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Ellagic Acid May Improve Mechanical and Barrier Properties in Films of Starch-A Review Paper

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Abstract

Packaging increases the shelf life of food and facilitates its handling, transportation and marketing. The main packaging materials are plastics derived from petroleum, but their accumulation has given rise to environmental problems. An alternative is the use of biodegradable materials. In this regard, starch is an excellent choice because it is an abundant and renewable source with film-forming properties. However, the films obtained from starch have some limitations with respect to their mechanical and barrier properties. Several strategies have been developed in order to improve these limitations, ranging from the addition of lipids to the modification of the polymer structure. The aim of this review was propose the use of ellagic acid as a cross-linking agent that may improves the mechanical and barrier properties in films based on exists reports that phenolic compounds interact with starch-based materials decreasing their rate of retrogradation. Furthermore, ellagic acid is a powerful natural antioxidant, which would allow the production of active packaging with antioxidant properties, in addition to the improvement of the mechanical and barrier properties of starch films. In this concern more studies such as Fourier transform infrared spectroscopy, X-ray diffraction, differential scanning calorimetry and thermogravimetric analysis are necessary to verify the structural changes and interactions between starch and ellagic acid. We expect extensive use of it in the future of packaging materials.

Keywords: ellagic acid, starch, cross-linking, phenolic compounds, antioxidant

1. Introduction

Food packaging plays a key role in the conservation, distribution and marketing of food products. Packaging protects the product from mechanical, physical, chemical and microbiological damage (Falguera, Quintero, Jiménez, Muñoz, & Ibarz, 2011). Plastics are chemically synthesized polymers that are widely used in food packaging, as their production is relatively simple and inexpensive (Ghanbarzadeh, Almasi, & Entezami, 2011); however, its use has caused environmental problems (Marsh & Bugusu, 2007). An alternative is the use of edible films and coatings, which contribute to the reduction of environmental pollution. These materials can be obtained from renewable and biodegradable sources, such as polysaccharides, proteins, lipids, resins and their mixture thereof (Campos, Gerschenson, & Flores, 2011; Ribeiro, Vicente, Teixeira, & Miranda, 2007). Starch is

one of the most abundant polysaccharides in nature. It has a great variety of botanical sources, and it is relatively inexpensive to isolate (Bertuzzi, Armada, & Gottifredi, 2007; Jiménez, Fabra, Talens, & Chiralt, 2012). Generally, starch films have poor mechanical properties and can be highly hygroscopic (Chiumarelli & Hubinger, 2012; Ghanbarzadeh et al., 2011). The addition of substances that generate intermolecular bonds, improving the integrity of the film, is among the strategies to improve the properties of starch films (Olivato, Grossmann, Bilck, & Yamashita, 2012). Ellagic acid, besides being a powerful antioxidant, can interact with polysaccharides as cross-linking agent, retaining its antioxidant properties (Kim et al., 2009). Generally, the cross-linking of starch involves the formation of esters between the carboxyl groups of the cross-linking agent (generally a carboxylic acid) and the OH of the glucose in starch (Kim et al., 2009; Reddy & Yang, 2010). Ellagic acid it is a polyphenolic acid without carboxyl groups ; however, it is the product of the hydrolysis of ellagitannins (glucose esters and phenolic compounds) (Ascacio-Valdés, Aguilera-Carbó, Rodríguez-Herrera, & Aguilar-González, 2013), whereby it should be possible to make this acid work as a cross-linking agent in the presence of oxidized starches, which are characterized by the presence of carboxyl groups, to obtain biodegradable films with suitable properties for use as food packaging or coating. This article describes the findings that support our hypothesis.

