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Antibacterial and Fungicidal Coating of Textile-polymeric Materials Filled with Bioactive Nano- and Submicro-particles

Abstract
This paper presents a method of antibacterial and fungicidal active particles production and conditions of their use in textile-polymeric coating materials with a wide range of practical applications, including clothing or health preventive measures. The functional antibacterial and fungicidal active particles reported here consist of silica submicro-spheres made by the sol-gel technique, whose developed surface was simultaneously overlaid with antibacterial metallic silver and fungicide copper nano-precipitates. This active powder constitutes significant progress in relation to the materials known, such as SiO_2/Ag or SiO_2/Cu particles. Our SiO_2/Ag+Cu particles are incorporated into thin polymeric coats, mostly consisting of hydrophilic polyurethane with a compact structure, during their formation on the surface of textile fabrics to impart bactericidal and fungicidal properties to these fabrics at the same time. It is of importance that the additive used does not cause any perceptible deterioration in the basic performance properties of the coating materials modified, such as high resistance to water penetration, wind-proofness and good hygienic characteristics, determined by means of water vapour permeability. This paper presents assumptions for the manufacturing process and physico-chemical and morphological characteristics of submicro-particles of SiO_2/Ag+Cu, as well as conditions of their use in polymeric micro-coats formed on the surface of textiles and the results of testing the performance properties of the coating materials obtained, including their antibacterial and fungicidal characteristics.

Key words: *polymeric coating, bioactive fillers, nano-particles, submicro-particles, multifunctional textiles, polymeric matrix, rheological properties, coating pastes, silver, copper.*

Introduction

The basic direction of the development of the world textile industry concerns the increase in the production of multifunctional high-tech or smart fabrics designed for various practical applications. The manufacturing processes developed and used to make such fabrics are more and more frequently based on nanotechnologies that create splendid prospects for significant optimisation of the performance properties of textiles as well as for the development of new types of fabrics for new application areas [1]. Among such fabrics are multi-functional and multi-layer textile-polymeric coating materials that are quickly developed with the use of coating or laminating textile substrates with polymeric coats or membranes modified with appropriate functional nano-particles with specific features, e.g. antibacterial properties. This approach makes it possible to impart new additional functions to fabrics that already have several specific properties without their handicapping or handicapping them to an imperceptible extent for users [2]. Therefore it is possible to significantly increase the multi-functionality of such fabrics and to extend the areas of their practical use. The method presented consists in depositing thin, mostly multilayer polymeric coats filled with functional nano-particles on the surface of fabrics with structures appropriately selected for the applications anticipated to impart additional properties or functions required to these fabrics [3]. Fillers of this type are added in considerably lower quantities than those of corresponding micro-additives, but they interact more effectively owing to their large specific surface. Finally, both the relatively low nano-filler quantity required and its small dimensions eliminate the negative effect observed in the case of micro-particle additives on the rheological properties of film-forming coating pastes as well as on the structure and properties of the polymeric coats obtained. As shown by relevant tests, similar remarks may also be referred to submicro-particle fillers under the stipulation that their size is limited to a maximum of 600 nm and the quantity of addition to a maximum of 4% in relation to the dry weight of the polymeric matrix [1, 2, 4, 9]. One should also emphasise the generally high and invariable stability of the additional functions obtained, practically determined by the stability of the polymeric matrix and directly dependent on its structure. Hence it is extremely important not to allow any disturbances in this structure caused by fillers, which depend on the size and quantity of the functional particles added. The total thickness of such coats usually ranges from 30 to 80 μm. These coats most frequently consist of

