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INFLUENCE OF FUNCTIONALIZATION TECHNOLOGIES WITH NANOPARTICLES ON THE SUSTAINABILITY OF INDUCED EFFECTS

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Abstract: *Textile mats of 100% cotton, 55% polyester/ 45% cotton and 100% polyester, white and dyed, were functionalized by: CeO_2 NPs spraying technology on a test device made at UT Dresden after oleophobization with Rukostar EEF6 or Nuva N 2114 and impregnation by applying oleophobic treatment with NUVA N 2114 or Rukostar EEE 6 simultaneously with the functionalization with CeO_2NP. Analysis of the size and shape of CeO_2 NPs was achieved by using SEM electronic microscopy, TEM and dynamic light scattering (DLS) transmission microscopy. The durability of CeO_2 NPs deposition on the surface of the textile materials was studied for the initial samples compared with those tested for acid/ alkaline perspiration, washing and wear (rubbing) revealed by SEM determinations. The statistical indicator of dispersions (medium average, standard deviation, dispersion and variation coefficient) were used to compare the morphology of NPs on the surface of textiles materials (dimension and distances). The average amount of NPs deposited on the textile by the spraying technology was smaller than with the impregnation one. The antibacterial characteristics of textiles materials treated with CeO_2 in correlation with fibrous composition, color and the oleophobic agent were determined.*

Key words: *textile mats, spraying, nano-particles, functionalization, additives*

1. INTRODUCTION

The market of products using nanotechnology could reach about a thousand billion dollars a year in 2015. Nanotechnology is developing at a fast pace globally, with a short duration between the effective date of an invention and its commercialization. According to the Nanotechnology Consumer Products Inventory, over 600 such products are currently produced by 322 companies in 20 countries. Ultra-fine particles (UFPs) are a category of particles that, when inhaled, can cause negative health effects [1]. These particles have a diameter of up to 100 nm and are therefore true nanoparticles in terms of size. Their nanometre size differentiates them from large particles (with diameter of up to 10µm, PM10) and fine particles that pollute the air (with diameter up to 2.5µm, PM2.5) [2]. The most important properties of nanomaterials in nano-bio interactions are dimension, shape, purity, surface area, charge, hydrophobicity, aggregation state, crystallinity, electron energy level, and the potential to generate ROS. These properties can be correlated with the biological results according to a set of structure-activity flow diagrams, an example being shown in Fig. 1.

The surface properties of the particles determine the cellular uptake pathways, the subcellular processing mechanisms and the cytotoxicity [3,6]. The Fenton reaction is one of the mechanisms by which the metallic impurities on the CNT surface can induce ROS generation (Fig. 2)[5]

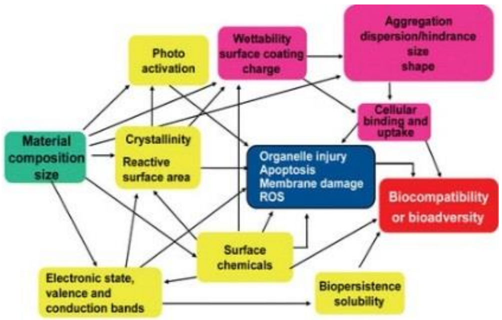

Fig. 1: *Structure-activity flow diagram*

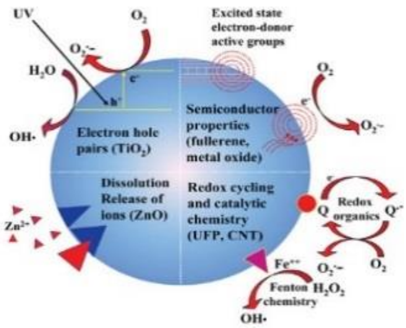

Fig. 2: *Fenton reaction*

Finally, the particle dissolution (e.g. ZnO, CdSe, Cu) can produce free ions capable of inducing ROS generation and toxic effects in cells. Fever of metal smoke may be an example of this type of toxicity [4]. Cerium was discovered in Sweden by Jöns J. Berzelius and Wilhelm von Hisinger and independently in Germany by Martin Heinrich Klaproth in 1803. The element's name comes from the asteroid Ceres, discovered two years earlier by Giuseppe Piazzi. Cerium is the most abundant of the lanthanides. It is not found freely in nature, but it is found in a series of minerals, mainly alanine, bastnaesite, monazite. From a commercial point of view, cerium is prepared by chloride electrolysis or by melted fluoride reduction with calcium. Cerium has 30 of isotopes whose half-life is known, with mass numbers of 123 to 152. Of these, three are stable, 136Ce, 138Ce and 140Ce. The most abundant isotope is 140Ce at 88,5%. SEM images of CeO2 were obtained by using the FEI Quanta 200 scanning microscope (Fig.3).