2. Mechanical Properties and Water Vapor Permeability, a Limitation of Starch Films

The use of plastic materials, mainly derived from petroleum, shows an upward trend. About 150 million tons of plastic are produced each year throughout the world, which generates large amounts of waste that pollute the environment (Shit & Shah, 2014). Among the various applications of petroleum polymers is their use for food packaging, which is why in recent years there has been an increasing interest in developing packaging from biodegradable polymers (Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002). In this sense, starch is a polymer with great potential for the manufacture of this type of material, since it is abundant, biodegradable and cheap (Mali et al., 2002; Wilhelm, Sierakowski, Souza, & Wypych, 2003). Starch is a reserve polysaccharide that is found in plant materials in the form of semi-crystalline granules which, depending on the botanical source, vary in shape, size, structure and chemical composition, which affects their functional properties and is composed of two glucose polymer molecules linked by a glycosidic bond; one is a linear molecule known as amylose, and the other a branched molecule known as amylopectin (Campos et al., 2011; Jiménez et al., 2012; Smith, 2001; Tharanathan & Saroja, 2001; Wilhelm et al., 2003). Although this polysaccharide has shown great potential as a film-forming material and has been extensively studied as such, its films are not suitable for commercial use, mainly due to their poor mechanical properties and high affinity for water (Mali et al., 2002; Schmidt, Porto, Laurindo, & Menegalli, 2013). The mechanical and barrier properties of the films prepared from polymers are determined by the structure of the polymer , its nature, the presence of polar and non-polar groups in the polymer chain, the glass transition temperature (Tg) and the degree of cross-linking (Gajdoš, Galić, Kurtanjek, & Ciković, 2000; Mrkić, Galić, Ivanković, Hamin, & Ciković, 2006). Films made only with starch are brittle; however, the addition of plasticizers such as polyols, mainly low molecular weight compounds, decreases the intermolecular attraction between adjacent chains in the amorphous region (Donhowe & Fennema, 1993), which in turn increases the flexibility and elongation of the films while decreasing their tensile strength (Jiménez et al., 2012). Moreover, it has been found that plasticizers increase the hydrophilicity of films, thereby increasing their permeability to water vapor, oxygen and other gases (Jiménez et al., 2012; Mali et al., 2002; Mali, Grossmann, & Yamashita, 2010). The high presence of OH- groups of the starch and some plasticizers makes films highly sensitive to contact with water or air at a high relative humidity, which produces an increased permeability to water vapor (Schmidt et al., 2013). According to Forssell, Mikkilä, Moates, and Parker (1997), the glass transition temperature (Tg) should be considered as the most important parameter of the mechanical properties of amorphous and semi-crystalline materials; thus, the process of recrystallization of these materials should be controlled. Materials such as films made from thermoplastic starch (gelatinized starch plus plasticizer) are able to recrystallize. This molecular rearrangement is accelerated when these materials are stored above their Tg (Mali, Grossmann, García, Martino, & Zaritzky, 2006; van Soest & Vliegenthart, 1997; Y. Zhang, Rempel, & Liu, 2014). The recrystallization of starch films, and the consequent modification of their mechanical properties and permeability, is a consequence of the retrogradation process, which is characteristic of starch-based systems (Campos et al., 2011). Retrogradation occurs after gelatinization, and it is the result of a molecular arrangement that consists in the formation of hydrogen bonds between the oxygen of the carbon atom 6 and the OH- of carbon 2 of the glucose residues from the molecules of amylose, and the OH- group of carbon 2 and the OH- of carbon 6 of the glucose residues from the short chains of the amylopectin molecule, respectively (Figure 1) (Y. Zhang et al., 2014). Under proper conditions, the molecular arrangement can be of the crystalline type (Buléon, Colonna, Planchot, & Ball, 1998). Mali et al. (2006) characterized the thermal, mechanical and barrier properties of films obtained from different starches (corn, yam and cassava) under controlled storage conditions (90 days, 64% relative humidity, 20 °C). These authors using differential scanning calorimetry noted that the type of starch

did not affect the Tg of the films, and that the variations in their mechanical properties and water vapor permeability were small. The authors noted also that starch-based films must have a Tg similar to the temperature at which they will be stored in order to reduce their crystallization (Mali et al., 2006).

