

PREPARATION OF ANTIMICROBIAL NANOADDITIVES AND THEIR CONCENTRATES BASED ON NANO CaCO_3 , NANO TiO_2 AND NANO ZnO FOR THEIR APPLICATION IN POLYPROPYLENE FIBRES, POLYPROPYLENE AND POLYETHYLENE FOILS

Jozef Šesták¹, Katarína Ščasníková¹, Andrej Dubec², Štefan Krivoš³ and Peter Michlík³

¹VÚTCH-CHEMITEK, spol. s r.o., Rybníky 954, 011 68 Žilina, Slovak Republic,

²Faculty of Industrial Technologies in Púchov, Alexander Dubček University of Trenčín
I. Krasku 491/30, 020 01 Púchov, Slovak Republic,

³Research Institute for Man-Made Fibres a.s., Štúrova 2, 059 21 Svit, Slovak Republic
jozef.sestak@vutch.sk, dubec@fptuni.sk, krivos@vuchv.sk, michlik@vuchv.sk

Abstract: The paper presents results of the research aimed at development of antibacterial (AMB) nanoadditives prepared by alternative methods using different types of nanocarriers. Results obtained by classical method of preparation-compounding of a carrier and a nanoadditive containing Ag ions, and by so-called progressive method using nanosols incorporating Ag, prepared by sol-gel technology, are compared. The prepared AMB nanoadditives were incorporated in two PP and PE polymer masterbatches with the aim to prepare solid AMB nanodispersions for additivation of PP fibres and PP, PE cast foils. Results from evaluation of antimicrobial efficiency of the AMB nanoadditives, applied on PP fibres and foils, against *Escherichia coli* CCM, performed according to the methods specified in AATCC 100: 2015 and ASTM E 2149, are reported. Application possibilities of the modified PP fibres and foils are outlined in the conclusion.

Keywords: antibacterial nanoadditive, nano CaCO_3 , nano TiO_2 and nano ZnO carrier, antibacterial efficiency, antimicrobial nanoadditive, PP masterbatch, color, processing and antimicrobial properties.

1 INTRODUCTION

Nanoparticles based on silver, copper, titanium or zinc are very interesting for commercial application aimed at achievement of antibacterial activity on fibrous and textile materials. Particular attention is paid to TiO_2 and ZnO carriers with a view to their unique optical, electrical and chemical properties, as well as silver-doped nanoparticles, prepared by sol-gel method [1]. Following methods are used advantageously to analyse nanoparticles trapped / fixed on the carrier surface: scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) or UV-Vis reflectance. Antibacterial, microstructural and fluorescent properties of silver (Ag) – doped TiO_2 nanoparticles were studied to investigate influence of silver on improvement of antibacterial properties of TiO_2 . Antibacterial activity of pure TiO_2 and Ag- TiO_2 against gram-negative bacteria *E. coli* and *Pseudomonas aeruginosa* and gram-positive bacteria *Bacillus subtilis* and *S. aureus* was studied by diffusion method in agar medium. It was found that doping with silver increases antibacterial activity of TiO_2 . Microstructures of these nanoparticles were studied by transmission electron microscopy (TEM) and atomic force microscopy (AFM) [2].

Attention is paid also to imparting antibacterial properties to polypropylene nonwovens, nonwovens made of cotton/PET blends and cotton woven fabrics, finished by padding – drying - curing as well as by electronic sputtering process. In the first place, surface modification of cotton/PET nonwovens and polypropylene fabrics was made to impart hydrophobic properties using RF plasma system and acrylic acid as monomer. After that silver-doped TiO_2 nanoparticles were prepared by sol-gel technology and processes of chemical reduction using titanium isopropoxide and silver nitrate as precursor. The nanoparticles were applied on the textile samples by padding – drying - curing and by electronic sputtering process. Antibacterial activity of the textile samples against bacteria *E. coli* and *S. aureus* was determined qualitatively and quantitatively according to the AATCC Method 147 and AATCC Method 100. Microstructural characteristics and surface morphology of the textile samples were studied by SEM-EDX and FTIR-ATR. The achieved results confirm, that silver-doped TiO_2 nanoparticles, synthesized by chemical reduction process, imparted good and permanent antibacterial activity to polypropylene nonwovens and to fabrics made of cotton/PET blend as well as to woven cotton fabrics [3].

