



# Preparation, characterization and barrier properties of silver/montmorillonite/starch nanocomposite films

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## ABSTRACT

The present work reports a strategy involving the preparation of nanocomposite films based on a natural biodegradable matrix. The polymer was a natural potato starch and the nanofillers were silver nanoparticles (AgNPs) and a natural montmorillonite (MMT). The AgNPs were prepared by an *ex situ* or an *in situ* method. The influence of the preparation method of AgNPs and the presence of MMT were investigated on the structure, morphology, water sorption and oxygen barrier properties of the nanocomposite films. Two distinct AgNPs populations in size were highlighted from the *ex situ* method, whereas one population was highlighted from the *in situ* method. Crystalline AgNPs were obtained only from the *in situ* method. The addition of MMT did not modify drastically the average size and size distribution of AgNPs despite the presence of some clusters of AgNPs in the vicinity of lamellar layers of MMT. The *in situ* formed AgNPs had a predominant role on the oxygen barrier properties with a 90% improvement independently of the presence of MMT for water activity ( $a_w$ ) equal to 0.45. This significant improvement was mainly related to the crystalline structure of the AgNPs and the cohesive interface between the AgNPs and the starch polymer matrix. Synergism effect of the AgNPs and MMT leading to 65% improvement for  $a_w=0.45$ , was observed when AgNPs were prepared by the *ex situ* method and was related to the intercalation of AgNPs between the lamellar layers of MMT which led to improve the dispersion of MMT within the polymer matrix.

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## 1. Introduction

Polymers reinforced by metal nanoparticles such as silver, gold, palladium have attracted great attention in the two last decades because of widened application scope [1,2]. Among them, silver nanocomposites are promising functional materials in fields such as optical, catalytic, magnetic, electronic and antimicrobial properties [3,4]. Performance level of silver based nanocomposites depends on the selection of the host polymer matrix as well as the controlled distribution of the uniformly shaped and sized nanoparticles. Improved properties are generally reached when small dispersed nanodomains are obtained [5]. In silver nanocomposite films, the host polymer can play a major role on the size and the uniform distribution of the nanoparticles [6]. Therefore, selection of polymer matrix with structurally compatible property is

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important to avoid silver nanoparticles (AgNPs) aggregation. Different methods to introduce AgNPs into polymer matrices have been developed [7]. Generally, silver nanocomposites are prepared by two different methods usually named *ex situ* and *in situ*. The *ex situ* method consists in dispersing beforehand preformed AgNPs within a polymer solution. The resulting mixture is subsequently cast in order to obtain the nanocomposite films. The main disadvantages of this technique are the formation of AgNPs clusters and the non-homogenous repartition of the AgNPs within the polymer matrix [8]. In the *in situ* method, a silver precursor is dissolved in a polymer solution. Then, the solution is cast to obtain a precursor film after solvent evaporation. Depending on the polymer and on the silver precursor chemical, physical or thermal treatments can be used to obtain the reduction of the silver ions [9–11]. The AgNPs are then formed directly within the polymer. The main disadvantages of this technique are the presence of by-products entrapped within the polymer and an eventual effect of the treatment on the polymer matrix [7]. Recently, efforts are made to develop green methods to prepare AgNPs [12]. Green synthesis of AgNPs involves three main aspects, which must be

evaluated taking into account the choice of solvent medium, non-toxic reducing agent and environmentally friendly agent for AgNPs stability. However, in the literature, very few studies are reported the comparison of preparation method of AgNPs and the resulting effects on the morphology and the corresponding properties of the nanocomposite films [6].

Layered nanoclays like montmorillonite (MMT) have also been largely used to improve properties of nanocomposite films [13]. MMT possesses a 2/1 layered structure with a single octahedral aluminum layer located between two layers of tetrahedral silicon. Each layer is about 1 nm thick with a lateral dimension of 100–1000 nm. MMT should be exfoliated as individual platelets uniformly dispersed within the polymer matrix in order to take full advantage of its potential high surface area. Exfoliated polymer-clay nanocomposite films are especially desirable to improve the barrier properties of polymeric materials [14]. When MMT are individually dispersed into the polymer, they create a structure that presents a tortuous path to penetrant molecules leading to slowing the diffusion rate [15]. Significant barrier improvement can be observed at very low loads (< 2% vol) [16].

