Disperse Azo Dyes-silica Hybrids for Modifying Cellulose Fabrics by Sol-gel Processes

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The paper presents disperse azo dyes-silica hybrids deposited as coating materials on the surface of cellulose fibres by sol-gel processes. Coatings are characterised by FT-IR spectrometry, UV-VIS reflectance spectra and colour measurements in CIELAB system, scanning electron microscopy (SEM) and thermal analysis (TA). Structure-properties relationships of the obtained coatings are discussed with respect to the structure of azo dyes embedded in the silica networks. The effect of functional groups grafted on the structure of disperse dyes was studied in relationship with leaching properties of the obtained coloured coatings.

Keywords: silica hybrids, cellulose materials, azo dyes, sol-gel, coatings

Multifunctional textile materials are the most important branch of investigation in textile chemistry during the last years. Several approaches were envisaged to modify the surface of textiles and to confer them special properties. Besides classical textile finishing techniques, which are already used since decades, the modification of textile fibres is carried out by chemical grafting methods or by modern entrapping techniques, with or without performing corona or plasma surface treatments [1].

Chemical modification of textiles using natural compounds such as chitosan [2] or cyclodextrines [3,4] and more recently semisynthetic monochlorotriazinyl-β-cyclodextrin or synthetic calixarenes are valuable approaches to obtain important effects due to their entrapping properties.

Sol-gel technology became more and more important in several sectors. From natural silicates and zeolites to synthetic silica hybrids [5-9] obtained from organosilanes through hydrolysis-condensation processes, important properties could be obtained due to adaptable porous networks developed during synthesis [10-12]. Applications of sol-gel technology in textile industry are becoming important due to film adherence on fibres and to chemical and thermal resistance of the obtained coatings. Nanocoatings of this type provide hosting nanocavities, which can include a wide variety of compounds such as dyestuffs [13,14], softeners [15,16], flame-retardants [17,18], UV absorbers [19-21], water or oil repellents [22-24], biocides [25,26], oils and flavours [27,28], enzymes [29-31], antistatic agents [32-34], conductive modifiers [35,36] or magnetic nanoparticles [37,38].

Our work is focused on studying hybrid silica materials containing embedded disperse azo dyestuffs which are deposited as coatings on cellulosic substrates. Sol-gel derived coatings are studied mainly as colouring materials for cellulosic supports. This approach is important due to possible applications, which can be developed by using non-specific dyes for colouring textile materials.

Experimental part

Materials and methods

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. Disperse dyes: Disperse Red 1 (DR1), Disperse Red 5 (DR5), Disperse Red 17 (DR17), Disperse Orange 5 (DO5), Disperse Brown 1 (DBr1), previously obtained by us [39], were purified by extraction with toluene in a Soxhlet extractor followed by re-crystallization. Textile material used was a 100% cotton fabric having a specific weight of 106 g/m^2, chemically whitened.

Obtaining the impregnation bath and pad-dry-cure treatment of cellulosic fibres

A solution made of 3.25 mL TEOS, 3.25 mL PhTES, 3.9 mL solution containing 1.7 g of a disperse dye selected from those mentioned above in 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. The mixture was maintained under vigorous stirring, at room temperature, and used immediately for padding cellulosic materials.

A textile test-piece of about 2 g was padded with sol with a pick-up 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 subject to heat treatment at 120^{0}C, for 1 h in a thermo-fixation oven.

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. 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).

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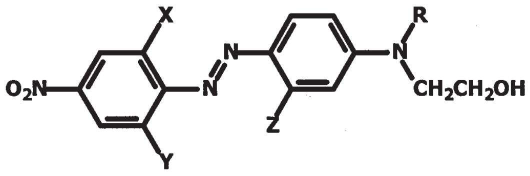
Leaching experiments

Coloured test-pieces were tested according to washing standards in place for determining the colour change on a course of eight repeated washing cycles. For this purpose was used a test like laundering household washing under conditions of ISO 105/C, using a solution of 1% by weight sodium dodecylsulfate, at a temperature of 60^{0}C, for 2 h, on a LINITEST type device. The test-pieces, consisting of a sample of the dyed cotton fabric were placed between a cotton fabric and a wool fabric, sewn on four sides. After washing, test-piece composite was rinsed with warm water 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 fabrics.

