

Photochromic organic-inorganic composite materials prepared by sol-gel processing: properties and potentials

L. Hou^{1,2}, M. Mennig¹ and H. Schmidt¹

1. Institut für Neue Materialien, D-66123 Saarbrücken, Germany

2. Shanghai Institute for Optics and Fine Mechanics, 201800 Shanghai, China

ABSTRACT

The sol-gel method which features a low-temperature wet-chemical process opens vast possibilities to incorporating organic dyes into solid matrices for various optical applications. In this paper we present our experimental results on the sol-gel derived photochromic organic-inorganic composite (Ormocer) materials following an introductory description of the sol-gel process and a brief review on the state of the art of the photochromic solids prepared using this method. Our photochromic spirooxazine-Ormocer gels and coatings possess better photochromic response and colour-change speed than the corresponding photochromic polymer coatings and similar photochemical stability to the latter. Further developments are proposed as to tackle the temperature dependence problem and further tap the potentialities of the photochromic dye-Ormocer material for practical applications.

1. INTRODUCTION

The last three decades have seen a rapidly growing interest in the research and development of organic dyes not only from a fundamental point of view but also for potential, possible or practical applications in optical, photoelectronic and photonic components or devices which exhibit lasing, switching, solar energy collecting, transmission controlling, optical storing, non-linear optical properties, respectively, to name a few. Among the others, a great number of organic dyes change colours when exposed to light (mostly near UV to blue) and return to the colourless form on cessation of light irradiation. This colour change stems from the reversible change of the organic dye between its two states having distinguishably different absorption spectra and is called photochromism. To make it easy to understand in plain terms, a photochromic dye is an organic compound which light makes dark and dark makes clear.

Up to now organic dyes are mostly used in their liquid solutions. Many kinds of solvents have been used as the hosts for them, especially in the early years for fundamental study on their physical and chemical properties. However, a dye in solution is always plagued by two thorny problems: severe aggregation at higher concentrations and poor stability against heat and particularly light irradiation. Therefore, it is desirable to host organic dyes in a solid-state matrix for uses requiring higher concentration and higher stability, because solid matrices for organic dyes possess apparent advantages over liquid hosts. Dye molecules in a solid matrix are much better isolated from each other, tendering it possible to reach a higher concentration without undesirable aggregation or association that deteriorate the expected performance, and the improvement in the thermal and photochemical stabilities of the dyes in solid matrices is self-evident. Finally, various shapes of the dye-in-solid matrix materials are achievable to meet different utilization purposes.

The high processing temperature of inorganic glasses excludes the incorporation of organic dyes because the decomposition temperature of most dyes are greatly lower than the glass-making temperature.

The logical development of this situation has been the employment of organic polymers as host matrices for organic dyes, because of their low temperature and low cost processing. There have already been a great deal of R&D activities in this field, and as the photochromic dyes are concerned, original papers on photochromic dye-in-polymer materials¹⁻³, detailed review articles on photochromic plastics⁴ as well as excellent books dealing comprehensively with photochromic molecules and systems^{5, 6}, and applied photochromic polymer systems⁷ indicate how highly interested people are in the area and indeed, big progress has been made.

In early 1980's, American Optical (AO) commercialized an spirooxazine (SO)-polymer lens as a result of systematical R&D activities⁷ from which it turned out that the photochromic response of the dye is deeply suppressed so that a high concentration (> 1 wt%) of the dye is necessary for obtaining a sufficiently high response and the fading rate of the coloured form activated by UV light is largely slackened by a factor of ca. 10 as compared with the SO-ethanol solution, hence the lens was unsuccessful and was later withdrawn. At present, two manufacturers, Rodenstock and Transitions Optical in USA, are producing and commercially marketing polymer lenses with photochromic coatings. It is evident from the values of photochromic response (ΔA_0) and half-life time ($t_{0.5}$) calculated based on the colouring-fading curves provided by the manufacturers at different temperatures that the fading rates are very slow and the temperature dependence of the photochromic responses is so serious that with a temperature change from ca. 20°C to ca. 30°C ΔA_0 decreases by a factor >2.

