Hybrid materials obtained from organic modified silica and an azo dye by sol-gel method

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The paper presents new types of organic-inorganic hybrid materials prepared from an azo dye bearing chelating groups and triethoxysilane residues, and tetraethoxysilane derivatives frequently used in sol-gel processes. Hybrid materials obtained were characterized by XRF spectrometry, FT-IR spectrometry, UV-VIS reflexion spectra, color measurements in CIELAB system and thermal analysis. Structure-properties relationships of the obtained organic-inorganic hybrid materials are discussed with respect to the structure and nature of the organic modifying agents.

1. Introduction

Hybrid materials obtained through sol-gel processes were studied in the last years because of large possibilities to tailor some specific properties as a necessity derived from the application domains [1]. As a major consequence many improvements were recorded in sol-gel chemistry for obtaining with minor changes in the structure of the precursors, major improvements in properties of the obtained hybrid materials [2]. Organic dyes are one of the most intensively studied classes of substances used for obtaining organic-inorganic hybrids [3]. As it was found in the scientific literature silica organic modified materials obtained through sol-gel processes containing organic dyes belong to two major classes due to the embedding of dyestuff molecules (class I) [4] or to the covalent linking to specific groups on the inorganic network (class II) [5].

The interest for obtaining organic-inorganic hybrid structures having organic dyes embedded or linked to an inorganic structure, such as silica networks, was due to important applications of the obtained materials [6]. Thus, materials with NLO properties, optical waveguides [7], chemical sensors [8], light concentrators, solid lasers, and photoresponsive materials [9] are some of the main applications of this type of hybrid materials.

Our research was focused on grafting of organic dyes bearing chelating groups on the silica organic modified networks formed by simultaneous sol-gel processes. The materials prepared by us can be tailored through modifying the environments of the organic dye with different organosilane reagents. Thus, optical and thermal properties of the obtained materials were studied in relationship with the structure of the organic modifying agents and interactions between them and dyestuff molecules.

2. Experimental

2.1 Materials

Tetraethylorthosilicate (TEOS), methyltriethoxysilane (MeTES), phenyltriethoxysilane (PhTES), octyltriethoxysilane (OTES), 3-glycidoxypropyltriethoxysilane (GPTES), titanium (IV) isopropoxide (TIP) and acetylacetone (AA) were purchased from Aldrich and used as received. Tetrahydrofuran (THF) was purchased from Carlo Erba and was purified by distillation followed by anhydrization on molecular sieves 3Å (Merck). Silicon anhydride (SiO_2 content: 83.71%) from Merck was used as standard for quantitative XRF measurements.

Azo chromogen [3-(triethoxy-silyl)-propyl]-carbamic acid 2-[4-(8-hydroxy-quinolin-5-yl azo)-benzenesulfonyl]-ethyl ester (HESAQTES) was synthesized by us through a usual method that was presented in detail elsewhere [10].

2.2 Procedures

For obtaining the hybrids it was followed a reaction pathway that consists of generating the inorganic matrix by hydrolysis-condensation of different TEOS derivatives in the presence of HESAQTES, in the usual manner of sol-gel processes.
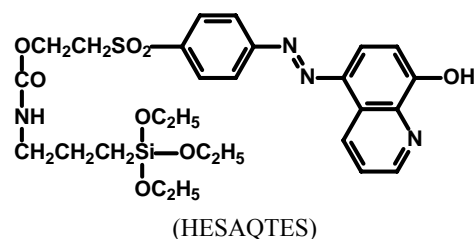

(HESAQTES)

Fig. 1. Chemical structure of the chromogen

Preparation of the hybrid composites

A solution made from 2.25 ml MeTES, 1.25 ml HESAQTES solution (1.66 g / 100 ml THF), 1.7 ml ethanol and a few drops of hydrochloric acid was stirred one hour at room temperature, and then it was added a mixture formed from 0.07 ml AA, 0.2 ml TIP and catalytic quantities of hydrochloric acid. The mixture was maintained under vigorous stirring at the room temperature and transferred into a rotary evaporator for the removal of the volatile solvents. The residue was dried at 70 °C and finely grounded into a laboratory vibrating ball mill. It was obtained 0.5 g hybrid material. All the other organic modified hybrid materials were prepared in a similar manner.

