

REVIEW

Starch-based films and food coatings: An overview

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Native and modified starches have received considerable attention for biodegradable films formulation due to their completely biodegradable nature, edible characteristics, and low cost. Development and characterization of starch films obtained by: (i) casting, (ii) blown extrusion and (iii) the thermo-compression moulding process are described. The rheological properties of filmogenic suspensions, the barrier properties, and the mechanical resistance of the obtained films are reported. Addition of specific additives to the formulations modifies the film functionality transforming them into active materials. Diffusion of antimicrobial agents such as potassium sorbate from the active starch film, as well as their efficacy in dairy products is discussed. Likewise, reinforcing agents lead to composite materials with improved mechanical resistance. Starch-based materials show higher permeability to carbon dioxide than to oxygen, which is useful to control the respiration rate of fruits and vegetables. The application of active starch-based coatings to strawberries and Brussels sprouts in order to prolong their refrigerated storage life is analyzed. A detailed overview on the formulation and performance of starch-based films employing industrial and lab-scale methods, as well as the application of starch coatings to improve food quality is presented, with the aim of analyzing the possibility of development and application of such materials.

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1 Introduction

Starch is the most commonly used agricultural raw material for biodegradable and edible film formulation, since it is widely available at relatively low cost. Nonetheless, starch structure presents several challenges to its potential applications in the bioplastics industry [1]. Botanical origin

and environmental factors along plants growth, result in distinct molecular structure and properties as well as diversity in shape, size and composition of the starch granules [2].

Compared with synthetic materials, starch has two main disadvantages. Firstly, the three hydroxyl groups per D-glycosylic unit impart a high degree of hydrophilicity to starch. Therefore, as water is an effective plasticiser for this polysaccharide, the gain or loss of moisture may result in significant changes in physical and mechanical properties of starch-based materials. Secondly, native starch is not thermoplastic, since pyrolysis occurs before the melting point of crystalline regions in starch is reached. Consequently, starch cannot be melt-processed via conventional plastic equipment without plasticisers addition [3].

In order to improve starch water resistance or impart specific functional properties or blend with other materials to achieve balanced characteristics, this biopolymer can be chemically or physically modified [4]. Consequently, starch

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Abbreviations: **DMA**, dynamic mechanical analysis; **GAB**, Guggenheim, Anderson, and de Boer; **HDPE**, high density polyethylene; **LDPE**, low density polyethylene; **PVC**, polyvinyl chloride; **TGA**, thermo gravimetric analysis; **TPS**, thermoplastic starch; **WVP**, water vapour permeability

compatibility with other biodegradable polymers, such as polycaprolactone or polylactic acid among others, as well as composites processing with micro- and nano-fillers have been broadly studied [5–7]. By varying the blend components and processing conditions, morphology and thus functional and structural properties can be carefully regulated to enhance the efficiency of biodegradable packages [8].

Starch films may be obtained by two technological processes: a “wet” one based on starch gelatinization (casting), and another “dry” based on the thermoplastic properties of this biopolymer at low concentrations of water and/or other plasticisers (Fig. 1). Wet process is mainly used at laboratory scale and is considered a highly energy-consuming process, since it typically involves the gelatinization of an aqueous starch suspension and its subsequent dehydration under controlled conditions [9–12]. Since it is not a continuous process, the casting technique has several limitations, including: restricted size and amount of the produced films, long production times, and large volumes of solvents disposal (as the relationship between the dry matter and the solvent is low and solids do not exceed 10–12% of suspension). Nevertheless, this technology is still extensively studied because it is closely related to coatings application on different surfaces such as paper coatings or on seeds and foodstuffs.

Biodegradable and edible films are generally prepared via casting though other techniques, such as semi-continuous tape-casting and spread-coating techniques can also be used for large-scale manufacture [13]. Nonetheless, the scale-up of the obtaining process of novel materials employing the existing technology for synthetic materials results indispensable [14]. In this regard, the widest used continuous

industrial methods are dry processes like extrusion followed by blown, injection or thermo-compression moulding, which are highly productive and energy-efficient [3, 10, 14–17].

A relevant trend in biodegradable materials development, involves the study of active packaging products and controlled-release materials of drugs, agrochemicals and dietary supplements. Active packaging technologies are aimed to extend the shelf life of foods maintaining their nutritional quality and safety. They offer new or extra functions such as gases scrap (O_2 , CO_2 , and ethylene), moisture regulation, flavours emission and preservation, among others. Since many food products contain components (lipids, aromas, pigments and vitamins) that are susceptible to oxidation processes, the incorporation of antioxidants leads to an active packaging system [18]. Moreover, as the growth of microorganisms is not only detrimental to the organoleptic characteristics of food (such as off-odours and accelerated changes in aroma, colour and texture) but also some microorganisms and their toxins may cause food recalls and serious foodborne outbreaks [19], antimicrobial active packages have also been thoroughly studied [20]. Besides, controlled release of agrochemicals is a possible alternative to surmount chemical pollution derived from their extensive use to increase productivity. Starch and other hydrocolloids, such as alginate or chitosan, have been studied as matrixes for controlled release systems of fertilizers and pesticides [21, 22].

