

# Silica-based Hybrid Coatings Containing a Non-ionic Dye as Colouring Materials for Cellulosic Fabrics

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*The paper presents experimental data regarding organic modified silica hybrids having embedded a non-ionic dye – Disperse Red 1, deposited on cotton fabrics. Hybrids were prepared by sol-gel processes using tetraethoxysilane and various trialkoxysilanes as organic network modifying agents, in acid catalysis and in the presence of Disperse Red 1. Control of the interactions between the organic non-ionic dyestuff and its embedding matrices allows tailoring the performance of the resulted coatings. Light and wash fastness and thermo-mechanical properties of the coated fabrics were investigated and correlated to the composition and morphology of the organic-inorganic coating materials. The results show that chemical composition of the impregnating bath have a decisive role in determining shade, intensity, fastness to light or washing of the coloured hybrid coatings as well as thermo-mechanical and hydrophobic properties of the coated textile fabrics.*

*Keywords: silica hybrids, non-ionic dye, cotton fabrics, contact angle, thermal stability*

Cellulosic materials are the most important natural textiles used in practice because of their availability, hydrophilic character, biodegradability and durability, thus becoming good candidates in obtaining multifunctional-coated textiles [1-3]. Moreover, the presence of reactive centres on the surface of the fibres can lead to the establishment of interactions between hybrid films used as coatings and textile substrate, which raise the adhesion and improve general properties of the coated materials [4-7].

Obtaining silica xerogel coatings on the surface of natural and synthetic fibres becomes a very important field of research during the last years. Concerns are centred mainly on acquiring multifunctional properties such as water and oil repellence, antibacterial, self-cleaning, antistatic, flame retardant or UV protective, without compromising original properties of the fabric [8-14]. Several works deals with obtaining hybrid coatings on cotton fabrics mainly in relationship with the improvement of thermal stability, flame retardancy and combustion behaviour of the coated fabrics [15,16]. Many attempts were made in order to achieve higher compatibility between silica coatings and cotton fabrics and moreover to enhance light and wash fastness correlated with maintaining the textile comfort [17,18]. The functionality of the fabrics depends on the intrinsic properties of the coating and on adhesion of the coating materials on textile substrate.

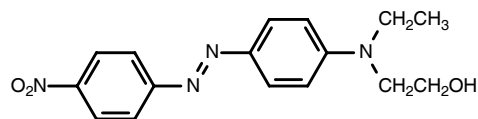
Our study was focused on investigating coloured organic-inorganic hybrid films obtained by impregnation and thermo-fixation on cellulosic substrates. In practice, the non-ionic dyestuff used as colouring material is not appropriate for dyeing this type of fibres. Impregnation baths were made of hybrid nanosols resulted after hydrolysis and co-condensation of different substituted alkoxyxilanes and tetraethylortosilicate in the presence of

Disperse Red 1. It is obviously that the nature of organic modifying agent in the hybrid films plays an important role in the design of the obtained coatings and will influence their properties as well as the visiting species such as dyestuff molecules [19-24].

## Experimental part

### Materials and methods

Tetraethylortosilicate (TEOS) (Merck), phenyltriethoxysilane (PhTES) (Aldrich), 3-glycidoxypropyltriethoxysilane (GlyOPTES) (Aldrich), vinyltriethoxysilane (VTES) (Aldrich), methyltriethoxysilane (MeTES) (Aldrich), octyltriethoxysilane (OTES) (Aldrich), 3-chloropropyltriethoxysilane (CIPTES) (Aldrich), ethanol (Chimopar), tetrahydrofurane (THF) (Fluka), hydrochloric acid (0.1 N) (Chimopar) were of laboratory reagent grade and were used without further purification. Silicon anhydride (Merck) was used as standard for quantitative XRF measurements. Disperse Red 1 - C.I. 11110 (DR1) with the structure shown in scheme 1, was obtained by us in laboratory [25], purified by extraction with toluene followed by recrystallization. Textile material used was a 100% cotton fabric having a specific weight of 106 g/m<sup>2</sup>, chemically whitened.



Scheme 1. Structure of Disperse Red 1 (DR1)

### Preparation of the colored hybrid coatings and impregnation of cotton fabrics

The impregnation bath was obtained by mixing under vigorous stirring, at room temperature, 3.08 g TEOS, 0.01 moles of one of the network modifying agents (PhTES, MeTES, OTES, CIPTES, VTES, GlyOPTES), 2.4 mL ethanol,

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0.4 mL HCl, 0.7 mL water and 0.05 g DR1 (added to the mixture as a solution in THF). After 24 h of reaction at room temperature, the resulted sol composition can be used as impregnating bath for cotton textile fabrics.

