

# PHOTOCHROMIC COATINGS DERIVED BY SOL-GEL PROCESSING FROM EPOXYSILANE, BISPHENOL-A, 1-METHYLIMIDAZOLE AND SPIROOXAZINE

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## Abstract

As photochromic organic dyes in solution suffer from heavy aggregation and poor thermal and photochemical stability, solid matrices are preferred as their hosts. The low-temperature wet-chemical characteristics of the sol-gel process, fortunately, offer vast possibilities for the incorporation of organic dyes into solid matrices.

In this work we present our experimental results on photochromic coatings containing 1,3,3-trimethyl-spiro[indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine] (SO) and derived from 3-glycidyloxypropyltrimethoxysilane (GPTMS), bisphenol-A (BPA) and 1-methylimidazole (MI) by sol-gel processing.

The experimental results of the investigation of the photochromic properties as a function of matrix composition and additives include four main aspects in terms of the photochromic intensity ( $\Delta A_0$ ) at the photostationary state under UV irradiation and the half-life time ( $t_{0.5}$ ) of the coloured form after cessation of the UV irradiation: (1) heat treatment temperature for densification of the coatings has a great effect on  $\Delta A_0$ . (2) The BPA content shows a significant effect on both  $\Delta A_0$  and  $t_{0.5}$ . While there exists an optimal content of BPA for  $\Delta A_0$ , there is a steadily increase in  $t_{0.5}$  with increasing BPA content. (3) The most encouraging result is that we are now able to increase the dye concentration in our samples to a similar concentration as is used in dye-polymer systems but with better photochromic intensity. (4) The effect of additives, e.g. fluorosilane (FAS), is also attractive to further work, because the addition of FAS not only leads to a further increase in  $\Delta A_0$  but also greatly enhances the photostability.

## Introduction

For all investigations and applications of organic photochromic dyes a suitable matrix has to be found. In order to solve the problems with dye solutions, i.e. concentration quenching of the photochromic effect and low photostability, solid matrices are preferred for the incorporation of organic photochromic dyes. Due to

the high temperature procedure inorganic glasses are not suitable for this purpose. The use of organic polymers as hosts decreases the aggregation problem and improves the photostability but at the same time leads to a deep suppression on both fading speed and photochromic response because of the rigidity of the matrix. Sol-gel matrices are expected to be better hosts for photochromic dyes as by the sol-gel method it is possible to develop matrices whose properties compromise between enough flexibility to allow the photochromic reaction to take place and enough rigidity to ensure good mechanical properties for practical applications.

The first approaches in this field, using tetraalkoxides or single organically modified silanes as starting precursors led to too rigid matrices that caused the photochromic activity to disappear[1-3] or to change to reversed photochromism[1]. Starting from a mixture of organically modified silanes, however, it was possible to develop a system with enough flexibility to allow good photochromic activity[3]. Yet only relatively thick coatings ( $\approx 100 \mu\text{m}$ ) with poor mechanical properties could be obtained although certain additives were also used. However, it was found that some additives, e.g. 1H, 1H, 2H, 2H-perfluoroalkyl-trimethoxysilane (FAS) improved the photostability of the dye[4, 5].

In the present work we report about a new system with increased mechanical strength that is achieved by the formation of an additional organic network within the inorganic network by amine-catalysed organic polymerisation of the epoxy groups of GPTMS with BPA. The photochromic properties are investigated as a function of processing parameters, matrix composition and additives and the results are discussed in terms of the photochromic intensity ( $\Delta A_0$ ) and the half-life time ( $t_{0.5}$ ) of the coloured form.

