Enhancement of the Photochromic Performance of Spirooxazine in Sol-Gel Derived Organic-Inorganic Hybrid Matrices by Additives

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Abstract. Organic-inorganic hybrid materials synthesized via sol-gel processing are excellent solid matrices for photochromic dyes like spirooxazine, and the photochromic performance can be further enhanced by introducing suitable additives. This work describes the effects of additives on the photochromic intensity (ΔA_0), decolouration rate (k) and photostability of spirooxazine in sol-gel derived organic-inorganic hybrid matrices. They include fluoroalkylsilane (FAS), bisphenol A (BPA) and methyl-imidazole (MI). FAS enhances both ΔA_0 and photostability, but has little effect on k. The higher the content of BPA, the higher the ΔA_0 and the higher the photostability, but the lower the k. The effect of MI on ΔA_0 and k is not so considerable as that of BPA and is a little complicated, while significant improvement in photostability is achieved by the addition of MI at an optimum concentration with the presence of BPA at a higher content.

Keywords: organic-inorganic hybrids, sol-gel, photochromic performance, spirooxazine

1. Introduction

Organic-inorganic hybrid materials (OIHMs), a new family of porous solid materials synthesized via sol-gel processing have been the subject of extensive research activities since they were first reported by Schmidt and Philipp [1] in 1984. The low-temperature processing method provides a new opportunity to organic dyes to be hosted in solid matrices. The porous structure of these materials offers free spaces for photochromic dyes to undergo reversible structural changes during photochromic transformations. In addition, their rigidity can be tailored by adjusting composition, employing proper precursors and introducing appropriate additives, so that the native structure of the photochromic dye can survive the shrinkage of the gels during drying, necessary heat treatment, and even UV irradiation. The existing publications have shown that the sol-gel derived OIHMs are ideal solid matrices for photochromic dyes such as spirooxazine [2–4], spiropyran [5] and 2,3-diphenylindenone [6], although the photochromic performance needs to be further improved for practical applications. Aiming at enhancing the photochromic performance of spirooxazine (SO), three additives (FAS, BPA and MI) were introduced into the SO-OIHM photochromic system in the present work. The effects of the additives on photochromic intensity (ΔA_0), decolouration rate (k) and photostability were investigated. The results show an encouraging enhancement of the photochromic performance by rational employment of the additives.

2. Experimental

Sols were prepared via the sono sol-gel process described in a previous paper [7] using ethyltriethoxysilane (ETES) and 3-glycidoxypropyltrimethoxysilane

(GPTMS) as starting precursors at a molar ratio of 3 : 7. Water was added in the form of 0.1N HNO_3 at a molar ratio of 1.5 to the total silanes. Concentrations of all the additives and the spirooxazine dye, 1,3-dihydro-1,3,3-trimethyl-spiro-[2H-indole-2,3′-[3H]-naphth[2,1-b][1,4]-oxazine (Aldrich Chem. Inc.), are expressed in their molar ratios (MRs) to the total silanes. Dip-coating method was used for the preparation of coatings on microscopic glass slides. After being dried in air for 12–24 hours the coatings were heated at 110°C for 2 h. A computer contolled apparatus [7] was used for the measurement of photochromic performance. Photochromic intensity (ΔA_0) defined as the absorbance at the photostationary state under UV irradiation, and decolouration rate (k) were deduced from the colouring-fading curve. For the evaluation of photostability, the coatings were subjected to UV irradiation at an intensity of 60 mW/cm^2. The variation of ΔA_0 with UV irradiation time (τ) up to 60 h was monitored and relative photochromic intensity, $\Delta A^\tau/\Delta A_0$, was plotted against UV irradiation time. The irradiation hours needed for ΔA^τ to reach 0.5 ΔA_0, $\tau_{0.5}$, was evaluated from the $\Delta A^\tau/\Delta A_0$ vs τ curve and is used as a measure of photostability.