Likewise, starch has been widely used in edible coatings. These are defined as thin layers of edible material applied on food products with the purpose of extending the food product shelf life and provide an effective barrier against hazards. Coatings reduce moisture migration, gas exchange,

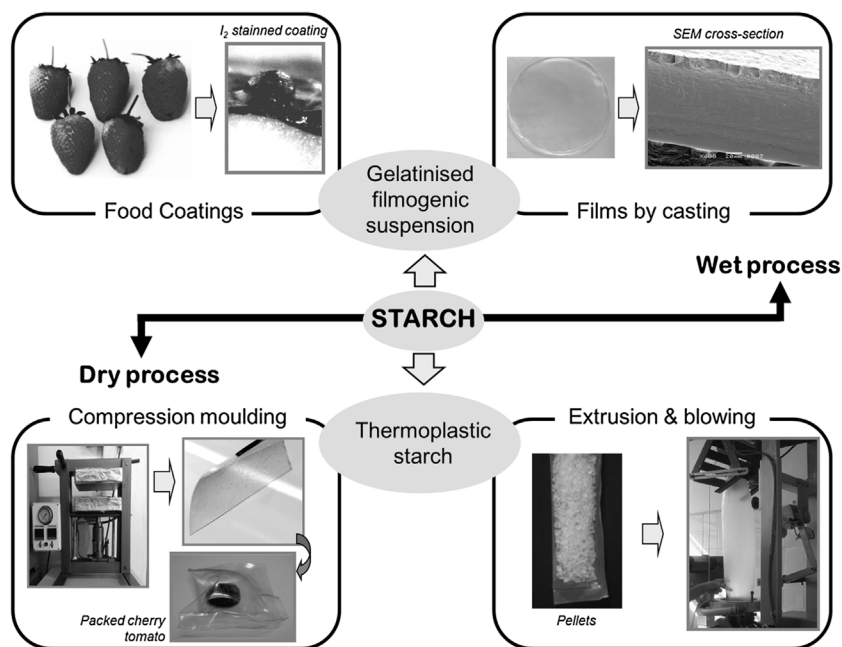


Figure 1. Representative scheme of starch potentiality in the formulation of edible coatings and biodegradable films by wet and dry processes. Image of packed cherry tomato: reproduced with permission [78]. Copyright 2015, Elsevier.

respiration and oxidative reaction rates, suppress physiological disorders, delay changes in textural properties, and improve mechanical integrity or food handling characteristics.

In this regard, this review intends to describe and analyze recent developments on starch-based materials from different processing techniques and applications.

2 Starch films obtained by casting

Films based on native starches of diverse botanical sources as well as chemically or physically modified have been widely studied by several authors [10, 11, 23–30]. Films formulation control allows tailoring of the mechanical and barrier properties of these materials, improving their efficiency as foods products packages. Study of films microstructure and the interactions between components provides insight into both the fundamental aspects of material science and the practical technologies for future applications.

Plasticisers are added to film formulations to aid processing operations and to modify final product properties, since they overcome material brittleness and improve their flexibility and extensibility. They are low molecular mass organic compounds that must be compatible with the film-forming polymers; they reduce intermolecular forces and increase polymer chains mobility [31]. Among others, oligosaccharides, polyols and lipids are chemically compatible with hydrocolloid-based films; being glycerol the most widely use [32–35].

2.1 Starch-based films physicochemical characterization

In casting method films thickness can be adjusted by controlling the ratio of filmogenic suspension weight to plate area. Drying conditions (rate and temperature) determine film characteristics (e.g., water content, crystallinity, etc.), affecting its microstructure and properties. Bader and Göritz [36] stressed that tailoring drying conditions, amorphous-crystalline structure could be controlled, which is strongly related to films barrier and mechanical properties.

Starch source has been reported to be critical for films optical properties, which ultimately determine packaged product acceptability by consumers. Ahipa starch films, for instance, exhibited lower UV barrier capacity than cassava and corn starch ones [26]. Transparency values of cassava and corn starch films were similar to those of some synthetic films, such as polyvinyl dichloride ($4.58 A_{600}/\text{mm}$).

Similarly, starch type did not affect film water solubility, regardless the assayed temperature (25 or 100°C), though it significantly ($p < 0.05$) increased with temperature and glycerol addition, due to the hydrophilic characteristic of the plasticiser.

Considering that hydrocolloid films are very sensitive to relative humidity, physicochemical characterization generally

includes water sorption isotherms determination, useful for the estimation of film stability under different ambient conditions. Sorption isotherms of yam, and native and acetylated corn starch films were reported in previous works [27, 37], being experimental data satisfactory fitted by GAB model, estimating the monolayer water content values.