The poor mechanical properties and high water vapor permeability of the starch films are closely related to the recrystallization or retrogradation of starch. Retrogradation, and the consequent increase in crystallinity, can be observed as the time of storage of films increases. Increasing the retrogradation kinetics, i.e., decreasing the rate of retrogradation in starch films, is one of the outstanding challenges in the field of packaging materials.

Recently, there has been an increasing interest in obtaining biodegradable active packaging; this has led to the use of natural extracts with antioxidant and antimicrobial properties. These extracts could also function as cross-linking agents. Cross-linking is a phenomenon that improves the stability and the mechanical properties of hydrocolloid-based polymeric matrices (Hager, Vallons, & Arendt, 2012; Silva-Weiss, Bifani, Ihl, Sobral, & Gómez-Guillén, 2014), and is characterized by the formation of intermolecular bonds between the polymer chains (Hager et al., 2012). It has been observed that the mechanical properties of films of cross-linked starch are significantly better than those of non-cross-linked starch (Ramaraj, 2007; Reddy & Yang, 2010). Many substances with antioxidant capacity are characterized by being phenolic compounds; ellagic acid, a phenolic acid that can form complexes with some proteins and polysaccharides, is one of the natural antioxidants (Kim et al., 2009).

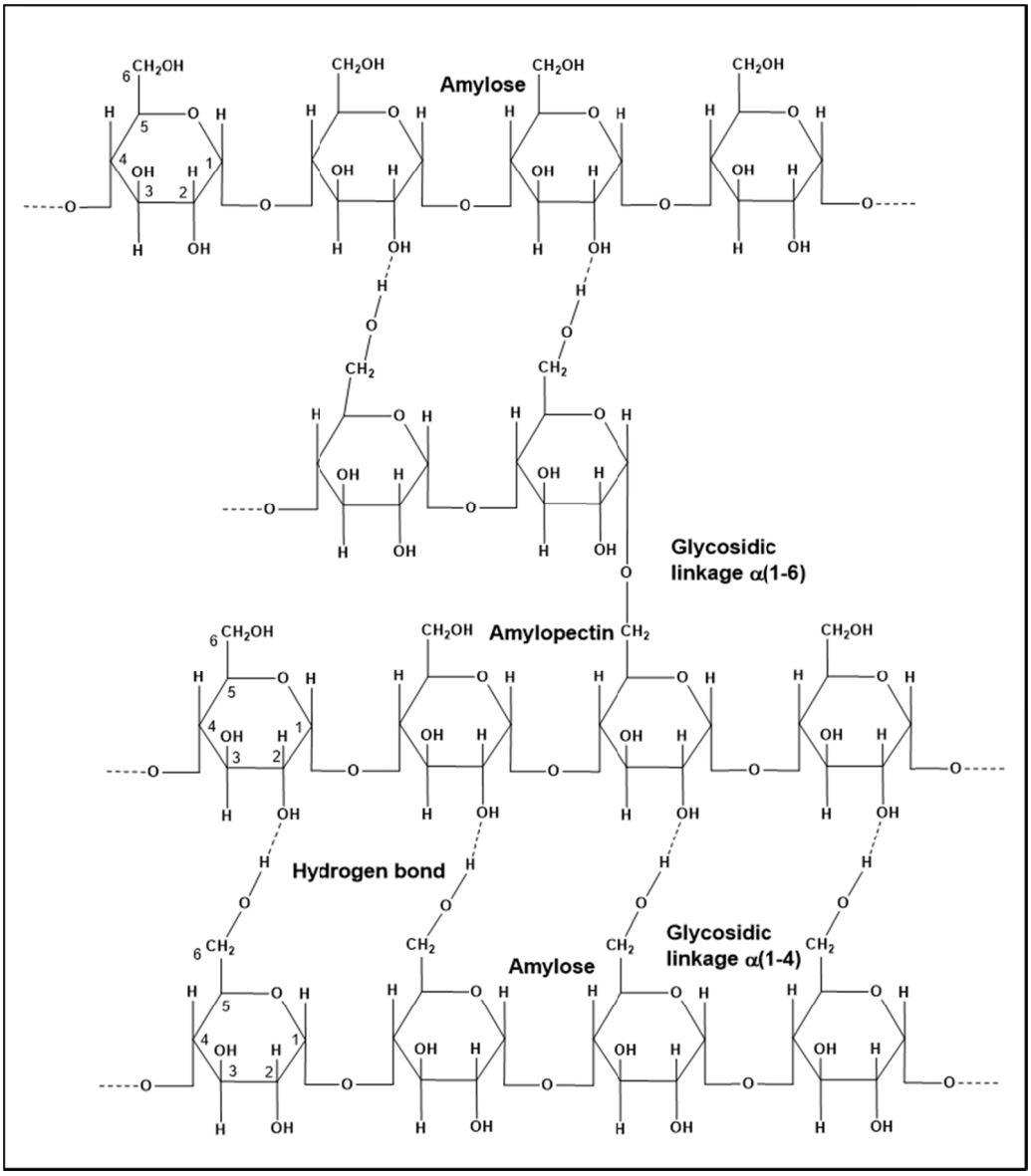

Figure 1. Formation of hydrogen bonds during starch retrogradation

