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Molecular characterization of silver–stearate nanoparticles (AgStNPs): A hydrophobic and antimicrobial material against foodborne pathogens

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ABSTRACT

In this study, silver–stearate nanoparticles (AgStNPs) have been produced from silver nitrate solutions by replacing the nitrate by stearate ions and then reducing by thermal treatment. AgStNPs were characterized by particle size, zeta-potential, ATR-FTIR, contact angle and SEM (scanning electron microscopy) analyses. The mean particle size and zeta potential of AgStNPs were determined to be 69.22 ± 7.30 nm and +8.02 ± 0.88 mV. ATR-FTIR analysis showed characteristic IR bands of stearate, revealing the two strong peaks at 2848 and 2915 cm^{-1} associated to symmetric ($\nu_s(CH_2)$) and asymmetric ($\nu_{as}(CH_2)$) stretching vibrations of methylene groups, respectively. On the other hand, the scissoring and rocking modes of methylene group were observed at 1470 and 718 cm^{-1}, respectively. Nanomorphological characterization by SEM revealed a layered morphology of AgStNPs. Contact angle measurements demonstrated that a contact angle of water drop on glass coated with AgStNPs was found to be 108.76°, which proved the strong hydrophobic properties of AgStNPs. AgStNPs seemed to be very effective in inhibiting foodborne pathogens (*Salmonella* Typhimurium, *Escherichia coli* O157:H7, *Staphylococcus aureus*, *Listeria monocytogenes* and *Candida albicans*). The results suggest the use of AgStNPs as a coating material to reduce biofilm or biofouling formation in terms of achieving appropriate food contact surfaces and higher hygiene/easier sanitation due to their strong hydrophobic and antimicrobial properties.

1. Introduction

The food industry has been faced with serious problems due to biofilm or biofouling formation on the surfaces of food processing equipment. Biofilms are generally biologically active matrix of cells and extracellular substances in association with a solid surface or a functional group of microorganisms attached to food-contact surface (Myszka & Czaczyk, 2011). Although microbial cells can adhere to food-contact surfaces within minutes (Hall-Stoodley, Costerton, & Stoodley, 2004), biofilm formation can form within hours or days (Schlisselberg & Yaron, 2013) as a result of activity of saprophyte microorganisms and foodborne pathogens as well.

Foodborne pathogens can be totally eliminated by efficient thermal treatments; however, food contact surfaces may be recontaminated during the processing steps when the risk of cross-contamination is elevated, leading the risk of foodborne illnesses to increase. In the last decade, new techniques which lower thermal or high pressure treatments have been offered to prevent biofilm formation on food contact surfaces as an alternative to food-thermal technologies. However, these alternative technologies have been observed to allow pathogenic bacterial growth in some cases (Valero & Francés, 2006). Other techniques mainly include physical methods such as hand washing, high pressure sprays, super-high magnetic field, ultrasound treatment, and high pulsed electric field and application of chemical reagents such as hypochlorites, iodophores, and quaternary ammonium compounds (Kumar & Anand, 1998). Although these techniques theoretically appear to be effective in removal of biofilm, in practice, they are not feasible in terms of economic aspects since the processing lines should be shut off to allow application of these techniques. Therefore, the food industry has followed some new strategies to develop the surfaces consisting of antimicrobial agents with significant lethal effects; for example, incorporation of antibacterial substances into materials with an aim to

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come in contact with food products. However, in application of such antimicrobial surfaces, another drawback has been the case; namely, formation of surface debris layer of dead cells, remarkably decreasing lethal efficiency of antimicrobial surface after a certain time period (Crick, Ismail, Pratten, & Parkin, 2011).

All the aforementioned challenges reveal the necessity to take precautions that would prevent or control adherence of microorganisms to food contact surfaces and subsequent biofilm formation to ensure consumer safety without any external interventions mentioned above. In this respect, the use of self-cleanable surface or packing materials incorporated with special coating materials appears to be a very promising approach to avoid such drawbacks. Accordingly, a couple of recent studies have shown that strong hydrophobic coatings could have a potential in minimizing microbial adhesion to solid substrates (Crick et al., 2011; Lai et al., 2012; Nosonovsky & Bhushan, 2009; Su, Zhao, Wang, & Bendavid, 2010). The reason is attributed to the lotus effect in association with the stream of liquid such as water (Epstein, Wong, Belisle, Boggs, & Aizenberg, 2012). In this respect, a number of recent studies have been conducted to reduce biofilm formation, reducing surface wettability by strong hydrophobic properties (Crick et al., 2011; Fadeeva et al., 2011; Kobayashi et al., 2012; Miyahara, Mitamura, Saito, & Takai, 2009; Privett et al., 2011). For this purpose, some coating materials like titanium dioxide (TiO_2) and, more recently, nitrogen-doped titanium dioxide (N-TiO_2) coatings have been successfully used as a coating material to eliminate adhesion of *Listeria monocytogenes* to food-contact surfaces due to their strong hydrophobicity (Rodriguez, Teixeira, Tavares, & Azeredo, 2013).

