Interaction of a spirooxazine dye with latex and its photochromic efficiency on cellulosic paper

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ABSTRACT

Spirooxazine (SO) is a class of important photochromic dyes for many applications, such as anti-counterfeiting printing, reversible memory photo devices and optical switching elements in molecular electronics. Since these dyes are expensive, improving their coloration efficiency in response to photo stimuli is of practical importance. In this study, a spirooxazine dye, 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphtha[2,1-b][1,4]oxazine], was dispersed into the substrate of a polystyrene acrylic latex emulsion to obtain a stable photochromic dye loaded latex. The photochromic latex was then applied on cellulose paper, and its coloration efficiency was significantly higher than the control (without the latex). Transmission electron microscope (TEM) observation revealed that the spirooxazine dye was well dispersed into the matrix of the latex particles, which functioned as a carrier/dispersant for the photochromic dye. Other results, including color stability, and fatigue resistance, were also discussed.

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1. Introduction

In the past decade, photochromic dyes have attracted considerable attention (Ercole, Davis, & Evans, 2010; Nigel, Partington, & Towns, 2009; Paramonov, Lokshin, & Fedorova, 2011). Spirooxazine (SO) is a well-known photochromic dye that turns blue upon irradiation with UV light, and rapidly returns to colorless state when the UV irradiation ceases. SO has good fatigue resistance and can have a wide range of applications, such as optical memory (Andersson, Robinson, & Berggren, 2005), color-changing textiles (Little & Christie, 2010), optical switches (Nunzio, Gentili, Romani, & Favaro, 2010), photo-sensitive paper coating (Pardo, Zayat, & Levy, 2009), inkjet printing, security and authentication.

However, SO is insoluble in water and there has been a strong interest in improving the water solubility of SO, for example, by introducing hydrophilic groups, which may lead to an increase in its color changing efficiency upon photo-irradiation (Chu, 2003; Billah, Christie, & Sharney, 2012). It was reported that hydrophilic groups can be introduced to SO structures by grafting (Chu, 2003). Billah et al. (2012) applied two isomeric water-soluble spirooxazine-based photochromic acid dyes to wool, and obtained positive results, which were largely due to increased SO uptake. The development of other potential methods to improve the coloration efficiency of these photochromic dyes would be of practical interest.

The coloration and de-coloration of SO are affected by both the physical and chemical conditions (Cheng, Lin, Brady, & Wang, 2008). One effective method to avoid SO aggregation and improve its stability, thus its photochromic efficiency, is to incorporate SO molecules into polymer matrices by binding them covalently to polymer backbones (Lee, 1999), or dissolving or suspending them in polymer solids (doping) (Bahajaj, Asiri, Alsoliemy, & Al-Sehemi, 2009), or by encapsulating SO in sol–gel matrices (Nishikiori, Tanaka, Takagi, & Fujii, 2007). Fu, Sun, Chen, and Yuan (2008) prepared a water-soluble photochromic polymer by grafting copolymerization of 9′-allyloxyindolinospiro-naphthoxazine onto carboxymethyl chitin. The resulting polymer had both good water solubility and superior photochromic characteristics.

Novel engineering technologies play significant role in functional modification for engineered fibers/papers. For example, nano-coated cellulosic paper exhibited electrical conductivity or thermosetting property (Jopson, 2008), the use of different fillers can impart cellulosic paper with unique functions, such as magnetic, antibacterial and deodorizing properties (Shen, Song, Qian, & Ni, 2011). Notably, the security paper, e.g. currency paper, can be made by using chemical or physical modifications, such as coating (Altaf, Adel, Houssni, & Mohamed, 2011).

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In this study, polystyrene acrylic based latex was used as the carrier/dispersant for SO to improve its solubility/dispersability in an aqueous system. An SO photochromic dye, 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphtha[2,1-b][1,4]oxazine], (SO) was first dissolved in acetone and then dispersed into a polystyrene acrylic latex emulsion. The obtained latex-dispersed SO was miscible with water, which was then applied to cellulosic paper by impregnation, and the photochromic efficiency was evaluated in terms of light absorption increase in the visible light range upon UV irradiation. The distribution of SO on latex particles was examined based on transmission electron microscope (TEM) technique.

2. Experimental

2.1. Materials

The spirooxazine (SO) photochromic dye, 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphtha[2,1-b][1,4]oxazine], was purchased from Sigma Aldrich. Polystyrene acrylic latex (solid content 50%, 210 cP) was purchased from Dow Chemical. All other reagents were analytical grades from Sigma Aldrich, and were used without further purification.

2.2. Methods

To prepare the latex-dispersed SO sample, SO was first dissolved in acetone at desired concentration at room temperature in an ultrasonic bath. The SO/acetone solution was then added into a latex dispersion drop by drop, under intensive mixing with an IKA digital Ultra-Turrax homogenizer operated at 15,000 rpm. The temperature was maintained at 0 °C by using an ice/water bath. Upon the completion of adding SO/acetone, the mixing speed was increased to 20,000 rpm, and the mixing was continued for another 30 min, followed by 15 min of ultrasonic degassing to remove air from the dispersion.

To prepare paper strips treated with latex-dispersed SO or SO dissolved in acetone (acetone-dissolved SO), filter paper strips (Waterman No.1006-110) were immersed into the prepared acetone-dissolved SO or latex-dispersed SO solutions, and treated with ultrasound for 15 min to ensure uniform impregnation. The impregnated paper strips were air-dried under a fume hood at room temperature.