A cotton fabric of about 2 g was impregnated with sol compositions prepared as previously described by several successive passes (2-6) through a laboratory Ernst BENTZ horizontal pad mangle, at a constant rate of 0.5 m/min. and a pickup of 80%. Coated material was dried at room temperature for 2 h and then subject to heat treatment at 120°C for 1 hour in a thermo-fixation oven.

#### *Characterization techniques*

Total colour differences and reflectance spectra were measured using a Jasco V-570 UV-VIS-NIR spectrophotometer equipped with a Jasco ILN-472 integrating sphere (150 mm), at a 10° standard observer, and using spectralon as reference. From reflectance the color strength expressed as K/S values is calculated using Kubelka-Munk equation:  $K/S = (1-R)^2/2R$ , where K is the absorption coefficient, S is the scattering coefficient and R is the reflectance ratio measured at the wavelength of maximum absorbance.

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

A CAM 200 optical contact angle and surface tension goniometer (KSV Instruments) was used to assess wetting of the surfaces. A quantity of 6.5  $\mu\text{L}$  deionised water was dropped onto the surface of each sample in order to measure the static contact angle and the volume of water absorbed in time. Four water droplets were deposited on textile samples and contact angles were measured at different points on the surface. Surface morphology of coated cotton samples was investigated by the FEI Quanta 200 scanning electron microscope (SEM) at an accelerating voltage of 10-20 kV and at magnifications up to 10000X.

Thermal measurements were conducted on samples of 5-10 mg, in alumina crucibles using a SDT Q 600 instrument from TA Instruments, coupled with Pfeiffer ThermoStar Mass Spectrometer (0-300 amu, resolution 1 amu), in air, at a heating speed of 10°C/min. and in the temperature range 25-900°C. 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  $\mu\text{m}$ , temperature ramp of 3°C/min. and temperature range 28-200°C.

Light fading tests measurements were performed on a XENOTEST 150S+ (ATLAS). Light fastness was determined in accordance with ISO 105 B02 and was evaluated with the blue scale, which includes eight fastness grades and is exposed to light simultaneously with the analyzed samples.

In order to determine the stability of the fabrics dyed with different sol compositions, coloured samples were tested according to washing standards EN ISO 105 A01, A02 and A03 / 1999 in place for determining the colour change and transfer to the accompanying textiles. Washing test was made under conditions of ISO 105/C, using a solution of 1% by weight sodium dodecylsulfate, at a temperature of 40°C, for two hours, on a LINITEST type

device. After washing, test-piece composite was rinsed with warm and cold water and then left to dry in air, seams being disposed on three sides. After drying test-pieces were evaluated comparatively with original coloured textile fabrics and accompanying material non-tested by using gray scale (five fastness grade) for colour change and the staining on the accompanying materials. Both scales used for the evaluation of fastness includes also half grades and the highest values on the scale represent the best fastness, while the lowest values represent the worst fastness.

#### **Results and discussions**

Besides TEOS, several network modifying agents, in different ratio were used for the achievement of mixtures that can be used for obtaining coatings which have the appropriate properties on cellulosic fibres. During preparation of the sols using organically modified alkoxide precursors, the non-hydrolysable organic groups remain linked into the pores of the matrix. Thus, the network modifying agents allow controlling the polarity and the size of the pores according to the nature and amount of the non-hydrolysable organic group. During the sol-gel process Disperse Red 1 used as non-ionic dyestuff, remained entrapped in the organic modified pores of the resulted matrices. It was observed that colour properties were very sensitive to dye-matrix interactions and thus one of our objectives was to study the effect of different organic functional silanes used as network modifiers on the dyestuff embedded molecules.

As it was seen, during experiments colour properties of the coatings are strongly influenced by the polarity of the environment where DR1 embedded molecules are located. The pores of the inorganic network formed during sol-gel process have also an important effect on the optical properties of the coatings, size and distribution being the most important parameters that influence colour and finally fastness of the obtained coatings. Silicon alkoxides modified with organic groups used for preparing hybrids affect the chemical composition of the inner pore surface and are responsible for the environments of the entrapped dyestuff molecules and influence them by many mechanisms such as steric inhibitions, affinity with the non-ionic dyestuff or by limiting interactions between dye and the inorganic matrix.

The absorption spectra have been measured for different organically modified matrices and compared as a function of the nature and amount of network modifying agent. As it was observed the colour depends on the polarity of the pores where DR1 molecules are located. Thus, a progressive shift of the absorption maximum to the ultraviolet is observed as the ratio between organic residue and silicon in the hybrid matrix is increased, as in case of PhTES modified matrices showed in figure 1. For these matrices, wavelength of the absorption maximum varies in the range 504-512 nm corresponding to a TEOS:PhTES=1:1-3:1 molar ratio. As it was observed during experiments hybrid coatings prepared with phenyl groups showed more important hypsochromic shifts as compared with samples prepared with methyl groups at the same molar ratio referring to TEOS.

