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Biocomposite films intended for agriculture application based on polysaccharide/quinoa saponin/Ag nanoparticles

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ABSTRACT

This study aims to develop novel alginate-based composite films intended for agricultural practices. The films were prepared by the solution casting method using alginate, hydroxyethyl cellulose, and saponin-silver nanoparticles. The film formation was supported by hydrogen bonds formed between the components, as evidenced by FTIR/ATR analysis. The addition of hydroxyethyl cellulose decreased the tensile strength and Young's modulus of alginate films, and this trend was further promoted with the addition of saponin-silver nanoparticles. However, the composite film still possessed a satisfactory mechanical resistance of 31 MPa, which is higher than that of commercial synthetic agricultural films. In addition, all composite films were not phytotoxic, demonstrated a high positive effect on the germination of radish seeds (131%), and acted as plant growth promoters. The obtained results showed that the combination of both polysaccharides with saponin-silver nanoparticles resulted in interesting bio-inspired films with the potential to replace commercially used synthetic agricultural films.

Keywords: alginate; hydroxyethyl cellulose; silver ions; composite films; agriculture.

1. Introduction

Covers and mulching films are plastic materials commonly used in agriculture to protect the fruit surface from pathogens, wind damage, leaf scars, dust, hail, sunburn, bird feeding and damage during harvest period. Plastic covers have also been used to protect fruits from low temperatures (Kasirajan & Ngouajio, 2012). For example, significant reduction in peel surface damage from insect pests can be obtained by covering bananas/grapes/onions soon after pollination (*Https://Www.Fruitnet.Com/Eurofruit/Reyenvas-Creates-Insect-Repellant-Banana-Film/166545.Article*, n.d.). Furthermore, agricultural films have been used not only to cover fruits, but even to cover the soil surface during seed germination and crop ripening (agricultural mulching sheets), to prevent weed growth (Thakur & Kumar, 2021). Up to date, insecticide-impregnated polyethylene and polypropylene bags have been used commercially to protect crops. Some of the farmers have been using pesticides to maintain pest free soil and remove blemishes. However, both methods do not fit with the sustainable environmental scope, as plastic materials have low degradation rate and after the use can remain intact in nature for more than 100 years. Moreover, extensive use of pesticides can contaminate fruits and easily transfer through food chains to the human body, causing serious health problems.

Biobased agricultural films present a sustainable alternative to traditional plastic films, because they are made of renewable resources and can fully degrade soil. One of the interesting biopolymers is alginate, that can be found in cell walls of brown algae. It is a polysaccharide comprised of β-D-mannuronic acid and α-L-guluronic acid units. Alginate has a unique property to gel in the presence of divalent cations, which allows widely use in food industry as a thickener and emulsifier, and pharmaceutical industries for drug delivery (Nesic et al., 2020). Recently, alginate-based films in combination with other biopolymers or natural fillers have been investigated as mulching film for agricultural application, due to high biodegradation rate and nontoxicity (Gao et al., 2022; Immirzi et al., 2009; Su et al., 2022; Wang et al., 2024). Alginate is often blended with hydroxyethyl cellulose, a cellulose ether derived from cellulose, to improve film forming, rheological properties and gelling abilities (Dmitrenko et al., 2021; Liu et al., 2021; Xie et al., 2024). Hydroxyethyl cellulose is a biocompatible and nontoxic gelling agent, commonly used in food products to increase viscosity and in pharmaceutical industry as capsules to carry drugs (Kapoor et al., 2020).

The main objective of this work is to develop composite bio-based films as a substitute for plastic agricultural films and covers. To obtain

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the films, alginate, hydroxyethyl cellulose and their blends were prepared by solvent-casting method. Additionally, saponin modified with the silver ions was used, to improve the biological functionalities of films. Namely, saponin belongs to the group of naturally occurring compounds found in various plants, including legumes, cereals, and medicinal herbs, and has been shown to exhibit antifungal and insecticidal properties (Chapagain et al., 2007; Cui et al., 2019). In addition, saponins can potentially improve soil health by promoting microbial activity, and can help in nutrient cycling and soil structure (Trdá et al., 2019). Modification of saponin by silver ions improves antifungal activity, and promotes growth of plants (Segura et al., 2020). Hence, it is hypothesized that incorporation of saponin modified with silver ions into mulching films could help to protect crops from pests and diseases, reducing the need for chemical pesticides. The obtained films were characterized by FTIR-ATR and mechanical analysis. In addition, the phytochemical toxicity of films was assessed.

