# Improvement of photofatigue resistance of spirooxazine entrapped in organic-inorganic composite synthesized via the sol-gel process

L. Hou[1,2], M. Mennig[1] and H. Schmidt[1]

1. Institut für Neue Materialien, Geb. 43, Im Stadtwald, D-66123 Saarbücken, Germany
2. Shanghai Institute of Optics and Fine Mechanis, Academia Sinica, 201800 Shanghai, China

## ABSTRACT

A photochromic dye, spirooxazine (SO), was incorporated in organic-inorganic composite (OIC) materials by taking the advantages of sol-gel processing. It has been found that the photochromic response is high enough and the fading rate is similar to the dye-in-ethanol solution while the photofatigue resistance is strongly dependent on the matrix composition and the starting compounds. In the present work, we present results on the effect of matrix composition and starting compounds as well as additives on the photofatigue resistance of SO-OIC photochromic coatings. Sol-gel coatings synthesized from methyltrimethoxysilane (MTMS) and glycidyloxypropyltrimethoxysilane (GPTMS) as starting compounds, and using 1H,1H,2H,2H-perfluoroalkyltrimethoxysilane (FAS) and 1-methylimidazole (MI) as additives provide the SO dye with a favourable matrix environment in terms of photofatigue, so that the overall photochromic performance of the dye can be optimized. The photofatigue resistance reaches the same level as, while both the photochromic response and fading rate are much better than the SO-PMMA coatings.

Key words:    photofatigue, sol-gel, organic-inorganic composite, photochromism, spirooxazine

## 1. INTRODUCTION

Many potential applications of photochromic dyes have been proposed, either as passive devices or as active devices. The former is related to the ability of the dye-containing materials to act as a transmission-controlling light-valve, for example, photochromic windows, eye protecting glasses, privacy shields, switching, photomasking and photoresisting components, while the latter is based on light-induced changes in the photochromic materials themselves, UV or visible dosimeters, reusable optical storage media and self-developing photographic films are examples in this connection. As for all practical applications, in general, the stability of the materials as a function of application time and/or under certain harsh conditions must be considered and improved if necessary. The stability, particularly the photochemical stability which is sometimes also called photofatigue resistance, of organic photochromic dyes has been a most formidable problem which puts a severe limit on their practical applications. This is because UV light irradiation is a conflicting factor to photochromic materials: it is indispensable for the photochromic transformation to take place but meanwhile detrimental to both the dye molecules and the host matrix by affecting and even breaking their chemical bonds, leading to the so-called photofatigue phenomenon, i.e. the photochromic dyes lose their photochromic efficiency gradually with increasing exposure time and intensity of UV irradiation. Since photofatigue of a photochromic material stems from both the photodegradation of the matrix resulting in less protection effect on the dye molecules and the photodeterioration of the dyes

themselves due to side reactions, its improvement lies naturally in the employment of matrices and dyes with better photochemical stability.

The utilization of polymer matrices leads to significant enhancement of photofatigue resistance of SO dyes[1], but at the same time poses a deep suppression on both the photochromic response and the fading rate[2]. A question arises as to wether solid matrices can be exploited for encapsulating photochromic dyes to realize combination of the advantages of dye solutions (high photochromic response, high fading rate) and dye-polymers (higher stability, low aggregation). Organic-inorganic composite materials synthesized by the sol-gel method are favourable matrices for photochromic dyes as demonstrated by the research works summarized in Table 1. It is clear from this table that most of these works were concentrated on fundamental research about the interaction between photochromic dyes (spiropyran, DPIO, azobenzene) and the matrices in order to demonstrate the feasability of using the dyes as probes to gather information on the structural changes of the matrices during the sol-wetgel-xerogel conversion, but only a few publications in the last 5 years were directed to problems associated with practical applications of the dye-in-gel systems. In addition, spiropyranes were more frequently used than the others because they are easy of access and more sensitive to the environmental circumstance in the matrices. We have been engaged in this area since 1991 and oriented our research work to developing practical photochromic systems. Considering that spirooxazine possesses similar photochromic sensitivity and fading rate to those of spiropyrane whereas its photofatigue resistance is much higher ($\approx 10^3$ times) than that of the latter[3] and has already been used in photochromic plastics[1], we have focussed our studies on the effect of sol-gel derived matrices on the photochromic properties of spiorooxazine dyes, particularly on the improvement of photofatigue resistance by optimizing the composition of organic-inorganic composite (OIC) matrix and employing appropriate additives. The experimental results presented in this work show that the photofatigue resistance of spirooxazine has been significantly improved in the OIC coatings prepared via sol-gel processing using MTMS and GPTMS as starting precursors and FAS and MI as additives.

