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Photochromic sol-gel derived hybrid polymer coatings: the influence of matrix properties on kinetics and photodegradation

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Photochromic dyes undergo a reversible change in their absorption characteristics upon UV light irradiation. By incorporating such photochromophores into sol-gel derived inorganic-organic hybrid polymers, versatile coatings with a fast photochromic response and high photochromic activity can be obtained. In the present study, the isomerization kinetics of spirooxazine dyes entrapped in hybrid polymer coatings were investigated in situ. The chemical properties of the matrices used were characterised in terms of their inorganic network connectivity (NMR measurements) and paramagnetic properties (EPR spectroscopy). Their photodegradation behaviour was studied by means of artificial weathering.

Key words: photochromic dyes; switching kinetics; sol-gel materials; hybrid polymer 1

1. Introduction

Sol-gel derived inorganic-organic (hybrid) molecular composites are used in a wide range of applications, such as laser optics, data storage, and antiscratch and antireflective coatings, e.g., on optical and ophthalmic components. This is due to the multiple advantages offered by their high transparency and low processing temperatures and the availability of suitable precursors [1]. Hybrid polymers (ORMOCER®s**) combine, to a certain extent, advantages of inorganic glasses (hardness, transparency, chemical resistance) and organic polymeric materials (modification of

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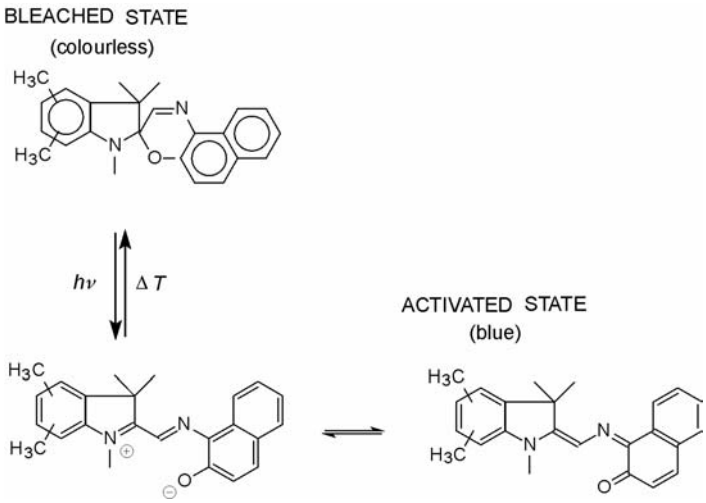
chemical environments, control of composite properties, low processing temperatures).

A photoinduced change in the absorption of a molecule by a reversible process is referred to as photochromism [2]. Usually an uncoloured form A undergoes isomerisation to a coloured form B, exhibiting a different absorbance behaviour. The spirooxazine dyes investigated in this work are characterised by a relatively week C_{spiro}–O bond, which, by a heterolytic cleavage caused by UV irradiation ("on-reaction"), forms a planar merocyanine-type structure (Scheme 1) [3].



Scheme 1. Photochromic reaction of Blue D

The half-life time of the thermally induced bleach back process ("off-reaction") can range from seconds to minutes [4]. Organic photochromes can be chemically modified in such a way that covalent attachment to an inorganic network becomes possible (see the inset in Fig. 1) [5]. Sol-gel matrices provide a stable environment for the chromophores, preventing their self-aggregation and interaction with the degradation products. Optical transparency in both the UV and visible light region and low processing temperature makes these kinds of materials attractive for the incorporation of photochromic dyes [6–8]. By tuning the nature of the matrix and dye the optical response can be optimized. The photochromic properties can be strongly modified by the presence of polar groups (i.e. Si–OH), complexation, protonation, matrix rigidity and steric hindrance [9, 10]. Strong interactions between the dye and host matrix reduce dye mobility and thus the thermal decoloration rate. A very good example are matrices made from hydrophobic polydimethylsiloxane species cross-linked by hydrophilic zirconium oxopolymers, used as hosts for spirooxazine (SO) and spiropyran (SP) dyes. The amount of the coloured form after irradiation depends on the molar percentage of the zirconium oxopolymer domains. In the hydrophobic matrix, where the Si–OH groups are fully hydrolysed, direct and very fast photochromism can be

observed [11]. Some advantages of this type of incorporation, such as an increase in photochromic activity and photochemical stability, have been reported earlier [6].