For coatings prepared without organic substituents on the silica network the surface of the pores consists mainly of silanol groups which confers a more polar environment for the dyestuff. The incorporation of organic groups lead to a decrease in the polarity of the matrix, on the one side because of the lower polarity of the organic groups linked to the pore surface and on the other side due to the large organic groups, such as phenyl, that may hinder OH groups

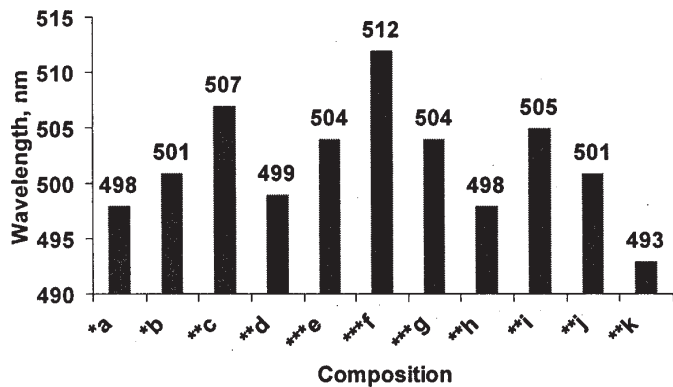


Fig. 1. Wavelength of the absorption maximum as a function of composition (a=TEOS/MeTES=1/1; b=TEOS; c=TEOS/PhTES=1/1; d=TEOS/OTES=1/1; e=TEOS; f=TEOS/PhTES=3/1; g=TEOS/PhTES=1/1; h=TEOS/CIPTES=1/1; i=TEOS/VTES=1/1; j=TEOS/PhTES/GlyOPTES=2/1/1; k=TEOS/PhTES/GlyOPTES/cat.=2/1/1; \*=2, \*\*=4, \*\*\*=6 successive impregnations)

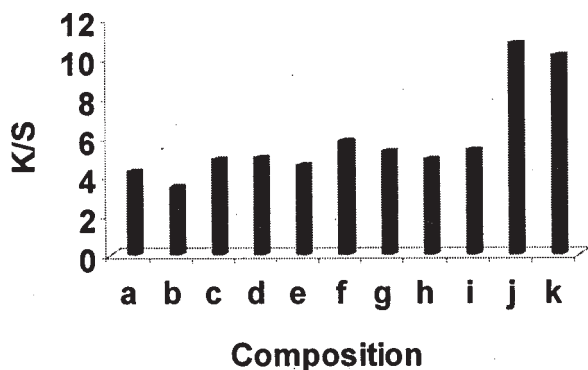


Fig. 2. Colour strength (K/S) as a function of coating composition

onto the matrix surface to interact with other groups of the dyestuff.

A more effective screening of the OH groups was observed when in sol gel-process was used GlyOPTES which contain epoxy groups capable of homopolymerization. In this case, the wavelength of the absorption maximum was recorded at 493 nm, the lowest value in the series, as it is observed from figure 1. During polymerization of the glycidyl residues are generated OH groups and it is probable that, hydrogen bonds with silanols from the silica network occurs. Thus, groups are oriented at the organic-inorganic interface in a such manner that the overall polarity of the pores is decreased due to the organic polymeric chains. This is indicated by a hypsochromic shift of the visible absorption bands.

Yellowish shades were obtained at higher dyestuff concentration and also when organic modified hybrid networks were generated from mixtures of precursors. Besides interactions between chromogen molecules and organic groups from the network, another explanation is that bulk organic groups on the surface of the silica network prevent interactions of alcoholic functionalities of the dyestuff with Si-OH groups which normally can lead to bathochromic effects. Moreover, the possible interactions between non-ionic dye and organic vicinities are in this case only of van der Waals type. Under these conditions it is very probable that in the case of GlyOPTES modified networks due to formation of hydroxyl groups during homopolymerization of epoxy groups, hydrogen bonds with hydroxyl groups of the dyestuff molecules occurs. The higher K/S values (fig.2) obtained in this case may be explained by the formation of hydrogen bonds.

The same situation is observed from total colour measurements in CIELAB system, as it can be seen in

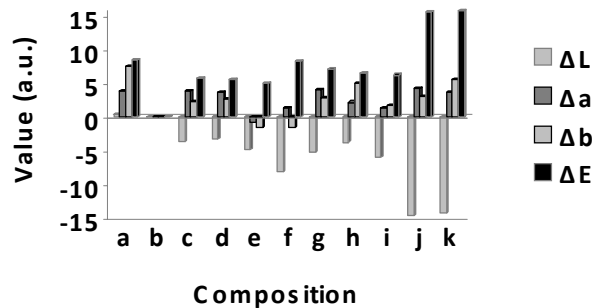


Fig. 3. Colour differences in CIELAB system

figure 3. Results show marked differences between compositions containing GlyOPTES and the others mainly due to hydrogen bonds as it was previously mentioned. Total colour differences are determined in this case by important differences in luminosity which is mainly influenced by the existence of hydrogen bonds. Using signs of  $\Delta a$ ,  $\Delta b$  parameters it is observed that colours of organic modified silica coatings become yellowish in almost all cases comparatively with coatings obtained using TEOS.