## Experimental

The preparation of the photochromic coatings starts with an 2 h pre-hydrolyzation of the 3-glycidyloxypropyltrimethoxysilane (GPTMS) with acidic water. Under stirring at room temperature a solution of bisphenol-A (BPA) in EtOH to achieve different molar ratios of BPA : GPTMS in the range from 10 to 40 mole% is added together with 1-methylimidazole (MI) and stirring is continued for 1 h. After the addition of a tenside to provide better dispersion of the dye and a certain amount of the spirooxazine (SO) dye to get concentrations from  $1 \times 10^{-3}$  to  $5 \times 10^{-2}$  mole/l and another 30 min stirring the sol can be used for dip-coating on glass slides. Afterwards the coatings are dried for 1 h in an electric oven at temperatures between  $90^\circ\text{C}$  and  $120^\circ\text{C}$  and directly after cooling down to room temperature the measurements are carried out with a home-made apparatus described in a previous paper[3]. To investigate the effect of additives, e.g. FAS, certain volume ratios to the total amount of the sol in the range from 0 to 10 vol% are added prior to the addition of the tenside and the dye and stirring is continued over night. UV irradiation for the photostability measurements is carried out in a SUNTEST device with an output of  $600 \text{ W/m}^2$ .

## Results and discussion

By the use of GPTMS, BPA and MI as starting precursors and SO as photochromic dye coatings ( $\approx 10 \mu\text{m}$ ) were obtained for the investigation of the

photochromic properties as a function of processing parameters and matrix composition. Fig. 1 depicts the change of the photochromic intensity ( $\Delta A_0$ ) as a function of densification temperature at various dye concentrations. For all concentrations one can see a decrease of  $\Delta A_0$  with temperature which is due to the increasing rigidity of the matrix. For the highest dye concentration all values of  $\Delta A_0$  are higher than 0.6 which is the commonly accepted lower limit for practical applications as it equals to a transmission change from 80 to 20 %.

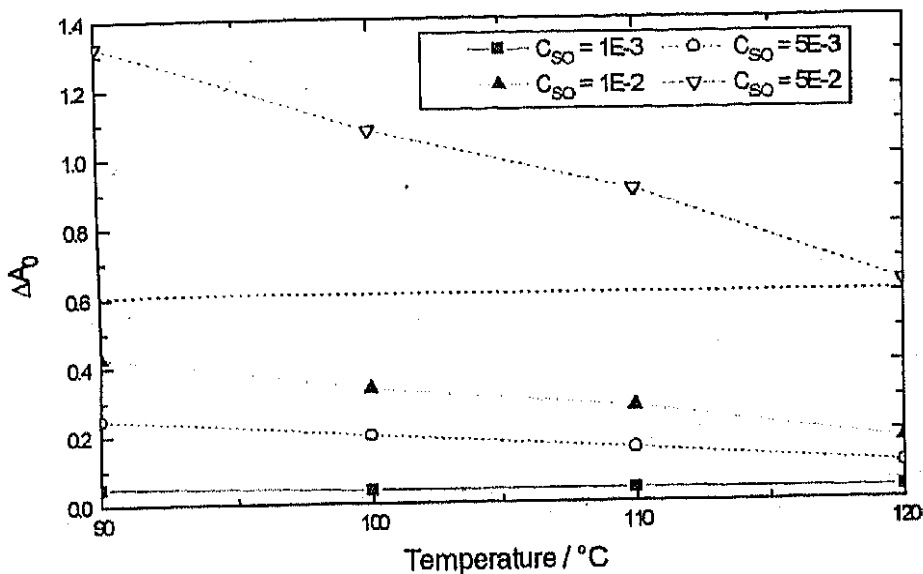
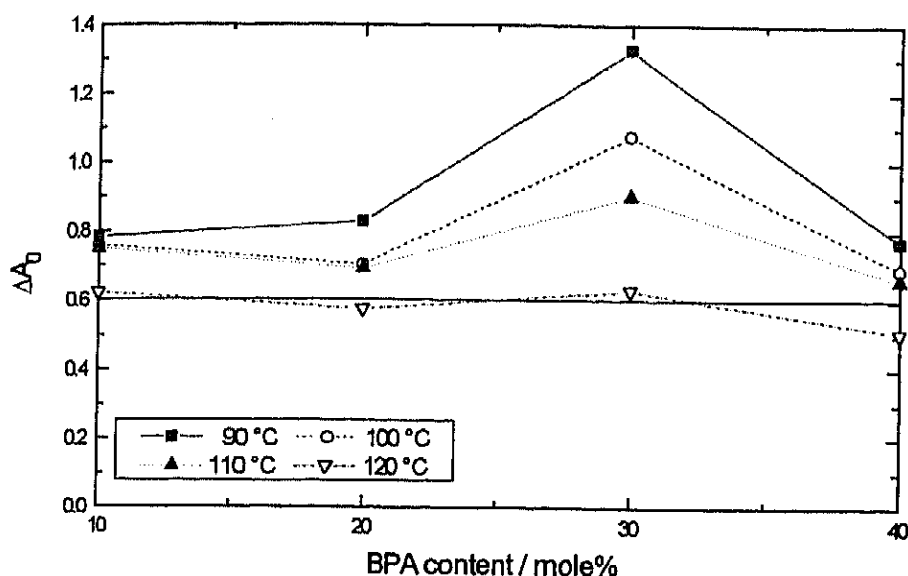