3. Polyphenolic Compounds as Cross-linking Strategy in Biodegradable Films

Oxidation is one of the most common mechanisms among food degradation process, which cause a reduction in shelf life (Miller & Krochta, 1997). Oxidation alters the nutritional quality of foods, which may decrease and potentially lead to the formation of compounds with toxic effects. Oxidation causes the production of undesirable odors and affects other quality attributes such as color and texture (Finley & Given Jr, 1986). Recently, consumers have shown some concern regarding the use of synthetic chemicals in food such as aspartame, monosodium glutamate and high fructose corn syrup, preferring foods with natural antioxidants, which, in addition to being safe, have potential benefits to human health (Song, Bae, & Park, 2013). Ellagic acid is a phenolic acid derived (a dimer) from gallic acid (Komorsky-Lovrić & Novak, 2011). Ellagic acid is present in many fruits, especially in fruits such as red raspberries, pomegranates, nuts and in grape seeds (Kim et al., 2009; Priyadarsini, Khopde, Kumar, & Mohan, 2002). It can be found in free form or as a result of plant metabolism, or it can be found as ellagitannins, which are its precursors (Ascacio-Valdés et al., 2011; Ascacio‐Valdés et al., 2014). Ellagitannins are ellagic acid esters and a polyol, usually glucose; upon contact with strong bases or acids, they undergo hydrolysis and release hexahydroadiphenine acid which forms ellagic acid by spontaneous lactonization (Figure 2).