## 2. EXPERIMENTAL

Fig. 1 depicts the preparation procedure of our photochromic dye-doped organic-inorganic composite coatings. Appropriate amounts of different silanes, MTMS and GPTMS in most cases, were first mixed in a plastic container (∅ 30 x 70 mm) for ten minutes by magnetic stirring and water in the form of 0.1 N $HNO_3$ solution was then added into the mixed silanes, followed by additional 10-min stirring and 20-min sonication by 20 kHz ultrasonic radiation at a power of 20 W and cycle duty of 70%. The ultrasonic radiation was generated by a SONIFIER Model 450 device (Branson Ultrasonics CT) and supplied to the liquid mixture through a standard horn tip. The plastic container was immersed into a ice-water bath during sonication. FAS and an additional amount of water were added successively into the sol which was subsequently magnetically stirred for three hours. In order to promote monomeric dispersion of the dye and enhance adhesion of coatings to the glass substrates a non-ionic surface active agent (SAA), Triton X-100, was introduced into the sol at 8 wt.% prior to the addition of the dye-ethanol solution. A commercially available spirooxazine dye, 1,3-dihydro-1,3,3-trimethyl-spiro[2H-indole-2,2'-[3H]-naphth[2,1-b][1,4]-oxazine (Aldrich Chem. Inc.), was used in this work. After an 1h-stirring the sol was exposed to the ambient air with continuing magnetic stirring until the dye concentration in the sol reaches $10^{-3}$ mol/l. Finally, an appropriate amount of MI was introduced into the sol followed by another 2h-stirring and the sol was ready for coating preparation. Coatings of different thickness were prepared by spreading

Table 1    Summary of research works on sol-gel derived photochromic solids

| Year | Dye | Matrix (precursor) | Result(s) | Authors |
|------|-----|--------------------|-----------|---------|
| 1986 | Aberchrome-670 | SiO$_2$ (TMOS) | feasability | Kaufmann et al [4] |
| 1988 | Spiropyrane | SiO$_2$ (TMOS) | NPC $\rightarrow$ RPC | Levy and Avnir [5] |
| 1989 | Spiropyrane | SE (ETES)<br>SP (TMOS-Pdms) | NPC<br>RPC | Levy et al [6] |
| 1989 | Spiropyrane | SiO$_2$ (TEOS) | RPC | Matsui et al [7] |
| 1990 | Spiropyrane | Al$_2$O$_3$-SiO$_2$ (ASE) | NPC<br>$\Delta A_0$ (-) $\rightarrow$0<br>$t_{0.5}$ (+) | Preston et al [8] |
| 1992 | DPIO | SiO$_2$ (TMOS)<br>Ormosil (TMOS-MMA-TMSPM)<br>Al$_2$O$_3$-SiO$_2$ (ASE) | $t_{0.5}$ (-) | Yamanaka et al [9] |
| 1992-1993 | Azobenzene | SiO$_2$ (TEOS) | $(\Delta A_0)_{gel} \ll (\Delta A_0)_{PMMA}$ | Ueda et al [10, 11] |
| 1993 | Spiropyran | Al$_2$O$_3$-SiO$_2$ (Al(OBu)$_3$-TEOS) | $\Delta A_0$ strongly dependent on composition | Nogami and Sugiura [12] |
| 1992-1994 | Spirooxazine | O-I composite (MTMS-GPTMS) (ETES-GPTMS) | stable NPC<br>less dye aggregation<br>thermal and photo-stability similar to DIP | Hou et al [13-18] |
|  |  | Al$_2$O$_3$-SiO$_2$ (ASE) | $\Delta A_0$ (-) $\rightarrow$0<br>$t_{0.5}$ (+) |  |

(+):            increase during drying
(-):            decrease during drying
ASE:          diisobutoxyaluminoxytriethoxysilane
DIP:           dye-in-polymer
DPIO:         diphenylindenone oxide
PdmS:         polydimethylsiloxane
TMPSM:      methacroyloxypropyltrimethoxysilane
(For other abbreviations refer to text)

