yield strain and resilience modulus, as well as, toughness values. Resilience is the ability of a material to absorb energy when it is deformed elastically up to yield strain, and release that energy upon unloading. In this sense, resilience modulus is defined as the maximum energy that can be absorbed per unit volume without creating a permanent distortion. From tensile tests results, a significant ($p < 0.05$) increment in U_r values of TPS films was observed for talc concentrations higher than 3% w/w, while the same effect was detected from 1% w/w talc addition in quasi-static assays. Particularly, incorporation of 5% w/w talc particles to starch based films caused an increment of 634 and 229% determined by tensile and quasi-static tests, respectively. Resilience modulus and yield strain increment are indicative of the relevance of adding talc nanoparticles to TPS materials in order to reinforce the matrix improving their elastic response. On the other hand, toughness is defined as the material ability to absorb energy up to fracture. TPS films toughness was raised with talc concentration reaching an increment of 94 and 59% for 5% w/w talc addition, determined by tensile and quasi-static tests. Talc contribution to TPS films toughness could be associated to particle reinforcement of starch matrix as it was reflected in the mechanical properties previously discussed.

Once mechanical behavior of TPS films was studied, the feasibility to develop packaging bags for food products was evaluated. Thus, films thermo-sealing capacity was studied in first instance. TPS films and composites containing talc nanoparticles were able to be thermo-sealed obtaining a good quality seal. This could be attributed to the disappearance of the interface between both individual layers, due to their high molecular interaction, allowing to form a new homogenous layer (Cho et al., 2007). TPS films thermo-sealing resistance, which determines package integrity, was studied by tensile tests. Fig. 2 shows tested specimen's photographs of TPS films and its bionanocomposite containing 5% w/w talc particles, as well as the corresponding stress-strain curves. Talc addition modified the failure mode of TPS films. Break near the seal was detected for TPS films while adhesive-cohesive failure was found for films with talc nanoparticles (Fig. 2A and B). Stress-strain curves shown in Fig. 2C were in agreement with the observed failure modes (López et al., 2011). TPS film's failure mode revealed that the corresponding juncture was resistant enough to bear the applied

Table 1
Mechanical properties determined by tensile tests and quasi-static assays of thermoplastic corn starch (TPS) films with 0, 1, 3 and 5% w/w talc nanoparticles (T).

Film formulation	E (MPa)	σ_m (MPa)	ε_b (%)	ε_y (%)	U_r (MJ/m^3)	Toughness (MJ/m^3)
Tensile tests						
TPS + 0 %T	22.7 ± 1.7^a	1.19 ± 0.04^a	62.2 ± 4.1^a	1.63 ± 0.13^a	0.29 ± 0.02^a	49.6 ± 4.6^a
TPS + 1% T	23.4 ± 2.6^a	1.48 ± 0.07^b	60.6 ± 1.0^a	1.85 ± 0.16^a	0.33 ± 0.03^a	60.8 ± 4.9^b
TPS + 3% T	25.7 ± 2.4^a	1.80 ± 0.13^c	59.1 ± 1.5^a	3.10 ± 0.25^b	1.16 ± 0.09^b	77.5 ± 5.3^c
TPS + 5% T	38.2 ± 3.0^b	2.34 ± 0.04^d	59.0 ± 1.1^a	4.02 ± 0.36^c	2.13 ± 0.17^c	96.2 ± 8.6^d
Quasi-static assays						
TPS + 0% T	74.9 ± 1.9^a	2.94 ± 0.36^a	17.0 ± 0.1^a	1.83 ± 0.15^a	1.00 ± 0.10^a	40.4 ± 0.4^a
TPS + 1% T	72.3 ± 3.9^a	3.14 ± 0.28^a	17.0 ± 1.6^a	2.01 ± 0.16^a	1.31 ± 0.10^b	43.3 ± 3.5^{a,b}
TPS + 3% T	86.3 ± 3.6^b	3.46 ± 0.03^b	17.0 ± 1.1^a	2.23 ± 0.18^a	2.02 ± 0.16^c	47.2 ± 5.2^b
TPS + 5% T	135.3 ± 1.1^c	4.32 ± 0.02^c	17.0 ± 0.5^a	2.68 ± 0.24^b	3.29 ± 0.26^d	64.1 ± 5.8^c

Reported values correspond to the mean ± standard deviation. Values within each column followed by different letters indicate significant differences ($p < 0.05$).

