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Simple synthesis of active films based on PVC incorporated with silver nanoparticles: Evaluation of the thermal, structural and antimicrobial properties

Lilian Rodrigues Braga*, Ellen Tanus Rangel, Paulo Anselmo Ziani Suarez, Fabricio Machado

Institute of Chemistry, University of Brasilia, Campus Universitário Darcy Ribeiro, P.O. Box 4478, CEP 70904-970, Brasilia, DF, Brazil

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ABSTRACT

In this work, active antimicrobial films were synthetized with 1.0% to 8.0% silver ions incorporated into polyvinyl chloride (PVC), utilizing a simple solvent casting method was accomplished in a single step. The incorporation of silver in the PVC affected the thermal, structural and antimicrobial properties of the films, which were observed *via* different characterization techniques. The antimicrobial activity was evaluated through disk diffusion method against the following bacterial and fungi species: *Bacillus subtilis*, *Aspergillus niger* and *Fusarium solani.* In addition, a practical evaluation was performed in order to observe the shelf life extension of breads. $PVC_{Ag1\%}$ exhibited better antimicrobial activity for *Fusarium solani* with halos (13.5 ± 0.3 mm), and $PVC_{Ag2\%}$ for *Bacillus subtilis* (15.3 ± 0.7 mm). The resulting bread sample displayed an absence of microorganisms to $PVC_{Ag1\%}$ after 15 days of storage. The results showed that the synthesis of the PVC-based films incorporated with silver nanoparticles (AgNPs) can be easily performed, resulting in films with antimicrobial activity, which may be applied to food storage at room temperature without use of a modified atmosphere.

1. Introduction

In recent years, the packaging industry has showed a continuous growth and technological development regarding the types of materials used to package products, and kind of packaging systems employed to prolong food preservation and reduce food waste (Pezzuto et al., 2015; Vermeiren, Devlieghere, Van Besst, Kruijf, & Debevere, 1999). In various production sectors, active packaging systems have emerged as a promising trend to reduce, inhibit, and/or retard the growth of microorganisms, while lowering food degradation, by using antimicrobial agents (Jofré, Aymerich, & Garriga, 2008; Kanmani & Lim, 2013), antioxidants (Chen, Lee, Zhu, & Yam, 2012; Dopico-Garcia, López-Vilariño, & González-Rodriguez, 2007) and preservatives (Suppakul, Miltz, Sonneveld, & Bigger, 2003). There is a growing interest in the construction of antimicrobial films containing nanocomposite materials such as: natural antimicrobial agents such as nisin (Imran, Klouj, Revol-Junelles, & Desobry, 2014), carvacrol (Shemesh et al., 2015) alginate (Seo et al., 2012) synthetic antimicrobial agents and organic acids such as EDTA (Suppakul et al., 2003), propionic (Rivero, Giannuzzi, García, & Pinotti, 2013), sorbic acids (Hauser & Wunderlich, 2011) and metal ions (silver, copper, gold, platinum) (Kuuliala et al., 2015; Suppakul et al., 2003).

Recently, several combinations of antimicrobials have been exploited and or incorporated into different materials such as plastics, fibers and paper with the intention of increasing the shelf life, quality, and stability of foodstuff during storage (Cooksey, 2005). Among antimicrobial agents, silver (Ag) and silver salts (*e.g.* silver nitrate, $AgNO_3$) seem to present larger antimicrobial potential, mainly due to its effectiveness to a broad spectrum of bacteria, fungi and yeasts. The silver can destroy microorganisms by altering their metabolism (Lubick, 2008). This characteristic makes it widely used in both the pharmaceutical industry and in water treatment (Appendini & Hotchkiss, 2002). In the United States, the use of $AgNO_3$ is accepted by the FDA (Food and Drug Administration) as a food additive, and in the European Union it is accepted as a colouring agent, with no restrictions. Additionally, the European Food Safety Authority (EFSA) has a positive list of additives for food contact with restrictions (Quintavalla & Vicini, 2002).

