ANTIBACTERIAL NANOADDITIVES PREPARED WITH NANO-SiO_2 CARRIER AND RESULTS OF THEIR APPLICATION IN POLYPROPYLENE FIBRES, POLYPROPYLENE AND POLYETHYLENE FOILS

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Abstract: *Research topic was to investigate preparation of antibacterial (AMB) nanoadditive using alternative nanotechnological procedures and three various types of nanocarriers based on SiO_2. Results of so-called standard method used to prepare AMB nanoadditive are compared with results of antimicrobial efficiency of a nanoadditive prepared by a method in which antibacterial nanosol containing Ag is used, or by direct incorporation of $AgNO_3$ into siloxane mixture and subsequent doping of nanoSiO_2 on the carrier surface. Results of Ag-content in different types of powder nanoadditives determined using atomic absorption spectrometry (AAS) and antimicrobial efficiency of the nanoadditive determined according to ASTM E 2149-13a method on Escherichia coli CCM 3954 bacterium are presented in table form. Besides, images of the nanoadditive surface obtained using SEM method and results obtained by analysis of Ag-content and form of the Ag ion using XPS method (X-ray analysis of atomic structure) are shown. Results from application of the AMB nanoadditive in polypropylene (PP) fibres, PP and polyethylene (PE) foils in the form of evaluation of antimicrobial efficiency using AATCC 100: 2015 method on Escherichia coli CCM 3954 bacterium are given in final part of the paper. Evaluation of the antimicrobial efficiency on the modified PP and PE foils was performed according to ASTM E 2149 method using Escherichia coli CCM 3954 bacterium. Results acquired on applying the AMB nanoadditive in PP fibres, PP and PE foils are focusing on fibre, textile and food industry.*

Keywords: *antibacterial nanoadditive, nanoSiO_2 carrier, antimicrobial efficiency*

1 INTRODUCTION

1.1 Methods for preparation of an antimicrobial (AMB) nanoadditive

It is possible to state on the base of our study and acquired knowledge that the issue of antimicrobial nanoadditives and their application in fibres, foils and fabrics is highly topical and significant from a viewpoint of human health protection [1, 2]. Numerous available information sources [1-5] confirm that it is an interesting theme for the scientists and researchers who explore it using various experimental procedures, different methods and source materials [3, 4-7]. Originality of our research solution, focusing on preparation of the AMB nanoadditive, consists in detailed examination of an innovative method to make AMB nanoadditive using AMB nanosol, prepared by coagulation and dispergation procedure or using siloxane nanosol to dope surface of SiO_2 nanocarrier with Ag particles in ionic form. Originality of preparation of solid dispersions of the AMB nanoadditive in polymeric matrix consists in detailed examination of compatibility of the system and investigation of influence of the nanoadditive on processing, rheological and colouristic properties of the developed solid dispersions as well as on morphological structure, mechanical and coloristic properties as well as performance characteristics (antimicrobial activity) of the nanocomposite PP fibres, PE and PP foils [8, 9].

Philosophy of our research focusing on preparation of the AMB nanoadditive is based on two options: so-called classical method and progressive one. The classical method arises from physico-mechanical compounding by means of a separate chemical reaction of the prepared Ag^+ ions in dispersion solution with subsequent surface doping of a silicate SiO_2 based nanocarrier [6, 7]. This method corresponds to a certain extent with knowledge about methods, currently used in the world, with subsequent preparation of concentrates in powder form and their application to the polymeric systems [4]. The progressive method assumes separate preparation of a silver-containing antimicrobial nanosol using specific procedures. Subsequent process involves compounding of the AMB nanosol with silicate nanocarrier in a solution, under specified conditions, from which powdered nanoadditive suitable for preparation of solid AMB nanodispersion in polymeric matrix is prepared. Another option is application of a sol-gel method using selected polysiloxane types in objectified ratio and subsequent incorporation of $AgNO_3$ into the nanosol solution. The prepared solution is subsequently

compounded with the powdered SiO_2 nanocarrier. The above-mentioned methods to prepare the AMB nanoadditive (application of sol-gel method, compounding the nanosol with a nanocarrier, preparation of powdered nanoadditive from a solution) has not been described anywhere yet, what points to high topicality of the proposed research solution.