appropriate volumes of the viscous sols on defined areas of slide glass substrates. After being held overnight in the ambient air at room temperature, the coatings were first heated to 65°C and maintained at this temperatur for 15 hours, then at 100°C and 120°C for two hours, respectively, and subsequently allowed to undergo spontaneuos cooling down to room temperature in the electric oven (MEMMERT Model 100).
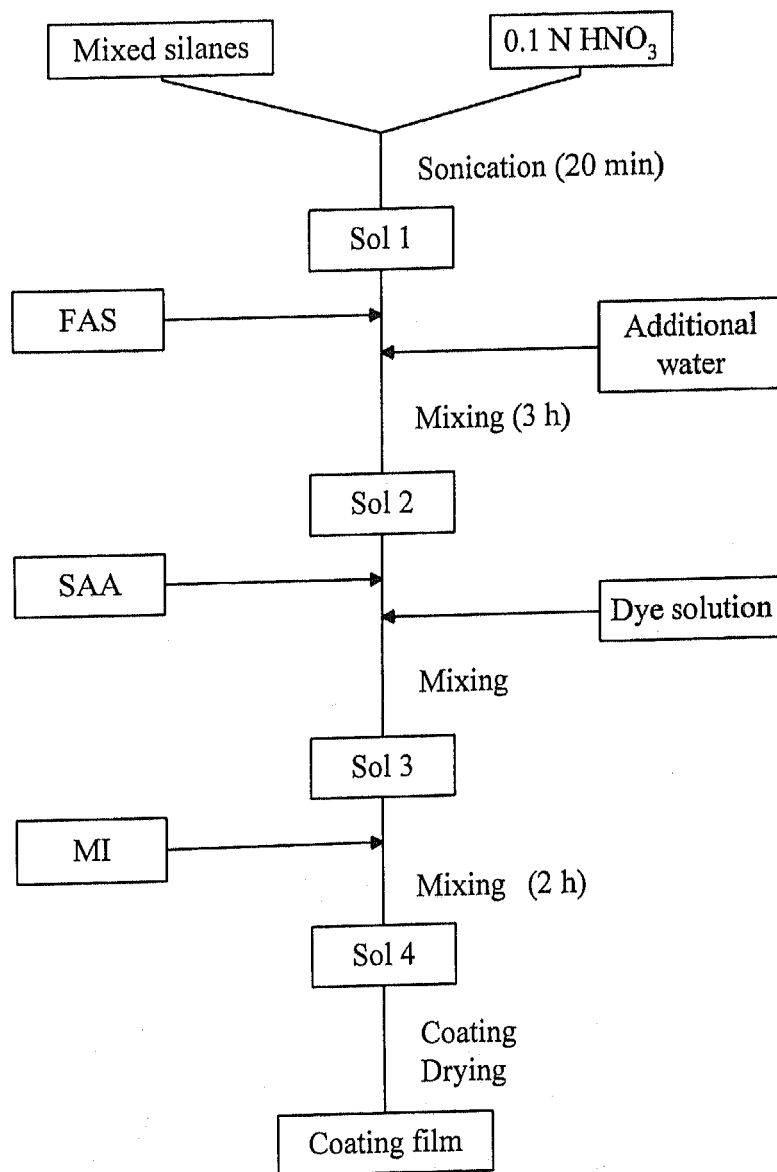
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   ┌──────────────┐              ┌──────────────┐
   │ Mixed silanes│              │  0.1 N HNO₃  │
   └──────────────┘              └──────────────┘
            \                    /
             \                  /
              Sonication (20 min)
                   ┌────────┐
                   │ Sol 1  │
                   └────────┘
   ┌──────────┐        │        ┌──────────────┐
   │   FAS    │───────▶│◀───────│  Additional  │
   └──────────┘        │        │    water     │
                       │        └──────────────┘
                   Mixing (3 h)
                   ┌────────┐
                   │ Sol 2  │
                   └────────┘
   ┌──────────┐        │        ┌──────────────┐
   │   SAA    │───────▶│◀───────│ Dye solution │
   └──────────┘        │        └──────────────┘
                    Mixing
                   ┌────────┐
                   │ Sol 3  │
                   └────────┘
   ┌──────────┐        │
   │    MI    │───────▶│
   └──────────┘        │
                   Mixing  (2 h)
                   ┌────────┐
                   │ Sol 4  │
                   └────────┘
                    Coating
                    Drying
                   ┌──────────────┐
                   │ Coating film │
                   └──────────────┘
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Fig.1   Preparation procedure of photochromic dye-doped organic-inorganic composite coatings.

For comparison, SO-PMMA coatings were also prepared by spreading SO-PMMA-EA (ethylacetate) solution containing 15 g PMMA in 100 ml EA on slide glass substrates. These plastic coatings underwent the same drying and heat treatment procedures as the SO-doped organic-inorganic composite coatings.

A SUNTEST CPS (Heraeus) apparatus was used to test the photofatigue of the heat treated coating samples against UV irradiation at an intensity of 600 W/cm$^2$. The decrease of photochromic intensity with increasing UV irradiation time was monitored and used as a measure of photofatigue.
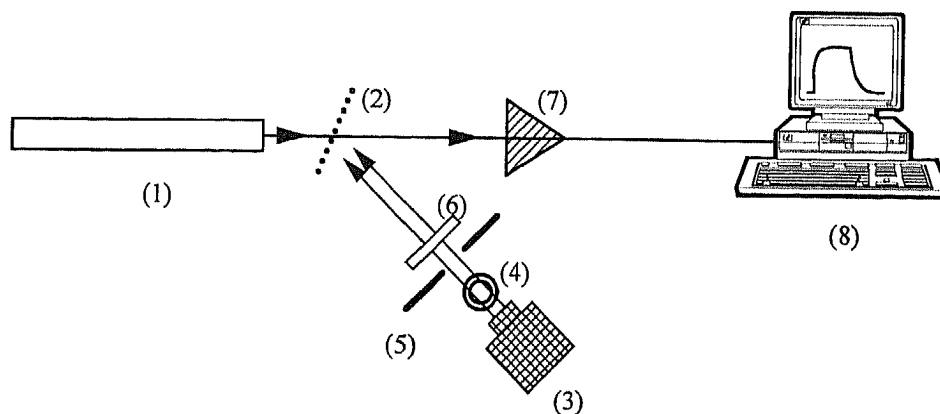


Fig.2  Schematic layout of the apparatus used for photochromism measurement. (1) Laser, (2) SO-OIC coating, (3) Hg-lamp, (4) Focussing system, (5) Shutter, (6) UV pass filter, (7) Detector, (8) PC

The computer-controlled apparatus used for the photochromism measurement is shown schematically in Fig. 2. A Hg-lamp is employed as UV irradiation source and a UV-pass filter (SCHOTT UG5) is used to reduce the influence of heat from the Hg-lamp on the colouring-fading process which is temperature dependent. The variation of transmission with time during the colouring and fading process is probed by a He-Ne-laser beam (633 nm) and processed by a personal computer. The photochromic intensity ($\Delta A_0$) expressed by the absorbance of the sample at the photostationary state under UV irradiation, and half-life time ($t_{0.5}$) of the coloured form, i.e. the time length required for the photochromic intensity to decay to its half value, are evaluated by the computer from the transmission vs. fading time curves.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of matrix composition

As is always the case for reactions that involve broken bonds, both the thermodynamics (reaction extent) and the kinetics (reaction rate) of the colouring (ring-opening) and the fading (ring-closure) processes of photochromic dyes are strongly affected by their surrounding environment in the matrices. The affecting factors include steric (viscositiy, rigidity, porosity) and electronic (polarity, acidity, hydrogen bond) ones. In order to achieve better photofatigue resistance, the matrix itself should be photochemically stable in the first place and could offer a favourable environment to the photochromic dye so as to improve its photostability without degradation in photochromic efficiency and colour change speed.

