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Bacteriostatic textile-polymeric coat materials modified with nanoparticles

Summary — The aim of the present study was to develop a process for the preparation of nanoparticles with antybacterial/bacteriostatic properties including the conditions of using these particles in textile-polymeric coating materials with stable bacteriostatic properties. The developed functional particles consist of submicro-spheres (mainly of SiO_2 — Fig. 1) made by the „sol-gel" technique. On their developed surface, „nanoislets" of an antibacterial agent such as metallic silver (Ag) were durably deposited (Figs 2 and 3). Such bioactive particles were then incorporated into either hydrophobic (with micro-porous structure) or hydrophilic (with compact structure) polyurethane coats during their production, obtaining the required uniform dispersion of single functional nanoparticles in the polymeric matrix (Fig. 4). To assess the performance stability of the bacteriostatic coating materials they were subjected to 10 standard laundering tests and no deterioration was found in their bacteriostatic properties, as well as in their structure and characteristics such as barrier and hygienic properties (watertightness, water vapor permeability or resistance of water vapor flow) as compared to those of corresponding unmodified materials (Figs 5, 6, 7, Tables 1 and 2).

BAKTERIOSTATYCZNE WŁÓKIENNO-TWORZYWOWE MATERIAŁY POWŁOKOWE MODYFIKOWANE NANOCZĄSTKAMI

Streszczenie — Celem badań przedstawionych w niniejszej publikacji było opracowanie technologii wytwarzania nanocząstek o właściwościach antybakteryjnych/bakteriostatycznych i warunków zastosowania tego rodzaju cząstek we włókienno-tworzywowych materiałach powłokowych o trwałych właściwościach bakteriostatycznych. Opracowane cząstki funkcjonalne stanowią wytworzone techniką „zol-żel" submikrokule (głównie z SiO_2 — rys. 1), na których rozwiniętej powierzchni został trwale osadzony czynnik antybakteryjny w postaci „nanowysepek" srebra metalicznego (Ag) (rys. 2, 3). Takie bioaktywne cząstki wprowadzano następnie do powłok poliuretanowych na etapie ich tworzenia — hydrofobowych o strukturze mikroporowatej oraz hydrofilowych o strukturze zwartej — uzyskując wymagane równomierne monocząstkowe rozproszenie cząstek funkcjonalnych w tworzywie matrycy polimerowej (rys. 4). W celu oceny trwałości użytkowej tak wytworzonych bakteriostatycznych materiałów powłokowych, poddawano je 10-krotnemu znormalizowanemu praniu, nie stwierdzając obniżenia właściwości bakteriostatycznych, ani też pogorszenia ich struktury i właściwości barierowych — wodoszczelności i higienicznych — przepuszczalności lub oporu przepływu pary wodnej, w stosunku do odpowiednich materiałów niemodyfikowanych (rys. 5, 6, 7, tabela 1, 2).

NANOCOATING OF TEXTILE MATERIALS — PRESENT SITUATION

One of the most rapidly developing fields of textile finishing research and technology is so-called nanocoating technique. This method relates to deposition on the surfaces of textiles the very thin (20—40 μm) polymeric coats or membranes, filled with appropriate functional nanoparticles with specific properties, such as *e.g.* antibacterial ones. The use of fillers of this type does not deteriorate the rheological properties of coating pastes or structures and performance characteristics of the resultant coats. Such nanofillers are added in considerably lower quantities than corresponding micro-materials, but they act more effectively, which is, among others, due to their large specific surface [1]. All in all, the use of nanoparticle additives of functional materials makes it possible to impart permanent additional specific functions to the coated fabrics without any deterioration in the existing properties. This creates also beneficial prospects for industrial applications of nanocoating to produce the fabrics whose main or additional feature is bio-

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activity. Hence, despite still high prices of such nanomaterials, the economical aspects of coating finishes are also acceptable.