2 EXPERIMENTAL

2.1 Results from preparation of the AMB nanoadditives using SiO_2 based nanocarriers

Following three types of commercially available silicate nanocarriers were used in the experiments:

a) **S** - SiO_2 content 98 wt.%, particle size 18 nm, specific surface 190 m^2/g

b) **M** - SiO_2 content 44 wt.%, particle size 30 nm, specific surface 100 m^2/g

c) **U** - SiO_2 content 94 wt.%, particle size 25 nm, specific surface 15-30 m^2/g

The specific samples were marked according to method used for preparation of the AMB nanoadditive as follows:

I. **KM** – ***classical method***: physico-mechanical compounding of the nanoSiO_2 carrier + $AgNO_3$ + NaCl + distilled water, (samples marked KM/S - Table 1 and KM/M - Tables 1-2),

II. **PM – *progressive methods*:**

PM/A – physico-mechanical compounding (when cold) of the AMB nanosol and nanoSiO_2 carrier with formation of dissociated silver citrate (using citric acid) in a form of a nanoadditive (samples marked PM/A/S, PM/A/U - Tables 1-4),

PM/B – direct formation of the AMB nanoadditive by hydrolysis of triethoxysilane + vinyltriethoxy-silane mixture (sol formation) with subsequent reduction using $AgNO_3$ or silver citrate and gradual addition of the nanoSiO_2 carrier under determined conditions (samples marked PM/B/S, PM/B/U - Tables 1-4 and PM/B/M - Table 1). Selected samples of the prepared AMB nanoadditives including basic data on Ag-content and antimicrobial activity are given in Table 1.

Figures 1 and 3 show SEM images of surfaces of the prepared AMB nanoadditives using S and U carriers with identification of silver nanoparticles. Presence of biogenic nanoparticles in the form of Ag^+ ions was confirmed by X-ray photoelectron spectroscopy (XPS method) of the nanoadditive as is shown in the Figures 2 and 4.

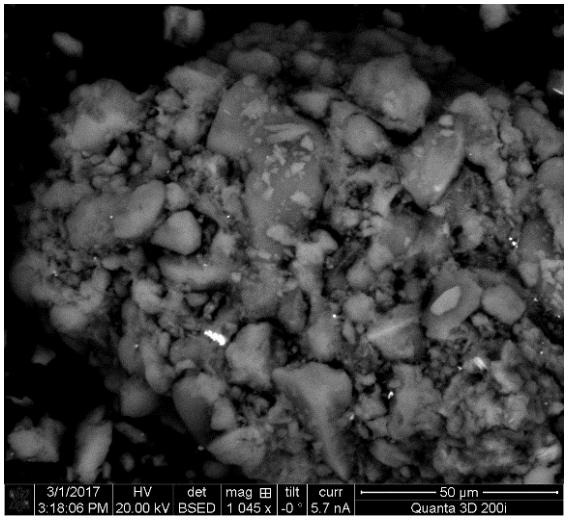

Figure 1 SEM image of AMB nanoadditive surface **with S** carrier (PM/B/S sample), magnification 1453x