For all the coated fabrics analyzed by FTIR spectroscopy the main characteristic vibrations belongs to the textile cellulosic material, as in figure 4. Some of the absorption bands were influenced in position and shape by particular bands, usually strong, belonging to the network modifying agent from the coating material. Thus, the absorption attributed to the O-H stretching vibration is composed of two vibrations located at 3272-3293  $\text{cm}^{-1}$  and 3320-3336  $\text{cm}^{-1}$  attributed to inter-molecular and respectively intra-molecular hydrogen bonds. The doublet at 2888-2921  $\text{cm}^{-1}$  and 2850-2861  $\text{cm}^{-1}$  is attributed to  $\text{CH}_2$  asymmetric and respectively symmetric stretching vibrations and was intensified by the presence of OTES as network modifying agent. The band at 1632-1646  $\text{cm}^{-1}$  is due to the bending mode of the absorbed water in the textile fabric and is present also in the FTIR spectra of blank cotton fabric. The peak situated at 1427  $\text{cm}^{-1}$  originate from the  $\text{CH}_2$  symmetric bending, at 1356-1366  $\text{cm}^{-1}$  was seen a band corresponding to OH bending, while at 1314  $\text{cm}^{-1}$  was recorded a band due to C-C stretching vibrations.

The band at 1154-1158  $\text{cm}^{-1}$  arises from asymmetric bridge C-O-C stretching vibration and 1096-1105  $\text{cm}^{-1}$  was assigned to C-OH skeletal vibration. The C-O-C asymmetric in plane ring stretching vibration gives a prominent band at 1050-1053  $\text{cm}^{-1}$ , in the same range with Si-O-C asymmetric stretching vibration. The peak characteristic of organic modified silica coatings was situated for all the samples at 1250-1285  $\text{cm}^{-1}$  corresponding to Si-C symmetric bending vibrations. This is the most important band which attests the presence of Si-C bonds from network modifying agents on the textile fabric surface. Other bands characteristic to cellulosic fabrics are located at 1026-1028  $\text{cm}^{-1}$  and attributed to C-O stretching vibrations while at 891-907  $\text{cm}^{-1}$  are found vibrations attributed to  $\beta$ -glycosidic linkages, at 694-703  $\text{cm}^{-1}$  are bands belonging to  $\text{CH}_2$  rocking vibrations and at 659-666  $\text{cm}^{-1}$  are found OH out of plane vibrations.

Overlapped with some of these bands were found peaks near 1100  $\text{cm}^{-1}$  and 1053  $\text{cm}^{-1}$  that could be assigned to Si-O-Si stretching vibrations. For VTES coatings, C=C stretching vibrations are found together with a band at 773  $\text{cm}^{-1}$  corresponding to C=C-H out of plane vibration. In the case of CIPTES coatings C-Cl stretching vibration was found at 783  $\text{cm}^{-1}$ , while for PhTES, CH ring out of plane deformation was situated at 778-788  $\text{cm}^{-1}$  and in the case of MeTES coating band situated at 771  $\text{cm}^{-1}$  corresponds to Si- $\text{CH}_3$  deformation. GlyOPTES modified silica coatings

present a band at 904  $\text{cm}^{-1}$  due to epoxy ring symmetric stretching vibrations which disappeared after polymerization under thermal treatment and in the presence of N-methylimidazole, used as a catalyst.

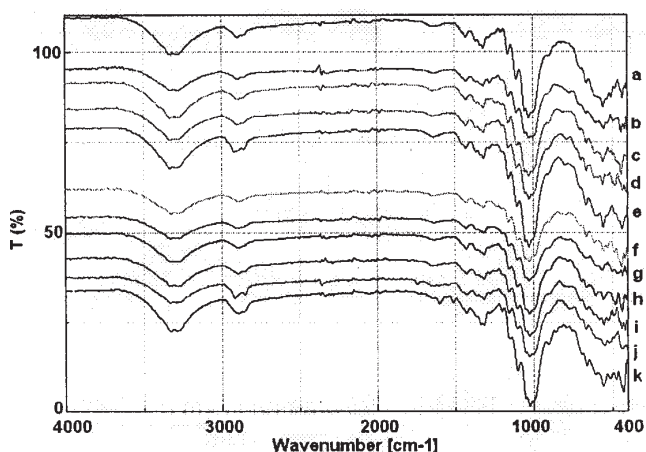


Fig. 4. FT-IR spectra of cellulosic coated fabrics

XRF analysis of coated cotton fibres showed the presence of silicon on the surface of the textile materials, the amount depending on the composition of the coating materials. The results obtained revealed that silicon at the surface of textile materials was situated in the range 8.2-9.4%, as it is show in figure 5. The highest value was recorded for coatings obtained using PhTES and TEOS at a 1:1 molar ratio after 6 successive passes on the impregnation machine. The results obtained for all the samples are in good agreement with residues at 900°C determined by thermogravimetry.