The feasability of incorporating a photochromic dye into SiO$_2$ gels derived from tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) via the sol-gel process was first demonstrated in 1986 by Kaufmann and co-workers[4]. However, results published by other authors later on revealed that photochromic dyes

doped in pure $SiO_2$[5, 7, 9-11] or aluminosilicate[8, 9, 12] gels would either lose their photochromic activity rapidly or change the direction of photochromism, i.e. from normal photochromism (NPC) to reversed photochromism (RPC), even during the sol-wetgel stage, while gels synthesized using organically modified silanes, for example, ethyltriethoxysilane (ETES)[6] as starting compounds, and Ormosils[9] (organically modified silicates) seemed to be promising hosts for photochromic dyes. But nothing was mentioned about the photofatigue resistance in all these works.
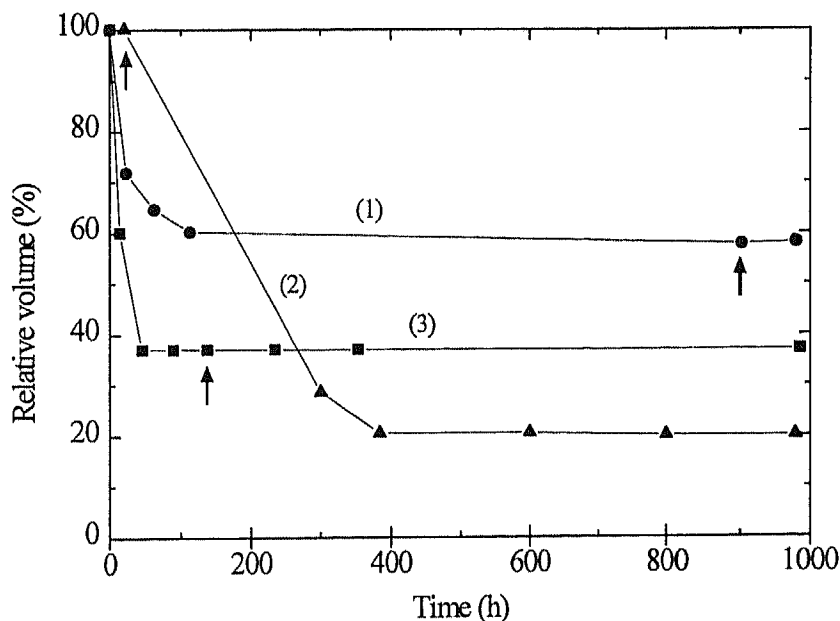


Fig. 3  Gelling time and volume change of samples in (1) GPTMS, (2) MTMS and (3) ETES-GPTMS systems during the sol-gel transformation. Arrows indicate gelling points.

Using mixed organically modified silanes, MTMS (or ETES) and GPTMS as starting precursors, we synthesized organic-inorganic composite gels and coatings containing photochromic spirooxazine. The photochromic efficiency of the dye can be maintained at a reasonably high level even after heat treatment at up to 120°C and no reversed photochromism occurs. This lays a necessary foundation for further improving the photofatigue resistance. But we failed to obtain satisfactory matrices for the dye when either MTMS or GPTMS was used as a single starting compound. Fig. 3 shows the gelling time and volume change of samples of different composition during the sol-gel transformation. When only GPTMS was used, the gelling time will be as long as 900 h even under conditions of exposure to ambient air. The volume decrease from the sol to the wetgel was only 40% mainly due to evaporation of solvent and the produced alcohol. In addition, the GPTMS coatings were too soft to be used practically. On the other hand, when only MTMS was used, the gelling time was as short as 20 h in a hermetically sealed container. By perforating the sealing foil the gel shrinked progressively to a final volume which is only ca. 20% of the initial one. Meanwhile the initial colourless gel became yellow- or even brown-coloured. This implies that the dye molecules have been passivated or even destroyed due to the high volume shrinkage (ca. 80%). Evidences supporting this argument can be found in Fig. 4 by comparing the absorption spectra of the SO dye in ethanol, MTMS-GPTMS and MTMS dry gels. In the near-UV absorption spectra of spirooxazine there are two absorption bands peaking at 311.4 nm and 341.5 nm, respectively. The concentration of the

