Romanian Academy

Institute of Physical Chemistry "Ilie Murgulescu"

THESIS SUMMARY

PROCESSES FOR THE HYDROPHOBISATION OF TEXTILE MATERIALS: PHYSICO-CHEMICAL CHARACTERISTICS AND MATHEMATIC MODELING

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Bucharest
2017

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The Summary keeps the numbering of Figures and Tables as it is in the Thesis.

INTRODUCTION

Textiles are well-known materials largely used since the dawns of mankind. Their study was also initiated for centuries. Nowadays, the textile research focuses on imparting various functionalities to the materials, e.g.: self-cleaning, water-proofing / oleophobisation / super-hydrophobisation; breathability; moisture absorbency; photosensitivants / adhesive-proofing; usage-proofed / anti-ageing; thermal insulator; antistatic; antiallergic; UV blocking; smart textiles; controlled release of active chemical reagents like drugs, cosmetics, odours, etc. For any of these functionalities there are alternative non-nano technologies, competing with the new nano-activating ones. The main processes using nano products for applying on textiles can be enumerated as:

- processes for introducing functional nano-materials in raw fibre products, leading to combining the original characteristics of the fibres with the functionality of nano-materials;
- coating fibres or textile materials with functional nano-products, resulting functional textiles with high added value;
- using electrospinning for producing nanofibres which are used further for producing textiles with improved, or even novel features, allowing various new applications.

The liquids transport in fabrics and the wetting of materials are common problems in processing and using of textile materials. These are of particular interest in evaluating the comfort and performances of fabrics destinated to leisure and active sport garments, for interior textiles, or for the materials destinated to medical use, etc. Research performed in this field aims at finding the suitable characteristics and testing methods [1].

The Thesis goals are as follows: to deepen the methods for studying the hydrophilic / hydrophobic properties; to apply the methods to the study of woven and knitted fabrics made of wool, a natural fibre less investigated for these features; to apply selected processes for render wool materials hydrophobic; to process the measured data and detail the wetting process of wool textiles; and to derive conclusions for further research.

The Thesis is structured in four main chapters.

Chapter 1 contains a survey of the literature concerning the wool textile materials, providing the meaning of textile terms used therein and of the elements of characteristic technological processes used in textile industry. The chapter contains also the description of physical and chemical structure of wool (particularly Merinos bred), the relation between the structure and fibre properties and details on various finishing treatments applied on wool yarns used in throughout this work. The issue of hydrophilic / hydrophobic properties of wool materials is discussed and some examples of

treatments used to control it, including the deposition of semiconductor oxides, are given. Finally it is given a short account of the statistical methods applied generally at physical-chemical studies and of those used in the Thesis.

Chapter 2 describes the experimental methods used for studying the modifications of wool textiles, as well as own contributions to these. The materials, the methods to treat them and, briefly, the analytical methods and equipment used for characterizing them are all detailed. The samples of knitted and woven wool fabrics (made of Merinos or Tigaie, Romanian semifine wool bred) are discussed comparatively with woven fabrics made of other fibres (e.g. polyester and linen). Further on the fabric surface modification by oxygen plasma treatment, and by deposition of ZnO, or TiO2 particles using sol-gel (SG) or sputtering (SP) method, are described, detailing the functional groups available on various textile fibres present in the treated sample. The equipment used for characterizing the wetting performance (contact angle), as well as those for measuring the photocatalytical effects (related to self-cleaning property induced by oxide particles) are explained, together with the laboratory set up for investigating the kinetics of wetting and the software developed for data acquisition and processing of the images of wet surfaces. The kinetics of drop penetration in the fabric allows statistical approaching to data processing based on the software of acquiring images of drops; the soft for processing the wet surface images is also presented (least square method). The statistical data processing algorithm follows several steps [2]] which are also retrieved in Chapter 3, dedicated to the presentation and analysis of experimental data.

The evaluation of photocatalytic activity of TiO_2 and the subsequent self-cleaning effect is performed by studying the kinetics of colour decolourization of Methylene Blue (MB), Rhodamine 6B (R6B) or Brilliant Blue (E133), respectively, in the laboratory set up and in Checker PCC2. The study is based on following the decolourization of colour for various dyestuff concentrations and UV exposure times, until the stain is cleaned.

The self-cleaning effect of textile samples can be explained by the fact that high energy species produced by TiO_2 under UV irradiation may react with chemicals from the stains (dyestuff, coffee, wine, etc.) decomposing them to CO_2 and H_2O.

Chapter 3 is dedicated to the presentation of the results and the discussion of the salient points. This Chapter is developed further.

Chapter 4 lays down the Conclusions of the investigations carried out within the framework of this Thesis.

The hygroscopicity of textile surfaces depends on the composition of chemical coating and on their topography. Increasing the amount of TiO_2/ZnO nano-particles on wool surface leads to the increase of its hydrophilicity. Fabrics treated with TiO_2 nanoparticles gain efficient protection against bacteria and staining due to the catalytically effect of this reagent [3]. When irradiated, ZnO nanoparticles impart similar properties with TiO_2 ones and as a consequence they are used also for antibacterial treatments of textiles [4- 7].

The wetting properties of wool can be modified by two ways, i.e.: acting at the level of individual fibre by reducing the scales and stripping the hydrophobic layer of natural fatty acids; this takes place before dyeing and has the purpose of improving the dyeability of the fibres and their long-lasting protection at care operations or acting for altering the surface of textile woven or knitted fabric by new methods of functionalizing the surfaces, methods which are used quite limited industrially.

The hydrophilic / hydrophobic properties of textiles treated this way were in the focus of research worldwide, including Romanian teams from INCDTP, ICECHIM, INCDFM, Universities such as Politehnica Bucharest, Politehnica from Brasov and from Iasi, etc.

Nanotechnologies open new directions in textile field, providing novel tools able to meet market demands and answer properly the competition.

The wool samples investigated in the present work are made of fine wool (Merinos) by Lanerossi and Raumer (Italy) and of semi-fine wool (Tigaie) by industrial or individual producers from Vaslui, Bacau or Neamt.

Modification of the textile surface was carried out firstly by a pre-treatment with oxygen plasma followed by the deposition of TiO_2 [8], or ZnO [9] nanoparticles. TiO_2 is a known photocatalyst [10- 12], acting both in bulk (powder) and as a thin layer coat. There are several methods of deposition, e.g.: TiO_2 can by applied by immersion, using sol-gel technique [13]; ZnO is increasingly applied by electroless method [14], due to several advantages; also ZnO can be deposited by RF sputtering.