The paper strips treated with acetone-dissolved SO or latex-dispersed SO were exposed to UV irradiation for 5 min in a photo reactor with 8 mini UV lamps (360 nominal wavelength and 2.7 mW/cm^2) (He & Ni, 2009), and then tested on a Technidyne TB-1 C spectrophotometer for the diffuse reflectivity of red light (R_X), green light (R_Y) and blue light (R_Z). The light absorption coefficient was calculated from the reflectance data according to the following Kubelka- Munk equation (Eqs. (1) and (2)).

$$\frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{1}$$

$$sw = \frac{1}{\left(1/R_\infty - R_\infty\right)} \ln \left(\frac{\left(1 - RR_\infty\right)\left(R_\infty - R_g\right)}{\left(1 - R_g R_\infty\right)\left(R_\infty - R\right)} \right) \tag{2}$$

where k is the light absorption coefficient, m^2/kg; s is the light scattering coefficient, m^2/kg; R_∞ is the diffusive reflectance; R_g is the background reflectance; w is the paper sheet grammage, g/m^2.

The paper strips treated with acetone-dissolved SO or latex-dispersed SO were gold coated and examined on a JEOL 6400 scanning electron microscope (SEM) by following earlier procedure (Wang, Ni, Jahan, Liu, & Schafer, 2011; Zaman, Xiao, Chibante, & Ni,

2012). For comparison, the original (untreated) paper sample was also examined by SEM under the same conditions.

For transmission electron microscopy (TEM) analysis, a small volume of the latex-dispersed SO solution (about10 μL) was transferred to a carbon-coated copper grid using a micropipette and the grid was dried in the air at room temperature overnight. The TEM observation was then taken on a JEOL 2010 transmission electron microscope with 200 kV acceleration voltages. Elemental analyses in combination with TEM were also conducted on the SO/latex particles.

To examine the effect of solvents on the photochromic behavior of SO, SO solutions of 350 mg/L concentration were prepared by dissolving SO in different organic solvents. The light absorbance of the SO solutions was measured on a UV-Vis spectrophotometer (Milton Roy Spectronic 1001 Plus) at 360 nm before UV irradiation, and at 600 nm immediately after UV irradiation for 5 min.

3. Results and discussion

3.1. Photochromic efficiency of the latex-dispersed SO in paper

The photochromic efficiency of SO in paper was improved significantly when it was loaded on latex. Intensive photo coloration of the paper was obtained even at low SO concentration in paper (2 mg/g). Fig. 1 compares the photo coloration efficiency of the paper strips treated with the acetone-dissolved SO or latex-dispersed SO. The color of the paper strips changed from essentially colorless to blue upon UV irradiation. It can be seen that the color intensity of the paper strips treated with the latex-dispersed SO was much higher than that treated with the acetone-dissolved SO
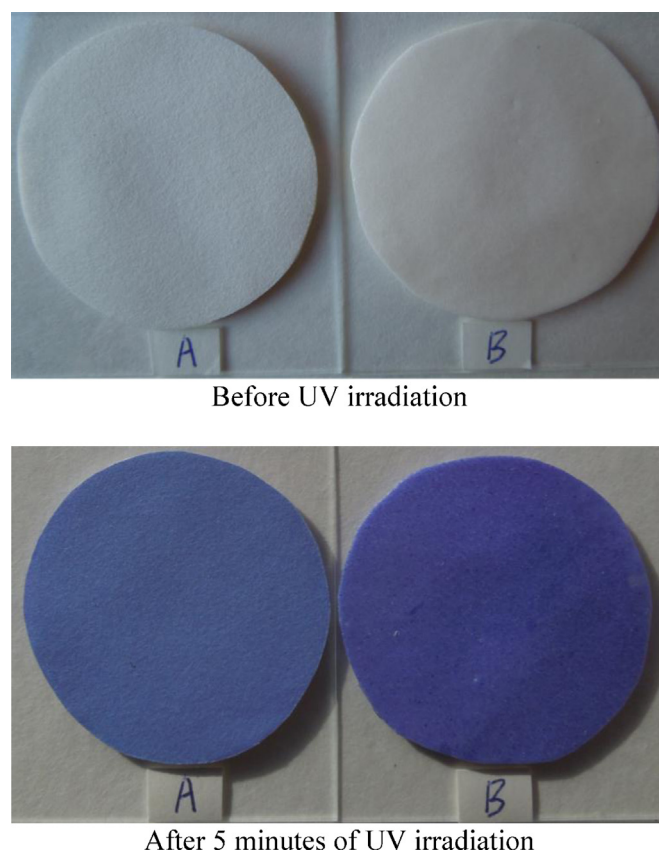

