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Coloured silica hybrids for functionalizing cellulose materials

A. RADITOIU, V. RADITOIU[*], V. AMARIUTEI, M. GHIUREA,
C.A. NICOLAE, R. GABOR, R.C. FIERASCU, L.E. WAGNER
National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, 202 Splaiul Independentei, 6-th district, 060021, Bucharest, Romania

The paper presents new types of coloured organic-inorganic hybrids deposited as coating materials on the surface of cellulose materials by sol-gel processes. Coated materials were characterized by: XRF spectrometry, FT-IR spectrometry, UV-VIS reflectance spectra and colour measurements in CIELAB system, scanning electron microscopy (SEM), thermal analysis (TA) and dynamic mechanical analysis (DMA). Structure-properties relationships of the obtained coated cellulose materials are discussed with respect to the structure and nature of the hybrid organic-inorganic coloured coatings.

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1. Introduction

In the last years the interest showed for textile fibres has changed with obtaining nanodispersions having a high solid content and particle diameters below 50 nm. Nanosols used as coating materials have the advantage of high storage stability, a good adhesion to textile fibres and require a short drying time at relatively moderate temperatures. Coatings obtained are interesting in particular to functionalize textile surfaces because they can be easily chemical or physical modified allowing changes of the resulting properties in a very extensive domain [1].

There are many studies on the modification of textile fibres using organosilane compounds, many of them focusing on their impact on mechanical properties of the obtained composites. This type of treatments involves condensation of silanole groups with functional groups from the fibre surface. Thermal curing processes, that occur after chemical grafting, leads to a chemical change of textiles surface [2] and as a consequence properties are strongly influenced.

Regarding usage of dyes in sol-gel systems on textile substrates, is to be mentioned an enhanced activity for achieving applications of such systems in the biomedical field [3,4], but also in textile dyeing of hydrophilic [5] or hydrophobic [6,7] substrates as: anionic, cationic and non-ionic dyes embedded in various silica networks. Properties of the obtained coatings and the influence of the host matrix on the washing fastness, stiffness, water contact angle, is also subject of several works [8-10].

2. Experimental

2.1 Materials

All of the chemicals used were of laboratory reagent grade and were obtained from Merck (Germany) and Aldrich (USA). Hydrochloric acid (0.1 N), tetraethylortosilicate (TEOS), phenyltriethoxysilane (PhTES), ethanol, tetrahydrofuran (THF) were used in this study as they were received. Silicon anhydride (SiO_2 content: 83.71%) from Merck was used as standard for quantitative XRF measurements. Disperse Red 1 - C.I. 11110 (DR1) was obtained by us as it was described elsewhere [11] and purified by extraction with toluene in a Soxhlet extractor followed by re-crystallization. The preparation of Disperse Red 1 chemically modified with NCOTEOS (DR1-PTES) followed a published procedure [12]. Textile material used was a 100% cotton fabric having a specific weight of 106 g/m^2, chemically whitened.

2.2 Procedures

2.2.1 Obtaining the impregnation bath

A solution made of 3.25 ml TEOS, 3.25 ml PhTES, 3.9 ml solution (DR1 or DR1-PTES 1.7 g / 100 ml THF), 0.65 ml water, 2.35 ml ethanol and a few drops of hydrochloric acid was stirred one hour at room temperature. Reactions were conducted in the usual manner of sol-gel processes [13]. The mixture was maintained under vigorous stirring, at room temperature and used immediately for padding cellulose materials.

2.2.2 Pad-drying procedure

A textile test-piece of about 2 g was padded with sol to a degree of assumption of 80%, by several successive passes in a laboratory Ernst BENTZ padding mangle, at a constant rate of 0.5 m/min. and pressure of 0.4 kg/cm^2. Coated materials were dried at room temperature for 2 h and then subjected to heat treatment at 120^{0}C for 1 h in a thermo-fixation oven.

2.3 Measurements

FTIR spectra were recorded on a Jasco FTIR 6300 spectrometer equipped with an ATR Specac Golden Gate (KRS5 lens), in the range 400-4000 cm^{-1} (30 scans at 4 cm^{-1} resolution).

