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A Study on the Photostability of Photochromic Fabrics from Hybrid Organosilica Coatings

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ABSTRACT

Photochromic fabrics were prepared using a coating solution containing photochromic dyes and silica sol-gel. The photochromic effect was rapid. The effect of three different post treatments on the optical and durability of the photochromic fabrics was evaluated. These included incorporating a UV stabilizer, increasing the surface hydrophobicity by fluorinating the pores, and blockading the dye-containing pores with additional silica coating. All the treatments improved photostability, without significantly affecting response/fading speeds.

INTRODUCTION

Photochromism is a color changing response to light stimulus, resultant from structural transformation in the dye molecule. It has been used in developing optical devices such as sensors, shutters, and switches. It could have novel applications in UV protecting, environment-sensing, and fashionable color-changing clothing. We previously produced a hybrid organosilica coating with encapsulated photochromic dye via the sol-gel method [1]. Although the optical performance response was very fast, the photochromic fabric showed low photostability. The following processes were assessed for this purpose: adding UV stabilizer, increasing surface hydrophobicity by incorporation of fluorine, and blockading the dye-encapsulating pores with addition coating layer.

APPROACH

Silica sols were prepared by mixing tetraacetoxysilane (TAS), alkyltriethoxysilane (RSi) and ethanol, stirring vigorously until TAS was dissolved. Water was subsequently added at a 1 ml/h rate and the mixture was stirred for 24 hours. The molar ratio of TAS: RSi: H₂O: EtOH was 1:32:100:320. Alkyltriethoxysilanes included octyltriethoxysilane (OTES) and phenyltriethoxysilane (PhTES), used in a 1:2 (mol/mol) combination, respectively. To incorporate photo stabilizers, a photochromic dye-ethanol solution containing stabilizer was mixed with the synthesized sol-gel solution. Wool fabric was dip-coated with the coating solution, air-dried and cured at 110 °C. To adjust the wettability of the coating, FAS was added to the silane combination at the beginning of synthesis (before adding water). To seal off the dye-containing pores, a second layer of sol containing no dyes was applied after air-drying the first layer.

RESULTS AND DISCUSSION

The typical structure of the Spirooxazine class of photochromic dyes and its ring-opening reaction with UV stimulation are shown in Figure I.

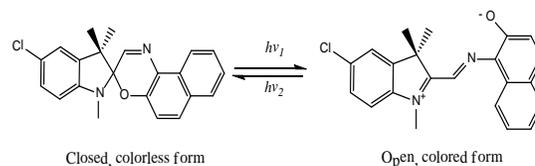


FIGURE I. Structure and photochromic reaction of spirooxazine

Figure II (a) shows the absorption spectra of the control sample in the presence and absence of UV radiation. Figure II (b) illustrates the ascent and descent of absorption with time as UV light was turned on and off. The time required for absorbance to rise and subsequently fall to half of its maxima, indicated as $t_{1/2}$ and $t'_{1/2}$, were calculated to signify the response and fading speeds of photochromic coatings.

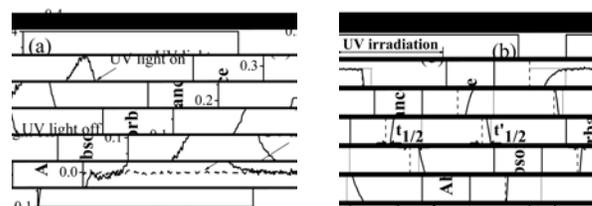


FIGURE II. a) Absorption spectra and, (b) colouration-decolouration curve of the control sample.

TABLE I. Coating descriptions

	Name	Constituents
	Control	OTES:PhTES 1:2 sol + dye
Adding UV stabilizer	UV-1084	O:P 1:2 sol + UV-1084 + dye
	HALS-622	O:P 1:2 sol + HALS-622 + dye
	Tinuvin 329	O:P 1:2 sol + Tinuvin 329 + dye
	HMBP	O:P 1:2 sol + HMBP + dye
Fluorination	FAS	O:P 1:2 + FAS sol + dye
Dbl. coating with extra silica	APS	1 st layer O:P 1:2 sol + dye 2 nd layer APS sol only
	MPS	1 st layer O:P 1:2 sol + dye 2 nd layer MPS sol only
	Same silica	1 st layer O:P 1:2 sol + dye 2 nd layer O:P 1:2 sol only

UV-1084: 2,2'-thiobis(4-tert-octylphenolato)-Nbutylamine nickel (II), HMBP: 2-hydroxy-4-methoxy-benzophenone, Tinuvin 329: 2-(2Hbenzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol, HALS-622: poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidine) ethanol-alt-1,4-butanedioic acid, FAS: Tridecafluorooctyltriethoxysilane, APS: (3-Aminopropyl)triethoxysilane; MPS: 3-(Trimethoxysilyl)propyl methacrylate

Coating descriptions are given in Table I, and full names of additives are listed below the table. The optical

properties of the coatings, namely, differential absorption at maximum ($\lambda \approx 620$ nm) or $\Delta A_{max} = A_{light} - A_{dark}$, photostability, and response/fading half-life times, $t_{1/2}$ and $t'_{1/2}$ are presented in Table II.

