



## Chitosan coated-phosphorylated starch films: Water interaction, transparency and antibacterial properties



Danila Merino<sup>a,\*</sup>, Andrea Y. Mansilla<sup>b</sup>, Tomy J. Gutiérrez<sup>a</sup>, Claudia A. Casalongué<sup>b</sup>, Vera A. Alvarez<sup>a</sup>

<sup>a</sup> Grupo de Materiales Compuestos Termoplásticos (CoMP), Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA), Facultad de Ingeniería, Universidad Nacional de Mar del Plata (UNMdP) y Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Colón 10850, 7600 Mar del Plata, Argentina

<sup>b</sup> Instituto de Investigaciones Biológicas, UE CONICET-UNMDP, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Deán Funes 3250, 7600 Mar del Plata, Argentina

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### ABSTRACT

Since there is a current need for developing biodegradable mulch films that keep the advantages of those manufactured with polyethylene but offering earlier biodegradation, new starch-based formulations were proposed and analyzed. In this work, starch was chemically modified by phosphorylation with sodium triphosphate and resulting films were later coated with chitosan. Starch phosphorylation was performed by two different methodologies: chemical modification in aqueous suspension (AS) and reactive extrusion (REx). The content of phosphorus and the degree of substitution (DS) were determined and calculated, respectively, for the purpose of evaluating the efficiency of the phosphorylation reaction. This was used as a reference to analyze its incidence on the structure of the materials tested. Fourier Transform infrared spectroscopy (FTIR) and X ray diffraction (XRD) techniques were used to analyze chemical and structural modifications of the starch. Results show that higher DS was achieved by REx method and that was supported by the analysis of FTIR and XRD spectra. Films characterization indicates that phosphorylation by REx contributed to lower film moisture content and to increase opacity and antimicrobial activity. With regard chitosan (CS) coating, SEM micrographs indicate that it presented a porous structure that produces an increment in hydrophilicity, opacity and antimicrobial activity.

### 1. Introduction

The development of biodegradable agricultural mulch films is highly attractive and necessary in order to replace the conventional polyethylene (PE) mulch films. The latter, are degradable in at least 100 years, time that exceeds their life use [1]. The use of PE mulch films offers several advantages to farmers: they produce an increase in yields and accelerate crop harvesting time by keeping a proper soil moisture and raising soil temperature [2]. Moreover, mulch films contribute to reduce the amount of herbicide utilization, since they filter the photosynthetically active radiation (PAR) and thus, prevent weed growth [1]. However, the main disadvantages of their use are the economic costs that imply their collection after harvesting and the disposal of great amounts of agrochemically-polluted PE [3]. Recent publications have described that the long-time usage of non-biodegradable mulching can produce soil deterioration [4,5]. At the same time, current trends argue

that the agricultural sector will be required in the coming years due to the continuous increase in the world population and the consequent need to increase food production [6]. This way, the development of new agro-inputs and innovative technologies that let to increase yields, the cultivation of poor soils and that allow to care for the environment and resources, such as water and soils, are urgently required [6]. In this context, starch appears as an interesting polymer that can be used as base of new mulch formulations. Starch is cheap, highly and naturally abundant, and can be processed in a continuous and traditional way in order to obtain thermoplastic films [7]. Their main disadvantages such as, poor mechanical properties and high hydrophilicity can be at least partially overcome by adopting different strategies [8].

Crosslinking reactions are widely used in the chemical modification of starch. In particular, phosphorylation allows to generate intra and intermolecular bonds, and in this way contributes to decrease the rate of retrogradation of their films [9]. In addition, crosslinking through

\* Corresponding author.

E-mail addresses: [danila.merino@fi.mdp.edu.ar](mailto:danila.merino@fi.mdp.edu.ar) (D. Merino), [amansill@mdp.edu.ar](mailto:amansill@mdp.edu.ar) (A.Y. Mansilla), [tomy.gutierrez@fi.mdp.edu.ar](mailto:tomy.gutierrez@fi.mdp.edu.ar) (T.J. Gutiérrez), [casalong@mdp.edu.ar](mailto:casalong@mdp.edu.ar) (C.A. Casalongué), [alvarezvera@fi.mdp.edu.ar](mailto:alvarezvera@fi.mdp.edu.ar) (V.A. Alvarez).

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phosphate groups is highly attractive for the application of thermoplastic starch (TPS) films as biodegradable and functional agricultural mulches. Plants require large amounts of phosphorus for their growth and development and it is expected that it could be available for plants once the mulch has been biodegraded [10].

Starch phosphorylation can lead to the formation of mono-starch and di-starch phosphates. The latter are obtained when two hydroxyl groups are esterified by the same phosphate [11]. Phosphorylation can occur in any of the carbons C-2, C-3 and C-6 and both amylose and amylopectin can react, although the former has a lower tendency towards crosslinking [9]. The most commonly used crosslinking agents are sodium tripolyphosphate (TPP), sodium trimetaphosphate (TMP), phosphoryl chloride and epichlorohydrin. The last one is highly toxic and therefore its use is becoming less frequent [12].

