NANOCOATING PROCESS FOR TEXTILES APPLICATIONS AND WOOD PROTECTION

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Abstract: *This paper presents the research results obtained in ERA NET MANUCOAT project, coordinated by INCDTP in collaboration with the following partners: INCDMNR-IMNR, SC MGM STAR CONSTRUCT SRL – Romania and IRIS-Spain.*
The objective of the research was to develop and obtain textile and wood surfaces with self-cleaning, photo catalytic, antibacterial and antifungal properties.
An innovative method of manufacturing nanoparticles by hydrothermal process in a single step without any further heat treatment and controlled stoichiometry, tested spray coating technology (sputtering) were developed. Full characterization of nanostructured powders in terms of chemical, physical, structural, thermal and technological characteristics was performed.The most important features to be considered in the treatment of wood by sputtering in order to deposit thin layers of TiO_2 NPs or TiO2/Ag as the humidity should be below 12% and the maximum roughness P150, depending on the species of wood.
Future works envisage optimizing the existing sputtering systems for pilot stage, in order to make nanoparticles deposits on large areas of textile and wood. The results of the research are photocatalytic textiles for surgical gowns, operative fields, hospital bed sheets and curtains and drapes for public spaces.

Key words: *TiO_2 nanoparticles, sputtering coating, photocatalytic textiles, antibacterial/antifungal, durable wood*

1. INTRODUCTION

In the global competition environment textile companies will always try to obtain a significant market share through product quality improvement and new technologies or products development. Also, consumers demand high performance textiles for both casual wear and for technical textiles.

Textiles with antimicrobial, antifungal efficacy and photocatalytic properties are required by fields such as medicine, defense, sports and leisure, for covers and draperies for public spaces and passenger compartments.

At its turn, wood is an excellent material for building, furniture, art objects but in natural state it is unfortunately not resistant to weather, insects and fire. Structures, surfaces and wood objects must be long lasting in order to be attractive to customers and to compete with other materials.

Photocatalytic activity, non-toxicity, high availability, biocompatibility, and low price make TiO2 nanoparticles particularly attractive for manufacturing textiles and wood products with high performances. When nano TiO_2 are irradiated with light of higher energy than its band gap, electrons and holes pairs are generated on its surface. Holes produced during an oxidative reaction can react with water and generate hydroxyl radicals and electrons. Anions of superoxide radical are created during reduction with oxygen. Active oxygen species and hydroxyl radicals can oxidize organic compounds to carbon dioxide and water as shown in the following reaction [1].

$C_nO_mH_{(2n-2m+2)} + \bullet OH + O^{-}_2 \rightarrow nCO_2 + (n-m+1)H_2O$ **(1)**

Different methods for fabric treatment with nanoparticles are known and were studied: padding, ultrasonic treatment, plasma and electro-spray and sputtering.

This paper presents the lab experiments of TiO_2 nanoparticles deposition on textiles and wood by physical methods, sputtering.

2. EXPERIMENTAL PART

2.1. Technology for obtaining TiO_2 nanoparticles

The characteristics of TiO_2 nanoparticles depend mainly on the method applied for their synthesis. The size, shape, crystalline structure and specific surface determine the electrical, chemical, optical properties and the photocatalytic activity of TiO_2 nanoparticles.

The innovative technology for obtaining nanostructured powders of TiO_2 and TiO_2 doped with Ag was developed by IMNR at laboratory level. Hydrothermal synthesis in one step, at high pressures (1000-3000 atm) and low temperatures starting from soluble inorganic salts of titanium and silver, is used to prepare silver doped nanostructured anatase. Hydrothermal process approach represents an alternative to the sol-gel, ball milling or spray pyrolysis processes used to prepare doped TiO_2. Hydrothermal synthesis presents some advantages, namely: it is an environmentally friendly procedure, it enables the formation of nanostructured anatase phase (>95%) and the dopant level can be controlled [2] [3].

The nanostructured powders were characterised in terms of chemical, physical, structural, thermal characteristics and photo catalytic properties, toxicity and antibacterial properties.