2.3 Measurements

UV-VIS absorption spectra of the filmogene materials were acquired in the range 380-780 nm using a spectrometer UV-VIS-NIR Jasco V-570.

FTIR spectra of the hybrid materials 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 color differences were measured by CIELAB method with a spectrophotometer UV-VIS-NIR Jasco V-570 equipped with an integrating sphere Jasco ILN-51 (150 mm), standard observer 10^0 (reference –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.

Thermal analysis was conducted on a TA Q 5000 IR instrument, in nitrogen atmosphere, at a heating speed of 10^0C/min. and the temperature range 25-900^{0}C (samples of 5-10 mg in platinum crucibles).

3. Results and disscusion

The aim of this work is to study colored hybrid organic-inorganic materials obtained through hydrolysis – condensation reactions of mixtures which contain an organic dye modified with alkoxysilane groups, tetraalkoxysilane and different organic trialkoxysilanes. This type of materials could be used as ion sensors for different environments due to the properties of the organic dye linked to the inorganic matrices.

All the hybrid materials obtained by sol-gel methods from mixtures of silane precursors at specific ratio exhibit major differences in optical, chemical and thermal properties. As it was remarked during the experiments, the reason for using MeTES as main component in sol-gel

synthesis was determined by superior results obtained for filmogen materials in relationship with good transparency and uniformity. All the others components were used only as modifiers at a sufficient level to establish major differences in properties.

Table 1. Typical compositions for the hybrid materials.

Material number	Silane precursors	Volume of silane precursors (ml)	HESAQTES solution (ml)	TIP (ml)	AA (ml)
1	MeTES	2.25	1.25	0.2	0.07
2	MeTES/PhTES	1.00/1.25	1.25	0.2	0.07
3	MeTES/GPTES	1.00/1.20	1.25	0.2	0.07
4	MeTES/OTES	1.00/1.60	1.25	0.2	0.07
5	MeTES/TEOS	1.10/1.00	1.25	0.2	0.07

Hybrid composites obtained as a result of sol-gel reactions, which generate the inorganic matrices by hydrolysis-condensation of different organic modified trialkoxysilanes in the presence of HESAQTES, were analyzed by means of XRF spectrometry.

The analysis performed for hybrid materials confirmed (Fig. 2) the presence of silicon in organic-inorganic hybrid samples. Quantitative analysis shows a silicon content of about 11.61-13.96% for all the hybrid materials studied.

The hybrid materials obtained as a result of hydrolysis – condensation processes, were characterized also through UV-VIS absorption and reflexion spectra and several characteristics were pointed out. Thus, because of the environments created in the inorganic matrices, through variations in the organic residues from organic substituted trialkoxysilanes used for sol-gel reactions, the organic dye interacts in different ways and thus optical properties of the obtained materials are modified in a large domain.