The fundamental condition for successful incorporation of nanoparticles into polymeric matrices is to ensure their uniform mono-particle dispersion in the membrane or coat material. Otherwise, the agglomerates of nanoparticles in the crosslinked membrane would act as micro-particles with all the negative effects of such a state. The agglomerates deteriorate the strength properties of coats or membranes and are insufficiently effective, which requires to use large quantities of such materials [2]. Due to the natural susceptibility of nanoparticles to agglomerate, it is difficult to obtain their stable mono-particle dispersion and uniform distribution in the crosslinked polymeric matrix, which creates the major technical problem in the preparation of this type of textile-polymeric coat materials [3—9].

OWN RESULTS

The Institute of Textile Materials Engineering (IIMW) in co-operation with the Institute of Material Science and Technical Mechanics (IMMT) of the Technical University of Wrocław undertook the studies aimed at the development of technology of the preparation of appropriate nanoparticles with antibacterial properties, and conditions of their use in the production of textile-polymeric coat materials with stable bacteriostatic properties (PBZ-KBN-095/T08/2003). Appropriate antibacterial materials have been developed with the use of the "sol-gel" technique by the group of IMMT. Their carriers consist of submicroglobules, mainly SiO_2 and TiO_2. On their surface an antibacterial agent was permanently deposited in the form of "nano-isles" of metallic silver, Ag^0, to impart the required bio-activity to the final products. It was of paramount importance to make these materials capable of dispersing, required by the technological processes of coating, ensuring also a good stability of the obtained dispersions in coating pastes as well as in the crosslinked polymeric matrices-membranes [7, 10—14].

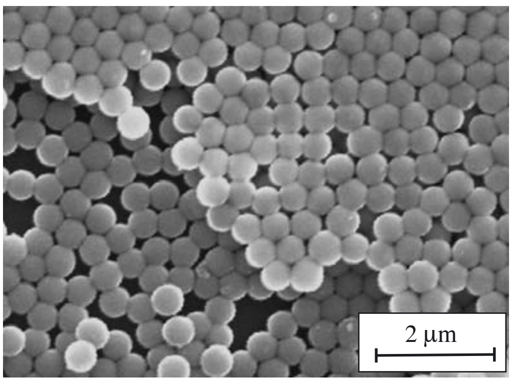

Fig. 1. SEM image of sol-gel SiO_2 submicron spheres [11]

The sol-gel submicron-sized silica particles (Fig. 1 [11]) were modified by production on their surfaces tightly bound nanoclusters of metallic silver Ag^0. This method of production of modified silica nanoparticles has been recently implemented in Poland in developed scale. The SEM micrograph of this material is presented in Figure 2 [11] and the scheme of its structure is shown in Figure 3 [10].

The prepared silica submicro-spheres with deposited silver nanoparticles were incorporated into polyurethane membranes/coats — hydrophobic with microporous structure or hydrophilic with compact structure to obtain the materials with permanent bacteriostatic and good hygienic and barrier (*e.g.* watertightness) properties. These membranes are produced at IIMW from monocomponent not-crosslinked polyurethanes by the method of phase separation induced by the solvent evaporation [8, 15, 16]. The incorporation of bioactive nanopowders into the polymeric membrane takes place during the preparation of three-phase emulsion [prepolymer/organic solvent/non-solvent (water)], through the addition of aqueous mono-particle dispersion of submicro-globules with precipitated silver nanoparticles to the external phase of the aqueous emulsion. Such an emulsion is the base of coating pastes. The choice of micro-porous membrane structure was justified by the ex-

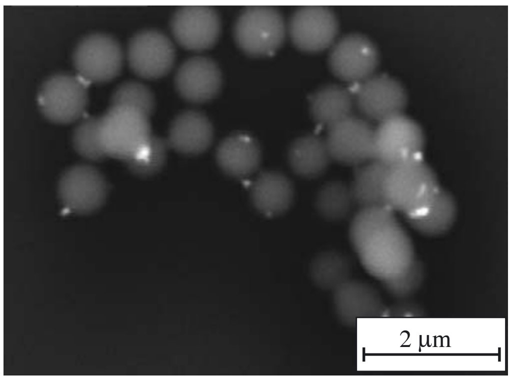

Fig. 2. SEM image of bacteriostatic submicro-globules (nanopowders). The bright dots are Ag^0 nanoclusters [11]