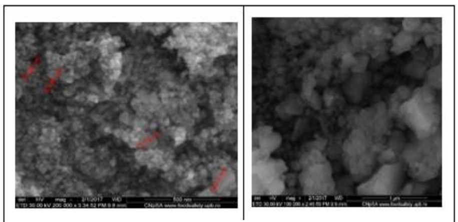

Fig.3: *SEM images*

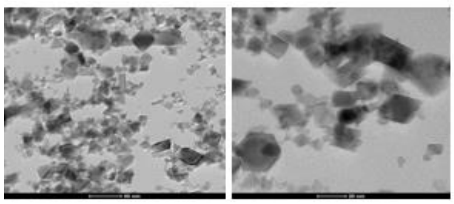

Fig. 4: *TEM images*

The TEM images in the light field (Fig. 4) on the CeO_2 NP reveal that the sample is made up of particles of a polyhedral shape with an average size of 11.86 nm ± 0.49 nm. The particles have a very large variation in size and shape (Fig. 5).

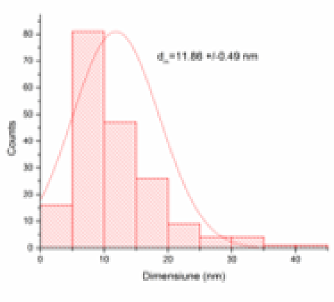

Fig. 5: *Size distribution diagram*

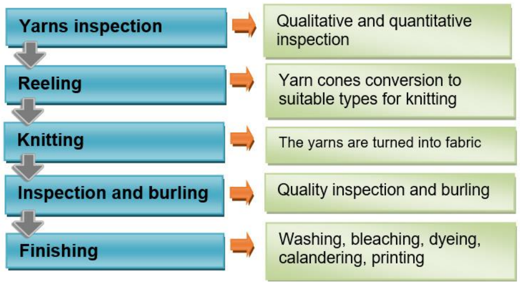

Fig.6: *Technological process*

100% cotton, 45% cotton/ 55% polyester and 100% polyester knitted fabrics were made according to the technological process presented in Fig. 6.

Table 1: *The obtained characteristics*

No.	Parameters	Variant		
		100% cotton	45% cotton/ 55% polyester	100% polyester
1	Yarn diameter, mm	0,18	0,17	0,12
2	Loop width/ loop height, mm	0,81/0,97	0,77/0,92	0,25 si 0,26/2,26
3	Stitch density, wales/50mm	62	65	217
4	Stitch density, rows/50mm	52	54	192
5	Loop length, mm	3,82	3.63	1,29
6	Mass, g/m^2	98,53	84,96	44,45
7	Coverage linear factor	21,22	21,35	35,0
8	Coverage surface factor	0,88	0,87	5,6

The knitting process was done on the 12 GG Shima Seiki SIG 123 machine and the characteristics of the obtained structures are presented in Table 1 that relives a higher values of coverage linear and surface factors of 100% polyester, compared to knits of 100% cotton and 45% cotton/ 55% polyester (35 vs. 21.22 and 21.34 respectively 5.6 vs 0.88 and 0.78).

Dispersion formula with UPW and solvent were prepared for which the following were used: 742 g UPW (MilliPure) and 1026 g ethanol (w> 99.9%) in a glass flask of 2 l; there were added 14.40 g of 2-butanone (MEK, w=9.5%), 10.80 g of HCI (w=37%) and 7.20 g of triethanolamine (w=100%); after sonication for 15 min., the dispersion was manually shaken for 1-2 minutes.

The EDS spectra for the CeO_2 dispersions in UPW/ solvent are presented in Fig. 7, show that the CeO_2 mass is of 62.0% in the UPW dispersion and of 24.5% in the solvent.

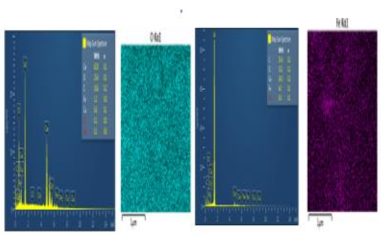

Fig. 7: *Spectre EDS-UPW /solvent*

The knitted fabrics were treated with Nuva N2114 or Rukostar EEE6 oleofobizing agents and functionalized with CeO_2 in UPW/ solvent dispersions by spraying (different steps) or impregnation (pad-roll) technology (in the same phase). For the application of CeO_2 NP by spraying technology, the equipment designed and developed by the Dresden-Germany Technical University was used. The 20x20 cm samples of 100% oleophobeized cotton knits with Nuva N 2114 and Rucostar EEE6 were spray-treated in the test chamber with CeO_2 dispersions in UPW and solvent. The spraying of various CeO_2 NP dispersions was done with 5 second spraying pulses. The treatment recipe used in pad-roll technology included: 70 g/ l Nuva N2114/ Rukostar EEE6, 20 ml/l dispersion of 5% CeO_2 NP in ethylene glycol/ water dispersion, 0.5 ml/l 60% acetic acid (1 ml/100% dog), 80% degree of take-up, drying at 110°C, condensation at 140°C for 2 min.

