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Optical and thermal behavior of some colored silica hybrids deposited on polyester fabrics as coating materials

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Different silica hybrid film forming materials were obtained and deposited on polyester fabrics and their optical and thermal properties have been investigated. Structural characteristics of network modifying agents determined vicinities of the embedded or chemically grafted nonionic dyestuffs and decisively influenced the optical behavior of the hybrid coatings. By modifying the hybrid materials using specific organic groups it is possible to tailor adhesion forces between the coating and textile substrate and thus can be determined fastnesses to wash and light of the colored coatings. Thermogravimetric analysis revealed the flame retardant effect manifested by the hybrid silica films deposited on polyester fabrics.

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Keywords: Silica hybrids, Disperse dyes, Polyester fibers, Thermogravimetric analysis, Color measurements

1. Introduction

Polyester fibers are the second most important category of textiles in terms of production and applications after cellulose fibers and the most important synthetic fibers.

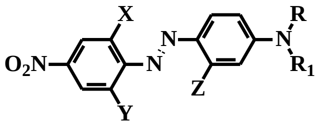
The sol-gel process used in order to generate silica film-building materials is a versatile method [1-6] that can be easily applied to obtain coatings on different type of substrates [7-14]. Silica hybrids which can be obtained at relatively low temperatures and at normal pressure are good hosting materials for a wide range of compounds, such as: flame retardants [15,16], UV absorbers [17-19], coloring materials [20-23], antibacterial [24-27], softeners [28,29], antistatic agents [30], oils and flavors. Beside the easy synthesis there are a lot of other advantages provided by the inorganic hosting materials: mechanical resistance [31-34], transparence in the UV-Vis domain and thermal resistance [35,36]. Thus, properties of the coated materials can be tailored by changing the guest molecules or by modifying the precursors used to generate the silica hybrids.

Starting from the need to find out dyeing solutions containing a single dye for blends of cellulosic with polyester fibers and taking into account the results obtained in the case of dispersion dyes entrapped into hybrid silica networks deposited onto cellulosic fabrics [37-40], experimental works were initiated for the application of such film-forming composition on the polyester substrates. The ultimate objective of the experiments is to find optimal compositions for subsequent application on cellulosic and polyester fibers with good resistance to wash and light.

2. Experimental

Materials

The precursors used were of laboratory reagent grade and were obtained from Merck - Germany and Aldrich - USA. Hydrochloric acid (0.1 N), tetraethylorthosilicate (TEOS), phenyltriethoxysilane (PhTES) diphenyldiethoxysilane (DPhDES), 3-glycidoxypropyltriethoxysilane, (GlyOPTES), vinyltriethoxysilane (VTES), 3-chloropropyltriethoxysilane (ClPTES), methyltriethoxysilane (MeTES), ethanol, 1,4-diazabicyclo [2.2.2.] octane (DABCO), tetrahydrofuran (THF), sodium dodecylsulfate (SDS) were used in the study without further purification. Disperse dyes: Disperse Red 1 (DR1), Disperse Red 5 (DR5), Disperse Red 17 (DR 17), Disperse Orange 5 (DO5) and theirs triethoxysilyl derivatives (Fig. 1) were previously obtained by us [41] and purified by extraction with toluene in a Soxhlet extractor, followed by recrystallization. The fabric used was 100% polyester (PES) fabric with a specific weight of 170 g/m^2 obtained from Matasea Romana - Romania. Silicon anhydride (SiO_2 content: 83.71%) from Merck was used as standard for quantitative XRF measurements.