2.2 Textile substrates

The selection of textile substrates takes into account the following requirements: breaking and tear strength, elongation, abrasion resistance, thermal resistance, surface and volume resistivity, air permeability, water-vapour resistance, water permeability, the user and last but not least the cost. The textile materials were selected for areas of application where the functional effects, photo catalytic, antibacterial and antifungal properties are the most requested: hospitals, public spaces, clothes, home interior. We analysed nine textile substrates with different fibre compositions in terms of the characteristics mentioned above. The selected textiles were: Rafia-fabric from textured yarns, 100% polyester with crepe weave, for covers and curtains used in public spaces; Mihaela-fabric from shiny three lobe yarns and microfilaments yarns, 100% polyester with satin weave, for surgical gowns and drapes; Ivona-fabric made of 100% cotton, with combined pattern weave (vertical stripes), for hospital and home bed linen; Fabric code 154-5069 made of 55% polyester + 45% wool, for women dress. The selected textiles were used as substrates for the deposition of nanostructured layers which give them photocatalytic, antimicrobial and antifungal properties [4].

2.3 Wood substrates

For the selection of the wood substrates to be used during the project, the partners had intense discussions to ensure the compatibility of the substrates with the different set-ups of the project and their industrial relevance. Three wood types were selected to be analysed in the project: oak, beech and cherry. The oak was chosen for its intensive use for interior works and furniture. High density and high tannin content give this wood resistance against fungi, but its aspect is strongly affected by UV radiation and aging. TiO_2 nanoparticles surface treatment removes these disadvantages. Beech is one of the most common species of deciduous wood for interior applications. Its low porosity prevents protective treatment by impregnation, making it difficult to use for outdoor applications. Surface activation and treatment with TiO_2 nanoparticles provide the opportunity for its use in outdoor applications. Cherry wood was selected for its use in the manufacturing of art objects.

The most important characteristics to be considered in the treatment of wood by plasma or sputtering in order to deposit thin layers of TiO_2 or TiO_2/Ag nanoparticles are:

- Humidity, must be below 12%; first tests will be done with samples with humidity between 10-15% (depending on species);
- Roughness depends on wood species, ideally P150 grit ISO / FEPA.

Rugosity and humidity are the only parameters usually provided by wood manufacturers.

2.4. Sputtering technology

Experimental deposition of nanostructured thin layers was performed by sputtering [5] [6]. Sputtering technology is a physical method deposition which involves removing the source material deposition at a temperature much lower than evaporation. The experiments for the deposition of TiO_2

and Ag/TiO_2 nanoparticles on small size substrates of textiles and wood were performed on VU-2 M vacuum equipment. Basically, the method involves placing the substrate and material deposition in a vacuum chamber in the presence of an inert gas. TiO_2 and TiO_2/Ag nanoparticles powders was pressed into 2 g pills. Then it was sintered in high vacuum equipment VU-2M, equipped with 2 inch sputtering, e-gun and resistive sources, glow discharge plasma cleaning system, carousel and thickness monitoring. Sintering was tested by electron beam heating and resistive method. It was concluded that resistive method is preferable because the electron beam pulverizes the material. The equipment has rotation and monitoring system of deposition rate and thickness control. Before the deposition process, textile and wood substrates were treated in Argon-Oxygen plasma to purify the surface. Sputtering deposition system performs simultaneously two functions: surface activation and deposition of TiO_2 nanoparticles or TiO_2/Ag. The deposition rate and thickness was monitored by Inficon XTC quartz controller with parameters set for TiO_2 (density of 4.26 g / cc and Z-ratio of 0.4). The sputtering deposition cannot be included in the continuous wood and textile production process, being used in a discontinuous –offline process (in comparison with the plasma treatment method that can be used in a continuous – online process).The sputtering experimental works were performed at laboratory scale on small textile and wood areas. Textile substrates have been covered with 5 and 10 nm TiO_2 and with 5 and 10 nm Ag/TiO_2 by RF sputtering.