Characterization of the analysed textile surfaces focused on: structural investigations of textiles materials / surfaces; wetting properties by measuring contact angles; relating the textile material properties with those of wetting. Due to the importance of wetting properties some details are also mentioned [15, 16]. Hydrophobicity is evaluated by measuring the contact angle of a water drop laid on a surface. A surface on which the water drop contact angle is higher than 150° is termed

as an ultra-hydrophobic surface. Such a surface can be achieved by rendering a certain rugosity to the surface of a material with a low surface free energy [17].

RESULTS AND DISCUSSIONS

1. Complex characterization of initial samples and of those treated with plasma and functionalized by deposing TiO_2 or ZnO

Below are shown the **optic images** of initial samples investigated by using transmission and reflected light, respectively.

Table 4: Images of optic microscopy of initial Romanian wool samples

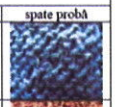
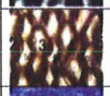
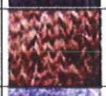
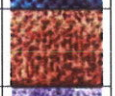
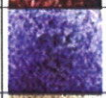
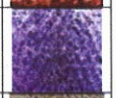
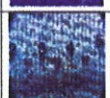
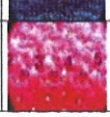
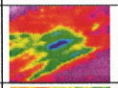
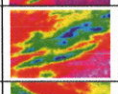
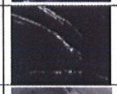
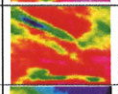
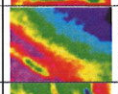
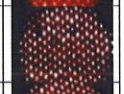
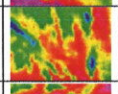
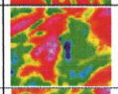
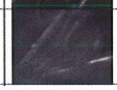
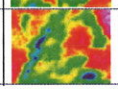
Notație probă tricot (element 3D)	Imagini lumină transmisă	Imagini în lumină reflectată	
	față probă	față probă	spate probă
VSKBG			
VSKMa			
BVFrB			
BCFsK			
BCFpR			

Table 5: Images of Merinos wool samples

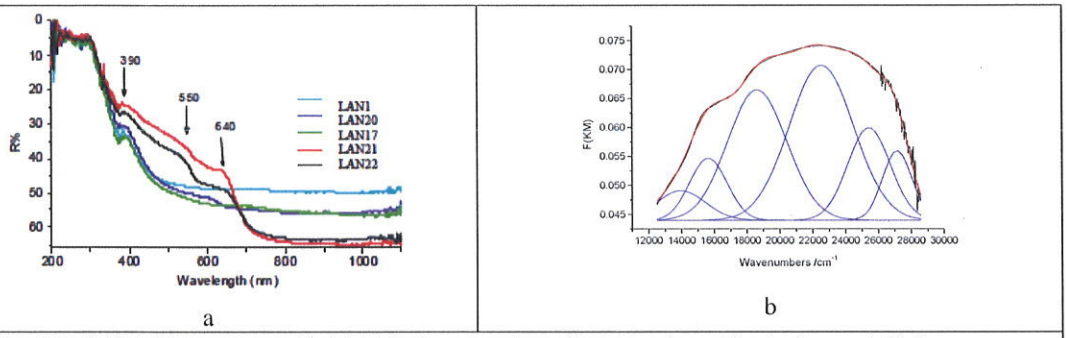
Notație probă	Imagini cu microscopul optic al Spotlight	Imagini cu FTIR Imaging microscop	Imagini cu microscopul optic
LAN1			
LAN24			
LAN18			
LAN17			
LAN19			
LAN R18			
LAN R19			

*The colour of wool samples by optic microscopy is not relevant.

The images from microscopy examination (Tables 4 and 5) contain also the length scale for easily compare the "pores". This direct observation of the samples was performed for evaluating the sizes of the voids on knitted / woven fabrics and the homogeneity of their distribution across the surface. The images acquired with Spotlight microscope are focused on yarn / fibres and allow comparing samples.

UV-VIS spectra of functionalized samples are graphed in Fig. 25, both as the variation of reflectance and as change of Kubelka Munk function [18, 19] which is made of the coefficients of absorption, K, and of spectral scattering, S, and of minimum reflection, R_{min}, and diffused reflexion,

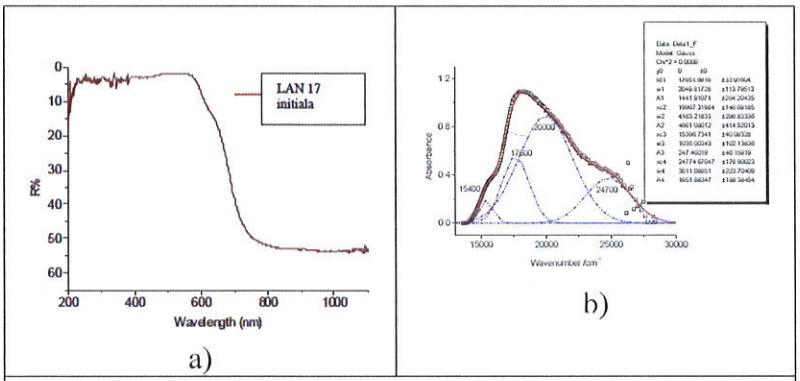
R, measured on wool samples. UV spectra exhibit a strong absorption at around 284 nm, corresponding to the specific absorption of certain amide groups [20].



a b

Fig. 25: a) UV-VIS spectra of initial Merinos wool textiles, mentioned in the Legend. b) Spectrum corresponding to the sample TiO2/LAN22P deconvoluted, according to Kubelka Munk representation