TABLE II. Optical properties

Coating	ΔA_{max}	Photo-stability (h)	Response/Fading (s)	
			$t_{1/2}$	$t'_{1/2}$
Control	0.32±0.01	9.5	1.6±0.1	3.3±0.1
UV-1084	0.32	47.5	1.7	3.9
HALS-622	0.24±0.09	13.5±3	2.1±0.1	3.7±0.5
Tinuvin-329	0.13±0.05	23±1.5	2.1±0.3	3.5±0.3
HMBP	0.19±0.02	12.7±2.6	2.1±0.4	3.7±0.2
FAS	0.34±0.02	11.9±1.6	2±0.2	3.9±0.2
APS	0.19±0.01	44.3	1.1±0.3	2.1±0.2
MPS	0.3±0.02	19±2.6	1.6±0.3	2.5±0.2
Dbl. SS*	0.42±0.003	12.7±1.5	2.1±0.2	4.3±0.3

Photochromic dye: RSi 1:100 (mol/mol); UV stabilizer: photochromic dye 1:1; * Dbl. SS: Double-coating with same silica

All the treatments improved the photo-lifetime of the coating. The incorporation of UV-1084 produced the best results, followed by double-coating with APS sol-gel. A comparison of the optical data of these two treatments with that of the control indicates that double-coating with APS reduced ΔA_{max} , and increased fading speed, while UV-1084 affected neither attributes. Among the UV stabilizers, the quencher UV-1084, was the most effective, followed by UV absorber Tinuvin-329, free radical scavenger HALS-622, and UV absorber HMBP. As expected, both Tinuvin-329 and HMBP as UV absorbers reduced ΔA_{max} , although without significantly retarding response and fading rates.

TABLE II. Durability

Coating	A.D.	W.F.	G		Q		C.A.
			warp	weft	warp	weft	
Control	83.3±5	60.85±1.6	85.01	21.4	2.03	0.51	137.6±7.8
UV1084	87.8	75.1	106.5	16.7	2.3	0.4	142.9±5
HALS622	88.1±2	58.5±8.3	148.6	29.1	3.7	0.7	143.7±7.2
Tin.329	81.7±3.9	62.8±9.2	106.6	21.01	2.7	0.5	143.03±6.3
HMBP	81.3±4.7	53.6±6.8	102	19.1	2.2	0.4	139.1±6.3
FAS	74±3.4	53.35±8	97.6	20.5	2.9	0.6	141.6±3.2
APS	93.8±4.5	55.35±5.9	12421	1618	444	57.8	138.9±6.3
MPS	75.5±15	44.75±11	168.2	27.7	4.7	0.8	141.5±6.4
2x SS*	92.1±1.9	58.75±4.3	287.8	31.5	12.6	10.6	138±6.9

A. D.: Abrasion Durability (%); W. F.: Wash Fastness (%); G: Flexural Rigidity (mg.cm); Q: Bending Modulus (kg/cm²); C.A.: Contact Angle (°)

The quencher type of UV-stabilizer (e.g. UV-1084) is thought to protect the dye by capturing and disposing of its energy in the excited state. UV absorbers (e.g. Tinuvin-329 and HMBP) prevent the dye's degradation by absorbing the UV irradiation and thus, minimizing the amount of radiation available to excite the dye. This predictably leads to reduced photochromic activity, as observed in Table II. The free radical scavenger type (e.g.

HALS-622, a Hindered Amine Light Stabilizer) protects the dye by disposing of the degrading free oxygen radicals, which react with the dye in its excited state.

FAS enriches the pores with fluorine, reducing the surface energy and thus, preventing degrading elements such as water from reaching the dye [2].

A positive effect on photostability was observed from sealing the pores with additional silica coating. This effect was less pronounced in the case of double-coating with the same silica, and more in the case of APS and MPS. In other words, APS and MPS coupling agents proved more effective in creating a protective, less permeable layer than the OTES/PhTES sol-gel.

The durability data of the coatings is given in Table III. Although some of the treatments decreased the durability to abrasion, the overall level was satisfactory, with APS showing the highest abrasion durability. Durability to washing was lower, with UV-1084 exhibiting the highest wash fastness. The stiffness induced by APS was notable, indicated by the significantly increased flexural rigidity and bending modulus. The contact angle data confirmed that all treatments induced hydrophobicity.

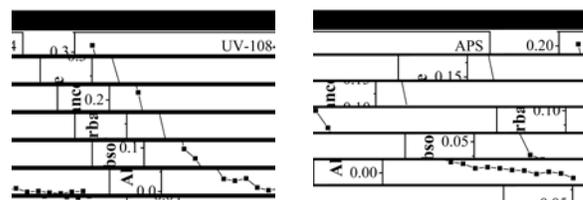


FIGURE III. Loss of photochromic effect with exposure time for UV-1084 and APS

Figure III illustrates the loss of photochromic effect with time for UV-1084 and APS coatings. The slope of the graph varied for different cycles. In both graphs, the absorbance dropped with a rate of 0.03 in the first cycle (3.2 hours). This was followed by a 0.04 and 0.01 drop in the following cycle for UV-1084 and APS, respectively. Generally, the loss of photochromic effect was most rapid in the first few cycles of irradiation.

CONCLUSIONS

A photochromic organic-inorganic silica coating on fabric with fast response and reasonable durability was produced. The effect of three types of treatments, namely, incorporating UV stabilizers, modifying wettability, and adding an extra silica layer, on the coating property was examined. The highest photostability was obtained by incorporation of a quencher UV stabilizer. The addition of an extra layer of APS sol-gel was the next most effective treatment in terms of photostability, although it lowered maximum absorbance and increased coating rigidity.

REFERENCES

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