Maximum wavelengths of the colored materials were close to MeTES when phenyltrietoxysilane was used as network modifier. After a thermal treatment of 2 hours at 100^{0}C it was recorded a hypsochromic shift of the absorption maximum wavelength with one notable exception (MeTES+GPTES). The hypsochromic shift could be explained probably by removing of the residual water and solvents from the networks. This process was accompanied by broken of the hydrogen bonds established between the chromogen and solvent molecules and a significantly changes in polarity of the dyestuff environments take place. Thus, a hypsochromic shift of 2-16 nm was observed, while the absorption coefficient is slightly raised due to an apparent dyestuff concentration in the hybrid material.
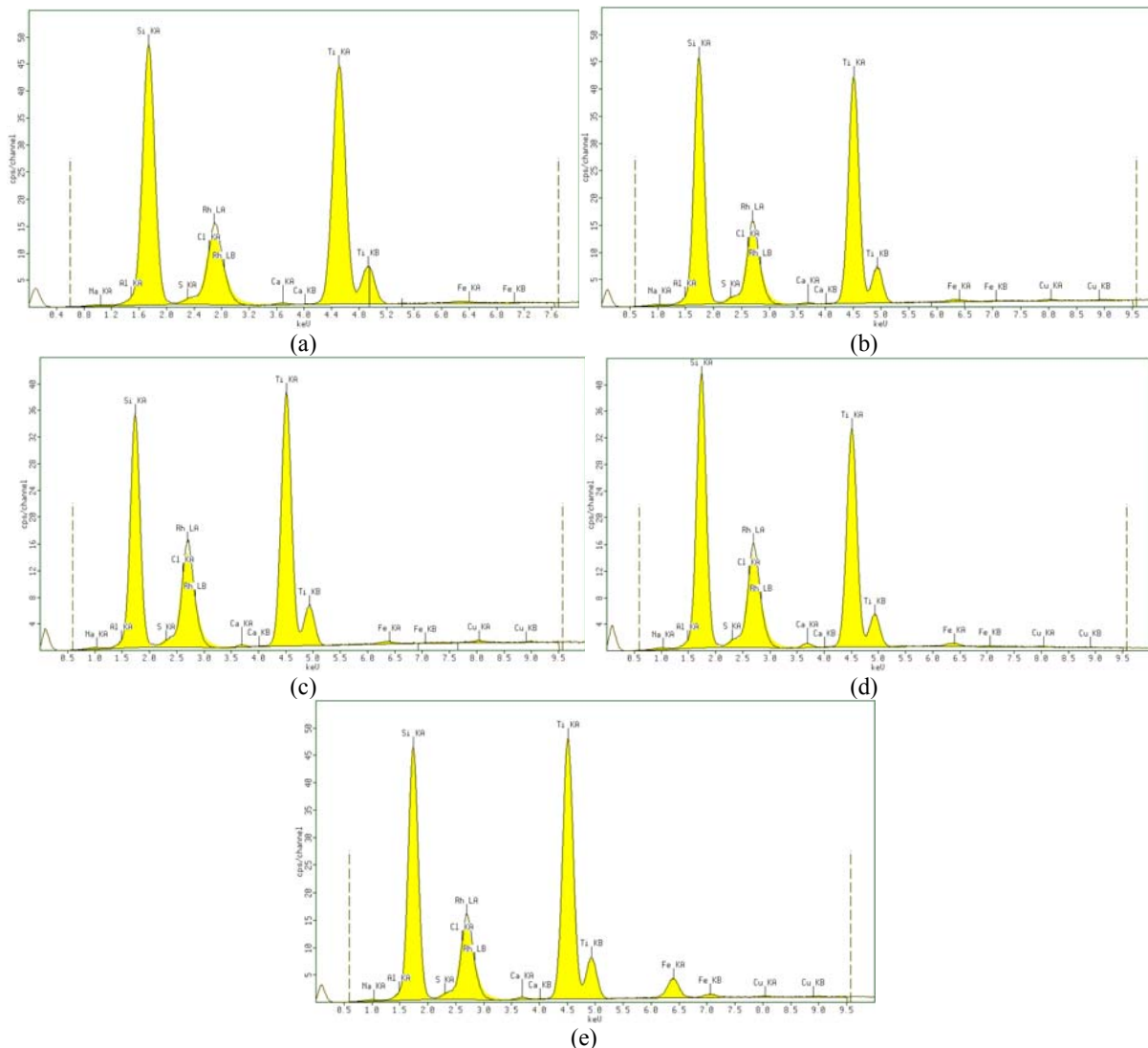
Fig. 2. X-ray fluorescence spectra for hybrids made from (a) MeTES; (b) MeTES+PhTES; (c) MeTES+GPTES;
(d) MeTES+OTES; (e) MeTES+TEOS

Only a single different situation was recorded for the hybrid material containing GPTES as a precursor, probably due to reactions that could take place at this temperature, because of the reactive epoxy groups. Addition reactions at epoxies generate secondary alcohol groups that could establish hydrogen bonds with the dye molecules, and that's why in our opinion this was the main reason for the bathochromic effect recorded in this case.