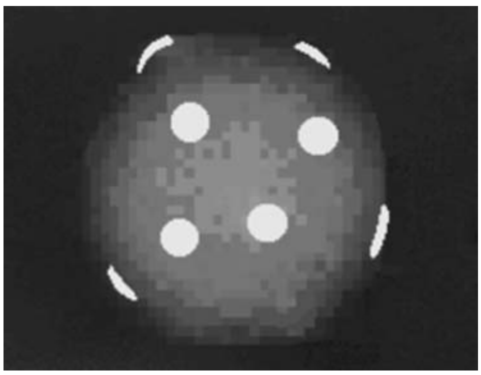

Fig. 3. Scheme of the structure of bacteriostatic submicro-globules (nanopowders) shown in Figure 2 [10]

pected areas of using coat materials, *i.e.* required high watertightness and good hygienic properties determined by water vapour permeability or flow resistance. It was also assumed that after the modification with bioactive nanomaterials, the microporous membranes would show greater capability of active silver ions to diffuse to their surfaces than in case of membranes showing compact structure. Hence, a better bacteriostatic effect could be expected. The basic research problem was to obtain a homogeneous, possibly mono-particle stable dispersion of nanopowder in water and then in the aqueous phase of coating paste and the crosslinked polymer coat [4, 10, 11, 17].

This problem was solved by the modification of nanopowder synthesis as well as by improving of the conditions of preparation of their dispersions, among others, by changing the PCD potential (PCD = *Particle Charge Detector*) and by addition of proper dispersing agents and stabilizers and of course by improving of the mechanical conditions of the process [10, 11, 16]. Eventually, the development of proper process conditions made possible to obtain the uniform mono-particle distribution of nanopowders in the coating pastes as well as in the crosslinked polymeric membrane, as shown in the SEM photograph (Fig. 4) [10, 17].

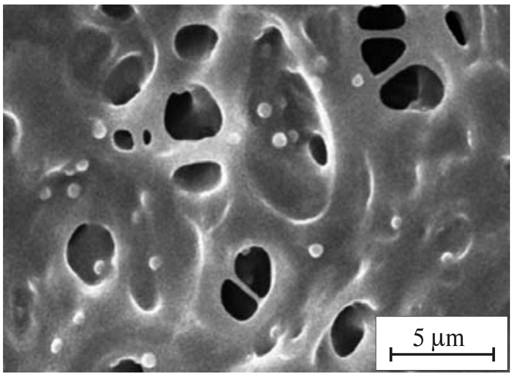

Fig. 4. SEM image of mono-particle dispersion of submicro-globules with precipitated silver nanoparticles in the polymeric microporous membrane [10]

The modified coat materials show good bacteriostatic effects when tested by the method of diffusion on a plate with agar-agar according to PN-EN ISO 20645:2005 (U), using three bacterial strains: *Escherichia coli*, *Klebsiella pneumonice* and *Staphylococcus aureus*.

To test the performance stability and resistance to washing of the coat materials (microporous or compact) and their bacteriostatic properties, they were deposited on the polyester fabric and such coated textiles were subjected to repeated washing (10 cycles) according to ISO 6330:1984, procedure 5A (40 ^{o}C). It has been found that the repeated washings caused no significant deterioration in the performance of coat materials as well as in their bacteriostatic properties.

The beneficial test results of the bacteriostatic properties of the obtained textile-polymeric coated materials filled with the developed SiO_2/Ag^0 submicro-globules create possibilities of wide practical applications of these new materials and prospects of launching their industrial production.