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polyurethanes and polyacrylates [3, 6, 9]. Eventually the use of nano-fillers and submicro-fillers (with the above-given limitations) makes it possible to impart additional specific functions to textile coating materials without deterioration in their previous properties. Examples of such products include coating materials used to make outer sports or recreation garments characterised by barrier properties such as resistance to water penetration and wind-tightness, as well as hygienic properties determined by water vapour permeability, strength properties (including resistance to mechanical effects occurring during use), and high bioactivity [2, 5, 7]. This property, determined by bacterio- or mycostatic interactions or bacteri- or fungicidal effects, has decisive significance for the safety and comfort of using various textile goods, not only for clothing application. Considering that textiles generally constitute a perfect substrate for the development of various bacteria, including dangerous pathogenic bacteria and even fungi, the problem of imparting bioactivity to various textile fabrics is gaining greater and greater importance as a result of growing concern for human health [2,5,10 - 14]. In the case of coating materials, bioactivity is imparted by incorporating appropriate nano- and submicro-particles. Nowadays it is bioactive metals such as silver and copper in the form of nano-particles that have gained the greatest importance due to their unlimited biological activity with no adverse side effects, as observed in the case of other biocides [1, 2, 5, 7, 15 - 18]. These metals in the form of ions strongly act on bacteria and fungi. The highest antibacterial activity is shown by silver ions, while copper ions show fungicide interactions. Under conditions of garment wearing, the slow ionisation of metal nano-particles occurs, and the ions released diffuse through the polymeric matrix onto the coat surface and further onto the garment user's skin to kill bacteria and fungi spores and even the whole fungi colonies present there. The basic condition for obtaining expected results of incorporating specified types of nano- or submicro-particles into polymeric matrices is to provide their mono-particle dispersion in the material of such a film or coat [1, 2, 4]. Only in such cases do the particles incorporated cause no structural destruction of the coat matter and provide the functional quality of the modified materials expected. The large active surface of metallic nano-particle materials, such as Ag and Cu is of paramount importance for their microbiological effectiveness as it increases their contact with bacterial strains or fungi colonies. Unfortunately, a large active surface also causes natural nano-particle aggregation resulting in the formation of greater forms (aggregates of nano-particles) and a decline in the specific properties of materials with nanometric dimensions. Various methods are used to prevent aggregation, one of which consists in depositing bioactive metal nano-particles on the surface of greater (submicron) ceramic carriers, mainly SiO_2 [2, 4, 7, 8, 16 - 18]. Our previous studies resulted in the development of SiO_2 submicro-spheres with the use of the sol-gel method. Their developed surface was overlaid with metallic silver nano-particles showing antibacterial effects [2, 4, 7, 8]. The material obtained turned out to be particularly suitable for producing textile-polymeric coating materials with antibacterial properties. It should be added that a similar method for the production of bioactively modified silica submicro-particles SiO_2/Ag^0 has been implemented on an industrial scale and such a material is commercially available [8]. A similar material (SiO_2/Cu^0+Cu_2O) was developed by us by depositing copper ions on silica submicro-spheres. In order to obtain a possibly wide range of bioactivity of the polymeric coats deposited in relation to both bacteria and fungi, it was attempted to use a blend of both materials developed, which, however, failed to give a satisfactory solution. This made it difficult to obtain stable dispersions of these materials and deteriorated the rheological properties of pastes modified in this way, causing adverse structural disturbances of the polymeric coats obtained, similar to that observed for SiO_2/Ag^0 [2].

Taking into consideration all of abovementioned arguments, we decided to develop a bioactive SiO_2/Ag+Cu submicro-particle with capabilities of simultaneous antibacterial and fungicidal effects. We decided to obtain such a material by depositing silver and copper nano-particles in metallic and/or ionized forms on the surface of a silica carrier prepared by the sol-gel method. Such an incorporation of bioactive submicro-spheres of SiO_2/Ag+Cu into polymeric coats deposited on fabric surfaces allows one to obtain good microbiological effects in relation to both bacteria and fungi colonies. At the same time the amount of nonactive fine-particle silica incorporated into the polymer structure is reduced, consequently the structure is not disturbed, and the performance properties of the coats are not deteriorated.

Experimental

Preparation and characteristics of submicro-particle bioactive silver and copper doped silica materials

The authors used the term 'silver and copper doped silica materials' when they write about two types of powders: SiO_2/Ag^0+CuO, and a mixture of SiO_2/Ag^0 and SiO_2/Cu^0+Cu_2O.

Monodisperse silica spheres were prepared by the Stöber method [16]. In a typical synthesis, a mixture of ethanol, water and 99.9%tetraethoxysilane [TEOS] (Alfa Aesar) in the presence of ammonia as catalyst were used. The evaporation of water and alcohol results in a dry white powder consisting of homogeneous submicro-spheres, which are subsequently doped with metal ions. Metal ions in the form of aqueous solutions of their salts, e.g. silver nitrate ($AgNO_3$) and copper nitrate ($Cu(NO_3)_2 \times 2.5\ H_2O$) were added to the submicro-sphere suspension in appropriate weight rations, followed by stirring and drying. The dry material was then reduced by thermal treatment. After the thermal reduction, performed under specified conditions, the silica still remained in a safe amorphous form. The product of these processes consists of silica submicro-spheres with a size of about 500 nm doped with nano-particles of metallic silver and copper in an ionised form.

The nano-particles of metals or metal oxides synthesised on the surface of silica submicro-spheres developed are durably combined with the carrier surface, which makes them resistant to external effects occurring during the use of textiles modified in this way, providing the invariability of their biological activity for a very long period of time. The functional bioactive material obtained is in the form of loose brown submicro-particle powder, whose biological properties are stable during storage. It is important for the textile applications intended that the material developed shows a reduced susceptibility to particle aggregation and good dispersing capability, making it possible to obtain stable mono-particle dispersion in water or organic solvents [19]. The obtained silica submicro-spheres with nano-particles of metallic Ag and

CuO formed on their surface are shown in an XRD pattern in ***Figure 1*** and as an SEM image in ***Figure 2***. The presence of silver and copper on the surface of silica submicro-spheres was additionally confirmed by elementary microanalysis (EDX) with the use of a Vega TS 5135 scanning electron microscope (Tescan) and an X-ray microanalyser, system ISIS Link 300 (Oxford Instruments, UK) – ***Figure 3***. As mentioned in the introduction, in addition to the SiO_2/Ag^0+CuO modifier developed, we also used a mixture of SiO_2/Ag^0 and SiO_2/Cu^0+Cu_2O for the purposes of comparison. It was then necessary to develop a synthesis of appropriate powder materials also based on Stöber's method [16] and similarly performed a synthesis of SiO_2/Ag^0+CuO. The presence of Ag^0 nano-particles in the SiO_2/Ag^0 material prepared and Cu^0 in SiO_2/Cu^0+Cu_2O is shown in the XRD diagrams in ***Figures 4*** & ***5***.