Nevertheless, one of the main requirements for the efficiency of these active antimicrobial films is the intense contact with food, which restricts the number of compounds that can be used for the film manufacture. Since direct contact must not cause any contamination or leave residuals that are harmful to human health or that, modify food properties (Robertson, 2006).

* Corresponding author.
E-mail address: lilianrodribraga@gmail.com (L.R. Braga).

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Furthermore, the type of polymer employed in the process may affect the synthesis and effectiveness of active antimicrobial polymeric films with silver for active packaging. Among desirable polymers the incorporation of metal ions, the industrial preference has leaned towards polyethylene (Colin-Chávez, Soto-Valdez, & Peralta, 2014), polyacrylonitriles (Rujitanaroj, Pimpha, & Supaphol, 2010), nylon-6 (Park et al., 2009) ethylene vinyl alcohol copolymer (Martínez-Abad, Lagaron, & Ocio 2012; Muriel-Galet, Cran, Bigger, Hernández-Muñoz, & Gavara, 2015) and poly(vinyl chloride) – PVC (Summers, 1997).

Among these polymeric materials, the PVC may be one of the most applied thermoplastic materials in the world, and perhaps being an interesting synthetic polymer in the development of active films. This may be due to its specific properties such as versatility, non-toxic resin, light weight, low cost and simplicity of processing (Cushen, Kerry, Morris, Cruz-Romero, & Cummins, 2013). Due to all these characteristics, the PVC is used in the manufacture of a series of products in various sectors, as for instance, industries of food and beverages, hospital products, textiles, civil construction, automobiles, among others.

Studies indicate that the use of PVC in active packaging and exploring its role in antimicrobial action of this thin film loaded with nano-silver (Afzal & Akhtar, 2010; Pongnop, Sombatsompop, Kositchaiyong, & Sombatsompop, 2011), silver (Ag) nanoparticles intercalated graphene (Ag/G) (Saadatabadia, Nateghib, & Zarandia, 2015), nano-copper (Becerra et al., 2012), nano-TiO_2/Ag (Liu et al., 2012), silver zeolite (Zampino et al., 2011).

In order to incorporate the nanoparticles into the polymer surface, different deposition techniques have been proposed, such as electrospinning, steam coating, ion implantation, sputtering or electrochemical deposition from solution. However, there are some drawbacks of the techniques should be highlighted: expensive methods, larger amount of material for synthesis which may affect the transparencies of the films. On the other hand, the solvent casting technique is a relatively simple and inexpensive method for film production, which enables the synthesis of homogeneous films on a small scale (Hannon, Kerry, Cruz-Romero, Morris, & Cummins, 2015; Merchan et al., 2013). For these reasons, the casting method is widely applied for the study of the polymeric properties on a small scale in the academic field. However, most of the reported procedures employing the casting method requires more than one step (synthesis of the silver nanoparticles and posterior incorporation in the films), which can be time consuming.

In a recent study, Azlin-Hasim et al. (2016) reported the synthesis of antimicrobial PVC films with 0.5% of AgNPs by solvent casting method following two steps, thus requiring more than two hours to synthesize the nanoparticles and afterwards incorporate them into the films. The authors evaluated the effects of PVC/Ag nanocomposite film in chicken breast fillets, applying modified atmosphere packaging (60% N_2/40% CO_2) and stored at 4 °C. The results showed that Gram-negative bacteria were most sensitive to film AgNPs, reducing the lipid oxidation of the chicken fillet and consequently increasing the shelf life.

In the present work, the evaluation of the active films performance on bread conservation was chosen due to the lack of studies evaluating PVC-Ag films on this food. There is a high value of bread in all cultures and its relatively short shelf life. Fresh bakery products are highly perishable and very sensitive to storage. The most common reason of bread spoiling is the growth of filamentous fungi of the genera *Penicillium, Aspergillus, Endomyces, Cladosporium, Fusarium, Alternaria and Rhizopus*, which can reduce the shelf life to no more than 3–4 days at room temperature (Bello et al., 2007; Nielsen & Rios, 2000).