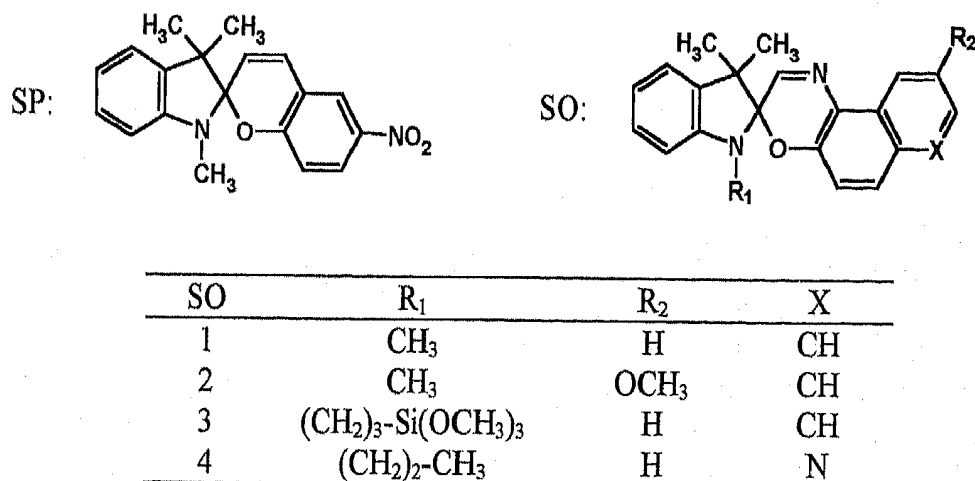


Fig.1 Photochromic dyes (SP, SO) involved in this work

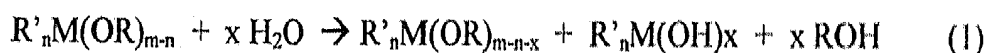
There are mainly three most important materials requirements for a photochromic system consisting of dye and matrix material: sufficiently high photochromic response to UV irradiation, very high or very low fading rate of the coloured form for switching or storing devices, respectively, and high stability, both thermal and photochemical. The fulfilment of these requirements lies both on the exploitation of high performance photochromic dyes themselves and on the development of suitable solid matrices which take the advantages of dye solutions (high fading rate, higher photochromic response) and dye-polymers (higher stability, low aggregation). Fortunately, organic-inorganic composites, a new family of porous solid materials derived via sol-gel processing, provide an exciting answer to the demand for better matrices for organic dyes. These organic-inorganic hybrid materials can be prepared at room temperature and cured at < 150°C. The low temperature processing opens a new door for organic dyes. The pores in the matrix offer free spaces for photochromic dyes to undergo reversible structural changes leading to

photochromism with sufficiently high photochromic response and fading rate and the hybridization between organic network modifiers and inorganic network formers is rationally expected to enable the material to inherit advantages of both inorganic glasses and organic polymers. In the past two years we have been engaged in the synthesis of photochromic organic-inorganic composite materials using spirooxazines as photochromic dyes whose molecular formulae are given in Fig. 1. In this paper we present our results on the spectral and photochromic properties of these photochromic composites and discuss their potentials for applications; following a brief review on the state of the art of the sol-gel derived solids for photochromic dyes.

2. THE SOL-GEL METHOD

The sol-gel process is a wet chemical method for synthesizing materials of network structure, e.g. inorganic glasses and organically modified ceramics (Ormocers), using metal alkoxides of network-forming cations as starting precursors. It involves the sequential hydrolysis and poly-condensation of the metal alkoxides in solutions at around room temperature leading to gels through ageing and/or slow evaporation of the solvents, liberated alcohols and excessive water, as shown in the following equations:

Hydrolysis:



Polycondensation:



Where M can be Si ($m = 4$), Ti ($m = 4$), Zr ($m = 4$), Al ($m = 3$), B ($m = 3$) etc., R is an alkyl group, R' can be an alkyl, vinyl or phenyl group. When $n = 0$ and x is large enough to ensure complete hydrolysis, inorganic glasses could be obtained by subsequent drying and firing of the gels. On the other hand, if $n > 0$, the unhydrolyzable alkyl groups, R', would remain in the network resulting in Ormocer gels. Moreover, if the R' groups themselves are polymerizable under certain conditions by thermal- or photo-curing, additional cross-linking can be obtained as to tailor the flexibility or rigidity and mechanical properties of the gels. Using the sol-gel process the composition, structure and properties of the gels can be varied in a broad range in response to different material requirements by the chemical design of starting precursors and the elaborate control of the hydrolysis-polycondensation process through changes in the experimental kinetic parameters, i.e. solvent, catalyst, water and other additives for promoting complexations or cross-linking etc. Therefore, it cannot be overstated that the possibilities opened by the sol-gel process for materials science and technology are limited only by one's imaginative faculty. This so broad spectrum of possibilities offered by the sol-gel method originates from the many unique and attractive advantages of the process.

The sol-gel process possesses many unique advantages. First of all, the low temperature characteristics enable one to prepare inorganic glasses at relatively low temperatures: amorphous oxide gels can be obtained at near room temperature, followed by thermal densification of gels into fully dense oxide glasses at temperatures far below those needed in the conventional melting method. For example, pure SiO₂ glass of high optical quality comparable to that of the commercial SiO₂ glass can be made by heat treatment of

gels at 1200°C⁸ and for borosilicate glass the firing temperature is less than 600°C⁹. Furthermore, the curing temperatures of Ormocer gels can be as low as < 150°C and UV-curing can be applied together with thermal curing or even alone at room temperature. This may be a most exciting feature of the sol-gel method which is desirable to the incorporation of organic dyes into a solid matrix. Next, gels prepared via the sol-gel process feature the porous network structure, the pores are generally interconnecting, but in certain cases closed pores may be created¹⁰. Both the porosity and the pore size distribution can be controlled by adjusting preparation parameters. These pores provide ideal cages for dye molecules in the solid matrices. As we will see later in this paper, this point is especially critical to photochromic dyes which need free volumes of certain sizes to undergo structural changes between the colourless and coloured states. Moreover, it is expected that closed pores are better cages for dye molecules than the connecting ones in terms of resistance to oxidation and photofatigue. Last but not the least, the versatility of the sol-gel process in preparing gels of different shapes, bulk (monolith) solids, fibers or coating films, provide a very bright future for further exploitation of its potentials. Up to the present sol-gel derived coatings have demonstrated most promising applications and what is more impressive, organic-inorganic hybrid coatings can be applied to both organic and inorganic substrates easily through optimizing composition and coating parameters.