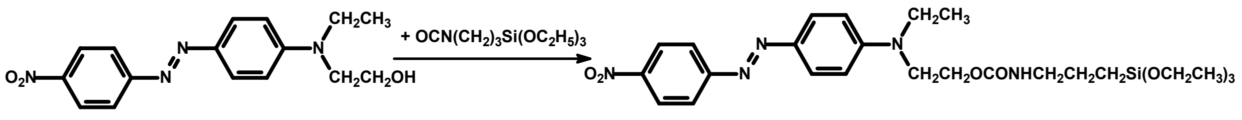
Total colour differences by CIELAB method using standard observer functions (D65/10^0) and diffuse reflectance spectra were measured with a spectrophotometer UV-VIS-NIR Jasco V-570 equipped with an integrating sphere Jasco ILN-51 (150 mm) against spectralon.

XRF analyses were performed on a PW4025-MiniPal-Panalytical EDXRF Spectrometer. Measurements were carried out in helium atmosphere, for 300 sec., without any filter, at 20 kV and automatically adjustment of the current intensity. SEM images were obtained with a scanning electron microscope FEI Quanta 200 (Philips).

Thermal measurements were conducted on a TA Q 5000 IR instrument, in air, at a heating speed of 10^{0}C/min. and the temperature range 25-700^{0}C (samples of 5-10 mg in platinum crucibles), while dynamic mechanic analysis was performed on a TA Q 800 instrument, in multi-frequencies-strain mode using a shear sandwich clamp, operated at a fixed frequency of 1 Hz, oscillation amplitude of 20 μm, temperature ramp of 3^{0}C/min. and temperature range 28-200^{0}C.

3. Results and disscusions

The aim of this work is to study coatings for cellulose textile materials made of coloured hybrid organic-inorganic materials. Coating materials were obtained through hydrolysis – condensation reactions from mixtures which contain azo dyes with or without alkoxysilane groups, TEOS and PhTES. Hybrid materials obtained by sol-gel methods from mixtures of silane precursors at specific ratio, exhibit major differences in optical, chemical and thermo-mechanical properties.



DR1 **DR1-PTES**

Fig. 1 Structures of disperse dyes contained in hybrid materials

The shade of the coating was slighter yellowish when the PhTES content was higher, probably because of π- π interactions between the chromogen and phenyl residues from the hybrid network and also hindering possible hydrogen bonds between chromogen and inorganic silica network [14]. Intensities of the obtained coloured coatings rise also in the same direction, stereo hindering being probably the main reason for obtaining a similar effect when the chromogen is forced to stay at a certain distance as in the case of DR1-PTES hybrids. In the later case, at the same intensity, the shade obtained is more yellowish than that obtained with DR1.

Colour difference measurements show that total colour difference is almost the same for DR1 and DR1-PTES hybrid materials, a little higher in the last case. Luminosity is higher for DR1-PTES coatings while the shade is shifted toward yellow comparatively to DR1 coatings, because Δa>0 and Δb>0.

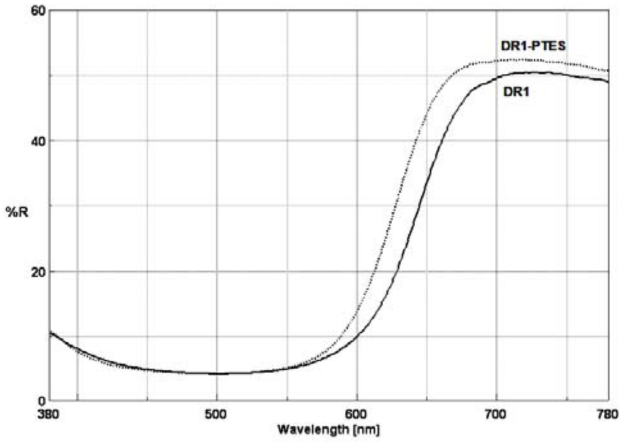


Fig. 2 Diffuse reflectance spectra of the coated textile fabrics

Table 1.Colour differences of coated materials

Coating composition	**D65**											
	Tristimulus values			**Trichromatic coordinates**		**CIELAB values**			**Colour differences**			
	X	**Y**	**Z**	**x**	**y**	**L**	**a**	**b**	**ΔL**	**Δa**	**Δb**	**ΔE_{ab}**
DR1	9.67	7.12	5.28	0.4383	0.3225	32.07	26.43	9.60	-59.92	26.87	10.14	66.45
DR1-PTES	12.60	8.66	5.06	0.4789	0.3289	35.32	34.00	16.23	-56.68	34.44	16.77	68.41

