AN ORGANIC-INORGANIC HYBRID GLASS HOSTING PHOTOCHROMIC DYES

L. Hou*, M. Mennig and H. Schmidt

Institut für Neue Materialien, Universitätscampus, Gebäude 43, Im Stadtwald
W-66123 Saarbrücken, Germany

An organic-inorganic (O-I) hybrid glass hosting photochromic spirooxazine dyes has been prepared via the sol-gel method with organically modified silicon alkoxides as starting materials. The utilization of methyltrimethoxysilane (MTMS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) at appropriate mole ratios led to different shapes of the glassy materials. The photochromic response, colour-decay speed, thermal and photochemical stabilities of the dye in the hybrid glass were studied and compared with the dye-in-ethanol (DIE) and dye-in-polymer (DIP) systems. The results reveal that (1) the photochromic response is better than both the DIE and DIP systems; (2) the colour-decay speed is similar to the DIE and much higher than the DIP system, and (3) the thermal stability is better than the DIE and similar to the DIP system, while the photostability is between them. Matrix effect is discussed on the photochromism of the dye in the hybrid glass.

1. INTRODUCTION

In recent years, the importance of organic dyes used for various optical purposes has been increasing significantly. Take photochromic dyes for example, fundamental and applied research work on them have been receiving more and more interests. It is well known that the matrix materials which host photochromic dyes are of great importance to the performance of a photochromic system and that solid matrices possess a number of advantages over liquid matrices, especially in overcoming the aggregation problem of dye molecules and in the improvement of photostability. Since the high temperature-melting of inorganic glasses precludes them from hosting organic dyes, most of the research work on solid matrices for photochromic dyes have been focussed on organic polymer systems (1~3) to date. In a dye-in-polymer (DIP) photochromic system, however, the photochromic response of the dye is deeply depressed so that a high concentration (> 1 wt%) of the dye is necessary to obtain an acceptable photochromic intensity, and the bleaching speed of the activated colour is largely lowered by more than 10 times so that certain applications which require fast bleaching become impossible. Therefore, efforts to seek for better matrix materials for organic photochromic dyes have never ceased. J. A. Blair and co-workers (4) reported the preparation of a new glass for hosting organic compounds by low temperature (< 200 °C) melting of mixed metal carboxylate salts and the dyes. The photochromic dyes, photochrome I and photochrome II, doped in the glass (2 mm thick discs) at a concentration of 0.5 wt% showed photochromic response to sunshine. Other authors have concentrated their efforts on the exploitation of the sol-gel method for the preparation of inorganic oxide glass (5~8) or organic-inorganic hybrid (5, 8) glass matrices hosting photochromic dyes, e.g. spiropyranes (SP) (5~7) and 2,3-diphenylindenone oxide (DPIO) (8), because of the many unique and desirable features of the sol-gel process: near-room temperature wet-chemical synthesis, formation of highly homogenous and highly pure porous solids. The composition, structure and properties of the gels can be tailored in response to different material requirements by the chemical design of molecular precursors and the elaborate control of the hydrolysis-condensation process. These

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* On leave from Shanghai Institute of Optics and Fine Mechanics, Academia Sinica 201800 Shanghai, China

gels offer encouraging possibilities for the incorparation of a broad variety of organic dyes. We have focussed on a class of photochromic dyes, spiroindolinonaphthoxazine (abbreviated as spirooxazine, SO). They possess good photochromic response to UV irradiation, higher fading speed of the coloured form and higher photostability than the SP dyes, but little work has been published on the incorporation of them into sol-gel derived matrices. In our previous work (9~11) the spectral and photochromic properties of the dyes in aluminosilicate and ORMOCER coatings and gels were reported as compared with those in ethanol solutions. In this paper we describe the preparation of O-I glass rods and discs in various dimensions and coatings of different thickness in the MTMS-GPTMS system by tailoring the viscosity of the sols through optimizing composition and introduction of appropriate additives. We also present experimental results on the photochromic intensity, colour-decay speed, thermal and photochemical stability of the dyes in the O-I glass as compared with DIE and DIP systems.