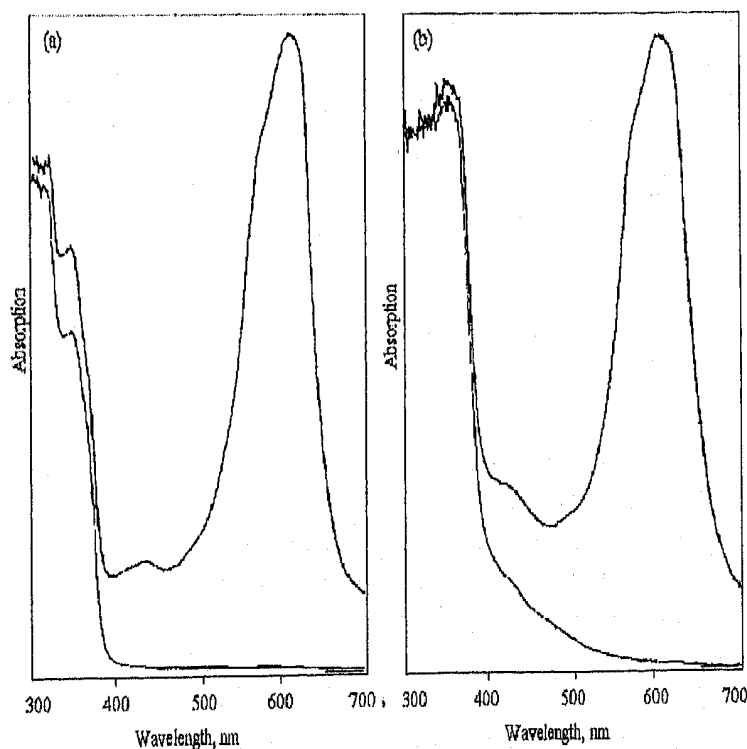


Fig.2 Absorption spectra of spirooxazines (a) SO1 and (b) SO3 in Ormocer gels before and immediately after UV irradiation. Dye concentration: 2×10^{-3} mol/l, gel thickness: 2.0 mm, cooled down to -20°C.

3. SOL-GEL DERIVED PHOTOCHROMIC SOLIDS

The first successful incorporation of a well-known laser dye, Rhodamine 6G, into silica matrix via the sol-gel process was reported ten years ago (1984) by Avnir and co-workers¹¹. Coincidentally, also in 1984 a new family of sol-gel derived organic-inorganic hybrid materials, presently known as Ormocers, was first reported by Schmidt et al¹². Since then more and more organic dyes of different kinds and functions have

been doped into both pure inorganic oxide and organic-inorganic hybrid solid matrices either for the investigation of structural evolution of the matrices during the sol-gel-xerogel transition with the incorporated dye molecules as probes to extract informations on structural changes or for the study of physical and chemical properties of the dyes themselves. Functions of the organic dyes involved in these research activities include laser (light emitting)¹³, non-linear optics¹⁴, photochromism (light absorbing), optical storage (hole burning)¹⁵, chemical luminescence¹⁶, chemical sensors¹⁷, solar energy concentrators¹⁸ and so forth. A vast and fast-growing bibliography of publications is indicative of a very active research field.

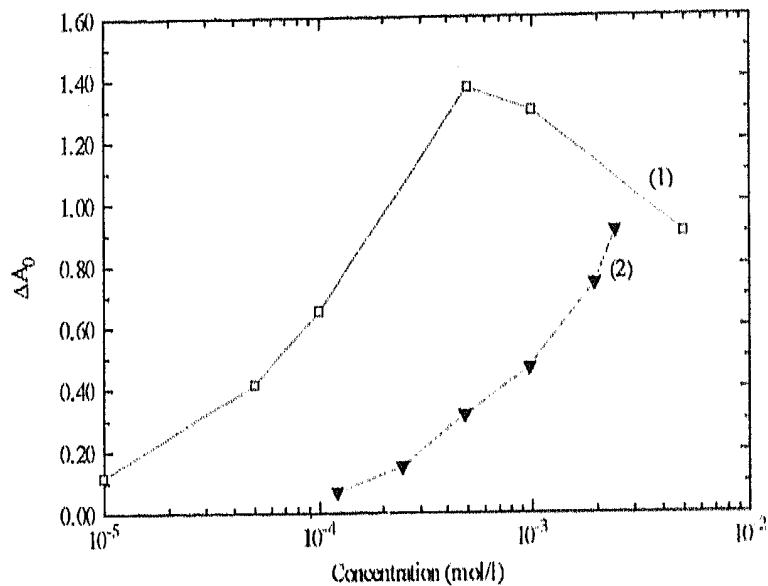


Fig.3 Photochromic intensity (ΔA_0) of SO1 in (1) ethanol and (2) Ormocer gel as a function of concentration