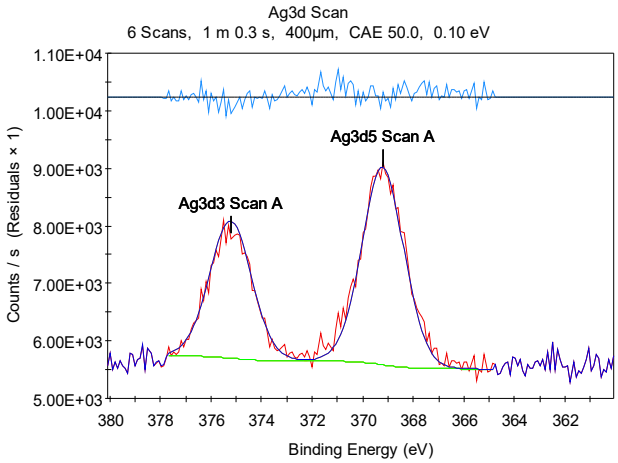

Figure 2 Graphical record of XPS analysis of PM/B/S sample with identification of Ag^+ ion at energetical wavenumber 369.3 eV

Table 1 Results of silver content and antimicrobial activity determined on powdered AMB nanoadditives prepared using nanoSiO_2 based nanocarriers

Sample	Nanocarrier type	Determined Ag content - AAS method [wt.%]	Antimicrobial activity (AMA) – determined bacterial reduction [%]
KM/S	S	1.19	R = 56.0
PM/A/S	S	0.025	R = 19.1
PM/B/S	S	0.32	R = 13.6
KM/M	M	0.90	R = 84.0
PM/A/U	U	0.06	R = 84.0
PM/B/M	M	0.28	R = 10.3
PM/B/U	U	0.52	R = 44.0

Notice: R - mean value of bacterial reduction, AAS - atomic absorption spectroscopy, AMA - antimicrobial efficiency of the nanoadditive determined according to ASTM E 2149-13a method on *Escherichia coli CCM 3954*

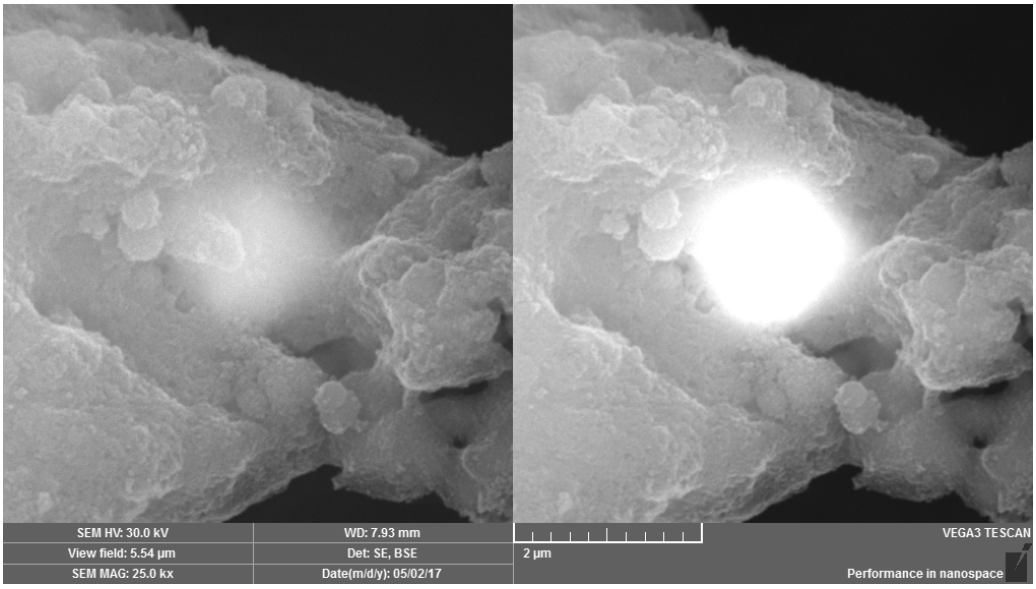

Figure 3 SEM image of AMB nanoadditive surface with **U** carrier (PM/B/U sample), magnification: 25000x, left: secondary ray, right: reflected ray

