Polyester fabrics coated with SiOx nanoparticles by vacuum deposition at small angle. Structural characterization and wetting properties

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Vacuum deposition at small angle was successfully applied in deposition of SiOx particles onto polyester textile materials; this deposition is here presented in comparison with that upon other materials made from poly(lactic acid), polyamide or hemp. Structural and spectroscopic characterization of deposited samples has been performed and compared with that of the raw materials. The deposited particles are amorphous. Contact angle measurement by the sessile drop method, was used to study the wettability behavior of the investigated composite systems. The hierarchical roughness structure generates hydrophylic properties onto polyester fabrics and the other functionalized samples after deposition. The deposition technique was proven to be highly reproducible, easy scalable and cheap, allowing a wide range of applications.

1. Introduction

Silicon oxide SiOx or even silicon dioxide SiO_2 were deposited last years onto polymeric supports as the alternative to the metallic depositions used for packing matter due to their transparency, recyclability, microwave use and impressive barrier properties [1], to produce textiles with hydrophobic properties [2]. In addition, small amounts of silica were immobilized onto textile surface to lead to flame retardant properties [3].

SiOx deposition can be performed by several physical techniques, such as sputtering [4] and ion beam evaporation [5], plasma enhanced chemical vapor deposition [6-9]. However, due to the columnary nanostructured relief of deposited layer it was expected to increase the roughness of the textile surface; in addition, it was own experience as concerning vacuum deposition at small angle [10-13]: thus we preferred this technique for a SiOx deposition onto textile materials. Polyester (P) textiles used have different sizes of the meshes [14]; other materials investigated for comparison were polyamide (PA), poly(lactic acid) (PLA) and natural cellulosic hemp (H) textiles.

2. Experimental

Fabric samples

The investigated textile elements differ by the chemical nature of the substrate fibers and by the surface roughness (see Table 1).

Table 1. Textiles chosen to be deposited.

Label	Textile 2D-element/thread	Nature of the fibres	Color
P1	Knitted/ interlock/Nm 70/1	polyester	White
P2	Knitted/ interlock/Nm 50/1	polyester	White
P3	Knitted/ glat/ Nm 50/1	polyester	White
P4	Fabric/ Nm 70/2 + Nm 40/2	polyester	White
PA	knitted	polyamide	White
PLA	non-vowen	poly(lactic acid)	White
H	fabric	hemp	Beige
P27	fabric	polyester	White
P28	fabric	polyester	White
P30	fabric	polyester	White

Prior to functionalization by deposition the plain weave was cut at the dimensions of ~20×20 mm and washed in n-propylic alcohol by 5 min sonication to remove the impurities. The drying was performed at room temperature with caution against dust.

Surface functionalization

SiOx was deposited under vacuum in a B30.2 (Hochvakuum Dresden) installation at small angle of 30°

against the surface namely 60° against the surface normal direction. The conditions (pressure of 10^{-5} bar, the deposition rate of 0.1 nm/s) were thus to lead to an estimated thickness of ca. 60 nm. Deposition matter was pure silicon oxide for coatings (Balzers) [10-13].

Characterization

The sample characterization was complex and considered both the original and the deposited fabrics as well. The structure and surface morphology were studied by X-ray diffraction, optical and electron microscopy, while the deposition changes were measured in addition by means of FT-IR spectroscopy. We have then applied the following techniques:

- *Direct visualization* of the samples to assess the mesh size. We used an optical microscope at diffuse illumination as already described [15] the receiver could be a photo camera, giving the possibility to save the observed images.

- *Scanning Electron Microscope* (SEM) micrographs taken with a Zeiss Evo 50 XVP instrument after conventional metallization of the samples by means of a plasma sputtering apparatus.

- *X-ray diffraction* with a D8 Advance equipment (Bruker-AXS) with a CuK_{α} radiation (K_{β} radiation being eliminated using a nickel filter) allowed phase identification. The qualitative aspects were obtained by Rietveld refining.

- *Fourier Transform Infrared Spectroscopy (FTIR)* in attenuated total reflection (ATR) or transmission mode with a Spectrum BX II (Perkin Elmer) instrument by collecting 28 scans at a resolution of 4 cm^{-1} or with a Scanning Microscope Spotlight 400 (Perkin Elmer) coupled with a Spectrum 100 FTIR spectrometer which was working in steps of 6.25 μm.

