NANOPARTICLES AND DEPOSITION METHOD FOR PHOTOCATALYTIC TEXTILES AND DURABLE WOOD

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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. Requirements for the textiles with multi-functional properties and durable wood are increasingly higher. New photocatalytic textiles with sensitivity in the visible spectrum, antibacterial and antifungal properties and wood with increased durability to environmental conditions were developed. To this aim, the obtaining of nanostructured undoped and Ag-doped TiO2 powders with characteristics that enable their deposition by physical methods and with an extended absorption in the visible region and establishment of the technological parameters for physical deposition technique represents the main issue. The innovative elements presented consist in the development of hydrothermal technology to obtain doped TiO2 NPs Anatase with extended absorption in the visible region and increase of the photo degradation rate and the manufacturing of new flexible, smooth nanostructured layers on textile and wood materials through improved physical method (plasma electro-spay, RF sputtering). The influence of different nanoparticles composition and coating methods of textile and wood is discussed through the main analyses and their results: contact angle, SEM/EDX, surface and volume resistivity, degradation rate of the methylene blue/methyl orange, antifungal and antibacterial effect, washing fastness.

Keywords: TiO_2 nanoparticles, sputtering method, photocatalytic textiles

INTRODUCTION

During the past several years the demand of different textiles with multifunctional properties such as self-cleaning and antibacterial was intense. Also TiO_2 NPs was selected for it photocatalytic activity, non-toxicity, high availability, biocompatibility, and low price. In order to obtain textile materials with antimicrobial performances, many procedures are used: impregnation of the fibrous material with a solution, suspension or emulsion of the bactericidal (fungicidal) product; padding of an antimicrobial product, from its soluble state into an insoluble one on the fibrous material; binding of an antimicrobial product on the fiber through chemical bonds (ionic, coordinative, covalent); immersion of a bactericidal product either in the spinning solution or melt, during preparation of the chemical fibers (Coman *et al.*, 2010).

The increasing environmental concerns and demands for an environmentally friendly processing of textiles leads to the development of new technologies like physical methods for deposited of NPs on textiles and wood substrate: plasma electrospray and RF sputtering.

In the same respect we are develop the synthesis of TiO_2 nanoparticles is an economical alternative to relatively expensive and highly polluting multi-steps wet chemical processes. Based on the relationships between the physical and chemical characteristics of doped titanium and their photocatalytic and antibacterial performance revealed by the literature data, the powders selected to be deposited on textile and wood substrates and their expected properties are: titanium Anatase phase amount > 95%, crystallite size at the nanoscale, silver dopant type, dopant concentration 0,5-2,0 mol%, photocatalytic activity in the visible range and antibacterial properties (Gupta *et al.*, 2013).

EXPERIMENTAL PART

Nanoparticles

The Anatase TiO_2 nanoparticles or TiO_2 doped with Ag were synthesized through an innovative hydrothermal technology in aqueous media, at low temperatures and high pressures in one step without any further thermal treatment.

The characteristics of NPs synthesized and used in our experiments are:

- TiO_2 nanoparticles: Anatase = 26.16 nm, Brookite = 8.19 nm in percentage of 98% Anatase and 2% Brookite;

- TiO_2 doped with silver nanoparticles: Anatase = 23.13 nm, Brookite = 25.73 nm and Silver = 59.90 nm in percentage of 93.5% Anatase, 6.0% Brookite and 0.5% Silver.

Textiles and Wood

Perla fabric designed for curtains, covers and other uses in public spaces. Diferent Wood samples

Physical Deposition Methods

For the electrospray deposition the nanoparticles was dispersed into a liquid that is forced with a controllable solvent pump to go through an electrified capillary, typically made of steel. Before nanoparticles deposition the fabric surface was activated in DBD atmospheric plasma, non-thermal, in order to improve nanoparticles adhesion on surface, decontaminate fabrics prior to deposition, removing or decreasing the microorganism load, clean the surface from dirt or fats. The speed of fabric was between 1-10 m/minute. For this deposition method, IRIS Spanish partner up-scaling the equipment at pilot scales.