Starch phosphates can be obtained by different methodologies. One of them, contemplates their modification in dry and consists in heating a reactive mixture of starch, sodium sulfate and TPP, or TMP, at a predetermined pH [11]. Another approach is the modification of starch in aqueous solution. For this purpose, starch dispersion is generally used together with TPP, TMP or a mixture of both, a catalyst such as  $\text{Na}_2\text{SO}_4$  and the pH, temperature and stirring time are controlled. Finally, the mixture is dried in an oven at 40 °C [13]. Nevertheless, these techniques have great disadvantages when compared to extrusion. Modification in solution involves using large volumes of water and amount of salts (10–30% w/w) to inhibit the gelatinization of the starch and be able to work in a wider range of temperatures. Additionally, the residence time in the reactor can be between 2 and 24 h. These requirements make the process industrially expensive [14]. On the other hand, the dry-mixing followed by oven-heating method usually gives low yields of phosphorylation [13]. Finally, starch phosphates can be obtained by reactive extrusion (REx). The extrusion technique itself offers numerous advantages over other methods of starch modification that must finally be processed by this technique to obtain the TPS [14]. REx allows incorporate perfectly mixed reagents with starch in the extruder and by the temperature, pressure and shear allows the reaction progress simultaneously with the processing of the material [14,15].

The objective of this work was to develop and study the properties of native and phosphorylated thermoplastic corn starch films obtained in two different ways: modification in aqueous suspension with subsequent extrusion and compression molding; and phosphorylation by REx and subsequent compression molding. Additionally, the effect of a chitosan coating on each of the materials developed was studied. CS is a linear chain cationic polymer derived from chitin, the second most abundant polymer in nature [16,17]. It has numerous properties that make it highly attractive for its application in agriculture, among which its antibacterial, antifungal and biostimulant capacity stand out [18]. The interaction between starch-based films and water was studied by measuring its moisture content, moisture absorption, solubility and contact angle. In addition, its superficial morphology was observed by scanning electron microscopy (SEM) and was related with water interaction results. The transparency of each film was also determined by measuring its light transmittance. Antibacterial properties of starch-based films were evaluated against *Pseudomonas syringae* pv. *tomato* DC3000 (*Psy*), a phytopathogenic bacterium that affect tomato crop [19].

It should be noted that the novelty of this research work does not lie in the methodology of phosphorylation by wet chemistry. The novelty of this work was centered in the comparison of the CS-coated modified TPS by means of two methodologies: a traditional one by means of wet chemistry and another one by REx. This last methodology can be considered as a green methodology, since it is energy efficient and does not require water consumption [20]. In particular, the phosphorylation reaction was selected with a view to the application of these materials as agricultural mulch films, which once biodegraded can enrich the soil in a mineral such as phosphorus, which is beneficial for the growth of food crops. Besides, the surface of these materials was covered with

chitosan with the aim of giving antimicrobial protection to the food crops in an ecological way. Thus, the proposed material formulation for application in agriculture as biodegradable mulches has not been previously published and represents an innovative approach for the replacement of traditional ones.

## 2. Experimental section

### 2.1. Preparation of phosphorylated corn starch in aqueous suspension

The chemical modification of corn starch was carried out according to the procedure reported by Gutiérrez et al. [21] with some modifications. Briefly, 4 l of distilled water was placed in a 10 l capacity reactor and 1 kg of corn starch was dispersed using stirring at 150 rpm. Then 34.90 g of 0.05 M  $\text{K}_2\text{SO}_4$  were added and the pH of the dispersion was brought to 11 with 1 M NaOH. Then, 30 g of TPP (3% w/w) was added. Reaction conditions such as pH and phosphate forming agent were chosen as reported by other authors. According to O'Brien et al. [22] pH 11 favors the formation of di-starch phosphates and according to Moad [14], TPP gives better yields than SMP. Once all the reagents were added, the mixture was heated to 45 °C and the stirring was maintained for 3 h. After this time, 2% (v/v) HCl was added to set the pH at 7.0 and the modified starch was allowed to decant for later filtering and drying in an oven at 40 °C for 48 h.

### 2.2. Preparation of phosphorylated corn starch via reactive extrusion (REx)

The preparation of corn starch phosphate films by REx was carried out by processing a mixture of corn starch with 20% (w/w) glycerol and 10% (w/w) water as plasticizing agents. The water used as a plasticizer was further used to dissolve TPP and  $\text{K}_2\text{SO}_4$  in the same concentrations used for the modification in solution 3% (w/w) and 0.05 M, respectively and the pH was brought to 11 using 1 M NaOH. The employed extrusion conditions are detailed below.

### 2.3. Preparation of thermoplastic films

The following films were obtained by extrusion and subsequent compression molding: thermoplastic starch (TPS), TPS phosphorylated in aqueous suspension (TPS-P-AS) and TPS phosphorylated by REx (TPS-P-REx). For that, an Extrualex Doble Argentina (Buenos Aires, Argentina) double screw extruder with six heating zones was used. In each case, a mixture of distilled water 10% (w/w) and 20% (w/w) glycerol was used as plasticizer, the screw speed was set at 130 rpm and the following temperature profile was used: 90/100/105/110/120/120 °C. According to Salay et al. [23] subsequent temperature increments (130–175 °C) decrease the amount of phosphate bound to the starch, so that the temperature was kept below these values.

Once extruded, approximately 90 g of each material were pressed using a hydraulic press at 130 °C and 70 Bar for 20 min. The mold was cooled by circulating water and was not opened until its temperature reached 40 °C. An aluminum mold of 30 cm × 30 cm and 0.2 mm of thickness was used to obtain each film.

### 2.4. CS coating

The TPS, TPS-P-AS and TPS-P-REx films were placed on aluminum foil under a hood and then a solution of CS at 1% (w/v) in 1% (v/v) acetic acid was poured over them and spread over the entire surface with the help of a glass rod. Once dry, the same procedure was carried out on the other side of the films. The resulted samples were labeled TPS-CS, TPS-P-AS-CS and TPS-P-REx-CS and were stored in polyethylene bags at 60% RH.

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