The matrix systems chosen in the present study have been proven to be suitable systems for the incorporation of organic photochromes. Epoxy-functional alkoxysilane hydrolysates were cross-linked with anhydrides and amines to produce matrices of different network density and polarity.

2. Experimental section

2.1. Chemicals

The photochromic dyes Variacrol® Blue D (1,3,3,5,6-pentamethylspiro-[indolino-naphthoxazine]), its silylated derivative (hereinafter called graftable Blue D, gr. Blue D; inset in Fig. 1, Table 2), a spiro-isoindolinooxazine analogous in structure to Blue D (Blue C, Table 2), a spiro-indolinooxazine with a 5'-morpholino-1,3,3-trimethyl substitution (PNO, Table 2), a red-switching chromene with proprietary structure (Red A, Table 2), and the chromene 3,3–diphenyl-3H-naphtho[2,1-b]pyran (Photo L, Table 2) were kindly supplied by Great Lakes Chemical Corporation, Italy.

Blue A (1,3-Dihydro-1,3,3-trimethylspiro[2H]-indole-2,3-[3H]naphth[2,1-b][1,4] oxazine], CAS-No. 27333-47-7) was purchased from Aldrich.

3-Glycidoxypropyl trimethoxysilane (GPTMS), 3-aminopropyl triethoxysilane (APTES), and methyl diethoxysilane (DH) were ABCR products. 3-triethoxysilylpropyl succinic anhydride (TESSA), cis-hexahydrophthalic anhydride (HHPA), and phenyl trimethoxysilane (PhTMO) were purchased from Wacker Chemie, Fluka, and Aldrich, respectively. All chemicals were used without further purification. THF and *n*-Propanol were purchased from Promochem and used as received.

2.2. Preparation of materials

Preparation of the GG matrix: H_2O and an amine catalyst were added to GPTMS placed in a round bottom flask in the molar ratio GPTMS : H_2O : cat. = 1 : 1.5 : 0.05, and the mixture was stirred. After hydrolysis was complete (as determined by Raman spectroscopy [12]), *n*-PrOH (100 g per mole of GPTMS) and TESSA (molar ratio GPTMS : TESSA = 1 : 0.5) were added. After stirring for 1 h the mixture was in a ready-to-apply condition.

Preparation of the GB matrix: GPTMS and PhTMO in the molar ratio 0.75 : 0.25 were placed in a round bottom flask and stirred. Subsequently, H_2O and an amine catalyst in the molar ratio GPTMS : H_2O : cat. = 0.75 : 1.5 : 0.0375 were added and the mixture was stirred until hydrolysis was complete. Finally, *n*-PrOH (100 g per mole of GPTMS) and HHPA (molar ratio GPTMS : HHPA = 0.75 : 0.375) were added. After stirring for 1 h the sol was in a ready-to-apply condition.

Preparation of the GA10 matrix: H_2O and an amine catalyst were added to GPTMS placed in a round bottom flask in the molar ratio GPTMS : H_2O : cat. = 1 : 1.5 : 0.05, and the mixture was stirred. After hydrolysis was complete, *n*-PrOH (100 g per mole of GPTMS) and APTES (molar ratio GPTMS : APTES = 0.9 : 0.1) were added. After stirring for 1 h the mixture was in a ready-to-apply condition.

Preparation of the GAD matrix: H_2O and an amine catalyst were added to GPTMS placed in a round bottom flask in the molar ratio GPTMS : H_2O : cat. = 1 : 1.5 : 0.05, and the mixture was stirred. After hydrolysis was complete, *n*-PrOH (100 g per mole of GPTMS) and APTES (molar ratio GPTMS : APTES = 0.9 : 0.1) were added. After APTES was fully hydrolysed, DH (GPTMS : DH = 0.9 :0.25) was subsequently added. After 30 minutes of stirring the mixture was in a ready-to-apply condition.

The dyes were dissolved in mixtures of THF and *n*-PrOH (wt. ratio 2:1), so that the total amount of additional solvent in the coating sol did not exceed 30 wt. %. In order to ensure that materials with identical chromophore concentrations were investigated, the mass of the side chain was taken into account in the mass calculation of the silylated dye. Variacrol® Blue D was added to the prepared sols as an additive. Graftable Blue D was added at an earlier stage, in order to allow its co-condensation with the polysiloxane oligomers that formed during the sol-gel process. For the hydrolysis of the dye, an additional amount of water was added in the molar ratio graftable Blue D : H_2O = 1 : 1.5.

The chromophore concentration was 3 wt.% with respect to the solids of the sols.