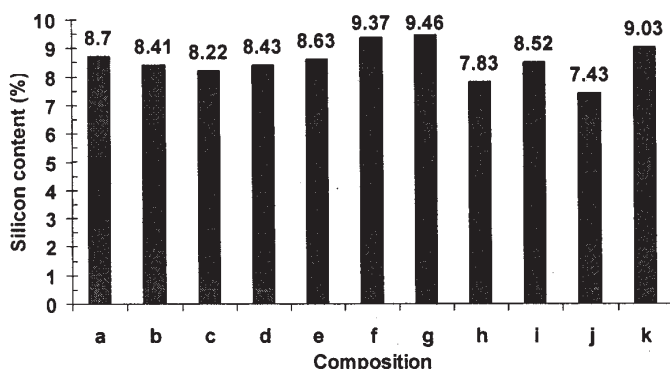


Fig. 5. Silicon content onto the fabric surface determined by XRF

Light fastness is a parameter that shows large variations as a function of dyestuff concentration and composition of the impregnation bath. As it was found the lowest value for the light fastness was recorded for the composition which contains only TEOS, at a dyestuff concentration of 0.2%. For the same concentration of the dyestuff but using a mixture of TEOS and MeTES as network forming agent, the light fastness was higher probably because of the generated matrix characteristics and differences in interactions established between the dyestuff molecules and organic vicinities from the hybrid network. It is obviously that a higher compatibility between dyestuff molecules and inorganic network was obtained in the case of organic residues present on the surface of the pores. Another reason may be in connection with a more porous material that can be obtained when it was used an organic modified trialkoxysilane. Due to the volume of organic residue it can be provided a more protective environment for the dyestuff molecule that finally leads to a rise in light fastness. Good results are observed when a mixture of PhTES and TEOS was used as network precursor, probably due to the large volume of the phenyl ring comparatively with other type of organic groups of network modifiers, as it is show in table 1.

The dye loading has an important effect on photodegradation and an increase of the amount of dye relatively enhances the photostability of the coloured coatings. Increasing the amount of network modifying agent results in a more effective screening of the silanole groups at the surface of the inner pores where DR1 molecules are located, hindering possible interactions that are responsible for promoting photodegradation. However, using substituted alkoxy silanes in the sol-gel process, the formation of oligomeric cyclic siloxanes is favoured and wash fastness is lowered. During the experiments we found that increasing the volume of the organic substituent, the wash fastness was improved probably due to a better accommodation of the organic dye in the silica network.

The films obtained on the cotton textile surface are in all cases uniform and free of cracks as it can be observed in Fig. 6. A coarser surface was observed after impregnation by several successive passes through the padding machine. The SEM images shows that mixtures used as impregnation baths are sufficiently diluted to obtain relatively thin coatings due to a significant reduction of the sol viscosities. Thus the surface morphologies of all silica hybrids deposited on textile fabrics are almost the same and it is not observed hybrid material between fibres that could lead to joining together fibres of the fabrics. Coatings are homogeneously distributed at the fibre surface and no

Silane content (%)		Dye content (%)	Shade / Standard intensity	Light fastness (grade)	Wash fastness (grade)			
TEOS	Modifying agent (%)				Change in colour	Staining on		
						cotton	wool	polyamide
100	---	0.2	1/2	1	1-2	4-5	2	2-3
75	MeTES (25)	0.4	1/3	3	2-3	3-4	4	4
50	MeTES (50)	0.4	1/2	3	2-3	4-5	4	4
---	MeTES (100)	0.2	1/2	3-4	1-2	4-5	4	3-4
50	OTES (50)	0.2	1/2	3	2	4-5	3-4	3-4
50	OTES (50)	0.4	1/1	3-4	2	4-5	2-3	2-3
50	VTES (50)	0.4	1/1	3	2	4-5	3-4	3-4
75	VTES (25)	0.4	1/1	2-3	2	4-5	3	2-3
50	CIPTES (50)	0.4	1/1	3-4	3	4-5	4-5	4
75	CIPTES (25)	0.4	1/1	2-3	3-4	4-5	3-4	3-4
75	PhTES (25)	0.2	Bluish-red / 1/2	2-3	3	4-5	4-5	4-5
50	PhTES (50)	0.2	+ Y / 1/2	3-4	3	4-5	4-5	4