Over the past decades, in the context of sustainable development, interests in biopolymer based nanocomposites are increased considerably owing to their biodegradability, biocompatibility for potential application in biotechnology and food packaging sectors. Various biopolymers such as gelatin, chitosan, alginate and starch are often used as host matrices [4,17–19]. Among natural polymers, starch is one of the most promising materials because of wide availability, attractive combination of price and very fast biodegradability without the formation of toxic residues [20]. It is a semi-crystalline polymer composed of a mixture of amylose, an essentially linear polysaccharide, and amylopectin, a highly branched polysaccharide. Nevertheless, pure native starch films are water sensitive and present poor gas barrier properties at high moisture content [21]. The addition of nanofillers like AgNPs or/and MMT in order to improve the properties of the nanocomposite films is considered as a promising option. Furthermore, starch polymer possesses large number of hydroxyl groups which can permit on the one hand a good control size of the formed AgNPs and on the other hand favorable interactions with natural MMT leading to an intercalation of the polymer chains into the interlayers of MMT [15,22]. Therefore, silver/montmorillonite/starch polymer as bionanocomposite film can be considered as a promising material for improved properties. To our best knowledge, the incorporation of both MMT and AgNPs into starch polymer matrix using a green chemistry process, to achieve improved barrier properties was never studied. The present work reports a strategy involving the preparation of nanostructured starch based film containing AgNPs and MMT using a completely green chemistry process. A particular attention was given to compare the influence of the preparation method of AgNPs and the presence of MMT on the structure, the morphology and barrier properties of the nanocomposite films.

## 2. Experimental

### 2.1. Materials

Silver nitrate (ACS reagent > 99.0%) and soluble starch were purchased from Aldrich. Native potato starch with a weight ratio of amylopectin to amylose equal to 77/23 was purchased from Sigma. Glycerol (99% purity) was purchased from Aldrich. Nanofil<sup>®</sup> 757 was supplied by Süd Chemie. It is a natural purified montmorillonite with a cation exchange capacity of 100 meq/100 g. Deionized water was used as solvent.

### 2.2. Film preparation

#### 2.2.1. Neat matrix film (SG)

The film preparation consisted in the dissolution of potato starch with glycerol (weight ratio 85:15) in deionized water at a concentration of 3 wt%. The starch/glycerol (SG) aqueous solution was heated to the gelatinisation temperature ( $85 \pm 0.5$  °C) and continuously stirred at this temperature for 3 h. The resulting SG aqueous solution was poured in polystyrene petri dish and water evaporation was carried out at ambient temperature.

#### 2.2.2. Silver nanocomposite films (SG/Ag<sup>in</sup> and SG/Ag<sup>ex</sup>)

Two methods to elaborate AgNPs starch nanocomposite films were investigated. The preparation methods were described in previous papers [8,23]. Typically, in the *ex situ* method, 85 mg of soluble starch was dissolved in 25 mL of deionized water at  $85 \pm 0.5$  °C for 30 min. Soluble starch was used as AgNPs stabilizing agent. Then, 10 mL of a  $6 \times 10^{-2}$  M silver nitrate aqueous solution was added into 25 mL of hot aqueous solution of soluble starch under vigorous stirring away from light. The colloidal dispersion was cooled down to room temperature after 48 h of reaction. The already prepared colloidal AgNPs was added to the SG aqueous solution and stirred at room temperature for 5 min. The mixture was poured into polystyrene petri dish and water evaporation was carried out at ambient temperature away from light. In the second approach called *in situ* method, 10 mL of a  $6 \times 10^{-2}$  M silver nitrate aqueous solution was added to the SG aqueous solution and stirred at room temperature for 5 min. The resulting mixture was poured into polystyrene petri dish and water evaporation was carried out at ambient temperature away from light. The obtained films were removed from the petri dish and then directly heated in an oven at  $85 \pm 0.5$  °C for 48 h away from light. These temperature and duration of treatment were chosen to allow a comparison between the *in situ* and the *ex situ* methods.

#### 2.2.3. Montmorillonite nanocomposite film (SG/MMT) and silver/montmorillonite nanocomposite films (SG/Ag<sup>in</sup>/MMT and SG/Ag<sup>ex</sup>/MMT)

For the MMT nanocomposite films, a 0.3 wt% dispersion of MMT was prepared by adding MMT to deionized water. The aqueous suspension was stirred for 12 h with a magnetic stirrer at room temperature. Then, the MMT aqueous suspension was added to the SG aqueous solution and stirred at room temperature for 5 min. Depending on the preparation method of AgNPs, the silver/montmorillonite/starch nanocomposite films were obtained using the same experimental conditions as those previously described.

Whatever the process, the silver content in the films was 2 wt% and MMT content was also 2 wt%. For all films, the thickness was approximately  $60 \pm 5$  μm. The films were conditioned in dark place at 25 °C and 40% of relative humidity, between two aluminum sheets before characterization. The compositions and the sample code of the prepared films are compiled in Table 1.

**Table 1**  
Compositions and sample code of the different films.

Silver amount (wt%)	MMT amount (wt%)	Silver generation method	Sample code
0	0	–	SG
0	2	–	SG/MMT
2	0	<i>ex situ</i>	SG/Ag <sup>ex</sup>
2	0	<i>in situ</i>	SG/Ag <sup>in</sup>
2	2	<i>ex situ</i>	SG/Ag <sup>ex</sup> /MMT
2	2	<i>in situ</i>	SG/Ag <sup>in</sup> /MMT

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