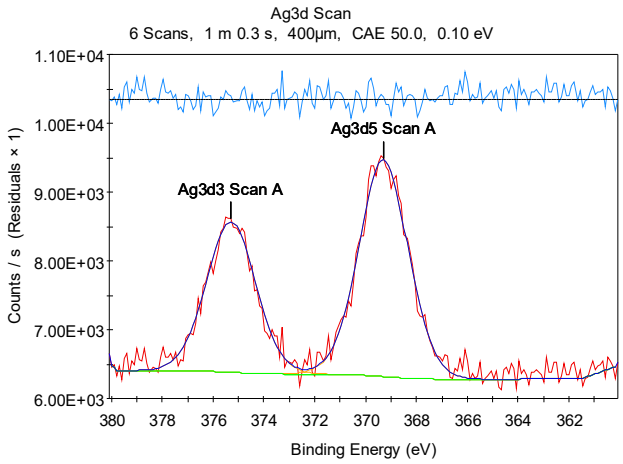

Figure 4 Graphical record of XPS analysis of the sample PM/B/U with identification of Ag^+ ion at energetical wavenumber 369.3 eV

Comparison of silver content in the AMB nanoadditives determined by different analytical methods shows that the samples are rather inhomogeneous and detected silver content depends also on sensitivity of the specific analytical method. It is possible to state that the XPS method, enabling also determination of ionic forms of Ag atom, has the best informative value. It can be concluded on the base of results, given in Table 2, that the progressive method using siloxane nanosol incorporating $AgNO_3$, in which biogenic silver form (Ag^+) arises, is most appropriate from a viewpoint of suitability of technology applied to prepare the AMB nanoadditive. This method used for preparation of the nanoadditive seems to be the best option to achieve considerable bacterial reduction in final products by means of biogenic silver nanoparticle.

Table 2 Results from evaluation of silver content (silver in various forms) using different analytical methods

Sample	AAS method [wt.%]	EDAX method [wt.%]	XPS method [wt.%]
Samples of the AMB nanoadditive prepared using different technologies with the same nanoSiO_2 carrier			
KM/S	1.190	9.76	1x0.3 (Ag^0)
PM/A/S	0.042	0.04	0,0
PM/A/M	0.023	0.87	5x0.1 (Ag^0)
PM/A/S	0.025	0.64	0.0
PM/B/S	0.390	2.13	4x0.2 (Ag^+)
PM/B/S	0.220	7.41	5x0.3 (Ag^+)
Samples of the AMB nanoadditive prepared with carrier U			
PM/A/U	0.060	undetermined	undetermined
PM/B/U	0.520	undetermined	0.3 (Ag^+)

Notice: For two samples PM/B/S and PM/A/S the different amount of carrier was used in the preparation of the nanoadditives,
EDAX method - X-ray fluorescence analysis method in combination with SEM analysis,
1x0.3 indicates determined one value with concentration of 0.3% by weight,
5x0.1 indicates determined five values with concentration of 0.1% by weight,
4x0.2 indicates determined four values with concentration of 0.2% by weight,
5x0.3 indicates determined four values with concentration of 0.3% by weight.

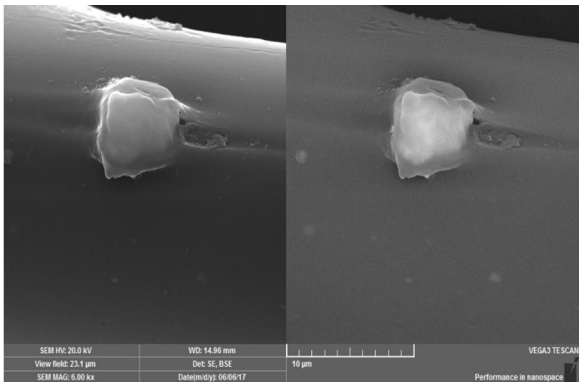

Figure 5 SEM image of PP fibre surface with a particle of AMB nanoadditive (sample PM/B/U – 10 wt.%, additive concentration 0.75 wt.%), magnification 6000x