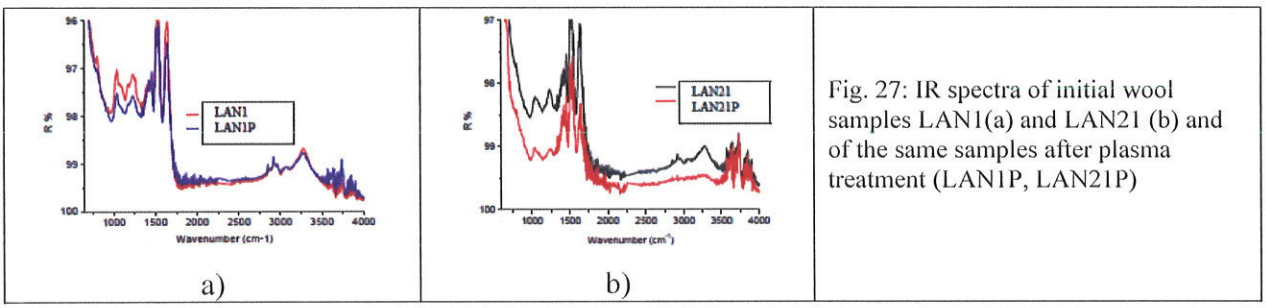
In order to extract more information **the least square method** (soft of ORIGIN) was used to deconvolute the absorption maxima of DRS spectra and to relate the result with the colour of the fabric. Fig. 26 shows such an example: Fig. 26 b gives the positions (noted xc_n), half-peak width values (w_n) and the area of the respective peaks (A_n). The deconvolution of the peak puts clearly into evidence the differences among samples, and allows calculating the values of deconvoluted parameters such as to achieve the best fit of model function to the experimental data.



a) b)

Fig. 26: a) DRS spectrum of LAN17 and b) its deconvolution by Gaussian functions [29]

FTIR spectra put in evidence that treated samples do not differ significantly from those initial; wool has many hydrophilic groups responsible for the stretching vibrations at 3300-3400 cm^{-1}. Such investigations provide information about characteristic groups of fibres and their involvement in the deposition of TiO_2 particles on the substrate.



a) b)

Fig. 27: IR spectra of initial wool samples LAN1(a) and LAN21 (b) and of the same samples after plasma treatment (LAN1P, LAN21P)

Plasma treatment (Fig. 27 a,b) does not modify significantly the spectrum of substrate, producing only slight changes of stretching vibrations of –OH and –COOH; in case of sample LAN21 one notices also a change of characteristic vibration of amide group –CONH (~3300 cm^{-1}). The characteristic bands of protein and polypeptides include also amide I and amide II bands, the former is due to stretching C=O vibration of amide group, whilst the absorption assigned to later comes from bending vibration of N-H bond [21]. Its deconvolution by Gaussians is shown in Fig.37.

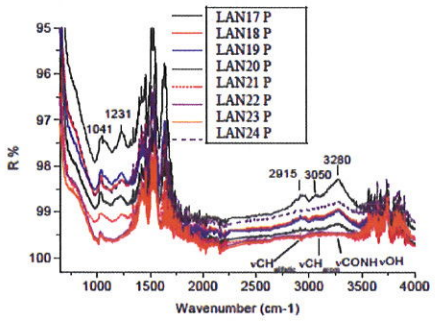


Fig. 30: IR spectra of some plasma treated Merinos wool samples and the assignment for the main peaks.

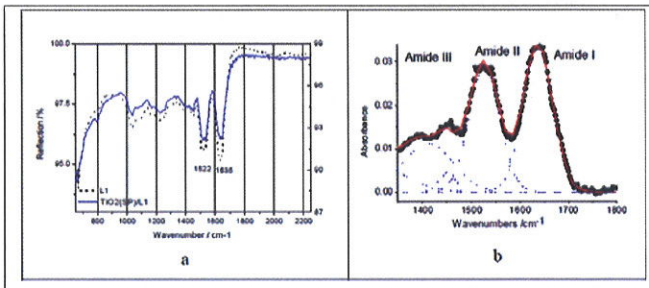


Fig. 37: a) FTIR-ATR spectra of wool sample LAN1 initial (dotted line) and with deposited TiO_2 (SP) (continuous line); b) Deconvolution of initial sample spectrum (dots) with Gaussians (dotted lines) and their sum (continuous line).

The morphology of initial samples was studied by **SEM** and some significant micrographs are shown in Fig. 28. The images are successive snapshots zooming from the overview of the knitted fabric to the individual fibres. One observes that the plasma treated surfaces (Fig. 31) appear more irregular than of the initial samples (Fig. 28). In case of sample TiO_2(SG)/LAN20P at high magnification one notices well that the deposition is even, round the fibre, as the scales are clearly exhibited. Table 7 and the next ones contain SEM images at various magnifications acquired for some of the investigated samples.

Proba/Mărirea Sample/ Magnification	100x	1000x	2000x	5000x	10000x
LAN1					

Fig. 28: SEM images of some initial wool sample.

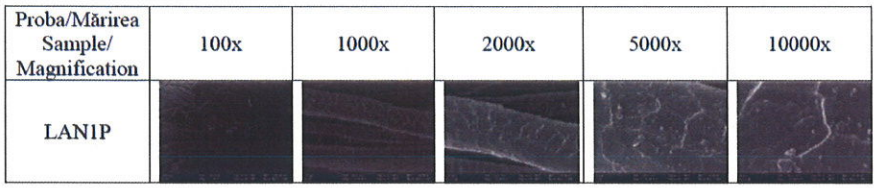
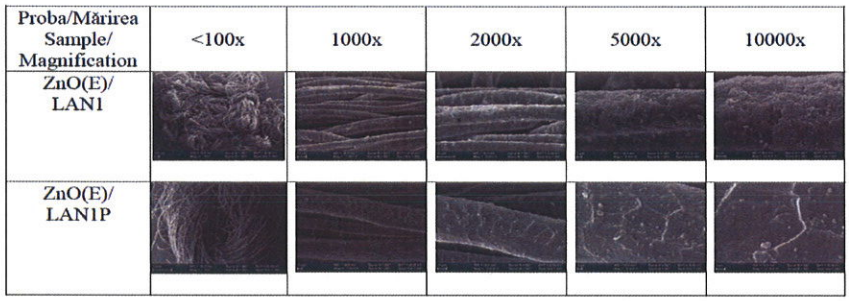


Fig. 31: SEM images of a plasma treated sample

Table 7. Samples initial / plasma treated and functionalized with TiO_2 or with ZnO by electroless (E)



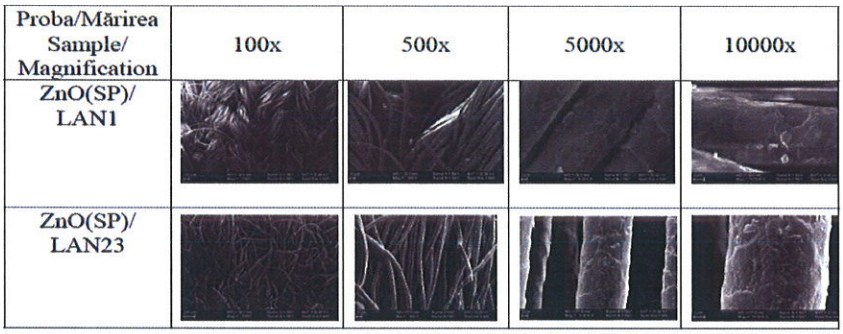


Fig. 34: SEM images of samples LAN1 and LAN23 coated with ZnO by sputtering.

