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Photochromic hybrid sol–gel coatings: preparation, properties, and applications*

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Inorganic-organic hybrid polymer (ORMOCER®) coatings with a fast photochromic response and high photochromic activity were prepared by incorporation of the photochromophore Variacrol® Blue D into hydrolysates of organofunctional alkoxysilanes, with subsequent thermal curing. Besides the traditional way of doping the sol–gel materials by physically dissolving the dye, a graftable derivative was prepared and covalently attached to two matrices of different rigidity. The resulting thin films showed good photochromic activity, no blooming, mechanical properties at least comparable to the pure host material, and can be applied to different glass and plastic substrates. Photochemical degradation was studied by means of artificial weathering and factors influencing the fatigue behaviour of the coatings assessed. The graftable dye showed improved photochemical fatigue resistance. The more rigid matrix was preferable, too, in terms of photodegradation.

Key words: photochromic dyes, covalent dye attachment, hybrid sol–gel materials

1. Introduction

Materials prepared via the sol–gel process [1] enable the development of abrasion-resistant, durable and optically clear coatings, that can act as hosts for organic species such as dyes [2, 3]. Inorganic-organic hybrid polymers derived from organofunctional alkoxysilanes (ORMOCER®s****) are especially suitable for this application [4]. Besides their alkoxy groups, that can be hydrolysed and polycondensed to form silica-like inorganic domains, these compounds provide reactive organic moieties, that

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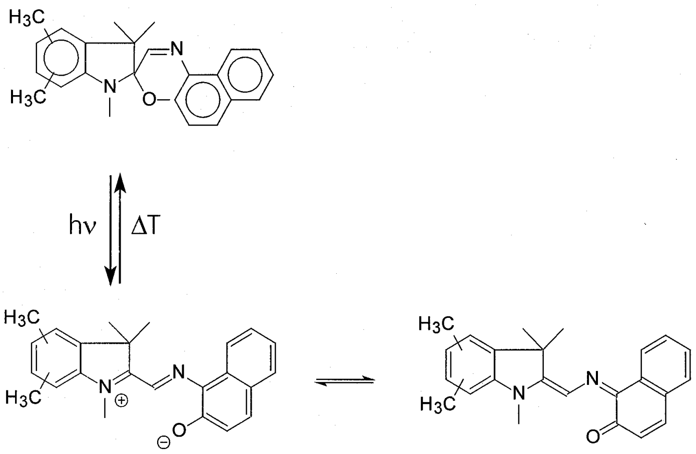
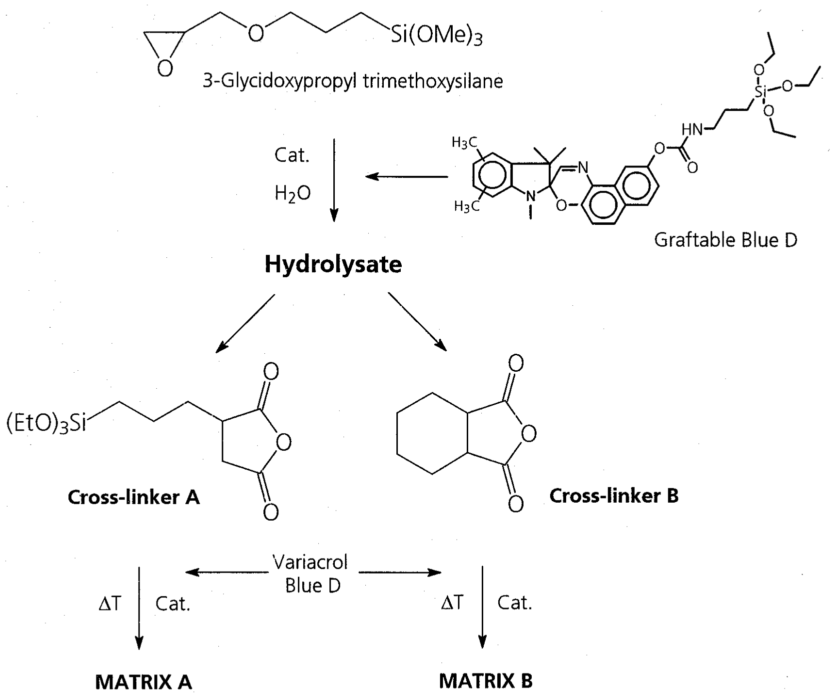
can be cross-linked to form an organic network at elevated temperatures or upon UV irradiation. By appropriate choice of network formers and modifiers the materials properties can be controlled and tailored within a certain range. Dye-doped hybrid polymers, in recent years, have been utilised to design and produce materials with new, unique properties, e. g., materials for optical storage [5] or coatings for decorative use [6].