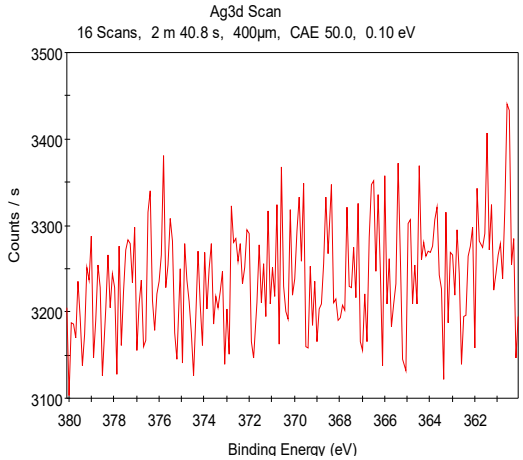

Figure 6 Graphical record of XPS analysis on a sample of PP fibre PM/B/U; where it was not possible to determine Ag ionic species using this method due to high scattering of Ag

2.2 Results from application of the prepared AMB nanoadditives using polymer dispersions of their concentrates in PP fibres, PP and PE foils

Samples of modified PP fibres (smooth fibre with fineness of 3 dtex) were prepared with 10 wt.% and 15 wt.% of the nanoadditive in the concentrate. Content of the AMB nanoadditive in the fibre was 0.75 wt.%. Results from the evaluation are shown in the Table 3.

It was not possible to identify exactly Ag ionic species on some samples of PP fibres using XPS analysis method due to its low content in the fibre or high scattering in the polymeric mass. Results of analysis of Ag content in various form (i.e. Ag^+ and/or Ag^0) have confirmed, that there is a direct relation between concentration of Ag ions and antimicrobial activity (AMA) of PP fibre, in a form of bacterial reduction of bacterium *Escherichia coli CCM 3954* determined according to ASTM 100:2015 method. The so-called progressive method, supporting existence of Ag^+ ions, enables to achieve relatively high bacterial reduction even without any need to increase content of dispersion of the concentrate with AMB nanoadditive in the polymeric system regardless which type of nanoSiO_2 carrier was used (see AMA results of PM/B/S and PM/B/U samples in Table 3). Besides, it was confirmed that the method of preparation according to PM/A alternative (see PM/A/S, PM/A/U in Tables 2 and 3) does not support formation of suitable Ag form (it generates colloidal form of Ag^0 only) and/or that it ensures low content of silver in the AMB nanoadditive, which is not sufficient for adequate antimicrobial activity.

Experimental research in the field of application of the AMB nanoadditives and solid dispersions, made from them, used in polymeric systems designed for preparation of extruded foils, allowed to ensure also sufficient level of AMA in selected types of PP and PE foils. The experiments have confirmed necessity to increase content of dispersion of the concentrate in the mass up to min. 15 wt.% and to ensure this way at least 2 wt.% content of the nanoadditive in the mass, so that AMA on PP and PE foils close to 50% bacterial reduction could be achieved.

However, in this case methods of PM/A as well as PM/B alternative have proved the most appropriate for preparation of suitable types of AMB nanoadditives. Results from evaluation of AMA on samples of PP and PE foils are shown in Table 4. Evaluation of the antimicrobial efficiency on the modified PP and PE foils was performed according to the ASTM E 2149-13a standard using bacterium *Escherichia coli CCM 3954.*

Table 3 Results from the analysis of antimicrobial activity (AMA) on selected types of modified PP fibres containing 10 and 15 wt.% of the nanoadditive in the concentrate

Bacterium	***Escherichia coli CCM 3954*** **CFU/sample**			
Sample of PP fibre (containing 10 wt.% of the additive in the concentrate), additive concentration in the fibre 0.75 wt.%	PM/A/S (carrier S)	PM/B/U (carrier U)	PM/A/U (carrier U)	PM/B/S (carrier S)
Bacterial reduction [%]	0	99.32	0	84.52
Sample of PP fibre (containing 15 wt.% of the additive in the concentrate), additive concentration in the fibre 0.75 wt.%	non-prepared fibre	PM/B/U (carrier U)	PM/A/U (carrier U)	PM/B/S (carrier S)
Bacterial reduction [%]	-	95.6	0	87.6

Notice: antimicrobial efficiency using AATCC 100: 2015 method on *Escherichia coli CCM 3954,*
CFU - the number of colonies of bacteria in the volume of the inoculum.