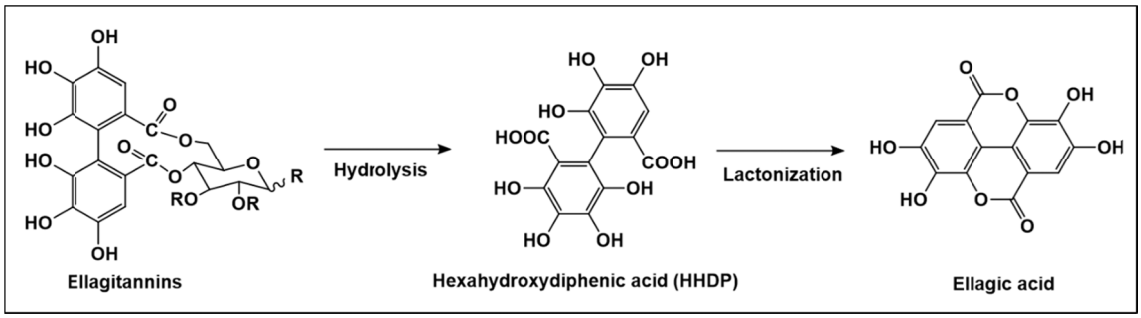

Figure 2. Hydrolysis of ellagitannins to ellagic acid

Ellagitannins, like other plant tannins, are found in vacuoles of intact cells. When plants are attacked by microorganisms (bacteria, fungi and viruses), they release phenolic compounds to prevent their tissues from becoming infected (Sepúlveda, Ascacio, Rodríguez-Herrera, Aguilera-Carbó, & Aguilar, 2011). Due to its presence in foods, and its antioxidant and antimicrobial properties, ellagic acid can be used as food additive (Komorsky-Lovrić & Novak, 2011); however in the EU countries ellagic acid has no status of the food additive. Ellagitannins can be found in some sub-products such as the shell of the pomegranate (*Punica granatum L.*) (Panichayupakaranant, Tewtrakul, & Yuenyongsawad, 2010). Ascacio-Valdés et al. (2013) analyzed the content of ellagic acid in the shell of ripe pomegranates; they reported a concentration of ellagic acid of 83.2 and 121.7 mg/g plant obtained by hydrolysis with methanolic hydrochloric acid and by hydrolysis with H2SO4 2 N, respectively. Compared with ellagic acid, the extracts from pomegranate shells have a similar antibacterial, anti-allergenic and anti-inflammatory activity (Panichayupakaranant et al., 2010).

At the moment, there are no reports of the effect of ellagic acid on the properties of biodegradable films regarding their use as packaging; however, there are studies with extracts or acids with others polyphenols similars to ellagic acid. For example, Kim et al. (2009) developed films of autoclaved chitosan with ellagic acid at different concentrations (0, 0.05, 0.1, 0.5 and 1%) as drug-eluting systems for the treatment of tumors in rats. Fourier transform infrared spectroscopy (FTIR) revealed that the autoclave process dissolved the amino groups of chitosan and the OH- of ellagic acid and the weak hydrogen bonds also affect changes in the FTIR spectrum. Siripatrawan and Harte (2010) obtained chitosan films that contained aqueous extracts of green tea as an antioxidant; the authors reported that the permeability coefficient decreased from 0.256 ± 0.023 to 0.087 ± 0.012 g mm m-2 d-1 kPa-1, while the density ranged from 1.21 ± 0.03 to 1.67 ± 0.03 g cm-3. These changes were attributed to the interactions between the functional groups of chitosan and the polyphenolic compounds of green tea extracts, as evidenced by FTIR spectra. Rivero, García, and Pinotti (2010) evaluated the cross-linking ability of tannic acid and its effect on chitosan-based biodegradable films. Adding tannic acid increased tensile strength up to 29% without affecting flexibility and decreased permeability to water vapor by 24% compared to films without acid; this was attributed by the authors to the effect of the cross-linking of the polymer matrix with tannic acid, which promoted a more rigid and compact structure, decreasing the elongation percentage.

Cross-linking is a strategy that improves the mechanical properties (Hager et al., 2012; Qiu, Hu, & Peng, 2013;

Reddy & Yang, 2010) and reduces the permeability to water vapor (Ghanbarzadeh et al., 2011; Olsson, Hedenqvist, Johansson, & Järnström, 2013) in biodegradable films. During cross-linking, the cross-linking agent promotes the formation of inter- and intra-molecular bonds in starch, generating films with a stronger structure and more uniform and compact surfaces (Qiu et al., 2013).

So far we have seen that phenolic compounds such as ellagic acid can be used in the production of films with antioxidant properties. It has been reported that ellagic acid can interact with polymers such as chitosan by autoclaving, which indicates the great thermal stability of this antioxidant, which has a melting point of 350 °C (Ascacio-Valdés et al., 2013). While it is true that there are no studies on starch films with ellagic acid, it would be interesting to know the effect of phenolic compounds on the physical and chemical properties of starch-based material.