The other publications present general overview of preparation of functional sols by doping functional materials in sol matrix and methods for modification of textile substrate by sol-gel technology. Combination of chemical and physical modification offers an unlimited potential for development and application of hybrid sol coatings, which can be used to develop functional and smart fabrics.

Structures of organofunctional trialkoxysilane sol-gel precursors are presented and compared with other organic-inorganic silicon-based hybrid materials. Functional properties, e.g. hydrophobicity and oleophobicity, flame-resistancy, antimicrobial properties, electric conductivity and antistatic properties are described in relation to chemical structure of the organic part of the precursor, mechanism and principle of activity of the coating and its washing resistance. Silver nanoparticles were synthesized by sol-gel technology, in the presence of CH_3COONa and hydrazine as reducing agent in water at room temperature. Structure and size of the prepared particles was characterized by SEM method and spectroscopically [4-6].

Functional modifications of chemical fibres imparting protective, hygienic and comfort properties to the fabrics are essential in the textile industry. The functional modifications include mainly permanent antimicrobial (AMB) modification of the fibres [7-10].

Nowadays the market offers AMB additives with average size of the particles in microscopic range ($d_{50} = 2-4 \mu\text{m}$) or polymer dispersions of these additives. Application of a nanoadditive as a carrier of an active component with significantly higher specific area than current microadditives is presumed to result in more uniform scattering of the antimicrobial active component on the surface of an inorganic carrier. Besides, antimicrobial efficiency at lower concentrations as compared to microadditives will be achieved.

2 EXPERIMENTAL

2.1 Materials and methods

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 consists of physico-mechanical compounding by means of a separate chemical reaction of the prepared Ag^+ ions in dispersion solution and subsequent doping a nanocarrier surface. 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. The progressive method assumes separate preparation of a silver-containing antimicrobial nanosol using specific procedures. Subsequent process involves compounding of the AMB nanosol with 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 sol-gel method using selected polysiloxane types in objectified ratio and subsequent incorporation of AgNO_3 into the nanosol solution. The prepared solution is then compounded with the powdered nanoCaCO_3 , nanoTiO_2 and nanoZnO 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.

Three types of commercially available nanocarriers, used in the experiments, were as follows:

- C type: nanoCaCO_3 content - 98 wt.% CaCO_3 , particle size 30-70 nm, specific surface $120 \text{ m}^2 \cdot \text{g}^{-1}$,
- T type: nanoTiO_2 content - 88-92 wt.% TiO_2 , particle size 10-12 nm, specific surface $100 \text{ m}^2 \cdot \text{g}^{-1}$,
- Z type: nanoZnO content - 99.8 wt.% ZnO , particle size 10-30 nm, specific surface $80-100 \text{ m}^2 \cdot \text{g}^{-1}$.

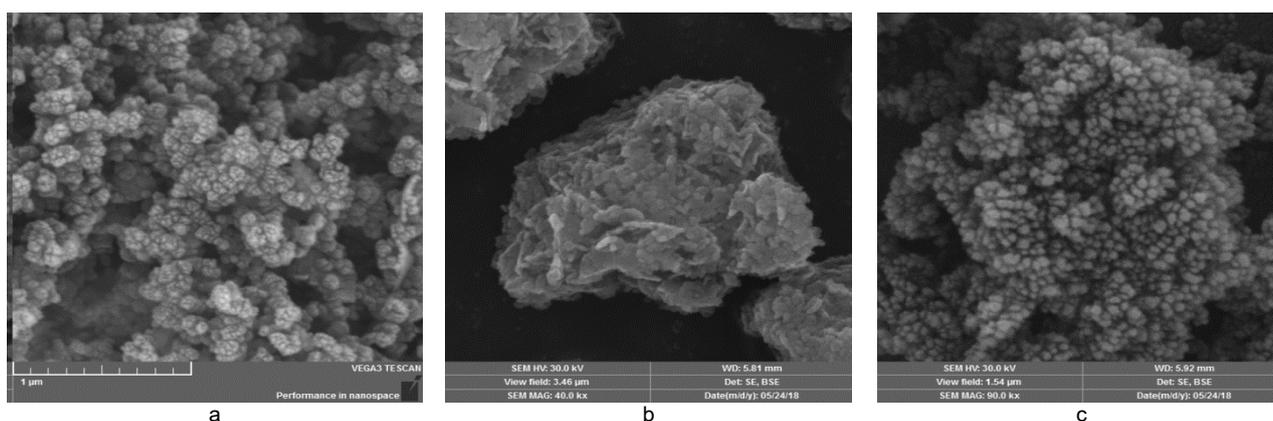


Figure 1 SEM images of nanocarrier surfaces (a) nanoCaCO_3 , (b) nanoTiO_2 and (c) nanoZnO