Photochromism is defined as the reversible change between two chemical species characterized by different absorption spectra. Light of wavelength l_1 is absorbed by the usually uncoloured compound A, which gives after isomeration coloured form B, absorbing at λ_2. B reverts back to A thermally or photochemically [7]. The most interesting group of photochromic dyes are spirooxazines, being characterized by a relatively week C_{spiro}–O bond that, upon an UV light irradiation, undergoes a heterolytic cleavage to form a planar, merocyanine-type structure (Scheme 1). The first electronic transition of such photomerocyanine usually occurs in the visible spectral region [8].



Scheme 1. Photochromic reaction of Variacrol® Blue D. Above: bleached spirooxazine state (colourless); below: activated, mesomeric merocyanine states (blue)

According to Crano et al. [9] an optical lens equipped with a physically dye-doped photochromic coating would be inherently limited with respect to its photochromic performance. In order to produce a coated lens with a performance acceptable to the market, the concentration of photochromic dye needs to be at least 25 wt. % of the film composition, which is impractically high. As a result, the physical and mechanical properties of the film would be significantly altered and the matrix integrity might not be maintained. Graftable dyes, with the chromophore linked to a hydrolytically unstable trialkoxysilyl group, are able to covalently attach onto the sol–gel matrix, thus present a possibility to circumvent this problem and realize higher chromophore concentrations without affecting the mechanical integrity of the coating.



Scheme 2. Coating preparation and composition

The objective of this work was to develop photochromic coatings for application on plastic substrates such as polycarbonate sunglass lenses. This should be achieved by incorporation of organic photochromophores into hydrolysates of organofunctional alkoxysilane compositions based on 3-glycidoxypropyl trimethoxysilane. Besides the traditional way of physically dissolving the dye, a graftable derivative was synthesized and subjected to the sol–gel process with the matrix material (Scheme 2). The photochromic behaviour of both dyes was investigated in two coatings of different cross-linking degree. The influence of grafting on the photophysical behaviour and fatigue resistance will be discussed.

2. Experimental section

2.1. Educts

3-Glycidoxypropyl trimethoxysilane (GLYMO), 3-triethoxysilylpropyl succinic anhydride (TESSA, cross-linker A), cis-hexahydrophthalic anhydride (HEPA, cross-linker B), and phenyl trimethoxysilane (PhTMO) were purchased from ABCR, Wacker Chemie, Fluka, and Aldrich, respectively, and used without further purification. THF and *n*-propanol were purchased from Promochem and used as received.

The photochromic dyes Variacrol® Blue D and a silylated derivative thereof (hereinafter called graftable Blue D) were made available by Great Lakes Chemical Corporation. Molecular structures are given in Schemes 1 and 2.

2.2. Procedures and coating materials

Preparation of matrix A: To GLYMO placed in a round bottom flask H_2O and an amine catalyst were added in molar ratio GLYMO : H_2O : cat. = 1 : 1.5 : 0.05, and the mixture stirred. After completion of the hydrolysis as determined by Raman spectroscopy [10], *n*-PrOH (100 g per mole of GLYMO) and TESSA in molar ratio GLYMO : TESSA = 1 : 0.5 was added. After stirring for 1 h the mixture was in a ready-to-apply condition.

Preparation of matrix B: GLYMO and PhTMO in molar ratios GLYMO : PhTMO = 0.75 : 0.25 were placed in a round bottom flask and stirred. Subsequently, H_2O and an amine catalyst in molar ratio GLYMO : H_2O : cat. = 0.75 : 1.5 : 0.0375 were added and the mixture stirred until the hydrolysis was complete. Finally, *n*-PrOH (100 g per mole of GLYMO) and HEPA in molar ratio GLYMO : HEPA = 0,75 : 0,375 were added. After stirring for 1 h the sol was in a ready-to-apply condition.