Analyzing UV-VIS diffuse reflexion spectra for the obtained hybrids it was found that the largest value for the dominant wavelength was recorded for the hybrid material having OTES as a modifying agent, while the lowest value was recorded for the material having PhTES. An explanation was the bulky phenyl ring that leads to a material with large pores and establishment of π-π interactions between dyestuff molecules and phenyl rings. It was verified also the hypothesis that for the material having GPTES as a modifying agent the generation of the hydroxyl groups lead to the possibility of establishing

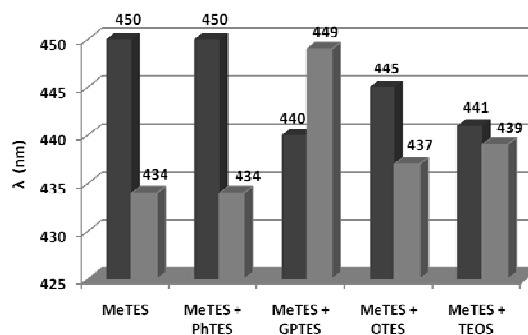hydrogen bonds with specific groups of the dyestuff molecules.

Fig. 3 Absorption maxima before and after thermal
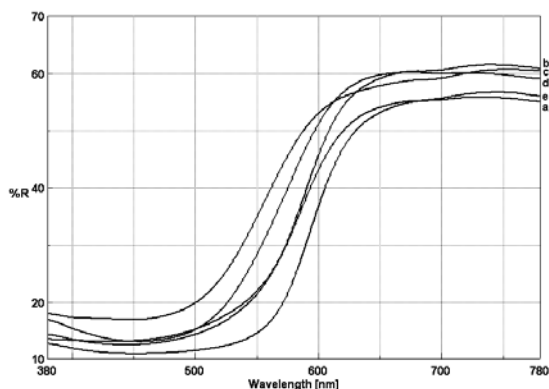*treatment of the transparent hybrid films*

Fig. 4. Diffuse reflexion spectra of hybrid materials made from: (a) MeTES; (b) MeTES+PhTES; (c) MeTES+GPTES; (d) MeTES+OTES; (e) MeTES+TEOS.

It is important to notice that dyestuff molecules are grafted on the network and because of the dimensions of the pores in some cases dyestuff molecules are far enough interact to each-other. That's why it was concluded that shifts of the absorption maxima are due to the polarities variation in the pores of the network at the points of dye anchoring. It was assumed also that steric hindering, due to bulky organic groups from the silica matrices, diminishes the network influences onto the chromogen, modifies the environments of the dye surroundings and probably hinders hydrogen bonds establishing, leading to a hypsochromic shift of the absorption maxima.

This process was characteristic for the hybrid materials having PhTES and MeTES as precursors, while for those having OTES, TEOS and GPTES as precursors, the absorption maxima are situated at higher wavelengths. These data are correlated with the results obtained from color measurement experiments in CIELAB system and in concordance with shade deviations.

All the hybrid materials were comparatively studied from the color differences in CIELAB system point of view. Luminosity is negative, as it was remarked for all

type of matrices and illuminant (A, B, C, and D65) used. The lower value of the luminosity was recorded when TEOS was used as a network precursor and this is due to interactions that could take place in this type of inorganic matrix, because of water molecules and residual solvents hold into the network. As it was observed for illuminant D65 (representative of average daylight) all the colors of the hybrid materials are much darker that those remarked for the same probes when illuminant A (representative of incandescent light) was used. Luminosity increased in the series of the hybrid materials in order: TEOS<MeTES<PhTES<OTES<GPTES, which can be fully explained on the basis of interactions of the dyestuff molecules with their environments.
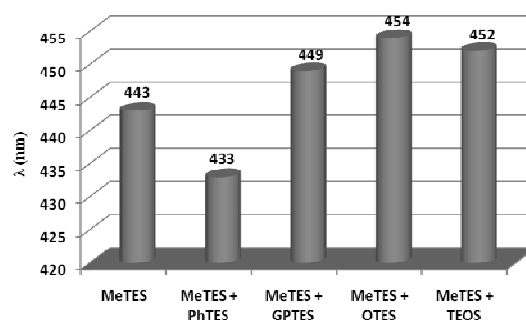

Fig. 5. Dominant wavelengths from diffuse reflexion spectra of the hybrid materials.