**Table 1**  
EFFECT OF THE NETWORK MODIFYING AGENT ON THE COATINGS FASTNESS

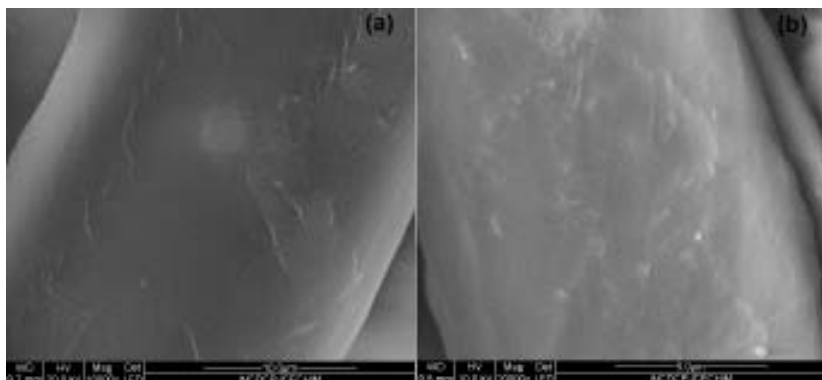


Fig. 6. SEM Images of: (a) pure and (b) TEOS/PhTES=1/1 silica coated cotton samples

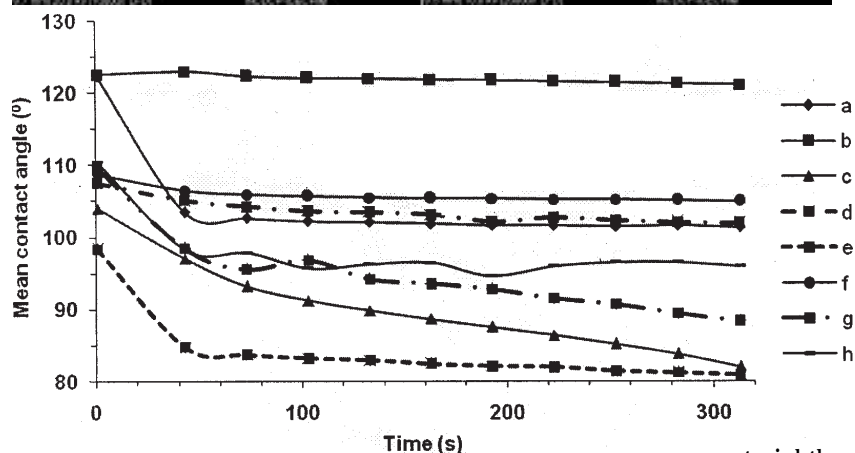


Fig. 7. Water contact angle for cellulosic fabric coated with sols containing TEOS and : a) PhTES (50%); b) OTES c) PhTES (25%); d) PhTES (50%); e) CIPTES; f) VTES; g) GlyOPTES; h) MeTES

island-like or agglomerations have been seen on the impregnated fabrics. Thus, it can be concluded that all compositions studied by us were compatible for application on the cotton textile surfaces.

Cotton fabrics exhibit a marked hydrophilic character, while silica hybrid coatings applied on their surfaces induce a rapid increase of the water contact angle. An earlier study reports on the hydrophobic properties of silica sol coatings on textiles in relationship with influence of solvents and sol concentration [26].

Water instantaneously impregnates uncoated cotton samples owing to the porous structure and hydrophilic character of the support. As it was seen, substrates impregnated with sols containing OTES exhibit the most hydrophobic character, with a water contact angle of 121°. When a short aliphatic chain was used for modifying inorganic silica coating, as in case of MeTES, it was obtained a lower water contact angle, of about 96°. Between these values for coatings made of VTES was obtained a water contact angle of about 105° and when it was used PhTES and TEOS at a 1:1 molar ratio the value was about 101° independent of number of passes through the impregnating bath, as it can be seen in figure 7.

It is interesting to note that a lower value of about 82° was obtained for coatings made of mixtures containing PhTES and TEOS in a 1:3 molar ratio. If it was used GlyOPTES as modifying network agent it was obtained a coating having a mean contact angle of 88°. In these cases probably due to a more polar character of the obtained coatings and to the possible hydrogen bonding between Si-OH groups of the inorganic network and respectively C-OH generated from epoxy groups, the contact angles decreased continuously without visible stabilization. Framing in this trend, for coatings made of TEOS exclusively it can not be measured the water contact angle. Probably in this case roughness and porous structure of the coatings play an important role for this behaviour.