- *Spectro-ellipsometry (SE)* with a DUV-VIS-XNIR Variable Angle Spectroscopic Ellipsometer (Woollam); the spectral domain spreads between 193 and 2200 nm while three incidence angles (65°, 70°, 75°) were set to measure the ellipsometric angles ψ and Δ. Cauchy model with optical constant variation was then applied to interpret the SE data.

- *Thermogravimetric measurements* were performed with a Diamond TG-DTA apparatus (Perkin Elmer) in a temperature range of 30-800 °C, at a heating rate of 10 °C /min.

Wetting properties

The water repellency was considered for the performance properties and was evaluated by measuring static (equilibrium) contact angles at room temperature with Drop Shape Analyzer DSA 100 (Krüss). The working mode has been described previously [16]. A fixed needle supplied a water drop of 3 μL onto the solid sample to be investigated. The data resulted from capturing the image of the sessile (static) drops which was processed using specific programs to fit the profile with the Young-Laplace or polynomial of 2nd degree equations. Finally, one obtains the value of the equilibrium contact angle (CA). At least five different points on each sample were thus tested.

3. Results and discussion

The results obtained from this experimental study can be divided into two main parts. The first part considers the characterization of the original and deposited fabrics and the second evaluates the effects of the functionalization with SiOx nanoparticles on the wettability properties against water drops. The deposition onto polyester textiles and the comparison with the textiles of other chemical nature is discussed on the basis of these investigations.

XRD studies

XRD studies were performed in the aim to observe the phases and the crystallinity of the samples. Some diffractograms of the original textile materials (P1, PA, H, PLA) were already shown and discussed in ref. [14]. However, since the layer deposited is expected to be rather thin, the crystallinity was checked onto test glass plates: The deposited SiOx layer was found amorphous.

Morphology features by SEM

The morphologies of SiOx particles grown on the investigated fabrics were characterized by SEM. Representative micrographs are given in Fig. 1 for SiOx functionalized samples at different magnifications.
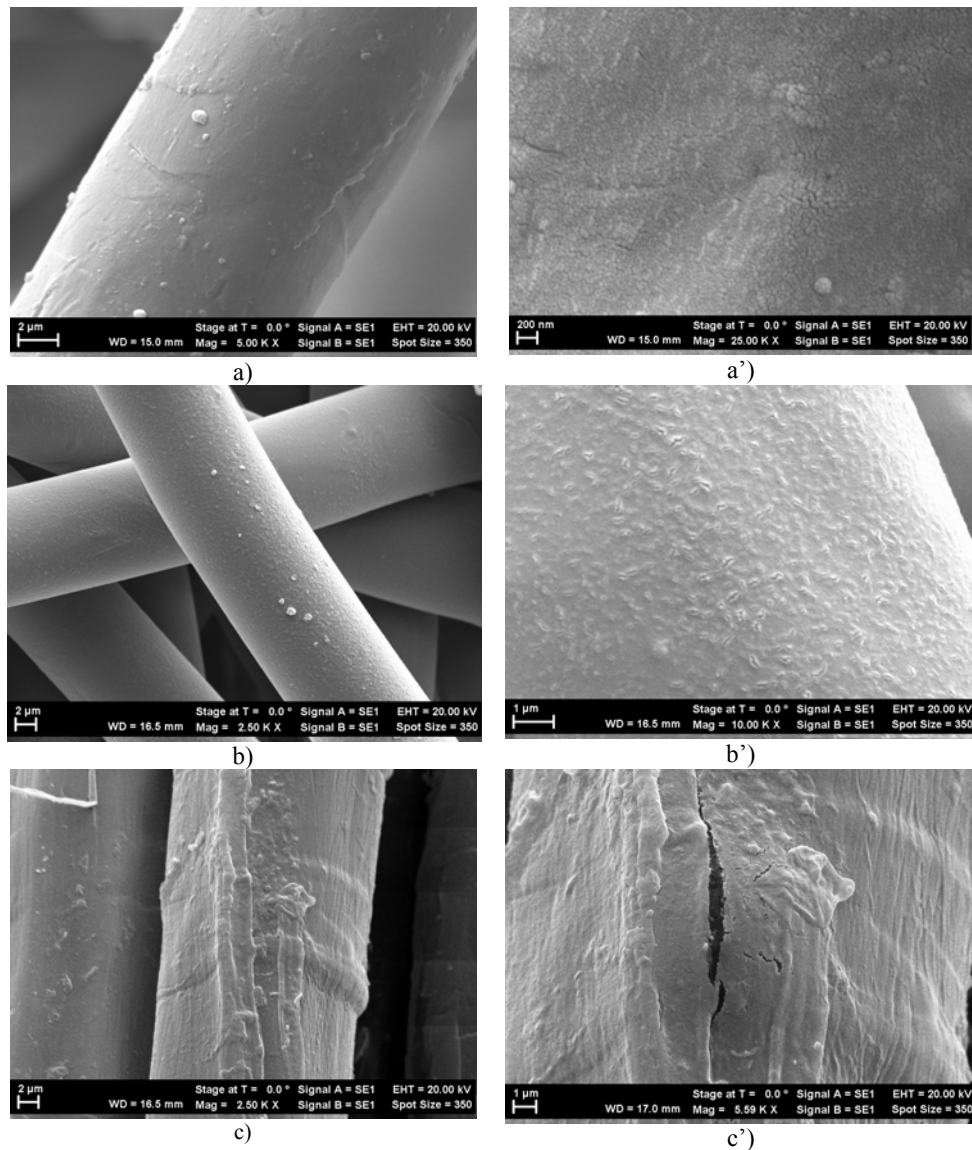
Fig. 1. SEM images of some investigated textiles, deposited by SiOx layer, at two magnifications: a,a')
SiOx/P2; b,b') SiOx/PLA; c,c') SiOx/H sample.