Shade shifting is an important parameter and was evaluated from the sign recorded for the variation of a, b parameters, in correlation with sign for ΔH. Thus, a>0, b>0 and ΔH>0 for all hybrid materials and type of illuminant used, define the direction of change in hue toward yellow. The shift to yellowish hues was recorded in order: GPTES<MeTES<TEOS<PhTES<OTES.

Table 2. Color measurements of hybrid materials.

Hybrid material made from :			MeTES	MeTES PhTES	MeTES GPTES	MeTES OTES	MeTES TEOS
A	Tristimulus Values	X	43.54	46.28	53.89	51.45	37.78
		Y	31.06	32.67	41.43	37.53	25.34
		Z	4.55	4.79	6.17	4.80	3.90
	Trichromatic coordinates	x	0.5501	0.5527	0.5310	0.5486	0.5638
		y	0.3924	0.3901	0.4082	0.4002	0.3781
	CIELAB	L	62.55	63.89	70.47	67.67	57.40
		a	27.24	29.01	20.06	26.11	32.56
		b	34.32	34.89	37.14	41.35	30.51
B	Tristimulus Values	X	34.51	36.52	43.80	41.01	29.40
		Y	27.58	28.91	37.82	33.45	21.99
		Z	10.80	11.35	14.62	11.39	9.32
	Trichromatic coordinates	x	0.4734	0.4756	0.4551	0.4777	0.4842
		y	0.3784	0.3765	0.3930	0.3896	0.3623
		L	59.51	60.70	67.89	64.52	54.02

Hybrid material made from :			MeTES	MeTES PhTES	MeTES GPTES	MeTES OTES	MeTES TEOS
	CIELAB	a	26.19	27.73	19.15	25.40	31.54
		b	29.38	29.76	33.14	36.23	24.76
C	Tristimulus Values	X	31.68	33.46	40.62	37.66	26.80
		Y	26.30	27.54	36.39	31.88	20.82
		Z	14.83	15.58	20.05	15.64	12.82
	Trichromatic coordinates	x	0.4351	0.4370	0.4185	0.4421	0.4434
		y	0.3612	0.3596	0.3749	0.3743	0.3444
	CIELAB	L	58.32	59.47	66.82	63.25	52.75
		a	23.65	25.03	16.73	22.82	29.02
		b	27.41	27.74	31.42	34.11	22.59
D 65	Tristimulus Values	X	31.06	32.81	39.83	36.95	26.27
		Y	26.16	27.40	36.24	31.71	20.69
		Z	13.73	14.41	18.56	14.48	11.86
	Trichromatic coordinates	x	0.4378	0.4397	0.4209	0.4444	0.4466
		y	0.3687	0.3672	0.3830	0.3814	0.3518
	CIELAB	L	58.19	59.34	66.70	63.10	52.61
		a	24.91	26.29	17.99	24.26	30.23
		b	27.14	27.47	31.17	33.80	22.32

The total color difference (ΔE) measured by CIELAB method was broken down into its main components: the chroma difference (ΔC), the difference of lightness (ΔL) and the hue difference (ΔH) as function of illuminant used. For hybrid materials obtained from OTES that generates non polar neighborhoods for the organic dye, the values recorded for the total color differences indicate that only weak interactions could take place between molecules. The hydrophobic character in the neighborhood of the dye molecules diminishes the possibility of the existence of hydrogen bonds, because residual solvent and water molecules are practically absent into the pores of the material. The volume of the pores is small comparatively with the pores obtained when PhTES was used as a starting material. From the influences of these factors and the values obtained for the main components of the total color differences, we can conclude that materials obtained from OTES had the highest recorded values for chroma and hue, while luminosity was governed mostly by the possibility of hydrogen bonding.

Table 3. Color differences of hybrid materials.