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

a) **KM** - classical method:

Preparation of a nanoadditive is based on physico-chemical compounding of the active agent (AgNO_3) with selected nanocarrier type: nanoCaCO_3 or nanoZnO . In the course of compounding, while cold, doping of nanocarrier surface by Ag^+ ions, released in the process of dissociation in the presence of reducing agent (chlorid natrium), takes place (samples designated KM/C and KM/Z, Tables 1-3).

b) **PM** - progressive methods:

PM/A - preparation of a nanoadditive by this method is based on physico-chemical compounding of the active agent (antimicrobial nanosol) with selected nanocarrier type: nanoTiO_2 or nanoCaCO_3 . In the course of compounding, while cold, doping of nanocarrier surface by Ag^+ ions, released in the process of dissociation in the presence of reducing agent (citrid acid), takes place (samples designated PM/A/C, PM/A/T, Tables 1-3),

PM/B - development of a nanoadditive by this method is based on preparation of nanosol by hydrolysis of a mixture of selected siloxane precursors (triethoxysilane + vinyltriethoxysilane), subsequent incorporation of an active agent (AgNO_3) and compounding with selected nanocarrier type: nanoTiO_2 or nanoZnO . In the course of compounding, while cold, doping of nanocarrier surface by Ag^+ ions (samples designated PM/B/T, PM/B/Z, Tables 1-3).

Selected samples of the prepared AMB nanoadditives and basic data on Ag-content and antimicrobial activity are given in the Table 1.

2.2 Preparation and evaluation of functional properties of PP and PE solid dispersions

Following materials were used to prepare samples of PP and PE masterbatches containing nanoadditives (Table 2):

Isotactic powdered PP (Lyondell Basell Company) with flow index (MFI) 10.2 g/10 min.

PE homopolymer, foil type, with melting flow index 19.6 g/10 min

1) **Inorganic AMB nanoadditives:**

- **KM/C, PM/A/C** ultrafine calcium carbonate with particle mean diameter 45 nm and surface area $120 \text{ m}^2 \cdot \text{g}^{-1}$ modified by an antimicrobial active component (VÚTCH-CHEMITEK, spol. s r. o).
- **PM/A/T, PM/B/T** nano TiO_2 rutile type with inorganic surface finish with rutile content 88÷92% TiO_2 ; specific surface $100 \text{ m}^2/\text{g}$; inorganic surface finish 8÷11% Al_2O_3 with primary particle size 10÷12 nm modified by

an antimicrobial active component (VÚTCH-CHEMITEK, spol. s r.o).

- **KM/Z, PM/B/Z** nano ZnO containing 99.8% ZnO; particle size 10÷30 nm with specific surface $80\div 100 \text{ m}^2/\text{g}$ modified by an antimicrobial active component (VÚTCH-CHEMITEK, spol. s r.o.).

2) **Dispersants:**

- D1 - PE wax with flow index 520 g/10 min (Clariant Corp.)
- D2 - copolymer of ethylene and acrylic acid with adjusted acid value by zinc salt (Honeywell Corp.)
- D3 - mixture of glycols and aliphatic amines (Clariant Corp.)
- D4 - condensing product of stearic acid and polyethylene glycol (Clariant Corp.)
- D5 - amidated PP wax (Clariant Corp.) with flow index 230 g/10 min (Clariant Corp.)

2.3 Evaluation methods

Functional properties of PP masterbatch

MFI of the masterbatches was evaluated using Dynisco Kayness capillary rheo-viscometer according to the STN EN ISO 1133 standard. The filterability index was evaluated using a filtration single-screw extruder with screw diameter of 25 mm and pore density of the filtration sieve of 16000 pores per cm^2 .

Coloristic characteristics of PP fibres

Coloristic characteristics of the drawn PP fibres of 3.0 dtex with concentration of nanoadditives 0.75 wt.% were measured using Hunterlab UltraScan XE under conditions as follows: illumination D65 - daylight with temperature 6500 K, observer 10° , CIELAB color space. The evaluated chromatic characteristics included: L^* (CIELAB) D65 10° color gradient light to dark, a^* (CIELAB) D65 10° - color gradient red to green, b^* (CIELAB) D65 10° - color gradient yellow to blue, WICIE - whiteness index, YIE-313/96 - yellowness index.