3. RESULTS AND DISCUSSIONS

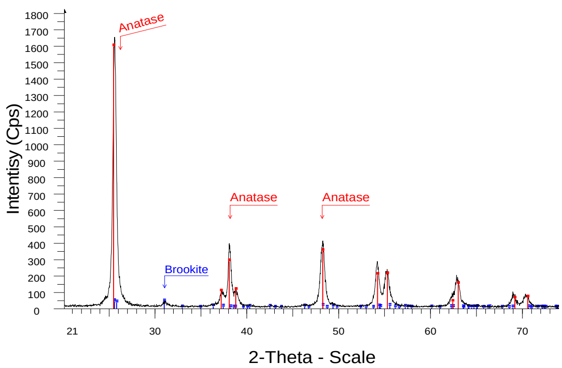
3.1. Technical characteristics of nanoparticles obtained by hydrothermal technology

Chemical components of NPs obtained at lab scale are presented in table 1:

***Table 1**: Chemical components of NPs*

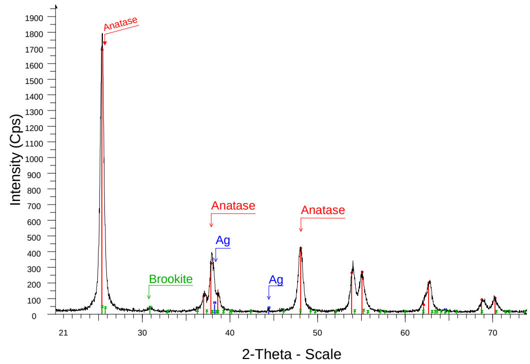
Sample code	Components %	
	Ti	Ag
MCTi	59.5	-
MCTiAg	58.4	0.52

XRD spectrum for lab nanoparticle samples is presented in figures 1 and 2.



Compound Name	Formula	S-Q(%)
Anatase	TiO_2	98.3
Brookite	TiO_2	1.7
Silver	Ag	0.0

***Fig.1**: XRD spectrum for MCTi samples.*



Compound Name	Formula	S-Q(%)
Anatase	TiO_2	93.5
Brookite	TiO_2	6.0
Silver	Ag	0.5

***Fig.2**: XRD spectrum for MCTiAg* samples

The best photocatalytic activity (100%) of the MCTiAg sample was measured at 75 min. For the MCTi sample the best photocatalytic activity (97.071%) was measured at 150 min.

3.2. Characteristics of textiles and wood samples nanocoating by sputtering

The textile and wood samples coated with TiO_2 and TiO_2 /Ag were analysed in terms of morphology and elemental composition of the deposited layers and the functional effects namely: hydrophobicity / hydrophilicity, photocatalytic effect, surface and volume electric resistant, antibacterial and antifungal effect.

3.2.1 The morphology of the textile materials and structure of the deposited layers have been analysed by scanning electron microscopy, (Quanta 200, FEI, Netherlands), figure 3.

