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Green synthesis of colloid silver nanoparticles and resulting biodegradable starch/silver nanocomposites

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ABSTRACT

Environmentally friendly silver nanocomposite films were prepared by an ex situ method consisting firstly in the preparation of colloidal silver dispersions and secondly in the dispersion of the as-prepared nanoparticles in a potato starch/glycerol matrix, keeping a green chemistry process all along the synthesis steps. In the first step concerned with the preparation of the colloidal silver dispersions, water, glucose and soluble starch were used as solvent, reducing agent and stabilizing agent, respectively. The influences of the glucose amount and reaction time were investigated on the size and size distribution of the silver nanoparticles. Two distinct silver nanoparticle populations in size (diameter around 5 nm size for the first one and from 20 to 50 nm for the second one) were distinguished and still highlighted in the potato starch/glycerol based nanocomposite films. It was remarkable that lower nanoparticle mean sizes were evidenced by both TEM and UV–vis analyses in the nanocomposites in comparison to the respective colloidal silver dispersions. A dispersion mechanism based on the potential interactions developed between the nanoparticles and the polymer matrix and on the polymer chain lengths was proposed to explain this morphology. These nanocomposite film series can be viewed as a promising candidate for many applications in antimicrobial packaging, biomedicines and sensors.

1. Introduction

Biodegradable polymers from renewable resources have attracted much attention in recent years (Averous, Faucaonnier, Moro, & Fringant; Peterson, 2000; Hartman, Albertsson, Söderqvist Lindblad, & Sjöberg, 2006; Petersson & Oksman, 2006). Renewable sources of polymeric materials offer an alternative for maintaining the sustainable development of economically and ecologically attractive technologies. Indeed, the complete biological degradability of these polymers can contribute to a reduction in the volume of garbage and the protection of the climate through the reduction of the carbon dioxide release. Thus, there is considerable interest in replacing some or even a large amount of synthetic polymers by biodegradable materials and in combining them with inorganic nanofillers to achieve designed functional properties. Metal nanoparticles incorporated polymers attracted great attention because of widened application scope (Clémenson, Léonard, Sage, David, & Espuche, 2008; Nesher, Marom, & Anvir, 2008; Nimrodh Ananth, Umapathy, Sophia, Mathavan, & Mangalaraj, 2011; Wang, Wu, & Zhu, 2002; White, Budarin, Moir, & Clark, 2011). Particularly, polymer–silver nanocomposites are promising functional materials in fields such as optical, magnetic, electronic and antimicrobial properties (Duan, Huang, Cui, Wang, & Lieber, 2001; Huang & Yang, 2004; Huang, Yuan, & Yang, 2004; Jin, Cao, Mirkin, Kelley, Schatz, & Zheng, 2001; Lahav, Gabriel, Shipway, & Willner, 1999; Narayanan & El-Sayed, 2005; Sanpui, Murugadoss, Prasad, Ghosh, & Chattopadhyay, 2008). Different routes to introduce silver nanoparticles into synthetic polymer matrices have been developed over the past few years (Akamatsu et al., 2000; Chen, Chen, Serizawa, & Akashi, 1998; Dirix, Bastiaansen, Caseri, & Smith, 1999; Heilmann & Werner, 1998). In the last decade, many efforts have been made in the incorporation of silver nanoparticles into biodegradable polymers for their potential application in biotechnology (Murugadoss & Chattopadhyay, 2008). Polysaccharide polymers, such as chitosan, alginate and starch are the most extensively used as host matrices (Bozanic et al., 2011;

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Brayner, Vaulay, Fievet, & Coradin, 2007; Djokovic, Krsmanovic, Bozanic, McPherson, & Van Tendeloo, 2009; Khan et al., 2013; Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006; Vimala, Murali Mohan, Samba Sivudu, Varaprasad, Ravindra, 2010; Wei, Sun, Qian, & Ye, 2009). The general method consists in the dispersion of already prepared colloidal nanoparticles (AgNPs) in the polymer matrix solution (Lim & Ast, 2001). This method is often referred to as the evaporation method since the polymer solvent is evaporated from the reaction mixture after AgNPs dispersion. In all cases, the performance level of the nanocomposites depends on the controlled distribution of the uniformly shaped and sized nanoparticles. Improved properties are generally obtained when small dispersed nanodomains are obtained (Wiley, Sun, & Xia, 2007). Therefore, the controllable synthesis of AgNPs is the first key challenge to achieve their better applied characteristics. Colloidal silver nanoparticles can be prepared by physical, biological and chemical methods. The chemical approach is mostly used and consists in the treatment of silver salts with a chemical reducing agent, such as hydrazine, ethylenediaminetetraacetic acid and above all sodium borohydride (Bright, Musick, & Natan, 1998; Evanoff & Chumanov, 2004; Merga, Wilson, Lynn, Milosavljevic, & Meisel, 2007; Wang, Efrima, & Regev, 1998). However, most of these reducing agents are considered as non-environmentally friendly component. Increasing awareness about the total elimination or at least the minimization of the generated waste has led researchers to focus on alternative synthesis routes. Recently, efforts have been made for developing green methods to prepare silver nanoparticles (Anastas & Warner, 1998; Huang & Yang, 2004; Raveendran, Fu, & Wallen, 2003). The preparation of AgNPs via a green chemistry process should be evaluated from three specific aspects: the choice of the solvent medium, the choice of a non-toxic reducing agent and finally the choice of environmental friendly materials for the stabilization of the silver nanoparticles. Water is generally used as the environmental friendly solvent. Saccharide molecules such as aldehyde are generally used for the reduction of silver ions. Monosaccharide like glucose, galactose and fructose and disaccharide like maltose, lactose have been reported to lead to AgNPs of controllable sizes (Panacek, Kvıtek, Prucek, Kolar, & Vecerova, 2006; Mehta, Chaudhary, & Gradzielski, 2010). Glucose is one of the most widely-used green reducing agent due to its chemical reaction rate which allows a compromise between the number of nuclei created and the rate of growth of the silver nanoparticles (Mehta et al., 2010; Panigrahi, Kundu, Ghosh, Nath, & Pal, 2004). Polyethylene glycol and polysaccharides such as starch, chitosan and heparin are reported to stabilize silver nanoparticles (Fanta, Kenar, Felker, & Byars, 2013; Shameli et al., 2012; Sharma, Yngard, & Lin, 2009). In some cases, polysaccharides serve as both reducing and capping agent (Huang & Yang, 2004). In a nanocomposite approach, the choice of the capping agent is crucial to allow a good incorporation and final dispersion of AgNPs in the polymer matrix.