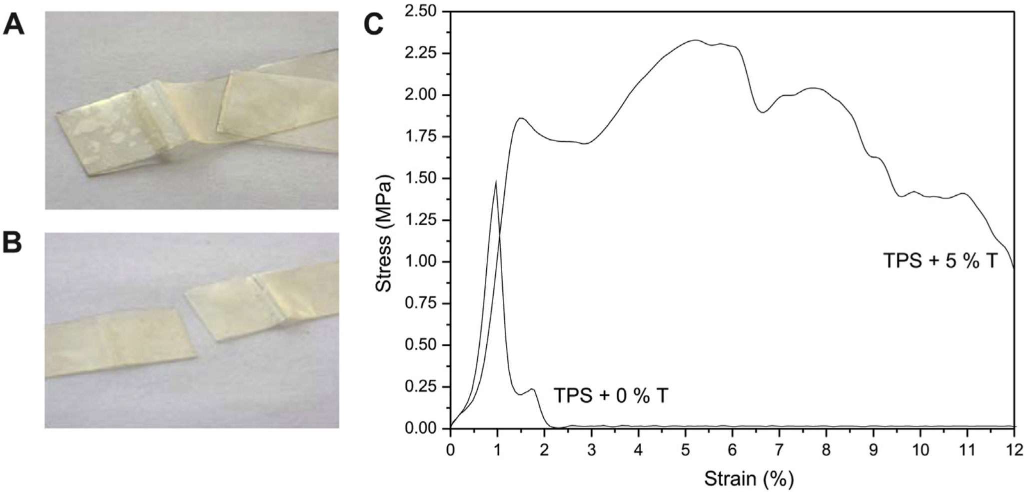

Fig. 2. Tested specimens of TPS films with: A) 0 and B) 5% w/w talc. C) Stress-strain curves of thermo-sealed films based on TPS with 0 and 5% w/w talc nanoparticles.

tensile stress failing thereby the material film before the seal. Maximum tensile resistance was 1.6 ± 0.3 MPa, being this value closer to the maximum strength of TPS films determined by the aforementioned tensile test (Table 1). The fact that both values were similar regardless different crosshead speed used in tensile tests is an indicative that TPS films material failed before the seal. On the other hand, film juncture of TPS composite with 5% w/w talc nanoparticles failed before material breakage. This result is in accordance with TPS matrix reinforcement by talc addition, demonstrated through tensile and quasi-static tests (Fig. 1 and Table 1). For these composite films the involved energy to cause adhesive-cohesive seal failure was 19.1 ± 1.7 J/m. Moreover, average thermo-sealing resistance of composite films was 1.7 ± 0.1 MPa. The fact that this value resulted significantly lower than the maximum tensile strength obtained by tensile tests (Table 1) demonstrates that seal was less resistant than film material. In addition, talc incorporation to TPS matrix increased the resistance around 11% to cause specimen failure, regardless the breakage mode. SEM observations of the seal zone of tested specimens were carried out in order to analyze if failure of TPS films with 5% w/w talc corresponded to an adhesive or a cohesive mode. Fig. 3 presents SEM micrographs corresponding to both films which were in contact before tensile tests. Fig. 3A and B are like specular images between them. When seal was opened, part of the material corresponding to one of the films was pulled out, causing a cohesive failure mode. Resulting hollows due to the material pulling are indicated with arrows in Fig. 3A. On the other hand, in Fig. 3B are marked the remaining material which corresponds to the hollows observed in its specular image. The fact that thermo-sealed TPS films with talc particles presented a cohesive failure indicates that packaging bags based on this kind of bionanocomposites could be easily opened by the peeling off method.