Preparation of textile-polymeric coating materials with antibacterial and fungicidal properties

Description of technological processes

The preparation of materials of this type consists in depositing polymeric coats containing bioactive submicro-particles of silver and copper doped silica materials on the surface of textile fabrics with specified structures such as woven fabrics, knitted fabrics and nonwovens. Owing to the presence of bioactive components, such materials should show antibacterial and fungicidal properties, but at the same time their polymeric coat can impart other specified functional properties to them, such as resistance to water penetration (not only water but also e.g. the impenetrability of blood and body fluids), waterproofness and windproof properties, protection against allergens (domestic dust mites) depending on the type of polymer used and the method of its deposition on the textile substrate. Moreover, the general features of textile-polymeric coating materials made in this way include hygienic properties and physiological comfort of use, determined by the water vapour permeability. The polymeric coat, strongly combined with the surface of fibres/fabrics, is resistant to wear and care conditions, including prolonged laundering, constituting an element that binds the functional submicro-particles with the textile carrier, which protects them against external effects occurring during use, e.g. abrasion. This coat also controls the intensity of releasing bioactive ions of Ag and Cu and consequently provides a long duration of antibacterial and fungicidal effects of the textile-polymeric coating materials. These materials are made by coating the textile carriers with appropriately prepared polymeric pastes of non-cross-linked polymers, mostly urethanes in the form of aqueous dispersion or solutions in organic solvents by the thin-layer multi-coating method. Stable woven fabrics were coated with pastes in the form of aqueous dispersion by the technique of direct multi-layer coating with a so-called air blade. Knitted fabrics susceptible to deformation were coated with solutions of appropriate prepolymers in organic solvents by the reversible technique using an indirect paper carrier [6].

In order to impart the bioactive properties expected to the coats, appropriate quantities of functional submicro-particles of silver and copper doped silica materials were added to the pastes prepared. As established in preliminary tests, the content of this modifier per dry weight of the polymeric coat should be at a level of 2.5 – 3.5%. It should be emphasised here that to obtain the biological effectiveness of the bioactive coats required, it is necessary to create a high, uniform mono-particle dispersion of the submicro-particles of silver and copper doped silica materials in the coating paste as well as in the cross-linked coats. Therefore a homogeneous, mono-particle suspension of silver and copper doped silica materials in water or organic solvent (depending on the polymer used) is prepared by means of an ultrasonic homogeniser and then incorporated into the aqueous dispersion of noncross-linked urethane polymer under intensive stirring. The suspension of silver and copper doped silica materials should be stable and resistant to sedimentation. In the case of coating knitted fabrics by the reversible technique with pastes of non-cross-linked polymers in organic solvents, the suspension of silver and copper doped silica materials should be prepared in the same medium. The conditions of the preparation of the suspension as well as the coating paste are the same as those for the pastes in the form of aqueous dispersions. The coat layers deposited in succession are dried

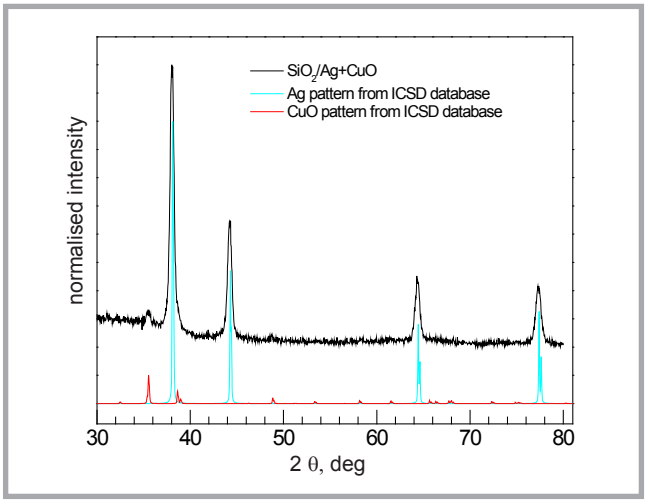

Figure 1. *XRD diffraction pattern of silica spheres overlaid with nano-particles of Ago and copper ions. The clear peaks visible in the diffraction patterns originate from the nano-particles of metallic Ag. Based on Scherrer's formula, it has been determined that the size of Ag crystallites is about 30 nm.*

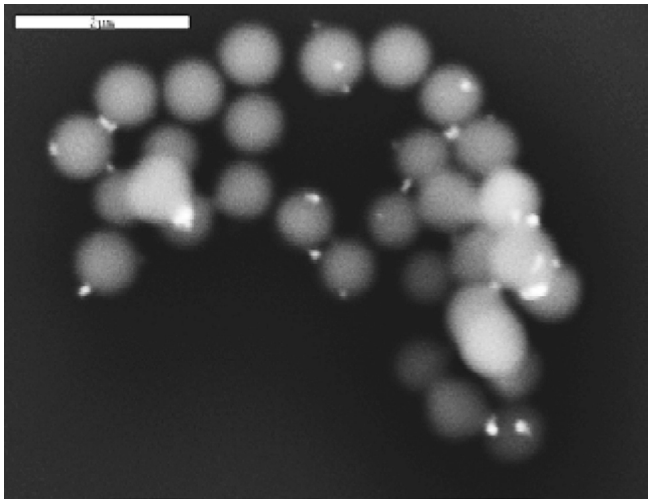

Figure 2. *SEM image of silica spheres with a size of about 500 nm overlaid with Ag0 nanoparticles.*

at temperatures of 80 – 120 °C, and then reheated/cross-linked at a temperature of about 150 -160 °C.