The sputtering deposition was made in the vacuum equipment VU-2M that were pilot up-scaled, by sputtering circular source TORUS 2’’ HV, radio frequency power supply R301 MKII, automatic matching network EJAT3 and matching network controller EJMC2.

The nanoparticle of titanium dioxide and silver doped titanium dioxide were sintered in targets that were bonding with an electrically conductive silver-filled epoxy paste on copper backing plates. The Bonding Sputtering Targets has many benefits for the sputtering process: faster transfer heat and the possibility to be used even after the target crack occurs. A glow discharge process, plasma treating is necessary for cleaning and activating the surfaces prior to deposition. The sputtering process occurs in vacuum and argon atmosphere.

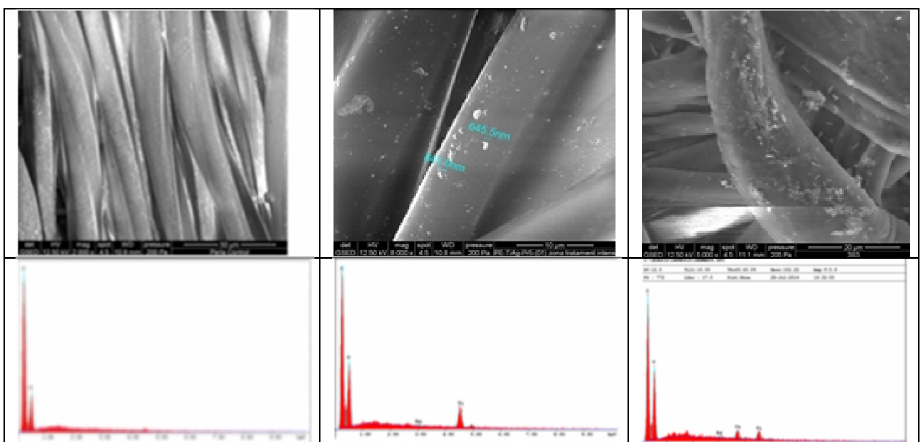
The assessment of characteristics of samples treated with TiO_2 Ag1% by electrospray and sputtering methods was made in terms of SEM images, EDX pattern, phisical-mecanical properties, bactericidal action and self-cleaning effect.

The methods used for tests are scanning electron microscopy (SEM) and EDX spectra, photocatalytic activity after stained with Methyl Orange (MO) and Methylene Blue (MB), Antibacterial effect was assessment according SR EN ISO 20743:2013-Textiles. Antibacterial activity of textile products, SR EN ISO 20645:2005-Textile fabrics. Antibacterial activity control. Agar diffusion plate test and ASTM E2149-10 Standard test method for determining the antimicrobial activity of immobilized agents under dynamic contact conditions.

RESULTS AND DISCUSSION

SEM/EDX Analyses

The SEM/EDX images of Perla sample treated with TiO_2Ag1% by electro-spray and sputtering are shown in figure 1.



Sample: Perla -control	Sample: Perla electro spray TiO_2Ag1% (5m/minute)	Sample: Perla sputtering TiO_2Ag1% (10 minute)

Figure 1. SEM and EDX images for sample Perla

- SEM images for electro- spray deposition at fabric speed 5m/minute, show a non uniform deposition of nanoparticles in the form of clusters; the size of nanoparticles agglomerations are 640÷840nm; EDX identified Ti in smaller amounts and Ag characteristic peaks are not visible;

- SEM images for 10 minute Sputtering deposition, show a non uniform deposition of nanoparticles; on the surface of samples the amount of Ti is 7.65% by weight and the amount of Ag i is 1.74% by weight;

Regarding to samples wood treated by sputtering, these was stained very hard.

Physical-Mechanical Characteristics

The physical-mechanical characteristics, tensile strength, elongation, tear strength and abrasion resistance, were determined only on electro-spray NPs deposition sample. The tensile strength and elongation aren't influenced by plasma treatment. A small influence is on tear strength and abrasion resistance is greatly enhanced. Also surface and volume resistivity is not significantly influenced by plasma treatment and electrospray deposition, table 1.

