

INCORPORATING OF COLORED AZODERIVATES IN HYBRID MATRICES

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From a scientific and practical point of view, it is of great interest to investigate the behavior of different chromophor systems (organic pigments and azo dyes) after their incorporation during the formation of boron hybrid matrices. For the synthesis, we used 5% solutions of the following chromophors: yellow light-resistant dye, green nitroso dye, red azo dye, and violet azo dye with an incorporated UV-filter. The starting components for the sol-gel matrix were $(\text{CH}_3\text{O})_3\text{B}$, $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$, PEG_{400} and PVA_{72000} . The hybrid matrix: chromophor ratio was 10:0.3. Visible estimation after mixing and subsequent formation of the hybrid network showed that well colored gel films (yellow light resistant, green, red, violet), with good hydrophobic properties, could be obtained with minimum quantities of chromophor. All the gel films retained their color characteristics up to 100 °C. Coatings derived with green nitroso-dye had the best thermal stability (up 230 °C). In the other combinations, there were color changes and a decrease in the elasticity of the gel films, which became brittle and not monolithic. UV-VIS analysis confirmed the retention of the chromophor system after incorporation in the hybrid boron matrix.

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1. Introduction

Incorporating organic dyes with inorganic and hybrid products, obtained through the sol-gel process, allows the achievement of colored layers for optics applications such as filters, transformers of solar energy, non-linear optics and laser environments etc. In addition, a higher photochemical stability of the dye is observed inside the hybrid matrix, compared to its presence in solutions, organic and inorganic matrices [1]. The most frequently used dyes are rodamines, pyranines, phthalocyanines etc., which have fluorescent, photochromic or non-linear optic properties [2-5]. They can be connected through chemical bonds [6-9] in matrices based on Si, Al, Ti, Zr and others. Due to their better solubility, easy recycling and the diversity of colors, these dyes are preferred for coloring glasses obtained through the classic technology.

Photoactive layers with the participation of azo dyes have been described in a matrix of liquid crystals [10], sensors for connecting them to polysiloxane networks [11], silica hybrid films from polyvinylpyrrolidone, and by characterization of their non-linear optic properties [12]. The siliceous organic-inorganic films were functionalized with organic dyes, for use as matrices for solar energy, mesoporous hybrid films, membranes, etc. [13]. There are cosmetic products of a high SPF based on hybrid hydro-gels. The PVA-PEG- B_2O_3 - SiO_2 system has been the subject of study in our previous works [14, 15]. The processes of gel forming have been studied together with the achievement conditions (pH, composition, type of precursor, etc.), on the basis of the homogeneity of the gel hybrid films and their thermal stability.

From a scientific and practical point of view, we were particularly interested in studying the behavior of the different chromophor systems (azo dyes and organic pigments), after their incorporation during the formation of hybrid borate matrices from the system PVA-PEG- B_2O_3 - SiO_2 .

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2. Experimental details

The borate hybrid matrices were obtained through a sol-gel method, employing the following starting compounds: PVA₇₂₀₀₀-4% water solution, PEG₄₀₀, (CH₃O)₃B and (C₂H₅O)₄Si. Dyes were introduced as 5% solutions (yellow, red and green pigment in a DMSO solution), and the pink-violet dye as a water solution. The preparation scheme is described in [14, 15].

Gels of the following mass composition were formed:

A) 55% PVA, 40% PEG, 5% B₂O₃ and

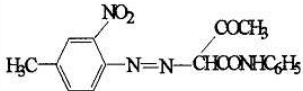
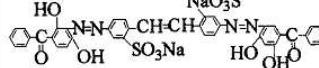
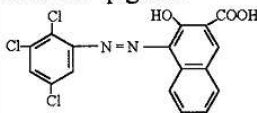
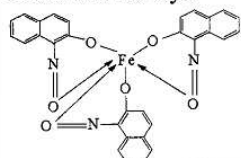
B) 70% PVA, 5% PEG, 5% B₂O₃, 20% SiO₂.

Dyeing solutions were added in the precursor mixture. The volume ratios of the matrix/ dyeing solution were 10:0.3 cm³. The films were obtained by casting equal volumes of each dyeing mixture into glass vessels with the same diameter, and drying in the environment. Homogeneous films were formed, from which we determined the optic characteristics with the aid of UV-VIS spectroscopy (Perkin Elmer Lambda 40) and structural changes with IR spectroscopy (Perkin Elmer SPECTRUM 1000). Subsequent thermal treatment in the range (25-300 °C), in air, realized media with retention times of 2 hours.

3. Results and discussion

Table 1 presents the results achieved by studying the gel-forming properties as functions of the synthesis, compound and type of azo dye.

Table 1. Gelation as a function of the conditions, and of the kind of chromophore.