Antimicrobial activity

Antimicrobial activity of the PP fibres with concentration of AMB nanoadditives 0.75% and PP and PE foils incorporating 2.25% additives was measured as well.

POY discontinuous technological process and TS-32 equipment was used to prepare 3 dtex PP fibres. Technological conditions of preparation:

| | |
|--------------------|--|
| PP homopolymer | Flow index 25.4 g/10 min |
| Melt temperature | 220°C |
| Additivation level | 0.75% of the AMB nanoadditive in the fibre |
| Melt dosage | 20 g/min |
| Spinning nozzle | 25×0.3/1.2 |
| Winding speed | 1500 m/min |

Drawing process:

| | |
|---------------------------|----------|
| Temperature of the heater | 108°C |
| Draw ratio | 2.0 |
| Winding speed | 80 m/min |

Influence of the Filterindex parameter (unquantifiable value) became evident during preparation of the fibres, containing PM/A/T and PM/B/T additives, by increase of operating pressure in the die block, what influenced negatively its lifetime.

3 RESULTS AND DISCUSSION

3.1 Results from preparation of the AMB nanoadditives using nanocarriers based on nanoCaCO₃, nanoTiO₂ and nanoZnO

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

| Sample | Nanocarrier type | Ag content [wt.%] determined by AAS | Antimicrobial activity (AMA) - determined bacterial reduction R [%] |
|--------|------------------|-------------------------------------|---|
| KM/C | C | 0.29-0.59 | 60-97.1 |
| PM/A/C | C | 0.010 | 88.6 |
| PM/A/T | T | 0.06 | 38.0 |
| PM/B/T | T | 0.05 | 35.6 |
| KM/Z | Z | 0.61 | 98.3 |
| PM/B/Z | Z | 0.14 | 77.4 |

Notice: 1/ R - mean value of bacterial reduction, AAS - atomic absorption spectroscopy, AMA - antimicrobial efficiency of the nanoadditive against *Escherichia coli* CCM 3954 determined according to the ASTM E 2149-13a method. 2/ It was not possible to use the PM/B type technology on application of nanoCaCO₃ due to oxidation processes taking place after addition of a mixture of the siloxanes and the additive.

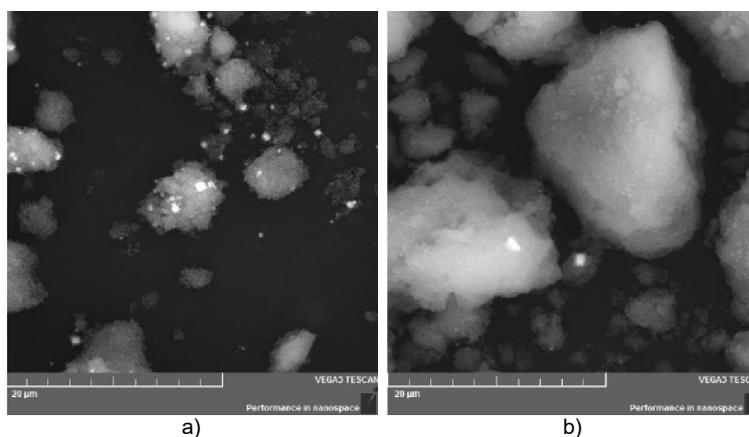


Figure 2 SEM images of surface morphology with 4000x magnification: (a) AMB PM/A/T nanoadditive (nanoTiO₂ carrier) and (b) of PM/B/T nanoadditive (nanoTiO₂ carrier)