2.2 Film microstructure

Materials based on corn starch exhibited a more homogeneous and compact structure than films obtained from tuberous starches as observed by SEM [26]. Compact and homogeneous matrix of films is an indicator of structural integrity and, consequently good mechanical properties are expected. In general, unplasticised starch-based films presented a multi-layered structure being those containing plasticisers more dense and compact without evidence of pores or cracks on their surfaces (Fig. 1).

Topography and roughness of starch films surface can be evaluated by AFM. Use of acetylated starch led to softer film surface, with lower roughness, in the same way as plasticiser addition did [12].

Interactions among film-formulation components are commonly studied by FTIR; spectra of unplasticised native corn starch films showed typical signals of stretching, bending and deformation for the main functional groups of starch. Acetylated corn starch films also exhibited a peak located at 1726 cm^{-1} , which is specific to CO bond stretching vibration of acetyl groups [38]. Furthermore, Guerra-DellaValle et al. [39] observed a decrease in the vibration signal corresponding to stretch ($3000\text{--}3900 \text{ cm}^{-1}$) and bending vibration (1650 cm^{-1}) of the OH groups due to the introduction of acetyl substituents on the starch constituent molecules.

X-ray diffraction patterns of native starch films corresponded to amorphous-crystalline structures. Films crystallinity depends on the following processing conditions: (i) biopolymer source and plasticisers, (ii) completeness of biopolymer dissolution in water, (iii) film drying conditions and (iv) final moisture content of the samples [36, 40]. Unplasticised starch films showed higher crystallinity than those containing plasticiser. Likewise, acetylated starch films yielded less crystalline structure than those from native starch.

X-ray diffraction patterns of starch-composite films generally represent a mixture of component features in which the characteristic peaks of each one can be identified.

Evolution of film matrix crystalline structure during storage can also be evaluated by DSC, which allows the glass-transition temperature (T_g) to be determined. As described for X-ray diffraction, film preparation and storage conditions influence their thermal transitions. Films obtained by yam starch thermal treatment, did not show any peaks in DSC thermograms at the initial time neither after 90 days of storage, indicating the matrix stability [27]. A similar trend

Table 1. Relevant physicochemical, mechanical and barrier properties of starch-based materials obtained by casting

Starch type	Film composition	Tensile strength (MPa)	Elongation at break (%)	WVP (g/m s Pa × 10 ¹⁰)	T _g (°C)	Opacity (AU × nm)	Ref.
Corn	Native corn starch	31.78 ± 2.40	4.15 ± 0.30	1.20 ± 0.01	48.3 ± 1.4	109.6 ± 0.9	[11, 12]
	Acetylated corn starch	41.85 ± 2.44	5.44 ± 0.26	0.16 ± 0.01	61.95 ± 0.81	56.78 ± 0.9	[12, 34]
	Corn starch + 50% acetylated corn starch	38.29 ± 1.51	3.95 ± 0.42	0.99 ± 0.03	53.32 ± 1.25	Nd	[12, 34]
	Corn starch + 50% Chitosan	20.9 ± 3.52	4.67 ± 0.58	2.13 ± 0.087	46.78 ± 0.65	88.7 ± 0.7	[11, 58]
Cassava	Native cassava starch	2.03 ± 0.85	248.4 ± 18.8	0.95 ± 0.19	22.57 ± 4.96	19.45 ± 1.34	[45]
	Cassava starch + 50% cassava bagasse	18.01 ± 0.19	4.4 ± 0.1	1.46 ± 0.07	51.50 ± 6.31	155.2 ± 1.32	[45]
Other	Ahipa starch	4.70 ± 0.30	21.80 ± 0.60	1.60 ± 0.01	42.9 ± 6.9	Nd	[26]
	Banana starch	4.6 ± 0.20	37.5 ± 0.50	4 ± 0.1	Nd	Nd	[59]
	Potato starch	1.7 ± 0.1	140 ± 15	0.72 ± 0.007	Nd	Nd	[60]

Notes: a) Composition is expressed in % w/w respect to starch content; b) All samples were plasticised with glycerol; c) The polysaccharides employed present different MW for their main components depending on their botanical source: being amylose MW 2×10^4 and 2.7×10^6 , 9×10^6 and 2.7×10^5 g/mol for corn, cassava, potato and banana, respectively, while amylopectin MW ranges from 2×10^5 and 1×10^6 g/mol for corn, 7×10^7 and 1.7×10^8 g/mol for cassava and potato, respectively [61–64]. There are no available data on ahipa starch amylose and amylopectin MW.

was observed for native starch films from other botanical sources, as well as, those based on acetylated corn starch. However, starch films obtained by alkaline treatment showed an endothermic transition at around 50°C during storage (90 days); this peak became narrower and its melting temperature and the corresponding enthalpy increased with storage time. This thermal transition could be associated with several processes, such as crystal growth of short chains (products of hydrolysis), recrystallization of amylose or other long lateral amylopectin chains [11, 28]. As it was previously described, plasticiser presence limited starch crystal growth and recrystallization, leading to lower enthalpy values and peak melting temperatures: additives may interfere with the polymeric chains association due to steric hindrances, likely decreasing films crystallinity.