2. Experimental part

2.1. Materials

Sodium alginate (A) and Hydroxyethyl cellulose (HEC) was purchased from Merck-Chile. Glycerol (G) was purchased from Sigma Aldrich and used as received. The synthesis of saponin-silver nanoparticles (with estimated particle sizes in the range between 5 and 50 nm) and detailed characterization are reported in our previous paper (Segura et al., 2020).

2.2 Preparation of films

The films were prepared by solvent casting method. The polymer solutions with a mass fraction of 2 wt.% were prepared by dissolving the alginate, glycerol and hydroxyethyl cellulose in 50 mL of distilled water, under stirring, at the temperature of 35 °C. The glycerol amount in all solutions was 20 wt.% per total mass of biopolymers, whereas amount of hydroxyethyl cellulose varied from 50 wt.% to 80 wt.% with the respect to the mass of alginate. After complete dissolution of biopolymers, saponin-silver nanoparticles were added into solutions at concentration of 5 wt.% per mass of biopolymer. All solutions were poured into Petri dishes and placed in oven at 40 °C, where films were allowed to form after drying for 2 days. The sample codes are presented in Table 1.

Table 1. The film formulations and codes.

Sample code	Alginate, wt.%	Hydroxyethyl cellulose, wt.%	Glycerol, % per total weight of biopolymers	Saponin-silver extract, % per total weight of biopolymers
A	100	-	20	-
HEC	-	100	20	-
A/HEC 80/20	80	20	20	-
A/HEC 50/50	50	50	20	-
A-S-Ag	100	-	20	5
A/HEC S-Ag	80	20	20	5

2.2. Characterization of films

2.2.1. Mechanical analysis

Tensile tests were performed by means of a dynamometer model 4301, Instron (Canton, USA) equipped with a 5 kN load cell. The measurements were performed on dumbbell-shaped films. The width and the length of investigated films were respectively 5 mm and 30 mm, while the thickness of each film was measured at five random points using a micrometer and the result was expressed as the average value. All measurements were carried out at 23 ± 2 °C and 50 ± 5% RH, at a crosshead rate of 5 mm min^{-1}. The reported data are the average values of four measurements. The obtained stress-strain curves were used to calculate tensile strength (σ_m, MPa), elongation at break (ε, %) and Young's Modulus (E, MPa). Tensile strength represents the maximum tensile stress a material can withstand before breaking. Elongation at break describes the flexibility or extensibility of the material up to breaking, whereas Young's modulus is an indicator of the rigidity or stiffness of the material. The following equations were used:

$$\sigma_m = F/A$$

$$\varepsilon = \Delta L/Lo \times 100$$

where F is the maximum tensile force up to breaking (N), A (mm^2) the nominal cross-section of aerogel sample, Lo (mm) initial length of aerogel sample and ΔL (mm) change of length up to breaking point.

2.2.2. FTIR/ATR spectra

FTIR-ATR spectroscopy was carried out on the surface of all films by means of a Perkin Elmer Spectrum 100 spectrometer (Waltham, USA) equipped with a diamond crystal Perkin Elmer Universal ATR diamond crystal sampling accessory. All the samples were analyzed at room temperature. Spectra were recorded on samples as an average of 16 scans in the range 4000–480 cm^{-1}, with a resolution of 4 cm^{-1}.

2.2.3. Germination test

Reddish seeds were disinfected with ethanol for 5 min, then washed three times with sterile distilled water and dried on sterilized paper towels. Thereafter, 10 seeds per treatment were placed in Petri Dishes to be treated as follows: control seeds (without alginate solutions), seeds treated with alginate, HEC and blends containing insecticides (1 ml). The Petri Dishes were stored in chamber with controlled temperature of 23 °C and relative humidity of 50%, in dark. The percentage of seed germination (G, %) was checked after 4. day and calculated according to the following equations:

$$G\ (\%) = \frac{RL \times RG}{100}$$

$$RL\ (\%) = \frac{average\ length\ of\ samples}{average\ length\ of\ control} \times 100$$

$$RG\ (\%) = \frac{number\ of\ germinated\ test\ seeds}{number\ of\ germinated\ control\ seeds} \times 100$$

where RL (%) is relative length of root and RG (%) relative germination. If G <25, the substrate is highly phytotoxic, if 26 <G <65, the substrate is phytotoxic and if 66 <G <100 then the substrate is not phytotoxic and can be applied in agriculture. However, if the G> 101, substrate is characterized as phytonutrient-phytostimulant and can be used in agriculture as a fertilizer.