Results and disscusions

The aim of this work is to study silica hybrids containing embedded disperse azo dyes and coatings obtained on cellulose textile materials using this type of materials. Coatings were obtained by sol-gel processes which consist of hydrolysis and condensation reactions of silica precursors (TEOS and PhTES) in the presence of azo dyes. The progress of the sol-gel process lead to the formation of the inorganic network which provide suitable nanocavities for the organic dyestuffs ensuring necessary conditions to obtain stable and adherent coatings to cellulose materials. Textile materials are impregnated with previously prepared nanosols and then are subject to thermal crosslinking.



X = Y = Z = H, R = CH_2CH_3 ; - C.I. Disperse Red 1
X = Y = H, Z = CH_3 , R = CH_2CH_2OH ; - C.I. Disperse Red 17
X = Cl , Y = H, Z = CH_3 , R = CH_2CH_2OH ; - C.I. Disperse Red 5
X = Y = Cl , Z = H, R = CH_3 ; - C.I. Disperse Orange 5
X = Y =Z= Cl , R = CH_2CH_2OH ; - C.I. Disperse Brown 1

Fig. 1. Structures of disperse dyes contained in hybrid materials

Besides normal reactions of alkoxysilanes hydrolysis, followed by condensation of alkoxysilanes with silanols and between similar or different silanols leading to Si-O-Si linkages, on the cellulosic materials other two reactions could take place. Esterification reactions of silanols with cellulose alcoholic groups and transesterification of unhydrolysed alkoxysilanes with cellulose alcoholic groups lead to the formation of Si-O-C linkages. The last type of reactions provides chemical linkages between hybrid coatings and textile substrate. Additionally, physical forces such as hydrogen bonds and van der Waals interactions ensure coatings adhesion on the cellulosic surface. Phenyl groups provided by PhTES lead to a better compatibility of the organic dyes with the inorganic network. If TEOS is used in excess comparatively to PhTES, thicker coatings are obtained on the fibres surface. However, when the TEOS content become more important in sol composition the colour strength of coatings on cellulose materials is affected and colour of the obtained coatings is uneven. The best results in terms of colour and thickness on cellulose fibres were obtained when PhTES : TEOS molar ratio was situated at around 1.

For coatings obtained using optimal conditions established for impregnating sols used as coatings for textile fabrics, were studied the shade and colour differences in CIELAB system using spectralon as standard material. At the same content of PhTES in coating material, from diffuse reflectance spectra it is observed that for all disperse azo dyes used in this study we obtained similar intensities on the cellulose fabrics. This behaviour is due to almost the same molar coefficient of absorption of azo dyes involved in the obtained hybrid coatings. At the same intensity, the absorption maximum of coloured coatings obtained on cellulose fibres varied from 460 nm in case of DO5 and DBr1 to 524 nm in case of DR5 (fig. 2). The hypsochromic effect of more than 60 nm recorded for DO5 and DBr1 can be explained by the deactivating effect on the aromatic structure shown by chlorine atoms grafted on the benzene rings near the azo group.

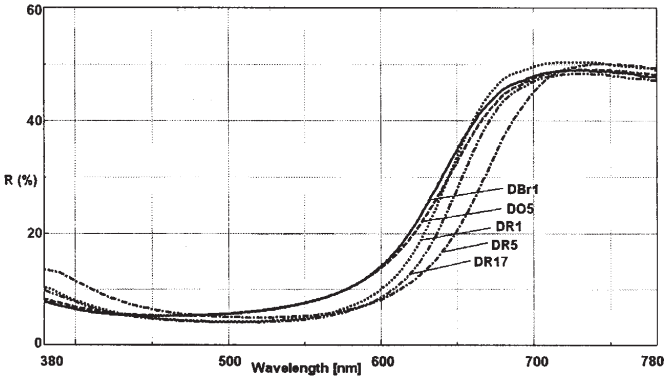


Fig. 2 Diffuse reflectance spectra of the coated textile fabrics

Colour differences were calculated in CIELAB system using D65 as illuminant and at 10^0 measurement angle using equation: $\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$ where ΔE is the total colour difference between reference and sample, ΔL^* is the difference in lightness, Δa^* is the difference in red-green colour component and Δb^* is the difference in the yellow-blue component.

