Bulgarian Chemical Communications, Volume 49, Special Issue L (pp.210-214) 2017

Study the possibilities of using silver nanoparticles in packaging paper

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Submitted December 12, 2016; Accepted May 23, 2017

Nanotechnology offers an enormous opportunity for innovations in food packaging, which can benefit both, the consumers and the industry. The application of nanotechnology shows significant advantages for improving the quality of packaging materials. Innovations related with the use of nanotechnology in food packaging and quality control is a core focus in the modern food industry. The packaging can be made to be "smart", which means that it can ensure the conditions of a safe environment or to send a signal to the user of pollution and pathogens. Silver nanoparticles have become the dependable antimicrobial material with a variety of applications. Packaging materials with nanoparticles of silver or related cationic silver nanocomposites, provide a possibility for effective and safe antimicrobial packaging.

In the present study are examined the opportunities for using silver nanoparticles in the composition of packaging paper. The physic-mechanical properties of laboratory obtained packaging papers, with and without silver nanoparticles, are been examined. Microbiological tests of the paper samples are also been made. The obtained results show bacteriostatic effect of silver nanoparticles over the packaging paper properties.

Key words: *nanoparticles, silver particles, packaging paper, antimicrobial properties, physic-mechanical properties*

INTRODUCTION

The application of nanotechnology shows significant advantages for improving the quality of packaging materials. Innovation related to the use of nanotechnology in food packaging and quality control is the main focus in the modern food industry. The silver nanoparticles can be relatively uniformly distributed in a matrix of other materials such as pulp, plastics, and others and thus be more effective at killing bacteria and fungi. Packaging materials with nanoparticles of silver, or cationic associated silver nanocomposites allow to create effective and safe antimicrobial packaging. Similar technology is used in many countries for the production of containers for food storage.

In terms of nanotechnology, the selected key technologies with significant quality and food safety are:

- Nano-encapsulation of biologically active substances (amino acids, vitamins, peptides, proteins, antioxidants, etc.) with the purpose of controlled release of their contents.

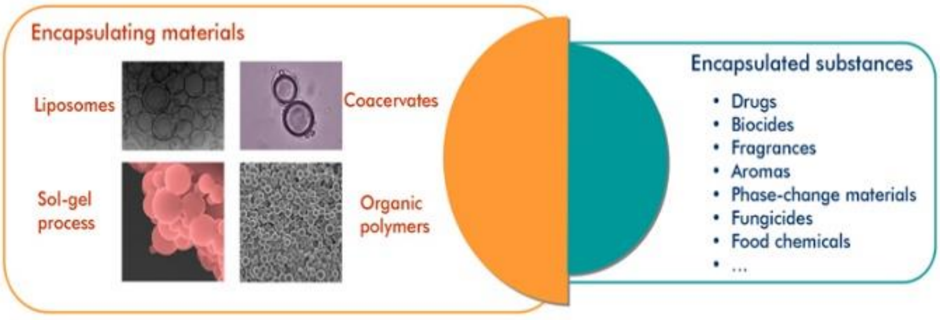

Fig.1. Encapsulation process.

The process is carried out as a fraction of the active substance is surrounded by an encapsulating agent with dimensions of micro and nano particles, thereby isolating the substance from the external environment.

Nano and microsensors are used to detect toxins, pathogenic microorganisms, pesticides, contaminants and residues of antibiotics in food products throughout their production cycle and storage in the distribution network.

A device based on optical fluorescence biosensors is provided. Each nanoparticle contains thousands of molecules which are suitable to be attached to each bacterium. When antibodies and antigens react efficiently the fluorescent signal

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amplified by allowing the bacterial concentration can be readily determined using a fluorescence microscope and spectrum-fluorescence analysis [1-5].

The most popular method for the synthesis of silver nanoparticles is the chemical reduction of silver salts in aqueous solutions in the presence of a stabilizer.