As mentioned before, several studies have focused on the incorporation of antimicrobial agents into different polymeric films to extend the shelf life of foods. However, there is still a lack of direct methods able to incorporate the AgNPs *via* casting method in a single step, which can simplify the synthesis and significantly reduce time and costs. Therefore, the goal of this current study was to synthesize PVC-based films incorporating AgNPs *via* a simple, single step, solvent casting method. In order to evaluate this protocol of synthesis, the AgNPs were incorporated in different concentrations, and the thermal, structural and morphological properties all the films were characterized. Moreover, the antimicrobial activity of the films was evaluated by *in vitro* analysis against the bacterial strain *Bacillus subtilis* and the fungal pathogens *Aspergillus niger* and *Fusarium solani* as well as for bread preservation.

2. Materials and methods

2.1. Chemicals

Poly(vinyl chloride) (PVC) was donated generously by Braskem S.A., with physical properties of average molar mass equal to 130 kDa. The reagents silver nitrate (99.8%) were furnished from Merck (Brazil), trisodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$) (99.8%) from were provided Ecibra (Brazil) and the solvent tetrahydrofuran (THF) (99.8%) was obtained from Tedia (Brazil).

2.2. Formation of PVC/silver active films

Active films were prepared by the solvent casting method, according to Amar and Parisi (2013) with some modifications. This technique is simple and did not require any specialized equipment. Initially, 0.5 g of PVC was dissolved in 20 mL THF, which contained 200 μL of industrial epoxidized soybean oil as a plasticizer. This was kept under constant agitation using a magnetic stirrer (model Go-Stirrer MS-H-S Go-Lab) and under boiling conditions (66 °C) for 90 s. Subsequently, the appropriate volume of a 1.0 $molL^{-1}$ silver nitrate solution was added to the mixture to obtain the concentration of 1.0% (w/w) of silver ions, with respect to the mass of PVC. Upon completion of agitation, the volume of the liquid mixture was reduced to 17 mL, and was dispersed onto flat surface glass plates and kept at 25 °C, until the complete evaporation of the solvent and the formation of the film was evident. The films with silver concentration of 2.0%, 4.0%, and 8.0% were prepared by replicating the same experimental procedure. Along with the preparation of these films, a control PVC film was also arranged. Next, active films ($PVC_{Ag\%}$) obtained were immersed into a trisodium citrate solution (1 mM), a reducing agent, for 10 min for the formation of the silver nanoparticles (AgNPs). The formation of the silver nanoparticles and its incorporation to the films was confirmed by UV–vis spectrophotometer analysis (model 8453, Agilent).

2.3. Characterization

The surface images of the films, PVC, $PVC_{Ag1\%}$, $PVC_{Ag2\%}$, $PVC_{Ag4\%}$ and $PVC_{Ag8\%}$ were morphologically observed by employing a Scanning Electron Microscope (SEM model JEOL JSM-7001 F). Each film was fixed onto a port sample and coated with gold under inert atmosphere (Argon) for 1 h.

The silver inserted in the films were analyzed by using a Spectrometer Fluorescence X-Ray Energy Dispersive (FRX-EDX), (SHIMADZU, model EDX 720) in triplicate.

The infrared spectra were acquired in triplicate on a spectrophotometer (VARIAN, model 640-IR), with a resolution of 4 cm^{-1} by accumulation 32 scans at 17 °C.

The structure of the PVC/silver films were evaluated through X-ray diffraction (XRD, BRUKER, model D8 Focus), using CuKα radiation. All samples were scanned at a 2θ range, from 1° to 70°, at a scan rate of 2° min^{-1} at 25 °C.

Thermal stabilities of the PVC/silver films were examined *via* thermogravimetric analysis (TGA, SHIMADZU, model DTG-60). Hence, ~10 mg of each film sample was added to a platinum crucible, and was heated from 30 °C to 600 °C at a rate of 10 °C min^{-1}, under a nitrogen atmosphere with a flow rate of 30 mL min^{-1}.