DMA is an alternative method to study relaxation processes associated to glass transition temperatures. Starch source and its chemical modification strongly affect T_g (Table 1), while plasticization decreases the intermolecular forces between polymer chains and consequently reduces T_g values. DMA patterns of plasticised film show two relaxations, one located around -50°C, associated to the glass transition of the glycerol-rich phase, and other about 60°C, attributed to the starch-rich phase. A similar trend was also reported by other authors for films formulated with native starches from different sources of cereals, legumes and tubers [25, 41–44].

2.3 Barrier properties

Unplasticised films often yield significantly higher WVP values than plasticised ones, due to pores and cracks presence. Plasticisers, although generally are hydrophilic compounds, could induce structural modifications of starch network leading to a less ordered and compact structure.

Sorbitol generally resulted in lower WVP values compared to glycerol in plasticised starch-based films (Table 2). Amylomaize films, with higher amylose content, denser matrix structure and higher degree of crystallinity than those of standard corn starch, also exhibited relatively lower WVP values. However, amylose content effect on WVP of starch film was minimized by the incorporation of sunflower oil to the formulation, which considerably improves the films barrier capacity (Table 2).

A reduction of 87% in WVP value was obtained for plasticised acetylated corn starch films due to the hydrophobic character of the substituent (Table 1). Filler addition, such as the remaining residue of starch extraction, reduce WVP values for cassava starch films, due to the presence of the reinforcement agent increases the tortuosity pathway (Table 1) [45].

In general, starch films exhibit lower WVP values (an order of magnitude) compared to both protein films and other polysaccharide-based films [46–49], although they are much higher than those of synthetic polymers such as polyethylene.

With regard to gaseous permeability, O₂ permeation of starch-based films was much lower than those of CO₂, indicating a variable permeability of these films to select gases (Table 2); this effect can be attributed to a higher solubility of CO₂ than O₂ in film matrix. Similar results were obtained by Arvanitoyanis *et al.* [50] working with potato and rice starch films. Likewise, lipid addition maintained the selective gas permeability properties of the starch-based films (Table 2). Synthetic films, such as LDPE, has a relatively low CO₂ to O₂ permeability ratio (around 4), compared to an average ratio of 13 for starch-based films [51–53]. Development of composite edible films and coatings with selective gas permeability could be promising for controlling respiratory exchange and improving the conservation of

Table 2. Filmogenic suspensions properties and characteristic of coatings applied on food products

Coating formulation	Apparent viscosity (η_{app}) (mPa s)	Surface tension (dyn/cm)	Characteristic of applied coating	Film barrier properties			Ref.
				WVP ^{a)}	CO ₂ permeability ^{b)}	O ₂ permeability ^{c)}	
Corn starch (CS)	12.85 ± 0.06	60.7 ± 0.12	Extremely brittle	3.68 ± 2.24	29.21 ± 13.89	15.92 ± 2.99	[48, 52, 53, 73]
CS + glycerol (G)	11.95 ± 0.18	59.6 ± 0.8	Only adhesive on irregular surface products	2.57 ± 1.04	5.69 ± 0.97	4.61 ± 0.51	[48, 52, 53, 73]
CS + G + sunflower oil (SO)	11.31 ± 0.09	59.1 ± 0.7	Good adhesion on irregular and regular surface products	1.92 ± 0.47	5.87 ± 0.58	3.83 ± 0.76	[48, 73]
CS + G + SO + tween 40	Nd	46.1 ± 0.9	Good adhesion on irregular, regular and smooth surface products	Nd	Nd	Nd	[66]
CS + sorbitol (S)	12.59 ± 0.18	51.40 ± 0.08	Only adhesive on irregular surface products	1.75 ± 0.14	4.19 ± 0.81	2.48 ± 0.32	[48, 52, 53, 73]
CS + S + SO	9.64 ± 0.18	54.0 ± 0.3	Good adhesion on irregular and regular surface products	1.22 ± 0.11	4.72 ± 0.65	3.77 ± 0.03	[48, 73]
CS + S + SO + tween 40	Nd	47.4 ± 0.8	Good adhesion on irregular, regular and smooth surface products	Nd	Nd	Nd	[66]

Notes: Corn starch amylose and amylopectin present a MW of 2×10^4 g/mol and $2 \times 10^5 - 1 \times 10^6$ g/mol, respectively [61].

a) WVP $\times 10^{10}$ ($\text{g s}^{-1} \text{m}^{-1} \text{Pa}^{-1}$).

b) CO₂ permeability $\times 10^9$ ($\text{cm}^3 \text{m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$).

c) O₂ permeability $\times 10^{10}$ ($\text{cm}^3 \text{m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$).

fresh or minimally processed vegetables, as well as, oxygen susceptible products.