Table 1
COLOUR DIFFERENCES OF COATED MATERIALS

Coating composition	Illuminant D65 / 10^0 standard observer											
	Tristimulus values			Trichromatic coordinates		CIELAB values			Colour differences			
	X	Y	Z	x	y	L	a	b	ΔL	Δa	Δb	ΔE_{ab}
DBr1	12.29	9.72	5.66	0.4442	0.3512	37.34	23.17	16.94	-55.87	23.73	17.51	63.18
DO5	11.93	9.52	5.77	0.4383	0.3498	36.97	22.23	15.86	-56.24	22.79	16.43	62.87
DR1	9.67	7.12	5.28	0.4383	0.3225	32.07	26.43	9.60	-61.14	26.99	10.17	67.60
DR5	8.03	6.54	7.01	0.3723	0.3029	30.73	18.19	0.03	-62.48	18.75	0.60	65.23
DR17	8.37	6.36	5.13	0.4215	0.3202	30.29	23.08	7.24	-62.92	23.64	7.81	67.66

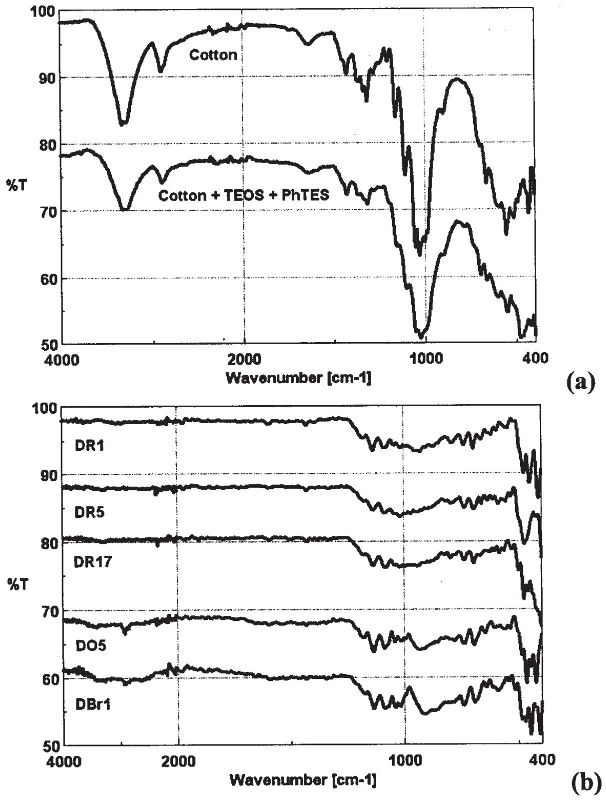


Fig. 3 FTIR spectra of (a) coated and uncoated cotton fabrics and (b) subtracted spectra of coating materials

Measurements show that total colour difference is in the same range for all the dyestuffs used for colouring cellulose materials in sol-gel systems, as it is presented in table 1. Luminosity is higher for DBr1 comparatively to DR17 due to the halogen atoms while the shade is shifted toward yellow because Δb value is positive and high. The reddish shade is recorded for DR5 when Δb value has the lowest value at almost the same value of Δa parameter as for the other dyes.

Infrared absorption spectra of coated cellulosic materials shows the structural characteristics of cellulose such as bands situated at 3334-3283 cm^{-1} due to hydroxyl stretching vibrations and at 2897-2853 cm^{-1} for methylene symmetric and asymmetric stretching vibrations from linear chains of glucopyranosic units. At 1636 cm^{-1} was identified the band specific to bending vibration of water molecules contained in the fibres.

FTIR spectra performed on untreated cotton fabric shows important peaks situated at 1427 cm^{-1} which correspond to methylene wagging vibrations, while at 1314 cm^{-1} is situated C-OH stretching vibration. In spectra it can be identified a band which correspond to CH bending vibration situated at 1278 cm^{-1} together with OH in plane bending at 1247 cm^{-1}. But the most important bands are found at 1159 cm^{-1} assigned to the asymmetrical bridge C-O-C stretching vibration, at 1107 cm^{-1} due to asymmetrical in plane ring stretching, and also at 1053, 1030 and 1000 cm^{-1} bands belonging to C-O stretching mode. Another important band was found at 710 cm^{-1} and is due to CH_2 rocking vibrations. Other bands which correspond to out of plane OH deformation and methylene groups vibrations are found in the range 700-400 cm^{-1}.