Technology of making bioactive coating materials

Textile carriers

The following textile substrates were used:

- Woven fabric with a plain weave made of multi-filament continuous polyester yarns: warp – PET DTY WP dtex 84f36; weft – PET DTY WP dtex 84f144×2, surface weight 93 g/m^2, designed for the deposition of coats by the direct technique.
- Warp knitted fabric with the following stitches: warp I – cord stitch, warp II – chain stitch of continuous multi-filament polyester yarn, warp I – PET dtex 56f20, warp II – PET dtex 56f20), fabric surface weight – 70 g/m^2; this knitted fabric was designed for the deposition of coats by the reversible technique.

The pretreatment processes (preparation for coating) included:

washing → drying in hot air at 70 - 120 °C → thermostabilisation in hot air in a frame drier-stabiliser at 185 °C for 30 s.

Film-forming polymers

The selection of polymers for the preparation of coating pastes depends on the structure of the textile substrate as well as on the practical applications of coating materials and consequently their expected properties. Therefore in the case of coating materials designed for outer sports or recreation clothing and some types of protective garments, non-cross-linked hydrophilic urethane polymers were used to provide high durability, resistance to water penetration and satisfactory hygienic properties – good water vapour permeability (user's perspiration).

- Non-cross-linked hydrophilic aliphatic polyester-urethanes in the form of aqueous dispersion from Dr. Petry (Germany) for the preparation of coating pastes deposited by the direct technique:
  - Pericoat PUBK – a white highly viscous aqueous dispersion containing 50% of an active substance (anion-active product)
  - Pericoat PU 340 NEW – a white low viscous aqueous dispersion

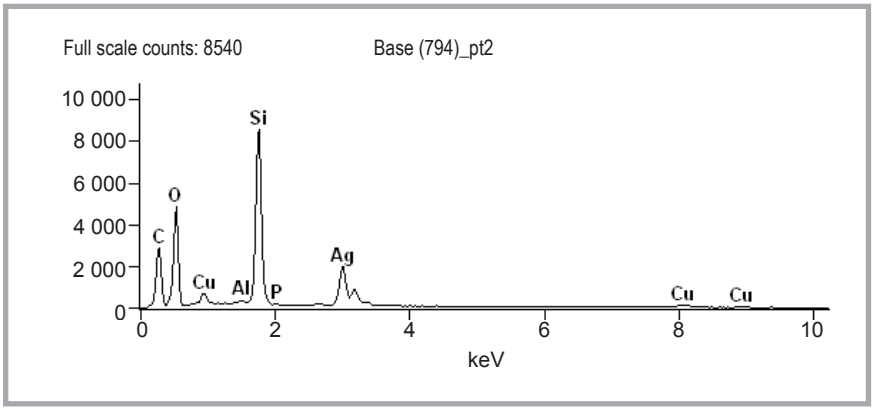

Figure 3. *EDX elementary analysis.*

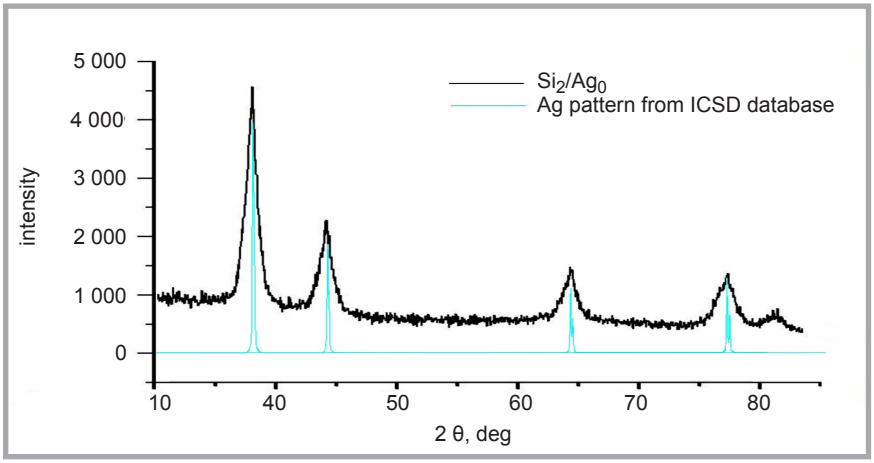

Figure 4. *XRD diffraction pattern of silica spheres overlaid with nano-particles of Ag_0. The clear peaks visible in the diffraction patterns originate from the nano-particles of metallic Ag. Based on Scherrer's formula, it has been determined that the size of Ag crystallites is 19 nm.*