The lowest value is obtained when a mixture of TEOS and CIPTES in a 1:1 molar ratio was used as coating

material the mean angle value recorded being about 81° probably because of the higher polarity of the coating. From the evolution of the mean contact angle in time we can conclude that a low content of network modifying agent lead to a lower value of this which decrease in time continuously. This is probably due to an inefficient covering of the silica coating surface with organic hydrophobic groups.

Coated textile fabrics were studied by thermogravimetric analysis in air at a heating rate of 10°C/min. and in the range 25-900°C. All the samples present the main steps of decomposition characteristic to cotton fibres. In the case of pure cotton fibres the first stage of decomposition consists of releasing water from the hydrophilic fibre that takes place with maximum speed at about 40°C. For coated materials this stage represents 1-3% of the total mass loss, consists of water and residual solvents from the sol-gel processes and takes place at 50-60°C. As it can be seen from figure 8, in the case of coated fabrics, the maximum decomposition temperature was shifted to higher values because water and residual solvents are better entrapped inside the pores of the silica network comparatively with uncoated cotton fibres.

Another decomposition step characteristic to uncoated cotton fabrics is situated at about 345°C, represents 85% of the total mass loss and is due to thermal decomposition of cellulose chains into carbon dioxide, carbon monoxide and carbonaceous char. For coated materials this step is situated at 337-351°C and represents about 40-75% of total mass loss.

The last step of decomposition for cotton fabrics consists of oxidative decomposition of the charcoal formed previously, that takes place at around 463°C and represents about 15% of total mass loss. For all coated materials this step is also present in the thermograms, takes place in range 457-482°C and is about 13-20% of the mass loss, depending on the organic group grafted on the silica network.

Residues at 900°C varies as a function of the coating composition and amount of coating material from 9% in

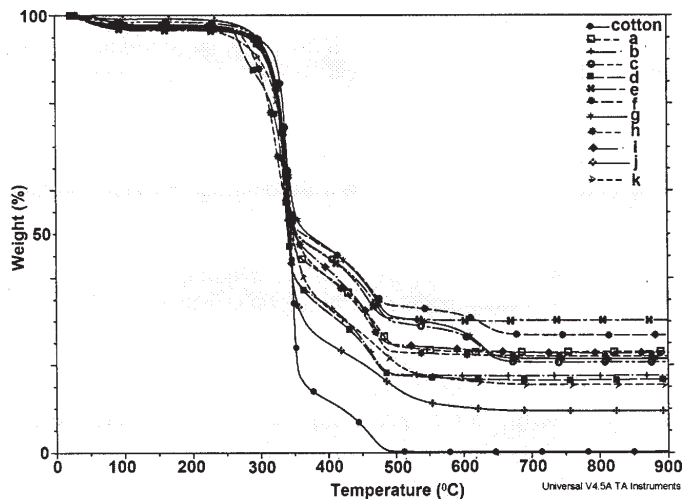


Fig. 8. Thermogravimetric analysis of pure and coated textile fabrics

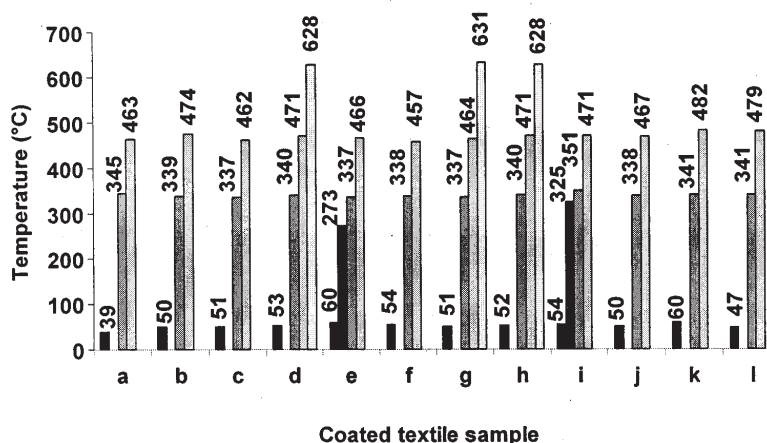


Fig. 9. Temperature of thermal decomposition with maximum speed from TGA

Sample	Loss Modulus		Loss Factor		Storage Modulus G' at 30 °C, (MPa)	Stiffness S (N/m)
	G'' peak max (MPa)	Temp, (°C)	Tan δ peak max	Temp, (°C)		
Blank (cotton fabric)	111.8	133	0.5555	129	500	736452
MeTES (2 passes)	73.95	92	0.03108	107	2531	4640990
TEOS (2 passes)	56.65	59	0.01804	60	3139	5022800
OTES (4 passes)	98.78	96	0.04098	120	2554	4596860
TEOS (6 passes)	62.15	61	0.02020	61	3187	5144300
PhTES 25% (6passes)	70.56	103	0.02433	120	3040	5067340
PhTES 50% (6passes)	64.17	76	0.02526	85	2634	4740780
CIPTES (4 passes)	71.48	69	0.02466	75	2978	4963390
VTES (4 passes)	69.81	97	0.02633	103	2783	4730840
PhTES25%/GlyOPTES 25% (4 passes)	85.86	70	0.03651	70	2403	4245180
PhTES25%/GlyOPTES 25% cat. (4 passes)	60.95	53	0.02508	56	2433	4297970