$X = Y = Z = H, R = CH_2CH_3$ $R_1=CH_2CH_2OH$ (DR 1) $R_1=CH_2CH_2OCONHCH_2CH_2CH_2Si(OCH_2CH_3)_3$ (DR 1-PTES)
$X = Y = H, Z = CH_3$ $R = R_1= CH_2CH_2OH$ (DR 17) $R = R_1=CH_2CH_2OCONHCH_2CH_2CH_2Si(OCH_2CH_3)_3$ (DR 17-PTES)
$X = Cl, Y = H, Z = CH_3$ $R = R_1= CH_2CH_2OH$ (DR 5) $R = R_1=CH_2CH_2OCONHCH_2CH_2CH_2Si(OCH_2CH_3)_3$ (DR 5-PTES)
$X = Y = Cl, Z = H, R = CH_3$ $R_1=CH_2CH_2OH$ (DO 5) $R_1=CH_2CH_2OCONHCH_2CH_2CH_2Si(OCH_2CH_3)_3$ (DO 5-PTES)

Fig. 1. Chemical structure of the chromogens.

Methods

Preparation of the nanosol film-forming material and coating of the polyester fabrics

A solution obtained from 3.25 ml TEOS, 3.25 ml DPhDES, 3.9 ml of a solution containing 1.7 g of disperse dye, selected from those mentioned above, in 100 ml of THF, 0.65 ml water, 2.35 ml ethanol and a few drops of hydrochloric acid was stirred for 1 h at room temperature. The mixture was used immediately for the impregnation of textile materials. Thus, a test sample of polyester fabric of about 2 g was impregnated with a 40% degree of uptake in several successive passes, on a laboratory impregnation device Ernst Bentz, at a constant speed of 0.5 m / min and a pressure of 0.4 Kg/cm^2. The coated materials were dried at room temperature for 2 h and then were subjected to heat treatment at 120^0C for 1 hour in a thermo-fixation oven.

Measurements

Diffuse reflectance spectra and total color differences in CIELAB system, using a 10 degrees standard observer and illuminant D65 were measured with a JASCO V570 UV-VIS-NIR spectrophotometer equipped with a JASCO ILN - 472 (150 mm) integrating sphere, using spectralon as reference. Color measurements are used to express differences, as we perceive them visually and color attributes, named hue, chroma and lightness are parameters necessary for the assessment of total color differences in CIELAB color space. The total color difference is an important value, which can be calculated from the equation: $\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$, where: L^* is the lightness, a^*,b^* are red-green, respectively yellow-blue color components and calculated differences indicate how much two samples differ from one another. Composition of the total color difference is evaluated using the equation: $\Delta H^* = \sqrt{(\Delta E^*)^2 - (\Delta L^*)^2 - (\Delta C^*)^2}$, where: H^* is hue and C^* is chroma.

XRF analyzes were performed on a spectrometer PW4025 - MiniPal - Panalytical EDXRF. The measurements were carried out in an atmosphere of helium for 300 sec. without using a filter, at 20 kV and automatically adjusting the intensity of the current.

Thermogravimetric analysis was carried out with an SDT Q600 instrument (TA Instruments) under an atmosphere of air or helium, at a heating rate of 10^0C/min., in alumina crucibles. The instrument was coupled to a Pfeiffer Thermostar mass spectrometer (0-300 amu, resolution of 1 amu).

To assess the stability of the fabrics coated with different sol compositions, colored test-pieces were tested according to washing standards in place for determining the color change and transfer to the accompanying textiles. For this purpose was followed a test like laundering household washing under conditions of ISO 105/C, using an aqueous solution of surfactant (1% by weight SDS), at a temperature of 40^0C, for 2 h, on a LINITEST type device. The test-piece consisting of a sample of the coated fabric was placed between cotton fabric, on the one side and wool fabric, on the other side, 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 the original colored fabric textile and accompanying materials. The color change of the specimen and the staining on the adjacent fabrics are assessed with the grey scale, which includes five shades (grades), according to EN ISO 105 A01, A02 and A03 / 1999. The light-fastness tests were carried out with a Xenotest 150 S+ (Atlas), in accordance with ISO B02. Light fastness is evaluated using a blue scale, which includes eight grades. Both procedures are based on the comparison of the contrast between the color of the sample before and after performing the test and the contrast on the scales, taking into account that the highest value is the best and the lowest is the worst.