The dyes were dissolved in 2:1 mixtures of THF and *n*-PrOH, in amounts corresponding to a chromophore concentration of 3 wt. % with respect to the solids content of the resulting sol. For calculation the additional mass of the silylated side chain of graftable Blue D was taken into account in order to make sure that materials with identical chromophore concentrations were investigated. Variacrol® Blue D was added to the final sols (as an “additive”). Graftable Blue D was added at an earlier stage in order to allow co-condensation (as shown in the Scheme 2). For the hydrolysis of the dye additional water was added in molar ratio graftable Blue D : H_2O = 1 : 1.5.

The freshly prepared systems were spin coated on different substrates such as glass slides, PC lenses or CR 39® sheets, and cured thermally at 130 °C for 20 min.

2.3. Test devices and measurements

Hydrolysis reactions of alkoxysilanes were followed by means of a FT-Raman spectrometer (Bruker, *model RFS 100*). Spin coating was performed by means of a KSM Karl Süss spin coater, *model RC8*. Thermal curing was done by means of Heraeus drying ovens. For activation a commercially available face tanner (Philips, *model HB170*) with Philips CLEO 15 W UV-A bulbs was used. Integrated power density was 44 $W\cdot cm^{-2}\cdot min^{-1}$ between 250 and 410 nm. Bulb-sample distance was 12 cm. Transmittance spectra were measured and ΔY values calculated by means of a colorimeter BYK-Gardner, model the Color Sphere. Prior to each measurement, the samples were activated, manually transferred into the measurement chamber of the spectrometer and the spectra measured with a 2 seconds delay. An average of 10 individual measurements per sample was taken in each case.

Microhardness was determined by means of a Berkovich indentor (Fischerscope H 100). Coating thickness was measured by means of a Laser Profilometer UBM, equipped with a microfocus device. For assessment of adhesion properties, a cross hatch test according to ASTM D 3359 was performed.

Photochemical degradation was studied by means of an air cooled Suntest chamber (ATLAS Material Testing Technology BV, model Suntest CPS+) with a 1100 W Xenon lamp as a light source (according to DIN ISI 9000ff specification). The average irradiance was 750 $W \cdot m^{-2}$. After each irradiation interval all samples were subjected to a bleach-back procedure comprising heat treatment at 75 °C for 20 minutes, irradiation with visible light (standard fluorescence bulbs) for 1 h, followed by storage in the dark for at least 2 h.

3. Results and discussion

In order to form matrices of different rigidity, two different anhydride cross -linkers were used, i.e., the bifunctional silylated cross-linker A (to form matrix A with additional inorganic cross-linking, Scheme 2) and organic cross-linker B (to form matrix B, Scheme 2). Variacrol® Blue D and its graftable derivative were incorporated into both matrices with amounts corresponding to a chromophore concentration of 3 wt. %. Table 1 compiles some physical and mechanical properties of the four resulting coatings (samples 1–4), compared to the pure host materials (first two lines). The data were obtained from coatings on glass slides. The microhardness of matrix A comprising the silylated anhydride cross-linker A (81 MPa) was about twice the hardness of matrix B (39 MPa). The microhardness was taken as a measure of rigidity and residual free volume in the coating materials.

Table 1. Physical properties of coatings

Sample No.	Matrix type	Dye	Thickness/μm	Microhardness/MPa	Photochromic activity/%
			(standard deviation in parantheses)		
	B			39.27 (0.98)	
	A			80.84 (13.18)	
1	B	3 wt. % Blue D	4.29 (0.26)	40.80 (6.26)	20
2	A		4.95 (0.25)	98.34 (5.80)	24
3	B	3 wt. % gr. Blue D	6.98 (0.38)	48.38 (5.37)	39
4	A		12.35 (0.27)	114.1 (8.01)	35