In 1986 Kaufmann et al¹⁸ demonstrated primarily the feasibility of incorporating a photochromic dye (Aberchrome 670) into SiO_2 gels synthesized from tetramethoxysilane (TMOS). The photochromism of this dye was observed despite the rigidity of the cage matrix because the molecular movement associated with the photochromism is minimal. Levy and Avnir¹⁹ reported in 1988 the effect of the changes in the properties of silica cage along the gel-xerogel transition on the photochromic behaviour of trapped spiropyranes (SP). They found that the normal photochromism (NPC) changed to reversed photochromism (RPC) at a certain point (called reversal point) which is sensitive to substituent effects. These observations were rationalized in terms of a gradual change in the environment of the photochromic molecules from dissolved in the solution encapsulated in a small cage to adsorbed on the cage surface accompanying by changes in the environmental polarity. The same authors²⁰ described the next year two types of photochromic gels, which are modified SiO_2 matrices containing spiropyranes. SE gels derived from ethyltriethoxysilane (ETES) using sodium acetate (NaAc) as catalyst to create mild basic conditions exhibited normal photochromism, while SP gels synthesized by co-polymerisation of TMOS with polydimethylsiloxane (Pdms) showed reversed photochromism which they interpreted as the stabilization of the coloured form by the strong bonds to the silanols of the silica cage. Experimental results of Matsui et al²¹ also revealed reversed photochromism (RPC) of spiropyran in SiO_2 -gels prepared by acidic hydrolysis of TEOS. Photochromism of spiropyranes in Aluminosilicate ($\text{Al}_2\text{O}_3\text{-SiO}_2$) gels derived from diisobutoxy-aluminoxy-triethoxysilane (ASE) was investigated by Preston et al²². No reversed photochromism was observed though both the photochromic response and the colour change rate

decreased during the drying process, and drying to a weight loss of ca. 75% caused the photochromism to cease. Yamanaka et al²³ doped 2,3-diphenylindenone oxide (DPIO) into three kinds of gels, SiO₂ from TMOS, organically modified silicate (Ormosil) from TMOS, 3-(trimethoxysilyl)-propylmethacrylate (TMSPM) and methylmethacrylate (MMA), and aluminosilicate from ASE. A long lifetime ($t_{0.5}^1$) component was found in all three types of samples. In addition, a short lifetime ($t_{0.5}^s$) of the dye was also demonstrated in the ASE samples. All of the samples showed a decrease in the lifetime of the coloured form with processing time. The lifetime in the Ormosil samples changed much faster than either the TMOS or the ASE samples. This may be, as the authors considered, a result of increasing polarity in the gel environment during ageing and drying. Photoisomerization of an azobenzene (AB), 4-methoxy-4'-(2-hydroxyethoxy)azobenzene (MHAB), in sol-gel SiO₂ gel films was investigated by Ueda et al²⁴ and compared with the same dye in poly(methylmethacrylate) (PMMA) films. Their results showed that the cis-fraction in the photostationary state in the sol-gel films was much smaller than in PMMA, suggesting a higher rigidity of the sol-gel matrix than PMMA. In a recently published work²⁵ Ueda reported the effects of introduction of one or two trimethoxysilyl (TES) groups into the AB molecules on the photochromism and found that introduction of one TES group had a slight influence on both the photoisomerization and thermal reversion while those of the AB dye with two TES groups was apparently depressed in sol-gel films. Nogami and co-worker²⁶ studied the effect of Al₂O₃ content on the photochromism of spiropyran doped in Al₂O₃-SiO₂ gels using TEOS and AL(OBu)₃ as starting compounds. The photochromic response decreased with increasing Al₂O₃ content and no photochromism was observed in 33 Al₂O₃ - 67 SiO₂ gels. Thus a strong dependence of the photochromism on gel composition was concluded.

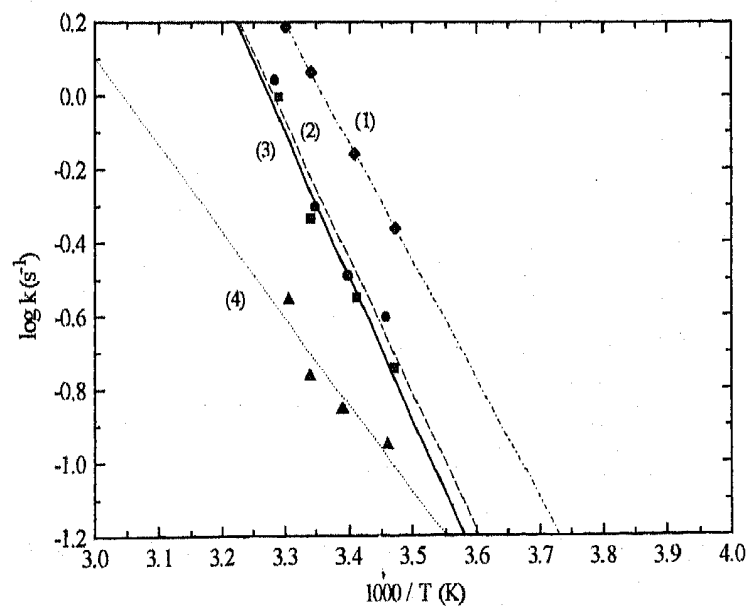


Fig.4 Arrhenius plots for colour-fading of SO1 ($c = 1 \times 10^{-3}$ mol/l) in (1) PMMA (15wt.%) - EA solution, (2) Ormocer coating, (3) Ethanol, (4) PMMA coating