3. Results and discussion

Composition of the impregnation baths and fastness of the coatings

One objective of our study was to obtain different compositions containing film-forming materials able to provide highly adherent and resistant colored coatings on polyester fabrics by varying the type and the amount of network modifying agents. For hybrid coatings of class I (corresponding to the entrapped dyes) or of class II (corresponding to the chemically linked dyes) were considered materials achieved by simultaneous hydrolysis of TEOS and different organosilanes used as network modifying agents in order to control domains where are found nonionic chromogens or derivatives thereof with trialkoxysilane groups. Nonionic chromogens used to obtain hybrid coatings of class I were chemically modified by performing an addition reaction with 3-isocyanatopropyltriethoxysilane (NCOTEOS), following a procedure published previously [41], to synthesize dyes containing trialkoxysilane groups, able to provide covalent bonds with the inorganic network, as in the case of hybrid coatings of class II.

Based on structural changes operated during obtaining of sol compositions, which constitute the film-forming materials, it can be analyzed the influence of different organic groups belonging to the structure of network modifying agents on the dyestuffs entrapped or chemically linked in the silica network. In addition, by comparing the obtained colors with the same types of coating compositions deposited on polyester fibers it can be studied the influence of the substrate on the color in relation to the chromogen positioning relatively to the textile fiber. Thus, were analyzed variations of the wavelength of the absorption maximum, in the case of nanosols of different compositions obtained from mixtures of silanes combined in different proportions and in the presence of DO5. It can be observed that the color of coating compositions made from TEOS and MeTES, respectively VTES, a hypsochromic effect of about 9-14 nm is obtained, greater the higher the organosilane content in the composition.

A particular behavior is noticed in the case of the film-forming materials containing ClPTES when there was recorded a high value of the wavelength of the absorption maximum. In the case of compositions containing the two components (TEOS and ClPTES) in equal proportions, a diminishing of the quantity of one component, lead to a slight hypsochromic effect, as shown in table 1. Such behavior can be explained only in the terms of the higher polarity of ClPTES and by the engagement of the halogen atom through hydrogen bonds with silanol groups of the silica. It is noted also a hypsochromic shift of the absorption maximum of about 10-15 nm for the colored coatings obtained with dyes covalently bonded on the silica, compared to the coatings containing dyes embedded into the inorganic network. The effect is more important as the number of anchoring groups on the silica network increases due to steric hindrance exerted by these groups on non-bonding electrons of amino auxochromes belonging to the dyestuff molecules. The existence of such interactions between dyes and the host matrix was demonstrated in several studies regarding colors variation obtained with dyestuffs entrapped in different organically modified silica matrices [42] and could explain some of our results.

Table 1. The effect of network modifying agent on fastness of the coatings.

Silanes content (%)		**Dyestuff (%)**	**Wavelength of the absorption maximum (nm)**	**Light fastness (grade)**	**Wash fastness (grade)**		
TEOS	**Network modifying agent (%)**				**Color change**	**Staining on**	
						wool	**cotton**
50	PhTES 50	DR1 (0.5)	507	4-5	3	3	4-5
50	PhTES 50	DR1-PTES (0.5)	495	4-5	4	4	4-5
50	PhTES 50	DR5 (0.5)	529	6-7	3	3-4	4-5
50	PhTES 50	DR5-PTES (0.5)	516	4-5	3-4	4	4-5
50	PhTES 50	DR17 (0.5)	506	5-6	3	4	4-5
50	PhTES 50	DR17-PTES (0.5)	496	4	3-4	4-5	4-5
50	PhTES 50	DO5 (0.5)	472	4-5	3	3-4	4-5
50	PhTES 50	DO5-PTES (0.5)	463	4	3-4	4	4-5
25	MeTES 75	DO5 (0.5)	469	4-5	2-3	2	4
50	MeTES 50	DO5 (0.5)	472	5-6	4	2	4
75	MeTES 25	DO5 (0.5)	478	5-6	3	3	4
25	VTES 75	DO5 (0.5)	469	6	1-2	2-3	3-4
50	VTES 50	DO5 (0.5)	471	6	4	3-4	4-5
75	VTES 25	DO5 (0.5)	483	6	4-5	3-4	4-5
25	ClPTES 75	DO5 (0.5)	478	5	1-2	2-3	3-4
50	ClPTES 50	DO5 (0.5)	480	6-7	3-4	3	4
75	ClPTES 25	DO5 (0.5)	472	6-7	3	3	4