The raw material images allow us to observe some defects like a few kink bands, dislocations, nodes and slip planes which are in fact usual in hemp materials [17]. The diameter of the fibers can be also seen as being of ~10 μm.

The images of the deposited samples show that the SiOx particles are grown on the fibers surfaces in a continuous and non-columnar layer. Apparently, each individual fiber of all the samples look like uniformly covered with this amorphous layer.

Thermogravimetric investigations

These were performed in order to evaluate the sample loading with deposition material and the deposited layer-substrate interaction [18]. Representative curves are shown in Fig. 2.
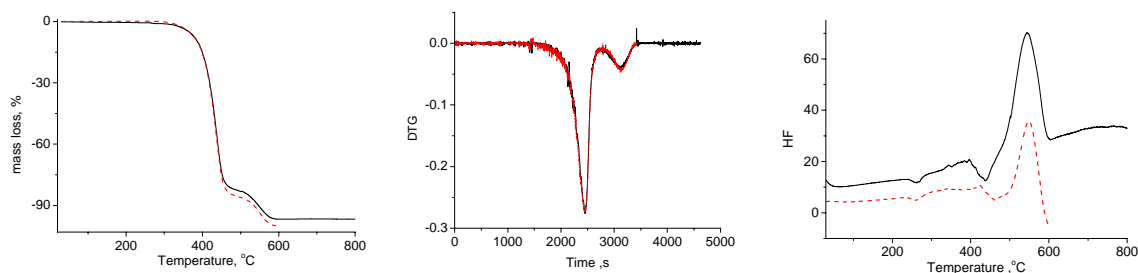
Fig. 2. TG, DTG and HF curves for P2 sample (black continuous) and SiOx/P2 sample (red dashed).

Fig. 2 shows a mass loss which is similar for all the P samples. The differences among the samples are in a rather narrow interval of around 10%, which allows their direct comparison. The small differences might indicate the interaction of the deposited layer with the surface. The filling degree calculated on the basis of the TG data is ca. 1-2%.

The biggest step of TG curve corresponds to a endothermic peak in the heat flow. The samples V2 and SiOx/V2 present differences as concerning the onset temperature which is higher for the deposited sample than for the original one, indicating that there is an interaction between the deposited layer and the substrate. The maxima in the HF curve do not coincide with those in the TG curve, showing that surface phenomena were involved.

Ellipsometric data

The spectra were registered for SiOx/glass sample which was deposited together with textile samples allowing to evaluate the thickness of the deposited layer. This layer is less uniform, in the thick part rising to 440 nm.
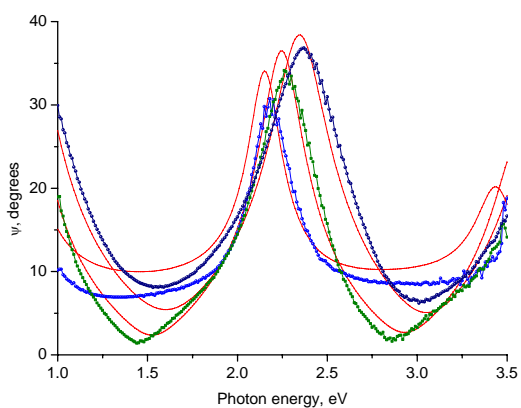

Fig. 3. Ellipsometric spectra and their Cauchy fit for the reference SiOx/glass sample. The angles are as follows: 50° (bleu), 55° (green) and 60° (black); the fit line are red continuous.