From the above brief survey one can see that most of these studies focussed on fundamental research concerning the interaction between photochromic dyes (SP, DPIO, AB) and sol-gel derived matrices, aiming to demonstrate the feasibility of using these dyes as probes to extract information about the structural changes of the matrices during the gel-xerogel transition process, but few was devoted to problems associated with applications of these dye-in-gel photochromic systems. We must say that this area has not been studied so extensively and intensively as those involving laser dyes or non-linear dyes.

Photochromic dyes are generally much more delicate and hypercritical than the others to the surrounding environment in the matrices, both sterically (viscosity, rigidity, porosity) and electronically (polarity, acidity, hydrogen bonding). It is more difficult to tap practical applications of them also in view of the fact that almost no dye can meet all the three important requirements mentioned in the introduction part of this paper. Moreover, mechanical constraints imposed for some applications also exclude many organic photochromic materials from consideration.

4. PROPERTIES OF SOL-GEL PHOTOCHROMIC ORMOCERS

Spiroindolinonaphthoxazine, usually called spirooxazine (SO), is a most promising kind of photochromic dyes that possess photochromic response to UV irradiation and fading rate of the coloured form as high as spiropyranes but photofatigue resistance²⁷ much higher (10^3 times) than the latter and have therefore been used in photochromic plastics⁴. As we know, however, this class of photochromic dyes had not been studied in sol-gel derived solids before we started our research project. In the first stage of our research a commercially available spirooxazine, SO1 (Aldrich), was used to optimize matrix parameters, and then several new SO dyes have been synthesized in order to improve the overall performance of the dye-in-Ormocer (DIO) photochromic systems.

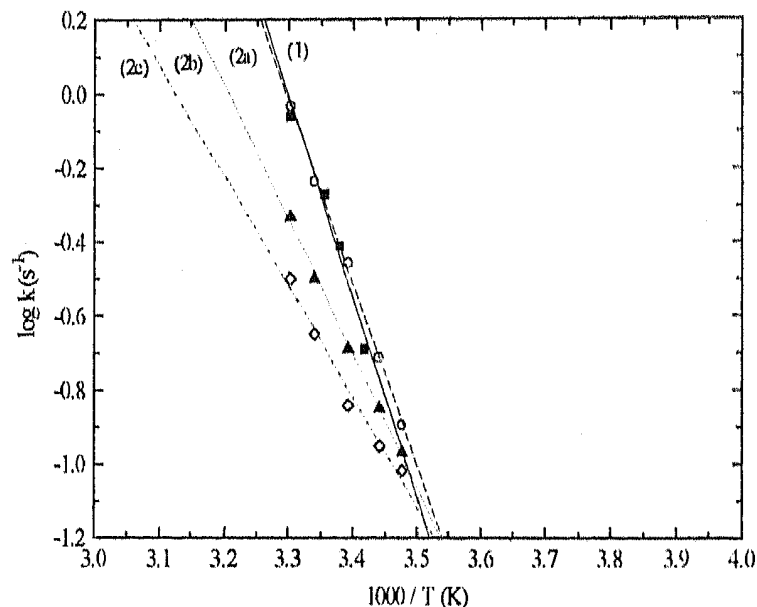


Fig.5 Arrhenius plots for colour-fading of SO3 in (1) Ethanol, (2) Ormocer gel

Considering that photochromic dyes doped in pure TEOS or TMOS gels would either lose their photochromic activity rapidly or change to undesirable reverse photochromism even during the sol-wetgel stage, we started our gel preparation from organically modified silicon alkoxides, $R'Si(OR)_3$. At first, we tried pure methyltrimethoxysilane (MTMS). It was found that although the doped SO dye exhibited detectable photochromism in the sol-wetgel stage, the photochromic response (ΔA_0) would decrease rapidly during ageing and drying and vanished as the rigidity of the gels reached a certain level. In addition, the initial colourless gels changed to yellow- or even brown-coloured implying that the dye molecules were passivated or even destroyed due to the high volume shrinkage ($> 80\%$). SO-doped gels were also prepared from 3-glycidyoxypropyltrimethoxysilane (GPTMS) whose long glycidyoxypropyl (GP) chain was expected to be helpful in creating a more flexible matrix for the dyes and the additional polymerization