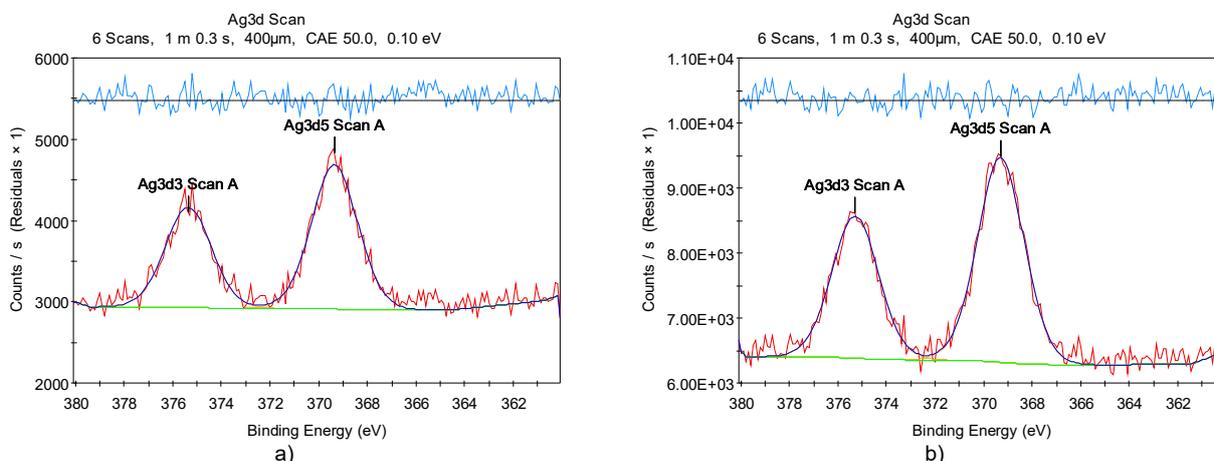


Figure 3 Diagram of XPS analysis of PM/A/T with identified form of Ag at wavenumber of 369.3 eV (a), Diagram of XPS analysis of PM/B/T nanoadditive with confirmation of content of 0.3 % mol. Ag⁺ ions at wavenumber of 369.3 eV (b)

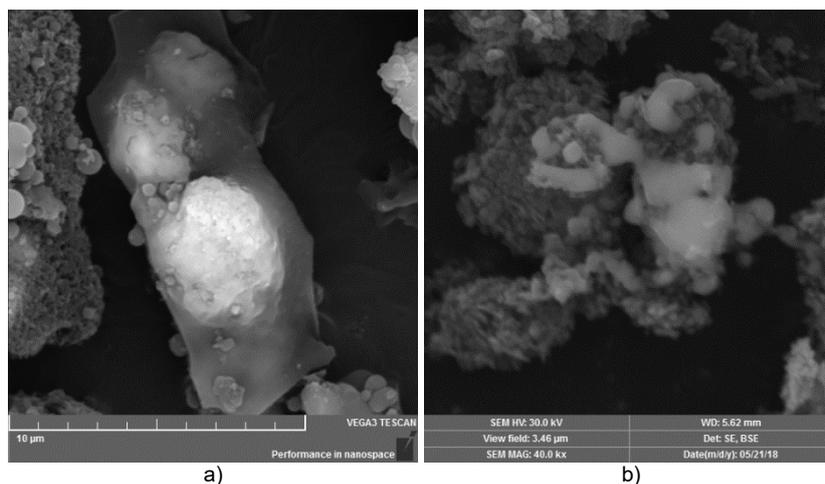


Figure 4 SEM image of AMB KM/Z nanoadditive surface with nanoZnO carrier (25 000x magnification) (a), SEM image of AMB PM/B/Z nanoadditive surface with nanoZnO carrier (25 000x magnification) (b)