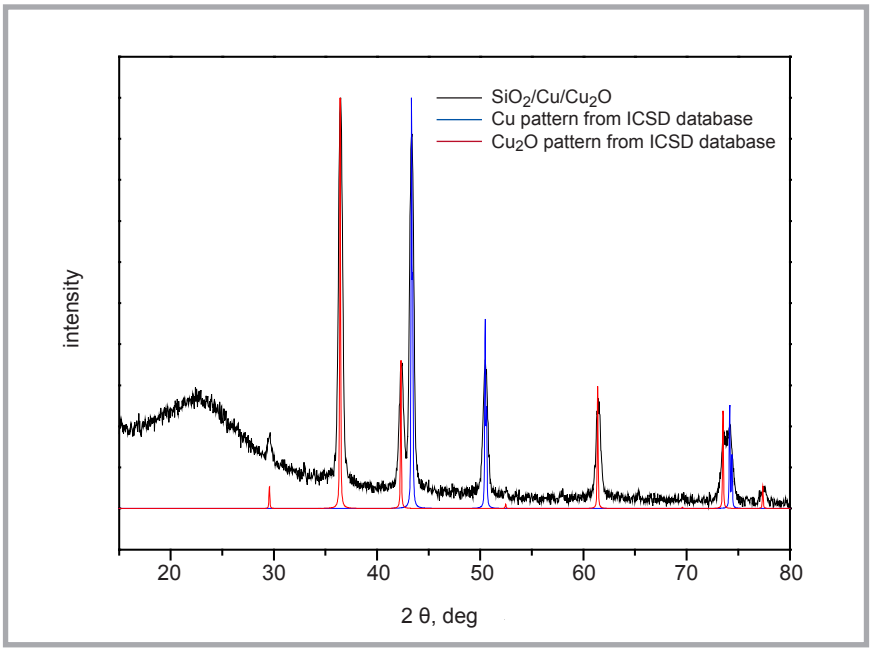

Figure 5. *XRD diffraction pattern of silica spheres overlaid with nano-particles of Cuo and Cu_2O with diffraction patterns of Cu0 and Cu_2O from the ICSD database (Inorganic Crystal Structure Database). The clear peaks visible in the diffraction patters originate from the nano-particles of metallic Cu. Based on Scherrer's formula [D=0.94/(β1/2×cosΘ)], it has been determined that the size of Cu crystallites is 17 nm.*

containing 40% of an active substance (anion-active product)
- Non-cross-linked hydrophilic aromatic, mono-component or two-component polyester-urethane in the form of solutions in organic solvents from Bayer (Germany) for the preparation of coating pastes by the reversible technique:
  - Impraperm AD03 – a highly viscous solution in a mixture of DMF and toluene (35:35) containing 30% of an active substance
  - Impraperm AD01 – a highly viscous solution in a mixture of DMF and toluene (35:35) containing 30% of an active substance
  - Impraperm LH03 – a highly viscous solution in a mixture of toluene and isopropanol (25:50) containing 50% of an active substance.
- Aqueous dispersions of fluoro-organic compounds used as the padding of woven fabrics before coating to prevent paste penetration into the fabric structure, which causes considerable fabric stiffening – Periguard UFC (Dr Petry, Germany).

Fine-particle functional bioactive compounds

The original silver and copper doped silica materials in the form of SiO_2/Ag^0+CuO [19], whose characteristics are presented in Part A, in a quantity of 2.5% in relation to the dry weight of coats were used in the study. Also the submicro-powders of SiO_2/Ag^0 and $SiO_2/Cu^0/Cu_2O$ obtained were used for comparison purposes, in the form of a mixture that was added to the coating paste in a total quantity of 3.5%, which corresponded to the total content of both metals in 2.5% of SiO_2/Ag^0+ CuO.

Coating material technologies

Depending on the type and characteristics of the fabric and coating paste, two technologies were used:

1) the thin-layer (two-layer) direct coating of woven fabrics by means of an 'air' blade using coating pastes in the form of aqueous dispersion;
2) the two-layer reversible coating of knitted fabrics by means of a blade supported on a roller using coating pastes in the form of solutions in organic solvents.

For both layers of coats, i.e. the base or tie and top, pastes of the above-presented polymers with different compositions were used. Regardless of the type of coating paste, the bioactive modifier - silver and copper doped silica materials was used exclusively as a paste forming the top layer of the product. This modifier - SiO_2/Ag^0+CuO or a mixture of SiO_2/Ag^0 and SiO_2/Cu^0+Cu_2O in the form of a highly dispersed mono-particle suspension, either in a water medium or organic solvent, was added under intensive stirring to the other components of the paste.

The deposition of coating pastes on textiles, by both the direct technique (pastes in the form of aqueous dispersions) and the reversible technique (pastes in the form of solutions in organic solvents) was carried out with the use of a laboratory coating-drying line from Mathis (Switzerland) [6].

1) Technological process of coating PET woven fabrics by the direct technique using pastes in the form of aqueous dispersion [19]:
   - Padding with a bath containing a fluoro-organic compound and drying.
   - Base – coating with Pericoat PUBK paste with no modifier and drying.
   - Top – coating with Pericoat PU 340 NEW paste containing silver and copper doped silica material submicro-particles in the form of homogeneous mono-particle aqueous suspension in a quantity of 2.5% or 3.5% in relation to the dry weight of the paste, followed by hot-air drying (temperature 90 °C→120 °C).
   - Curing at 160°C for 60 s to cross-link the polymeric coat and combine it with the surface of the textile substrate.