between the epoxy groups under certain conditions would possibly play a role in improving the mechanical properties of the gels. It was found, however, that the gelling time was too long to allow aquirement of a wetgel within one month, while gel coatings obtained were too soft even three month after preparation. Using both MTMS (or ETES) and GPTMS as starting compounds SO-doped gels of good optical quality were successfully prepared with significantly reduced gelling time and improved mechanical property^{28, 29}. Fig. 2 shows the absorption spectra of SO1 and SO3 in the Ormocer gels before and immediately after UV irradiation. Because the fading rate of the coloured form is very high ($t_{0.5} < 2$ s) at room temperature, the samples were first cooled down to -20 °C, followed by subsequent UV irradiation and measurement of absorption spectra. No apparent differences had been observed between the absorption peak wavelengths of the coloured form in ethanol solution and Ormocer gel. The improvement in the aggregation of the dye molecules in Ormocer gels is clearly depicted by Fig. 3. In ethanol solutions the dye (SO1) shows a maximum around 5×10^{-4} mol/l in the ΔA_0 vs concentration curve. The aggregation of the dye molecules at higher concentrations is responsible for this phenomenon. In the Ormocer gel, however, ΔA_0 increases monotonically with dye concentration ranging from 1×10^{-4} up to 3×10^{-3} mol/l, indicating a great reduction of aggregation.

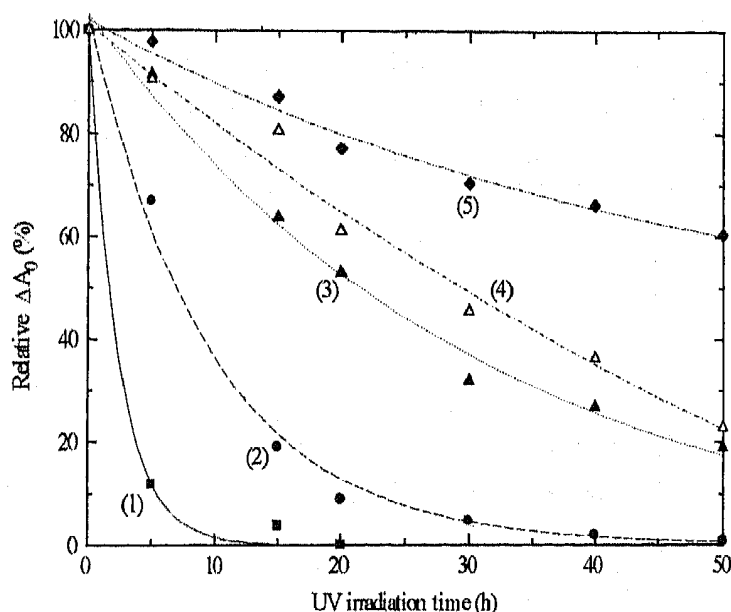


Fig.6 Decrease of ΔA_0 of SO1 under UV irradiation in (1) Ethanol, (2) Ormocer coating, (3) PMMA coating ($c = 1 \times 10^{-3}$ mol/l), (4) Ormocer coating ($c = 1 \times 10^{-3}$ mol/l) containing an additive, (5) PMMA coating ($c = 5 \times 10^{-3}$ mol/l)

The kinetics investigation of the colour-fading process of SO dye-in- Ormocer (DIO) coatings was conducted and compared with the dye-in-solution (DIS) and dye-in-polymer (DIP) photochromic systems by tracing the absorption change (ΔA) as a function of fading time (t). Fig. 4 shows the Arrhenius plots for colour-fading of SO1 in different media. The most interesting result from this figure is that the Arrhenius plot of the dye-Ormocer coating is almost the same as that of the dye-ethanol solution indicating the thermal decay rates (k) at a same temperature for these samples are identical to each other^{30, 31}. In other words, the dye molecules in the Ormocer are as free as in ethanol solution. This is because, we consider, the dye molecules are trapped in the pores in the Ormocer matrix. The fading speed of the dye in PMMA coatings is largely reduced as compared with the dye-in-ethanol solution and the dye-Ormocer coating whereas the dye-PMMA-EA-solution shows a much faster fading speed than the others. This phenomenon

can be attributed to the much lower polarity of ethyl acetate than ethanol. A non-linear kinetics characterizes the SO₃-Ormocer coatings especially at relatively higher temperatures (> 25°C), meaning that the colour-fading mechanism is not a first-order one. The Arrhenius plots for colour-fading of SO₃ in Ormocer gel at the beginning (2a), middle (2b) and final (2c) stages are given in Fig. 5, from which it follows that the fading speed in the beginning stage is similar to that in ethanol solution and undergoes a gradual decrease during the fading process. This implies that the dye exists in different states within the pores of the matrix: completely free or with one to three -OR groups hydrolyzed and the Si atom in the dye molecule connected to other Si atoms through one to three bridging oxygens so that the freedom of the dye molecules is degraded to different extent.