Unfortunately for the coated fabrics in the range 1000-1100 cm^{-1}, vibrations are overlapped and hard to evaluate, because Si-O-Si, Si-O-C, and C-O-C give vibration bands in the same region. For silica coatings spectra obtained by subtraction revealed characteristic bands located at 1592-1596 cm^{-1} due to C-C aromatic stretching vibration, at 1429-1435 cm^{-1} and 1136-1137 cm^{-1} bands corresponding to Si-phenyl stretching vibration, and also at 776-790 cm^{-1} together with 692-695 cm^{-1} bands belonging to aromatic ring deformations. These bands confirm the existence of aromatic residues in the coating materials due to the network modifying agent – PhTES and also belonging to disperse azo dyestuffs.

Hybrid coatings present characteristic peaks in the FTIR spectra due to Si-O-Si stretching vibration recorded as an intense peak at 1083-1087 cm^{-1}, while specific intense peaks characteristic for silica networks were also recorded at 1014-1019 cm^{-1} and 1040-1042 cm^{-1} corresponding to Si-O-C, respectively Si-O-Si stretching vibrations. A single band due to Si-O-Si group is clearly visible in the FTIR spectra of the coated fabrics and identified also in the spectra obtained by subtraction. This is due to Si-O-Si rocking motions and is situated in the range 473-487 cm^{-1},as it is presented in figure 3.

Thermo-stability was investigated by performing thermo-gravimetric analysis on cotton fabric and comparatively on cotton coated fabrics. As it is observed textile support presented a specific decomposition pattern which can be used further for comparative experiments. Thus, weight loss recorded during thermal decomposition of cotton fibres comprises three stages. The first stage is due to weight loss by dehydration and the amount of water released from the cellulose fabrics was about 2% by weight. The second stage is the main decomposition step and corresponds to a weight loss of about 85% due to hemicelluloses and cellulose decomposition [40] into carbon dioxide, carbon monoxide and carbonaceous char. In the last stage takes place an oxidative decomposition of the carbonaceous char which lead to a mass loss of about 12%.

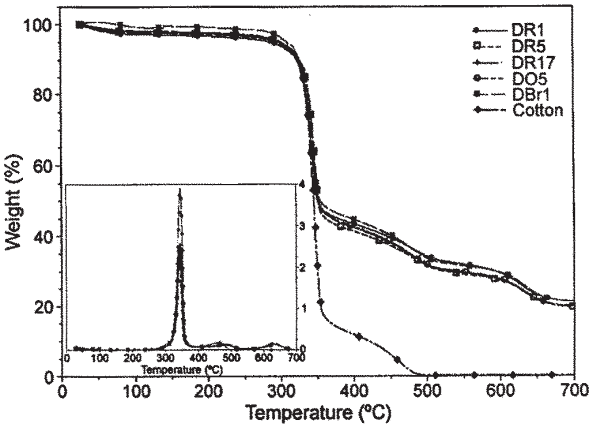


Fig. 4 Thermo-stability of coated cellulose fabrics

Regarding coated cellulose fibres the decomposition patterns (fig. 4) are similar whatever the type of disperse dye of the series studied, and include four steps. The first step is due to the releasing of water and solvents retained during the impregnation stage. The amount of solvents released at temperatures less than 130°C was about 1.7-2.6 % by weight. In the second and the third step takes place mainly the decomposition of the textile fibres. The mass loss is situated at 53-56% by weight in the second step and at 11-13% in the third step, which is similar to those recorded for the uncoated fabric.