Tear resistance is another important issue within packaging field giving information about the required strength to open the package when it is torn. Generally, materials present different tearing behavior. Some of them may be quite resistant to tear when they are in their full form, but when a pre-cut slit is made, they become susceptible and the effort needed to propagate the tear is lower. Fig. 4 shows load-time curves corresponding to TPS and TPS with 5% w/w talc particles, as well as, specimen photographs after they were tested. According to ASTM D 1938-02 standard test method, load dependence with time indicates that TPS based materials could be associated to low extensible films. Although talc incorporation did not modify tear propagation pattern of TPS, reinforced materials presented higher average tear propagation force than TPS matrix. Normalized load required to propagate tear across starch films without talc particles resulted 0.31 ± 0.02 kg_f/mm while for TPS bionanocomposites with 5% w/w talc was 0.44 ± 0.02 kg_f/mm. This increment of 1.4 times is attributed to the presence of mineral particles which act as reinforcement agent of TPS matrix. Tear propagation forces presented the same order of magnitude than those reported by Wawro and Kazimierczak (2008) for potato starch films. Other effect on this mechanical property caused by talc presence was evidenced through the visual analysis of the direction

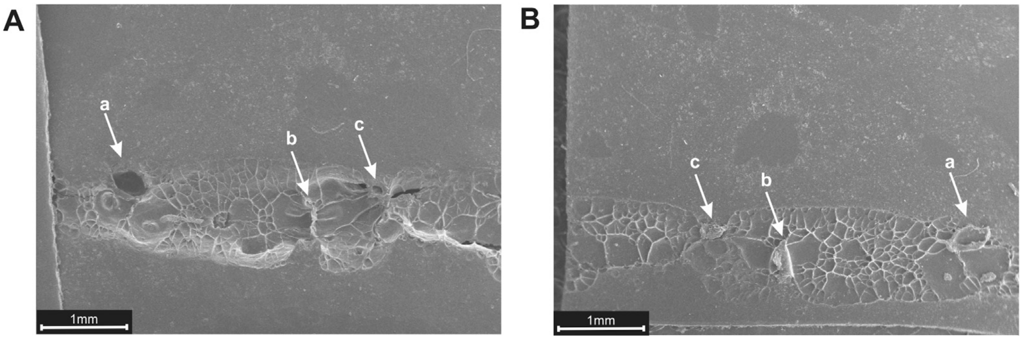

Fig. 3. SEM micrographs (58×) of seal zone of thermo-sealed films based on thermoplastic corn starch with 5% w/w talc nanoparticles after tensile tests. Ref.: same letters indicate the hollow and the corresponding remaining material in both specular images.