2) Technological process of coating PET knitted fabrics by the reversible technique using pastes in the form of solutions in organic solvents [6, 19]:
   - Deposition of the polymeric coat on a paper indirect substrate – coating by means of a blade supported on a roller using a paste consisting of two polymeric products: Impraperm AD01 and AD03 with an addition of submicro-particles of silver and copper doped silica materials in the form of homogeneous mono-particle suspension in organic solvents, in a quantity of 2.5% or correspondingly 3.5% in relation to the dry weight of the coat, followed by hot-air drying at 90 °C and curing at 150 °C for 60 s.
   - Deposition of a polymeric layer consisting of Impraperm LH03, cross-linker and catalyst on the coat previously deposited to combine it with the substrate surface.
   - Transferring the polymeric coat formed from the indirect paper substrate onto knitted fabric.
   - Curing at 150 °C for 60 s to cross-link the polymeric coat and combine it with the surface of the textile carrier.

The resultant bioactive coating materials, both the woven and knitted fabrics, showed uniform, smooth, non-sticking surfaces with a soft handle and without local discoloration.

Test methods used to assess the bioactive coating materials

- Determination of the total mass per unit area of the coating material and coat according to PN-EN ISO 2286-2:1999.
- Determination of the thickness of the coating material and coat according to PN-EN ISO 5084:1999.
- Determination of the tensile strength and elongation at break of materials on textile substrates with the use of a Zwick tensile testing machine, model 1120 (Germany) according to PN-EN ISO 1421:2001.
- Determination of the bursting strength of materials on knitted substrates according to PN-P-04738:1979.
- Determination of resistance to water penetration by the hydrostatic method with the use of a Penetrometer FX 3000 from TEXTEST (Switzerland) according to PN-EN 20811:1997.
- Determination of water vapour permeability by the gravimetric method according to Procedure NJC/2/95 (Textile Research Institute); tests under static conditions (temperature, RH) to determine the amount of water vapour (grams) permeable through the sample surface for a specified period of time.
- Determination of water vapour resistance under dynamic conditions according to PN-EN 31092:1998/Ap1:2004, with the use of a Sweating Guarded Hotplate M259B from SDL Int. Ltd.(UK), whose basic element consists of a special micro-porous plate simulating human skin.
- Assessment of the wear and care effect on the level of resistance to water

penetration and bioactive properties of coating materials simulated by 20-fold laundering according to PN-EN ISO 6330:2002/A1:2011, Procedure 5A (40 °C) in an automatic washing machine, type A from Electrolux (Sweden).

- Assessment of antibacterial and fungicidal properties according to ASTM 2180, by the quantitative method to determine the percentage reduction in bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumoniae* and percentage reduction in fungi: *Candida albicans*, *Aspergillus niger* and *Trichophyton mentagraphytes* in relation to unmodified materials.
- X-ray micro-analysis (EDX) was used to confirm the presence of silver and copper particles deposited on the surface of silica submicro-spheres developed and also to assess quantitative changes in metals in the bioactively modified polymeric coats resulting from wear and care processes such as multiple laundering.
- SEM analysis with the use of a scanning electron microscope HITACHI S-3400 N. Samples of the materials to be tested were in the form of a suspension in EtOH deposited on appropriate plates and dusted with carbon. The resultant photographs were used to determine the size and shape of spheres, the degree of their aggregation and location of metal particles. SEM analysis was also used to assess the uniformity of distribution of silica submicro-particles in the polymeric coat modified with the submicro-powders developed.
- XRD – X-ray diffractometry with the use of a polycrystalline X-ray diffractometer - ULTIMA IV/Rigaku/2008. The resultant measurement results confirmed the presence of nano-particles in the metallic materials, while a lack of reflection indicated the presence of metal in a non-crystalline form (e.g. ionic form). The size of metallic silver nano-particles was calculated on the basis of Scherrer's equation.

Results and discussion

Characteristics of the bioactive coating material obtained are given in ***Tables 1*** and ***2***. From the test results given in these tables it follows that the coated textiles containing 2.5% of SiO_2/Ag^0+CuO submicro particles incorporated into the polymeric coat show no adverse changes in their mechanical properties compared to those of corresponding unmodified materials (without the submicro-particle

Table 1. *Mechanical properties of coating materials.*

Samples		Surface weight, g/m²		Thickness, mm		Tensile strength, N		Elongation at break, %		Bursting strength, N
		total coating material	polymeric coat	coating material	polymeric coat	length wise	cross-wise	length wise	cross-wise	
PET knitted fabric	Impraperm AD03+01	121	53	0.33	0.08	-	-	-	-	31.40
	Impraperm AD03+01+2.5% SiO_2/Ag^0 + CuO	129	61	0.31	0.06	-	-	-	-	32.80
PET woven fabric	Pericoat PUBK +340 NEW	171	78	0.37	0.08	445	550	12.00	17.00	-
	Pericoat PUBK+340 NEW+2.5% SiO_2/Ag^0+CuO	171	78	0.33	0.08	457	551	14.00	20.00	-