Fig. 1 Densification temperature effect on  $\Delta A_0$  in GPTMS/BPA/MI system with various dye concentrations (BPA content: 30 mole%)  
Dotted line at  $\Delta A_0 = 0.6$  indicates a transmission change from 80% to 20%

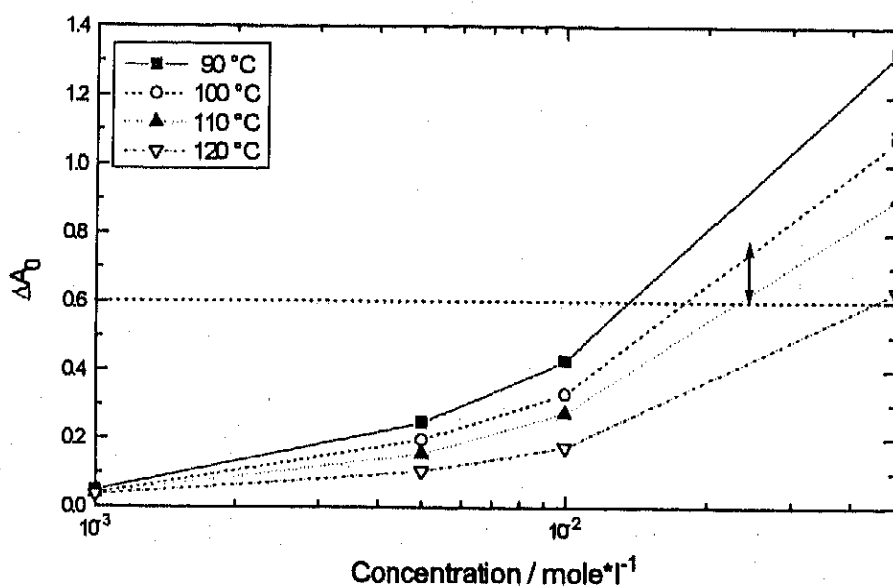
Fig. 2 shows the effect of BPA content on  $\Delta A_0$  at various densification temperatures of coatings with a dye concentration of  $5 \cdot 10^{-2}$  mole/l. As it can be seen from this figure BPA content has a great effect on  $\Delta A_0$  with an optimum at 30 mole%. Two reasons lead to the suggestion that the improvement in  $\Delta A_0$  is due to solvent and stabilization effects. First, the same result can be found when adding BPA to a dye-EtOH solution and second, the half-fading time ( $t_{0.5}$ ) also increases with increasing BPA content. Although its value is more than doubled from 1.8 s to about 5 s when increasing BPA content from 10 to 40 mole% the fading is still faster than in organic polymer systems which commonly show half-fading times  $> 100$  s.