FTIR investigations

Fig. 4 presents the FTIR ATR spectra of deposited samples in representative cases. The wavenumber domain reproduced contains the positions where the Si-O-Si vibrations are expected: bending around 800 cm^{-1} and stretching at 1000-1200 cm^{-1} [19].

The position of the main peaks in polyesters is as follows: the stretch vibration of the C=O group of the esters (and aldehydes or acids as well) which appears around 1730 cm^{-1}; the peak at 725 cm^{-1} which is due to the deformation of the C-H group; the valence vibration of the alkyl groups observed around

3000 cm^{-1} (Ref. [20]), e.g. at 2916 (C-H) and 2975 cm^{-1} (CH$_3$); CH$_2$ symmetric bending at 1425 cm^{-1}; C-O bending at 1247 cm^{-1}; stretching of H bonded (or free) OH groups in the region 3400 (3700) cm^{-1}. Hemp fibers, which are hydrophilic have large peaks in might give also [21] peaks in the frequency range of carbonyl stretching 1700-1750 cm^{-1}: The peak at 1732 cm^{-1} is addressed to functional groups of >C=O or -COOH, while 1738 cm^{-1} corresponds to hemicellulose, 1736 cm^{-1} to pectins and waxes. The structure of the poly(lactic acid) is very related to the polyester structure, consequently the spectrum of PLA is alike with those of P samples. PLA generally shows in this region either complex splitting with possible components at 1776, 1759 and 1749 cm^{-1} or only one centered at 1710 cm^{-1} [22].

The spectra of all the investigated P samples are perfect comparable indicating the same nature of these materials. In the case of PA sample, the most important region is that at 1700–1650 cm^{-1}. This region corresponds to the carbonyl amide stretching vibrations: 1663 – Amide I band of secondary amide; 1558 – Amide II band [23]. Also, it is important the stretch vibration of amine C-N appearing at ~1250 cm^{-1}.

Microscopic visualization of surface changes is illustrated in Fig. 2 in which representative microphotograps taken with the FTIR scanning microscope were displayed: The pictures give evidence for distinct variation of the textile surface due to SiOx deposition process, especially increased roughness and "grafting", such modifications were observed in other cases of fiber treatments as well [24].

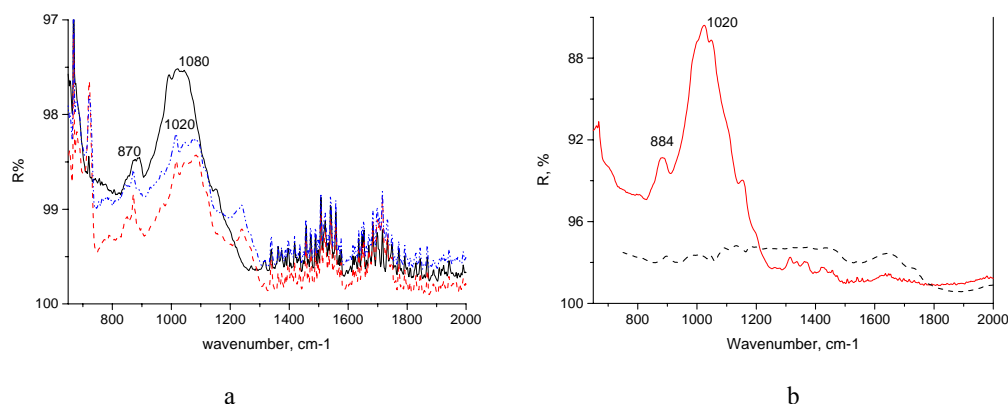a   b

Fig. 4. FTIR ATR spectra of deposited samples: a) SiOx/P2 (dashed), SiOx/P3 (dash dot) and SiOx/P4 (continuous); b) SiOx/H (continuous) and H (dashed).
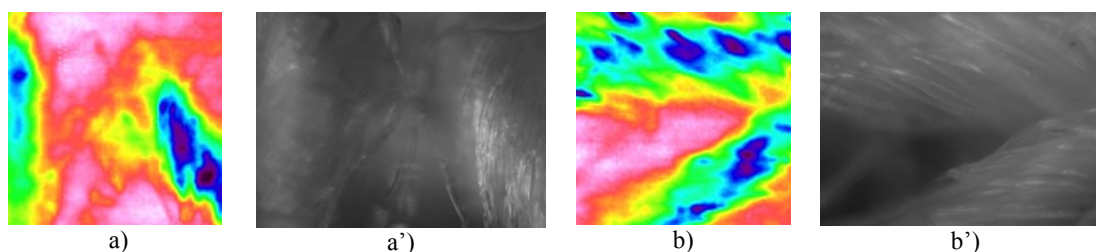

a)   a')   b)   b')

