ANTIMICROBIAL NANOMATERIALS FOR FOOD PACKAGING APPLICATIONS

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ABSTRACT: Food packaging industry presents one of the fastest growing industries nowadays. New trends in this industry, which include reducing food as well as packaging waste, improved preservation of food and prolonged shelf-life together with substitution of petrochemical sources with renewable ones are leading to development of this industrial area in diverse directions. This multidisciplinary challenge is set up both in front of food and material scientists. Nanotechnology is recently answering to these challenges, with different solutions-from improvements in materials properties to active packaging solutions, or both at the same time. Incorporation of nanoparticles into polymer matrix and preparation of hybrid materials is one of the methods of modification of polymer properties. Nano scaled materials with antimicrobial properties can act as active components when added into polymer, thereby leading to prolonged protective function of pristine food packaging material. This paper presents a review in the field of antimicrobial nanomaterials for food packaging in turn of technology, application and regulatory issues.

Key words: nanotechnology, antimicrobial systems, food packaging, legislation

INTRODUCTION

As human population is growing, changes in all spheres of life are inducing innovations through different solutions. Concept of bio economy as Europe’s response to key environmental challenges to reduce the dependence on natural resources, transform manufacturing and promote sustainable production of renewable resources (land, fisheries and aquaculture) and their conversion into food, feed, fiber, bio-based products and bio-energy (McCormick and Kautto, 2013). Food packaging is one of the most challenging research topics, concerning the balance between designing materials with specific properties and the demands of the packed food as well as satisfying four basic functions (protection and preservation, containment, convenience and marketing and communication) of food packaging (Sorrentino et.al., 2007; Petersen et.al, 1999). Adequate selection of food packaging materials as well as packaging conditions can contribute to a better sustainability of pa-
cked food and reduce the total food waste (Marsh and Bugussu, 2007; Duncan, 2011). However, novel technologies are pushing forward new trends, and opening new chapters in food packaging research: active packaging as extension of protection and preservation, and intelligent packaging as extension of communication and marketing (Figure 1.)

Development of nanotechnology has been growing in the last decade, opening the opportunity for innovation in many industrial sectors including food packaging. Nanotechnology presents the impeller of advanced food packaging technologies and gives optimal solutions that were not possible on micro- or macro-scales (Arora and Padua, 2010; Lagaron et al. 2005, de Azeredo, 2009).

Polymer nanocomposites present new class of composite materials with at least one component which is on nanodimension (between 1-100 nm). Nanotechnology is relying on incorporation of organic or inorganic nanoparticles into polymer matrix for improvement of material properties (mechanical, barrier, optical, thermal) (Duncan, 2011; De Azeredo, 2009; Silvestre et al., 2011). Small particle size and extremely high surface area of nanoparticles create large interfaces between nanofillers and polymer matrix and enhance the effect of particle-particle and/or polymer-particle interaction. This interaction promotes strong physical contact between the particles and polymer matrix causing the improvement in material properties. Depending on the shape, there are three types of nanoparticles: one-dimensional (layered), two-dimensional (nanotubes) or three-dimensional (spherical nanoparticles) (Silvestre et al., 2011).

Material properties are highly dependent on dispersion and distribution of nanoparticles in polymer matrix, and besides the particles behavior in different systems, preparation of nanocomposite films is also of great importance (Mihindukulasuriya and Lim, 2014).

Besides nanofillers used to improve materials properties, nanoparticles also find application in nanocomposite packaging materials with antimicrobial properties. Nanocomposite packaging materials with antimicrobial functions have a high potential in active food packaging. Taking in consideration the sensitivity of food products to growth of divers’ microorganisms, antimicrobial packaging systems present optimal solution for prolonged shelf-life influencing product quality and safety. Antimicrobial nanomaterials presents a part of active packaging concept designed to carry the active nanoparticles that can be integrated into a food package (Mihindukulasuriya and Lim, 2014). These antimicrobial systems are particularly effective, because of the high surface-to-volume ratio and enhanced surface reactivity of the nanosized antimicrobial agents, making them able to inactive microorganisms more effectively than their micro- or macro-scale features. Commonly used or tested antimicrobial nanocomposite materials include metal ions (silver, copper, gold, platinum), metal oxide (titanium dioxide, zinc oxide, magnesium oxide), and organically modified nanoclays. In real systems different combinations of antimicrobials are used by incorporating into packaging materials thus giving the best results in combination of their activity (de Azeredo, 2013).