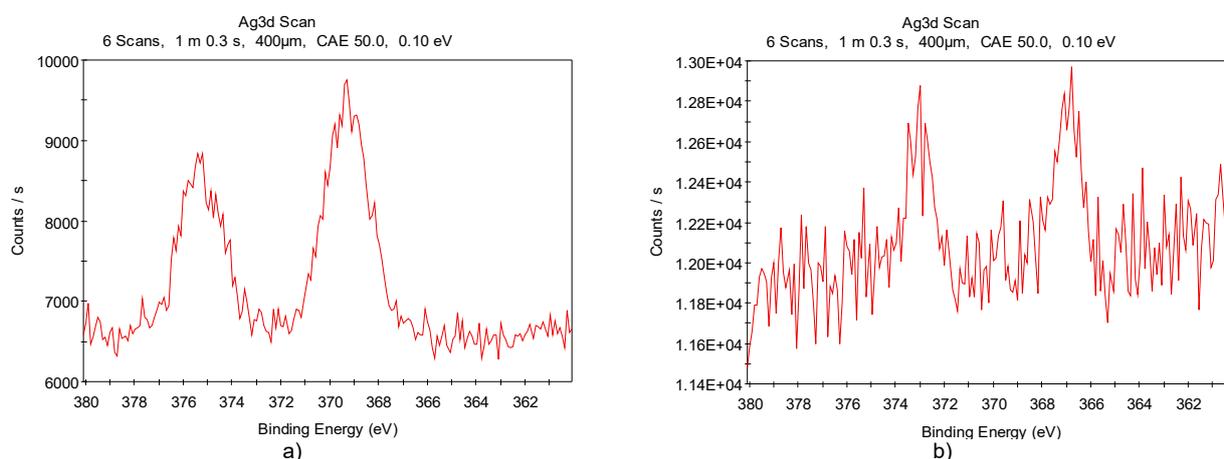


Figure 5 Diagram of XPS analysis of KM/Z nanoadditive (nanoZnO carrier) with determined atomic percentage of Ag⁺ ions 0.1% (a), Diagram of XPS analysis of PM/B/Zn nanoadditive (nanoZnO carrier) with determined atomic percentage of Ag⁺ ions 0.3-0.4% (b)

3.2 Results from preparation of polymer dispersions containing AMB nanoadditives and their application in PP fibers and PP, PE foils

Composition of PP and PE solid dispersions of AMB nanoadditives is given in the Table 2.

PP masterbatches were prepared from premix of powdery PP, nanoadditive and dispersing system using Werner-Pfeiderer ZDSK 28 twin screw extruder with 28 mm screw diameter. Preparation was performed at constant screw rotating speed 250 min^{-1} and constant extrusion temperature 220°C .

Functional properties of the prepared solid dispersions, describing suitability for their application in fibres and foils, were measured in the laboratory conditions.

Determined functional properties of PP and PE solid dispersions are given in the Table 3.

Preparation of the solid dispersions was trouble free. Functional properties, flow index and melt viscosity are on a level suitable for addition of PP and PE matter to be used for manufacture of PP and PE foils and PP fibres. The parameter filterindex is non-significant in the case of addition of PP and PE foils. However, the value of filterindex is important in the case of addition of PP fibres, because it determines time of functional use of the die block. Unquantifiable filterindex values of PP solid dispersions of AMB nanoadditives with TiO_2 nanocarrier of the antimicrobial component determine very short durability life of the die block.

Table 2 Composition of PP and PE solid dispersions of AMB nanoadditives

| Composition of PP solid dispersions of AMB nanoadditives | | | | |
|--|-------------------|----------------|-----|-------------------------|
| nanoadditive | Concentration [%] | Dispersant [%] | | Concentration of PP [%] |
| KM/C | 15.0 | D3+D4 | 3+2 | 80.0 |
| PM/A/C | 15.0 | D5+D4 | 3+2 | 80.0 |
| PM/A/T | 15.0 | D5+D4 | 3+2 | 80.0 |
| PM/B/T | 15.0 | D5+D4 | 3+2 | 80.0 |
| KM/Z | 15.0 | D2 | 10 | 75.0 |
| PM/B/Z | 15.0 | D2 | 10 | 75.0 |
| Composition of PE solid dispersions of AMB nanoadditives | | | | |
| nanoadditive | Concentration [%] | Dispersant | | Concentration of PE [%] |
| KM/C | 15.0 | D1 | 1.5 | 83.5 |
| PM/A/C | 15.0 | D1 | 2.5 | 82.5 |
| PM/A/T | 15.0 | D1 | 1.5 | 83.5 |
| PM/B/T | 15.0 | D1 | 1.5 | 83.5 |
| KM/Z | 15.0 | D2 | 10 | 75.0 |
| PM/B/Z | 15.0 | D2 | 9.4 | 75.6 |

Table 3 Functional properties of PP and PE solid dispersions of AMB nanoadditives

| Functional properties of PP solid dispersions with concentration of AMB nanoadditive 15 wt.% | | | | | |
|--|-----------------------|--------|------------------|--------|----------------------|
| Designation | Flow index [g/10 min] | Cv [%] | Viscosity [Pa.s] | Cv [%] | Filterindex [MPa/kg] |
| KM/C | 15.40 | 2.74 | 557.00 | 2.70 | 157 |
| PM/A/C | 14.72 | 1.61 | 582.60 | 1.60 | 191 |
| PM/A/T | 11.94 | 2.20 | 734.50 | 2.20 | Unquantifiable |
| PM/B/T | 12.58 | 5.05 | 667.10 | 5.10 | Unquantifiable |
| KM/Z | 12.97 | 1.87 | 694.50 | 2.00 | 88 |
| PM/B/Z | 12.24 | 2.84 | 695.00 | 2.60 | 2724 |
| Functional properties of PE solid dispersions with concentration of AMB nanoadditive 15 wt.% | | | | | |
| Designation | Flow index [g/10 min] | Cv [%] | Viscosity [Pa.s] | Cv [%] | Filterindex [MPa/kg] |
| KM/C | 13.50 | 2.08 | 666.20 | 2.10 | 165 |
| PM/A/C | 18.69 | 1.55 | 483.10 | 1.50 | 689 |
| PM/A/T | 13.03 | 2.42 | 683.10 | 2.40 | Unquantifiable |
| PM/B/T | 13.64 | 1.86 | 614.80 | 1.90 | Unquantifiable |
| KM/Z | 23.19 | 1.33 | 398.60 | 1.30 | 358 |
| PM/B/Z | 15.08 | 1.03 | 579.70 | 1.05 | Unquantifiable |