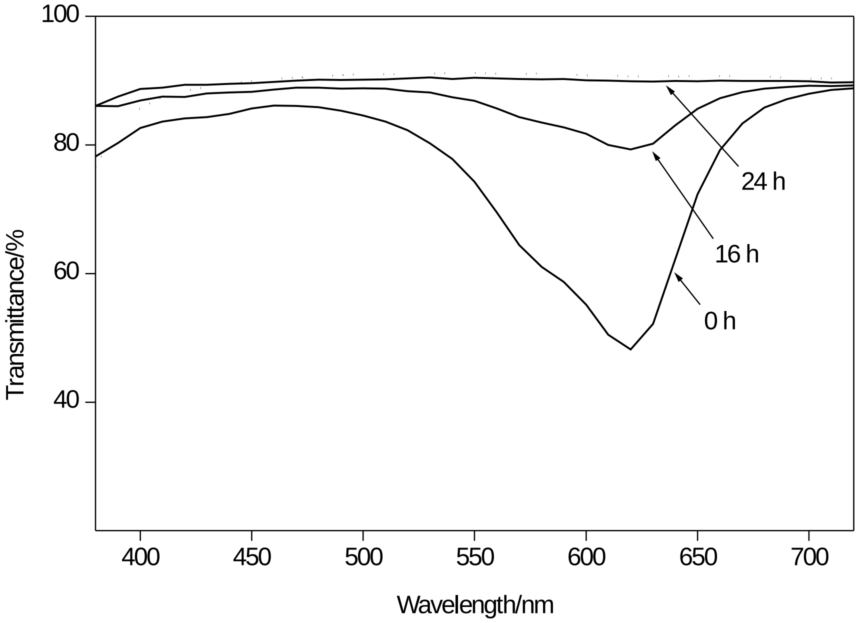


Fig. 1. Variacrol® Blue D incorporated physically into matrix B (sample 1)

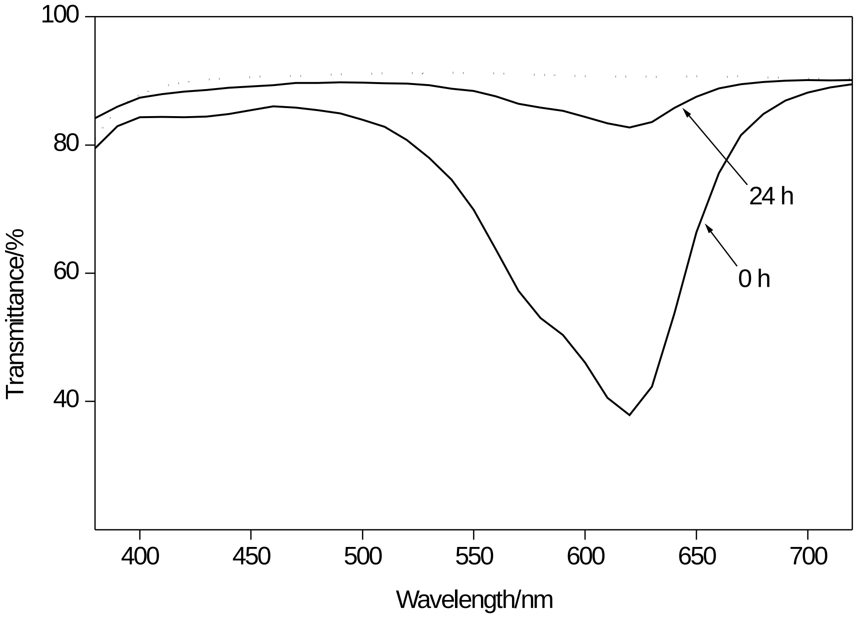


Fig. 2. Variacrol® Blue D incorporated physically into matrix A (sample 2)