Color differences	Illuminant type									
	A					B				
	MeTES	MeTES PhTES	MeTES GPTES	MeTES OTES	MeTES TEOS	MeTES	MeTES PhTES	MeTES GPTES	MeTES OTES	MeTES TEOS
ΔL	-30.55	-29.21	-22.63	-25.43	-35.70	-33.67	-32.47	-25.29	-28.66	-39.16
Δa	28.00	29.76	20.82	26.87	33.32	26.82	28.37	19.78	26.03	32.17
Δb	35.06	35.63	37.88	42.09	31.25	30.00	30.38	33.76	36.86	25.38
ΔE_{ab}	54.28	54.85	48.79	56.03	57.98	52.47	52.75	46.59	53.45	56.68
ΔC	42.76	44.31	41.16	47.84	43.56	38.47	39.79	37.38	43.36	39.21
ΔH	13.59	13.84	13.22	14.29	13.74	11.83	12.03	11.56	12.49	11.93
Color differences	C					D65				
	MeTES	MeTES PhTES	MeTES GPTES	MeTES OTES	MeTES TEOS	MeTES	MeTES PhTES	MeTES GPTES	MeTES OTES	MeTES TEOS
ΔL	-34.89	-33.74	-26.39	-29.96	-40.46	-35.02	-33.87	-26.51	-30.11	-40.61
Δa	24.18	25.56	17.26	23.35	29.55	25.46	26.85	18.55	24.82	30.79
Δb	27.99	28.32	32.00	34.69	23.17	27.71	28.05	31.74	34.37	22.89
ΔE_{ab}	50.85	50.93	44.93	51.45	55.20	51.41	51.53	45.32	52.00	55.87
ΔC	35.42	36.58	34.81	40.26	35.99	36.04	37.23	35.19	40.81	36.78
ΔH	10.66	10.83	10.49	11.32	10.71	10.85	11.03	10.64	11.50	10.93

From the infrared spectra of all organic-inorganic hybrids, it was distinguished some common structural particularities. Thus, the broad absorption band at 3000-3800 cm^{-1} corresponds to the fundamental stretching vibrations of different hydroxyl groups and it is composed of a superposition of: isolated vicinal SiO-H stretching vibrations situated at about 3700 cm^{-1}, mutually hydrogen bonded SiO-H stretching at about 3627 cm^{-1}, SiO-H stretching of surface silanols hydrogen bonded to molecular water at 3500 cm^{-1} and O-H stretching of hydrogen bonded molecular water situated at about 3330 cm^{-1}. As a particularity for hybrids obtained from PhTES it is to be noted the existence of an absorption band situated at 3063 cm^{-1} as a part of the broad absorption band from this domain, that correspond to ν(CH) aromatic stretching vibration of the aromatic nucleus.

Moreover, all materials presented in the spectra a band that correspond to asymmetric stretching vibration of the methylene group situated at 2925-2976 cm^{-1} and a band for symmetric stretching vibration situated at 2858-2919 cm^{-1}.

In addition to the envelope of vibrations corresponding to O-H stretching, it was observed a band at 1635-1647 cm^{-1} that is assigned to a deformation mode of adsorbed molecular water and for the material obtained from OTES, this band was present in the spectrum as a shoulder because of the hydrophobic character of the material and a lower content of water in the network.

In the spectra we are found deformation characteristic vibrations δ(OH), δ(NH) and δ_{asym} (H$_3$C-Si) at 1553-1570 cm^{-1}, respectively at 1432-1459 cm^{-1}, while at 1268-1272 cm^{-1} it was detected a characteristic strong and sharp signal δ_{sym} (H$_3$C-Si). The bands situated at 913-923 cm^{-1} correspond to Si-O-Si stretching vibrations and the intense peak situated at 773-776 cm^{-1} was attributed to γ (H$_3$C-Si) deformation. Also the band situated at 433-483 cm^{-1} correspond to Si-O-Si rocking motions of the oxygen atom perpendicular to the Si-O-Si plane accompanied by Si motion, as it was noted by other authors [11].
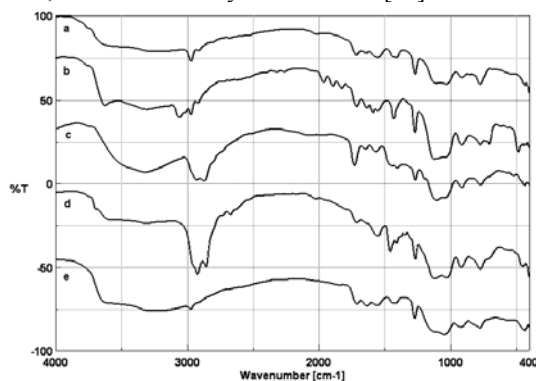

Fig. 6. FT-IR spectra of organic-inorganic hybrids: (a) MeTES; (b) MeTES+PhTES; (c) MeTES+GPTES; (d) MeTES+OTES; (e) MeTES+TEOS.