2. EXPERIMENTAL

2.1 Sol-gel preparation

The preparation procedure of the organic-inorganic glass rod, disc and coating is shown in Fig. 1 using MTMS and GPTMS as starting materials. The final mole ratio of H_2O to silanes (MTMS + GPTMS) is 3.0 and the volume ratio of EtOH to silanes is 0.3. Additives such as NaAc and NaF were introduced 1h before the addition of the SO dye in EtOH solution at a mole ratio of 1×10^{-2} and 5×10^{-4} to the silanes, respectively. All the samples are labelled with MGmn, where M and G represent MTMS and GPTMS, respectively and m/n denotes the M-to-G mole ratio. For the purpose of comparison SO-PMMA coatings were prepared by spraying on slide glass substartes using the SO-PMMA-EA (ethylacetate) solution. The concentration of PMMA is 15 g / 100 ml EA.
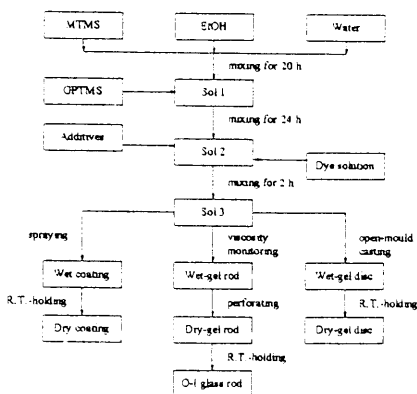

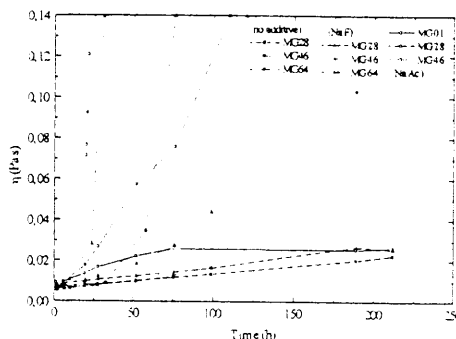Fig. 1: Preparation procedure of the O-I glass rod, disc and coating

Fig. 2: Viscosity vs. time during the sol-gel transformation with different additives (none, $R_{NaF} = 5 \times 10^{-4}$, $R_{NaAc} = 1 \times 10^{-2}$)

2.2 Measurement of properties

The viscosity at a rotation speed of 500 s^{-1} was taken using the Z_1 measuring system of a computer controlled PHYSICA rotationviscometer to monitor the viscosity evolution during the early stages of the sol-wetgel transformation. A SUNTEST CPS (Heraeus) apparatus was employed to characterize the photostability of the samples against UV irradiation at the

intensity of 600 W/m^2. Heat treatment was conducted in a MEMMERT model 100 electric furnace to various temperatures for estimating the thermal stability. The home-made apparatus used for the measurement of photochromism was described in a previous publication (10). The photochromic response expressed in terms of equilibrium absorbance at the steady state under UV irradiation, ΔA_0, and the fading speed of the activated colour on cessation of UV irradiation expressed in terms of half-life time, $t_{0.5}$, were deduced from the tansmission vs. time curves recorded by the apparatus during the colouring-fading process. Due to the temperature dependence of all the photochromism, organic or inorganic, a CONATEX 9010 thermometer was used to measure the real-time temperature at which a photochromism measurement was carried out.

3. RESULTS AND DISCUSSION

3.1 Effect of composition and additive on viscosity evolution

On account of the fact that photochromic dyes doped in pure silica or aluminosilicate gels would either lose their photochromic activity rapidly or change to inverse photochromism (5, 7, 11) even during the sol-wetgel transformation stage, we decided to use organically modified silicon alkoxides, $R'Si(OR)_3$, as starting precursors. At first, we tried pure MTMS. It was found that although the doped SO dye exhibits detectable photochromism in the sol-wetgel stage, ΔA_0 would decrease rapidly during the ageing and drying process and vanish as the rigidity of the gels reached a certain level. And what is more, the initial colourless gels changed to yellow or even brown implying that the dye molecules are either passivated or even destroyed due to the high volume shrinkage (> 80%). SO-doped gels were also prepared from GPTMS alone considering that it possesses properties favourable to photochromic dyes, i.e. the long glycidoxypropyl (GP) chain is helpful in creating a more flexible matrix for photochromic dyes and the polymerisation between the epoxy groups would play a certain role in improving the mechanical properties of the gels. However, it was found that the gelling time is too long to allow aquirement of a wetgel within one month although intense photochromic response is maintained.

Using both MTMS and GPTMS as starting precursors, sols having various m/n ratios were prepared via the procedure depicted in Fig.1. The viscosity evolution of the sols of various compositions and with different additives is shown in Fig.2. It can be seen that (1) the viscosity increase with time is significantly accelerated with increasing m/n ratio, (2) this acceleration process is enhanced greatly by the addition of NaAc and moderately by NaF, as is evidenced by the results that the viscosity increase of the MG64, MG82 with NaAc and MG82 with NaF is too fast to monitor, (3) in the case of NaAc-additive only the pure GPTMS sols, while in the case of NaF-additive and no-additive sols with the m/n ratisos less than 3:7 would remain ungelled for a pretty long period of time (>> 1 month) if the sols were air-tight. These results suggest that it is possible to tailor the viscosity by changing composition and additives in order to obtain different shapes of the glassy materials. It was in this way that we prepared our O-I glass rods and discs in various dimensions and coatings of different thickness. The utilization of the MG system at appropriate m/n ratios led to moderate gelling time (100~200 h) and volume shrinkage (around 50%) rendering it possible to monitor the variation of the photochromism (ΔA_0 and $t_{0.5}$) of the SO dyes during the sol-wetgel-xerogel transformation as a result of room temperature holding and due to heat treatment or UV irradiation and to make comparisons with the DIE and DIP systems.