The freshly prepared systems were spin-coated on glass slides and CR 39® lenses, and cured thermally at 125 °C for 20 min. The glass slides and lenses were cleaned prior to coating as follows: after immersion in NaOH for 5 minutes (50°C), the substrates were washed with deionized water, placed in a ultrasonic water bath for 3 min, washed again with deionized water and dried with compressed air.

For NMR and EPR measurements, powdered samples were prepared from dye-doped and undoped gels and dried in aluminum vessels at 125 °C for 20 min.

2.3. Test devices and measurements

The hydrolytic 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 the activation of the photochromic coatings, a commercially available UV-A source (Philips face tanner, model HB170) equipped with Philips CLEO 15 W UV-A lamps was used. The integrated power density on the sample was 44 W/(cm^2·min) between 250–410 nm. The lamp–sample distance was adjusted to 12 cm. The transmittance spectra were measured and ΔY values (photochromic acivity) 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 recorded with a delay of

2 s. Kinetic investigations were performed "in situ" by means of a custom-made set-up comprising a HBO 200 W Hg lamp, a water filter for heat absorption, a colorimeter, and a sample holder placed in the spectrometer. The sample holder allowed the sample to be fixed in the optical path with a tilt angle of 45°.

The photochemical degradation of the photochromic coatings was studied by means of an air cooled Suntest chamber (ATLAS Material Testing Technology BV, model Suntest CPS+), which was equipped with a 1100 W Xenon lamp (according to DIN ISI 9000ff specification). The average irradiance was 750 W/m^2. After each irradiation interval, all samples were exposed to a bleach-back procedure comprising a heat treatment at 75 °C for 20 min and irradiation with visible light (standard fluorescence bulbs) for 1 h, followed by dark storage for at least 2 h at ambient temperature.

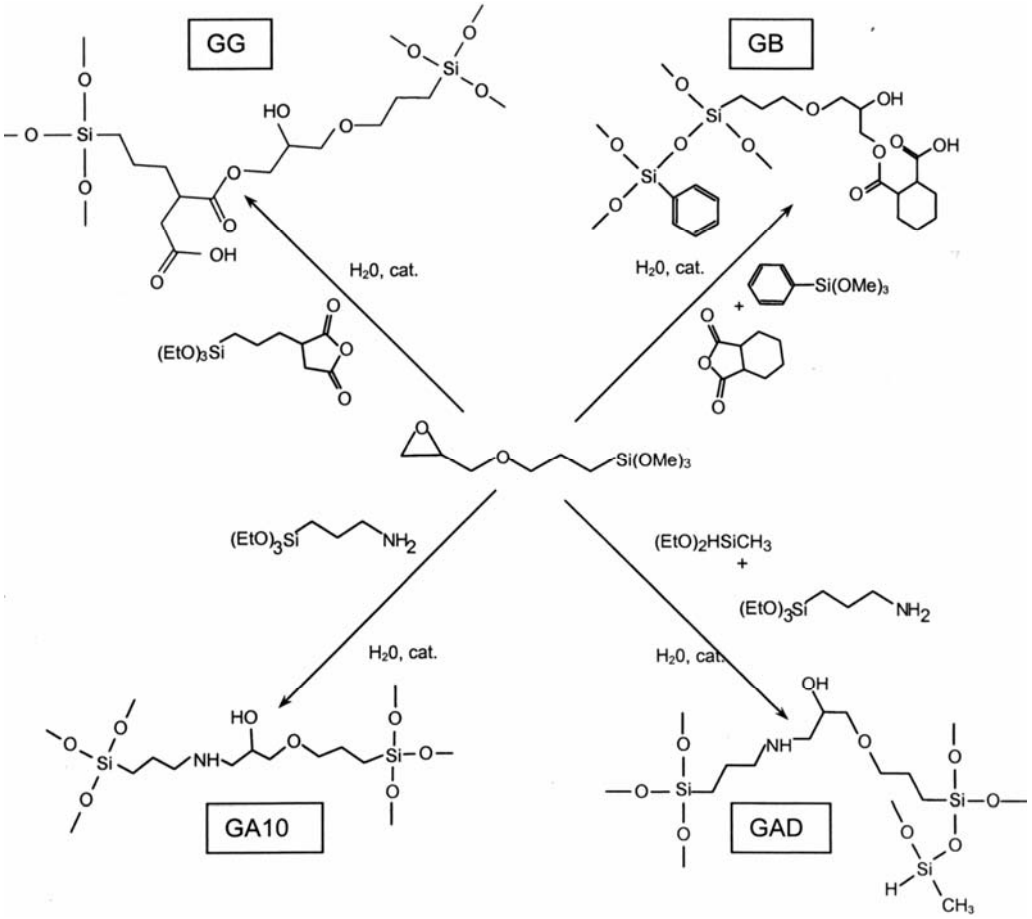
Solid state quantitative MAS-NMR measurements were performed on a Bruker DSX 400 spectrometer. The paramagnetic properties were investigated by means of a standard SE/X spectrometer (Radiopan, Poznań), the sample holders were sealed quartz capillaries (1 mm in diameter). The magnetic field was calibrated using diphenylpicrylhydrazyl (DPPH) free radicals and modulated at 100 kHz. The EPR spectra were obtained at 9.4 GHz (X-band) and displayed as the first derivative of the respective absorption curves. For the photochemical degradation of EPR samples, a HBO 200 W mercury lamp was used. The powders were irradiated for 4 h at a lamp-sample distance of 0.5 m.