3. Results

3.1. Mechanical analysis

Mechanical properties of the films were summarized in Table 2. Young modulus (E) specifies the stiffness or rigidity of the film, tensile strength (σ_m) indicates the tensile strength of the film up to breaking point and elongation at break (ε) describes the flexibility or extensibility of the films up to breaking. The results obtained show that tensile strength and Young's modulus of neat alginate films is significantly higher than for neat HEC film, probably due to the unique molecular structure of alginate, with less chain mobility, and its ability to form more self-associated hydrogen bonds. The A/HEC blends exhibit lower tensile strength and Young's modulus, but higher elongation at break in comparison to the control alginate films. This effect is more pronounced with an increase of HEC content in the blend films. The same trend is observed by Russo et al. for the alginate/HEC films plasticized with polyglycerol (Russo et al., 2010). Addition of saponin-silver nanoparticles into alginate matrix causes a significant increase in tensile strength and Young's modulus values, implying that this film is more rigid, due to reduced mobility of polymer chains. The same trend was observed when silver nanoparticles were incorporated into starch films (Rozilah et al., 2020). On the other side, it is interesting to note that addition of saponin-silver nanoparticles into A/HEC blend films causes a slight decrease in tensile strength and Young's modulus, but an increase in elongation at break value, in comparison to the control alginate film and A/HEC film. This result indicates that the presence of HEC allows a certain level of polymer chains mobility, thus diminishing the influence of silver nanoparticles on rigidity of films. The commercial agricultural plastic films are based on LDPE and their tensile strength is in the range between 7 and 17 MPa (Mark, 2007), whereas tensile strength values of films in this work are in the range between 31 and 76 MPa (except for A/HEC 50/50 film). This result proves that alginate-based composite films have higher mechanical resistance in comparison to plastic films and can potentially be used as sustainable solution in agricultural practices. Due to the lower mechanical stability of films that contain 50 wt.% of HEC, this film was not further characterized.

Table 2. Mechanical parameters of A, HEC and their blend/composite films.

Sample	σ_m, MPa	ε, %	E, MPa
A	37	9	402
HEC	6	20	48
A/HEC 80/20	37	12	313
A/HEC 50/50	8	11	76
A-S-Ag	76	4	1986
A/HEC-S-Ag	31	13	242

3.2. FTIR/ATR analysis

The main vibrational modes of alginate-based films are presented in Figure 1. The spectrum of A shows the characteristic peaks in the range 1595–1610 cm^{-1} and in the range 1405–1415 cm^{-1} due to the -COO asymmetric and symmetric stretching. The broad peak between 3200-3600 cm^{-1} corresponds to -OH stretching vibrational modes, due to inter- and intramolecular hydrogen bonding, while the moderately intense bands in the region between 3000-2500 cm^{-1}, are related to -CH, $-CH_2$, and $-CH_3$ stretching and bending vibrations. The main stretching vibrational modes of C-O-C and C-C bonds of carbohydrate ring can be detected in the range of 1360 and 800 cm^{-1} (Nesic et al., 2023). In the spectrum of HEC, specific vibrational modes similar to the spectrum of A are visible, such as peak in the range of 3200–3550 cm^{-1} which corresponds to -OH stretching vibrations, peaks in the range of 3000-2500 cm^{-1} ascribed to stretching of $-CH_2$, $-CH_3$ groups, and carbohydrate finger print region between 1100-800 cm^{-1} (Kalyani et al., 2006). The blending of alginate with HEC causes significant shifts of the peaks assigned to the stretching of –OH groups and asymmetric stretching vibrations of COO- to higher frequencies. The same trend is detected when the saponin-silver nanoparticles are incorporated into alginate matrix and A/HEC blends. The shift of -OH bands to higher frequencies indicates that the self-associative hydrogen bonding interactions of neat polymers are stronger than cross-associative hydrogen bonding between two polymers (Nešić et al., 2017).