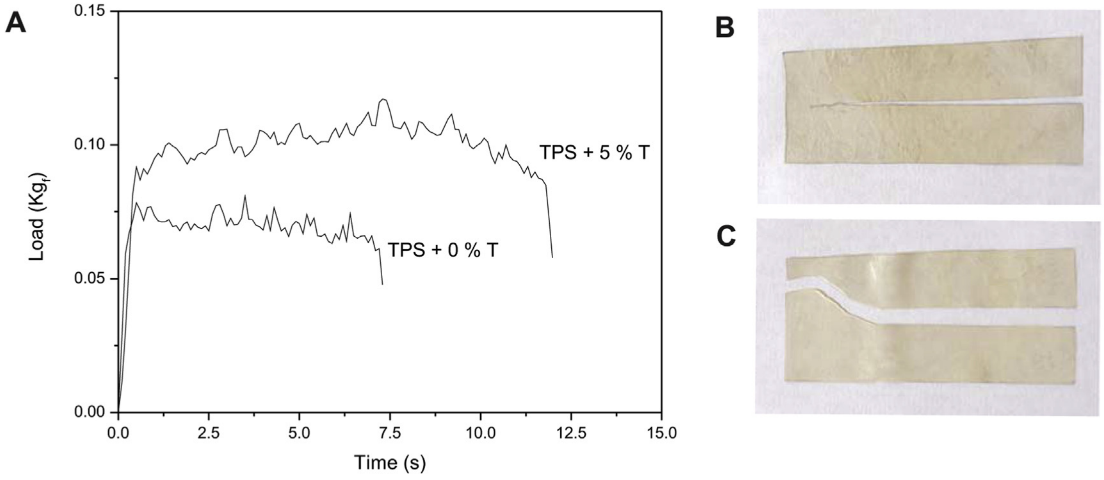

Fig. 4. A) Load-time curves of films based on thermoplastic corn starch (TPS) with 0 and 5% w/w talc nanoparticles obtained from propagation tear resistance assays. Tested specimens of TPS films with B) 0 and C) 5% w/w talc nanoparticles.

where tear propagated (Fig. 4B and C). During tensile assays, in TPS films tear propagated following the same slit direction, as it can be observed in Fig. 4B. Meanwhile, talc presence within starch matrix caused a tear propagation deviation of approximately 45° respects to slit direction (Fig. 4C). The fact that all TPS films with talc showed the same tear propagation direction could be related to a preferential particle orientation within the matrix reported in a previous work (Castillo et al., 2013).

Thermo-sealed packages tightness is an essential property to ensure its function for both domestic and industrial used products. Tightness is determined by inherent characteristics of packaging material and product's nature. Table 2 shows WVP values corresponding to the studied TPS-talc bionanocomposite films, determined by gravimetric method, as well as by measurement of gas flow. Comparing to synthetic polymers, TPS films shows a higher WVP attributed to two contributions. One of them is related to the inherent hydrophilic nature of starch and the other is associated to the swelling capability of starch–glycerol network which can hold substantial amounts of water. Swelling phenomenon disrupts matrix structural integrity affecting film barrier properties (Pushpadass et al., 2009). Talc addition at 1% w/w did not significantly modify ($p < 0.05$) moisture vapor permeability of TPS films. From both methods a WVP decrease of 1.4 times was observed for talc concentration of 3% w/w. For talc addition of 5% w/w, reduction percentages were 26 and 54% determined gravimetrically and by gas flow measurements, respectively. Despite obtained values using both techniques were significantly different, WVP tendency as a function of talc concentration resulted similar. These results indicate that layered talc structure hindered the transmission of moisture vapor through composite films. Similar results were reported by other authors for starch films reinforced with different mineral fillers (Gao, Dong, Hou, & Zhang, 2012; Kampeerapappun, Aht-ong, Pentrakoon, & Srikulkit, 2007; Park et al., 2002). Within nanocomposite structure, layers disposition led to a tortuous pathway for water molecules to move through polymeric matrix, thereby increasing the effective path length for diffusion (Tang, Alavi, & Herald, 2008). Moreover, moisture permeability decrease in TPS films by talc addition could be also attributed to starch molecules immobilization due to starch-talc particles interaction. In a previous work, this interaction was demonstrated using different complementary techniques such as X-ray Diffraction and Fourier Transform Infrared Spectroscopy (Castillo et al., 2013). Similar physical interpretation to this phenomenon was claimed by other authors for different reinforced bio-based materials (Gao et al., 2012; Gusev & Lusti, 2001; Tunc et al., 2007; Wang, Zhang, Han, & Bai, 2009). Oxygen permeability measurements were performed at 25 °C and 60% RH, which is a standard use condition. Obtained results for TPS-talc bionanocomposites are shown in Table 2. Oxygen permeation of TPS films was rather low compared to synthetic films such as low and high density polyethylene (2325 and 4650 cm^3 mil m^{-2} day^{-1}, respectively). Addition of 1% w/w talc to TPS formulations did not significantly affect ($p < 0.05$) films oxygen barrier property (Table 2). The presence of talc nanoparticles from 3% w/w reduced oxygen permeation through TPS matrix, reaching a decrease of about 26% for the formulation with 5% w/w talc. As it was previously described for WVP, the layered silicate could be viewed as an impermeable obstacle to oxygen molecules motion affecting films gas barrier properties. Moreover, good filler dispersion and distribution within starch matrix, studied by Transmission Electron Microscopy and Scanning Electron Microscopy in a previous work, also contributed to a reduction in oxygen permeation (Castillo et al., 2013).