3. Results and discussion

3.1 . Types of matrices used

Four matrix types were chosen as hosts for the photochromic dyes. The advantages and disadvantages of each of the hosts are demonstrated below. The main crosslinking reactions postulated to occur during thermal curing are shown in Scheme 2.

The GG system is a hybrid polymer with inorganic polysiloxane backbones and polyether/polyester-like crosslinks, which arise from the thermally induced polyaddition reaction of epoxide and anhydride groups. The hydrolysis and polycondensation of the alkoxysilane groups can be carried out at mild conditions and ambient temperature. Organic polyaddition starts at temperatures above approximately 100 °C. As was assessed by microhardness measurements, the GG matrix showed a relatively high rigidity. The universal microhardness was determined to be 110 N/mm^2 for this system. Contrary to that, the GB matrix, which exhibits a lower network density and higher amount of organics, showed the microhardness of only 60 N/mm^2. It is known that both GG and the GB coating solutions have very low contents of residual water (less than 1 wt.%) due to its immediate consumption by anhydride groups, which results in the formation of carboxylic acid species. Thus, GG and GB are both weakly acidic, and were expected to have a relatively low concentration in silanol groups and to differ in their cross-linking density.



Scheme 2. Main precursors and postulated structures of the hybrid polymer host materials GG, GB, GA10 and GAD

The GA10 matrix, whose characteristic structural feature is the β-aminoalcohol cross-link, is a basic system with no Brönsted acid components. The water content of GA10 coating solutions was in the range of approximately 5 wt. %. The GAD system, whose development was based on the GA10 system, has an even lower polarity in the cured state as a result of a linear silicone-type backbone and the incorporation of methyl groups. Therefore, GA10 and GAD are both basic in nature, but should differ in their polarities.

3.2. Network connectivity according to NMR spectra

The photochromic behaviour of the incorporated chromophores strongly depends on the network characteristics of the sol-gel matrix (the cage effect) [13]. When the rigidity of the host is high, organic molecules within it will be completely immobi-

lised and separated from each other (and their degradation products). This may positively affect the photochemical activity and result in significant stabilisation [6]. Kinetics are determined by factors such as dye structure and rigidity, matrix micropolarity, the type of incorporation, and temperature. In a less polar environment, the closed, uncoloured, less polar forms of spirooxazines would be favoured, while a more polar environment would stabilise the more polar merocyanine (or even zwitterionic) form [3, 14].

In the present study, solid state ^{29}Si-MAS-NMR and Raman spectroscopy were used to characterise the microenvironments supposed to surround the chromophores. The inorganic network density was measured for powdered bulk samples. Solid state ^{29}Si-MAS-NMR spectroscopy yielded valuable insight into the level of inorganic connectivity and allowed the concentration of relevant silicon structural units to be determined (Table 1).