Table 2. *Functional properties of coating materials.*

Samples		Resistance to water penetration, cm		Water vapor permeability, g/m² 24 h	Resistance of water vapor, m²Pa/W
		before laundering	after 20 launderings		
PET knitted fabric	Impraperm AD03+01	1000	560	1414	14.09
	Impraperm AD03+01+2.5% SiO_2/Ag^0 + CuO	1000	500	1426	13.04
	Impraperm AD03+01+3.5% [SiO_2/Ag + SiO_2 / Cu^0+Cu_2O]	923	298	1498	14.50
PET woven fabric	Pericoat PUBK +340 NEW	1000	420	1373	14.12
	Pericoat PUBK +340 NEW +2.5% SiO_2/Ag^0 + CuO	970	300	1396	15.13

Table 3. *Bioactive of coating materials.*

Samples		Reduction in bacteria, %R					
		Staphylococcus aureus		*Escherichia coli*		*Klebsiella pneumoniae*	
		Before laundering	After 20 launderings	Before laundering	After 20 launderings	Before laundering	After 20 launderings
PET knitted fabric	Impraperm AD03+01+2.5% SiO_2/Ag^0 + CuO	99.99	99.90	99.99	99.99	99.90	95.40
	Impraperm AD03+01+3.5% [SiO_2/Ag + SiO_2 / Cu^0+Cu_2O]	73.90	73.90	99.90	99.20	99.20	94.00
PET woven fabric	Pericoat PUBK +340 NEW +2.5% SiO_2 Ag^0 + CuO	99.80	99.80	99.99	99.90	99.90	99.90
Samples		**Reduction in fungi, %R**					
		Candida albicans		*Aspergillus niger*		*Trichophyton mentagraphytes*	
		Before laundering	After 20 launderings	Before laundering	After 20 launderings	Before laundering	After 20 launderings
PET knitted fabric	Impraperm AD03+01+2,5% SiO_2/Ag^0 + CuO	99.99	99.98	99.94	99.00	99.96	98.10
	Impraperm AD03+01+3,5% [SiO_2/Ag + SiO_2 / Cu^0+Cu_2O]	99.99	99.80	90.40	59.95	97.50	49.75
PET woven fabric	Pericoat PUBK +340 NEW +2,5% SiO_2/Ag^0 + CuO	99.99	99.99	99.40	56.40	96.50	92.10

modifier in the top coat layer). The coating materials modified in this way show the antibacterial and fungicidal properties expected, as presented in ***Table 3***. It is evident from ***Tables 2 & 3*** that the textiles modified with the mixture of two kinds of powders: SiO_2/Ag^0 and SiO_2/Cu^0+Cu_2O, in a total quantity of 3.5%, show a decrease in resistance to water penetration of about 10%, and a considerably greater drop in the resistance to water penetration can also be observed after 20 standardised launderings, indicating that the incorporation of increased quantities of inactive silica spheres constituting over 75 - 80% of the modifiers exerts an adverse influence on the respective properties.

As follows from the data given in ***Tables 1, 2 and 3***, the coating materials modified with submicro-particles of SiO_2/Ag^0+CuO, added in a quantity of 2.5% in relation to the dry weight of the polymeric coat, regardless of the coating processes and textile substrates, are characterised by high and stable antibacterial and fungicidal activity as well as other properties suitable for various functional applications. Owing to the gradual release of silver and copper ions from the polymeric coating containing active submicro-particles of SiO_2/Ag^0+CuO, the materials developed, in addition to a high level of biological features, are safe for users. The use of the same matrix as a carrier of bioactive nano-particles to obtain two different microbiological effects at the same time has important economic and technological aspects.

On the one hand, the fact that it is possible to obtain the expected antibacterial and fungicidal effects with the use of a considerably decreased quantity of submicro-particles, compared to that containing only nanoparticles of one metal (in a considerably increased quantity), significantly reduces undesired structural disturbances in the polymeric matrix. This has a beneficial influence on the coat quality - its mechanical resistance and functional properties – simplifies the technological process of coating paste preparation, and eliminates one of the possible sources of errors.

Nevertheless the cost of using lower quantities of SiO_2/Ag^0+CuO is simply smaller than that of adding appropriately increased amounts of SiO_2/Ag^0 and SiO_2/Cu^0+Cu_2O. This solution is of particular importance when coating materials are used for the bioactive modification of textile-polymeric coating materials. In this case, the incorporation of submicro-spheres of SiO_2/Ag^0+ CuO into the structure of the polymeric coat allows one to obtain good biological effects and simultaneously to reduce the addition of submicro-particles, consequently minimising the possible adverse influence of the mechanical characteristic and functional properties of the coat. Bio-actively modified coating materials made on woven or knitted carriers of polyester fibres, being characteristic of fabrics for sports and recreation outerwear, are characterised by a high resistance to water penetration amounting to about 1000 cm of the water column. Multiple standardised laundering (20-fold) of modified and unmodified materials results in the same drop in this parameter for both types of materials - ***Table 2***. The modifier used does not deteriorate either the resistance to water penetration, water vapour permeability or water vapour resistance of the materials modified, which indicates a good capability of carrying off human perspiration. The test results of water vapour resistance obtained at a level of about 14 $m^2 \cdot Pa/W$ should be accepted as very good and corresponding to the requirements of the highest class – 3 indicated by the standard concerning protective clothing – protection against rain, establishing that a water vapour resistance of $< 20\ m^2 \cdot Pa/W$ is required.