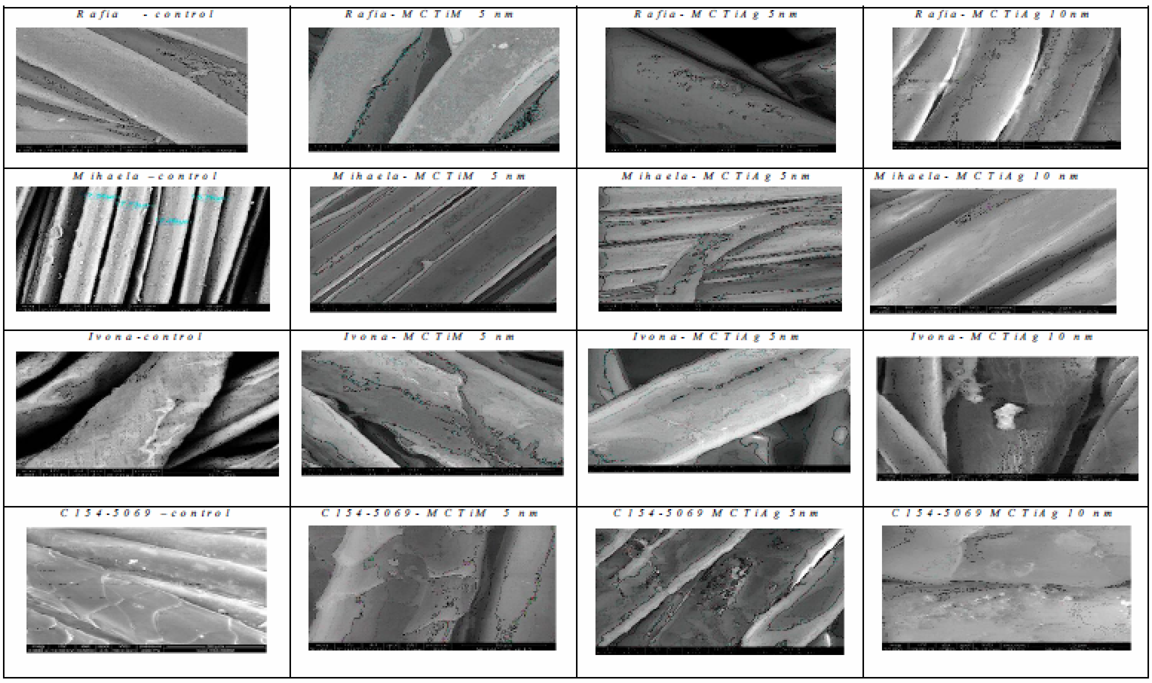


Fig.3: *The morphology of the textile materials and structure of the deposited layers*

The sputtering coatings of Rafia do not significantly modify the surface characteristics of the PET fibres. In the case of Mihaela only a few nanoparticles are seen on the fibres covered with 5nm TiO_2 layer (MCTi) while the fibre coated with a thicker layer (10nm) is very smooth and uniform. The difference could come from the smoother, finer fibres (76.3 den, 108 µm diameter) used in the warp of Mihaela sample compared to Rafia sample (168.4den, 179 µm diameter). In the case of Ivona sample with 10nm sputtering, the layers seem more uniform, covering the fibres better. After the deposition of TiO_2 and Ag/TiO_2, on code 154-5069 fabric, both the polyester and wool fibres composing the sample are covered with a thin layer of metal oxide, creating a smoother surface.

3.2.2 The identification of the metals deposited on samples

The EDX unit connected to the SEM microscope was used to determine the chemical contents of elements presented in the surface of coated fabrics.

EDX spectra for Rafia indicate the presence of TiO_2 and Ag/TiO_2 on the material. The dominant elements are carbon attributed to polyester fibres and oxygen attributed to polyester fibres and titanium oxide. The sample presents a higher Ag/Ti ratio for coatings with 10nm (Ag/TiO_2 = 0.21) than for those with 5nm (Ag/TiO_2 = 0.3). This behaviour is largely due to hydrophobicity and polyester fibres structure which allow uniform deposition of oxide films. For coated Mihaela material, the ratio Ag/Ti is 0.27 for 5 nm coatings and it increases to 0.42 for deposits thicker than 10nm. For the Ivona sample covered with 10nm Ag/TiO_2 spectra were performed for particles present on the surface of the material. Due to the presence of other elements and especially of large amounts of carbon and oxygen from the substrate, practically Ag/Ti ratio has relatively high error margins. EDX spectra for fabric code 154-5069 confirm the deposition of TiO_2 and Ag/TiO_2. The amount of silver and titanium increases as the layer thickness grows.

3.2.3 Hydrophobicity/hydrophilicity of the nanocoated samples are analysed by measuring their contact angle, using the VCA Optima equipment and distilled water as test liquid.

The materials' wetting capacity modifications induced by sputtering show the results:

- Rafia sample is initially hydrophilic, due to fibres type and to large interspaces between yarns and after sputtering nanocoating it becomes hydrophobic (about 124^0).
- Mihaela sample is initially hydrophobic (88^0) and after sputtering nanocoating it becomes hydrophilic due to polar groups: =C=O, -O-C= O, -COH, -COOH, -CH2OH and better adherence of TiO_2.
- Ivona sample is strongly hydrophilic (0^0), both initially and after deposition, the water drops being instantaneously absorbed by the materials.
- Fabric Code 154-5069 is initially and after deposition highly hydrophobic (about 130^0).

