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Cellulose nanocrystals (CNC) as carriers for a spirooxazine dye and its effect on photochromic efficiency

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ABSTRACT

Nanocrystalline cellulose (CNC) as a renewable/sustainable material, has received much attention. Herein we studied CNC as carriers for a hydrophobic spirooxazine (SO)-based dye, 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphtha[2,1-*b*][1,4]oxazine], which may have potential applications in reversible memory photo-devices, textiles, photo-sensitive paper coatings, and inkjet printing inks. Due to the high cost and water-insolubility of this dye, it is desirable to improve its coloration efficiency and water-dispersibility. The experimental approach was to use CNC as carriers for the SO dye, thus obtaining a stable photochromic dye in aqueous systems. Transmission electron microscope (TEM) observation confirmed that the SO dye adsorbed on the surface of the CNC, which functioned as carriers for the photochromic dye. An impregnation process was adopted to anchor the dye onto cellulosic paper. It was found that the use of CNC resulted in a significant improvement in the SO coloration efficiency. The color stability and fatigue resistance were also studied. The use of CNC as carriers for a hydrophobic compound, its enhancement of associated properties, and its subsequent application were demonstrated.

1. Introduction

Nanocrystalline cellulose (CNC) has generated a great deal of interest as one bio-based nanometer sized material (Yang, Han, Duan, Xu, & Sun, 2013; Jahan, Saeed, He, & Ni, 2011). The recent research and development activities related to CNC preparation and its applications have been extensively reported (Dong, Kimura, Revol, & Gray, 1996; Saito, Uematsu, Kimura, Enomae, & Isogai, 2011; Leyva et al., 2011), and it is part of society's drive toward sustainable bio-economy: the production of biochemicals, biomaterials, and biofuel from renewable resources. For example, numerous studies have been published regarding the integrated forest biorefinery concept (Shen, Kaur, & Baktash, 2013; Ruiz et al., 2013), and the production of value-added products from agricultural wastes (Hosseinpour, Fatehi, Latibari, Ni, & Javad Sepiddehdam, 2010; Haafiz, Eichhorn, Hassan, & Jawaid, 2013).

Photochromic dyes are specialty organic materials tailor-made for functional applications (Such, Evans, & Davis, 2006; Gushiken, Saito, Ubukata, & Yokoyama, 2010). Spirooxazine (SO) is a group of photochromic dyes that in liquid or solid matrix turn blue upon irradiation with UV light and rapidly turn back to colorless once the light source is removed. The photochromic mechanism of these compounds is well understood (Besugliy et al., 2009; Castro, Go′mez, Cossi, & Reguero, 2012).

However, SO is insoluble in water and considerable attention has been devoted to improving the hydrophilicity of SO, for example, by introducing hydrophilic groups (Billah, Christie, & Sharney, 2012), or encapsulating into sol–gel matrices (Nishikiori, Tanaka, Takagi, & Fujii, 2007). Alternatively, SO molecules can be covalently bound to polymer backbones (Lee, 1999). In a previous study (Sun et al., 2013), polystyrene acrylic based latex, a commonly used binder (Kugge, Craig, & Daicic, 2004) in the paper industry, was used as a carrier for SO to improve its dispersability in an aqueous system, and then applied onto the surface of cellulosic paper. The results showed that latex served as a good carrier for the SO molecules.

CNC may also be used as carriers or an emulsion stabilizer for tablets, cosmetic creams, and diet food (Kristensen, Schaefer, & Kleinbudde, 2000) or hydrogel-based products. Ougiya, Watanabe, Morinaga, and Yoshinaga (1997) studied the use of unmodified

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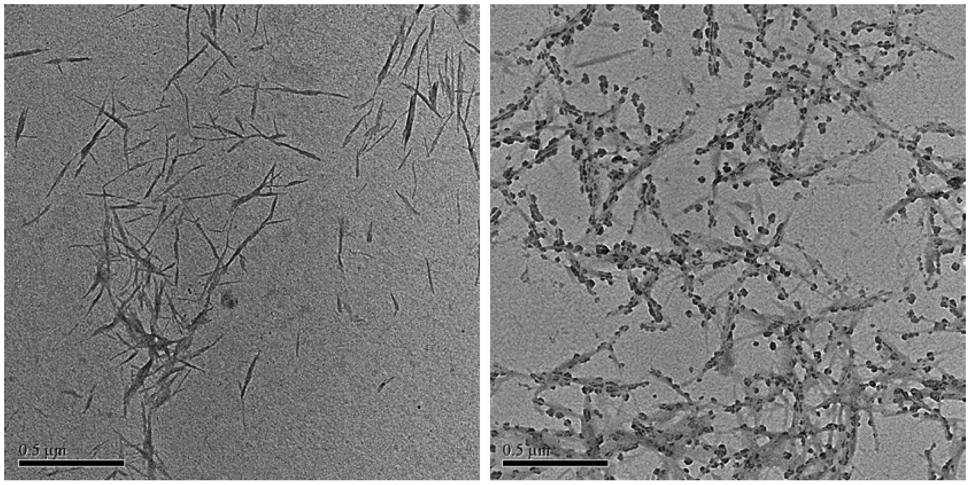