The purpose of this work was to explore the possibilities to obtaining silver nanoparticles using ultrasound and to include them in the composition of wrapping paper. Microbiological tests of the wrapping paper samples were conducted and the physical and mechanical properties with and without silver nanoparticles were studied.

MATERIALS AND METHODS

The silver nanoparticles can be synthesized using a variety of techniques. These include high temperature and a method (such as plasma, for example by formation of films) which are expensive and complicated for realization. The most commonly used methods which allows synthesis at moderate temperature are associated with the chemical reduction of silver ions in water [6-8] or in organic [9,10] solutions.

Because of its low cost and easy implementation, as well as in laboratory and in industrial conditions, the method for the synthesis of silver nanoparticles by means of ultrasound field represents an interesting alternative in comparison with the other known methods.

As a precursor has been used silver nitrate ($AgNO_3$), as a reducing agent - ethyl akohol (96%) and ammonia solution 25% as stabilizer.

For obtaining the solutions containing silver nanoparticles the following experimental work has been carried out :

Silver nitrate was dissolved in distilled water at room temperature using a magnetic stirrer. Consecutively has been added ethyl akohol and ammonia solution. The flask has been placed in an ultrasonic bath with thermostatically controlled temperature, while the color of the solution had been changed from transperent to light yellow or dark yellow. The yellow colour of the solution is a certain sign of the presence of silver nanoparticles.

The effect of time of exposure of ultrasound, the working volume, the concentration of silver nitrate, ammonia and ethanol over the resulting nanoparticles has been investigated. The resulting solutions has been analyzed by atomic-absorption analysis.

The measurments by fluorescence microscopy shows the presence of a very small amount of aggregated particles with sizes up to several microns. The obtained suspensions has been added into the pulp suspension, in order to obtain wrapping paper samples. They has been subjected to a microbiological and mechanical measurment.

RESULTS AND DISCUSSION

The process of preparing silver nanoparticles through chemical reduction requires the use of various substances performing specific functions. A reducing stabilizing agents are necessarily to be presented into the solution and sometimes also agents to accelerate the process. As a precursor of the silver is selected silver nitrate - $AgNO_3$, as it is relatively inexpensive (compared to other silver compounds or pure silver), widely used, especially for the synthesis of silver nanoparticles by chemical reduction and shows satisfactory results.

The reducing agent influences the size and distribution of the nanoparticles in the suspensions. The absence of a reducing agent in the system limits the yield of nucleus and their further growth due to low concentration or absence of silver atoms. As reducing agents in synthesis of silver nanoparticles are used most commonly ammonia [11] (Fig.2), ethanol [12] as well as sodium citrate [13].

The stabilizing agent is involved in the process by stopping the growth of the nanoparticles, which starts after the formation of germs, but also prevents the agglomeration and precipitation of already formed nanoparticles [8,9]. Ammonium hydroxide has been preferred by us as a stabilizer as it is significantly cheaper.

The accelerate agents, are intended to increase the rate of the reaction when it is too slow. Various salts are used mainly as an accelerate agents in the synthesis of silver nanoparticles. When using silver nitrate as raw material these salts act as catalysts participating in the process of formation of silver ions. When the process of synthesis is exposed to the external field (for example microwaves or ultrasound), it is usually necessary to use an accelerator, since its effect is weaker than that of the field.

The ultrasonic field may affect the mechanism of formation of nanoparticles due to the presumably activating this process thermally, and also it increases the speed of the particles, atoms and ions, as well as collisions between them.

The operating parameters, influencing on the process, the quantity and quality of the obtained silver nanoparticles are the following:

- The water temperature in the ultrasonic bath (40 °C or 50 °C);

- The amount of distilled water (50 ml; 100 ml or 200 ml);
- The concentration of silver nitrate solution;
- Concentration of NH_3OH (25%) in the solution;
- The concentration of ethyl alcohol (96%) in the solution.