4. Phenolic Compounds Interfere with Starch Retrogradation

It has been observed that the addition of some polyphenols purified from green and black tea can reduce the phenomenon of starch retrogradation. Wu, Chen, Li, and Li (2009) found that rice starch containing 10%, 14% or 20% of polyphenols showed no retrogradation in studies with DSC after 10 days of storage. The authors attributed this behavior to the interaction of the hydroxyl groups of tea polyphenols with the OH- groups of the starch molecules, which resulted in the formation of hydrogen bonds between polyphenols and starch. In a similar study, Xiao et al. (2011) reported that green tea polyphenols reduced rice starch retrogradation regardless of the content of amylose in rice. The results of the works cited above provide evidence of interactions between phenolic compounds and starches.

Moreover, Perazzo et al. (2014) developed biodegradable films based on cassava starch containing green tea extracts and palm oil extracts rich in carotenoids. They found that the mechanical properties and water vapor permeability of the films with extracts improved compared to controls (films with no extracts).

Zhu, Cai, Sun, and Corke (2008) evaluated the effect of 25 phenolic compounds on the paste- and texture-forming properties of wheat starch. The authors attributed the changes in the paste-forming profiles to possible interactions between the functional groups of phenolic compounds (methoxyl and hydroxyl) and amylose and amylopectin through hydrogen bonding and long-ranged interactions, such as van der Waals forces . With respect to the texture properties, phenolic acids reduced hardness and adhesion in greater proportion than flavonoids and other phenolic compounds. The possible interactions between amylose/amylopectin and phenolic compounds through hydrogen bonds and van der Waals forces could have affected the rearrangement of amylose and the retrogradation properties of amylopectin. The variation in the hardness of the gels was attributed to the different structures of the phenolic compounds, which can result in different degrees of interaction.

To date, it is believed that phenolic compounds interact with starch through hydrogen bonds. These interactions between phenolic compounds and starch can reduce the retrogradation process. Moreover, as mentioned above, ellagic acid can be found in nature interacting with glucose to form esters. Esters are the result of cross-linking reactions of starches; their formation requires the presence of carboxyls (carboxylic acids) and OH- groups. The presence of carboxyl groups is needed to attempt the possible cross-linking of ellagic acid with starch (Figure 3); one way to accomplish this is by previously oxidizing starch.

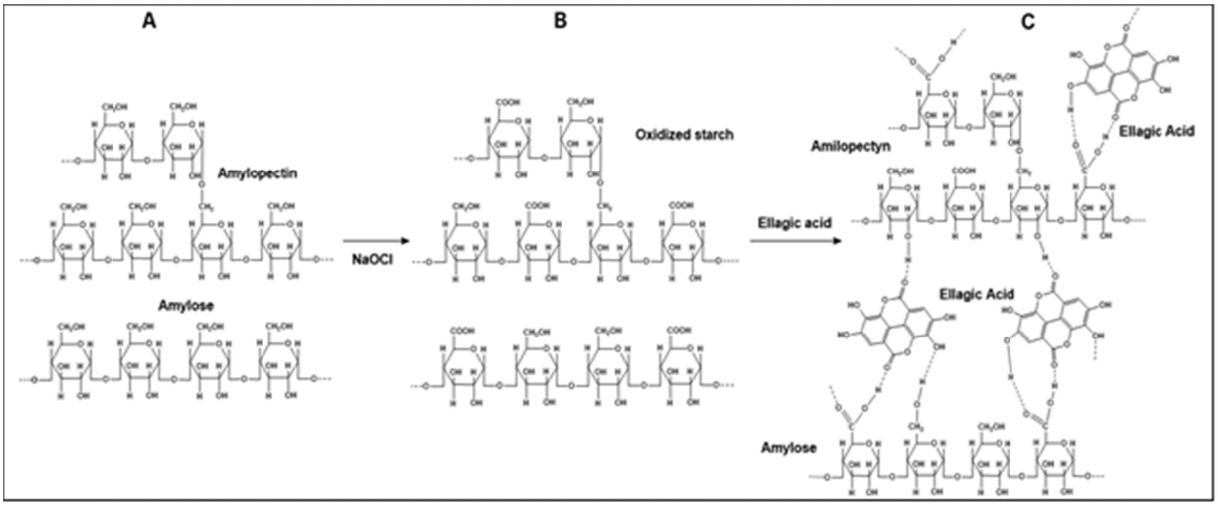

Figure 3. Cross-linking of starch with ellagic acid. (A) Native starch, (B) Oxidized starch and (C) Possible interaction of the cross-linking of oxidized starch with ellagic acid