Table 2
Barrier properties of thermoplastic corn starch (TPS) films with 0, 1, 3 and 5% w/w talc nanoparticles (T).

Film formulation	WVP × 10^{10} [g (s m Pa)$^{-1}$]		Oxygen permeation [cm^3 mil m^{-2} d^{-1}]
	Gravimetric method	Gas flow determination	
TPS + 0% T	12.9 ± 1.0^a	1.36 ± 0.05^a	527.8 ± 41.1^a
TPS + 1% T	13.1 ± 0.1^a	1.35 ± 0.01^a	525.6 ± 16.5^a
TPS + 3% T	9.3 ± 0.6^b	0.94 ± 0.08^b	406.4 ± 23.5^b
TPS + 5% T	9.6 ± 0.1^b	0.62 ± 0.04^c	388.7 ± 18.5^b

Reported values correspond to the mean ± standard deviation. Values within each column followed by different letters indicate significant differences ($p < 0.05$).

Finally, tightness of package bags based on TPS films was evaluated qualitatively. For this purpose, cherry tomatoes were packaged in developed bags and visual analysis was done during storage. In Fig. 5 it can be observed that packaging bags were inflated respect to their initial condition. This observation is a consequence of gases production due to tomatoes respiration and senescence mechanisms. On the other hand, gases accumulation within the bags is attributed to both good quality packages seal and high films barrier properties. Talc incorporation to TPS films allowed a high accumulation of gases within bags associated to barrier properties improvement by particles presence.

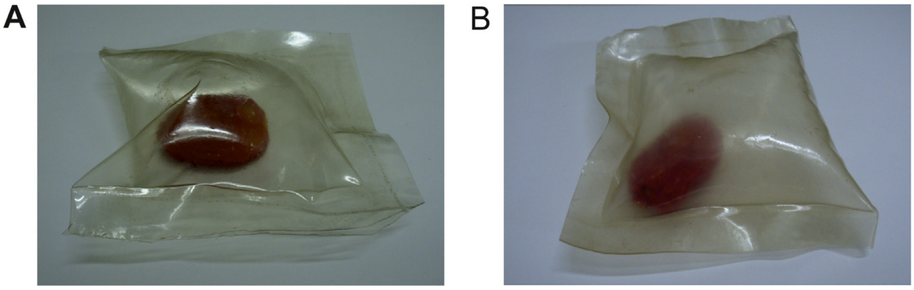

Fig. 5. Packaging bags containing cherry tomatoes based on A) thermoplastic corn starch (TPS) and B) TPS with 5% w/w talc nanoparticles.

4. Conclusions

Thermo-sealed packaging bags from films based on thermoplastic corn starch (TPS) and talc nanoparticles were obtained. Talc concentrations higher than 3% w/w increased significantly stiffness and yield stress of TPS films, without affecting their elongations at break. In addition, TPS films resilience was raised with 3% w/w talc incorporation, meanwhile significant differences in toughness values were observed from 1% w/w particles concentration. These results indicate that TPS films reinforced with talc nanoparticles could be used to develop tougher and more resistant packages without resigning ductility. Concerning packaging opening, it was demonstrated that TPS bags could only be torn, while talc incorporation allows a new bags opening way by peeling off. This asseveration comes from tensile tests performed on thermo-sealed films which evidenced talc effect on failure modes of thermo-sealed TPS materials. Tightness of TPS packaging bags was improved by 3% w/w talc mainly due to the enhancement of films water and oxygen barrier properties.

