

Effect of Heat Treatment and Additives on the Photochromic and Mechanical Properties of Sol-Gel Derived Photochromic Coatings Containing Spirooxazine

L. HOU

*Institut für Neue Materialien, Geb. 43, Im Stadtwald, D-66123 Saarbrücken, Germany; and
Shanghai Institute of Optics and Fine Mechanics, Academia Sinica, 201800 Shanghai, China*

B. HOFFMANN, H. SCHMIDT AND M. MENNIG

Institut für Neue Materialien, Geb. 43, Im Stadtwald, D-66123 Saarbrücken, Germany

Abstract. The experimental results on the photochromic and mechanical properties of coatings containing 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-(3H)-naphth(2,1-b)(1,4) oxazine] (SO) derived from 3-glycidyl-oxypropyltrimethoxysilane (GPTMS), bisphenol A (BPA) and 1-methylimidazole (MI) by sol-gel processing are presented. It is shown that heat treatment temperature is a conflicting factor to the photochromic intensity (ΔA_0), photostability and abrasion resistance of the photochromic coatings. With increasing densification temperature the matrix rigidity increases leading to a decrease of ΔA_0 and at the same time an enhancement of both abrasion resistance and photostability, the optimum heat treatment temperature is 110°C under our experimental conditions. By the use of certain additives, e.g., fluorosilanes (FAS), not only ΔA_0 but also the photostability and the abrasion resistance of the photochromic coatings have been further improved.

Keywords: photochromism, photochromic coatings, spirooxazine, photochromic properties, mechanical properties

1. Introduction

For all investigations and applications of organic photochromic dyes a suitable matrix is indispensable. In order to overcome the aggregation and improve the stability of the dyes solid matrices are preferred. Unfortunately inorganic glass cannot be used for this purpose due to the high temperature procedure. The use of organic polymers alleviates the commonly arising problems with dye solutions, concentration quenching and low photostability, but at the same time leads to a deep suppression on both fading speed and photochromic response of the dye [1]. As the sol-gel method enables the development of matrices whose properties compromise between enough flexibility to allow the photochromic reaction to take place and satisfactory rigidity to ensure good mechanical strength, sol-gel derived matrices are expected to be better hosts for photochromic dyes.

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 either to disappear or to change to reversed photochromism [2–4]. Starting from a mixture of organically modified silanes, however, it was possible to develop a system with enough flexibility to ensure good photochromic activity [4]. It was also found that some additives, e.g., 1H, 1H, 2H, 2H-perfluoroalkyltrimethoxysilane (FAS) improved the photostability of the dye [5, 6]. But the coatings are too thick and mechanical properties are not satisfactory for practical applications.

In the present work we report about a new photochromic system with increased mechanical strength that is achieved by the formation of additional organic cross-linking within the inorganic network by amine-catalyzed polymerization of the epoxy groups of

3-glycidyloxypropyltrimethoxysilane with the OH-groups of bisphenol A. The photochromic and mechanical properties of the coatings are investigated as a function of processing parameters and additives and the effects on photochromic intensity (ΔA_0), photostability and abrasion resistance are discussed.

2. Experimental

The preparation of the photochromic coatings started 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 was added to achieve BPA contents from 10 to 40 mole%, followed by the introduction of 1-methylimidazole (MI) and stirring was 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 a concentration of 5×10^{-2} mole/l, another 30 min stirring was conducted and the sol was used for dip-coating on glass slides. The coatings were then treated for 1 h in an electric oven at temperatures between 90°C and 120°C and cooled down to room temperature. The measurements of photochromic properties, e.g., the photochromic intensity, ΔA_0 , the absorbance of the sample at the photostationary state under UV irradiation, were carried out with a home-made apparatus described in a previous paper [4]. To investigate the effect of additives, a volume ratio of 2.5 vol.% of FAS to the total amount of the sol was added prior to the addition of the tenside

and the dye and stirring was continued overnight. UV irradiation for the evaluation of photostability was carried out in a Heraeus SUNTEST CPS device with an output of 60 mW/cm². The abrasion resistance is expressed by scratch hardness of the coating. It was defined as the load needed to create visible scratches in the sample surface while scratching it with a Vicker's diamond.

