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REVIEW ARTICLE

Silver nanoparticles in polymeric matrices for fresh food packaging

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Abstract The growing demand for increased fresh food shelf life as well as the need of protection against foodborne diseases urged the development of antimicrobial food packaging. Among the most efficient methods, the combination of organic–inorganic, packaging, i.e. polymer embedded metal nanoparticles proved to be highly effective. Silver nanoparticles (AgNPs), in particular, have antimicrobial, anti-fungi, anti-yeasts and anti-viral activities and can be combined with both non-degradable and edible polymers for active food packaging. The actual application of AgNPs in food packaging is regulated by EU and USA food safety authorities in a prudent way, due to the inability to make conclusive statements on their toxicity. Therefore, their use is evaluated in terms of Ag^+ migration into the packed food.

In this mini review, the most recent studies are reported on protection of meat, fruit and dairy products against the most common food pathogens by AgNPs-doped non-degradable and edible polymers and oils are reported.

Contents

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1. Introduction

In the last few decades, the demand for "ready to eat", "ready to cook" and "ready to use" food dramatically increased with a consequent increased necessity of the manufacturers to produce minimally processed food, in an attractive and hygienic way.

One of the main issues in food processing is the protection against foodborne diseases which still represent a global problem of public health. The Center for Disease Control and prevention (CDC) estimates that the impact of foodborne diseases in countries such as the United States results each year in 76 million sick people, 325,000 of which are hospitalized and 5000 die (Morris, 2011).

The urgency of preventing foodborne diseases required acceleration in the development of antimicrobial food packaging, a special packaging that releases active biocide substances in order to improve the quality of the food, extend shelf life, and prevent or delay the spoilage. The antimicrobial action may be obtained by releasing the biocide directly into the food or in the space around the food (Vermeiren et al., 2002) and can be exerted by both organic and inorganic materials (Malhotra et al., 2015). The former ones are mostly organic acids, enzymes and polymers, the latter ones are nanoparticles of metals or metal oxides. The organic antimicrobial materials are less stable at high temperatures compared to inorganic ones, whereas metal and metal oxide nanoparticles withstand harsher processing conditions (Metak, 2015; Metak and Ajaal, 2013).

The use of nanomaterials in several fields is growing (Carbone et al., 2015) and also for food packaging it largely increased over the past decade (Bumbudsanpharoke and Ko, 2015; Nasr, 2015). Nanotechnology-enabled food packaging can be divided into two different key points: (i) improved packaging, where nanomaterials are mixed into the polymer matrix to improve the gas barrier properties such as polymer/clay nanocomposites; (ii) "active packaging", where the nanoparticles interact directly with the food or the environment to allow a better protection of the food, such as silver nanoparticles as potent antimicrobial agents (Duncan, 2011). Metal nanoparticles with their potent antimicrobial properties are therefore used as "active packaging". Emerging metal nanoparticles with biocidal properties are Cu, Zn, Au, Ti, and Ag (Toker et al., 2013). Among them silver nanoparticles (AgNPs) demonstrated to have the most effective bactericidal properties against a wide range of pathogenic microorganisms, including bacteria, yeasts, fungi and viruses (Rai et al., 2009; Martinez-Abad et al., 2012). AgNPs showed better antimicrobial properties compared to metallic silver thanks to their extremely large surface area which can provide a better contact with the microorganism (Toker et al., 2013). Furthermore, they exhibit low volatility and stability at high temperatures (Youssef and Abdel-Aziz, 2013). AgNPs can be hosted in different matrices such as polymers and stabilizing agents (citrates and long chain alcohols) (Toker et al., 2013), through different strategies: they can be coated, absorbed, or directly incorporated in the synthesis processes (Martinez-Abad et al., 2012).

Although the use of AgNPs as antimicrobial agents in food packaging is a mature technology, concerns on the risks associated with the potential ingestion of the Ag ions migrated into food and drinks still exist. This leads to a prudent attitude of food safety authorities (Cushen et al., 2012).

The European Food Safety Authority (EFSA) panel on Food Additives and Nutrient Sources added to Food stated its inability to assess the safety of silver hydrosol (EFSA, 2011; Shenir, 2014) and, for extension, products for food packaging and food supplements that contain AgNPs are not allowed in the EU unless authorized (Bumbudsanpharoke and Ko, 2015). ESFA did provide upper limits of Ag migration from packaging. Recommendations are not to exceed 0.05 mg/L in water and 0.05 mg/kg in food. This implies that evaluations of silver migration profiles are necessary to assure antimicrobial effectiveness while complying with the current legislation. EFSA published in 2011 a document (EFSA, 2011) which indicates that *in vitro* genotoxicity, absorption, distribution, metabolism and excretion tests are required by manufacturers.

Similarly, in the United States the USFDA published in 2014 a document which provides guidance to manufacturers of food ingredients and food contact substances. The USFDA recommends that manufacturers should study and prepare a toxicological profile for each container with nanomaterials (USFDA, 2014). In March 2014 the United States Environmental Protection Agency (EPA) prohibited the sale of plastic food containers with nanosilver produced by an American company because their products have not been tested according to USFDA regulations (Martin, 2014). At the moment Canada does not have any regulation on nanomaterials and in many other countries only incomplete food safety regulations are introduced (Berekaa, 2015).

In this mini review, we overview the latest studies focused on the evaluation of the efficacy of AgNPs-containing hybrid materials to assure fresh food safety. The use of AgNPs in food packaging was investigated in order to obtain information about their benefits to food packaging and also about their possible negative and toxicological effects.

2. AgNPs based nanomaterials for food packaging

AgNPs based antimicrobial packaging is a promising form of active food packaging which plays an important role in extending shelf-life of foods and reducing the risk of pathogens.

A subdivision has been made according on the type of matrix used to host the AgNPs. Two subsections are made depending on the polymeric matrix employed, i.e. whether it is a (i) non-degradable polymeric one or a (ii) biodegradable edible coating film made by either a polymer or a stabilizing