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3.2 Photochromic response at room temperature

Fig.3 shows ΔA_0 as a function of dye concentration in ethanol, O-I glass coating and PMMA coating, respectively. Note that concentrations are referred to those in SO-EtOH, SO-PMMA-EA solutions and sols for O-I glass coatings. The volume shrinkage factors for the O-I glass coatings and the PMMA coatings are ca. 2.5 and 5.0, respectively. This means comparison between these two systems is reasonable. It is clear that (1) serious aggregation of the dye molecules occurs in the DIE system as the concentration becomes higher than 5×10^{-4} mole/l, (2) although the aggregation problem is overcome to certain extent in the DIP system the photochromic response intensity is at the same time badly depressed, (3) the ΔA_0 of a O-I glass coating is much higher than that of the corresponding PMMA coating and increases monotonically with dye concentration, implying that better photochromic response of the dye is obtained in the O-I glass than in the other two systems.
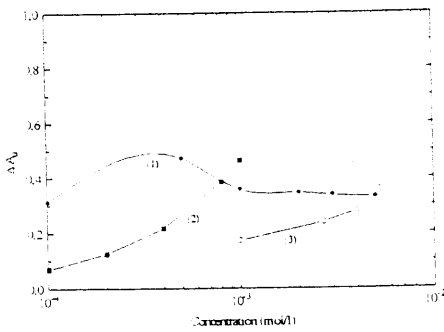

Fig. 3: ΔA_0 (T=25°C) as a function of SO1 concentration in (1) EtOH (10-mm plastic cell), (2) O-I glass coating (0.4 mm thick) and (3) PMMA coating (0.2 mm thick)
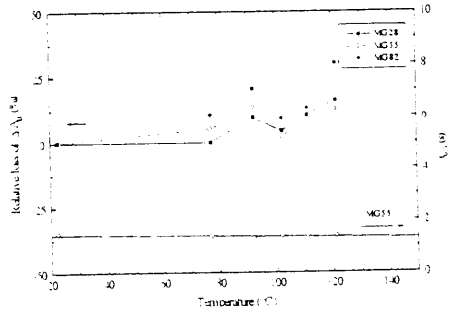
Fig. 4: $t_{0.5}$ and relative loss of ΔA_0 of SO1 (2.5×10^{-3} mol/l)-doped O-I glass coatings (0.2 mm thick) as a function of heat treatment (T=22.5 °C)

3.3 Effect of heat treatment on ΔA_0 and $t_{0.5}$

The $t_{0.5}$ and relative loss of ΔA_0 of SO1-doped O-I glass coatings as a function of heat treatment temperature are shown in Fig.4. It follows from the figure that (1) heat treatment has little effect on $t_{0.5}$ up to 120 °C, (2) relative loss of ΔA_0 increases with increasing heat treatment temperature and, the greater the content of MTMS, the greater the loss, (3) in the worst case (MG82) the relative loss of ΔA_0 is around 10% before 120 °C and amounts to 25% after a heat treatment at 120 °C for 6h. Fig. 5 presents the variation of $t_{0.5}$ and ΔA_0 of SO1-PMMA coatings with R.T.-holding and heat treatment. In contrary to the O-I glass coatings, $t_{0.5}$ increases very rapidly with increasing heat treatment temperature; even in the case of R.T.-holding without heat treatment, $t_{0.5}$ increases slowly, too. On the other hand, ΔA_0 shows no significant decrease before 140 °C. Heat treatment at 140 °C for 6h results in a relative loss of ΔA_0 less than 25%. Comparing Fig. 4 with Fig. 5, it is evident that the thermal stability of $t_{0.5}$ of the SO1-doped O-I glass is much better than the SO1-PMMA sytem, while the thermal stability of ΔA_0 of the SO1-PMMA system is a little better than the SO1-doped O-I glass.