Preparation and evaluation of coloristic characteristics of the smooth 3dtex PP fibre

The measured coloristic characteristics of the prepared fibres were compared with those of a standard non-additivated PP fibre. Coloristic properties are given in the Table 4. Very good coloristic characteristics were achieved by additivation of PP fibres with AMB nanoadditives KM/C; KM/Z; PM/A/C and PM/A/T. The fibres show low yellowness (yellowing degree 4÷2) and whiteness nearly on a level of a non-additivated standard (WICIE 66.61÷74.78). Delustering effect represented by RFS parameter is remarkable for

AMB nanoadditives KM/Z (998.5) and PM/A/T (594.06) Fibres containing AMB nanoadditives PM/B/T; PM/B/Z achieve coloristic parameters proper to yellow color shades with significant delustering effect.

Preparation of PP and PE cast foils

PP and PE cast foils with thickness 40 µm and 2.25% level of additivation of active substance were prepared on the Plasticizer equipment with screw diameter of 25 mm and temperature regime of 250°C. No negative phenomenons were observed during the preparation.

Table 4 Coloristic of smooth 3 dtex PP fibres with 0.75% concentration of the AMB nanoadditive

| AMB nanoadditive | L* | a* | b* | GS | RFS | WICIE | Yellowing degree | YIE313/10 |
|------------------|-------|-------|-------|------|--------|--------|------------------|-----------|
| Standard (PP) | 94.23 | -0.17 | 1.33 | 5.00 | 100.00 | 79.73 | 4.00 | 2.44 |
| KM/C | 92.00 | -0.27 | 1.27 | 3.00 | 189.00 | 74.78 | 4.00 | 2.29 |
| PM/A/C | 95.16 | -0.74 | 4.71 | 2.50 | 95.93 | 66.61 | 2.00 | 8.31 |
| PM/A/T | 94.22 | -0.15 | 3.10 | 3.00 | 594.06 | 71.62 | 3.00 | 5.82 |
| PM/B/T | 87.9 | 0.42 | 12.73 | 1.00 | 707.12 | 10.27 | 1.00 | 24.83 |
| KM/Z | 92.69 | 0.00 | 1.93 | 4.00 | 998.50 | 73.32 | 4.00 | 3.77 |
| PM/B/Z | 85.16 | -0.10 | 16.36 | 1,00 | 999.99 | -15.04 | 1.00 | 31.49 |

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

Samples of modified PP fibres (smooth fibres, 3 dtex) were prepared with 15 wt.% of the nanoadditive in the concentrate. Content of the AMB nanoadditive in the fibre was 0.75 wt.%. Results of the evaluation are shown in the Table 5.

Different results of antimicrobial activity on the surface of PP fibre have been achieved after addition of the prepared samples of AMB nanoadditives into fibre-forming PP polymer in a form of solid polymeric dispersion (concentrate). The highest efficiency was achieved after application of nanoadditives prepared by the classical method (KM), the lowest efficiency showed additives prepared by the PM/A method. Very good results of antimicrobial efficiency were established on the fibres, where additives prepared by PM/B sol-gel method were applied. When comparing the nanocarriers, the highest antimicrobial efficiency was found with the additive containing nanoZnO (KM/Z and PM/B/Z nanoadditives).

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 achieve 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 foils close to 50% bacterial reduction could be achieved. In this case PM/A method as well as PM/B alternative have proved the most appropriate for preparation of suitable types of the AMB nanoadditives. Results of AMA evaluation on the samples of PP and PE foils are shown in the Tables 6 and 7.