Composition of the impregnation bath was varied to obtain stronger adhesion forces between the coating and the substrate and to achieve a better compatibility of the non-ionic dyes with the neighboring molecules in the silica network. It was also aimed at changing the stiffness of coated materials within reasonable limits so as not to affect the properties of the original fibers.

Unlike cellulose fibers, in the case of the polyester fibers, the interactions between the coating and the textile substrate are achieved predominantly via van der Waals bonds and π - π type interactions. This finding is of great importance for obtaining coatings resistant to wet and dry processes. Thus, as can be seen from Table 1, the best wash fastness is obtained for hybrid coatings, which are formed from mixtures of silanes containing PhTES, due to a higher adhesion to the textile substrate. This is explained by the interactions established between phenyl residues existing at the surface of the hybrid network and benzene rings of the polyester substrate, as it was previously mentioned by other authors [43]. It can be seen that in the case of the staining on the cotton fiber to which the dyestuff does not have any affinity, the migration at the surface of the accompanying material is due to the displacement of parts of the hybrid silica network from the surface of the coating.

Comparing the behavior to washing tests of the coatings obtained with hybrids of class I and class II containing nonionic dyes, it was concluded that in the latter case the fastness is superior. This is due to the immobilization of dyes in the inorganic network and in this case staining on the accompanying material could be due only to the oligomers together with parts of the hybrid network displaced during the washing process. The most important method in the assessment of changes in color intensity of the hybrid coatings deposited on the surface of textile materials, in successive washing processes, under controlled conditions, was diffuse reflectance spectra, as shown in Fig. 2.

Analyzing changes of the absorbance obtained from reflectance spectra for polyester samples treated with hybrids of class I and II, during successive washing cycles, we can assert that if the parameters of the impregnation process are similar, coatings present higher intensity in the case of class I comparatively with class II hybrids. This can be observed from the absorbance values recorded for unwashed samples colored with DR1, probably because part of the dye was situated at the surface of the inorganic network during thermal cross-linking.

It is noted that for DR1, the maximum of the absorption wavelength for the hybrid of class I is situated at $\lambda_{max.}$= 507 nm comparatively to the value recorded for the hybrid of class II ($\lambda_{max.}$= 500 nm), probably due to steric hindrance caused by urethane group belonging to DR1-PTES. The more pronounced decrease of color intensity occurs after the first washing cycle in each case, while after four successive washes, decrease of intensity is almost the same for both types of hybrids. After six successive washes, the loss of colored films from polyester fabrics treated with hybrids of class I and II is in the first case around 25 %, while in the second case is only about 15 %, as is shown in Fig. 2. Taking into account that the determination is based on quantification of the substrate color remained after each washing cycle, it is obvious that in the case of class I hybrids a part of the dye is removed by extraction from the inorganic network during the washing process, probably due to the surfactant micelles. As it was previously mentioned by other authors [44], large quantities of water in the sol composition could lead to the appearance of cracks that affect the integrity of the coatings to successive washing cycles and therefore determine lower fastness properties of the coatings.