Fig. 3 indicates the change of  $\Delta A_0$  with increasing dye concentration at various densification temperatures of coatings with a BPA content of 30 mole%. As it is expected  $\Delta A_0$  increases with increasing dye concentration but it is important to stress two aspects. First, we are now able to increase the dye concentration to similar or even higher concentrations as in polymers and second, at similar concentrations our system is at least as good as and in some cases better than polymers concerning the photochromic intensity and in all cases faster concerning the half-life time as mentioned before.



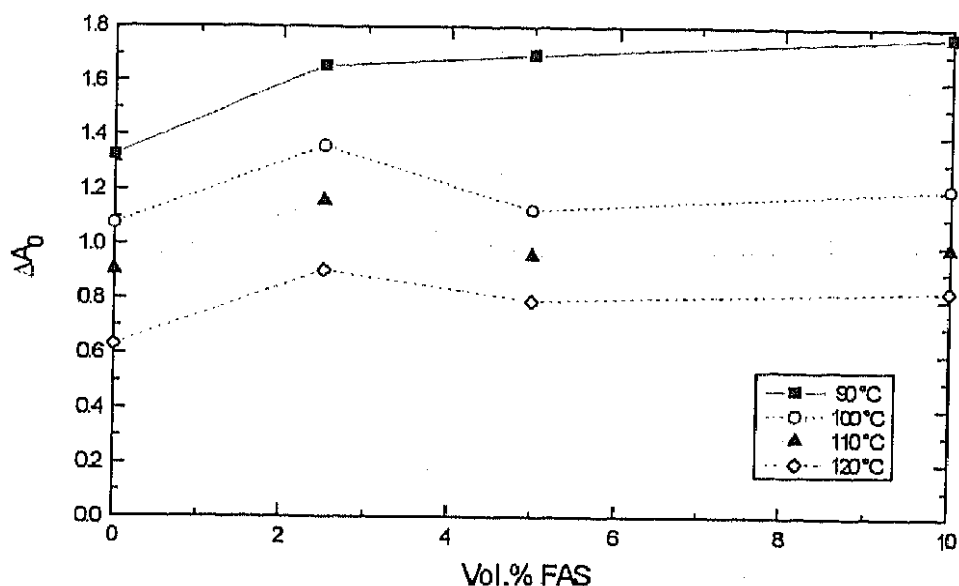
**Fig. 2** Effect of BPA content on  $\Delta A_0$  at various densification temperatures ( $C_{SO} = 5 \cdot 10^{-2}$  mole/l)

Fig. 4 shows the photochromic intensity as a function of the FAS content at various densification temperatures and a dye concentration of  $5 \times 10^{-2}$  mole/l and a BPA content of 30 mole%. In all cases there is an enhancement in  $\Delta A_0$  with an optimum at 2.5 vol% FAS. Only at a densification temperature of 90 °C there is a further enhancement with increasing FAS content but in those cases the optical quality of the coatings is bad caused by incomplete hydrolysis of the FAS or impurities in the FAS.



**Fig. 3** Effect of dye concentration on  $\Delta A_0$  at various densification temperatures (BPA content: 30 mole%)

Double arrow indicates range for organic polymer systems



**Fig. 4** Effect of FAS content on  $\Delta A_0$  at various densification temperatures (BPA content: 30 mole%,  $C_{SO} = 5 \cdot 10^{-2}$  mole/l)

A good means to investigate the photochemical stability is to measure the remaining photochromic intensity after certain time intervals of UV irradiation. Commonly the measurements are carried out until  $\Delta A_0$  has dropped to half of its initial value before the first irradiation.