3. Results and Discussion

By use of GPTMS, BPA and MI as starting precursors and SO as photochromic dye, coatings with a thickness of about 10 μm were obtained for the investigations of the photochromic and mechanical properties. Figure 1 depicts the change of the photochromic intensity, ΔA_0 , as a function of densification temperature.

The decrease in ΔA_0 with increasing temperature is due to the increasing rigidity of the matrix, more and more significantly prohibiting the structural changes of the dye molecules. The figure also shows that ΔA_0 can be enhanced by about 10% by FAS (2.5 vol.%). This is probably due to the hydrophobic environment created by FAS surrounding the dye molecules and the enhancement in matrix flexibility by the long alkyl chain of FAS. Figure 2 shows the effect of densification temperature on the abrasion resistance of the coatings with and without FAS, respectively. This figure demonstrates not only the improvement in scratch hardness with increasing temperature but also the enhancement in scratch hardness by the use of FAS.

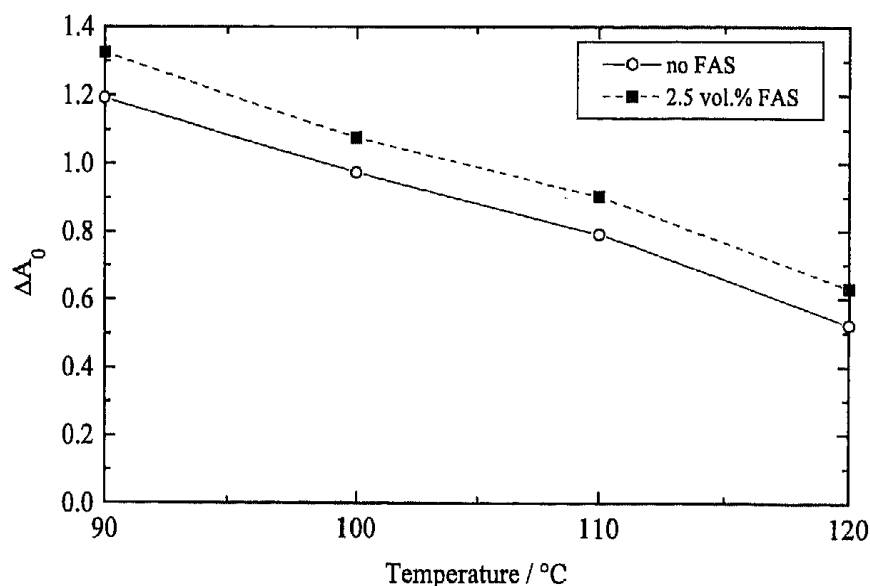


Figure 1. Effect of densification temperature on ΔA_0 in the coatings with and without FAS.