Fig. 5. Images scan FTIR (a,b) and visible (a', b') for representative polyester samples SiOx/P2 and SiOx/P4 respectively.

Wetting properties by contact angle measurements

In Fig. 6 the image of the water droplets onto the deposited P2 and H samples leading to the corresponding contact angle, is represented. The measurements were performed for a direction parallel to the privileged (that of vertically advance) one of the knitted matter; there are differences of a few degrees when the measurements are performed following a direction perpendicular to the privileged direction.

As resulted from Fig. 6, the surfaces investigated are far for being flat, smooth and homogeneous: Textile surfaces are rough to a certain degree; depending on the structure of the interlace of yarn strands, the fiber arrangement in the fabrics, woven, knitted and needled nonwoven ones. This particular structure makes difficult the application of the model algorithm. In addition, wetting of fabric surfaces is complicated by the heterogeneity, diffusion of liquid into the fiber, and the capillary action of the fiber assembly: therefore the experimentally measured contact angle is in fact an apparent one and can differ considerably from the true value.

The mean CA values of the raw or deposited samples are given in Table 2. One can observe that the CA generally decreases by functionalization, with a few degrees up to several tens of degrees. The investigated materials become more hydrophilic.
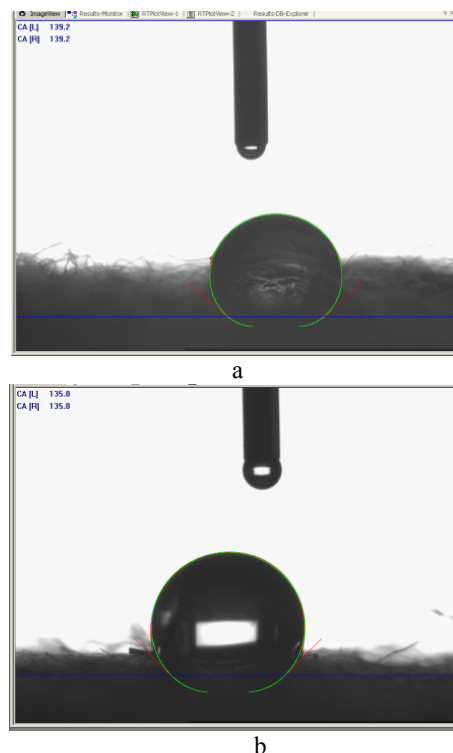

a

b

Fig. 6. Water droplets in contact with the surface of a) SiOx/P2; b) SiOx/H samples. The shape contour and the left/right tangents are drawn as well. Small fibers can be observed on the material surface.

Table 2. Static contact angle (degree) in raw and SiOx
functionalized form of the samples.

Sample	Raw	SiOx
P2	136,9	139,2
P3	138,1	128,9
P4	158,2	154,9
PA	165,1	97,6
PLA	129,6	hydrophylic
H	126,9	135,0
P27	hydrophylic	hydrophylic
P28	152,1	105,3
P30	124,8	75,5

4. Conclusions

Polyester textiles were successfully coated with SiOx particles using a vacuum deposition at small angle technique. Their behavior was compared with that of other representative fabrics made from poly(lactic acid), polyamide or hemp. The deposited samples were characterized and the structural investigations show that the SiOx layer is amorphous and leads to changes of the wetting properties toward hydrophylicity.

The filling degree calculated on the basis of the TG data is ca. 1-2%.

TG curves of raw and deposited samples show different onset temperature of the highest peak, higher for the deposited sample than for the raw one, indicating that there is an interaction between the deposited layer and the substrate.

The contact angle measurements confirm that the presence of SiOx particles on the fiber surface transforms the textiles into hydrophilic one.

The deposition process was successful for the polyester fabrics and for the other investigated fabrics, its main advantages compared to other techniques being related to its scalability and low cost.

Acknowledgements

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