2.4 Mechanical properties

Films mechanical properties are dependent on additive-matrix interactions, and are also strongly affected by physical, chemical and environmental conditions, which influence on the material stability and flexibility. Stress-strain curves of unplasticised films showed a typical pattern of brittle materials while plasticised materials exhibited a ductile one. When glycerol was incorporated the mechanical behaviour of these materials changed considerably, decreasing tensile strength, as well as elastic modulus, while elongation at break significantly increased (Table 1). However, starch-based films were less flexible and resistant than synthetic polymers like LDPE and HDPE [54]. Plasticisers facilitate polymeric chain slipping, decrease network rigidity, producing a less ordered structure increasing films flexibility. According to García et al. [48], plasticiser-matrix interaction showed similar trends for both corn starch and amylopectin films, though plasticised corn starch films were more flexible than those of amylopectin. The addition of lipid increased film flexibility, reducing the starch type effect.

In general, tuberos starch films, such as cassava ones, exhibited higher elongation at break and lower tensile strength than those of corn (Table 1). Numerous authors agree with the positive effect of amylose content on elastic modulus of starch films [55, 56].

Tensile strength of films containing acetylated starch were significantly ($p < 0.05$) higher than those of native

starch, regardless glycerol addition (Table 1). Although acetyl groups interfere with the chains alignment, they led to the development of a more resistant matrix due to the reinforcement by hydrogen bonds between aligned polymeric chains. Likewise, the addition of natural fillers increases film tensile strength confirming the material reinforcement (Table 1) [45]. This is a well-known behaviour of polymeric composites reinforced with natural fibres, which has been extensively described by Shalwan and Yousif [57].

Heat-sealing capacity of flexible films is a critical feature and determines the integrity of the package. Starch-based films were sealed by impulse sealing showing a rupture near the zip or adhesive failures whether unplasticised or plasticised, respectively. Acetylated starch films presented higher maximum traction resistance values compared to native starch, while an intermediate behaviour was recorded for their blend. Besides, the necessary energy to cause adhesive failure of native and starch blend films were comparable, while acetylated ones showed the highest value, indicating a better zip quality [12].

3 Food applications of starch-based films and coatings

Starch-based edible coatings allow control of the respiratory exchange ratio of coated fruits and vegetables, delaying their natural senescence and hence extending their shelf life. As was previously discussed, starch-based coatings exhibit highly selective gas permeability ratio (CO₂/O₂) compared with conventional synthetic materials (Table 2). The modified

atmosphere created by the coating generates a physical capture of CO₂ inside the fruit or vegetable and partial sealing of the pores, reducing the gas exchange and gas transfer rates.

Coating integrity is a critical factor that depends on film flexibility, surface tension and adhesion to the food product. Matrices without plasticiser are brittle and rigid because of strong interactions between the polymer chains that can also lead to aggregates formation. These structures may be incompatible with irregular surfaces such as that of some fruits. The incorporation of plasticisers can solve this problem by improving the coating flexibility, [52, 53, 65]. However, the plasticiser/polymer ratio should be optimized since high plasticiser concentrations reduce barrier properties and may cause segregation from the matrix.

In starch-based formulations glycerol or sorbitol are commonly used as plasticisers in concentrations between 5 and 50 g/L, depending on starch concentration. Garcia and co-workers [52] found that 20 g/L was the maximum amount of glycerol supported in corn starch coating-formulations, since surface migration occurs at higher plasticiser concentrations resulting in a sticky material. On the contrary, sorbitol concentrations greater than 20 g/L led to extremely long drying stages.

Furthermore, rheological properties of filmogenic suspension should be tailored to fit the coating process: spraying requires low viscosity while higher viscosity is needed for immersion coating. In general, starch-based filmogenic suspensions exhibit a pseudoplastic behaviour. Table 2 summarizes the effect of coating formulation on the main properties of filmogenic suspensions that affect the adhesion to food substrate and successful coating application.

On account of the broad spectrum of food products to which edible coatings could be applied to, many technical challenges regarded to surface characteristics and coating adhesion should be addressed. Products with smooth and soft surfaces (such as tomatoes, mushrooms and Brussels sprouts) require formulations with low surface tensions to ensure coating adherence and uniformity. For products with irregular and rough surfaces (such as strawberries) the formulation must include plasticisers to prevent the appearance of cracks or pores in the coating (Fig. 1).

An alternative to enhance coating adhesion is the addition of surfactants and lipids to filmogenic suspensions, reducing their surface tension (Table 2). Moreover, the incorporation of lipid phase in the film matrix reduces WVP owing to its hydrophobic character. With this purpose, Garcia, et al. [48] incorporated sunflower oil to corn starch filmogenic suspensions in an emulsion and found that concentrations greater than 2 g/L produce migration, similarly to what happened with plasticisers excess. These corn starch-based coating formulations containing lipids and plasticiser were applied on Brussels sprouts (*Brassica oleracea*), in combination with the packaging using commercial plastic films (PVC and RD106[®]) in order to assess their quality and nutritional

attributes during storage at 0°C [66]. The use of plastic films allowed the weight loss to be reduced in both the control and the coated sprouts. Although all treatments involving the use of synthetic plastic film presented an acceptable commercial quality up to 42 days of storage, the RD-106[®] film and the combination of PVC and coating application showed the highest values of commercial quality without compromising the nutritional quality, with respect to antioxidant capacity. Thus, edible coating applications can complement synthetic films packaging, which shows additional effect in terms of gas permeability. In addition, starch-based films have been used as biodegradable packaging for food products. Mali and Grossmann [18] proposed the use of yam starch (*Discorea alata*) films as packaging for strawberries contained within plastic trays, and compared the performance of these films with those of PVC.