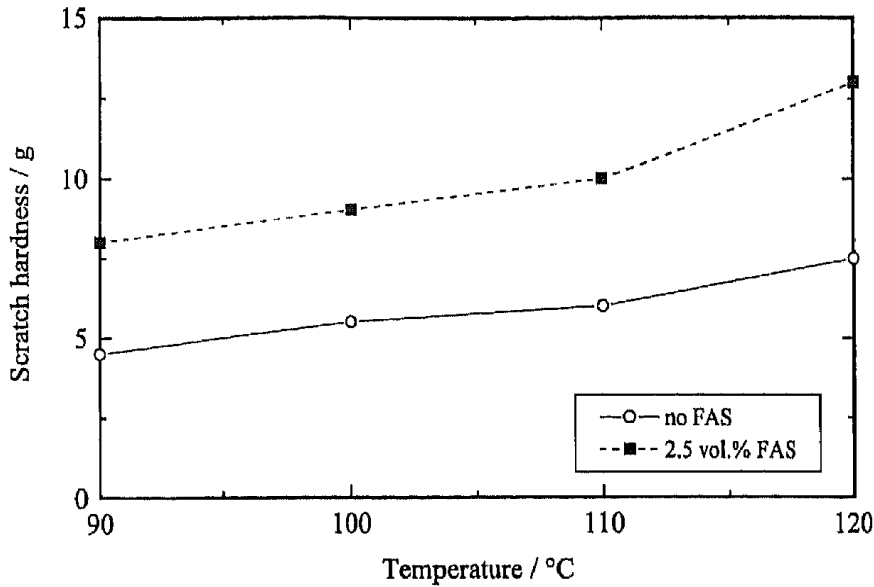


Figure 2. Effect of densification temperature on abrasion resistance of the coatings with and without FAS.

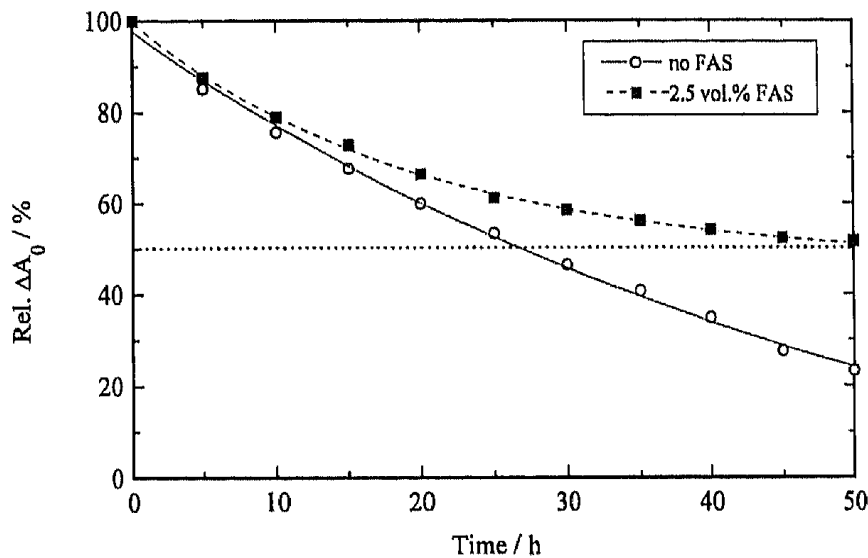


Figure 3. Effect of UV irradiation time (suntest) on ΔA_0 of the coatings with and without FAS and densified at 110°C.

To evaluate the photochemical stability the remaining photochromic intensity after certain time intervals of UV irradiation is measured and compared with the initial value. Table 1 shows the time required for the photochromic intensity of the samples with and without FAS to drop to half of its initial value. From this table and Fig. 3, which depicts the effect of UV irradiation time on ΔA_0 of the coatings densified at 110°C, it can be seen that the photostability is greatly improved by the addition of FAS, too.

An overall conclusion that can be drawn from the table and figures is that a compromise has to be made between maximum photochromic intensity, photostability and mechanical strength. While the samples densified at 90°C show higher photochromic intensity, the

abrasion resistance is better at higher densification temperatures. An optimum densification temperature is found to be 110°C. Although the higher rigidity of the matrix heated at this temperature hinders the structural

Table 1. Time length required for ΔA_0 of the coatings with and without FAS and densified at various temperatures to drop to 50% of the initial value.

	No FAS	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

change of the dye molecules to a certain extent, its better protection effect on the dye molecules leads to a great enhancement in the photochemical stability in addition to improvement in mechanical properties. The loss in photostability at densification temperatures higher than 110°C may be explained by two facts. First, the increased matrix rigidity blocks more and more dye molecules and prevents their photochromic reaction and second, it is possible that part of the dye molecules may be already decomposed at those temperatures. In this way less dye molecules are available to achieve a high photostability.

4. Conclusions

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

With FAS as an additive, photochromic coatings densified at 110°C show acceptable photochromic intensity along with good photochemical stability and improved mechanical strength. This lays a solid foundation for further research work on possible practical applications.

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