dye in the coating sols is 1x10-3 mol/l. Due to volume shrink concentrations of the dye in MTMS-GPTMS and MTMS gels are increased by a factor of ca. 2.5 and ca. 5.0, respectively. If no dye molecules in the gels are destroyed, the absorbance should be directly proportional to dye concentration. This is true for the MTMS-GPTMS gel from comparison between curves (1) and (3) in Fig. 4. In the case of MTMS gel, however, absorbance at the first peak (311.4 nm) is much lower than expected while the second absorption peak (341.5 nm) becomes almost indistinguishable and absorbance at this wavelength is lower than the dye-ethanol solution, suggesting that more than 80% of total dye molecules has been destroyed. This is the reason for the colour change of the MTMS gel during drying.
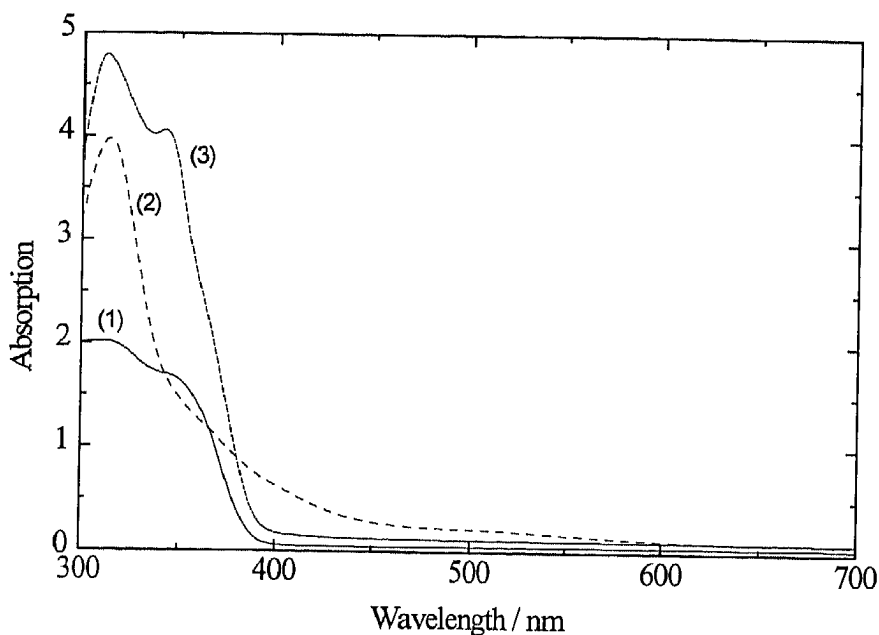


Fig. 4 Absorption spectra of the SO dye in (1) ethanol ($1 \times 10^{-3}$ mol/l), (2) MTMS dry gel ($5 \times 10^{-3}$ mol/l), and (3) MTMS-GPTMS dry gel ($2.5 \times 10^{-3}$ mol/l).

Aluminum, titanium and zirconium alkoxides were also introduced into the MTMS-GPTMS system at a molar ratio of 0.2 to total silanes. It was found that a yellow colour grew gradually and the photochromic activity of the SO dye disappeared during ageing of the gels or even before gelling in some cases. There must be some reactions between the dye and the three non-silicon alkoxides leading to the loss of photochromic activity.

## 3.2 Effect of additives

Severeal additives were introduced into the MTMS-GPTMS system at various molar ratios to total silanes, $R_x$ (x= NaAc, NaF, MI, FAS), to establish their effects on the hydrolysis-polycondensation reaction and thereby on stability of the SO dye in the organic-inorganic composite materials. Variation of photochromic intensity of the SO-OIC coatings containing different additives with UV irradiation time at a intensity of 600 W/cm$_2$ is shown in Fig. 5. It is apparent that when NaAc or NaF are used as additives photofatigue resistance of the coatings is not satisfactory, a 20 h-UV irradiation makes the photochromic

intensity decrease by a factor of >80%. With the addition of MI ($R_{MI}=1x10^{-2}$) photofatigue resistance is improved considerably, decrease in photochromic intensity resulted from a 20 h-UV irradiation is <60%. The cooperative effect of MI and FAS on the improvement of photofatigue resistance is so encouraging that photochromic intensity can be maintained at a level of >65% of the original value after a 20 h-UV irradiation. This is a little better than the corresponding SO-PMMA coatings. Considering that both photochromic efficiency and colour change (colouring and fading) speed of the SO dye are deeply suppressed in PMMA coatings[18] it can be concluded that overall photochromic performance of the SO-OIC coatings contrasts favourably with the corresponding SO-PMMA coatings.
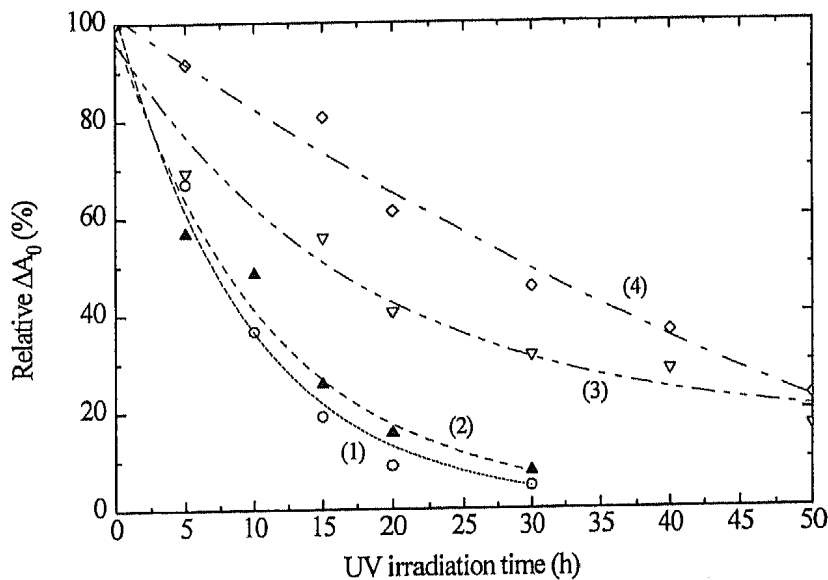