Moreover, composite starch-based edible coatings were also developed. Fakhouri et al [67] developed an edible coating based on gelatine and different types of starch: native corn starch, waxy and a commercially available waxy modified one. These formulations were applied by dipping on grapes and were effective as a natural postharvest treatment to extend grapes shelf-life under refrigeration conditions and to maintain fruit quality, particularly for reducing the total weight loss. Complete sensorial analyses were performed, showing that the coatings did not influence consumer acceptance, especially when taste was evaluated.

Similarly, Chinma and co-workers [68] reported that edible coatings formulated with 50:50 cassava starch and soy protein concentrate on toasted groundnuts extending their shelf-life for 14 days at 27°C preventing the rancidity onset.

Active starch-based coatings containing antimicrobial agents (potassium sorbate plus citric acid), plasticiser (sorbitol) and emulsified lipid (sunflower oil), were applied on strawberries, extending their storage life at 0°C and 84% relative humidity and decreasing microbial growth [48]. Weight loss was reduced, colour change delayed, and tissue firmness and fruit appearance improved with coating application. By visual inspection the edible coating could not be detected, thus coating integrity was evidenced by iodine staining (Fig. 1). In addition, alterations of the fruits physiological parameters, such as titratable acidity, sugars and anthocyanins content, were retarded due to the selective permeability of the coatings.

Recently, essential oils derived from plants, which are rich sources of volatile terpenoids and phenolic compounds with a recognized antimicrobial and antioxidant activity, have been incorporated into edible films and coatings. Bezerra de Aquino et al. [69] developed edible chitosan–cassava-starch coatings enriched with essential oils from *Lippia gracilis* mixtures and applied them on guavas (*Psidium guajava* L.), which are vitamin-C rich fruits but very perishable. The authors informed the efficiency of these edible coatings and emphasized that, in order to minimize their sensory impact;

essential oils should be incorporated at concentrations lower than 1.0%.

With regard to the application of films and coatings to other food products, López et al. [70] developed films based on blends of native and acetylated corn starches containing glycerol as plasticiser, potassium sorbate and citric acid. The developed active starch films were able to inhibit *Candida* spp., *Penicillium* spp., *S. aureus* and *Salmonella* spp. growth, which are responsible of some foodborne diseases. The minimal inhibitory concentration of this antimicrobial agent was determined and tested on refrigerated cheese samples, extending the products shelf life in 21% (from 14 to 17 days) regardless of pH. Besides, sorbate controlled release from the polymeric matrix was studied and diffusion coefficients in aqueous and semisolid media were also determined.

Similarly, Martins Sousa et al. [71] evaluated the shelf-life of fresh lasagna pasta intercalated with extruded films based on blends of rice flour, poly(butylene adipate-co-terephthalate), glycerol and potassium sorbate. These composite films guaranteed the microbiological safety of fresh lasagne pasta and avoided the excessive consumption of food additives.

Likewise, edible coatings may also act as carriers of specific nutrients; Gennevois and co-workers [72] developed a refrigerated ready-to-eat food fortified with Fe and ascorbic acid using pumpkin (*Cucurbita moschata*) as raw material. Both mineral and vitamin were included in the coating formulation; authors remarked that the Fe supported in the coating matrices tended to have a higher bioaccessibility at in vitro simulated lumen conditions.

4 Scale-up of film production

Starch is not a real thermoplastic material, but when it is processed at low moisture content with plasticisers, under high temperature and mechanical forces, starch semicrystalline granular structure is disrupted and the polymer melts, leading to TPS [42, 74–77]. Under these conditions, the polymer undergoes a glass transition forming a rubbery amorphous mass which can be shaped and stabilized by cooling and/or eliminating volatile plasticisers [78]. In addition to its biodegradable character, TPS is a renewable and flexible material that can be easily used in diverse standard processing equipment. However, as other starch-based materials, TPS present a high tendency to retrograde and unsatisfactory mechanical properties dependent on environmental conditions [10, 78–82].