The antibacterial effectiveness of the modified coating materials in relation to three common bacterial strains *Staphylococcus aureus*, *Escherichia coli* and *Klebsiella Pneumoniae* is very good, and the antibacterial effect obtained is resistant to 20-fold laundering under standardised conditions. The fungicidal activity of the woven and knitted fabrics modified with SiO_2/Ag^0+CuO in relation to fungi such as *Candida albicans*, *Aspergillus niger* and *Trichophyton mantagraphytes* is also very good and resistant to 20 standardised launderings. This result indicates that the bioactive submicro-particles are very well combined with the coat material and consequently with the textile substrate. The submicro-particles of SiO_2/Ag^0+CuO are neither released from the structure of the polymeric coat nor migrate to the coat surface, which is due to the uniform, mono-particle dispersion of SiO_2/Ag^0+CuO in the coat material, excluding the formation of aggregates or clusters of submicro-particles, the good adhesive combination of the nanoparticles of bioactive Ag^0 and CuO with the surface of matrices developed and the protection of the polymeric coat by surrounding submicro-particles against external effects - ***Figure 6***. Thus the bioactive submicro-particles incorporated have no adverse effect on the structure of the bio-actively modified polymeric coats.

Finally, the high bioactivity of the textile-polymeric coating materials obtained by the modification of coats with submicro-particles of SiO_2/Ag^0+CuO as well as the absence of adverse effects of the modifier

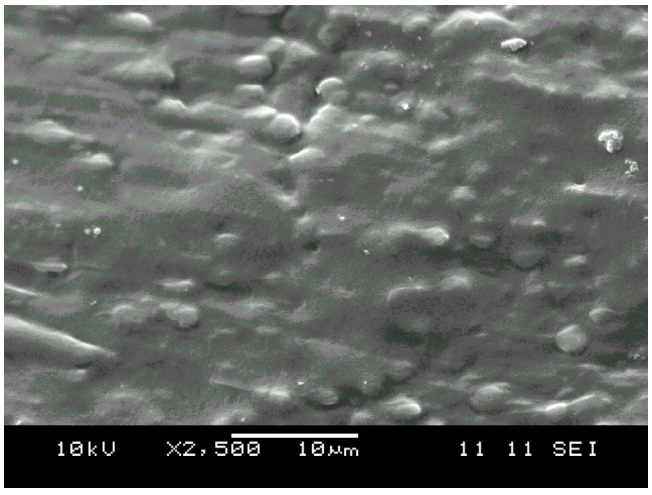

Figure 6. *SEM image of the polymeric coat surface with submicro-particles of $SiO_2/Ag0+CuO$.*

used on the barrier properties (resistance to water penetration) and hygienic properties (water vapour permeability and resistance) of both the polymeric coats and textile-polymeric coating materials make it possible to widely use these materials for various practical and functional applications.

Conclusions

1) The original submicro-particle functional material SiO_2/Ag^0+CuO developed is an effective bioactive modifier that simultaneously imparts remarkable antibacterial and fungicidal properties to textile-polymeric coating materials. The biological activity obtained is stable and resistant to intensive wear and care conditions, imitated by 20-fold laundering under standardised conditions.
2) The submicro-particle SiO_2/Ag^0+CuO modifier developed, when used in a quantity of 2.5% (in relation to the dry weight of the coat), imparting great biological activity towards common bacterial strains and colonies of fungi to the coating materials, causes no noticeable deterioration in the mechanical, functional and hygienic properties of these materials, including resistance to water penetration, water vapour permeability compared to those of corresponding unmodified coating materials.
3) The use of the bioactive submicro-particle SiO_2/Ag^0+CuO modifier developed is more beneficial than the application of a mixture of submicro-particle SiO_2/Ag^0 and SiO_2/Cu^0+Cu_2O modifiers. The technological advantage results from the fact that SiO_2/Ag^0+CuO is used in a lower quantity in relation to the indispensable addition of materials containing single metals, which brings about a smaller loading of the polymeric coats with inactive silica spheres and consequently smaller interference in the coat structure. Hence the final materials have both better durability and functional properties. Moreover, the preparation of coating pastes is simplified and they have better rheological properties.
4) The original submicro-particle SiO_2/Ag^0+CuO modifier can be used by means of various finishing methods such as direct coating and reversible coating with pastes in the form of aqueous dispersions or solutions in organic solvents.
5) Thanks to the great biological activity imparted to the coating materials modified as well as the durability and resistance of the bioactivity effect obtained to external conditions, these materials are suitable for miscellaneous and wide functional applications.
6) The submicro-particle bioactive SiO_2/Ag^0+CuO modifier developed is made in the form of a loose brown powder with well separated grains, which is suitable for the preparation of highly dispersed, mono-particle suspensions in both an aqueous medium and organic solvents. This submicro-particle shows no changes during prolonged storage.

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