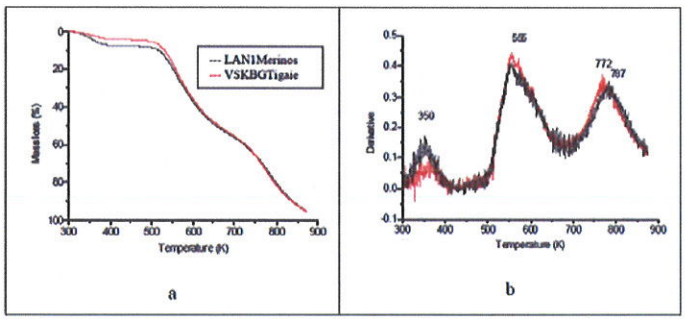


Fig. 29: TG (a) and DTG (b) recorded curves for samples LAN1 Merinos and VSKBO Tigaie, respectively

Thermogravimetric analysis was carried out on both types of Merinos and Tigaie samples. The recorded curves and their derivatives (DTG curves) indicate at least three mass loss steps, namely: first step (<150°C/423 K) due to moisture loss, without the damaging of the material; the second process, occurring above 200°C /560K, is due to the melting and degradation of various components which form wool structure; the last step occurs at high temperature (~780 K) and is related to the oxidative pyrolysis of wool. The two wools have similar curves suggesting an

expected similar thermal behaviour [22]. Also by comparing the TGA curves of plasma treated wool samples with those of initial ones (Fig. 32) [29] one may notice their similar behaviour.

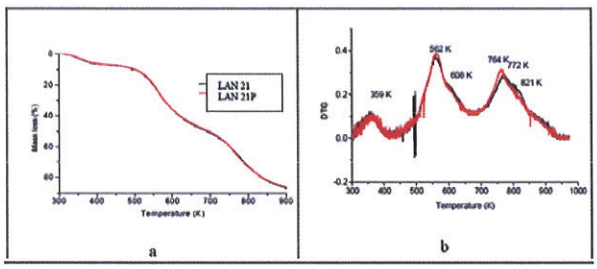


Fig. 32: TG (a) and DTG (b) curves for samples LAN21 and LAN21P

The pyrolysis process at high temperature appears to be slower for plasma treated samples than for those initial. A sample made of Romanian wool (VsKBH) is with about 50 degrees less stable than the commercial samples. The small effects can be easier noticed by comparing DTG than TGA curves.

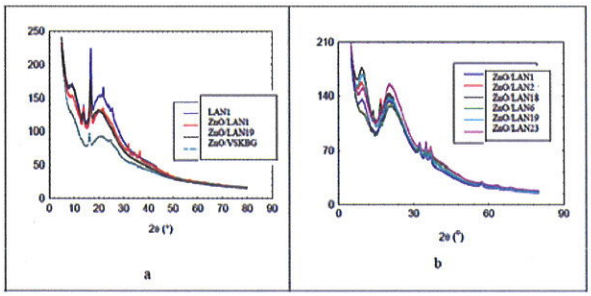


Fig. 36 XRD diagrams recorded for Merinos wool samples treated with ZnO: a) by electroless; b) by sputtering.

In the **XRD patterns**, the oxide is noticed only on one of the samples (LAN1), probably due to a too low amount of oxide deposited, and/or to a deposition of a weakly crystallized form. The deposition of ZnO by electroless method seems to be less favourable than by sputtering (Fig. 36 b). All samples recorded, as expected for wool, XRD patterns assigned to alpha-helix and antiparallel beta-sheet [23, 24].

Photoelectron spectroscopy measurements put in evidence the composition of samples coated with semiconductor oxides. Table 8 gives the general spectra from which the percentage of principal species was calculated (and listed in Table 9), and the high resolution spectra as well. The general spectra show the elements C and O, expected for the textile material, but coming also from any possible contamination of the surface; one may notice also peaks assigned to Ti and Zn, or coming from the deposition process (e.g. Sn, Pd from electroless process).

Table 8: General photoelectron spectra recorded for samples of indigene initial and coated wool

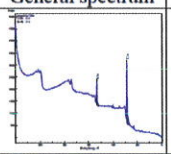
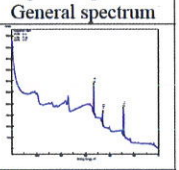
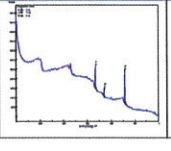
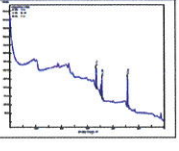
Proba/Tratament aplicat Sample/Treatment	Spectrul general General spectrum	Sample Treatment	Spectrul general General spectrum
VSKBG inițială/ initial		TiO_2(SG) VSKBG/ coated	
TiO_2(SP) VSKBG/ coated		ZnO(E) VSKBG/ coated	

Table 9: Percentage content of principal elements for the samples of indigene wool

Proba Sample	C %	O %	Ti (or Zn) %	Other elements
VSKBG	86.4	13.6		Not considered
TiO_2(SG)/VSKBG	66.8	29.0	4.3	
TiO_2(SP)/VSKBG	76.0	21.8	2.2	
ZnO(E)/VSKBG	75.7	21.2	no	Sn3d: 3.1%
Gs**	75.0	25.0		Si, Ca, Al etc.
TiO_2(SG)/Gs	62.3	34.9	2.7	
TiO_2(SP)/Gs	52.6	35.3	11.1	

*- Percentages are calculated from principal elements only. **- Glass

Initial samples contain largest amount of C and O; the coating treatment add titanium in a larger amount by sputtering (SP) than by sol-gel (SG). The signals of Si, Al and Ca in the glass sample (Table 9) are due to the glass composition. An extra-contamination by irradiation can be considered too for the coated samples.

2. Wetting properties. Contact angle of wool knitted samples

The wetting properties were investigated on samples at room temperature, by the help of analysing system of drop shape DSA 100. For the applications involving fibres of small diameter, the surface of the fibre may be the dominant parameter of most of the interactions. The contact angle of the analysed samples depends on the size of the loops on the side considered for the finishing treatment applied on fibres [25]. Some illustrative images are shown in Fig. 41. One may notice, in green, the contour of the drop drawn according to the used equation and the left and right tangents (in red) which serve to calculate the contact angle, CA.