XRF analysis of cellulose materials coated with DR1 and DR1-PTES hybrids, revealed the presence of silicon at the surface of the textile material. The amount of silicon at the surface of the fibres was about 9.5% (weight) for coating obtained with DR1, a little higher for the coating obtained with sol of same composition (without dyestuff) about 9.7% by weight, while for coating obtained with DR1-PTES the amount of silicon was about 10%. For pure cellulose sample silicon was absent at the surface of textile fibre.

The results obtained shows also that the difference recorded between fibres coated with sol containing DR1 and with sol containing DR1-PTES was about 0.5% by weight and comes from the amount of silicon of DR1-PTES.

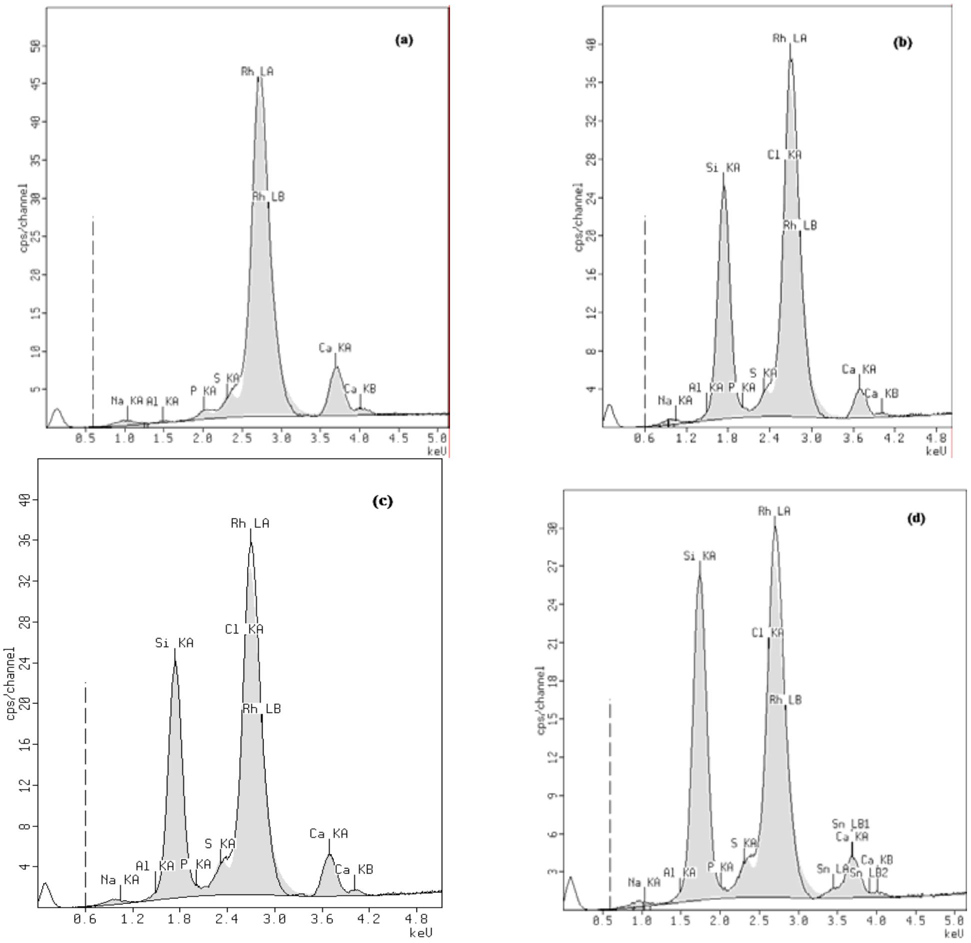


Fig. 3 X-ray microanalyses of a) untreated fibres; b) fibres with silica nanosol; c) fibres coated with DR1 hybrid; d) fibres coated with DR1-PTES hybrid