Before UV irradiation

After 5 minutes of UV irradiation

Fig. 1. Photochromic coloration of paper treated with acetone-dissolved SO (A) and latex-dispersed SO (B) (SO load of 2 mg SO/g paper in both cases; irradiation time of 5 min; UV lamps parameter: 360 nm of the nominal wavelength and UV lamps intensity of 2.7 mW/cm^2).
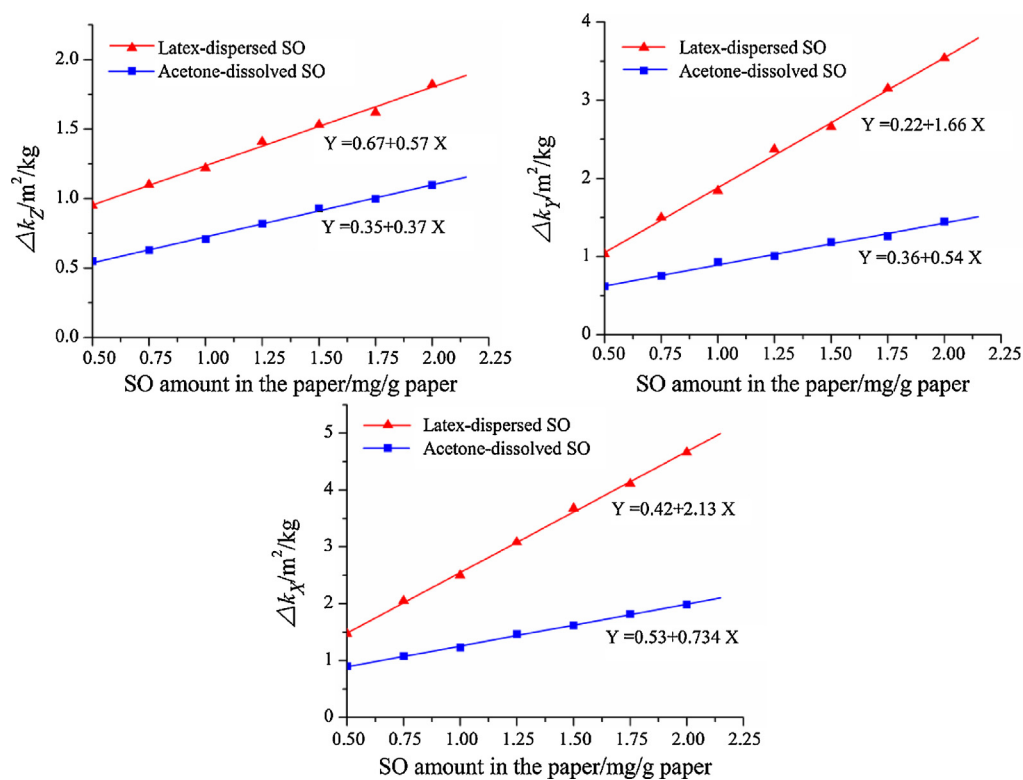
Fig. 2. Effect of SO load in paper on the change of the light absorption coefficient (Δk) in the red, green, and blue light ranges upon UV irradiation (Irradiation time of 5 min; UV lamps parameter: 360 nm of the nominal wavelength and UV lamps intensity of 2.7 mW/cm^2).
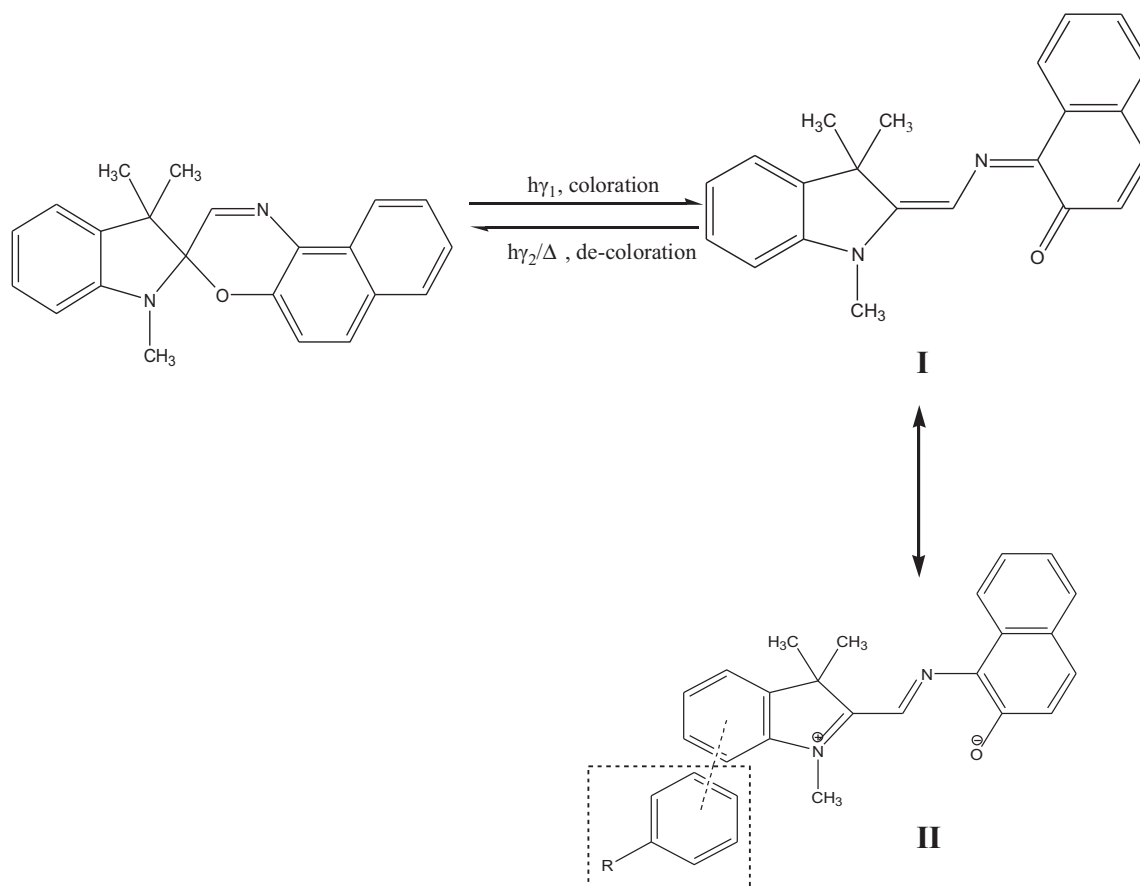