4.1 Blown extrusion

TPS can be obtained from extrusion or melt-mixing processing. Extrusion followed by blown or thermo-compression moulding is a viable alternative to produce starch-based films with a low-cost, continuous, energy-efficient and versatile

production system [10, 15, 17]. Operating conditions should be carefully selected, avoiding starch degradation but permitting a complete starch plasticization, as well as a good material flow through the extruder barrel. In a previous work an exhaustive analysis on extrusion processing of native and acetylated corn starches mixtures with glycerol was described [79]. The obtained pellets showed adequate processability to form films by blown extrusion resisting the tension exerted by rolling and the air flow pressure without tearing (Fig. 1). The blowing process conditions employed led to homogeneous films without bubbles, regardless of the TPS formulation. However, films did not always present regular thickness, because it depends on the insufflated gas flux during blowing step and it was very difficult to control [10, 79]. Another drawback observed was the greasy appearance or stickiness of TPS films, especially those derived from cassava and potato starches [10, 14]. To overcome this problematic, pellets could be dried prior to film blowing or sorbitol and urea could be used as a complement or replacement of glycerol [14, 80].

Composite mixtures can be processed by this technique, although Herrera-Brandelero et al. [76] stressed that when two polymers are mixed by extrusion it is relevant to achieve a single phase and avoid clusters formation from the entangled polymer chains. Within this context, blends based on starch–chitosan and starch–poly(vinyl alcohol) have been extruded and studied [81, 82]. Likewise, preformed bottles were obtained by blown extrusion of starch–gelatine matrix reinforced with cellulose [83].

Table 3 summarizes the mechanical and barrier properties of different films obtained from TPS by extrusion. WVP values of native and acetylated corn starch blend films obtained by blown extrusion varied between 0.88 and 1.41×10^{-10} g/s m Pa. Acetylated starch incorporation to film formulations decreased their WVP due to the hydrophobic character of the substituent [12, 34]. Films with the lowest WVP were those with low glycerol concentration and high acetylated/native ratio. A similar trend was observed for O₂ and CO₂ permeability, resulting CO₂ permeability values significantly ($p < 0.05$) higher than those corresponding to O₂ permeability [79].

With regard to mechanical behaviour, acetylated starch incorporation reinforced film matrix increasing the maximum tensile strength, as was observed for films prepared by casting [15]. Tensile strength for the developed films was higher than those reported by Zullo and Iannace [84] for blown films from different starch sources (Table 3). Meanwhile, it was observed that film flexibility was improved increasing glycerol concentration up to 20%.

4.2 Compression moulding and composite materials

Compression moulding is a useful processing method owing to its simplicity and the suitability for oversized products. These technologies allow composite materials, films for

Table 3. Mechanical and barrier properties of different botanical source and processing of starch-based materials

Starch type	Film composition	Processing method	Tensile strength (MPa)	Elongation at break (%)	WVP (g/m s Pa × 10 ¹⁰)	Ref.
Corn	Corn TPS	Thermo-compression	2.94 ± 0.36	17.0 ± 0.10	1.36 ± 0.05	[78]
	Corn TPS + 1.5% cassava bagasse	Thermo-compression	3.13 ± 0.045	4.57 ± 0.91	1.56 ± 0.31	
	Corn TPS + 1.5% cassava peel	Thermo-compression	4.20 ± 0.23	9.05 ± 1.04	1.30 ± 0.001	
	Corn TPS + 5% Talc nanoparticles	Thermo-compression	4.32 ± 0.02	17.00 ± 0.5	0.62 ± 0.04	[78]
	Corn TPS + 10% Chitosan	Thermo-compression	12.5 ± 0.8	1.64 ± 0.12	8.70 ± 0.40	[88]
	Corn TPS + ≈50% acetylated corn starch	Extrusion	17.54 ± 1.92	3.92 ± 0.25	1.36 ± 0.017	[79]
Cassava	Cassava TPS	Thermo-compression	1.68 ± 0.37	11.03 ± 2.58	1.49 ± 0.075	[89]
	Cassava TPS + 1.5% cassava bagasse	Thermo-compression	4.35 ± 0.52	15.69 ± 1.43	1.50 ± 0.15	[89]
	Cassava TPS + 1.5% cassava peel	Thermo-compression	2.96 ± 0.38	11.65 ± 2.75	1.53 ± 0.076	[89]
	Cassava TPS + potassium sorbate and xanthan gum	Extrusion	1.2–3.0	41.0–85.0	3.72–6.40	[10]
Other	Potato TPS	Extrusion	5.42 ± 0.35	52 ± 16	Nd	[84]
	Wheat TPS	Extrusion	1.86 ± 0.33	58 ± 23	Nd	[84]

Notes: a) Composition is expressed in % w/w respect to starch content; b) All samples were plasticised with glycerol; c) The polysaccharides employed present different molecular weight (Mw) for their main components depending on their botanical source: being amylose Mw 2×10^4 , 2.7×10^6 , 9×10^6 and 3.9×10^6 g/mol for corn, cassava, potato and wheat, respectively, and amylopectin Mw ranging from 2×10^5 and 1×10^6 g/mol for corn, and 7×10^7 , 1.7×10^8 and 3.1×10^8 g/mol for cassava, potato and wheat, respectively [61, 62, 64].

agricultural use, or moulded objects such as disposable food containers (for example, covers and disposable dishes), garbage and food bags, pots and insulating materials, among others, to be obtained [42, 74–77, 85, 86].