Because quantity of dyestuffs is small we couldn't identify any of their structural characteristics when we have analyzed coatings obtained onto the surface of the fibres [15]. That was the reason for comparing FTIR spectra for uncoated cellulose fibres, colourless sol and cellulose fibres coated with sol.

Analysis showed infrared spectral characteristics for cellulose materials such as bands situated at 3331-3282 cm^{-1} due to OH stretching vibrations and 2897-2861 cm^{-1} for methylene symmetric and asymmetric stretching vibrations. It was detected also a band at 1644 cm^{-1} that is due to bending vibration of water molecules from the fibre. As structural characteristics also in the range 1280-1427 cm^{-1} and 702-525 cm^{-1} are visible bands that correspond to in plane and respectively out of plane OH deformation, while in the range 1202-897 cm^{-1} are strong bands corresponding to C-O stretching vibrations. All these bands are present in the spectrum of the coated cellulose fabric also.

For the sol composition used as impregnation bath characteristic bands were situated at 3623 cm^{-1}, a sharp band that correspond to free Si-OH stretching vibration, 3363 cm^{-1} due to OH associated groups and 3077 cm^{-1} for OH stretching vibrations. Very important for the study were skeletal vibrations of the phenyl groups situated as sharp intense bands at 1595 cm^{-1} and 1431 cm^{-1}. Ring deformation of phenyl groups was seen at 695 cm^{-1} while C-H and C-C deformation vibrations were recorded at 734 cm^{-1}. These bands were observed also for coated cellulose fibres and proved the existence of coatings on the fabrics.

For coated cellulose fabrics Si-O-Si stretching vibration was recorded as an intense peak at 918 cm^{-1}, while specific intense peaks characteristic for silica networks and cellulose substrate were recorded at 1013 cm^{-1} and 1129 cm^{-1} corresponding to Si-O-C, Si-O-Si, respectively C-O-C stretching vibrations. Unfortunately for the coated fabrics in the range 1000-1100 cm^{-1}, vibrations are overlapped and hard to evaluate. A single band due to Si-O-Si group is clearly visible in the IR spectrum of the coated fabrics and identified in the spectrum of colourless sol also. This is due to Si-O-Si rocking motions and is situated at 473 cm^{-1} for colourless sol and at 482 cm^{-1} for coated fibres, respectively.

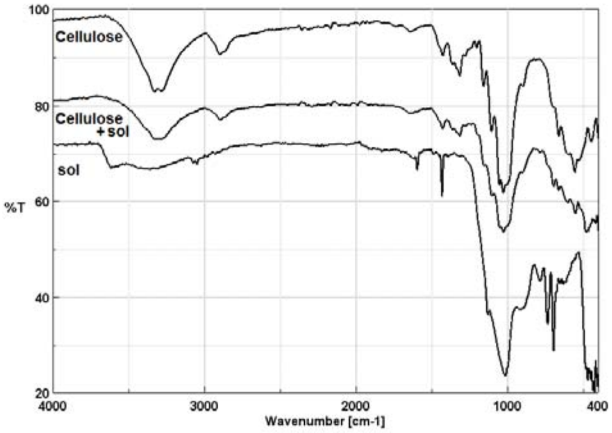


Fig. 4 FTIR characterization of silica coated cellulose fibres

For the evaluation of the thermo-stability of the coatings, comparative experiments were conducted before and after deposition onto the fabrics. Experiments were made in air at a heating rate of 10^{0}C/min. and in the range 25-700^{0}C. The mass loss observed in the first stage is due to dehydration of fibres, which is mainly the same for all the samples analyzed. For coated cellulose fibres weight loss in this temperature range was a little higher than that observed for untreated fibres, the difference being of 0.3% by weight. This can be due to the releasing of water and solvent retained during sol deposition, process that takes place at temperatures less than 100^{0}C.