Physical, physicochemical, useful (including hygienic — water vapor static permeability and dynamic water vapor flow resistance) (the method of wetting of thermally-insulated plate according to PN-EN 31092: 1998/Ap. 2004) and microbiological properties of these bioactive-modified textile products were investigated. These results were utilized to optimize the amounts of the nanopowders used — depending on the textile type, the coating method, the number of the coatings applied as well as the carrier structure and the final product character [10, 11].

In order to investigate the bacteriostatic properties of the obtained microporous coating materials doped with SiO_2-Ag^0 powders, the textiles were washed several times [5 and 10 washing cycles at 40 ^{o}C, 30 min; according to the ISO 6330:1984 washing standard, procedure 5A (40 ^{o}C)]. The samples were dried at room temperature after each cycle. The number of the washing cycles depended on the applications of the textiles with the obtained polyurethane coatings or membranes (bed cloths, sportswear). The washed materials were microbiologically investigated in order to establish the changes in their bacteriostatic (Table 1) and basic functional (*e.g.* water tightness; the hydrostatic method according to PN-EN 20811, PN-ISO 811:1997) properties (table 2). The results obtained suggest that addition of the bioactive powders does not influence negatively the working characteristics of the membranes produced.

T a b l e 1. Bacteriostatic effects of the textile samples with hydrophobic microporous coating with or without SiO_2-Ag^0 submicro-globules; comparison of the results for the samples as obtained and after 10 washings [PN-EN ISO 20645:2005 (U)]

Samples	*Staphylococcus aureus*	*Escherichia coli*	*Klebsiella pneumoniae*
No nanopowder, no washing	no effect	no effect	no effect
No nanopowder, 10 washings	no effect	no effect	no effect
With nanopowder, no washing	good effect	good effect	good effect
With nanopowder, 10 washings	good effect	good effect	good effect

These materials were also investigated by SEM (the micrographs were obtained using Jeol SEM microscopes JSM 550 LV or JSM 35C; the membranes were investigated in high vacuum with the secondary electron detectors). The results are presented in Figures 5 and 6 [10, 11].

T a b l e 2. Functional and protective properties of coated polyester textiles with SiO_2-Ag^0 — doped microporous hydrophobic coating (double layer)

Sample	Surface weight g/m^2	Loading g/m^2	Water tightness cm column of water	Water tightness after 5 washings, cm	Water tightness after 10 washings, cm	Water vapor permeability g/m^2 (24 h)	Water vapor resistance $m^2 \cdot Pa/W$
Textile with the microporous coating without bioactive nanopowder	130	26	220	165	148	2714	4.82
Textile with the microporous coating with bioactive nanopowder	133	29	222	154	145	2557	4.26

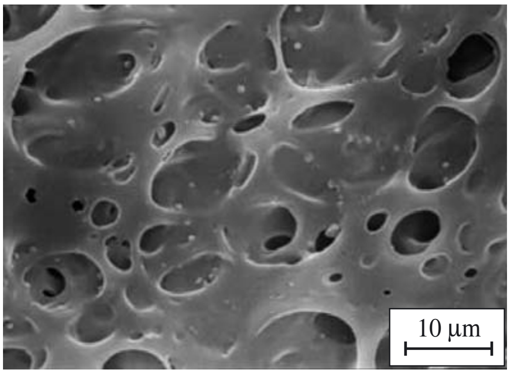

Fig. 5. Microporous membrane with SiO_2-Ag^0 submicro-globules before washing [10]

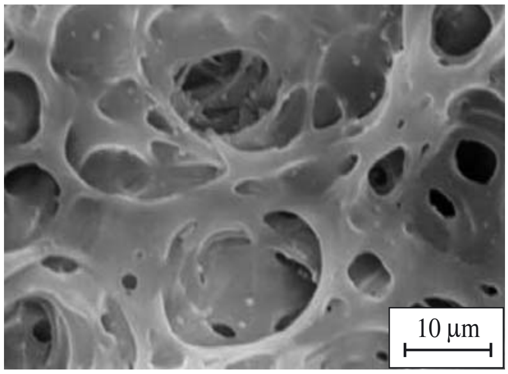

Fig. 6. Microporous membrane with SiO_2-Ag^0 submicro-globules after 10 washings [10]