Table 1. ^{29}Si solid state NMR chemical shifts and inorganic network connectivity

GG		GB		GA10		GAD	
δ [ppm]	Assignment	δ [ppm]	Assignment	δ [ppm]	Assignment	δ [ppm]	Assignment
66,5	T^3 (~74%)	80,9	Si-Ph (~21%)	67,5	T^3 (~77%)	67,8	T^3 (~78%)
60,1	T^2 (~22%)	67,3	T^3 (~79%)	59,9	T^2 (~23%)	60,1	T^2 (~22%)
52,8	T^1 (~4%)						

A signal with a chemical shift δ around 67 ppm in the 29Si-MAS-NMR spectrum can be assigned to the completely hydrolysed and polycondensed species T^3, which forms a three-dimensional polysiloxane network. In GG, GB and GAD matrices T^3 species were detected to a maximum of 79%. Partly condensed T^2 and T^1 species, bearing residual alkoxy or OH groups [1, 15], were found to be present to about 20 %. Only matrix GB behaves somewhat differently, in that solely T^3 moieties could be found. The resonance at δ = 80.9 ppm can be attributed to T^3 groups with the substituents on the silicon atoms being phenyl groups originating from the PhTMO component of the GB system [16]. Thus, unlike GG, GA10, and GAD, which contain residual hydroxyl or even alkoxy groups, the GB matrix is supposed to consist of a fully hydrolysed and completely condensed polysiloxane network. The pore size and distribution of the materials have not been investigated in this study. It can be, however, assumed that the free volume is higher in the GB than the GG matrix, which is due to the lacking contribution of the (purely organic) anhydride cross-linker to the polysiloxane network.

3.3. Photochemical stability

The photodegradation behaviour of Blue D and graftable Blue D under artificial weathering has been reported elsewhere [6]. For the sake of clarity, the transmittance

spectra of the activated state of a graftable Blue D doped coating after continuous irradiation for 28 h and 60 h are presented in Figure 1. The degradation mechanism of spirooxazines is known to involve radicals [17]. Therefore, in this study it was attempted to take their presence, i.e., the concentration of paramagnetic species as an indication of dye photostability.

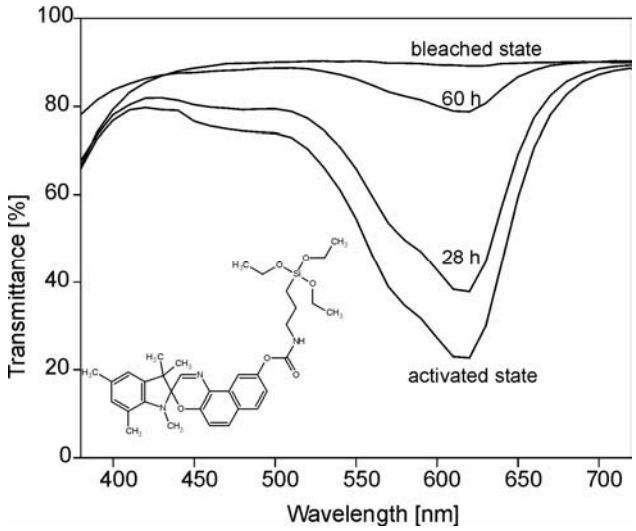


Fig. 1. Transmittance spectra of graftable Blue D (inset) entrapped in the GG host, prior to and after artificial weathering for 28 h and 60 h (Suntest®)

By means of EPR spectroscopy on powdered bulk samples of the pure matrices as well as on two series of doped samples (with Blue D and gr. Blue D), radicals could be detected in a few cases even though the samples were non-irradiated. The results are displayed in Figure 2a. Substantial amounts of radicals were found for undoped and doped GAD samples as well as for undoped GG and GA10 samples. The highest radical concentration was observed for the sample with gr. Blue D covalently bonded in the GAD matrix.

Figure 2b demonstrates the effect of continuous UV irradiation for 4 h. The EPR spectra were recorded immediately after the irradiated samples were transferred to the measurement chamber of the EPR spectrometer. As expected, the EPR signal intensity rose upon irradiation. This was particularly marked for Blue D doped samples, where the intensity signal increased by a factor of 10. Interestingly, the radical concentration of the graftable Blue D/GAD system was not affected by UV irradiation. Among all other samples, however, the GAD matrix was found to be the worst in terms of photoinitiated radical production.

The sharp single EPR signals showed a g factor between 2.003 and 2.0045, with neither splitting nor fine structure. This indicates an anisotropic location or migration of the detected radical species. Moreover, due to the absence of any Si–C or Si–O

splitting, the radicals are supposedly not associated with the photolysis of polysiloxane chains [18, 19].