In order to achieve the best performance in enhancing food contact surfaces in terms of higher hygiene and easier sanitation, the material of concern should also have antimicrobial properties in addition to aforementioned hydrophobic properties. In the last couple of decades, the use of inorganic nanoparticles has been very popular because of their potential applications in biological, pharmaceutical and food packaging (Brigger, Dubernet, & Couvreur, 2002; de Azeredo, 2009). As well known, nano-sized particles can show considerable physical, chemical and biological functions thanks to their large surface area and high reactivity. In this respect, silver ions and silver-based nanoparticles (AgNPs) were proved to show strong bactericidal effects on many foodborne pathogens like *Escherichia coli* (Kim et al., 2007; Lee et al., 2009; Sondi & Salopek-Sondi, 2004; Yang et al., 2009) and active against a very broad spectrum of bacteria, yeasts, fungi and viruses even at very low concentrations. Furthermore, silver ions are known to be nontoxic to mammalian and human cells (Bosetti, Masse, Tobin, & Cannas, 2002).

As far as the nanoparticle applications of the silver ions on food preservation technology were concern, there were some applications of AgNPs as reported by An, Zhang, Wang, and Tang (2008) and Zhang, Duan, and Shan (2005) who used silver ions to preserve the characteristic of vegetables and derived products. Effectiveness of AgNPs on foodborne spoilage microorganisms were tested in in vitro test conditions by Incoronato, Conte, Buonocore, and Del Nobile (2011) who revealed that an extended shelf life prolongation of mozzarella cheese stored in the active packaging. Although Limbach et al. (2007) reported that silver in the form of nanoparticles could be more reactive with its increased catalytic properties, suggesting that AgNPs would become more toxic than the bulk counterpart, it is still difficult to reach absolute conclusions about their toxicity without concrete results that would be obtained by their comprehensive characterization and description as well as their solutions used under experimental conditions (Beer, Foldbjerg, Hayashi, Sutherland, & Autrup, 2012). The same opinion is shared by the European Commission Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) who reached such conclusion based on the studies conducted on AgNPs, declaring that their risks should be assessed on a case-by-case basis in spite of different toxicological effects of the bulk substance (SCENIHR, 2006, 2009). Also, some others factors that should be taken into consideration to reach such a conclusion are size, shape, chemical composition, surface charge, solubility and their ability to bind as well as their metabolism and excretion which would affect the toxicity of the AgNPs (Castranova, 2011; Schrand et al., 2010). Furthermore, different findings in the literature have been attributed to different production methods, purification level, various size distributions and use of different cell cultures. (Gliga, Skoglund, Wallinder, Fadeel, & Karlsson, 2014). On the other hand, they were approved to offer novel advantages over current agents such as increasing blood half-life, saturation in the lungs at low concentration and increasing neurotransmission with no immune response appearing as non-toxic (Daniel, Tharmaraj, Sironmani, & Pitchumani, 2010).

Silver nanoparticles have become more and more popular for food applications in the past few years (Bosetti et al., 2002). In literature, some food applications of AgNPs have been reported by An et al. (2008) and Zhang et al. (2005) who used silver ions to preserve the characteristic of vegetables and derived products and by Incoronato, Buonocore, Conte, Lavorgna, and Del Nobile (2010) who tested effectiveness of AgNPs on food-borne spoilage microorganisms as well as applied the nanoparticles to mozzarella cheese to prove shelf life prolongation of fresh dairy product stored in active packaging. In addition, the AgNPs have been applied on a great variety of food-contact materials (Appendini & Hotchkiss, 2002; Bouwmeester et al., 2009; Simpson, 2003). Due to their versatility and cost-effectiveness, silver has been the most widely used polymer additive for food applications (Appendini & Hotchkiss, 2002; Quintavalla & Vicini, 2002).

In food applications, AgNPs have been applied in combination with phyllosilicate clays, such as montmorillonite as a support for AgNPs to develop a new class of antimicrobial systems. Different materials like stearate can also be more effective support materials for AgNPs Accordingly, we also observed that silver stearate nanoparticles (AgStNPs) had strong hydrophobic properties, which led us to think that they would be a promising coating or food packaging material in addition to their potential antimicrobial effects. Therefore, a study should be conducted on testing hydrophobic and antimicrobial effectiveness of AgStNPs as well as on their molecular characterization.

No study has appeared so far in literature focusing on molecular, hydrophobic and antimicrobial properties of silver stearate nanoparticles (AgStNPs) that would be potentially used as a coating and antimicrobial material for food applications. This is also presently the case for the food industry in which silver stearate has found no application. Therefore, the aims of this study were (1) to perform molecular characterization of AgStNPs in terms of particle size, zeta-potential, ATR-FTIR, surface characterization and nanostructural analysis and (2) to evaluate their effects on foodborne pathogens and yeasts in order to reveal if AgStNPs would be a promising coating or antimicrobial food packaging material for food applications.

2. Materials and methods

2.1. Chemicals and reagents

Analytical grade of silver nitrate, stearic acid and ethyl alcohol (Merck, Darmstadt, Germany) were used in the synthesis of silver stearate. All the glass and polyethylene containers were cleaned with 18 $M\Omega \cdot cm^{-1}$ deionized water before their use.

2.2. Preparation of silver stearate nanoparticles (AgStNPs)

In order to synthesize silver stearate [$CH_3(CH_2)_{16}COOAg$] nanoparticles (AgStNPs), a 0.05 M aqueous solution of $AgNO_3$ (99 +%, Merck) was put into clean conical flask and dissolved in 100 mL ethyl alcohol by using a magnetic stirrer. Then, equimolar stearic acid (99 + %, Merck) solution was added dropwise to the silver nitrate solution. After each drop, the solution became cloudy. Finally, the reactants were mixed and heated for 45 min at 65 °C to complete the reaction. Fig. 1 shows descriptive illustrations for the Ag–stearate (Ag–St) complex. As