Fig. 5 Variation of photochromic intensity ($\Delta A_0$) of the SO-OIC coatings with UV irradiation time. (1) $R_{NaF}=5x10^{-4}$, (2) $R_{NaAc}=1x10^{-3}$, (3) $R_{MI}=1x10^{-2}$, and (4) $R_{MI}=1x10^{-2}$, $R_{FAS}=2x10^{-2}$

NaAc was used as an additive to create a mild basic condition[6] both for stabilizing the dye and for catalyzing the hydrolysis-condensation reaction to obtain matrices with larger pores as cages for dye molecules, since it is generally recognized that low pH-values (acid catalysis) tend to result in gels which are weakly crosslinked and highly polymeric with a large amount of small pores while a higher pH-value (base catalysis) favours the formation of highly branched silica chains, leading to a more particle-like structure having larger interconnection channels, namely, larger pores. NaF was introduced into the organic-inorganic system based on a similar consideration. R. Winter and co-workers[19] reported that the presence of fluoride not only drastically accelerates the gelation process but also leads to a differnt polymerization process and formation of a loose and relatively open gel network with a large fraction of mesopores. This loose and relatively open gel network is apparently favourable to the photochromic dyes which undergo structural changes in the photochomic transformation process. Fig. 6 shows effects of NaAc and NaF on viscosity evolution of the MTMS-GPTMS system in the early sol-gel transformation stages. Acceleration of gelation process is obvious. It should be added here that gelling time of the same system was shortened to less than five hours when MI was used as an additive at the molar ratio ($R_{MI}$) of $2x10^{-2}$ and it is difficult to include this result in Fig. 6.
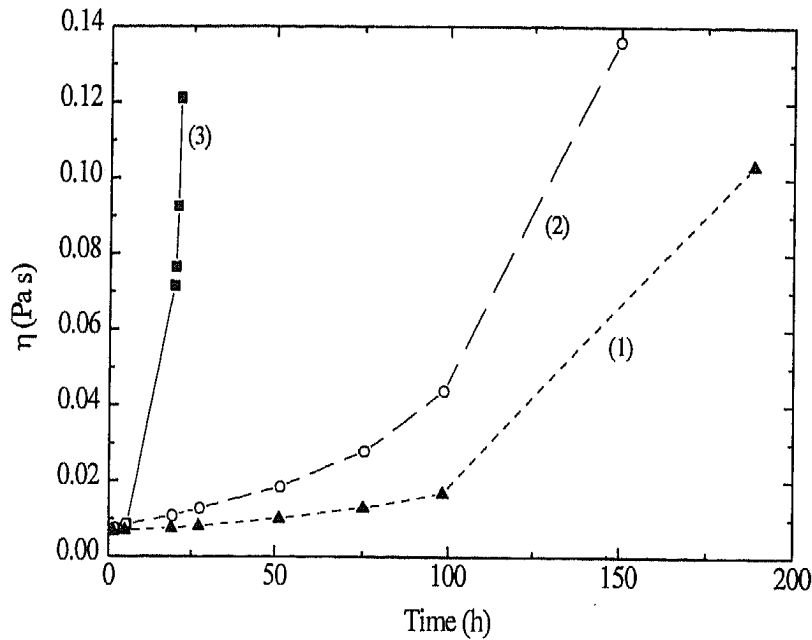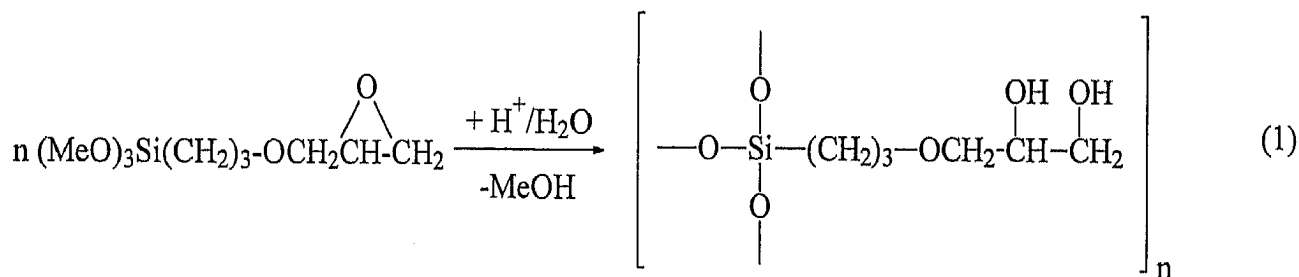
Fig. 6 Viscosity vs. time in the early stages of sol-gel transformation in MTMS-GPTMS system. (1) no additives, (2) $R_{NaF}=5\times10^{-4}$, and (3) $R_{NaAc}=1\times10^{-3}$