A particularity of thermal decomposition in case of the coated fabrics is the presence of a fourth stage in the temperature range 550-700°C. The weight loss in this stage for all these samples was around 9-10%. This stage is due to phenyl residues belonging to the network modifying agent - PhTES and to azo dyestuffs. Probably during thermal

Table 2
THEMOGRAVIMETRY RESULTS

Sample		Temperature range (^{0}C)				Residue
		20-130	130-400	400-550	550-700	
Cotton	Weight loss (%)	2.137	84.95	12.26	0	0
	$T_{max.}$ (^{0}C)	39	346	463	0	
DR1	Weight loss (%)	2.628	53.73	11.4	10.64	21.33
	$T_{max.}$ (^{0}C)	39	343	482	627	
DR5	Weight loss (%)	2.242	56.34	12.15	9.474	19.64
	$T_{max.}$ (^{0}C)	40	345	484	632	
DR17	Weight loss (%)	1.800	55.71	12.74	9.685	19.92
	$T_{max.}$ (^{0}C)	42	346	482	629	
DO5	Weight loss (%)	1.763	55.55	12.95	9.609	20.04
	$T_{max.}$ (^{0}C)	44	342	483	632	
DBr1	Weight loss (%)	1.766	54.03	13.65	10.13	21.26
	$T_{max.}$ (^{0}C)	43	342	483	633	

decomposition process, aromatic residues formed highly condensed compounds which lead to a carbonaceous deposit very resistant to oxidative thermal treatment. Thus, the final decomposition step in these cases is situated in the temperature range 550-700^{0}C. The amount of silica deposited on the fibres surface can be estimated from the residue recorded at 700^{0}C and was around 19-21% by weight, as it is presented in table 2.

Temperature at which takes place the oxidative thermal decomposition of maximum 5% by weight can be used as a measure of influence on the thermal stability of the obtained coatings. It was seen that thermal stability increases in order: uncoated cotton = DR1 < DO5 < DR5 < DR17 < DBr1. Probably this behaviour is due to the halogen content of the dyestuff present in the hybrid coating.

The surface of untreated cotton fabrics is relatively smoother but some fibrils are observed. When treated with sols containing TEOS and PhTES in the presence of disperse dyestuffs, the surface of cellulose fibres become more roughly and some clusters are seen. Compositions containing disperse azo dyes formed uniform and free of cracks coatings due to a high compatibility between the organic modifier and organic dyestuffs in the pores of the silica network.

Homogeneity and adhesion of the coatings on the fibres lead to obtaining of continuous films as a result of the greater number of nanoparticles adsorbed on the surface. Because of the organic content of the hybrids, coatings obtained are relatively flat and regular due to a better film formation. This behaviour is recorded for all disperse azo dyestuffs investigated in our work. It is observed that in some cases are formed bridges of coating materials between fibres usually because of a relatively high viscosity of the sol prior to impregnation of the cellulose materials.

We must notice also that in all cases investigated by us, there are no situations of unevenly distributed cavities, concave grooves or agglomerated islands of coating materials on the fibres surface visible in SEM images. The images analysis supported the conclusion that whatever the type of the disperse dyestuff investigated, by this approach we obtained uniform coating films on cellulose fibres (fig. 5).

The efficiency of the hybrid silica matrix in entrapping disperse azo dyes used in our experiments together with coatings adherence on the surface of the cellulose fabric was tested by performing leaching experiments. For textile fabrics is important to find out to what extent a multifunctional coating is useful in practical applications.