In the second stage, uncoated cellulose fibre exhibited a mass loss of 85% due to thermal decomposition into carbon dioxide, carbon monoxide and carbonaceous char. The TGA curves for coloured samples indicated a similar trend, the mass loss being situated at 52-54%, due to the hybrid silica coatings.

The char content undergoes oxidative decomposition, in the third stage resulting in another important mass loss of 11-12% which is almost the same for all the samples analyzed.

It appeared from the TGA curves that the condensation of silanole to siloxyl groups takes place in the fourth stage and thus it was recorded only for the coated samples. The weight loss for these samples was almost the same of about 10-11%.

For uncoated sample it wasn't recorded any residue, while for the coated samples the residue at 700^{0}C was about 21-22% and correspond to SiO_2, a little lower for the DR1 hybrid coating and in accordance with the results for silicon content determined by XRF.

We consider that the first three steps were common for all the samples and correspond exclusively to dehydration and decomposition of the fibre, while only the fourth step was common to the coated samples and also only for these were recorded residues at 700^{0}C. The amount of hybrid material on the fibres surface determined from TGA analysis was about 32-33% by weight.

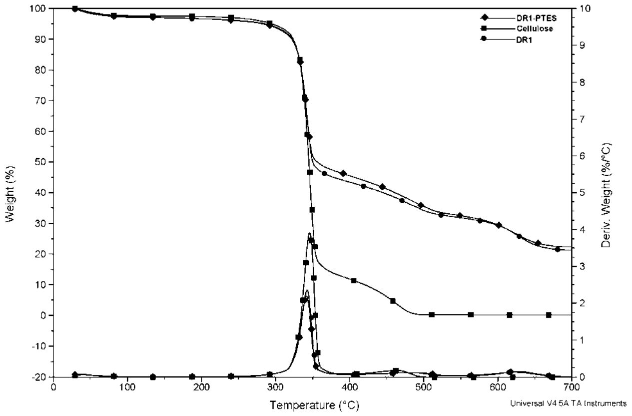


Fig. 5 Thermo-stability of coated cellulose fabrics

It was observed from SEM micrograph of uncoated fibres, that its surface has tiny cracks and is relatively uneven. As it was seen from SEM, using a mixture of TEOS and PhTES in a 1:1 weight ratio it was obtained a sol composition that cover uniform the surface of cellulose fibres. Coloured compositions obtained by adding DR1 or DR1-PTES to sol mixtures before impregnation lead to more uniform and free of cracks coatings.

After coating with hybrids, it was seen that tiny cracks on fibre surface disappeared as a result of the greater number of particles adsorbed onto the fabric pores. The phenomenon was similarly for both types of hybrids, the particles being relatively uniform distributed on the surface of the fabrics. Hybrid particles increased the hydrophobic character of the treated fabrics, because of the organic content and coatings obtained became more flat and regular due to better film formation.

Higher sol concentration, as was observed in case of cellulose fibres coated with silica sol without dyes, favoured formation of large particles and agglomerates, clearly seen in some regions on the surface of the textile fabric. Thus, the coatings obtained increased the roughness of the surface and induced a pronounced hydrophobic character to the treated fabrics.