Fig. 3. The SO photochromic process (Harada et al., 2010; Patel et al., 2010; Tsuzuli, 2005).
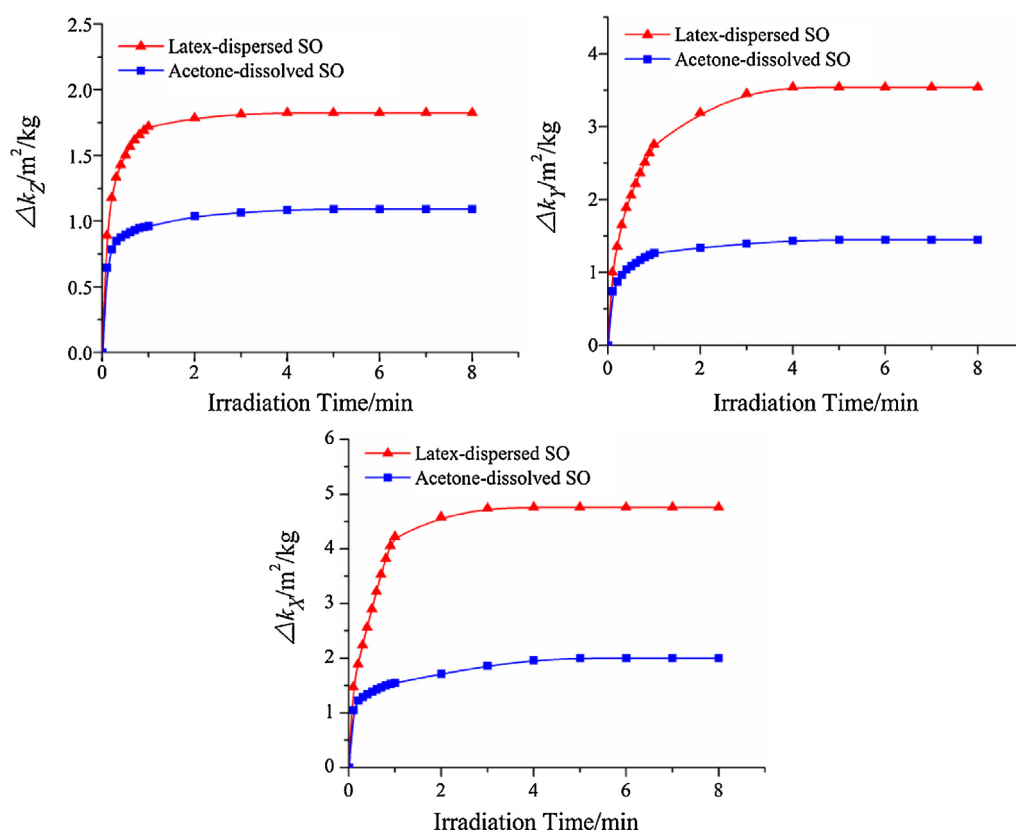
Fig. 4. Coloration of the paper treated with latex-dispersed SO or acetone-dissolved SO during the UV irradiation (SO load of 2 mg SO/g paper in all cases; UV lamps parameter: 360 nm of the nominal wavelength and UV lamps intensity of 2.7 mW/cm^2).

Table 1
Differential diffusive reflectance before and after UV irradiation ($\Delta R = R_{after} - R_{before}$).

	ΔR_X	ΔR_Y	ΔR_Z
Paper treated with latex-dispersed SO	−74.4	−70.0	−54.6
Paper treated with acetone-dissolved SO	−63.6	−57.9	−34.4

Note: SO load in paper was 2 mg/g in all cases; Irradiation time was 5 min under the condition of the nominal wavelength of 360 nm and 2.7 mW/cm^2 UV lamps.

after 5 min of UV irradiation, although the SO load was the same in both cases.

Shown in Table 1 are the Differential diffusive reflectance of the paper strips before and after UV irradiation in the red light (ΔR_X, $\lambda_{max} = 700$ nm), green light (ΔR_Y, $\lambda_{max} = 541.6$ nm) and blue light (ΔR_Z, $\lambda_{max} = 435.8$ nm). It is evident that the paper treated with the latex-dispersed SO had higher ΔR_X than those of the paper treated with the acetone-dissolved SO, in particular, ΔR_Z (for the blue color), under the conditions studied.

The color intensity of the paper can be better described by the light absorption coefficient that can be calculated from the data of the diffusive reflectance based on the well-known Kubelka- Munk theory. The higher the light absorption coefficient, the higher the concentration of the colored substances in the paper. Therefore, the photochromic coloration efficiency of the SO in the paper strips can be evaluated by the increase of the light absorption coefficient. In Fig. 2, the differential light absorption coefficients (Δk) before and after UV irradiation of the paper treated with the latex-dispersed SO or acetone-dissolved SO are plotted against the SO load in paper ($\Delta k = k_{after} - k_{before}$). It can be seen that the differential light absorption coefficients increased almost linearly with increasing SO load in the paper for both systems.