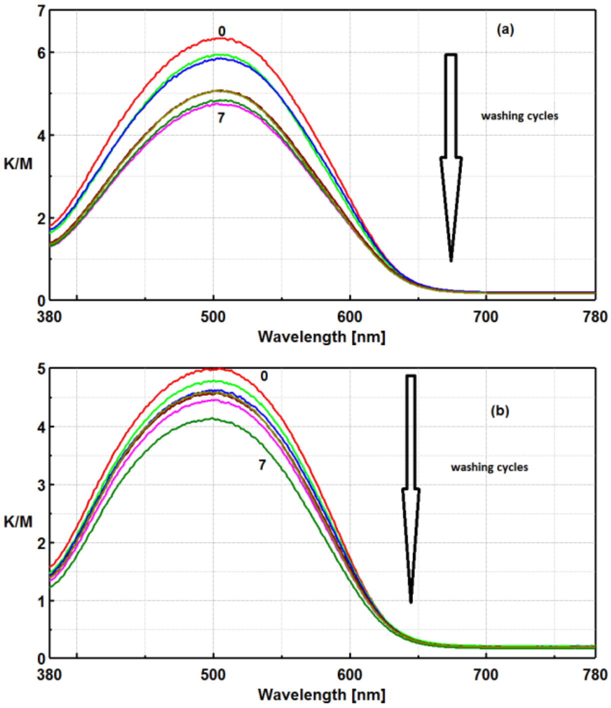


Fig. 2. Variations of K/S values during succesive washing cycles performed on PES coated with silica hybrids obtained from TEOS/PhTES with: (a) DR1 şi (b) DR1-PTES.

Regarding fastness to light, it is largely influenced by the chromogen structure, but it can be seen that in all cases the type and the amount of hybrid network modifier easily influence it. Increasing the amount of organic modifier leads to a decrease of the resistance to light due to the negative influence of the photodecomposition products on the dye molecules in the vicinity. The most significant example is the coating material obtained with DR17-PTES, which shows a lower value of the light fastness than that obtained in the case of DR17. The only possible explanation is the immobilization of the dye near the organic substituent located on the surface of the inorganic network. Probably, in these circumstances fragments obtained from photochemical degradation of organic groups interact more effectively with the dye molecules immobilized in the immediate vicinity thereof.

Table 2. Color differences of the coated textile materials.

Coating composition	**Illuminant D65 / 10^0 standard observer**												
	Tristimulus values			**Trichromatic coordinates**		**CIELAB values**			**Color differences**				
DO5/TEOS/	**X**	**Y**	**Z**	**x**	**y**	**L**	**a**	**b**	**ΔL**	**Δa**	**Δb**	**ΔE_{ab}**	**ΔH**
ClPTES	18.44	14.72	9.47	0.4326	0.3453	45.25	25.69	16.57	-47.96	26.25	17.14	57.30	9.83
MeTES	18.52	14.52	8.63	0.4444	0.3484	44.97	27.32	18.79	-48.24	27.87	19.36	58.98	10.25
VTES	22.65	18.80	12.54	0.4195	0.3482	50.45	23.83	16.79	-42.76	24.39	17.36	52.19	9.62
PhTES	17.99	14.25	9.12	0.4350	0.3445	44.58	26.16	16.53	-48.63	26.72	17.11	58.06	9.88

Color differences in the CIELAB system are useful to quantify the effects of various components of the total color difference. As can be seen from Table 2, the total color differences are mainly due to differences in lightness, darkness of the shades obtained being greater when aromatic nuclei, which interact with dyestuff molecules, are present in the structure of the hybrid material. Shifting the hue to red occurs when the volume of the organic substituent from the hybrid network is small (MeTES). This can be explained by the possibility of establishing interactions by hydrogen bonds between the auxochrome groups of the dye and silanol groups of the silica network, as it was shown by other authors in the case of dyed fabrics treated by sol-gel-process [45,46].

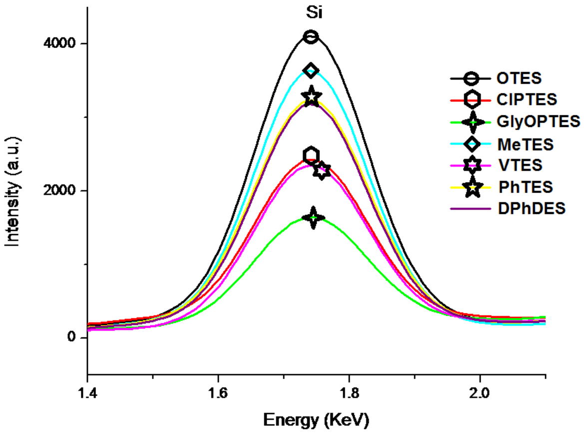


Fig. 3. Intensity of the silicon line on the surface of PES coated fabrics by XRF.