It is well known that the epoxy group in GPTMS may react with water under acid conditions to form hydrophilic diol units by hydrolytic ring-opening, providing dye molecules with an alcohol-like environment, while the methoxy groups in GPTMS hydrolyze to a certain extent depending on the amount of water added:

$$n\ (MeO)_3Si(CH_2)_3\text{-}OCH_2CH\text{-}CH_2 \xrightarrow[-MeOH]{+H^+/H_2O} \left[ -O-Si-(CH_2)_3-OCH_2-CH-CH_2 \right]_n \tag{1}$$

On the other hand, when proper catalyst is employed, polyaddition can take place among the epoxy groups to form polyethylene oxide chains:

$$HC-CH_2 + H_2C-CH \xrightarrow{cat.} CH-CH_2-O-CH-CH_2-O \tag{2}$$
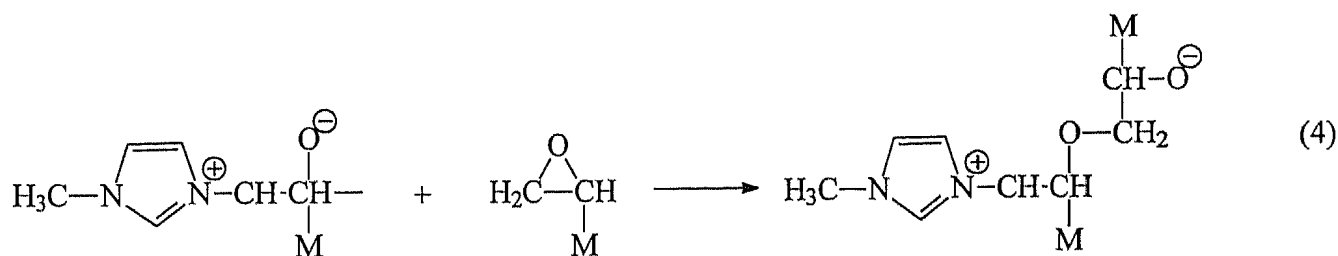
$$M = (MeO)_3Si(CH_2)_3\text{-}O\text{-}CH_2$$
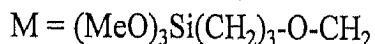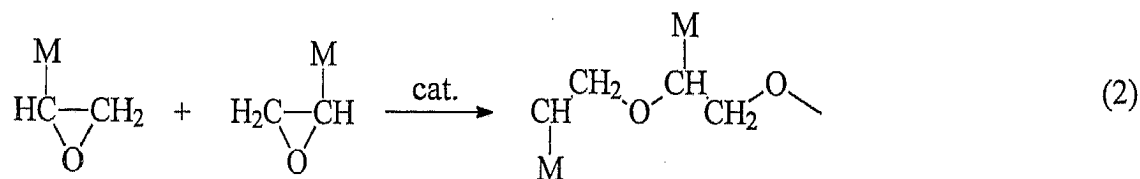
This makes it possible to optimize the flexibility of the organic-inorganic matrix by adjusting cross-linking in gel network through additional polymerization between epoxy groups. MI can act both as a base catalyst for condensation of silanol groups produced through hydrolysis of the methoxy groups and as an initiator for polymerization of epoxy groups in GPTMS. The mechanism of the polymerization may be as follows:

Ring-opened intermediate formation:

$$H_3C-N\diagdown N \quad + \quad H_2C-CH \quad \longrightarrow \quad H_3C-N\diagdown N-CH-CH \tag{3}$$
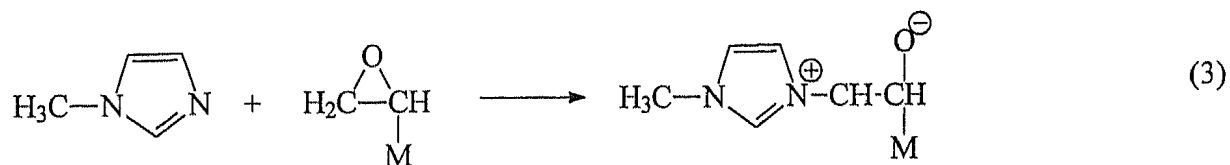
Polyetherification and network formation:

$$H_3C-N\diagdown N-CH-CH- \quad + \quad H_2C-CH \quad \longrightarrow \quad H_3C-N\diagdown N-CH-CH \tag{4}$$

It is evident that the higher the amount of MI added, the higher the connectivity in the network, and the higher the rigidity of the gel matrix. A high connectivity is favourable to the stability of matrix itself and thereby protection of dye molecules against degradation due to UV irradiation. But a too high connectivity will retard the structural change of dye molecules under UV irradiation and lead to a smaller or even vanishing photochromic response. Therefore, optimization must be conducted giving considerations to both photochromic intensity (high enough) and photofatigue resistance (acceptable). Fig. 7 shows the effect of concentration of MI on photochromic intensity of the SO-OIC coatings. The optimum concentration locates around $R_{MI}=1 \times 10^{-2}$, above which the higher the concentration the lower the photochromic intensity. This is why this concentration is usually adopted in the coatings, as shown in Fig. 5. The absorption spectra of the SO-OIC coatings with and without additives are compared in Fig. 8. The two absorption maxima, one in UVB (280-320 nm) and the other in UVA (320-400 nm) regions, vary distinguishably with additives: addition of MI causes both maxima to decrease whereas addition of FAS reduces the UVB absorption but exerts little influence on the UVA absorption. In general, the greater the quantity of UV irradiation absorbed, the higher the probability of deterioration of organic dyes and UVB is more harmful to the dyes because of its higher energy than UVA.