Azo dyes, samples	Composit ions		Observation of gelation				Water-resistance
	A	B	Closed vessel:		Open-air vessel:		
			2 days	60 days	2 days	4 days	
Without dyes (a)		*	Gel	Solid gel	Gelling	Solid gel	Hydrophobic film
	*		Liquid	Liquid	Poor gelling	Gelling	Hydrophilic film
Yellow light-resistant dye (b)		*	Liquid	Liquid	Gelling	Solid gel	Hydrophobic film
	*		Liquid	Liquid	Poor gelling	Gelling	Hydrophilic yellow film
Pink-violet azo-dye with incorporated UV-filter (c)		*	Liquid	Liquid	Gelling	Solid gel	Hydrophobic Pink film
	*		Liquid	Liquid	Poor gelling	Gelling	Hydrophilic Pink film
Red azo- pigment (d)		*	Liquid	Liquid	Gelling	Gel	Hydrophobic red film
	*		Liquid	Solid gel	Poor gelling	Gel	Hydrophilic red film
Green nitroso dye (e)		*	Liquid	Liquid	Gelling	Solid gel	Hydrophobic green film
	*		Liquid	Solid gel	Poor gelling	Gelling	Hydrophilic Green film

In direct contact with air, we observed gelling of all precursor mixtures; the gelling time of compounds from the SiO_2 modified system being the shortest. If the ageing of the mixtures from the PVA-PEG- B_2O_3 system was carried out without contact with air, gels could be obtained only when using red and green azo pigments, while the borosilicate system formed gels only in the absence of chromophores.

The reasons for the different gel-forming behavior are most probably twofold. One is the fact that, in the process of carrying out the complete sol-gel reactions, we need the excess water to be dissociated in the air when drying (the gel becomes stable). The other is the pH of the system. In the pure borate system, mixing takes place at a pH of 4-5, while with SiO_2 modified at a pH of 2-3, the behavior of the chromophores in different conditions would be different. The difference in the pH value would also influence the boron coordination and the stability of the BO_4 ester complexes participating in the cross linking.

Table 2. Information of UV-VIS spectroscopy for the obtained hybrids films (25 °C).

№	Films from compositions:		Colour	λ max [nm]
	A	B		
(a)	*		Colourless	280, 328
		*		280, 328, 385, 420, 548
(b)	*		Yellow	276, 328, 432, 465, 548
		*		278, 328, 420, 471, 548
(c)	*		Pink	275, 320, 385, 540
		*		280, 328, 385, 420, 550, 570
(d)	*		Red	311, 328, 507
		*		280, 328, 416, 504
(e)	*		Green	328, 417, 675
		*		285, 421, 438, 675

Table 3. Characterization of coloured films during heat treatment.

№	Films from compositions:		Visual changes of samples during heat treatment t [°C]								
	A	B	25	50	80	100	130	160	200	230	300
b		*	yellow	brown	brown	yellow	yellow	Yellow-brown	Yellow-brown	Yellow-brown	brown
	*		yellow	yellow	yellow	Dark yellow	brown	brown	brown	brown	brown
c		*	pink	pink	pink	darken	Pink-red	dark red	dark red	dark red	Dark
	*		pink	pink	pink	pink	pink	pink-brown	Orange-brown	Orange-brown	Dark
d		*	Red	Red	Red	Red	Red	Red	Red-brown	Red-brown	black
	*		Red	Red	Red	Red	Red	Red	Red-brown	Red-brown	black
e		*	Green	Green	Green	Dark green	Dark green	Dark green	Dark green	Dark green	black
	*		Green	Green	Green	Green	Green	Green	Green	Green	black

Table 2 presents data from the UV-VIS spectroscopy of gel hybrid films, while the changes taking place in the gel materials during thermal treatment in the interval 25-300 °C are systematized and presented in Table 3. Changes in the color of all gel films were not observed up to 100 °C, but some of them became more fragile and lost part of their elasticity. Dying with red pigment (up to 160 °C) and green pigment (up to 230 °C) proved to be thermally most stable. The most unstable

proved to be dying with yellow pigment (up to 100 °C). The chromophores participating in the borosilicate hybrid matrix preserved their color up to higher temperatures, while gel films with integrated pink dye demonstrated thermochromism (130 °C). At 300 °C, visible destruction of all hybrid films, together with a change in their color, took place.

IR spectroscopy was used to trace the influence of the hybrid matrix and type of chromophore on the structural changes in the dyed gel hybrid films. All spectra were characterized by the appearance of absorption bands in the range 3500–3200 cm⁻¹ (ν_s OH), 1400–1200 cm⁻¹ (B-O from BO₃, C-H from CH₂) 1200–1050 cm⁻¹ (ν B-O from BO₄, ν OH from C-OH and C-O-C).

Adding dyes to the hybrid borate matrix additionally decreased the pH of the system and influenced the quantitative ratio of BO₃ and BO₄ structural units in the hybrid network. Also, bands at 1225–1254 cm⁻¹ related to the polymerization of the borate network appeared.

4. Conclusions

The changes observed in the IR spectra led us to presume that there are reactions taking place between the chromophore functional groups and the matrix. The inhomogeneous surface of the borate hybrid films can be explained with a less polymerized hybrid matrix and absorption of atmosphere humidity. The introduction of a second glass-former to the system improves the homogeneity, mechanical, thermal stability of the films obtained. Increased content of the inorganic component and additional networking lead to improved density, better water stability and the duration of preservation in physical matrices. UV-VIS analysis confirmed the retention of the chromophore system after its incorporation into the hybrid boron containing matrix.

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