XRF analysis of the coated PES fibers shows the presence of silicon on the textile surface, the amount depending on the composition of the coating material. The results obtained show that the silicon content on to the surface of the textile material expressed as silica is situated in the range of 7.7 to 15.7%. The highest value was recorded for the coatings obtained from MeTES and TEOS at a 1:1 molar ratio, after four successive passes of the textile material through the impregnation machine. The results obtained for all the samples tested are showed in Fig. 3 and are in good agreement with the silica residues obtained at 700^0C, as measured by thermogravimetry.

Thermal stability of the PES fibers coated with hybrid materials

Some studies previously reported demonstrated the improvement in the thermal stability of textile fabrics subjected to sol-gel treatments, due to the presence of silica which have a protective effect during the thermal degradation [47]. Samples in our study were subjected to thermogravimetric analysis, in air, at a heating rate of 10^0C/min. and in the temperature range 25-700^0C, the results being presented in Fig. 4.

All samples show the main stages of decomposition characteristic of polyester fibers, with several specific features due to the coating materials. The first step is the removal of water from the textile substrate, which in this case is around 1-2 % of the total mass loss. In the case of PES coated with hybrid materials this stage represents 0.3 % of mass loss and is due to an enhanced hydrophobicity of the textile materials after coating with hybrids.

Another characteristic stage of the decomposition profile of the polyester fibers is situated at about 430^0C, represents about 83 % of the total weight loss and is due to the thermal decomposition of polyester chains into carbon dioxide, carbon monoxide and tar. For coated materials, this stage has the thermal decomposition peak located at 431 - 437^0C and represents 68-80 % of the total mass loss.

The last stage of decomposition of the polyester fabric consists of oxidative decomposition of previously formed tar coal, which takes place at about 540^0C, and is about 15% of the total weight loss. This stage is present in the range of 529-540^0C for all materials coated with hybrids, and represents about 10-15% of the total weight loss, based on the organic groups initially grafted on the inorganic silica network. It is obviously that in this stage also takes place the oxidative decomposition of tar formed as a result of the existence of aromatic nuclei in the structure of polyester fiber.

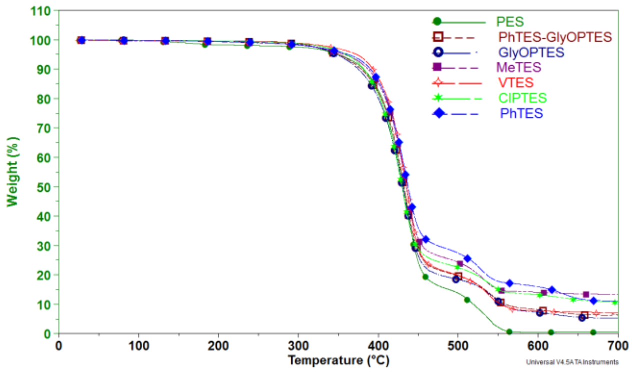


Fig. 4. Thermogravimetric curves for PES fibers coated with hybrids.

Residues at 700^{0}C vary depending on the composition and amount of coating material deposited on the fiber from 5% in the case of GlyOPTES to 13% in the case of coatings containing MeTES.

There are some major differences in the thermal decomposition of fibers coated with hybrid materials having different compositions. The existence of aromatic rings in the structure determines the formation of a highly heat-resistant layer of charcoal that burns in air with maximum speed at about 616- 634^{0}C. This behavior is characteristic only for impregnating compositions obtained with PhTES, as shown in table 3. The protection afforded by the silica network on which are grafted aromatic nuclei leads to oxidative decomposition of the tar at a temperature, which is significantly higher than that at which takes place the oxidation of the tar resulted from the decomposition of aromatic rings belonging to the PES structure.