5. Oxidized Starches: Inclusion of Carboxyl Groups in the Structure

In their native state, starches may have certain limitations for specific applications, while their modification increases their range of possible applications (Simsek, Ovando-Martínez, Whitney, & Bello-Pérez, 2012; Zamudio-Flores et al., 2015). The modification of starches is done to improve or change properties such as the paste-forming profile, viscosity, gelling properties, the stability of viscosity at different pH and shear stress values, retrogradation trends, surface properties, ionic character, among others (Abbas, Khalil, & Hussin, 2010; Ayoub & Rizvi, 2009; Kaur, Ariffin, Bhat, & Karim, 2012). The chemical modification of starch involves derivatization of its molecules through etherification, esterification, cationization, cross-linking, and oxidation. The oxidation of starch is a modification that has been practiced since the early nineteenth century (Steve, Qiang, & Sherry, 2005). Its use in food has increased because oxidized starches have high stability, low viscosity and binding properties (Sánchez-Rivera, García-Suárez, Velázquez del Valle, Gutierrez-Meraz, & Bello-Pérez, 2005). The oxidized starches used in the food industry are mainly modified with sodium hypochlorite (Sánchez-Rivera et al., 2005). During the oxidation of starch with sodium hypochlorite, the hydroxyl groups of the glucose residues are oxidized to carbonyl groups (C=O) and, finally, to carboxyl groups (COOH); the presence of these groups is used as an indicator of the extent of the oxidation process (Y. J. Wang & L. Wang, 2003). In order to evaluate the effect of the concentration of the oxidizing agent (sodium hypochlorite, NaClO), Y.-J. Wang and L. Wang (2003) oxidized corn starch with NaOCl (0.25 to 3%). The authors observed that the presence of carbonyl and carboxyl groups increased with the increase in the concentration of sodium hypochlorite in the reaction. Both amylose and amylopectin were degraded during oxidation, but amylose was more susceptible to oxidation. Similar results were reported by Sánchez-Rivera et al. (2005), who oxidized banana starches with different concentrations of sodium hypochlorite. Kuakpetoon and Y.-J. Wang (2001) investigated the effect of the botanical source of starch (corn, potato and rice) on the properties of starch oxidized by NaOCl. They analyzed the patterns of X-ray diffraction of the oxidized starches and found that the botanical source of starch had no effect on crystallinity, suggesting that oxidation takes place in the amorphous region of starch, which varies according to the type of starch. Kuakpetoon and Y. J. Wang (2006) evaluated the effect of amylose on the oxidation level of corn starches with different content of amylose. The authors used NaOCl (0.8, 2 and 5%) as oxidizing agent and found the highest concentrations of carboxyl and carbonyl groups in waxy starch, in which the concentration of NaOCl was higher (2 to 5%); they also reported that amylose was more sensitive to depolymerization, but that a higher content of it (70% amylose) hindered the formation of carboxyl groups. The authors explained the above by saying that it is probable that starches with up to 70% amylose do not allow the access of hypochlorite and water to their amorphous region, which would be necessary to carry out the oxidation of the OH- groups. As mentioned above, the modification of native starch changes its properties; thus, it is expected that the films obtained from modified starches also have different properties. Zamudio-Flores, Vargas-Torres, Pérez-González, Bosquez-Molina, and Bello-Pérez (2006) prepared films based on banana starch oxidized with three levels of NaOCl (0.5, 1.0 and 1.5%). Tensile strength increased with the oxidation level of starch, which probably was due to a greater oxidation. There were interactions between the carboxyl groups and the OH- of the glucose residues of starch through hydrogen bonds, which could have resulted in a greater integrity of the structure of the films. Moreover, S. D. Zhang, Zhang, Wang, and Wang (2009) evaluated the effect of the carbonyl groups on the properties of films based on oxidized corn starch plasticized with glycerol; the authors reported that the mechanical and thermal properties of the films improved with the increase of carbonyl groups, which in turn increased starch interactions (hydrogen bonds). Table 1 shows the concentration of carbonyl and carboxyl groups in starches oxidized with two concentrations of sodium hypochlorite. As can be seen, the carboxyl groups were present in greater concentration because they are the primary oxidation products. Similarly, it can also be seen that the presence of these groups depends on the type of starch.