Figure 1. Food packaging functions
Metal ions are usually used as nanoparticles incorporated into different polymer systems. Antimicrobial activity of metal ions when they are on nanodimension is accelerated and can be more effective against pathogen microorganisms. Antimicrobial activity of silver ions can be assigned to their ability to disrupt both inner and outer cell membranes. They can also inhibit respiratory chain enzymes and reduce the ATP levels (Li et al., 2017; Mihindukulasuriya and Lim, 2014). Recent researches on antimicrobial activity of different nanoparticles are summarised in Table 1.

Turalija et al. (2016) analysed the influence of silver nanoparticles as well as chitosan as antimicrobial agents in composite structure with PLA, however, this group also used plasma treatment for surface modification of polymer matrix as activation of polymer surface and antimicrobial components.

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Polymer matrix</th>
<th>Tested microorganisms</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/Chitosan</td>
<td>PLA</td>
<td>Staphylococcus aureus (ATCC 6538) Escherichia coli (DSMZ 30083)</td>
<td>Turalija et al. (2016)</td>
</tr>
<tr>
<td>Ag</td>
<td>Agar banana powder</td>
<td>Escherichia coli Lysteria monocytogenes</td>
<td>Orsuwan et al. (2016)</td>
</tr>
<tr>
<td>TiO₂/Ag/Cu</td>
<td>PVC</td>
<td>Mixed microorganism culture media</td>
<td>Krehula et al. (2016)</td>
</tr>
<tr>
<td>ZnO/Ag/Cu</td>
<td>PLA/PEG</td>
<td>Lysteria monocytogenes Salmonella typhimurium</td>
<td>Ahmed et al. (2016)</td>
</tr>
<tr>
<td>Ag</td>
<td>PE</td>
<td>Escherichia coli</td>
<td>Eslami et al. (2016)</td>
</tr>
<tr>
<td>Ag/Cu</td>
<td>Guar Gum</td>
<td>Lysteria monocytogenes Salmonella typhimurium</td>
<td>Arfat et al. (2017a)</td>
</tr>
<tr>
<td>Ag/TiO₂</td>
<td>PE</td>
<td>Aspergillus flavus</td>
<td>Li et al. (2017)</td>
</tr>
<tr>
<td>Ag/Cu</td>
<td>Fish skin gelatin</td>
<td>Lysteria monocytogenes Salmonella enterica sv Typhimurium</td>
<td>Arfat et al. (2017b)</td>
</tr>
<tr>
<td>Ag</td>
<td>Starch/PVA</td>
<td>Lysteria innocua; Escherichia coli Aspergillus niger; Penicillium expansum</td>
<td>Cano et al. (2016)</td>
</tr>
<tr>
<td>Ag/SiO₂/TiO₂</td>
<td>LDPE</td>
<td>Escherichia coli</td>
<td>Becaro et al. (2016)</td>
</tr>
<tr>
<td>Ag</td>
<td>PHBV3</td>
<td>Salmonella enterica Lysteria monocytogenes</td>
<td>Castro-Mayorga et al. (2017)</td>
</tr>
<tr>
<td>SiO₂</td>
<td>PBAT</td>
<td>Escherichia coli; Staphylococcus aureus</td>
<td>Venkatesan and Rajeswari (2016)</td>
</tr>
<tr>
<td>ZnO</td>
<td>LDPE</td>
<td>Bacillus subtilis; Enterobacter aerogenes</td>
<td>Esmalzadeh et al. (2016)</td>
</tr>
<tr>
<td>ZnO</td>
<td>MC</td>
<td>Staphylococcus aureus; Lysteria monocytogenes</td>
<td>Espitia et al. (2012)</td>
</tr>
<tr>
<td>Nanoclay (NaMMT, OrgMMT)</td>
<td>PVOH/chitosan</td>
<td>Escherichia coli</td>
<td>Giannakas et al. (2016)</td>
</tr>
</tbody>
</table>

¹Polylactic acid; ²Polyvinylchloride; ³Polyethylene glycol; ⁴Polyethylene; ⁵Polyvinyl alcohol; ⁶Low density polyethylene; ⁷poly(3-hydroxybutyrate-co-3mol%3-hydroxyvalerate); ⁸poly(butylene adipate co-terephatalate); ⁹Methyl cellulose
This system is a very good example of synergistic approach where more than two influences are included for improvement of material properties and also creating active packaging solution.