The Δk was much larger for paper treated with the latex-dispersed SO than that treated with the acetone-dissolved SO at a given SO load in the paper (Fig. 2). For example, to obtain Δk blue light of 1.1 (m^2/kg), the SO load in paper can be decreased from 2.00 to 0.758 mg/g. Thus if the latex-dispersed SO, instead of the acetone-dissolved SO, was used for the cellulosic paper, about 62% reduction of the SO dosage can be achieved. Similar results can be obtained when the calculation is based on the green light absorption coefficients. Based on the above results, it can be concluded that the latex-dispersed SO had higher photochromic efficiency than the acetone-dissolved SO.

3.2. Coloration and de-coloration processes of the SO impregnated paper

The observed higher photochromic efficiency of the latex-dispersed SO may be associated with the effect of the surrounding environment on the coloration and de-coloration process of the SO molecules. It is generally believed that the coloration and de-coloration reactions are reversible; they are in equilibrium under a given condition, and the concentration of the colorless and colored SO isomers in the system are determined by the ratio of the rate constants of the coloration and de-coloration reactions (Feczkó, Varga o. Kovács, Vidóczy, & Voncina, 2011; Harada, Kawazoe, & Keiichiro, 2010), as shown in Fig. 3. During the UV radiation process, both the ring opening and closing (coloration and de-coloration) reactions are taking place simultaneously, and the concentrations of SO in the open and closed forms are in equilibrium once a steady state is reached in the system. This equilibrium is determined by both the physical and chemical environment (Cheng et al., 2008). In different media the equilibrium concentration of the colored SO isomer species can vary greatly, even when other conditions,
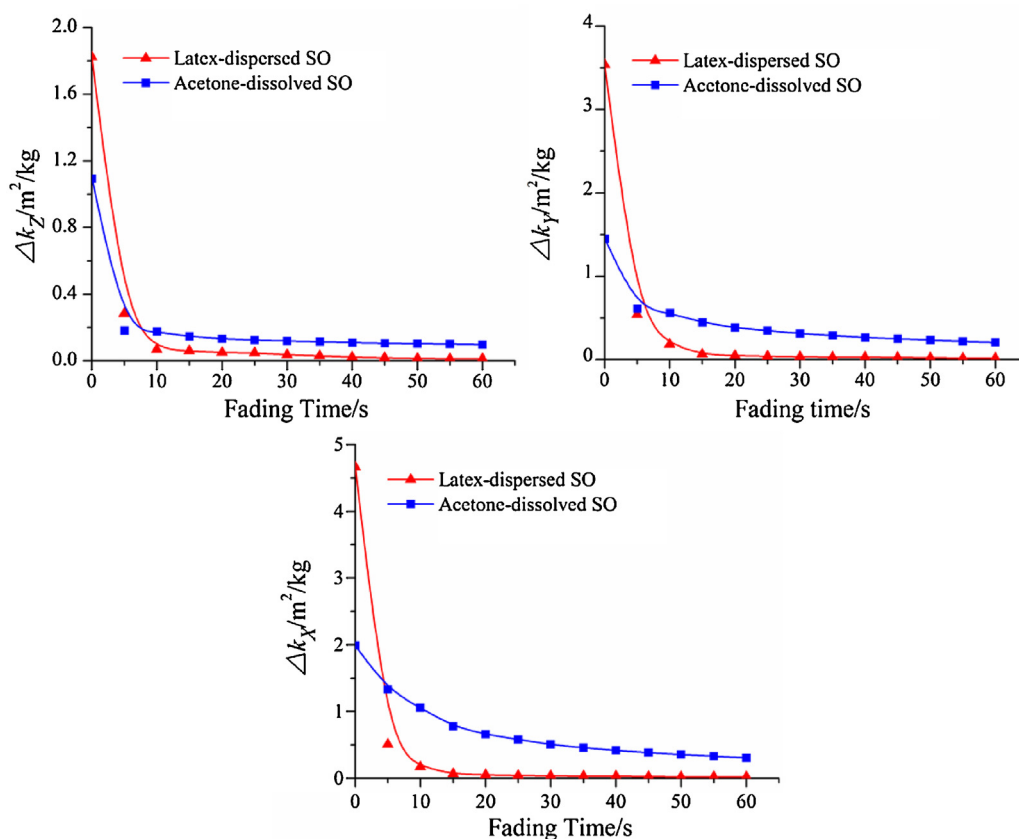
Fig. 5. De-coloration of the paper treated with latex-dispersed SO or acetone-dissolved SO after the termination of UV irradiation (SO load of 2 mg SO/g paper in all cases; Irradiation time of 5 min; UV lamps parameter: 360 nm of the nominal wavelength and UV lamps intensity of 2.7 mW/cm^2).

such as the total SO load, temperature, irradiation intensity of UV light and visible light are constant. Feczkó et al. (2011) reported that SO in PMMA polymer matrix had significantly higher light absorbance than in acetonitrile at 600 nm after UV irradiation, and they attributed this difference to the change of the rate constants of the ring opening and closing reactions in these two systems. They found that both the SO coloration and de-coloration processes slowed down significantly in PMMA polymer nano-capsules than those in acetonitrile. However, the rate constant of the ring closing reaction was more affected by the change of the medium, compared with the ring opening rate constant. Therefore, the relative equilibrium concentration of the colored SO isomer was higher in PMMA than it was in acetonitrile.

Fig. 4 shows the color development of the paper samples upon UV irradiation, in terms of light absorption coefficient changes (Δk) versus UV exposure time in blue, red and green light ranges. It can be seen that the light absorption in blue, red and green had rapid increase initially and then reached a plateau, for both the latex-dispersed SO and acetone-dissolved SO treated paper samples.