Oxidation can also be performed with peroxides. Sangseethong, Termvejsayanon, and Sriroth (2010) oxidized commercial cassava starch (Manihot esculenta) using sodium hypochlorite and hydrogen peroxide at the same concentration (3% of oxidizing agent). They observed that the concentration of carboxyl groups concentration was higher when using sodium hypochlorite because the conversion of carbonyl to carboxyl groups was slower when peroxide was used.

Table 1. Content of carboxyl and carbonyl groups in oxidized starches

Starch	0.8 % NaOCl		2.0 % NaOCl		Reference
	Carbonyl (%)	Carboxyl (%)	Carbonyl (%)	Carboxyl (%)	
Potato	0.030	0.021	0.070	0.039	Kuakpetoon and Y.-J. Wang (2001)
Corn	0.030	0.050	0.060	0.140	
Rice	0.030	0.070	0.060	0.240	
Common corn			0.044	0.061	Y.-J. Wang and L. Wang (2003)
Waxy corn			0.048	0.061	
Banana			0.048	0.760	Sánchez-Rivera et al. (2005)
Common corn	0.020	0.030	0.070	0.180	Kuakpetoon and Y.-J. Wang (2006)
Waxy corn	0.020	0.030	0.050	0.160	
Amylose corn 50%	0.030	0.030	0.050	0.140	
Amylose corn 70%	0.050	0.040	0.060	0.080	

6. Conclusions

This article proposes the use of ellagic acid as cross-linking agent; ellagic acid is a powerful antioxidant that is found in some plant tissues in the form of ellagitannins, which are esters of ellagic acid, and some polyol such as the anhydroglucose molecule. Ellagic acid is derived from the hydrolysis of a glucose ester and polyphenols presents in plants, which leads us to believe that it may participate in cross-linking reactions in starches, either reacting with the hydroxyl groups of glucose residues or with the carboxyl groups of oxidized starches, generating esters. This could improve the mechanical and barrier properties of starch-based films because cross-linking promotes strong interactions at the molecular level that strengthen the structure of the films and can reduce the interaction with water, providing bioactive films with high antioxidant capacity.

Further experiments should be carried out adding ellagic acid to the formulation of films based on native and oxidized starches in order to measure the effect of the presence of carboxyl groups in the interaction between acid and starch and its effect on the physicochemical and structural properties of the films. Ellagic acid has been used to autoclave chitosan, indicating its high stability at elevated temperatures. It would be interesting to subject native and oxidized starch to an autoclave process with ellagic acid and to elaborate films based on the obtained starches, to assess the effect of this process on the physicochemical properties of such films. FTIR studies should performed on the obtained films in order to verify the structural changes in the starch resulting from its possible interaction with ellagic acid, while X-ray diffraction studies should be done to observe any changes in the amorphous/crystalline arrangement of starch. It would also be interesting to evaluate the mechanical and barrier properties of these films to determine how these properties are modified by the inclusion of ellagic acid in the polymer matrix. Clearly, these studies could be performed simultaneously with thermal analysis by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to evaluate the stability and thermal degradation of the polymer matrix. Finally, in order to characterize their functioning as active films, the antioxidant properties of these films should be evaluated.

Conflict of Interest

The authors declare that there are no conflicts of interest

Acknowledgments

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