In this processing technique TPS material, commonly obtained by melt mixing, is placed in a mould and processed in a hydraulic press at high temperature (Fig. 1). Films based on TPS of different sources have been obtained by thermo-compression, and their main properties and film micro-structure were extensively studied [14, 87–89].

Blend compositions as well as processing conditions have to be optimized regarding to the desired properties for the specific application of the obtained material. Thereby, Castillo *et al.* [87] prepared mixtures of native corn starch, glycerol (30% w/w) and distilled water (25 and 45% w/w), which were processed in a Brabender Plastograph (Brabender, Germany) at 140°C and 50 rpm for 15 min, and later moulded at 150 kg cm⁻² at 140°C during 6 min. Obtained materials resulted homogenous and transparent, presented good integrity, adequate handling characteristics and their thickness varied between 178 and 223 μm. An increase in film flexibility was observed with higher water content in TPS formulations (Table 3).

Nevertheless, TPS films have still two main disadvantages in comparison to synthetic polymers: moisture absorption susceptibility and poor mechanical performance. To overcome these drawbacks, natural organic or mineral fillers are added to TPS matrix as reinforcing agents. There are many works dealing with TPS-based materials containing different clay minerals, especially montmorillonite [90–92].

Among mineral fillers, talc is a phyllosilicate with a layered structure with nanometric size thickness that make talc particles suitable to be intercalated by polymer chains during composite processing [87]. TPS films containing talc

nanoparticles (0–5% w/w) were obtained by thermo-compression moulding and their structural properties were analyzed [87]. López *et al.* [93] stressed that talc concentrations higher than 3% w/w significantly increased stiffness and yield stress of TPS films, without affecting their elongations at break (Table 3). Furthermore, 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 developed bags were used to package different foodstuffs such as cherry tomatoes, grapes and peppers (Fig. 1).

On the other hand, the use of natural lignocellulosic fibres is a good option to increase TPS mechanical performance preserving the environmental-friendly character of material [57, 94]. The use of industrial byproducts as reinforcement and/or support is still under study. Hereof, Versino *et al.* [89] used cassava byproducts (peels and bagasse) as natural fillers of TPS matrices. Under the processing conditions studied starch-filler interactions were favoured, thus leading to lower mixing energy requirements. The expected matrix-filler compatibility, due to their similar chemical nature, was demonstrated by FTIR and TGA analysis. Similarly to inorganic fillers, natural ones increased UV-barrier capacity and opacity of TPS materials. On the contrary, TPS water vapour barrier properties were not affected by cassava peel or bagasse inclusion. In spite of the low concentration used (1.5%), both byproducts reinforced TPS matrices, being bagasse the most efficient filler due to its high residual starch content and higher proportion of smaller particles. In comparison, films obtained from corn starch TPS reinforcing with 1.5% cassava peel exhibited similar tensile strength than those containing 5% talc nanoparticles, although nanocomposites presented improved elongation at break and WVP properties (Table 3).

Similar results were obtained in cornstarch TPS films reinforced with the residue of the starch extraction from *Pachyrhizus ahipa* roots, which is mainly constituted by remaining cell walls, starch granules and natural fibres [93]. AFM studies revealed the formation fibres agglomerates which seemed to be randomly oriented, increasing films roughness. Residue addition decreased 33% WVP values of TPS films and reinforced the matrix increasing maximum tensile strength and Young's modulus.

Correspondingly, other hydrocolloids, like chitin and chitosan, have been included in TPS matrices with some structural modifications as a result of the interactions between starch hydroxyl and chitosan/chitin amino groups, evidenced by FTIR analysis [88]. Moreover, the addition of both chitin and chitosan affected optical properties of TPS films being UV absorption capacity and opacity values higher than control ones. Likewise, WVP was reduced while tensile strength and elastic modulus increased with hydrocolloid addition. Chitosan incorporation increased antimicrobial capacity of TPS against *S. aureus* and *E. coli*, two important microorganisms responsible of foodborne illnesses.

5 Future prospects

TPS-based materials are being promoted, turning their processability easier and lowering industrial sector inversion. Organic or inorganic fillers reinforce biopolymeric matrixes and lead to films with special properties due to the synergic effect between components. TPS-composite films have a potential use as packaging materials for food, cosmetics, and pharmaceutical products, among others. Biodegradation in soil and water has been studied demonstrating that these materials are completely biodegradable [1, 38].

The potential of starch-based films and coatings has been recognised as an alternative or synergistic addition to conventional packaging to enhance food quality and protection. Further studies should continue optimizing film formulation, as well as, processing conditions to improve humidity susceptibility and films properties for specific applications. Nowadays, starch films are used as carriers of functional ingredients by incorporating antimicrobial, anti-browning, and nutraceutical agents to improve foodstuffs quality. The development of new technologies to improve the delivery properties of films and coatings still requires future researches. Most of the studies on food applications have been conducted at a laboratory scale, thus research on cost reduction and larger scale production and on stability and safety are necessary for promoting the feasibility of commercialised biodegradable packaged or coated products.

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6 References

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