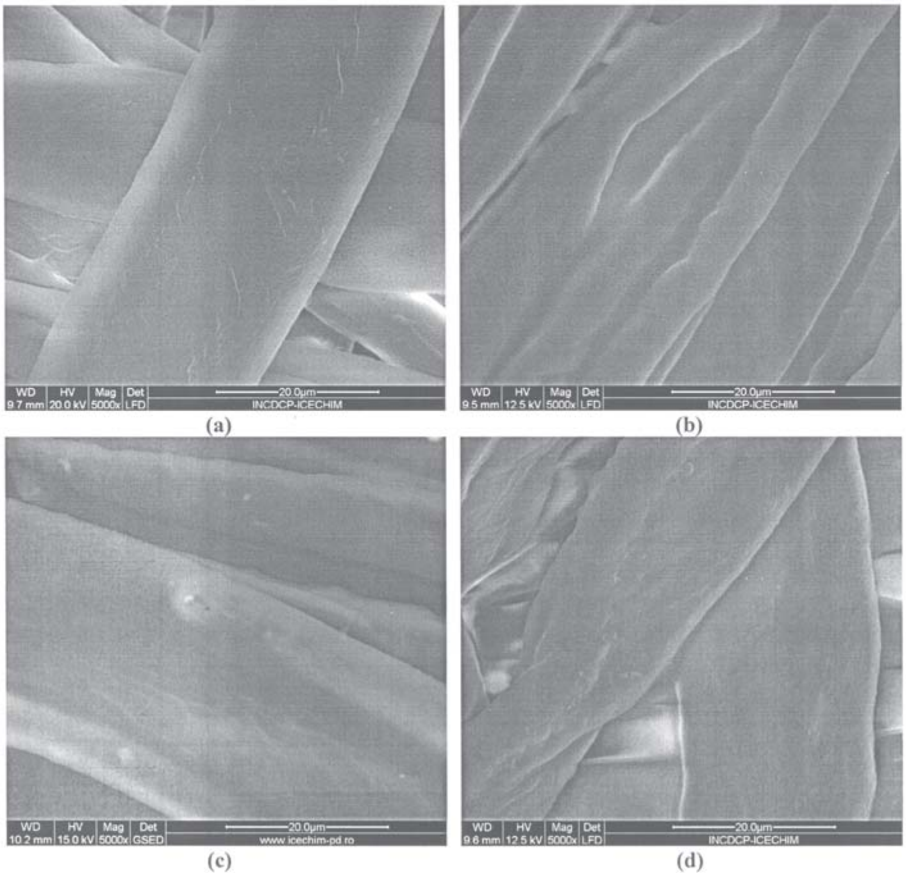


Fig. 5. SEM photographs of: **a)** untreated fabric; **b)** fabric coated with nanosol containing DR1 ; **c)** fabric coated with nanosol containing DR5; **d)** fabric coated with nanosol containing DR17

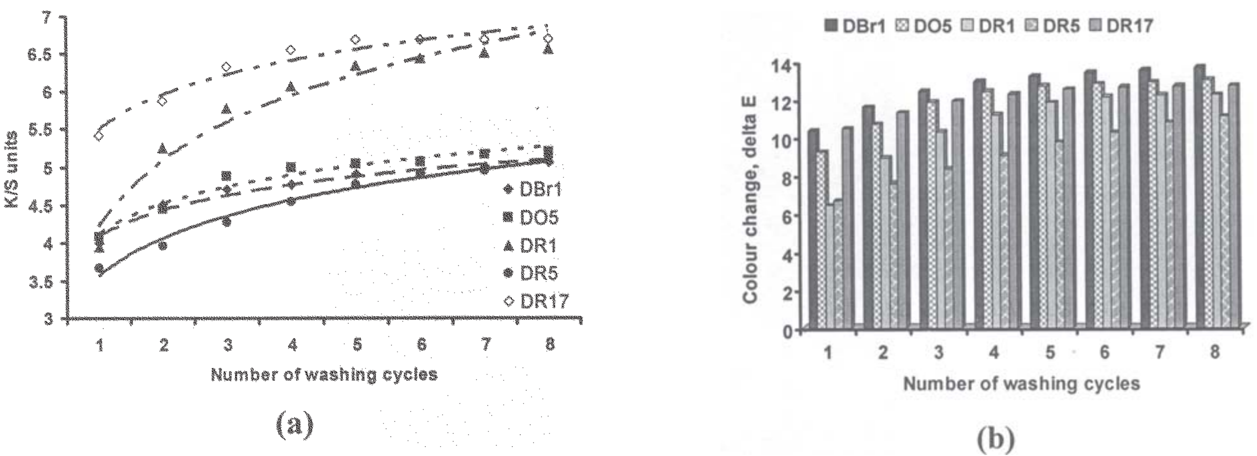


Fig. 6 Colour change during leaching experiments from: (a) K/S values and (b) CIELAB ΔE values

Thus in these cases a standard measurement of the obtained coatings efficiency consists of monitoring the change in intensity of the absorption bands recorded in visible spectra. These bands correspond to disperse azo dyes entrapped in the silica network deposited as a coating material on the textile fabric.

Leaching stability of the obtained coatings was evaluated from reflection spectra of coated fabrics before and after performing each washing cycle, using K/S values calculated using Kubelka-Munk equation at maximum absorption wavelength of each dyestuff $K/S = \frac{(1-R)^2}{2R}$ where R is the percent of remission value, K is the absorption of light and S is the scattering of light.