Table 4 Results of AMA analysis on selected types of modified PP and PE foils containing 15; 10 and 5 wt.% of the additive in the concentrate

Bacterium	***Escherichia coli CCM 3954*** **CFU/sample**			
Sample of PP foil (content 10% concentrate) additive portion 0.75 wt.%	PM/A/S (carrier S)	PM/B/U (carrier U)	PM/A/U (carrier U)	PM/B/S (carrier S)
Bacterial reduction (%)	8.4-19.5	17.2-20.5	11.6-12.1	0.0-14.4
Sample of PP foil (content 15% concentrate) additive portion 2.25 wt.%	Non-prepared sample	Non-prepared sample	PM/A/U (carrier U)	PM/B/S (carrier S)
Bacterial reduction (%)	-	-	46-53	38-45
Sample of PE foil (content 5% concentrate) additive portion 0.75 wt.%	PM/A/S (carrier S)	PM/B/U (carrier U)	PM/A/U (carrier U)	PM/B/S (carrier S)
Bacterial reduction [%]	0.0-10.9	0.0	0.0-5.5	4.2-7.9
Sample of PE foil (content 15% concentrate) additive portion 2.25 wt.%	Non-prepared sample	Non-prepared sample	PM/A/U (carrier U)	PM/B/S (carrier S)
Bacterial reduction [%]	-	-	36.7-48.5	35.6-43.5

AMA values confirm that after enhancement of the additive portion over 2 wt.% level bacteriostatic efficiency on PP and PE foils after application of AMB nanoadditives prepared using the alternative methods of PM/A and PM/B type is achieved.

3 CONCLUSION

Experiments with various nanoSiO_2 based carriers applied on preparation of the AMB nanoadditives were concluded by application of a new carrier U type, which has brought better results than carriers S and M type. Carrier U is characterized as spherical amorphous SiO_2, which is very suitable for dispergation in polymeric matrix. Surface area is set at 20 m^2/g, it contains small quantity of Fe_2O_3 and carbon (less than 0.20 wt.%). The carrier U assured good stability on preparation of the nanoadditive solution using the progressive method with application of AMB nanosol as well as $AgNO_3$. A positive result was achieved with variant PM/A, where high AMA was determined with relatively low Ag content, as well as with variant PM/B, where the progressive method enabled to suppress considerably negative influences in the method of nanoadditive preparation and where also Ag content increased up to the level of 0.5 wt.%. From a viewpoint of suitability of the specific nanoSiO_2 types for preparation of the AMB nanoadditive it is possible to determine sequence of their advisability as follows: carrier U – carrier S – carrier M. Besides, high antimicrobial activity of the prepared AMB nanoadditives with the carriers U and S after application in PP fibres (AMA at the level of min. 85% reduction – bactericidal efficiency), PP and PE foils (AMA at the level of min. 35-50% reduction, bacteriostatic or even bactericidal efficiency) was confirmed. The achieved level of antimicrobial efficiency in PP fibres surpasses highly practical requirements for application of PP fibres in the textiles (sufficient bacteriostatic level) and at the same time it is satisfactory in application in PP and PE foils for food packing (bacteriostatic level).

It is possible to expect also significant economical benefits whilst maintaining high antimicrobial efficiency in the final products - fibres and foils - regarding comparatively low Ag content in the polymeric mass of PP fibre, PP and PE foil after application of the AMB nanoadditive, prepared using the progressive methods (0.05-0.50 wt.%).

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