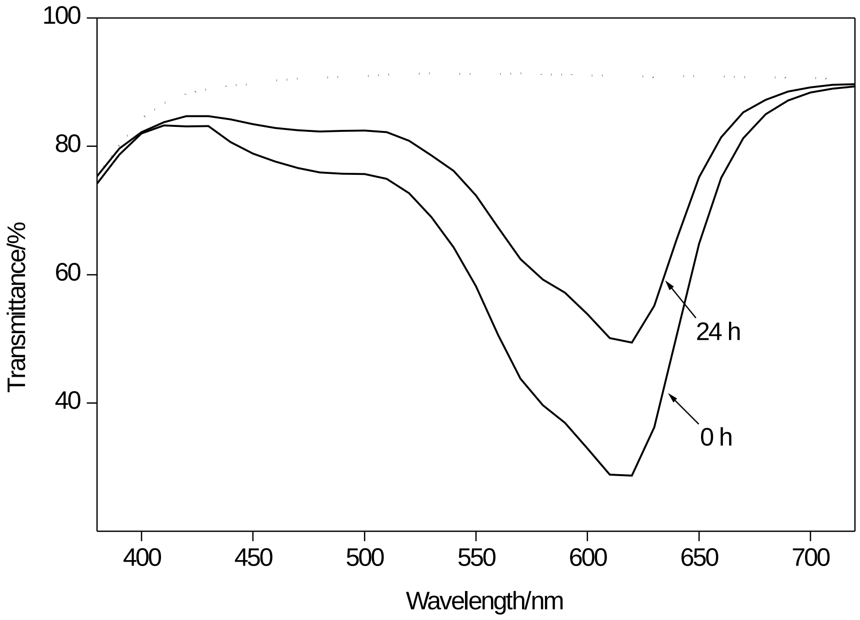


Fig. 3. Graftable Blue D covalently attached to matrix B (sample 3)

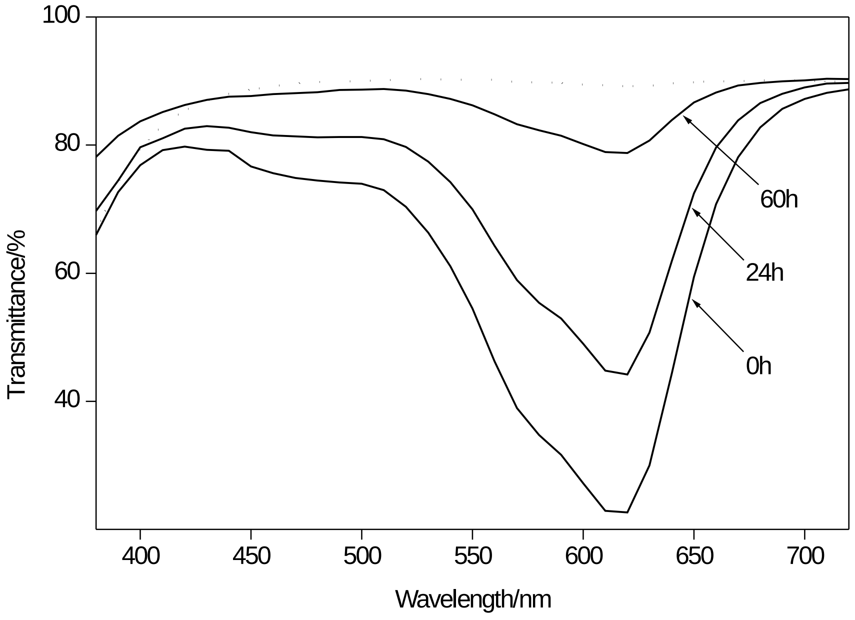


Fig. 4. Graftable Blue D covalently attached to matrix A (sample 4)

After physical incorporation of Blue D the microhardness remained essentially unchanged for sample 1, however, was slightly increased in sample 2. For the dye-grafted samples 3 and 4 the hardness rose to 48 MPa and 114 MPa, respectively. This apparent strengthening effect was attributed to the additional contribution to the matrix connectivity resulting from covalent attachment of the chromophore.

The transmittance spectra of samples 1–4 are shown in Figs. 1–4, respectively. The corresponding photochromic activities ΔY are given in Table 1. Variacrol® Blue D shows an absorption maximum at 620 nm in the activated state. This is in close agreement with the corresponding value obtained from alcoholic solutions [11]. The absorption of the graftable derivative was found to arise at approximately the same wavelength. Additionally, a further weak absorption was observed with a maximum at 460 nm, giving the activated form of the graftable dye a slight green hue compared to the colour of the parent dye.

Samples 3 and 4 showed higher activities compared to samples 1 and 2. However, this could not be attributed to a higher photochromic response of the grafted dye, because of the different layer thickness achieved with these samples. According to the law of Lambert–Beer, the absorbance is a function of the path length of light traversed through the sample. Normalization of ΔY to a layer thickness of 1 μm shows that all four samples had comparable activity.