Table 1. Physical-mechanical characteristics of Perla electro spray $TiO_2Ag1\%$

Sample / Characteristics		Perla Control	Perla electrospray $TiO_2Ag1\%$ (5m/minute)
Tensile properties, N	Warp	1687	1659
	Weft	854	850
Elongation, %	Warp	52.3	51.7
	Weft	39.4	42.2
Tear force, N	Warp	71.2	61.0
	Weft	55.4	51.4
Abrasion resistance by the Martindale method, cycles		38931	49441
Surface resistivity, Ω		2.98×10^{13}	1.84×10^{13}
Volume resistivity, Ω		1.08×10^{13}	1.84×10^{13}

Antibacterial Effect

Perla samples treated with TiO_2/Ag1% by sputtering presents inhibitory effect after 1h and 24 h for Gram-negative strains (Escherichia coli, Pseudomonas aeruginosa, Acinetobacter baumani, Klebsiella pneumoniae) and Gram-positive strains (Enterococcus faecalis, Staphylococcus aureus) and also for Candida albicans.

Photocatalytic Effect

The photocatalitic effect was evaluated by the color difference between treated samples and control sample according to standard EN ISO 105-B02:2013 Textiles - Tests for color fastness - Part B02: Color fastness to artificial light: Xenon arc fading lamp test (ISO 105-B02:2013). The half covered samples are exposed to light in Xenon Arc lamp light fastness tester equipped with a xenon lamp, suitable filter systems to simulate visible light. The light fastness of the dyes, measuring the degree to which a dye resist fading due to the light exposure is evaluated on grey scale (note from 1 to 5; 5 is best, meaning the dye is not destroyed by the light and 1 is worst, the dye is destroyed by light) or blue scale (1-8; 8 best). TiO_2, being a photocatalytic compound, accelerate the degradation. Consequently, if the dyes (methyl orange or methylene blue) show a high degradation noted by a small grade (e.g. 1 or 2) the textile material coated with TiO_2 Ag1% has a high ability to absorb visible light and to destroy the dye being a very good photocatalyst.

In parallel to the above mentioned Standard photocatalytic activity can be measurement with Hunterlab equipment (more objective).

The grade of photocatalytic activity to methylene blue and methyl orange of Perla sample treated by electrospray with TiO_2/Ag1% at a fabric speed of 5m/minute is presented in figure 2.

Color grade difference	Perla sample-Control	Perla sample stained by dipping 5 minutes in methylene blue (c=100 mg/L)
		
ISO 105 B02- grade	3-4	3
Color difference on Hunterlab equipment	4	3
Color grade difference	Perla sample-Control	Perla sample stained by dipping 5 minutes in methyl orange (c=100 mg/L)
		
ISO 105 B02- grade	4	2-3
Color difference on Hunterlab equipment	4	1.5

Figure 2. Images after 7h Xenon lamp exposure an grade of photocatalytic activity to of Perla sample treated by electrospray with TiO_2/Ag1%

Taking into account both measurements, it could be concluded that Perla samples treated by electro-spray with stable solution of TiO_2/Ag1% have a good an efficient photocatalytic activity.

CONCLUSION

The intermediaries' tests allow to conclude:

Perla samples treated with TiO_2/Ag1% by sputtering presents total inhibition of grows for all strains: Gram-negative strains (Escherichia coli, Pseudomonas aeruginosa, Acinetobacter baumani, Klebsiella pneumoniae) and Gram-positive strains (Enterococcus faecalis, Staphylococcus aureus) and also for Candida albicans;

Perla samples treated by electro-spray with stable solution of TiO_2/Ag1% have a good an efficient photocatalytic activity;

Samples wood treated by sputtering with TiO_2/Ag1% was stained very hard;

Physical-mechanical characteristics of sample are not affected by the plasma treatment applied before NPs deposition both by electrospray and sputtering.

As a general conclusion the result of treatment with TiO_2 and TiO_2 doped with Ag depends on substrate characteristics and the treatment technique should be selected according the application field of textile and wood.

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SR EN ISO 20743:2013-Textiles. Antibacterial activity of textile products;