3. Results and Discussion

Figures 1 and 2 show the effects of BPA and MI on ΔA_0 and k of the coatings, respectively. The concentrations of FAS (MR_{FAS}) and the dye (MR_{SO}) are 0.015 and 0.010, respectively. It can be clearly seen in the figures that the higher the content of BPA, the higher the ΔA_0, and the lower the k. The effect of MI on ΔA_0 and k, however, is not so considerable as that of BPA and is a little complicated. When there is no BPA a slow increase in ΔA_0 is shown with increasing concentration of MI, while for the BPA-containing coatings ΔA_0 decreases with increasing concentration of MI, and the higher the content of BPA, the faster is the decrease of ΔA_0. On the other hand, it is evident in Fig. 2 that k increases with increasing concentration of MI when the content of BPA is equal to 0.30 and decreases with increasing concentration of MI when no BPA is used, though the variations of k in both cases are very slow. It is worth noting that MI exhibits little influence on k when the content of BPA equals 0.15.

Table 1. $\tau_{0.5}$ at different content of BPA.

MR_{BPA}	$\tau_{0.5}$ (h)
0.05	12.8
0.15	18.5
0.20	31.5
0.25	49.8

The significant enhancement of photostability by BPA is undoubtedly demonstrated by the monotonic increase of $\tau_{0.5}$ with increasing content of BPA in Table 1. The effcet of MI on photostability is depicted in Fig. 3 by plotting $\tau_{0.5}$ against MR_{MI}. $\tau_{0.5}$ goes through a maximum with increasing MR_{MI}, suggesting an optimum concentration of MI around 0.05.

In order to achieve high photostability it is necessary to have both a high ΔA_0 before UV irradiation

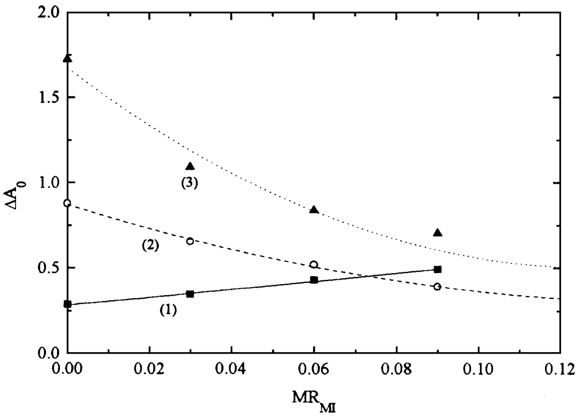

Figure 1. Photochromic intensity (ΔA_0) as a function of MI concentration (MR_{MI}) at different BPA content (MR_{BPA}): (1) 0, (2) 0.15, (3) 0.30.

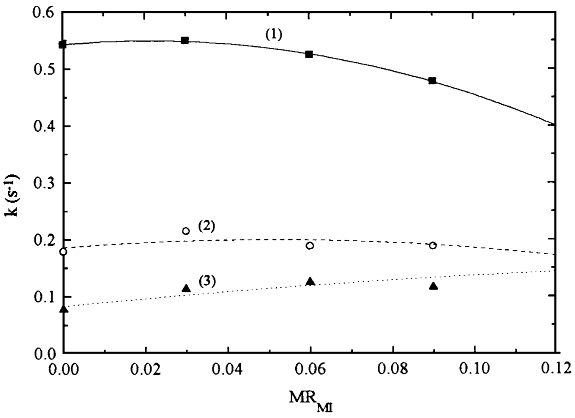

Figure 2. Decolouration rate (k) as a function of MI concentration (MR_{MI}) at different BPA content (MR_{BPA}): (1) 0, (2) 0.15, (3) 0.30.