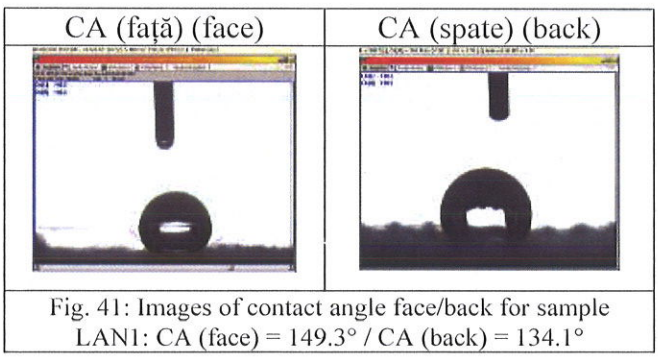


Fig. 41: Images of contact angle face/back for sample LAN1: CA (face) = 149.3° / CA (back) = 134.1°

One observes that:

- all initial samples are hydrophobic, CA> 90°;
- the plasma pre-treatment decrease the contact angle with 5...10°;
- the deposit of TiO_2 increases CA;
- the samples for which CA > 150° are termed superhydrophobic;
- the values of CA differ for measurements performed along the direction parallel versus those perpendicular to the privileged direction of the knitted fabric;

- comparing the CA values of initial against plasma treated, one notices the increase of CA of all plasma treated Merinos wool samples which become superhydrophobic;
- CA values of initial Merinos wool samples confirmed that the fibres were previously subjected to treatments for modifying their surfaces, like, for ex.: antipilling, shrink-proofing or Total Easy Care (TEC) finish;
- CA values of Merinos wool and Tigaie wool are similar, slightly increased for Merinos wool. This is probably due to the harsher industrial treatments used on Merinos fine wool before spinning than the domestic milder treatments applied on Tigaie semi-fine wool fibres.

Table 11: Contact angle measured on Merinos wool samples (*P – plasma treated)

Merinos wool initial samples			
Sample	Contact angle (CA°) face	Contact angle (CA°) back	Wetting behaviour face/back
LAN1	149.3	134.1	hydrophobe/hydrophobe
LAN17	147.0	143.5	hydrophobe/hydrophobe
LAN18	133.8	149.9	hydrophobe/superhydrophobe
Plasma treated Merinos wool samples			
Sample	CA°(Left/L)/(Right/R)		Wetting behaviour
LAN1	CAP1(L)=CAP1(R)=164.8		superhydrophobe
LAN1P	CA1P(L)=CA1P(R)=148.7		hydrophobe
LAN17P	CA17P(L)=CA17P(R)=159.1		superhydrophobe
LAN18P	CA18P(L)=CA18P(R)=161.5		superhydrophobe
TiO_2 coated Merinos wool samples (SG)			
Sample	CA° initial sample	CA° TiO_2 (SG)	Sample
LAN1	149.3	164.80	LAN1
LAN1P	148.7	148.70	LAN1 + Plasma
LAN17P	166.4	159.10	LAN17+Plasma
LAN18P	152.0	161.50	LAN18+Plasma

Summing up, all samples measured for contact angle exhibit hydrophobic / superhydrophobic features, CA values ranging from 134.1° to 166.4°.

The large CA values are probably due to the formation of the drops on a composite surface existing between air, water drop and material surface having nanorugosity, as suggested in reference [26]. This behavior was modeled by the help of Cassie-Baxter equation:

$$\cos\theta_C = f\cos\theta_0 - (1-f) \qquad (1)$$

where θ_C is the contact angle on treated fabric; θ_0 stands for the contact angle on the initial textile material, and f is the fraction of surface in contact with water drop [26]. The values of f were

calculated for each pair of initial-treated samples, as given in Table 15. Overall, the phenomena are complex and hard to be detected.

Table 15: Parameter *f* and contact angles for initial and treated wool samples

Sample	CA(°)				
	Initial value	ZnO(E)	*f*	ZnO(SP)	*f*
VSKBG	141.2	137.9	(132.39)	151.0	(134.65)
VSKMa	143.9	initial 112.6, absorbed extremely fast	1.033	155.7	0.654
BVFrB	152.3	initial 105.6, absorbed extremely fast	1.264		--
BCFsK	148.3	initial 155.2, absorbed extremely fast	3.463		--
LAN1	149.3	150.3, large roll off 180°	1.749	151.6	1.577
LAN3	133.8	156.0	2.039		--
LAN4	147.0	148.7, slowly absorbed	2.408		--
LAN6	143.9	145.7, double volume, large roll off 180°	0.756	168.8	0.914
LAN18	152.0	137.5, double volume, large roll off 180°	1.284	140.7	0.159
LAN19	149.9	145.3, double volume, large roll off 180°	1.050	165.8	0.146
LAN20	168.0	164.2, double volume, large roll off 180°	1.805		
LAN23	136,1			141.2	

3. Penetration of liquids in textile material. Liquid transport in woven fabrics (wicking)

The change of the profile of the drop during wetting the material allows inferring the kinetics of wetting [27]. The behaviour of a water drop / drop of a dyestuff solution on a wool knitted fabric, initial or functionalized with TiO_2 may characterize hydrophobic and self-cleaning properties of the deposited layer. Images illustrating the advancement of drops and wetting front are given below and allow obtaining the corresponding contact angles.

In order to follow the kinetics of drops penetration in fabrics we have did an experimental set-up where the liquid is spread radially from a tank of infinite capacity on a horizontally laid woven fabric sample. The experimental setup allows acquiring: 1- images of wet stain (first configuration), or 2 – images are acquired simultaneously with recording the weight of the tank with liquid (second configuration). The images are recorded with a WEB camera, which is useful for further image processing step.