Antimicrobial efficiency against *E. coli* CCM 3954 was evaluated on the modified PP and PE foils according to the ASTM E 2149-13a method. As for AMA evaluation, the highest efficiency with the both types of foils became evident after application of AMB nanoadditives prepared by the classical method (KM/C type), where even bactericidal effect was achieved. Nanoadditives with nanoTiO₂ carrier approved one selves on sufficient bacteriostatic level, the lowest level of antimicrobial efficiency was achieved with the nanoZnO carrier.

Table 5 Results from the analysis of antimicrobial activity (AMA) on selected types of modified **PP fibres** containing 15 wt.% of the nanoadditive in the concentrate

| Bacterium | <i>E. coli</i> CCM 3954, CFU/sample | | | | | |
|---|-------------------------------------|-----------------------|-----------------------|-----------------------|---------------------|-----------------------|
| | KM/C (C carrier) | PM/A/C (C carrier) | PM/A/T (T carrier) | PM/B/T (T carrier) | KM/Z (Z carrier) | PM/B/Z (Z carrier) |
| Sample of PP fibre (containing 15 wt.% of the additive in the concentrate), additive concentration in the fibre 0.75 wt.% | | | | | | |
| Bacterial reduction [%] | 99.9 | 0.0 | 0.0 | 36.0 | 99.5 | 84.8 |

Notice: antimicrobial efficiency against *E. coli* CCM 3954 determined according to the AATCC 100: 2015 method; CFU - colony forming unit (number of bacterial colonies in the volume of the inoculum)

Table 6 Results of AMA analysis on selected types of modified **PP foils** containing 15 wt.% of the additive in the concentrate

| Bacterium | <i>E. coli</i> CCM 3954, CFU/sample | | | | | |
|--|-------------------------------------|-----------------------|-----------------------|-----------------------|---------------------|-----------------------|
| | KM/C (C carrier) | PM/A/C (C carrier) | PM/A/T (T carrier) | PM/B/T (T carrier) | KM/Z (Z carrier) | PM/B/Z (Z carrier) |
| Sample of PP foil (15% content of the concentrate), 2.25 wt.% additive content | | | | | | |
| Bacterial reduction [%] | 61.1 | 9.8 | 10.1 | 23.9 | 9.1 | 7.3 |

Table 7 Results of AMA analysis on selected types of modified **PE foils** containing 15 wt.% of the additive in the concentrate

| Bacterium | <i>E. coli</i> CCM 3954, CFU/sample | | | | | |
|--|-------------------------------------|-----------------------|-----------------------|-----------------------|---------------------|-----------------------|
| | KM/C (C carrier) | PM/A/C (C carrier) | PM/A/T (T carrier) | PM/B/T (T carrier) | KM/Z (Z carrier) | PM/B/Z (Z carrier) |
| Sample of PE foil (15% content of the concentrate), 2.25 wt.% additive content | | | | | | |
| Bacterial reduction [%] | 77.0 | 19.4 | 18.2 | 13.4 | 6.2 | 9.4 |

4 CONCLUSION

The achieved level of antimicrobial efficiency in PP fibres exceeds significantly practical requirements related to application of PP fibres in the textiles (sufficient bacteriostatic level) and at the same time it is satisfactory for application in PP foils designed 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 and PP foil after application of the AMB nanoadditive, prepared using the progressive methods (0.01-0.14 wt.%).

Permanent AMB modification of PP fibres and PP and PE foils is achieved especially by addition of the main AMB additive into the basic polymer during spinning and foil forming. The masterbatch must have at the same time all functional, processing and coloristic characteristics together with the antimicrobial activity. Results presented in this document showed that all above-mentioned preconditions have been fulfilled with PP nanoadditived masterbatches with concentration 15 wt.%, in particular samples of the type: KM/C; KM/Z and PM/A/C with correctly selected dispersing system (D3 - mixture of glycols and aliphatic amines; D2 - copolymer of ethylene and acrylic acid with acid value adjusted by zinc salt; D4 - condensation product of stearic acid and polyethylene glycol) and their mutual combinations. It is possible to state on the base of these observations that the PP nanoadditived masterbatch with concentration 15 wt.%, KM/C; KM/Z and PM/A/C type are suitable for preparation of antimicrobial nanocomposite PP fibres. Bacteriostatic efficiency is sufficient for preparation of antimicrobial PP and PE packing foils. Positive effect of the dispersant D2 - ethylene copolymer and acrylic acid with acid value adjusted by zinc salt was observed for PE solid dispersions. The dispersant D1 - PE wax has limited application in higher concentrations over 2.5%.

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