3.2.4 Evaluation of the photocatalytic activity

Evaluation of photocatalytic effect was performed by two methods:

- Photodegradation of methyl orange solution with different concentrations (0.01, 0.005, 0.002 g /L) and exposure to UV radiation under stirring (λ = 254nm and 365nm);
- Measurement of the colorimetric coordinates of the initial samples and of the stained samples after exposure to artificial light. The samples coated with 5nm layer of TiO_2 and Ag/TiO_2 were spotted with 3 drops of 0.02g/L Methylene Blue(MB), 0.02g/L Methyl Orange(MO), coffee (C). The spotted samples have been exposed to artificial light according to standard ISO 105- B02:2013 in Apollo light fastness tester provided with Xenon lamp, simulating sunlight, wavelength: 300-700nm, the lamp irradiation: $42W/m^2$, humidity 45%, light exposure temperature:50^0C. UV-VIS spectra of solution 0.002g/L MO + Ivona coated with 5nm MCTiAg and 10nm MCTiAg exposed to UV radiation (365nm) are presented in figure 4 a) and 4b).

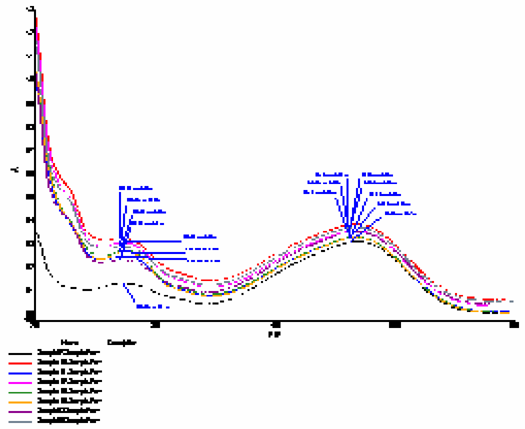


Fig.4 a): *UV-VIS spectra of solution*0.002g/L *MO + Ivona coated with 5nm MCTiAg*

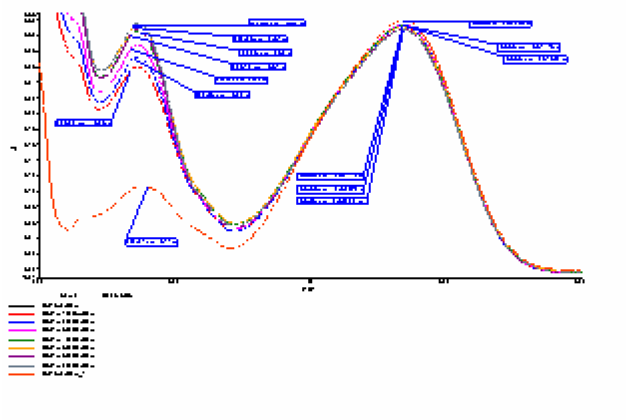


Fig.4 b): *UV-VIS spectra of solution*0.002g/L *MO + Ivona coated with 10nm MCTiAg*

Photodegradation efficiency after 4 hours is 15.38% for 5nm MCTiAg and 4.06% for 10 nm MCTiAg.

The second method for the evaluation of colours of stained samples after exposure to artificial light uses the spectrophotometer Hunterlab with 0/45 degrees geometry. Spotless original material was the reference.