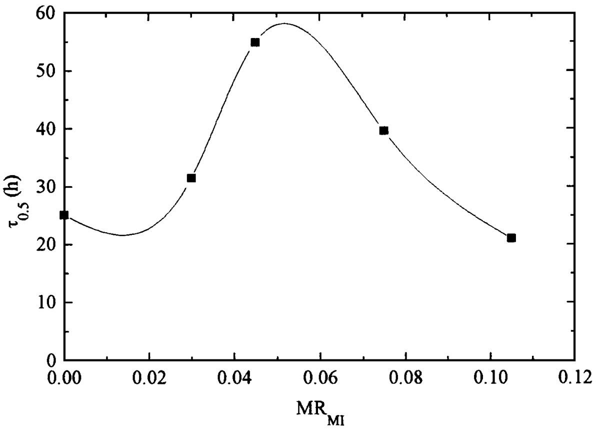

Figure 3. Variation of $\tau_{0.5}$ with MI concentration (MR_{MI}) at a BPA content (MR_{BPA}) of 0.20.

and a long $\tau_{0.5}$ against UV irradiation. There are two kinds of factors affecting ΔA_0 and $\tau_{0.5}$: electric and steric. In general, the higher the polarity of the environment in the matrix, the higher the thermal stability of the colored form, implying a higher ΔA_0 and a lower k. Addition of phenol compounds, which contain aromatic and OH-groups such as BPA, helps effectively stabilize the coloured form. The enhancement of ΔA_0 and retardation of k are due to the electric effect of BPA as it creates an environment with higher concentration of OH-groups.

The steric effect exerted by matrix on ΔA_0 and photostability is contradictory: a high matrix rigidity always suppresses ΔA_0 whereas it is favourable not only to the stability of the matrix itself but also to the protection of the dye molecules from UV irradiation. Therefore, it is advisable to optimize the matrix rigidity, taking both ΔA_0 and $\tau_{0.5}$ into account. MI is thought to act as a catalyst for the hydrolysis-condensation of the silanes and for the polycondensation between BPA and GPTMS, and as an initiator for the polymerization of the epoxy groups in GPTMS. The interaction between the silanes, BPA and MI results in the complicated effect of MI in the presence of BPA as shown in Figs. 1–3. The cooperative effect of BPA and MI leads to an optimum concentration of MI (ca 0.05) where the best photostability is achieved.

In a previous paper [4] we reported that the introduction of a small concentration of FAS leads to significant increase in both the photochromic intensity and the photostability of spirooxazine in OIHM coatings but has no influence on the decolouration rate. This is also true when BPA and MI co-exist with FAS in the coatings. The higher the concentration of FAS, the higher the ΔA_0 and the photostability. $\tau_{0.5}$ for the coatings with FAS at the concentrations of 0, 0.009 and 0.015 are 21.5 h, 25.5 h, and 31.5 h, respectively. The reason for the enhancement is that the enrichment of fluorine in FAS at the surface layer of the coating results in a non-stick surface due to the low surface energy. This non-stick surface prevents water, oil and other compounds from clinging onto and penetrating into the coating. These compounds themselves may be harmful to the photochromic dye or under UV irradiation they may generate new substances that are detrimental to the dye.

4. Conclusions

Great enhancement of the photochromic performance of spirooxazine in organic-inorganic hybrid matrices has been achieved by rational employment of BPA, MI and FAS as additives. BPA serves to maintain a high photochromic intensity, MI helps optimize the matrix rigidity and bulk protection of the dye, and FAS contributes to the surface modification so as to prevent harmful compounds from entering the coatings. In most cases the decolouration rate is sufficiently high ($>0.1\ s^{-1}$) and is not a problem to practical applications.

References

1. H. Schmidt and G. Philipp, J. Non-Cryst. Solids **63**, 283 (1984).
2. L. Hou, B. Hoffmann, M. Mennig, and H. Schmidt, J. Sol-Gel Sci. Techn. **2**, 635 (1994).
3. L. Hou, M. Mennig, and H. Schmidt, Chimica Chronica, New Series **23**, 175 (1994).
4. L. Hou, M. Mennig, and H. Schmidt, *Proc. SPIE* (1994), vol. 2255, p. 26.
5. D. Levy, S. Einhorn, and D. Avnir, J. Non-Cryst. Solids **113**, 137 (1989).
6. S.A. Yamanaka, J.I. Zink, and B. Dunn, *Proc. SPIE* (1992), vol. 1758, p. 372.
7. L. Hou, M. Mennig, and H. Schmidt, *Proc. SPIE* (1994), vol. 2288, p. 328.