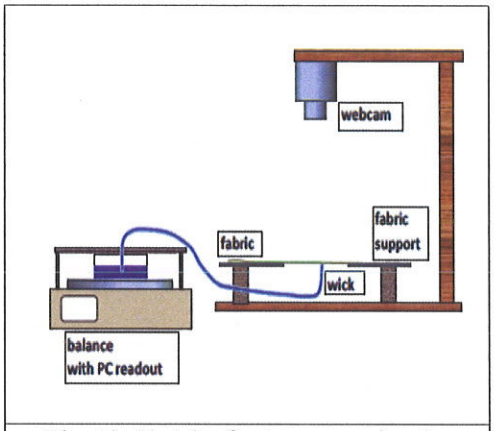


Fig. 10: Sketch of setup measuring the weight of liquid and obtaining the wet stain on the textiles [28]

The penetration of drop in the fabric is related to both **wetting** of fabric and **diffusion** of liquid through the fibres. Several softwares for data acquisition and quantifying the wet surface were developed [29]. LabVIEW language was used for writing a programme for image acquisition from AVI type movie. Fig. 18 displays the monitor screen during data acquisition. The commands of the programme logic chart can be related to those on the screen. Acquired data are processed statistically for describing the wet surface. The algorithm developed for the analysis of wet surface [30] is based on the distribution of the values of luminosity (pixels) and not on their spatial relationship. The AVI movies of wet stain were analysed for each frame with the programme written in LabVIEW, for evaluating the wet surface as a function of time [29, 30]. At the end of this processing the relation of wet area and number of frame (proportional with time elapsed) is graphed. The programme provides also a text file giving for each frame the wet area (in pixels) and the time of acquiring.

For improving the visualisation of wetting one uses a dyestuff dissolved in water at low concentration. For our experiments we have used Methylene Blue MB, Rhodamine 6B (red colour), or Brilliant Blue FCF (E133, a food dye). The dyestuff was choose for producing most suitable wet stains according to a separate investigation. It is mentioned in literature that the methods for investigating the wetting of textiles may be grouped either as gravimetrical or optical methods.

In this work the behaviour of wet stain was followed up: 1) - by watching the spreading of a drop of dyestuff solution laid on fabric; 2) - by a continuous feeding of liquid; 3) - by continuous feeding and simultaneous variation in time of the amount of absorbed liquid (fig.10, [28]).

Kinetics of wetting from optic investigation and increase of fabric weight.

Wetting achieved by continuous feeding

By using the mentioned experimental setups one may record the curves of sorbet surface versus time and of sorbet mass versus time, like those given below in Table 16 [29]. The histogram in Fig. 18b (right side) indicates that the centre of the stain is the most wet / coloured, as there is the contact with dyestuff solution tank.

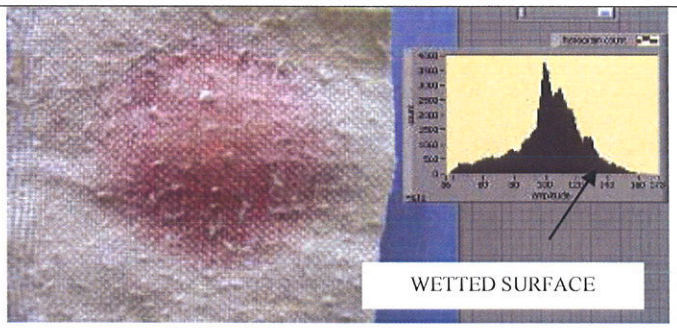
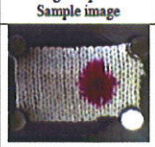
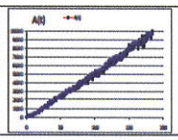
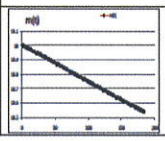
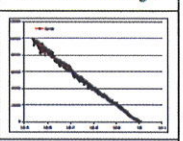
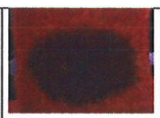
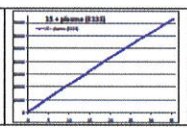
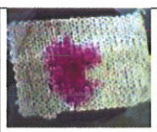
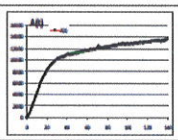
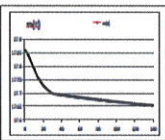
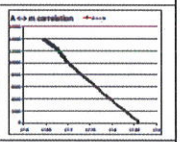


Fig. 18 b: Image of wetted surface (left) and corresponding histogram (right)

The change in time of the wetted stain is shown in Table 16 (for solution of Rodhamine 6B), for continuously feeding with liquid. The graphs plot the change of surface area in time, of the weight in time and the correlation area-weight. The diagrams obtained on polyester are also given to show the similarity of the process on various fibres. Each of the plots in Table 16 can be deconvoluted with the fitting programmes based on least square method. This way one may infer the kinetics of wetting from the evaluated fitting parameters.

Table 16: Change of wetted area and of dyestuff solution weight and the correlation area-weight

Probă Sample	Substanța test Test reagent	Imaginea probei Sample image	A(t)	M(t)	Corelație arie/masă Correlation area/weight
LAN21	R6Bconcentrat alimentare continuă/ R6B concentrated, continuously fed				
LAN18	E133 alimentare continuă/ E133 continuously fed				
LAN23	R6B diluat alimentare continuă/ R6B diluted continuously fed				

4. Statistical analysis of wetting process

The data acquisition programme allows the subsequent statistical processing of the wetting stain area. The algorithm developed for this purpose [30] is based on the distribution of luminosity values (in pixels) and not on their spatial relationship. The programme produces a histogram of luminosity (in pixels) of selected colour and calculates the total surface of it. The estimation of wetted area depends on the used threshold for processing the histogram of luminosity (in pixels) for each frame. In order to reduce the side effects (noise), one uses a second ROI. The graph relating wetted area to the number of frame (proportional to the time elapsed) is displayed at the end of this process. The programme, written in LabVIEW, may be used for both the results obtained with

continuous feeding and to those obtained by laying down the drops. The curves may be fitted with exponentials, polynomial functions, etc, for reaching understandable kinetic results. Each frame which leads to a point of a curve shows the wetted area variation, and may be reported also as a histogram [29].

Kinetics and the mechanism of wetting

The equations for describing the graphs given in Table 16 need to relate the variation of wetted surface in time and the weight of dyestuffs lost by tank and absorbed by textile material. The mathematics used to describe the wetting of yarns and fabrics offer a way to understand the transport of liquids through textile materials. In some cases the textile yarns were described as porous media through which the liquid is transported according to Darcy law [31]. Often it was assumed that the wetting acts through packages of capillaries; this is particularly the case when the pores are interconnected, homogeneously distributed, and, for the sake of simplicity, one may consider a single tube.