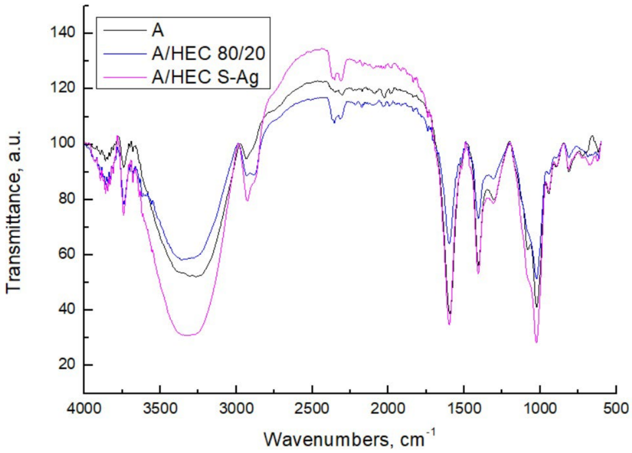

Fig. 1. FTIR/ATR spectra of A, A/HEC blend and composite A/HEC S-Ag film.

3.3. Germination test

To determine phytotoxicity of film formulations, germination test on reddish seeds were performed and results are presented in Table 3 and Figure 2. As can be seen, the germination index is higher for HEC (77%) control films than for A films (68%). This effect is even more pronounced for A/HEC blend films, reaching a germination index value of 93%. Addition of saponin-silver nanoparticles into alginate and A/HEC films promotes higher growth of reddish seeds, with germination index above 100%. These results imply that composite films don't have phytotoxic effect on reddish seeds growth and that act as plant growth promoters. The highest germination index is obtained for A/HEC S-Ag composite film reaching a value of 131%.

Table 3. Analysis of germination test at 4. day

Sample	RG, %	RL, %	G, %
Control	100	-	-
A	85	80	68
HEC	90	85	77
A/HEC 80/20	95	98	93
A-S-Ag	95	113	107
A/HEC S-Ag	100	131	131

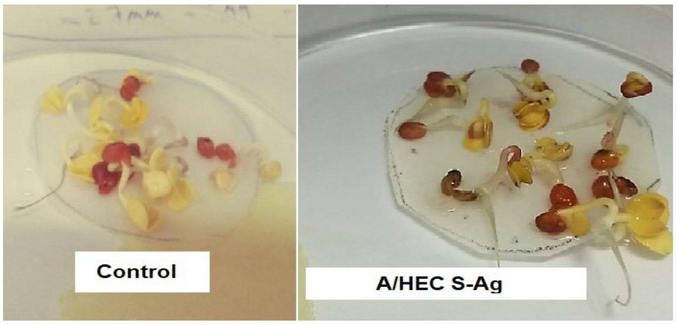

Fig. 2. Germination of reddish seeds after 4 days using water (control sample) and A/HEC S-Ag.

4. Conclusions

Alginate composite films were prepared successfully by solution casting method using hydroxyethyl cellulose and saponin-silver nanoparticles as additives. The film formation was supported by the creation of hydrogen bonds, most probably established between carboxyl and hydrogen groups from alginate and hydroxyl groups from HEC and saponin-silver nanoparticles. The increasing HEC concentration in alginate matrix led to decreased mechanical stability of composite films. The optimal concentration of HEC in film to provide satisfied mechanical resistance is 20 wt.%. Addition of saponin-silver nanoparticles into alginate matrix induced high rigidity, which was evidenced by significantly higher tensile strength and Young's modulus value in comparison to the control alginate films. Contrary, saponin-silver nanoparticles caused decrease in tensile strength of A/HEC blend films, but still provided sufficient tensile strength of 31 MPa, which is still higher than for commercial synthetic agricultural films. Finally, the composite films revealed high performances on reddish seed germination, thus confirming no phytotoxic effect, and acting as a plant growth promoter. The first results of alginate-based composite films presented in this work demonstrate that these films have potential to compete with the synthetic agricultural films on the market. Still, to keep the eco-friendly approach, additional tests in terms of biodegradation, insecticide and antifungal property should be assessed and will be part of future investigation.

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