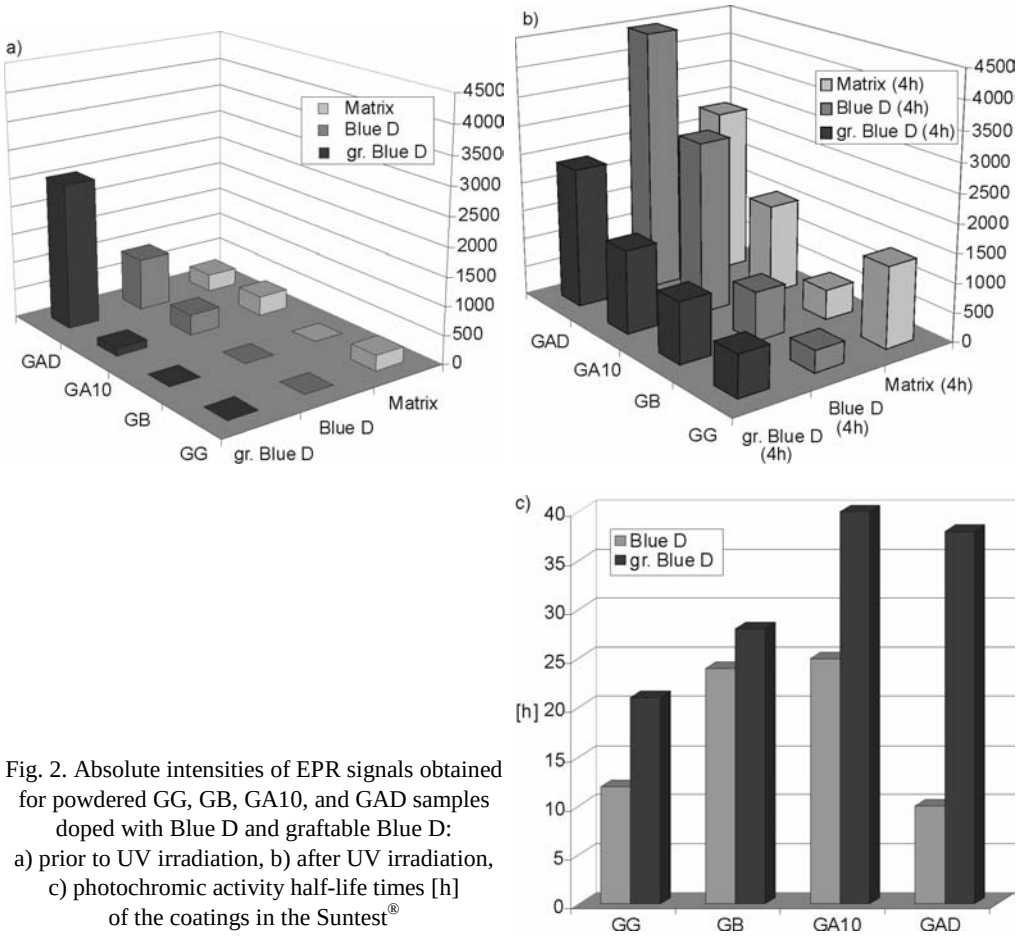


Fig. 2. Absolute intensities of EPR signals obtained for powdered GG, GB, GA10, and GAD samples doped with Blue D and graftable Blue D: a) prior to UV irradiation, b) after UV irradiation, c) photochromic activity half-life times [h] of the coatings in the Suntest®

Radical centres that are present before UV irradiation could originate from an accidental irradiation with visible light during sample preparation, the energy of which (~2.5 eV) is sufficient to create some magnetic centres. In the cases where no radical activity is observed after visible light irradiation only, the energy gap to the excited state may have been too high. After irradiation with UV light (energy ~5–10 eV) the number of the active centres rises. The form and *g*-factors of the EPR signals are not changed, which means that the characteristics of the magnetic species are the same. All EPR signals of the measured samples have a *g*-factor similar to that of a free electron (g = 2.0023), thus the magnetic centres are of the 1-electron "free radical" type. In most cases, the radicals have isotropic environments. In a few cases, when the asymmetric EPR signals are present, the isotropy is slightly distorted.

Upon storage for 24 h in the dark, the EPR signal intensities of previously irradiated samples decreased to the initial level, probably due to diffusion-controlled recombination processes. When irradiated again, the EPR signal intensities increased as before.

In order to correlate the EPR results with the actual photodegradation behaviour, coated glass samples were irradiated in a Suntest weathering device and the transmittance of the samples was measured after 4 h intervals of exposure. The non-silylated dye showed higher half-life times in soft and polar matrices (GB and GA10) (Fig. 2c). This finding did not correlate with the large difference in the amount of radicals detected after UV light irradiation in the respective powdered samples (Fig.re 2a, b). The GG and GAD matrices, rigid polar and soft non-polar systems, respectively, turned out to be less suitable for the physically embedded spirooxazine. This again was in disagreement with the concentration of radicals after irradiation (low for GAD, high for GG). For samples doped with graftable Blue D, an increase in the radical concentration identical to the pure matrix was found. This in general correlates with the previously obtained result that graftable dyes have higher photochemical stability than the corresponding physically entrapped dyes.