Since the textile fibres act as capillaries, the flux of liquid may be described by classical kinetic equation of Lucas-Washburn:

$$l^2 = \left(\frac{\gamma}{\eta}\frac{\cos\theta}{2}\right) rt \qquad (2)$$

where l stands for the length of capillary at which the liquid achieved; t is the wetting time; r is the rayon of capillary tube; η is the liquid viscosity; γ stands for the liquid surface tension; θ is the contact angle between liquid and solid absorbant. The proportionality factor is called the constant of capillary liquid transport.

All these dependencies lead to Washburn-type equations, generalized by Laughlin as:

$$l = a \cdot t^k \qquad (3)$$

where k may have values smaller than 0.5 for various fabrics.

It was observed that gravimetric method can be used for coloured fabrics with fairly good results.

5. Measuring the photocatalytical properties of samples coated with TiO_2 and ZnO

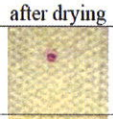
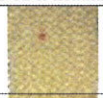
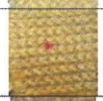
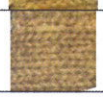
A) Irradiation with laboratory experimental device

The laboratory setup for irradiation was homemade. A photo camera takes the image of textile surfaces before and after irradiation. This way the stain resulting from a drop of dyestuff solution which was laid down on the surface was followed after various irradiation times. The irradiation was

performed with a xenon lamp of 150 W, placed at 30 cm away of the sample. The photographing of the stain was carried after various times of irradiation until reaching an ideal end result, the vanishing of the stain. In real cases we have observed only a decolourization of stain colour intensity.

The effect of TiO_2 nanoparticles concerning the self-cleaning properties of wool knitted fabrics was examined by following the decolourization of Methylene Blue stains. One notices that initial colour of initial wool knitted samples does not differ significantly from those of TiO_2 loaded ones. The image of sample 24 / TiO_2 in Table 18 shows clearly that after 12 hours of UV irradiation the stain of Methylene Blue stays almost unchanged on the wool knitted samples. Rhodamine 6B, both as 0.001 M solution and diluted 100 times, was also examined; the results are given in Table 20. This shows that the decolourization took place indeed.

Table 20: Drops of Rhodamine 6B laid down on fabrics, photoed before and after irradiation

Probă Sample	Rodamina 6B 0.04 mM, după uscare Rhodamine 6B 0.004 mM, after drying	Rodamina 6B 0.04 mM, după iluminare 12 h Rhodamine 6B 0.004 mM after 12 h irradiation
TiO_2/LAN1		
TiO_2/LAN17		
TiO_2/LAN21		

B) Decolourization of Methylene Blue after irradiation with UV, or Vis, using PCC2

The photocatalytical properties of the coated samples were tested also by the help of a professional tester, Photocatalysis Evaluation Checker, PCC2 type (ULVAC RIKO), using Methylene Blue (MB), as the testing dye to be degraded [32]. The equipment is drawn in Fig. 22 [33]. The photocatalytical experiments on PCC2 were performed by irradiating the samples with UV and Vis light. Some samples which at XRD, or SEM examination did not indicate crystalline deposition, exhibited still a signal of kinetic decay. These features, summed up, are given below.

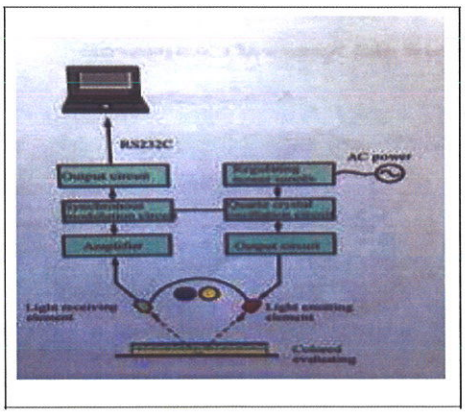
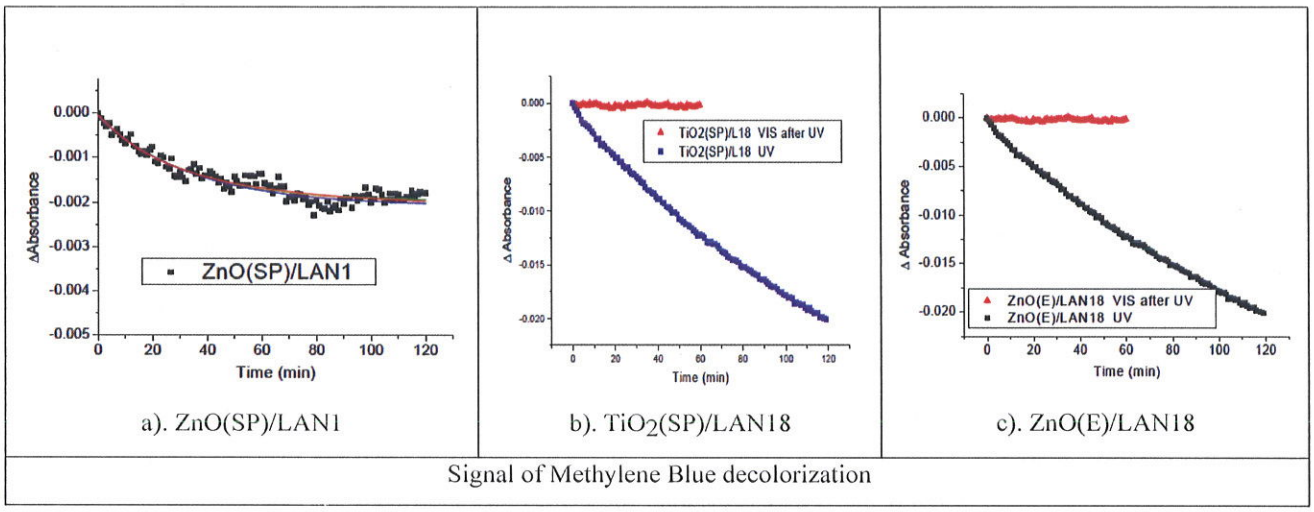


Fig. 22: The layout of the professional tester Photocatalysis Evaluation Checker PCC2 model (ULVAC RIKO).

Kinetic curves are shown below together with the structural properties of the samples required for explaining the photocatalytical behaviour.