The influence of the treatment solution on the shape and dimensions of CeO_2 NP was studied on the Auriga model workstation produced by Carl Zeiss SMT Germany FESEM-FIB with the GEm columnal field emission source in the beam spectra. There were used: the Everhart Thornley SESI Secondary Electron Detector with Faraday Cup in sample chamber or the columnal anular inLens Secondary Electron Detector.

In Fig. 8 are presented SEM images of solutions containing NUVA N2114 and dispersion in UPW and solvent of CeO_2 NP.

The average dimensions of CeO_2 NP in the Nuva N 2114 solution and CeO_2 dispersion are lower for UPW dispersion (16.1 nm vs. 23.7 nm), but the standard deviation and coefficient of variation are higher than the NUVA solution N 2114 and CeO_2 dispersion in solvent (46.2 and 5.78% vs. 21.14 and 3.52%).

From the analysis of the statistical indices of the evolution of CeO_2 sizes in solutions of the oleofobising agent Rukostar EEE6 and their dispersions in UPW and solvent it is observed that the average size of CeO_2 in the solution of RuKostar EEE6 and dispersion in UPW is at the same level as in the dispersion in solvent, with the difference that the standard deviation and the coefficient of variation are higher (80.6 and 8.06% vs. 46.5 and 5.8%). The statistical indicators of the CeO_2 size in the Nuva N2114 solution and in the UPW dispersions and in the solvent are better than in the case of the Rukostar solution and the same type of dispersions.

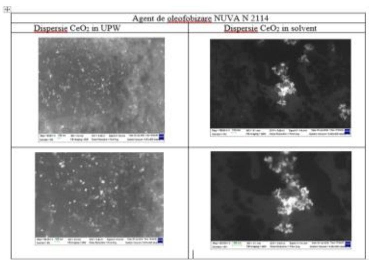

***Fig. 8**: SEM images of solutions*

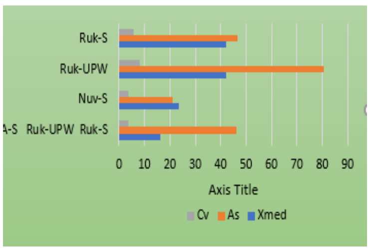

***Fig.9:** Statistical indicators*

From the analysis of the SEM images, a tendency of the NPs to agglomerate in the solvent/ polymer matrix was observed, but their morphology remains similar, respectively irregular polyhedrons and octagonal shapes (Fig. 9).

The NPs amount deposited on textile materials was analyzed by the Air ion counter and ICP-OES methods, which showed that it is less than 5 mg/kg for the spraying technology and more than 400 mg/kg for the impregnation and does not decrease significantly from the initial knits to those after the resistance tests on acid/ alkaline perspiration, washing and rubbing.

The statistical indicators of the dispersion (mean, coefficient of variation, standard deviation and dispersion) evaluated by the SEM images analysis (Fig. 10) showed the evolution of the sizes and distances between the CeO_2 NPs on the surface of the initial knits and after the resistance treatments on acid/ alkaline perspiration (Fig. 11), washing and friction (Fig. 12) which varies depending on: the nature of the dispersion and oleofobizing agents, the fibrous composition and the presence of the dyestuff on the textile support.

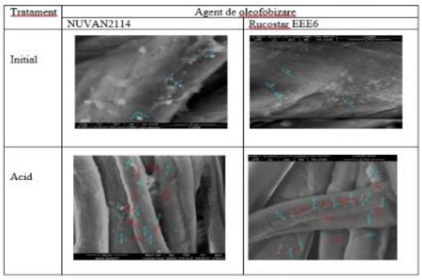

***Fig. 10**: Dispersion indicators evaluation*

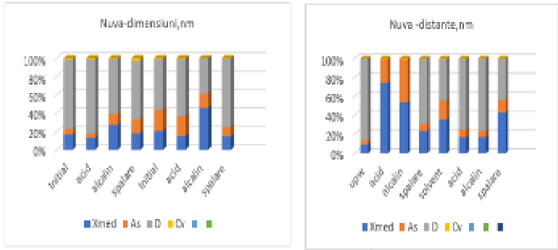

***Fig. 11:** NP Evolution (perspiration)*

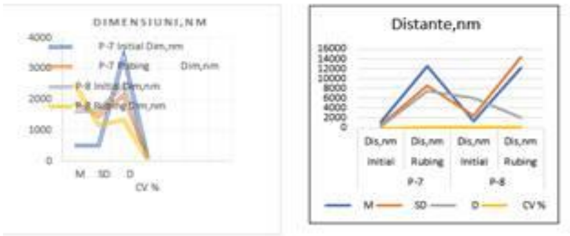

***Fig. 12:** NP Evolution (washing and friction)*

***Fig. 13:** Fungi*

The antifungal efficacy tests performed with Candida albicans, Trichophyton interdigitale and Epidermophyton floccosum showed that (fig.13):

- Testing for Candida albicans revealed high microbial reduction rates of over 80%, varying according to the material used (dyed/ undyed).