3.4. Switching kinetics

For the investigation of switching kinetics, coated glass samples were irradiated in situ in the measurement chamber by means of a UV lamp (HBO 200 W Hg lamp). The change in optical density was determined in intervals of 2 s during activation as well as during bleaching.

Dyes entrapped in hybrid polymers generally showed slower kinetics than the corresponding solutions in organic solvents (see Table 2) [4, 20]. This was particularly evident for the fading processes. Nonetheless, the differences were small and indicated a high degree of mobility for the incorporated chromophores.

Table 2. The kinetics of several photochromic dyes;
t_a – activation time for 50 % of the maximum transmittance, t_f – fading time, both in seconds

Dye	GG		GB		GA10		Methanol		Hexane	
	t_a	t_f	t_a	t_f	t_a	t_f	t_a	t_f	t_a	t_f
Blue A[a]	4.7	5.8	1.4	6.2	3.4	3.2	2	1	3	4
Blue C[b]	20.5	93.6	10.3	63	14.7	28.6	–	–	–	–
Blue D	6.2	9	5.3	9.6	5.5	8.9	6	12	4	4
PNO[c]	3.9	2.8	3.7	5.2	4.1	1.8	2	1	2	>24
Red A[d]	7.5	129.1	4.8	57	5.8	26.6	–	–	–	–
Photo L[e]	7.4	9.1	5.5	10	3.9	13.6	6	11	5	12

It is apparent that covalent attachment noticeably slowed down the “off-reaction“, which is probably due to steric hindrances and restricted chromophore mobility (i.e.,

restricted ability to re-orientate within the free volume of the matrix). The determined bleaching kinetic curves could be fitted by means of a second order exponential decay (Fig. 3).

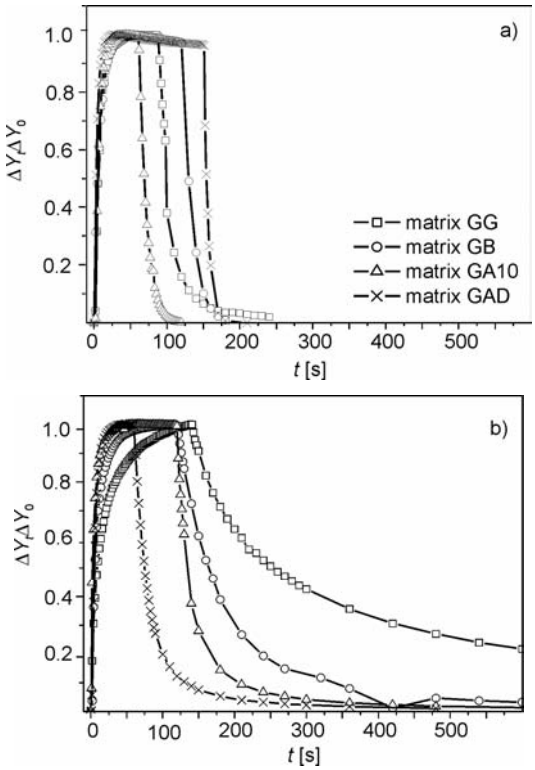


Fig. 3. On/off kinetics of spirooxazines entrapped in the four hybrid polymer matrices, GG, GB, GA10, and GAD: a) Blue D, b) Graftable Blue D. ΔY_t – change of luminous transmittance after irradiation for a given time t, ΔY_0 – change of luminous transmittance at maximum colouration (photochromic activity)

It can be seen that both matrix rigidity and polarity have an influence on the switching kinetics. The large difference between the covalently bonded and physically entrapped dyes is clearly evident, for example, in the off-reaction of graftable Blue D in the GG system, which proceeds slower than for Blue D by about a factor of 10 (squares in Figs. 3a, b). For the other matrices the effect is observable as well, but less pronounced. It is conceivable that on the one hand the polar carbonyl and silanol sites of the GG host material are particularly effective in stabilising the opened merocyanine form, thus causing slower bleaching, and on the other hand the back reaction is sterically hindered as a result of the covalent attachment to a matrix that is considered to be the most rigid one (GG). In agreement with this hypothesis, fast on- and off-kinetics were observed when the dyes were physically entrapped in the more soft and unpolar host materials.