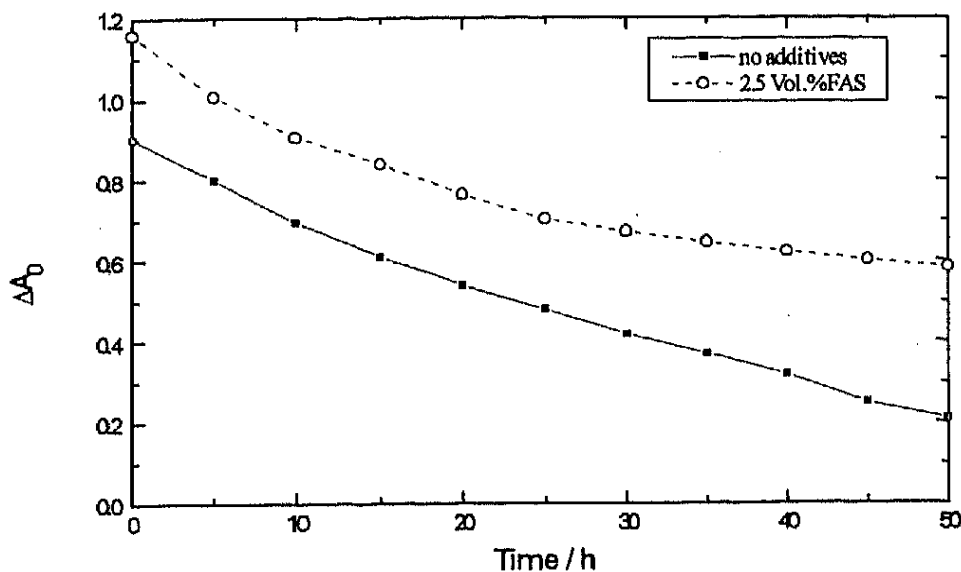
Table 1 shows the time length required for the photochromic intensity to drop to 50 % for samples with and without FAS densified at various temperatures. From this table and from Fig. 5 which depicts the effect of the UV irradiation time on  $\Delta A_0$  on samples with 30 mole% BPA and  $5 \cdot 10^{-2}$  mole/l SO dye densified at 110 °C it can be seen that the photostability is greatly improved by the addition of FAS and the decrease of  $\Delta A_0$  is slowed down.

**Table 1** Time length required for  $\Delta A_0$  of coatings with and without FAS densified at various temperatures to drop to 50 % of the starting value (BPA content: 30 mole%,  $C_{SO} = 5 \cdot 10^{-2}$  mole/l,  $I_{UV} = 600$  W/m<sup>2</sup>)

	without FAS	with 2.5 vol% FAS
90 °C	13 h	35 h
100 °C	19 h	29 h
110 °C	27 h	> 50 h
120 °C	19 h	35 h

Another conclusion that can be drawn from Figs. 2 and 4 and Table 1 is that one has to compromise between maximum photochromic intensity and photostability. While the samples densified at 90 °C show higher photochromic intensity, the photostability of the samples densified at 110 °C is much better. Although the increasing rigidity of the matrix hinders the structural change of the dye molecules its

better protection effect on the dye molecules leads to a great improvement in the photochemical stability.



**Fig. 5** Effect of UV irradiation time (suntest) on  $\Delta A_0$  at a densification temperature of 110 °C (BPA content: 30 mole%,  $C_{SO} = 5 \cdot 10^{-2}$  mole/l,  $I_{UV} = 600$  W/m<sup>2</sup>)

## Conclusions

The GPTMS/BPA/MI system is a suitable matrix for SO dyes. The photochromic properties can be tailored by processing parameters, matrix composition and additives.

By heat treatment at 110 °C good mechanical and good photochromic properties can be achieved. The dye concentration can be increased to a similar or even higher concentration as is used in organic polymers. In both cases the sol-gel coatings are as good as polymers concerning the photochromic properties or show even higher photochromic intensity and faster fading kinetics. The addition of FAS leads to an increase in  $\Delta A_0$  and to a great improvement in photostability.

All the results lay a solid foundation for further research work including investigation of the mechanism of the FAS and further improvement of the photochemical stability because the sufficiently high photochromic intensity and much higher fading speed are very encouraging to practical applications.

## References

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