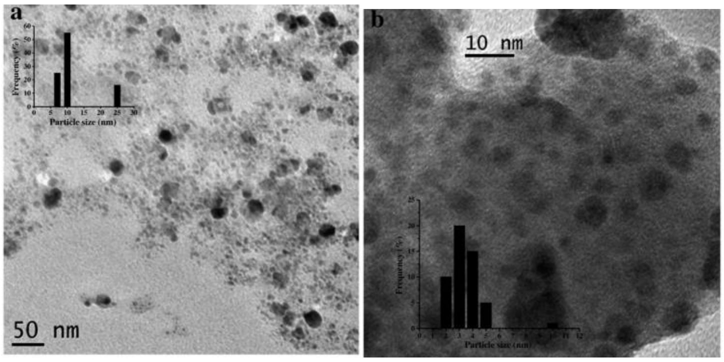

Fig.2 Transmission electron microscopy of silver nano-particles, prepared by reduction of silver nitrate and a stabilizing agent (a) and sodium borohydride (b) sodium citrate [11].

Table 1. Results of the atomic absorption spectrometry

Sample	$AgNO_3$ concentration in the solution before the synthesis, *mg/l*	Concentration of unbound silver after AAS analysis, *mg/l*	Converted silver, %
1.	1700	1110	65
2.	1700	770	45
3.	1700	790	46
4.	1700	1140	67

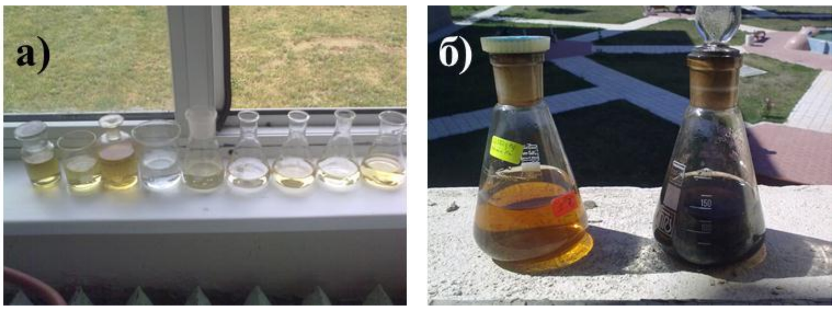

Fig.3. Different colors of suspensions prepared under different operating parameters. a) A solution, which does not change color or pale yellow suspensions; b) suspensions with dark yellow or black colour.

The resulting suspensions were analyzed using Atomic Absorption Spectrometry (AAS) and the results are represented in Table 1.

Between 45 and 65% of the silver in the solution has been gone from associated to free state. This gives us grounds to assume, that has been received solid silver particles that have nano-scale, probably due to the characteristic yellow color of yellow suspensions (Fig.3).The steadfast yellow colour of the slurry indicates the presence of silver nanoparticles.

Several laboratory experiments had been conducted to obtain wrapping paper. The used raw material was unbleached kraft pulp, beated in "Yokro" grinder to 36ºSR. the laboratory obtained paper samples were with a grammage of 70 g/m^2 and sizing degree of Cobb$_{60}$ = 22 g m^2. As sizing agent is been used rosin size in the amount of 3 % to o.d.f. and aluminum sulfate 4.5 % from the o.d.f. [14] .

During the paper formation process a solution of silver nanoparticles in different quantities were added into the fibrous suspension. The physico-mechanical properties (BDS EN 194-2:2000) of the received laboratory paper samples were examined and the results are represented in Table 2. The resulting samples were subjected also to microbiological tests to establish the barrier properties.

The obtained thensile strenght results shows that the tensile length of the of the paper samples containing silver nanoparticles, fell slightly compared to that of a zero sample. Paper samples containing silver nanoparticles virtually has no changes in the physical and mechanical characteristics or has slightly lower values. This decrease is probably due to the weaker hydrogen bonds between the fibers due to the decrease of the contact surface between the fibers.