Moreover, leaching stability was estimated from total colour differences between coated fabric before and after performing several washing cycles.

Measurements are performed on coated materials after successive washing cycles (fig. 6). The data show that the most significant colour lost, over the eight cycles performed, is during the first six cycles in cases of DR1 and DR5 azo dyes. This is probably due to size of the dyestuffs and thus to the probability to escape through the pores of the silica network. As it is seen, this tendency is more attenuated in case of DO5 and even more for DR17 and DBr1, which have the largest molecules. This suggests that the dyestuffs are efficiently entrapped inside the silica network, which is able to retain dyes in the pores due of steric hindrance. An explanation for this behaviour could be the existing functional groups grafted on the azo structure near the azo group.

It must be mentioned that in all cases investigated by us the differences inΔE values can be visually observed. From their analysis the same conclusion can be drawn, values are very close in each washing cycle in case of coatings containing DO5, DR17 and DBr1 while for coatings with DR1 and DR5 are recorded relatively large differences between ΔE values measured after the last washing cycle comparatively with the first. Thus, for DR17 difference between ΔE values recorded after eight washing cycles was about 2.2, while for DR1 this difference was about 5.7. Results obtained using both methods confirm the possibility to estimate the leaching stability of the coloured coatings either by K/S values or from CIELAB ΔE values.

Conclusions

The present study shows results obtained when cellulose fabrics are coated through sol-gel processes with silica hybrids containing disperse azo dyes. The efficiency of the obtained coatings is discussed with respect to the structure of disperse azo dyestuffs.

Coatings were analysed by means of UV-VIS diffuse reflectance spectra and FT-IR spectrometry to prove the structure of the obtained hybrids, colour measurements in CIELAB system to evaluate differences in colour, SEM analysis for studying coatings integrity and roughness and thermal analysis to evaluate their thermal stability.

Functional groups grafted on the structure in the immediate vicinity of the azo group have a positive effect on leaching properties of the obtained coloured coatings. Due to steric hindrance, voluminous molecules cannot leave so easily the pores of the silica networks and leaching stability of the coatings is significantly improved.

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References

1. MORALES, J., OLAYO, M.G., CRUZ, G.J., HERRERA-FRANCO, P., OLAYO, R., J. Appl. Polym. Sci., **101**, 2006, p. 3821
2. SUZUKI, K., ODA, D., SAIMOTO, H., SHIGEMASA, Y., Polym. J., **32**, 2000, p. 334
3. SAENGER, W., Angew. Chem., **92**, 1980, p. 343
4. OPWIS, K., BACH, E., BUSCHMANN, H.J., KNITTEL, D., SCHOLLMEYER, E., Melliand Textilber., **79**, 1998, p. 545
5. BLEDZKI, A.K., REIHMAN, S., GASSAN, J., J. Appl. Polym. Sci., **59**, 1996, p. 1329
6. POTHAN, L.A., THOMAS, S., GROEMINCKS, G., Compos. A, **37**, 2006, p. 1260
7. HERRERA-FRANCO, P.J., VALDEZ GONZALEZ, A., CERVANTES-UC, M., Compos. B, **28**, 1997, p. 231
8. HERRERA-FRANCO, P.J., VALDEZ GONZALEZ, A., J. Appl. Polym. Sci., **65**, 1997, p. 197
9. VALDEZ GONZALEZ, A., CERVANTES-UC, M., OLAYO, R., HERRERA-FRANCO, P.J., Compos. B., **30**, 1999, p. 321
10. RADITOIU, V., RADITOIU, A., WAGNER L.E., RADULY, M.F., NICOLAE, C.A., FIERASCU, R.C., Rev. Chim. (Bucharest), **62**, no. 4, 2011, p. 409
11. RADITOIU, V., RADITOIU, A., WAGNER L.E., RADULY, M.F., NICOLAE, C.A., FIERASCU, R.C., J. Optoelectron. Adv. Mat., **12**, 2010, p. 1566
12. RADITOIU, V., RADITOIU, A., WAGNER L.E., RADULY, M.F., AMARIUTEI, V., NICOLAE, C.A., FIERASCU, R.C., Optoelectron. Adv. Mat., **5**, 2011, p.363
13. MAHLTIG, B., KNITTEL, D., SCHOLLMEYER, E., BOETTCHER, H., J Sol-Gel Sci. Technol., **31**, 2004, p.293
14. MAHLTIG, B., KNITTEL, D., SCHOLLMEYER, E., BOETTCHER, H., Textile Res. J., **74**, 2004, p.521
15. BAJAJ, P., J. Appl. Polym. Sci., **83**, 2002, p 631
16. HAUSCH, F., Textilveredlung, **36**, 2001, p. 23