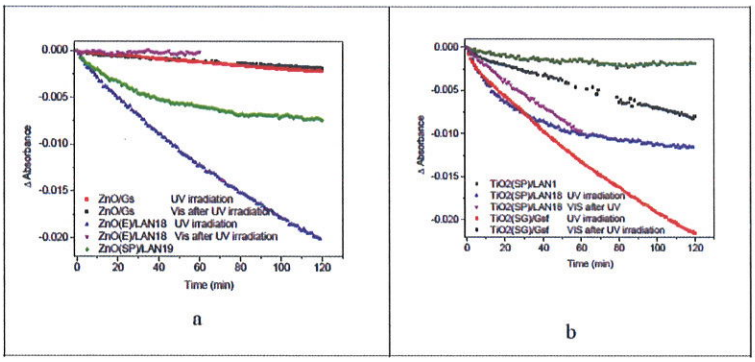
Although on some samples there are enough proofs that the semiconductor oxide is deposited, the photocatalysis still does not occur; it is likely that the semiconductor oxide is in a non-reactive state (crystalline), or air layer interposes between oxide and dye.

Time decay of MB by irradiation is plotted in Fig. 52 for some investigated cases [29].



a). ZnO(SP)/LAN1 b). TiO_2(SP)/LAN18 c). ZnO(E)/LAN18

Signal of Methylene Blue decolorization



a b

Fig. 52: Decay of Methylene Blue on the imbibed (and dried) sample of various fabrics containing: a) TiO_2 catalyst; b) ZnO catalyst, as in the corresponding inlets. Irradiation conditions are also mentioned in inlets. Gs stands for glass; Gsf - glass fabric

The variation of absorbency of investigated systems can be attributed to the two concurrent processes, namely: the desorbtion of MB dye from catalyst support, which increases the absorbency (case of reaction in solution) and degradation of MB dye, which leads to the decrease of absorbency. Although for certain samples there are proofs that the semiconductor oxide is deposited, the photocatalysis still does not occur; very likely in these cases the oxide is in a non-reactive state (amorphous), or there are air layers separating the oxide from dye.

Table 22: Apparent rate constants for decolourization MB process and the evaluated parameters from kinetic curves followed with PCC2 [34]

Sample	k' (min^{-1})		Chi^2
	UV	Vis	
ZnO(SP)/LAN1	31.8		$2.2741E^{-8}$
ZnO(E)/LAN18	155.0		$5.3785E^{-4}$
ZnO(SP)/LAN18	155.0		$5.3785E^{-4}$
ZnO(SP)/LAN19	36.4		$3.7453E^{-5}$
ZnO(E)/VSKBG	No signal		
TiO_2(SP)/VSKBG		No signal	
TiO_2(SG)/VSKBG	No signal		
ZnO & Ag(1-5%)-ZnO	0.004-0.013		
TiO_2	0.067		

* VIS irradiation took place after UV irradiation

Langmuir-Hinshelwood model developed for describing the kinetics of mineralizing process is applied to the reactions occurring on the surface of catalyst:

$$r = \frac{dC}{dt} \tag{4}$$

$$\ln\left(\frac{C_0}{C}\right) \simeq kKt = k't \tag{5}$$

r being the oxidation rate of reactant (mg/L/min), C stands for the concentration of the reactant (mg/L), t is the irradiation time (min), k is the rate constant (mg/min), K stands for the coefficient of absorption of dyestuff solution (L/mg) and k' is the apparent rate constant (min^{-1}) including the contribution of rate of dye mass transfer onto the surface of photocatalysor and subsequent surface reactions. The values of kinetic parameters are in good agreement with those found in literature for similar cases. The textiles coated at room temperature with TiO_2, or ZnO particles exhibit a photocatalytical activity by UV and Vis irradiation.

CONCLUSIONS

This work used several (20) Merinos or Tigaie wool samples, in form of knitted (17) or woven (3) fabrics, provided by industry (15+3), or home workshops (2), for comparatively study their hydrophobic / hydrophilic properties and processes to enhance either property. Two of the most known semiconductor oxides, TiO_2 and ZnO, respectively, were chosen for functionalizing the surface of textile materials with nano-particles of them via simple, efficient and relatively accessible

methods which allows controlling the coating oxide layer. The data were analysed by using methods based on multidimensional linear algebra and multilinear statistics.

In this Thesis:

- were deepened the methods for studying the hydrophobic / hydrophilic properties of wool fabrics (industrial or home processed);
- were developed various experimental devices;
- were developed data acquisition and processing programmes;
- were tested the mentioned experimental setups and programmes on samples made of natural fibres less investigated (wool) and on samples for which the behaviour at wetting is known (polyester fabrics);
- were chosen the solutions of testing dyes and the suitable concentrations from separate studies;
- were investigated the self cleaning properties on wool textiles functionalized by coating ZnO (SP)/TiO_2 (SG or SP); the behaviour of the samples was fitted with various models, either by considering the texture of the samples and the count of the yarns, or by taking into account the wetting mechanisms, transport and even photon excitation mechanisms;
- was developed a setup of fabrics irradiation and photographing before and after irradiation;
- were prepared 3 manuscript to be submitted for publication and 5 communications for national conferences with international participation.

Novelties of the Thesis

- functionalizing textile samples of less used fibres for such purpose, namely of wool, by depositing nano-particles of semiconductor oxides;
- developing new laboratory devices for studying the water transport through fabrics;
- use domestic wool samples of Tigaie, along with those of Merinos;
- developing a data acquisition programme from movies of drops, which allowed further processing of electronic image of textile surface;
- developing a programme for processing the images of wetted surfaces, for evaluating the area of wetted stain;
- analysis of hydrophobic / hydrophilic properties of knitted and woven wool fabrics by using the programme for evaluating the area of wetted stain;

- extract relevant information for characterizing textile surface after a treatment by using statistical methods used in spectroscopical analysis;
- study of textile wetting phenomena which allows to discriminate among woven/knitted structures for choosing most suitable one for removing the perspiration during wearing;
- investigate photocatalytical properties of coated materials for developing potential applications; textiles coated at room temperature with particles of TiO_2 or ZnO exhibit a photocatalytic activity when irradiated with UV or Vis light;
- investigating the self-cleaning properties of wool fabrics by the help of the dye decolourization test method;
- decolourization process appears to follow a pseudo-first order kinetics.

The results obtained so far consolidated the expertise of the working team regarding the characterization of textile material-semiconductor oxide systems by the help of wetting and liquid transport methods. This expertise is going to be valorised by finding new potential applications of such textiles in industry. The results were presented at five national conferences with international participation, and in three papers, out of which one is already published in a peer review journal, a second one is in publishing process also in a ISI journal and the third is going to be soon submitted for another ISI journal.

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