Among all the studies related with silver nanoparticles, very few works have been concerned with the whole steps of the preparation of biodegradable silver/polymer nanocomposites from green process including the synthesis of colloidal silver nanoparticles, their incorporation in a biodegradable polymer matrix and finally the characterization of the obtained nanocomposites. In the present paper, the synthesis of colloidal silver nanoparticles via a green chemistry process is reported. Water, glucose and soluble starch have been used as solvent, reducing agent and stabilizing agent, respectively. A kinetic study of the AgNPs formation was performed as a function of the concentration of reducing agent. The synthesis process was studied by using complementary techniques and the size and size distribution of the AgNPs were characterized. Starch based nanocomposite films were then prepared from the synthesized silver nanoparticles and their morphology was characterized. It was shown that by the green chemistry approach used in this study, it was possible at first to prepare very small silver nanoparticles and then to keep a fine dispersion of these nanoparticles within the biodegradable polymer matrix. This is a promising item for further functional fields such as medical applications and packaging.

2. Experimental

2.1. Materials

For colloidal silver nanoparticles preparation, $AgNO_3$ (ACS reagent > 99.0%) was purchased from Aldrich and used as silver precursor. D(+)-Glucose from Merck was used as reducing agent and soluble starch, supplied from Aldrich, was introduced as nanoparticles stabilizer. For the nanocomposite films elaboration, native potato starch with a weight ratio of amylopectin to amylase equal to 77/23 was purchased from Sigma and glycerol (99% purity-supplied from Aldrich) was used as plasticizer. In all cases, distilled water was used as solvent.

2.2. Preparation of the colloidal silver nanoparticles

In a typical experiment, 85 mg of soluble starch was dissolved in 25 mL of distilled water at 85 °C for 30 min. 10 mL of a 6.10^{-2} M silver nitrate was added into 25 mL of hot aqueous solution of soluble starch under vigorous stirring away from light. Then 15 mL of a glucose solution (0.06 M or 0.12 M) was added into the reactive system, which was held at 85 ± 0.5 °C with 700 rpm stirring. A thermostated oil bath and a magnetic stirrer were used to maintain a constant temperature and constant stirring throughout the reaction process. The molar fractions of $AgNO_3$/glucose used were 1:0, 1:1.5 and 1:3. The obtained colloidal suspension was cooled down at room temperature after different reaction times (between 1 and 72 h) and characterized. To avoid any photochemical reactions, all colloidal dispersions were kept in a dark place.

2.3. Preparation of the nanocomposite films

The film preparation consisted of the dissolution of potato starch in the presence of glycerol (weight ratio 85:15) in distilled water at a concentration of 3 wt%. The solutions were heated to the gelatinization temperature (85 °C) and continuously stirred at this temperature for 3 h. Then, an appropriate amount of colloidal silver nanoparticles was added and further stirred for 2 min at room temperature. The obtained mixture was poured into polystyrene Petri dishes and water evaporation was carried out at ambient temperature away from light during at least four days. The theoretical silver nanoparticles content in the films was 2 wt% and was expressed with respect to the total matter content including glycerol. Neat matrices were prepared by using the same experimental conditions. In all cases, the films were conditioned in dark place at 25 °C between two aluminum sheets before characterization. The thickness of the films was approximately 60 μm ± 5 μm.

2.4. Characterization methods

Different techniques were used to obtain complementary information about the size and the morphology of the silver nanoparticles in the colloidal suspensions and in the nanocomposite films.

2.4.1. Ultraviolet–visible absorption spectroscopy (UV–vis)

To follow the formation of silver nanoparticles and to investigate the influence of the embedded silver nanoparticles in the matrix, Ultraviolet–visible (UV–vis) absorption studies were performed on the colloidal silver nanoparticle dispersions and on the