Orsuwon et al. (2016) reported that addition of silver nanoparticles into Agar banana powder has significant antimicrobial activity against *Escherichia coli* and *Lysteria monocytogenes*, also increasing UV light absorption, water barrier properties and antioxidant properties, however leading to a decrease in mechanical properties. Combination of nanoscaled metal oxides with silver nanoparticles were incorporated into polyvinyl chloride and tested on mixed microorganism culture suspension.

Besides very good antimicrobial activity on tested microorganisms TiO$_2$ formed UV protection, and addition of silver together with Cu showed improvements in thermal stability of pristine polymer (Krehula, 2016). Similar results were reported from Ahmed (2016) with use of ZnO/silver and Cu nanoparticles against *Lysteria monocytogenes* and *Salmonella enterica* sv. Typhimurium).

Silver nanoparticles were effective as antimicrobials when incorporated into polyethylene polymer matrix against *E. coli* (Eslami et al., 2016) and in low density polyethylene (LDPE) in silver/silica/TiO$_2$ system (Becaro et al. 2016). Castro-Mayorga et al. (2017) reported on prolonged antimicrobial activity against food born pathogen (S. enterica and *L. monocytogenes*), and drop in oxygen permeability of PHBV3 polymer matrix with silver nanoparticles.

Nanosized metal oxides are also very effective as antimicrobial agents when incorporated into polymer matrix (Chaudhry and Castle, 2011). In particular, nano-shaped ZnO is commonly used as effective antimicrobial agent but also for improvements of mechanical and thermal properties of different polymers (Espitia et al., 2012). ZnO has been used as antimicrobial agent for different polymers (LDPE, MC) and showed antimicrobial activity against *Bacillus subtilis* and *Enterobacter aerogenes* (Esmailzadeh et al. 2016), and *Staphylococcus aureus* and *L. monocytogenes* (Espitia et al. 2013). Venkatesan and Rajeswari (2016) reported on antimicrobial activity (inhibition effect against *S. aureus* and *E. coli*) and improvement in material properties (mechanical and contact angle) for Poly(butylene adipate-co-terephthalate) (PBAT) films with 5% SiO$_2$ nanoparticles compared to neat PBAT films.

Modified nanoclays are one of the most reported nanoparticles for improvements in various materials properties. Because of their high water sorption and swelling capacity they are well dispersed in diverse polymeric matrices, and are influencing properties essential for food packaging materials.

Among others, improvements in barrier properties, are in the focus of packaging scientist (Rhim et al., 2013). Giannakas et al. (2016) has reported that addition of nanoclays are influencing the antimicrobial properties of PVOH/chitosan films and enhances antimicrobial activity up to 44% for NaMMT and up to 53% for OrgMMT. Hong and Rhim (2008) reported on antimicrobial activity of natural nano-clays (Cloisite Na$^+$) as well as organically modified nanoclays (Cloisite 20A and Cloisite 30B) against four pathogenic bacteria.

All reported systems are presenting up to date work in the development of antimicrobial nanocomposite food packaging systems, which were very effective against various microorganisms. These researches are very useful for further research and development of antimicrobial food packaging materials for the real food systems.

**LEGISLATION**

Rise of nanotechnology also opened new demands on the legislation side. In food industry adoption of nanotechnology is limited due to concerns on safety and also consumer’s acceptance; however in food
packaging this growth is significant. There are still concerns about the migration of nanoparticles into packed food as well as the effect on consumer’s health. There are only few published studies regarding the effects of nanomaterials upon ingestion, or the potential interaction of nanomaterial-based food contact materials with food components (Silvestre et al. 2011). In general, all food contact material are regulated with European Commission Regulation (EC) No. 1935/2004.

Some other regulations are considering the use of nanomaterials (for example Commission Regulation (EC) 450/2009 on “Active and intelligent materials and articles”), but in these regulations approach relies on case-by-case studies for the use of nano-materials with no specific requirements. Regulation (EU) 10/2011 (on plastic materials and articles intended to come into contact with food) is more specific.

This regulation applies on overall migration limit of 10 mg constituent per dm² surface area to all substances that can migrate from food contact materials to foodstuffs (Com- mission Regulation (EU) No. 10/2011). For a litre cubic packaging containing 1kg of food, this equates to a migration of 60 mg of substance per kg of food. There are only few materials specifically listed in Annex 1 of the legislation, and all the others nanomaterial risk assessment has to be performed on a case-by-case basis (Silvestre et al. 2011; Commission Regulation (EU) No. 10/2011).