The photochemical degradation (fatigue) behaviour of the coatings (on glass slides) was studied by means of artificial weathering in a Suntest device. The samples were continuously irradiated with simulated sunlight and their residual activity determined after intervals of 4 h. After each irradiation interval all samples were subjected to a bleach-back procedure in order to make sure that all photochromic species are in the bleached state prior to the transmittance measurement. Figures 1, 2 show the spectra of the physically doped samples obtained after the selected intervals. Whereas sample 1 was totally degraded after 24 h (Fig. 1) sample 2 had some residual activity after that time (Fig. 2). As both samples contained the same chromophore in identical concentrations, it can be concluded that – compared to matrix B – matrix A had a stabilizing effect on the fatigue of Blue D.

Figures 3, 4 show the spectra of the dye-grafted samples. It is apparent that the grafted dye had a strongly improved photostability. In matrix B after 24 h of irradiation still 51% of the initial activity was maintained (Fig. 3). An even better stability was observed for sample 4 where 74% and 17% of the initial activity was left after 24 and 60 h of irradiation, respectively (Fig. 4). From these data it is evident that grafting the photochromophore to a rigid, highly cross-linked host material leads to a significant photochemical stabilization, a phenomenon the occurence of which was expected also from energy dissipation and oxygen diffusion considerations [8]. The influence of the layer thickness, which might also be significant, however, was not investigated.

The developed coatings were applied to a variety of different substrates relevant for sunglass applications, such as bis-phenol A polycarbonate, a material that has been widely accepted to be utilized for safety-type lenses but cannot be tinted by state-of-the-art solvent dyeing techniques [9]. Bis-phenol-A polycarbonate lenses have been spin-coated with the matrix A system. In Fig. 5 are displayed photographs of the resulting photochromic samples. On the left hand side is shown the colouration of the samples immediately after switching off the UV source. The photographs on the right hand side demonstrate the status after 3 minutes of bleaching at room temperature. The shaded parts of the lenses shown here in different grey scales had a very pleasant deep blue colour. The bleached halves (covered during irradiation) were essentially colourless.

Fig. 5. Bis-phenol-A polycarbonate lenses equipped with photochromic hybrid polymer coatings. Left pictures: colouration immediately after switching off the UV-A irradiation source; right pictures: state after 3 minutes of bleaching under ambient conditions; upper row: 6 wt. % of graftable Blue D in matrix A; bottom row: 4 wt. % of graftable Blue D and 2 wt. % of Variacrol® Blue D in matrix A

Two different dye compositions were realized. The coating in the upper row was dyed with 6 wt. % graftable Blue D, whereas that one in the bottom row contained a mixture 2 wt. % Variacrol® Blue D and 4 wt. % of its graftable derivative. As the photographs prove, strong colouration depths result from these high concentrations, which, by using physically dissolved dyes only, could not have been achieved. The used grafting technique prevents aggregation, crystallisation or diffusion processes (blooming on the surface) to occur, thus, enabling higher dye concentrations to be incorporated without producing adverse effects. The switching kinetics of both dyes differed, in particular as far as the bleaching reaction is concerned, which proceeds about a factor of 10 slower for the graftable dye [12]. As can be understood from the illustration, the mixed composition (bottom row) consequently showed less residual colouration after 3 min of bleaching, although having a higher initial colouration depth. Hence, in principle, switching kinetics may be tuned in a limited range by means of mixtures of physically dissolved and grafted dyes.

4. Conclusion

Photochromic coatings with favourable mechanical and photochemical properties could be prepared from hybrid polymers and silylated graftable photochromophores. The resulting thin films exhibited a number of favourable features such as high colouration depths, absence of blooming and plasticizer effects, and improved photochemical fatigue resistance. The developed technology provides as a further benefit a more general applicability that should allow for the preparation of high-performance coatings to be used virtually independently of the substrate. The coatings may be preferably employed in the preparation of optical ophthalmic and non-ophthalmic articles such like prescription lenses or sunglasses. Besides, further possible application fields are visors, radiation protection devices, light filters, safeguard systems, sunroofs, shading devices, reversible markings, printing/publishing systems, and textiles. Where appropriate, the coatings may be equipped with abrasion resistant hybrid polymer top coats.

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