3.4 Effect of UV irradiation on ΔA_0 and $t_{0.5}$

The relative loss of ΔA_0 as a function of UV exposure (suntest) time on samples described in Table 1 is compared in Fig. 6. It turns out from Fig. 6 and Table 1 that (1) UV irradiation makes no detectable influence on $t_{0.5}$ of all the samples tested, (2) the photostability of the SO-doped O-I glass measured by the relative loss of ΔA_0 is between the DIE and DIP systems, suggesting that further improvement in the photostability is necessary before some applications can be put into effect, (3) with the addition of only a small amount of fluoroalkyltrimethoxysilane (SF) the photostability of the O-I glass can be considerably enhanced, indicating a promising future for the O-I hybrid glass hosting photochromic dyes.
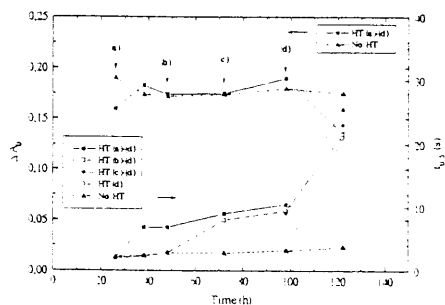

Fig. 5: Variation of ΔA_0 and $t_{0.5}$ (T=22.5 °C) of SO1 (1×10^{-3} mol/l)-PMMA coatings (0.2 mm thick) with R.T.-holding time and heat treatment (HT): (a) 100 °C 12 h, (b) 110 °C 6 h, (c) 120 °C 6 h, (d) 140 °C 6 h
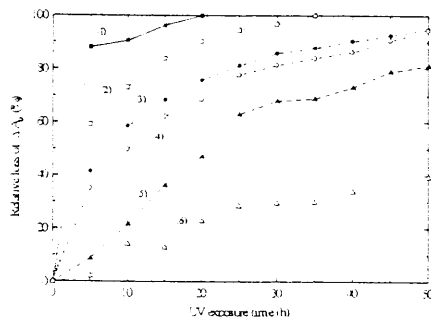
Fig. 6. Relative loss of ΔA_0 (T=25 °C) as a function of UV exposure (suntest) time on samples described in Table 1

The different photochromic performance of the SO dyes in the three matrices, ethanol, O-I glass and polymer, is closely related to their structures and thereby the environment surrounding the dye molecules. In ethanol solution, the degree of freedom of the dye molecules is high so that the speed of photochromic transformation is high, but at higher concentrations the probability of aggregation of the dye molecules becomes higher and the photochromic response is passivated. In addition, the poor thermal and photochemical stability of the DIE systems are self-evident. The degree of freedom of the dye molecules in the DIP systems is largely degraded due to the complexity of the structure of polymer with various architectures, e.g. linear flexible chains, graft, H-shaped, ring and star (12), resulting in the deep depression of the photochromic activity of the dyes, reflected by the decrease of ΔA_0 and increase of $t_{0.5}$. However, both the thermal and photochemical stabilities of the dyes in polymer are greatly improved as compared with the DIE systems, although still unsatisfactory. The dye molecules trapped in the pores of the sol-gel derived O-I glasses possess high degree of freedom for photochromic transformation and low degree of freedom to move together for aggregation, so that the photochromic response is better than both the DIE and DIP systems; the colour fading speed is similar to the DIE and much higher than the DIP systems. The porous structure of the O-I glass may favour the thermal stability while make it easier for oxygen to penetrate into the pores and degrade the photostability, behind which the mechanism is still unclear.

Table 1

Measured values of $t_{0.5}$ (s) (T = 25 °C) after various lengths of UV exposure (suntest) time

Sample No.	Dye (C, mol/l)	Matrix (thickness, mm)	Exposure timelength (h)		
			0~10	15~25	30~50
1	SO1 (4×10^{-3})	EtOH (10)	1.3	-	-
2	SO3 (1×10^{-3})	O-I GLASS (0.4)	1.9~2.0	1.8~2.0	-
3 *	SO3 (1×10^{-3})	O-I GLASS (0.4)	1.9	1.7~1.9	1.7~1.9
4 **	SO3 (1×10^{-3})	O-I GLASS (0.4)	1.9~2.0	1.8~1.9	1.7~1.9
5	SO1 (1×10^{-3})	PMMA (0.2)	2.8~3.1	2.9~3.0	2.8~3.0
6	SO1 (5×10^{-3})	PMMA (0.2)	2.9~3.0	2.7~3.0	2.7~3.0

* $R_{SF} = 1\times10^{-2}$
** $R_{SF} = 5\times10^{-2}$

4. CONCLUSIONS

Different shapes and dimensions of organic-inorganic hybrid glasses in MTMS-GPTMS system have been made by the sol-gel process for hosting photochromic dyes. Spirooxazines entrapped in the O-I glass show photochromic response better than both the DIE and DIP systems, colour-decay speed similar to the DIE and much higher than the DIP system, thermal stability similar to the DIP and of course much better than the DIE system. Efforts must be made to improve the photostability of the dye-doped O-I glass photochromic systems before certain applications can be put into practice.

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