Table 2: *Colour difference for stained samples after exposure to light*

Sample/Stained with	Initial				MCTiAg 5 nm			
	dL*	da*	db*	dE*	dL*	da*	db*	dE*
Rafia/ C	1.4	-0.43	0.67	1.61	1.36	0.77	1.14	1.93
Rafia/ MO	3.54	-0.65	-0.18	3.61	4.19	-0.62	-2.04	4.7
Rafia/ AM	2.39	-0.5	-0.02	2.44	2.53	-0.24	-1.41	2.91
Mihaela/C	-4.45	-1.84	16.37	17.07	-2.38	-2.94	13.67	14.18
Mihaela/MO	-0.69	-2.06	7.1	7.42	-1.31	-2.85	10.23	10.7
Mihaela/AM	-1.1	-1.89	5.79	6.19	-1.09	-2.79	8.87	9.36
Ivona/C	-9.5	-0.96	25.99	27.69	-9.47	-1.62	28.18	29.77
Ivona/MO	-2.6	-2.22	19.06	19.36	-2.83	-2.33	18.73	19.08
Ivona/AM	-10.38	-4.94	8.26	14.15	-7.22	-4	10.35	13.24
Code 145-5069/ C	1	-1.59	-2.09	2.81	0.95	-1.29	-2.08	2.63
Code 145-5069/ MO	1.09	-1.4	-2.64	3.18	2.82	-4.61	-5.38	7.63
Code 145-5069/ AM	1.08	-1.63	-2.58	3.23	1.58	-3.84	-4.4	6.05

Total colour difference (DE *) is almost double for all treated stained materials compared with the original material stained and exposed for 67 hours to artificial light, except for the sample code 154-5069.

3.2.3. Antibacterial and antifungal effect

Antibacterial effect was tested at E.Coli and E. Aureus in conformity with SR EN ISO 20645:2005 and antifungal effect was tested at Candida albicans and Trichophyton interdigitale in conformity with ASTM E2149-01 and ISO 20743:2007. The samples tested were Mihaela and Ivona for medical sector.Mihaela sample treated with MTTiAg 5 nm and 10nm presented a satisfactory antibacterial effect. Ivona sample treated with MTTiAg 5 nm presents antibacterial efficiency at limit.

Textile samples treated with Ag/TiO2 presented excellent results when tested against Candida albicans. All treated samples have a 100% reduction of microbial population, when compared to untreated control samples. The reduction rates were lowered on the same textile tested against strain of Trichophyton interdigitale, ranging from 47%, lowest reduction;

Materials treated only with TiO_2 didn't exhibit significant reduction in microbial population, compared to untreated control samples.

3.3. Characteristics of the wood samples' nanocoating by sputtering

Changes induced by nanocoating of wood samples were determined by measuring the contact angles using the same method and the same equipment as for textiles.

After nanocoating with TiO_2 by sputtering, 5 nm and 10 nm all 3 types of wood presented the contact angle higher by about 16^0 than initial samples.

After nanocoating with TiO_2/Ag, 5 nm and 10 nm all 3 types of wood presented the contact angle higher by about 30^0 than initial samples.

4. CONCLUSIONS

- All natural and synthetic fibres can be treated with TiO_2 or TiO_2/Ag nanoparticles by sputtering with technology conditions appropriate for each type of material;

-Powder TiO_2/Ag nanoparticle samples containing anatase phase in 93%;

- Powders componence is as follows: 59.5% titanium in TiO_2 and 58.4: titanium 0.52% silver for TiO_2/Ag ;

- The sample of MCTiAg presented the highest photocatalytic activity (100%) and was measured at 75 min;

- Sputtering deposition method has the advantage of two functions simultaneously, activation of the substrate surface in plasma and deposition of nanoparticles;

- Photocatalitic efficiency for 100% cotton sample after 4 hours is 15.38% for 5nm MCTiAg and 4.06%. for 10 nm MCTiAg;

- Textile samples treated with Ag/TiO_2 presented excellent results when tested against Candida albicans (100% reduction of microbial population) and 47% against Trichophyton interdigitale;

- Sample made of 100% cotton treated with Ag/TiO_2 5 nm and 10nm presented a satisfactory antibacterial effect and sample 100% polyester treated with MTTiAg 5 nm presents antibacterial efficiency at limit.

The results of technical characteristics of nanopowders and nanocoated textiles and wood will allow optimisation of the TiO_2 and Ag/TiO_2 synthesis at pilot scale.

The results of samples' characteristics obtained by lab scale sputtering technology provide important information for the optimization of the existing sputtering systems at MGM STAR CONSTRUCT for pilot stage.

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