The incorporation of natural and innocuous mineral filler like talc to films based on thermo-plastic starch allows obtaining a bionanocomposite suitable for packaging with enhanced functional properties.

References

Carvalho, O., Avérous, L., & Tadini, C. (2011). Mechanical properties of cassava starch-based nano-biocomposites. In *Proceeding of 11th International Congress of Engineering and Food. Athenas, Greece, 22–26 May* (pp. 111–112).

Castillo, L. A., Barbosa, S. E., & Capiati, N. J. (2012). Influence of talc genesis and particle surface on the crystallization kinetics of polypropylene/talc composites. *Journal of Applied Polymer Science, 126*(5), 1763–1772.

Castillo, L. A., Barbosa, S. E., Maiza, P., & Capiati, N. J. (2011). Surface modifications of talcs. Effects of inorganic and organic acid treatments. *Journal of Materials Science, 46*(8), 2578–2586.

Castillo, L., López, O., López, C., Zaritzky, N., García, M. A., Barbosa, S. E., et al. (2013). Thermoplastic starch films reinforced with talc nanoparticles. *Carbohydrate Polymers, 95*(2), 664–674.

Chabrol, K., Gressier, M., Pebere, N., Menu, M., Martin, F., Bonino, J., et al. (2010). Functionalization of synthetic talc-like phyllosilicates by alkoxyorganosilane grafting. *Journal of Materials Chemistry, 20*(43), 9695–9706.

Chillo, S., Flores, S., Mastromatteo, M., Conte, A., Gerschenson, L., Nobile, D., et al. (2008). Influence of glycerol and chitosan on tapioca starch-based edible film properties. *Journal of Food Engineering, 88*(2), 159–168.

Cho, M., Choi, Y., Park, H., Kim, K., Woo, G.-J., & Park, J. (2007). Titanium dioxide/UV photocatalytic disinfection in fresh carrots. *Journal of Food Protection, 70*(1), 97–101.

Chung, Y.-L., Ansari, S., Estevez, L., Hayrapetyan, S., Giannelis, E. P., & Lai, H.-M. (2010). Preparation and properties of biodegradable starch–clay nanocomposites. *Carbohydrate Polymers, 79*(2), 391–396.

Comard, M., Calvet, R., Balard, H., & Dodds, J. (2004). Influence of the geological history, particle size and carbonate content on the surface properties of talc as determined by inverse gas chromatography at infinite dilution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 238*, 37–42.

Corradini, E., De Carvalho, A. J. F., da Silva Curvelo, A. A., Agnelli, J. A. M., & Capparelli Mattoso, L. H. (2007). Preparation and characterization of thermoplastic starch/zein blends 2. Experimental section. *Materials Research, 10*(3), 227–231.

Davis, G., & Song, J. H. (2006). Biodegradable packaging based on raw materials from crops and their impact on waste management. *Industrial Crops and Products, 23*(2), 147–161.

De Azeredo, H. M. C. (2009). Nanocomposites for food packaging applications. *Food Research International, 42*(9), 1240–1253.

De Melo, C., García, P. S., Eiras Grossmann, M. V., Yamashita, F., Dall'Antônia, L. H., et al. (2011). Properties of extruded xanthan-starch-clay nanocomposite films. *Brazilian Archives of Biology and Technology, 54*(6), 1223–1233.

Ferrage, E., Martin, F., Boudet, A., Petit, S., Fourty, G., Jouffret, F., et al. (2002). Talc as nucleating agent polypropylene: morphology induced by lamellar particles addition and interface mineral-matrix modelization. *Journal of Materials Science, 37*, 1561–1573.