As the UV irradiation was stopped, the color of the paper samples started to fade away. As shown in Fig. 5, the de-coloration process of the latex-dispersed SO treated paper was markedly faster than that for the acetone-dissolved SO treated paper. The half life time of de-coloration (expressed as Δk) was about 5 s for the latex-dispersed SO treated paper and about 20 s for the acetone-dissolved SO treated paper. The flexibility of the latex matrix likely contributed to the faster de-coloration of the SO. It is known that polystyrene acrylic latex film is a much more flexible material than cellulose fibers, and it has been reported that SO in a more flexible polymer matrix had faster de-coloration (Feczkó et al., 2011).

The faster de-coloration rate of the latex-dispersed SO in paper suggested that the observed darker color under UV radiation cannot be explained simply by the rate constants of the coloration and de-coloration processes. The equilibrium concentration of the colored SO isomer in the latex-dispersed system must be higher than that in the acetone-dissolved SO system and it may be affected by the other factors, including the chemical interaction of the SO molecules with the medium.

3.3. SO distribution on fiber surface

Latex can be a good dispersant (Ström, Hornatowska, Xiao, & Terasaki, 2010) and emulsifier (Khorassani, Afshar-Taromi, & Pourmahdian, 2010), as well as an adhesive (Kan, Keefe, Olesen, & Saucier, 2011), binder (Lundqvist, Odberg, & Berg, 1995; Shen et al., 2011) and a reinforcing agent (Ramos-Fernández et al., 2012) in many applications. In the preparation of latex-dispersed SO, SO was well dispersed under high shear mixing, and the latex particles functioned as carriers/dispersants for these SO particles. As shown in the TEM pictures in Fig. 6, the latex particles were surrounded with many smaller particles that were confirmed to be SO, based on the nitrogen elemental mapping analyses. After evaporation, a latex film was formed, and the SO particles were well dispersed in the film to give a uniform SO distribution in the polystyrene acrylic matrix (Fig. 6).

In contrast, for the paper treated with acetone-dissolved SO, larger SO aggregates were formed on fiber surface after acetone was evaporated, due to the hydrophobic nature of SO and the hydrophilic nature of cellulose. As shown in Fig. 7, the SO particles of 500–3000 nm size can be found on the fiber surface, which was about 100 times larger than those SO particles found in the styrene
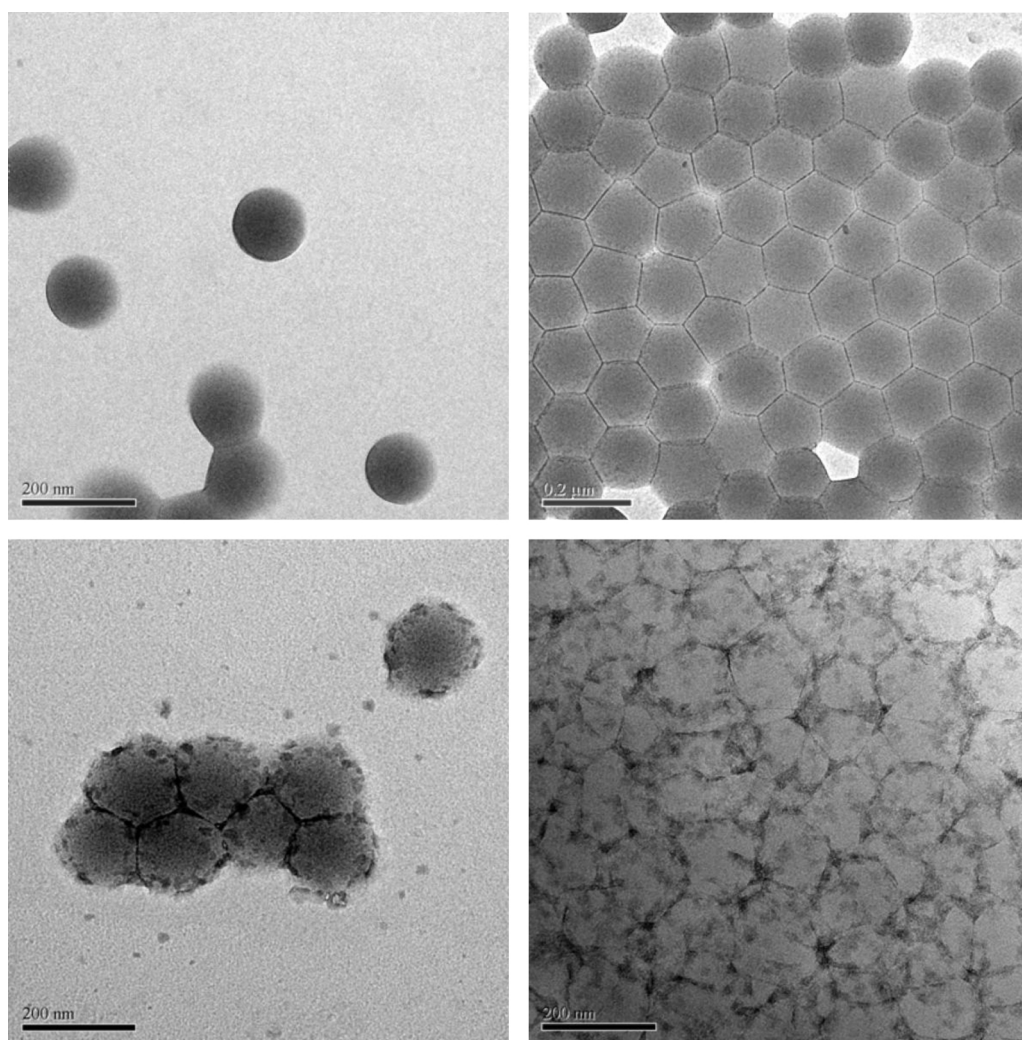
Fig. 6. TEM pictures of latex particles and film (top) and latex-dispersed SO particles and film (bottom) (Latex concentration: latex/water = 1/1; SO concentration: SO/dry latex = 10 mg/5 g).