Table 2. Physico-mechanical properties of the laboratory obtained wrapping paper samples

Sample	Tensile Strength, m	Elongation, %
Zero sample	5500	10.2
Sample 1	5300	10
Sample 2	5400	10.1
Sample 3	5200	10.3
Sample 4	5500	9.9
Sample 5	5500	10.1
Sample 6	4900	9.8
Sample 7	5300	10.2

The resulting paper samples were subjected to microbiological tests to identify the impact of silver nanoparticles. For this purpose single colonies of bacteria Escherichia coli strain LE392 were cultured. A solid nutrient medium Luria-Bertrand (LB) agar containing is used [3]. The optical density of the formed bacteria was measured on a spectrophotometer. On the surface of the paper samples are been made lineal strokes with bacteria. The samples were left for two weeks in a thermostat at a temperature of 37˚C. Observations shows (see Fig. 4) that Escherichia coli bacteria have been penetrated only in the zero sample. All other samples exhibit antibacterial activity, which was substantiate from the absence of gloss and odour of the samples.

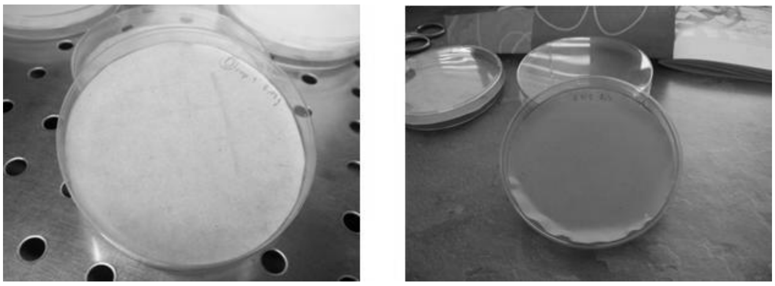

Fig. 4. (A) zero-sample showing visible traces of bacteria. (B) Sample containing silver nanoparticles in with no ingress of bacteria.

CONCLUSIONS

From the studies carried out it has been established that the application of nanotechnology shows significant advantages for improving the quality of packaging materials. The use of packaging paper with silver nanoparticles helps to keep food fresh and the effect of different types of bacteria such as Escherichia coli.

The paper acts as a barrier to bacteria and can be used as a material for food packaging.

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ПРОУЧВАНЕ ВЪЗМОЖНОСТИТЕ ЗА ИЗПОЛЗВАНЕ НА СРЕБЪРНИ НАНОЧАСТИЦИ В ОПАКОВЪЧНА ХАРТИЯ

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Подадено на 12 декември 2016 г .; Приет на 23 май 2017 г.

(Резюме)

Нанотехнологиите предлагат огромна възможност за иновации в опаковането на хранителни продукти, които могат да бъдат от полза както за потребителите, така и за промишлеността. Прилагането на нанотехнологиите показва значителни предимства за подобряване на качеството на опаковъчните материали. Иновациите, свързани с използването на нанотехнологиите в опаковането на хранителни продукти и контрола на качеството, са основен фокус в съвременната хранително-вкусова промишленост. Опаковката може да бъде направена като "умна", което означава, че може да осигури условия за безопасна среда или да изпрати сигнал до потребителя на замърсяване и патогени. Сребърните наночастици се превръщат в надежден антимикробен материал с разнообразни приложения. Опаковъчните материали с наночастици от сребро или сродни катионни сребърни нанокомпозити осигуряват възможност за ефективна и безопасна антимикробна опаковка.

В настоящото изследване са разгледани възможностите за използване на сребърни наночастици в състава на опаковъчна хартия. Изследвани са физико-механичните свойства на получените лабораторни опаковъчни образци - хартия, със и без сребърни наночастици. Извършени са и микробиологични тестове наобразците от хартия. Получените резултати показват бактериостатичен ефект на сребърните наночастици върху свойствата на опаковъчната хартия.