The investigated microporous polyurethane coatings with submicron-sized SiO_2-Ag^0 powders show after washings almost unchanged structure, what indicates their high mechanical durability. Also, the visible number of the immobilized powder grains was not diminished after washings. The graphical representation of these results is shown in Figure 7 [10].

The satisfactory results of the microbiological investigations of the textiles modified with SiO_2-Ag^0 nanopowder (before and after 10 washings) were confirmed by the quantitative and qualitative SEM analyses [the X-ray analysis was performed using an EDX microanalyzer IBIS Link 300 (Oxford Instruments)]. The silver content in the powders was virtually identical before and after the washings [10].

In order to obtain the materials with extremely high water resistance, the composite materials with compact hydrophilic polyurethane membranes were produced in addition to the basic microporous membranes. As compared to the microporous membranes, water vapor transport through the compact ones occurs only *via* diffusion. This is why they show different hygienic and barrier properties — the water vapor resistance is at the level of 15—20 $m^2 \cdot Pa/W$, while water resistance

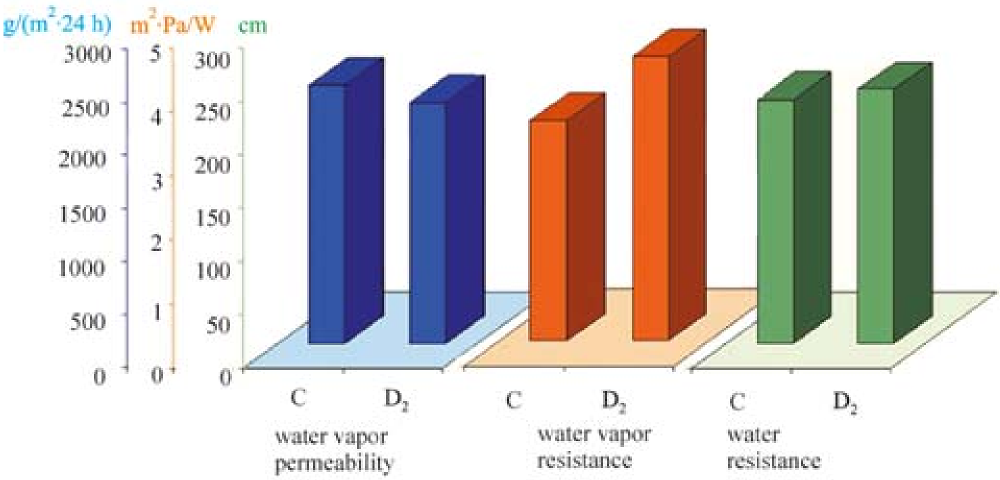

Fig. 7. Barrier and physiological comfort properties of the coated materials doped with SiO_2-Ag submicro-globules (nanopowders) — double layer coat; C — polyester fabric with the bioactive-modified polymer coating, D_2 — polyester fabric with the non-modified polymer coating

reaches 1000 cm of water. Due to the different conditions of the silver ions diffusion through such compact membranes it is necessary to adjust properly the amounts of the antibacterial nanopowders [10].

CONCLUSIONS

The encouraging bacteriostatic properties of SiO_2-Ag^0-doped materials open a way for their various practical applications. Examples of such coated or laminated products include [16, 17]:

— coated sport and recreational textiles,

— shoe linings,

— bed cloths Argo+ with additional antiallergic and antibacterial activities,

— layered systems for sport textiles — Ag stops bacteria multiplication and removes odors,

— bed linings for hospitals,

— bed linings for infants.

Thus, nanotechnology opens new areas of applications of bioactive textiles.

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