acrylic latex film (Fig. 6). The SO particles in the paper treated with the latex-dispersed SO were too small to be seen in the SEM pictures (Fig. 7), but the smoother fiber surface confirmed the presence of a latex film coating.

The much smaller particle size and more uniform distribution of SO in the latex-dispersed SO system provided more surface area for the SO molecules to receive and utilize the photon energy during the UV irradiation, so that the SO photochromic process is more effective. The effect of the polystyrene acrylic latex on the photochromic efficiency of SO may be similar to the effect of cellulose on the brightening efficiency of optical brightening agents (OBAs) or fluorescent whitening agents (FWAs) (Zhang et al., 2011; Zhang, Hui, & Ni, 2010). OBAs can have higher fluorescent brightening efficiency when absorbing onto cellulose fibers (He, Hui, Liu, Ni, & Zhou, 2010; Liu et al., 2012).
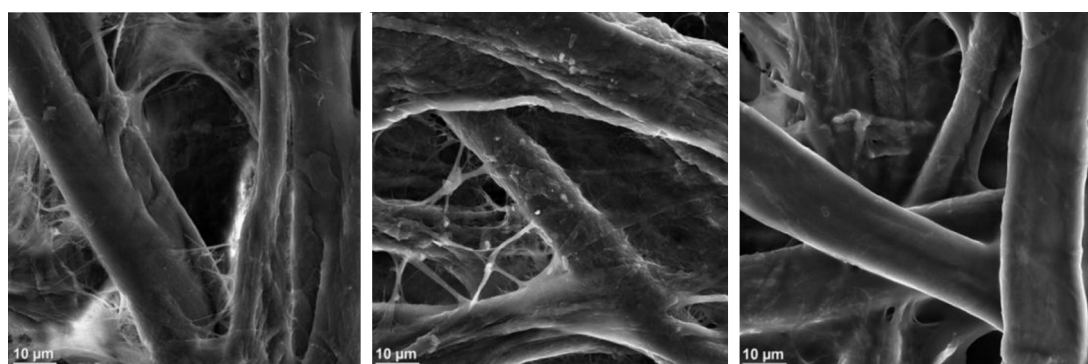

Fig. 7. SEM pictures of the original paper (left), paper treated with acetone-dissolved SO (middle) and paper treated with latex-dispersed SO (right) (Waterman No. 1006-110 filter papers; SO load of 2 mg SO/g paper in all cases).

Table 2
Effect of solvent on the absorbance of SO solutions.

Solvent	Absorbance at 360 nm without UV irradiation	Absorbance at 600 nm with UV irradiation
Acetone	1.703	0.050
Methanol	1.705	0.055
Toluene	1.700	0.098
Benzene	1.699	0.089
Styrene	1.702	0.087

Note: SO solutions concentrations were 350 mg/L in all cases; Irradiation time was 5 min under the condition of the nominal wavelength of 360 nm and 2.7 mW/cm^2 UV lamps.

3.4. Chemical interaction of SO and latex

Another factor that might also contribute to the observed higher photochromic efficiency of the latex-dispersed SO in paper is the chemical interaction of the SO molecules with the polymer matrix. It has been reported in the literature that solvents can have a significant effect on the coloring and de-coloring behaviors of photochromic agents (Chibisov, Marevtsev, & Görner, 2003; Castro, Gómez, Cossi, & Reguero, 2012). To confirm the effect of solvent on the photochromic behavior of the SO, different solvents were used to prepare SO solutions at the same concentration (350 mg/L). The SO solution had a characteristic absorption peak at about 360 nm before UV irradiation and at about 600 nm after UV irradiation, which is in agreement with those reported in the literature (Gaeva et al., 2007; Sai, Lüer, Polli, Garbugli, & Lanzani, 2011). As shown in Table 2, the SO solutions in toluene, benzene or styrene as the solvent had a significantly higher absorbance at 600 nm with UV irradiation, compared with those in acetone or methanol as the solvent. These results suggest that solvents with an aromatic ring structure can enhance the coloration of SO, or in other words

increase the concentration of the colored open-(merocyanine) form of SO isomer species in the system under UV irradiation at the steady state.

For the paper treated with the latex-dispersed SO, the polystyrene acrylic latex and SO may form a solid solution, wherein the polystyrene acrylic latex functioned as a solvent to interact with SO.

The merocyanine form of SO has two resonance structures (I, II, Fig. 3). In the presence of polystyrene acrylic latex or benzene ring containing solvent, the chemical interaction may occur between the aromatic ring of the solvent or latex with SO molecules via the π-π interaction (Patel et al., 2010; Tsuzuki, 2005; Tewari & Dubey, 2008), therefore stabilizing the merocyanine structures, resulting in the formation of more colored merocyanine isomers.