17. HRIBERNIK, S., SMOLE, M.S., KLEINSCHEK, K.S., BELE, M., JAMNIK, J., GABERSCEK, M., Polym. Degrad. & Stabil., **92**, 2007, p. 1957
18. SONG, L., HU, Y., TANG, Y., ZHANG, R., CHEN, Z., FAN, W., Polym. Degrad. & Stabil., **87**, 2005, p. 111
19. ABIDI, N., HEQUET, E., TARIMALA, S., DAI, L.L., J. Appl. Polym. Sci., **104**, 2007, p. 111
20. XU, P., WANG, W., CHEN, S.L., AATCC Review, **12**, 2005, p. 28
21. MAHLTIG, B., BOETTCHER, H., RAUCH, K., DIECKMANN, O., NITSCHE, R., FRITZ, T., Thin. Solid. Films, **485**, 2005, p. 108
22. SATOH, K., NAKAZUMI, H., MORITA, M., Textile Res. J., **74**, 2004, p. 1079
23. YEH, J.T., CHEN, C.L., HUANG, K.S., J. Appl. Polym., Sci., **103**, 2007, p. 3019
24. YEH, J.T., CHEN, C.L., HUANG, K.S., J. Appl. Polym., Sci., **103**, 2007, p. 1140
25. HAUFE, H., MUSCHTER, K., SEGERT J., BOETTCHER, H., J. Sol-Gel Sci. Technol., **45**, 2008, p. 97
26. HAUFE, H., THRON, A., FIEDLER, D., MAHLTIG, B., BOETTCHER, H., Surf. Coat. Int.B: Coatings Trans., **88**, 2005, p. 55
27. BOETTCHER, H., Textilveredlung, **42**, 2007, p. 8
28. VEITH, S.R., PERREN, M., PRATSINIS, S.E., J. Colloid. Interf. Sci., **283**, 2005, p. 495
29. LI, F.Y., XING, Y.J., DING, X., Enzym. & Microbiol. Techn., **40**, 2007, p. 1692
30. OPWIS, K., KNITTEL, D., BAHNERS, T., SCHOLLMEYER, E., Eng. Life. Sci., **5**, 2005, p. 63
31. OPWIS, K., KNITTEL, D., SCHOLLMEYER, E., AATCC Review, **11**, 2004, p. 25
32. AMBER-SCHWAB, S., Technische Textilien, **46**, 2003, p. 137
33. XU, P., WANG, W., CHEN, S.L., Melliand International, **11**, 2005, p. 56
34. SCHOTTER, G., Chem. Mater., **13**, 2001, p. 3422
35. CERVEAU, G., CORRIU, R.J.P., LEROUGE, F., BELLEC, N., LORCY, D., NOBILI, M., Chem. Commun., 2004, p. 396
36. BATAIL, P., Chem. Rev., **104**, 2004, p. 4887
37. THOMAS, S., SAKTHIKUUMAR, D., JOY, P.A., YOSHIDA, Y., ANANTHARAMAN, M.R., Nanotechnology, **17**, 2006, p. 5565
38. XU, Z.Z., WANG, C.C., YANG, W.L., FU, S.K., J. Mater. Sci., **40**, 2005, p. 4667
39. WAGNER, L.E., RADITOIU, V., RADITOIU, A., ARDELEANU, P., AMARIUTEI, V., RADULY, M.F., Rev. Chim. (Bucharest), **60**, 2009, p. 444
40. SERAPIGLIA, M.J., CAMERON, K.D., STIPANOVIC, A.J., SMART, L.B., Appl. Biochem. Biotechnol., **145**, 2008, p. 3

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