EFSA Nanonetwork is a network established for risk assessment of nanotechnology in food and feed sector responsible for harmonisation of methodologies and practice (practical recommendations on how to assess applications of engineered nanomaterials (ENMs) in industry as food additives, enzymes, flavorings, food contact materials, novel foods, food supplements, feed additives and pesticides) (EFSA, n. d.). The latest priority topics of EFSA (EFSA committee in 2016-2018) are considering nanomaterials in the section 3.2.3 and food contact materials are also included in this section. The guidance update should take into account the general extensions needed to cover also nanopesticides and nanoformulations, food contact materials, food and feed additives and novel foods; as well an update of the physico-chemical property measurements and the other data needed for food/feed assessment. In addition, a second guidance document should be produced on the environmental risk assessment for nanoparticles used in the food chain (EFSA, 2016).

European Chemical agency (ECHA) established a specific working group “Nanomaterials” for scientific and technical discussion answering the question related to nanomaterials under REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) and CLP (Classification, Labeling and Packaging of Substances and Mixtures).

Regulatory issues on nanotechnologies in diverse sectors are also changing and developing in other countries then EU (USA, Canada, Australia and New Zealand, Russia, Africa, South Africa), and are regulated by their national legislations (Amenta et al., 2015). General frameworks in the EU are applicable to the antimicrobial systems as well.

The growth of nanotechnology will produce new products on the global market, so the evolution of the legislation is also expected. Further increase in this area will require more detailed legislation, but until then, every system will be studied on case-by-case scenarios.

This approach is not the most efficient one from the safety and risk assessment point of view. For the future perspective legislation in food contact nanomaterials will require also harmonization of national with international legislative and more detailed analysis of various systems.

**CONCLUSION**

Antimicrobial food packaging is in focus of multidisciplinary scientific networks be-
cause it can answer more easily on various challenges that are placed in front food scientists and material scientist as well. Development of these systems requires multidisciplinary approach thus teams of scientist are working on research in this area. There are different studies on different nanoparticles incorporated into various polymeric matrices, and results are indicating a great potential of antimicrobial nanocomposite system for prolonging the shelf-life and preservation of different food stuff.

However, it is clear that this part of active packaging solution is still in the developing phase, because there are not so many studies on the real food systems. It is expected that the future research will provide more in vivo studies and real products on the markets world-wide.

Besides the great potential, antimicrobial nanocomposite systems need public acceptance. Therefore legislation that regulates nanomaterials for food contact materials is in focus of global international bodies responsible for improvements in legislative, aiming to provide sufficient documents and public acceptance on nanocomposite materials for food packaging application.

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Antimicrobial Nanomaterials for Food Packaging Applications

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Abstract: The food packaging material industry represents one of the fastest-growing industries today. New trends are leading to the reduction of food and packaging waste through preservation and prolongation of shelf life, as well as substitution of materials obtained from petrochemical sources, and thus, toward the development of food packaging materials in a number of directions. This multidisciplinary challenge is faced by scientists from the fields of food and materials. Nanotechnology provides some of the answers to these challenges with different solutions ranging from improved material characteristics to active packaging or a combination of both solutions. The incorporation of nanoparticles into a polymer matrix is one of the ways to modify its properties. Nanomaterials that contain active (antimicrobial) nanoparticles elevate the concept of active packaging to a higher level and provide a prolonged protective function of the packaging material. This paper presents an overview in the field of antimicrobial nanomaterials for food packaging with an aspect of technology, application, and legal regulations.

Key words: Nanotechnology, antimicrobial systems, food packaging, legal regulations

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Сазак: Индустрија амбалажних материјала за паковање хране представља једну од најбрже растућих индустрија данас. Нови трендови воде ка смањењу отпада од хране и паковања кроз презервацију и продушење одрживости, као и супституцију материјала добијених из петрохемијских извора природним, па самим тим и према развоју индустрије амбалажних материјала за паковање хране у неколико праваца. Овај мултидисциплинарни изазов постављен је како пред научнике из области хране, тако и пред научнике из области материјала. Нанотехнологија даје неке од одговора на ове изазове - са различитим решењима од побољшања карактеристика материјала до активног паковања или комбинацију оба решења. Уношење наночестица у полимерну матрицу, са циљем креирања хибридног материјала, јесте један од начина реализације његових својстава. Наноматеријали који у себи садрже активне (антибиотичне) наночестице, подижу концепт активног паковања на један виши ниво и обезбеђујући продушење заштитне функције самог амбалажног материјала. Овај рад представља преглед у области антимикробних наноматеријала за паковање хране са аспекта технологије, примене и законске регулације.

Кључне речи: Нанотехнологије, антимикробни системи, паковање хране, законска регулатива

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