Specific intense peaks for silica matrices are situated at 1031-1046 cm^{-1} (A$_{1000}$) and 1105-1125 cm^{-1} (A$_{1100}$), corresponding to Si-O-C, respectively Si-O-Si stretching vibrations. As it was observed the relative size of these peaks could be correlated with porosity of the materials and also with the hydrophobic character of the networks. Thus, for hybrid materials obtained from OTES, PhTES and GPTES (A$_{1100}$>A$_{1000}$) the hydrophobic character decreased in the order mentioned earlier, while for hybrid materials obtained from MeTES and TEOS (A$_{1100}$<A$_{1000}$) networks became hydrophilic and the porosity also became lower.

It is important to notice that for the hybrid material obtained from GPTES in the spectrum was found a more intense peak situated at 914 cm^{-1} that correspond to the epoxy ring stretching vibration, but after a thermal treatment for this kind of material, since the ring opening reactions causes generation of hydroxyl group, the characteristic stretching vibration of hydroxyl group became more intense and broad. Also, after thermal treatment the bands situated at about 1100 cm^{-1} became more intense and sharp.

All the materials obtained were examined through thermal gravimetric analysis (TGA). The experiments were conducted under nitrogen at a heating rate of 10^{0}C/min. and in the range 20-900^{0}C. The analysis of the thermogravimetry results shows that the release of the water and residual solvent from the networks occurs in the range 20-270^{0}C. The shape of the curves showed that the instability at heating is more pronounced for materials derived from GPTES, probably due to polymerization reactions that occur while the temperature was raised and followed by decomposition of the polymers formed.

For hybrid materials obtained from TEOS, because of the polar character of the network, water and solvent retained during synthesis are released at temperatures under 130^{0}C and the weight loss was about 4.6%. The weight loss for hybrid material obtained from OTES was only of 1.37% below 200^{0}C, because of the non polar character of the network which retain in the pores only small amounts of water and residual solvents from the synthesis.
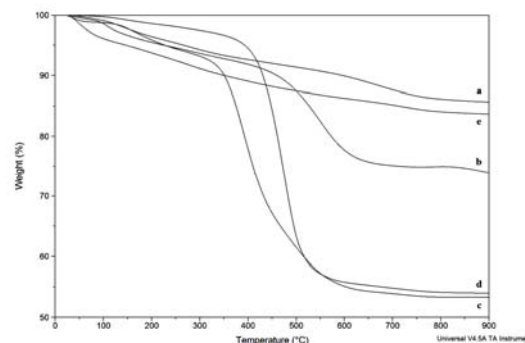

Fig. 7. TGA of the hybrid materials: (a) MeTES; (b) MeTES+PhTES; (c) MeTES+GPTES; (d) MeTES+OTES; (e) MeTES+TEOS.

Aliphatic long chains were thermal unstable as it was observed for GPTES and OTES hybrid materials. Thus at

temperatures between 200-700 °C organic residues were decomposed almost quantitatively, the weight loss recorded for GPTES and OTES being situated at about 40%. The residues for these hybrid materials at 900^{0}C were about 53-54%, while for MeTES and PhTES hybrid materials were situated at about 85% and 74%, respectively.

4. Conclusions

A series of hybrid materials were prepared through sol-gel processes from different alkoxysilanes and HESAQTES as an azo chromogen bearing triethoxysilane residues and structure-properties relationships of the obtained organic-inorganic hybrid materials are discussed with respect to the structure and nature of the organic modifying agents.

Hybrid materials were complete characterized by means of XRF spectrometry, FT-IR spectrometry, UV-VIS absorption and diffuse reflexion spectra, color measurements in CIELAB system and thermal analysis.

The potential usage of a large variety of silanization agents that allow great variations of the inorganic matrices, facile grafting of the azo chromogen on the silica surface and interactions between dyestuff molecules and organic groups of the network, lead to hybrid materials which exhibit major differences in optical, chemical and thermal properties.

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