Recently, several kinds of perfluoroalkylsilanes were incorporated into $ZrO_2$[20] and organic-inorganic composite[21] coatings via sol-gel processing to create non-stick hydrophobic and oleophobic surfaces due to their very low surface free energy, for which the enrichment of fluorine at the surface layer was found to be responsible. This may provide another reasonable explanation for the remarkable improvement in photofatigue resistance of the SO-OIC coatings containing only a small amount of perfluoroalkylsilane. The non-stick surfaces of the coatings prevent $H_2O$, oil and other possible compounds from clinging to the

surfaces and penetrating into interior of the coatings. These compounds themselves may be harmful to the dye or may generate new substances detrimental to the dye, for example, $O_2$ under UV irradiation.
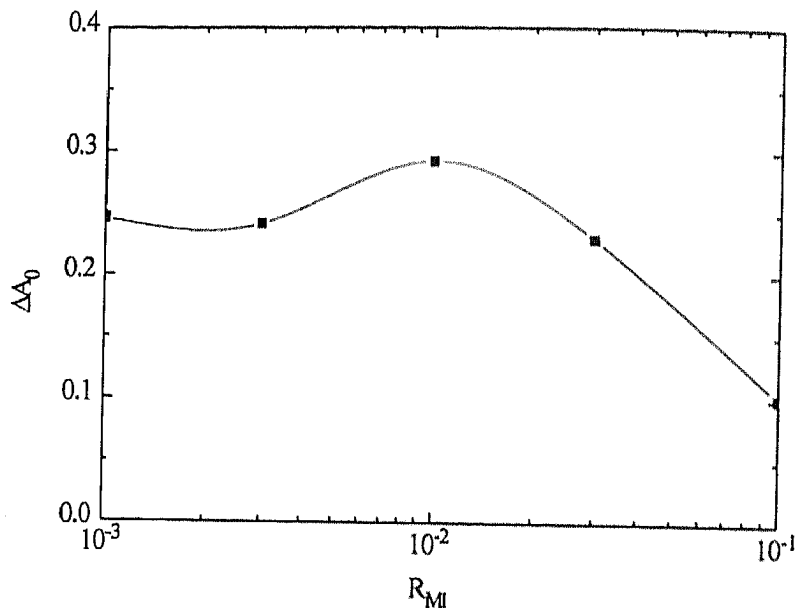


Fig. 7    Photochromic intensity ($\Delta A_0$) of the SO-OIC coatings as a function of concentration of methylimidazole (MI)

## 4. CONCLUSIONS

Based on elaborate selection of composition and starting materials, organic-inorganic composite coatings prepared by the sol-gel proces provide photochromic spirooxazine with a favourable matirx environment. Sufficiently high photochromic intensity ($\Delta A_0$) and colour change speed ($t_{0.5}$) are maintained after heat treatment at 120°C.

Addition of small amount of methylimidazol and perfluoroalkylsilane into the organic-inorganic composite coatings results in an encouraging improvement in photofatigue resistance. The former additive serves to optimize connectivity in the matrix by additional cross-linking so as to aquire a compromise between photofatigue resistance and photochromic intensity, while the latter leads to a fluorine-enriched anti-adhesion surface which protects the photochromic dye in the coatings from being attacked by detrimental substances.

## 5. ACKNOWLEDGEMENT
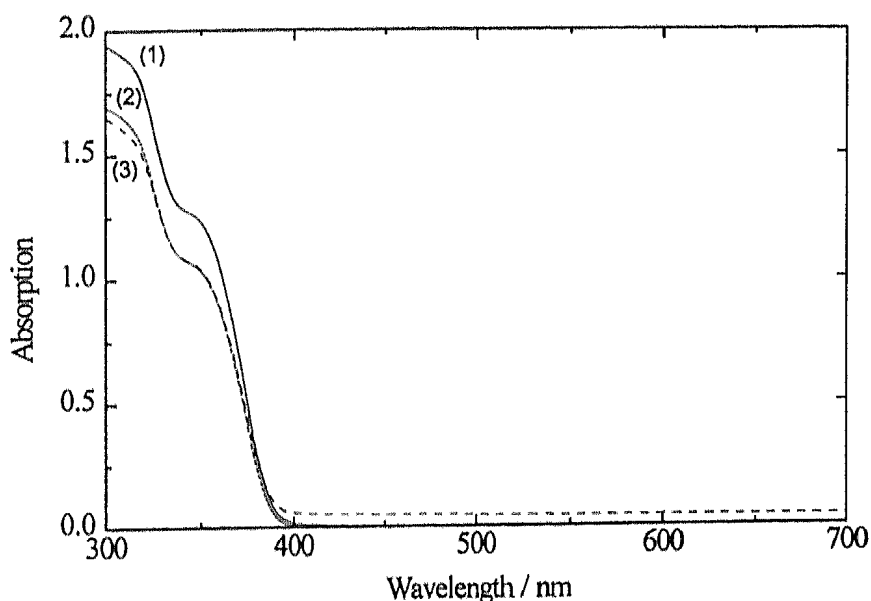
Fig. 8  Absorption spectra of the SO-OIC coatings. (1) no addtitives, (2) $R_{MI}=1x10^{-2}$ and (3) $R_{MI}=1x10^{-2}$, $R_{FAS}=2x10^{-2}$

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