Our results³⁰ show that: (1) ΔA_0 decreases rapidly in the initial stage, then continues decreasing but more slowly, and levels off in about one month after preparation. (2) $t_{0.5}$ increases in the early stage (< 100 h), then decreases and levels off much earlier than ΔA_0 . These observations can be explained as follows. In the sol-wetgel stage the viscosity of the sol increases gradually due to the increase in the extent of condensation. As a result, a greater and greater portion of the dye molecules is more and more tightly confined and even completely blocked from undergoing colour change. Meanwhile, the increasing hindrance due to the viscosity increase makes the fading speed decrease. At the gelling point, a certain portion of dye molecules have been „killed“ and lose their photochromic activity. Only those caged in the pores remain photochromically active. Therefore, both ΔA_0 and $t_{0.5}$ reach a steady value in the xerogel.

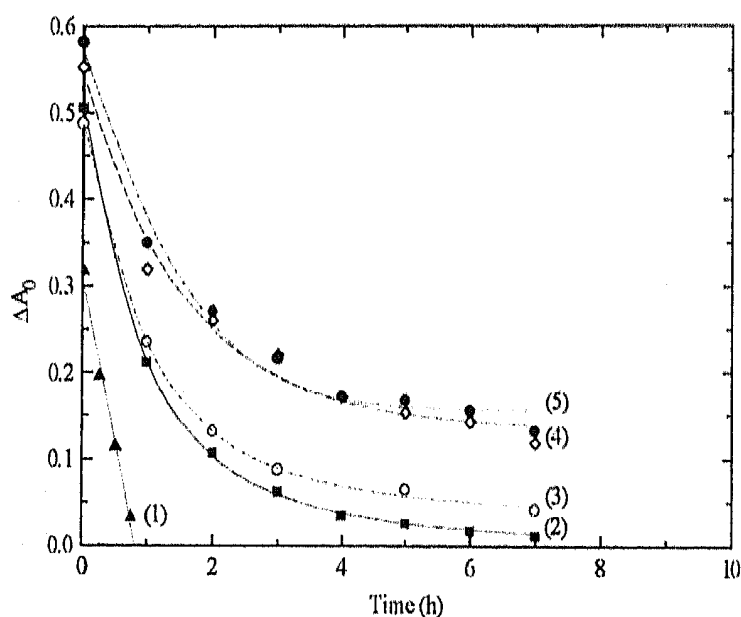


Fig.7 Photochromic intensity (ΔA_0) of SO₃ vs. UV-exposure time in (1) ethanol, (2)-(5) Ormocer gels containing an additive at various concentrations (R_{add}): (2) 0, (3) 0.005, (4) 0.02, (5) 0.1

It is worth highlighting that both ΔA_0 and $t_{0.5}$ show no further decrease up to the present (12 months since preparation). On the contrary, severe degradation of the photochromic response of SO in ASE-gels during ageing had been observed. The photochromic response decreases by a factor of ≈ 3 after 14 days and vanishes after 60 days. During the ageing process of the ASE-gels the structural change (ring-opening) of the SO molecules would face greater and greater hindrance due to the increase of condensation extent of the Al-O-Si network, therefore, the photochromic transformation is more and more heavily suppressed and finally nullified. Our previous work³² has already established that both the photochromic response and

the colour-fading rate of SO-Ormocer gels and coatings are much higher than the SO-PMMA coatings. In order to confirm the application potentialities of the SO-Ormocer material, a comparison in the photochemical stability was recently made experimentally between the dye-in-Ormocer (DIO) and the dye-in-polymer (DIP) materials³³. The result is shown in Fig. 6: (1) The photochemical stability of SO-Ormocer coating without additives is between the SO-ethanol and SO-PMMA systems; (2) A small amount of an additive leads to a great improvement of the photochemical stability of the SO-Ormocer coating, much better than the SO-PMMA coating with same SO concentration. Fig. 7 shows the remarkable effect of the additive on the photostability of SO-Ormocer coatings. (3) By increasing SO concentration in the SO-PMMA coatings up to 5×10^{-3} mol/l the photochemical stability is further enhanced. This suggests a helpful forthcoming step for SO-Ormocer coatings besides introducing more effective additives.

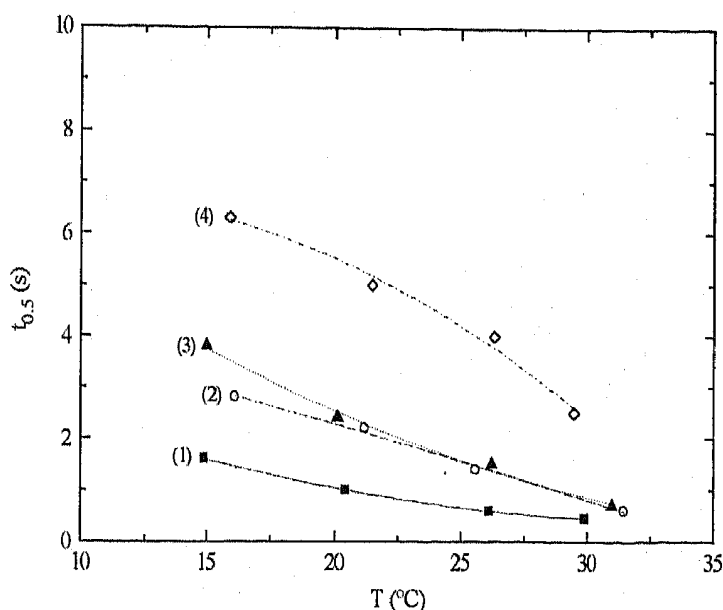


Fig.8 Temperature dependence of half-life time ($t_{0.5}$) of the coloured form of SO1 in (1) PMMA (15wt.%) -EA solution, (2) Ormocer coating, (3) Ethanol, (4) PMMA coating