Thus, it could be seen that for 100% cotton, higher degrees of microbial reduction were recorded, due to a mechanical retention rate of the cells on the material (compared to polyester). At the same time, it has been observed that the presence of the dye on the material can contribute to a slightly higher degree of microbial reduction.

- Tests for interdigital Tricophyton revealed variations in the degree of reduction in both the fibrous composition and the treatment variant from which the material was part (NUVA + CeO_2 in UPW or Nuva in solvent), not respecting a particular pattern. Thus, for the variant "NUVA + CeO_2 in UPW", the highest rate of reduction of the microbial population had knitted from 45% cotton/ 55% polyester, dyed, 79.3%, and the lowest, 100% polyester with 69.28%. For the variant "Nuva + CeO_2 in solvent, the highest discount rate was presented by 45% cotton/ 55% polyester, painted with 84.19% and the lowest 45% cotton / 55% polyester, white, with 79.41%.

- The tests for Epidermophyton floccosum revealed that for the variant "NUVA + CeO_2 in UPW", the highest rate of reduction of the microbial population had knitted of 100% polyester, dyed, with 67.76%, and the lowest knit: 45% cotton/ 55% polyester, white, with 52.06%. For the "Nuva + CeO_2 in solvent" variant, the highest reduction rate was 100% cotton, dyed, with 70.57% and the lowest, the 100% polyes ter, dyed with 55.31%.

2. CONCLUSION

- Knitted materials from 100% cotton, 45% cotton /55% polyester and 100% polyester, raw and dyed were treated after oleophobic treatment or in same process with CeO_2 NP by spraying and padding technology.

- SEM and TEM analysis of CeO_2 and dispersions of CO_2 in UPW (ultrapure water) and solvent have evidenced the medium dimension (10-50 nm) and their polyhedral shape; EDS analysis has evidenced that dispersion with CeO_2 with UPW contains a greater quantity of NP (62%) when compared with solvent dispersion (24,5%). The quantity of NP deposited on knitted materials surface has evidenced a value less than 5 mg/kg at the spraying technology and a value more than 400 mg/kg at padding, which do not decrease significantly after acid/ alkaline perspiration tests, washing, rubbing tests. Statistic indicators of dispersion have evidenced the evolution of dimensions and distances between CeO_2 on surface knitting in initial phase and treated of acide/ alkaline perspiration, washing and rubbing tests, which are depending on: nature of oleophobic agent, fiber composition and presence of dyestuff on the textile material.

- The antifungal efficacy tests performed with: Candida albicans, Trichophyton interdigitale and Epidermophyton floccosum showed that these are depending on the nature of the fiber composition, the colour and treatment of the textile support.

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REFERENCES

[1] Agency Toxic Subst. Dis. Regist. (ATSDR). 2005. "*Toxicological Profile for Zinc.*"Atlanta, GA: US Dep. Health Hum. Serv. Public Health Serv http://www.atsdr.cdc.gov/toxprofiles/tp60.pdf

[2] Araujo JA, Barajas B, Kleinman M, Wang X, Bennett BJ, et al. 2008. "*Ambient particulate pollutants in the ultrafine range promote early atherosclerosis and systemic oxidative stress*", Circ. Res. 102:589–96

[3] Arimoto T, Kadiiska MB, Sato K, Corbett J, Mason RP. 2005. "*Synergistic production of lung free radicals by diesel exhaust particles and endotoxi",* Am. J. Respir. Crit. Care Med. 171:379–87

[4] Brook RD, Franklin B, Cascio W, Hong Y, Howard G, et al. 2004. "*Air pollution and cardiovascular disease: a statement for healthcare professionals from the expert panel on population and prevention science of the American Heart Association"*, Circulation 109:2655–71

[5] Brown JJ. 1988. "*Zinc fume fever",* Br. J. Radiol. 61:327–29

[6] Chen HW, Su SF, Chien CT, Lin WH, Yu SL, et al. 2006, "*Titanium dioxide nanoparticles induce emphysema-like lung injury in mice"*, FASEB J. 20:2393–95