An interesting case is represented by the hybrid coatings containing ClPTES, which show the oxidative decomposition step at 634^{0}C and a total mass loss of about 3 %, probably due to the flame retardant effect of the halogenated derivative, which delays the oxidative decomposition of aromatic residues from the PES fibers.

Table 3. Results of thermogravimetric analysis on PES fabrics coated with hybrid materials.

Silanes (weight ratio)		**Temperature range (^{0}C)**				**Residue**
		RT-150	**150-490**	**490-590**	**590-700**	
-	**Weight loss (%)**	1.78	82.83	14.85	-	0.54
	T $_{max.}$ (^{0}C)	-	437	540	-	
TEOS/PhTES/ GlyOPTES (2/1/1)	**Weight loss (%)**	0.13	79.29	11.97	2.14	6.47
	T $_{max.}$ (^{0}C)	-	433	540	616	
TEOS/PhTES/ GlyOPTES (5/4/1)	**Weight loss (%)**	0.31	68.13	12.04	6.81	12.71
	T $_{max.}$ (^{0}C)	-	431	536	632	
TEOS/GlyOPTES (3/1)	**Weight loss (%)**	0.16	80.98	11.28	2.22	5.36
	T $_{max.}$ (^{0}C)	-	433	542	623	
TEOS/MeTES (1/1)	**Weight loss (%)**	0.26	73.58	11.77	0.86	13.53
	T $_{max.}$ (^{0}C)	-	435	534	-	
TEOS/VTES (1/1)	**Weight loss (%)**	0.26	78.78	13.11	0.66	7.19
	T $_{max.}$ (^{0}C)	-	437	539	-	
TEOS/ClPTES (1/1)	**Weight loss (%)**	0.18	75.96	10.08	2.96	10.82
	T $_{max.}$ (^{0}C)	-	429	538	634	
TEOS/PhTES (1/1) (DR5)	**Weight loss (%)**	0.26	70.45	12.17	5.97	11.15
	T $_{max.}$ (^{0}C)	-	435	529	631	
TEOS/PhTES (1/1) (DR5-PTES)	**Weight loss (%)**	0.32	69.28	11.47	6.93	12
	T $_{max.}$ (^{0}C)	-	435	537	631	

4. Conclusions

Analyzing polyester fabrics colored using nanosols of the type shown as impregnating compositions, was revealed that the coloring of polyester fabrics could be made in one-step, with good uniformity and satisfactory intensity. The shades obtained for the dyes used were red-brown (DO5), ruby (DR5) and red (DR1 and DR17).

Using of dyes with anchoring groups and modifying agents for the inorganic network lead to modification of shades obtained with a deviation towards red. Disperse dyes produce a coloration of the hybrid material with standard intensity at a concentration of about 0.5 %.

The best compatibility of non-ionic dyes with inorganic silica network is obtained by the use of modifiers containing aromatic residues, and in this case an increase in thermal stability of coated materials occurred.

Thermal cross-linking of the coatings performed at a temperature of 120 - 150^{0}C, for 1/2 to 1 hour is sufficient to obtain hybrid networks stable to successive washing cycles. Under these conditions, the colored coatings are sufficiently intense and uniform, and resistance to washing of polyester textiles colored with nonionic chromogens by sol-gel method, is good and very good.

The more pronounced decrease in intensity occurs after the first washing cycle in each case of hybrid material, while after four successive washing cycles the decrease in intensity is similar for both types of hybrids. After six successive washes the loss of colored filmogen materials is around 25% in the case of hybrids of class I, while in the case of class II it is only about 15 %.

By varying the parameters, which influence the nanosol obtaining procedure or impregnation conditions, as well as by combining of the agents used as network modifiers can be controlled the properties of the colored silica coatings.

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