Sometimes heat treatment (HT) is necessary to the aquirement of Ormocer with desired mechanical properties. The effect of heat treatment on the photochromic property of the SO-Ormocer coatings was also investigated and compared with the SO-PMMA coatings³³. It was revealed that heat treatment of the SO-Ormocer coating up to 120°C had little influence on $t_{0.5}$ and led to only limited decrease in ΔA_0 (< 10%), while in the case of SO-PMMA coatings ΔA_0 showed no significant decrease, but $t_{0.5}$ increased very rapidly with increasing heat treatment temperature between RT and 120°C.

5. FURTHER DEVELOPMENTS

From the results given above we can say that our sol-gel derived photochromic spirooxazine-Ormocer materials possess the thermal and photochemical stabilities comparable to, and both the photochromic response and the colour-change rate much better than the SO-PMMA materials. However, problems encountered by most photochromic materials are far from having been solved, especially in terms of practical applications. Although we are now in a position to achieve photochromic SO-Ormocer materials with good photochemical stability about which the previous publications on photochromic dyes doped in sol-gel derived solid matrices say nothing, much work is still to be done in further optimizing concentration

concentration of the dye, the thickness and the mechanical properties of the coatings. We think our studies are still in a demonstration stage at the present. The optimization of the pore structure may be a promising approach for further improvement of the photofatigue resistance. The density of our photochromic Ormocer is about 1.2 g/cm^3 , but its BET surface area is surprisingly low, only ca. $1 \text{ m}^2/\text{g}$. This implies possibly that the pores are either very big or closed pores. The latter possibility is very attractive, if we can create closed pores in the matrix by controlling the composition and synthesizing parameters the photochemical stability of the photochromic coatings could be greatly enhanced. More fundamental research is certainly claimed in this connection.

There is another common problem with most photochromic materials, inorganic silver halides or organic dyes, organic polymer-, inorganic glass- or Ormocer-based. That is the temperature dependence which is shown clearly by Fig. 8. This problem should be tackled by more elaborate and sophisticated efforts devoted to the improvement of both the matrix and the dye itself. Recently we made a comparison between different SO dyes and fortunately we found that SO4 in ethanol is less sensitive than the others to temperature change in the range of 15°C to 30°C especially in terms of photochromic response as shown in Fig. 9. This arouses our great interest to dope this dye into Ormocer coatings for further developments.

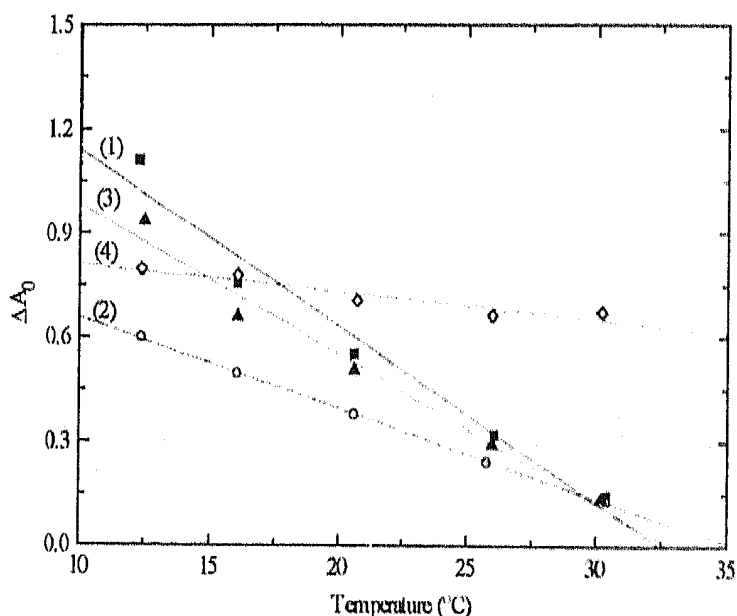


Fig.9 Temperature dependence of ΔA_0 of spirooxazine dyes in ethanol at same concentration: (1) SO1, (2) SO2, (3) SO3, (4) SO4

6. CONCLUSIONS

The „cold“ and „wet-chemical“ characteristics of sol-gel process provides a new and successful way for the incorporation of photochromic dyes into organic-inorganic composite materials. The flexible porous solid matrix allows the encapsulated spirooxazine dyes to undergo reversible photochromic transformations with the photochromic response and colour change speed being much better, and the thermal and photochemical stabilities comparable to the dye-polymer materials. The temperature dependence is hopefully to be improved by introducing a more stable spirooxazine dye and optimizing the pore structure of the Ormocer matrix.

7. ACKNOWLEDGEMENT

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