Table 2  
RESULTS OF DYNAMIC  
MECHANICAL ANALYSIS

the case of GlyOPTES to 30% for TEOS coatings deposited on the fabrics after 6 passes on the padding machine.

There are several major differences in the thermal decomposition behaviour recorded for coated fabrics due to different compositions of the coating materials. The existence of aromatic rings in the structure favoured the formation of a thermally resistant carbonaceous char which burns in air with maximum speed at about 630°C. This behaviour is characteristic only for PhTES modified sols used as coating materials. In the case of OTEs hybrid coatings a supplemental step in weight loss was recorded at around 273°C due to decomposition of long aliphatic chains. This represents about 11% of the total mass loss, while for CIPTES hybrid coatings this step is centred at around 325°C, as is shown in figure 9.

Adhesion of the hybrid coatings to the surface of the cellulosic fibres is due to various molecular interactions that lead to an inter-phase of higher stiffness than that of uncoated fabrics and increases the storage modulus of the obtained composite material. Storage modulus shows that the highest values were obtained when only TEOS was used for obtaining coloured coatings mainly due to a more pronounced inorganic character and as a consequence to a higher rigidity. When the number of passes on the impregnation machine was increased, the quantity of coating material on the textile surface increased and storage modulus was rise together with stiffness of the material. Coatings obtained using network modifying agents are more flexible and stiffness and storage modulus are decreased, as it is observed in table 2.

Interactions between silanol groups of the network and cellulosic OH groups are the main factor influencing the storage modulus and results obtained showed good interfacial adhesion between the hybrid coatings and cellulose fibres. In the case of organic modified silica coatings a slighter decrease in storage modulus and stiffness was recorded in the following order: PhTES (25%) > CIPTES > VTES > PhTES (50%) > OTES > MeTES > GlyOPTES. For all coated textile materials stiffening occurs due to the lower flexibility of the hybrid coatings and moreover when the number of impregnation cycles was risen the stiffness increases because thick coatings are obtained and probably silica bridges between the fibers are formed. Because coatings with TEOS restricted the mobility of cellulose macromolecules increased the storage modulus and reduced the viscoelastic differences between the stress and the strain. Since peak high is associated with mobility it was observed that after applying hybrid coatings molecular mobility was reduced diminishing the possibility to dissipate the energy by fibre-network interactions or by friction between fibres and thus the intensity of  $\tan \delta$  decreased. Thus when hybrid coatings were obtained using silane derivatives having voluminous organic groups (PhTES, OTES, VTES) the  $\tan \delta$  peaks are shifted to higher temperatures and are broadened.

A special case was recorded when GlyOPTES was used as network modifier probably because HO groups which are generated during polymerization interact with Si-OH groups from inorganic network. This induced the decrease of the  $\tan \delta$  peak value of the composite and produced a shifting to the lowest temperature recorded in this series. The molecular motion in coated fabrics was restricted and loss modulus is decreased comparatively to pure cotton fabric. The peak maximum was shifted to lower temperatures as strong interactions are established between coatings and fabric and consequently improved adhesion of the coating occurs.

## Conclusions

The aim of the study was to determine in which way we can modify silica sol used as impregnation bath, to obtain optimal conditions for coating cellulosic fibres with significant improvements in light and wash fastness of the coloured coating material. Selection of the network modifying agents was one of the most important steps for the achievement of a high degree of compatibility between the embedded organic non-ionic dyestuff and inorganic matrix. The type and the amount of modifiers in the impregnation bath determine the hydrophobic behaviour, thermal and mechanical properties of the coated textile fabrics. The important achievement of the work was that we obtain compositions suitable for colouring cellulosic fibres with DR1 which usually cannot be used in dyeing of such type of fibres. Hybrid matrices obtained from PhTES and TEOS are the best choice for the entrapment of DR1 molecules and lead to an improvement of photostability and wash fastness of the obtained coloured coatings. The treatment on the cellulosic fibres contributed to an improving of their dynamic mechanical properties due to the efficient surface interactions between coatings and fibres. Stiffening that occurs after coating cellulosic fabrics with sol-gel hybrids was of the same order of magnitude with that recorded in the case of uncoated polyester fabrics. This finding is important in order to use such type of coating materials for colouring textile blends.

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