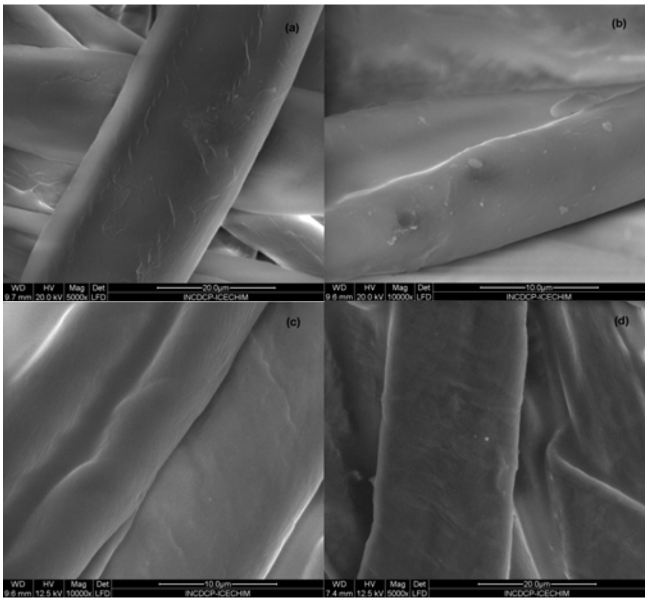


*Fig. 6 SEM: **a)** untreated fabric; **b)** fabric coated with silica nanosol; **c)** fabric coated with silica - DR1 hybrid; d) fabric coated with silica - DR1-PTES hybrid*

From DMA experiments we intend to compare properties of coated samples in relationship with dyestuff content and thermal after-treatment of the fabrics coated with organic-silica hybrids and formation of a reinforcing organic-mineral network on the fibres that lead to nanocomposites.

The dynamic storage modulus of the cellulose coated with silica increased when increasing the silane content, while the tan δ peak shifted to higher temperatures, broadened and decreased in intensity. This demonstrates the formation of a continuous rigid network coating on the surface of the cellulose materials.

The DMA studies of the DR1 hybrids indicate that the motion of the cellulose chains is constrained in the matrix. If the content in organic dye embedded into the network was rise, the storage modulus decreased and $T_{max.}$ decreased also. By modifying the surface with sols the storage modulus at 30^0C rise from about 500 MPa to more than 2000 MPa. Thermal treatment at 120^0C produces a more reticulated product and thus, storage modulus rise and loss modulus is lowered. The product became more stiffness at DR1 content of about 0.6% and after performing a thermal treatment at 120^0C.

During the experiments analysis reveals that for the fibres coated with coloured hybrid silica sols the tan δ peak corresponding to $T_{max.}$ is shifted to high temperatures (from 130^0C to 151^0C) by comparison to unmodified fibres. Since the relaxation peak height is associated with molecules mobility, it was observed that hybrid coatings had greatly reduced molecular mobility and in turn decreased the intensity of tan δ of more than 10 times compared to uncoated fibre. Coating has a considerable effect on the stiffness which affects the dynamic mechanical behaviour of the composites.

Table 2. DMA properties of coated cellulose materials

Sample	**Storage Modulus**		**Loss Modulus**		**Tan Delta**		**Stiffness (N/m)**
	T (^{0}C)	**G' (MPa)**	**$T_{max.}$ (^{0}C)**	**G" (MPa)**	**$T_{max.}$ (^{0}C)**	**Tan δ**	
Blank	30	(500)	133	111.8	129	0.5553	736452
DR1 0.6%	30	1782	128	88.46	139	0.05729	3293800
DR1 0.8%	30	2009	123	80.89	129	0.04731	3683890
DR1 0.6% 120^0C/1h	30	2222	114	86.89	130	0.04476	4072870
DR1-PTES 0.6% 120^0C/1h	30	2872	102	61.89	110	0.02276	4978570

4. Conclusions

Cellulose textiles coated with hybrid materials were obtained through sol-gel processes from non-ionic azo dyes bearing or not triethoxysilane residues and mixtures of alkoxysilanes. Structure-properties relationships of the obtained organic-inorganic hybrid materials are discussed with respect to the structure and nature of organic azo dyestuffs and silica network modifying silanes.

Hybrid materials were complete characterized by means of XRF spectrometry, FT-IR spectrometry, UV-VIS absorption and diffuse reflectance spectra and thermo-mechanical analysis.

Grafting of the azo dyestuff on the silica network and interactions between dyestuff molecules and organic groups of the network, lead to hybrid materials which exhibit different optical, chemical and thermal properties comparatively with hybrids containing embedded azo dyestuff.

Interactions between hybrid coatings and cellulose textile materials lead to composites having improved thermo-mechanical properties comparatively to uncoated textile materials.

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*Corresponding author: vraditoiu@icechim.ro