3.5. Fatigue resistance of the SO in paper

Fatigue is the loss of photochromic properties upon prolonged exposure to UV irradiation. Fatigue resistance is an important parameter of photochromic materials for outdoor applications. Continuous UV irradiation is a commonly used technique to study the fatigue resistance of photochromic materials. In the current study, the paper samples treated with the latex-dispersed SO or acetone-dissolved SO were exposed continuously to UV radiation in a photo reactor (2.7 mW/cm^2 and 350 nm nominal wavelength), and the color intensity of the paper (Δk) was monitored.

As shown in Fig. 8, with extended UV irradiation, the color intensity of both the latex-dispersed SO and the acetone-dissolved SO treated paper samples decreased. However, the decreasing rate of the Δk for the paper treated with the latex-dispersed SO was markedly slower than that treated with the acetone-dissolved SO, indicating that the SO in the polystyrene acrylic latex matrix
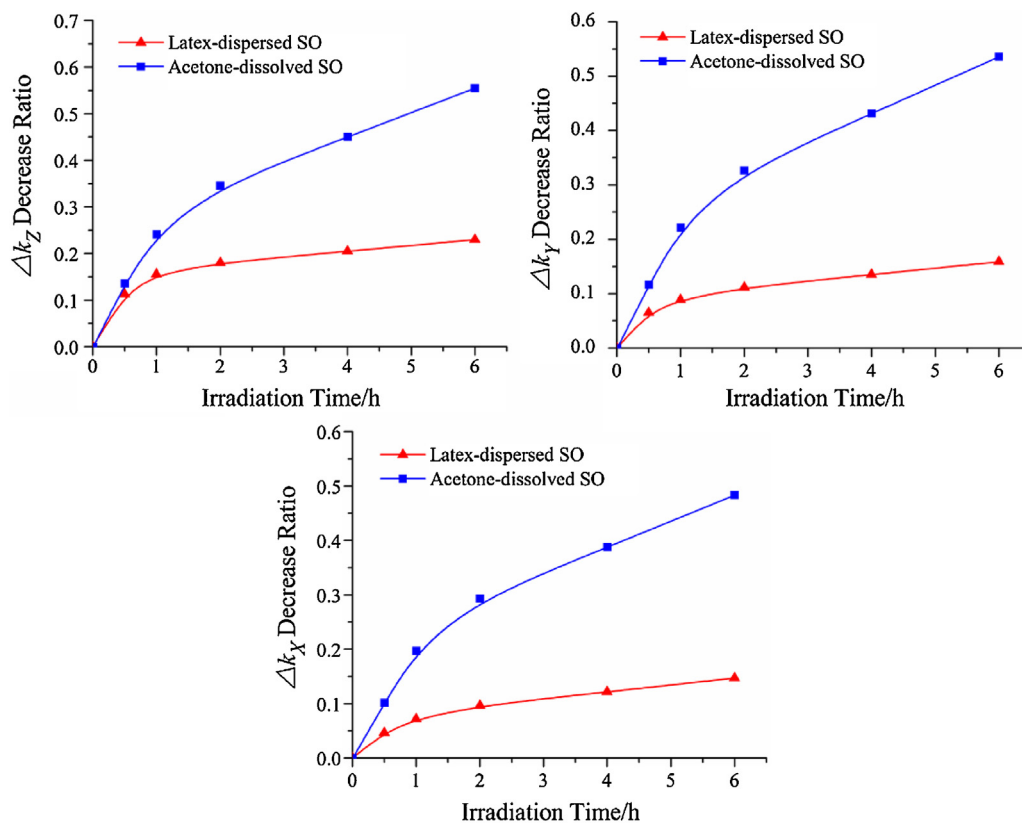

Fig. 8. Comparison of the fatigue resistance of the paper treated with the latex-dispersed SO or acetone-dissolved SO during the continuous UV irradiation (SO load of 2 mg SO/g paper in all cases; UV lamps parameter: 360 nm of the nominal wavelength and UV lamps intensity of 2.7 mW/cm^2).

improved the fatigue resistance. After 6 h of UV irradiation, the Δk decreased about 52% for the paper treated with acetone-dissolved SO, and only about 13% for the paper treated with the latex-dispersed SO, under otherwise the same conditions.

The photo-degradation of spirooxazine is generally believed to be caused by oxidative degradation reactions through free radical or singlet oxygen mechanism (Uznanski, Amiens, Donnadieu, Coppel, & Chaudret, 2001). It was found that the radical transfer efficiency was significantly reduced in the system with a heavy coating of an electro-steric stabilizer (Lucotti, Bertarelli, & Zerbi, 2004). The latex-dispersed SO system may have the similar radical transfer suppression, thus decreasing the radical-induced SO photo-degradation. As a result, the latex-dispersed SO system exhibits better fatigue resistance, as shown in Fig. 8.

4. Conclusions

The improvement of spirooxazine (SO) induced photochromatism on cellulosic paper was investigated by using polystyrene acrylic-based latex. The results showed that the latex-dispersed SO exhibited higher photochromic efficiency than the acetone-dissolved SO. In addition, the color stability and the fatigue resistance were improved in the presence of latex. Latex served as a good carrier/dispersant for the SO molecules, which was supported by the TEM results, and the adsorption of the SO dye on the latex particles prevented the dye aggregation. The π-π interactions of the styrene-based latex and SO molecules may also be partially responsible for the observed improvements.

Acknowledgement

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