Gao, W., Dong, H., Hou, H., & Zhang, H. (2012). Effects of clays with various hydrophilicities on properties of starch–clay nanocomposites by film blowing. *Carbohydrate Polymers, 88*(1), 321–328.

Gusev, A. A., & Lusti, H. R. (2001). Rational design of nanocomposites for barrier applications. *Advanced Materials, 13*(21), 1641–1643.

Hishinuma, K. (2009). *Heat sealing technology and engineering for packaging: Principles and applications*. DEStech Publications, Inc.

Kampeerapappun, P., Aht-ong, D., Pentrakoon, D., & Srikulkit, K. (2007). Preparation of cassava starch/montmorillonite composite film. *Carbohydrate Polymers, 67*(2), 155–163.

Lim, S. H., Lee, M. W., & Tay, Y. C. (2009). Development of biopolymeric nanocomposites for sustainable packaging. *SIMTech Technical Reports, 10*(4), 191–196.

López, O. V., García, M. A., & Zaritzky, N. E. (2008). Film forming capacity of chemically modified corn starches. *Carbohydrate Polymers, 73*(4), 573–581.

López, O. V., Lecot, C. J., Zaritzky, N. E., & García, M. A. (2011). Biodegradable packages development from starch based heat sealable films. *Journal of Food Engineering, 105*(2), 254–263.

Mbey, J. A., Hoppe, S., & Thomas, F. (2012). Cassava starch–kaolinite composite film. Effect of clay content and clay modification on film properties. *Carbohydrate Polymers, 88*, 213–222.

Park, H.-M., Li, X., Jin, C.-Z., Park, C.-Y., Cho, W.-J., & Ha, C.-S. (2002). Preparation and properties of biodegradable thermoplastic starch/clay hybrids. *Macromolecular Materials and Engineering, 287*(8), 553–558.

Pushpadass, H. a., Kumar, A., Jackson, D. S., Wehling, R. L., Dumais, J. J., & Hanna, M. a (2009). Macromolecular changes in extruded starch-films plasticized with glycerol, water and stearic acid. *Starch – Stärke, 61*(5), 256–266.

Robertson, G. L. (2013). *Food packaging: Principles and practice, third edition*. Taylor & Francis (CRC Press, Boca Raton, Florida, USA).

Russo, G. M., Simon, G. P., & Incarnato, L. (2006). Correlation between rheological, mechanical, and barrier properties in new copolyamide-based nanocomposite films. *Macromolecules, 39*(11), 3855–3864.

Siracusa, V. (2012). Food packaging permeability behaviour: a report. *International Journal of Polymer Science, 2012*, 1–11.

Slavutsky, A. M., Bertuzzi, M. A., & Armada, M. (2012). Water barrier properties of starch-clay nanocomposite films [Propriedades de barreira à água de filmes de nanocompósitos de amido e argila]. *Brazilian Journal of Food Technology, 15*(3), 208–218.

Sorrentino, A., Gorrasi, G., & Vittoria, V. (2007). Potential perspectives of bio-nanocomposites for food packaging applications. *Trends in Food Science & Technology, 18*(2), 84–95.

Tang, X., Alavi, S., & Herald, T. J. (2008). Effects of plasticizers on the structure and properties of starch–clay nanocomposite films. *Carbohydrate Polymers, 74*(3), 552–558.

Tunc, S., Angellier, H., Cahyana, Y., Chalier, P., Gontard, N., & Gastaldi, E. (2007). Functional properties of wheat gluten/montmorillonite nanocomposite films processed by casting. *Journal of Membrane Science, 289*(1–2), 159–168.

Wang, N., Zhang, X., Han, N., & Bai, S. (2009). Effect of citric acid and processing on the performance of thermoplastic starch/montmorillonite nanocomposites. *Carbohydrate Polymers, 76*(1), 68–73.

Wawro, D., & Kazimierczak, J. (2008). Forming conditions and mechanical properties of potato starch films. *Fibres & Textiles, 16*(6), 106–112.