It is apparent (squares and circles in Fig. 3b) that the bleaching kinetics differ for GG and GB matrices. This may be attributed to both the differences in network densities (i.e., free volume) and polarities. As pointed out before, GB, derived from an organic anhydride cross-linker should have a higher free volume and lower rigidity than the GG material, whereas GG is clearly more polar than GB. All these factors may have contributed to the observed differences in kinetic behaviour.

The amine cross-linked systems GA10 and GAD behaved very similar in terms of colouration, but showed higher bleaching rates as compared to the anhydride cross-linked systems GG and GB.

4. Conclusions

The switching kinetics and photochemical stability of photochromophores were found to depend strongly on the chemical properties of the matrix they are entrapped in, and on the type of entrapment. Significant differences were observed for physically entrapped and covalently bonded chromophores. The results allow the most suitable molecular environment to be chosen for a given dye in terms of photostability, kinetics and activity – this is considered to be relevant for potential applications in the ophthalmic sector. In order to create optimised microenvironments, further investigations on the micropolarity and chemical character of the radical species present in the irradiated samples are necessary. Low temperature EPR is considered to reveal valuable information in this respect.

Acknowledgements

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References

[1] BRINKER C.J., SCHERER G.W., *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press Inc., San Diego, 1990.
[2] BROWN G.H. (Ed.), *Photochromism*, Wiley-Interscience, New York, 1971.
[3] Fischer E., Hirshberg Y., J. Chem. Soc., 1952, 4522.
[4] MALATESTA V., *Photodegradation of Organic Photochromes*, [in:] J.C. Crano and R. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, Kluwer, New York, 1999, p. 65.
[5] SCHOTTNER G., Chem. Mater., 13 (2001), 3422.
[6] KLUKOWSKA A., POSSET U., SCHOTTNER G., WIS M.L., SALEMI-DELVAUX C., MALATESTA V., Mat. Sci. 20 (2002), 95.
[7] CRANO J.C., KWAK W.S., WELCH C.N., *Spirooxazines and their use in photochromic lenses*, [in:] C.B. McArdle (Ed.), *Applied Photochromic Polymer Systems*, Blackie & Son Ltd., New York 1992, p. 31.
[8] KWAK W.S., CRANO J.C., PPG Technology Journal, 2, (1996), 45.

[9] LEVY D., EINHORN S., AVNIR D., J. Non-Cryst. Solids, 113 (1989), 137.
[10] LEVY D., AVNIR D., J. Phys. Chem., 92 (1988), 4734.
[11] SANCHEZ C., RIBOT F., LEBEAU B., J. Mater. Chem., 9 (1999), 35.
[12] POSSET U., LANKERS M., KIEFER W., STEINS H., SCHOTTNER G., Appl. Spectr., 47 (1993), 1600.
[13] AVNIR D., LEVY D., REISFELD R., J. Non-Cryst. Solids, 74 (1985), 359.
[14] GUGLIELMETTI R., *4n+2 systems: Spiropyrans*, [in:] H. Dürr and H. Bouas-Laurent (Eds.), *Photochromism; Molecules and Systems*, Elsevier, Amsterdam, 2003, p. 314.
[15] MARSMANN H.C., [in:] P. Diehl, E. Fluck and R. Kosfeld (Eds.), *NMR 17: Oxygen-17 and Silicon-29*, Springer-Verlag, Berlin, 1981, p. 66.
[16] TAYLOR R.B., PARBHOO B., FILLMORE D.M., *Nuclear Magnetic Resonance Spectroscopy*, [in:] *The Analytical Chemistry of Silicones*, A. Lee Smith (Ed.), Wiley, New York, 1991, p. 347.
[17] MALATESTA V., NERI C., WIS M.L., MONTANARI L., MILINI R., J. Am. Chem. Soc., 119 (1997), 3451.
[18] ALBERTI A., CAMPREDO M., GIUSTI G., LUCCIONI-HOUZE' B., MACIANTELLI D., Magn. Reson. Chem., 38 (2000), 775.
[19] MATSUI K., MOTEGI M., ITO K., Nucl. Instr. Methods Phys. Res. Sect. B, 116 (1996), 253.
[20] *Photochromes GLCI Variacrols*, Great Lakes Chemical S.r.l., Milan, Italy, 1994, p. 1.

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