Fig. 1. TEM images of pure CNC rods (a) and CNC-dispersed SO (b) (CNC/SO ratio: 16 mg/0.5 mg). CNC are good carriers for the hydrophobic SO.

bacterial cellulose to stabilize oil-in-water (o/w) emulsions. Wege, Kim, Paunov, Zhong, and Velev (2008) found that microcrystalline cellulose could be used to stabilize oil droplets without surface modification.

In the current study, a SO photochromic dye, 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphtha[2,1-*b*][1,4]oxazine], was dissolved in acetone and then dispersed into CNC dispersion. Subsequently, cellulosic paper was treated with the CNC-dispersed SO by impregnation, and the role of CNC in the photochromic efficiency of the dye was explored.

2. Experimental

2.1. Materials

Cotton fibers were received from Shandong Silver Hawk Co., Ltd, China. The spirooxazine (SO) photochromic dye (1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphtha[2,1-*b*][1,4]oxazine]) and other chemicals were obtained from Sigma Aldrich and used as received.

2.2. Methods

For the preparation of CNC, cellulose fibers (cotton) were used to produce CNC by acid-catalyzed hydrolysis according to previously reported procedures (Jahan et al., 2011; Dong et al., 1996). Organic solvent (benzene-ethanol) extraction of cotton fibers were ground to smaller than 20 mesh powder in a mill. The ground fibers (5 g) were mixed with sulfuric acid (55 ml, 63.8%) and stirred at 45 °C for 1 h. The acid was removed by centrifugation, and then residual sulfuric acid was removed by dialysis with deionized water until neutrality was reached. The suspensions were freeze-dried for 48 h in a vacuum at 50 °C.

To prepare the CNC-dispersed SO dye, SO was first dissolved in acetone. 0.5 wt% CNC was added under mixing at 10,000 rpm, and the temperature was kept at 0 °C by using an ice/water bath. CNC was added to the dye solution. Upon the completion of CNC addition, the mixing speed was increased to 20,000 rpm, and it was continued for 30 min. The mixture was then subjected to ultrasonic treatment for 10 min. 1 g CNC/SO/acetone mixture was added to 10 g water under mixing at 10,000 rpm. The mixing speed was increased to 20,000 rpm when the addition of the mixture was completed. Subsequently, ultrasonic degassing was conducted at 30–40 °C for 15 min to remove the air in the aqueous system. The resulted CNC-dispersed SO dye was dried at 50 °C to a final concentration of 5 wt%.

For the preparation of SO-impregnated paper and determination of coloration efficiency, filter paper strips (Waterman No.1006-110) were impregnated with CNC-dispersed SO or acetone-dissolved SO. During the impregnation process, an ultrasonic treatment (15 min) was conducted. The impregnated paper strips were then air-dried under room temperature. The SO was weighed and its load was 2 mg SO/g paper, unless otherwise specified. The SO-impregnated paper strips were exposed to UV radiation for 5 min in a photo reactor with 8 mini UV lamps (360 nominal wavelength and 2.7 mW/cm^2). A Technidyne TB-1C spectrophotometer was used to determine the diffuse reflectivity for red light (R_X, 595 nm), green light (R_Y, 557 nm) and blue light (R_Z, 455 nm). We followed the same methods for data processing as described in a previous publication (Sun et al., 2013).

For transmission electron microscopy (TEM) analysis, the CNC-dispersed SO or acetone-dissolved solution was transferred to a carbon-coated copper grid (about 10 μL by using micropipette) and then air-dried at room temperature overnight. The TEM observation was then conducted on a JEOL 2010 transmission electron microscope with 200 kV acceleration voltages. Elemental analysis in combination with TEM was also conducted.

For the UV–vis analysis, SO-containing system with a concentration of 2 mg/g was prepared by adding SO into a mixture of acetone and water (1:5), or CNC-dispersed SO to water. The light absorbance of the SO dispersion was measured using a UV–vis spectrophotometer (Milton Roy Spectronic 1001 Plus) upon UV irradiation for 5 min.

3. Results and discussion

3.1. CNC as carriers for SO Dye

In the preparation of CNC-dispersed SO, SO was well dispersed under intensive shear mixing, and the CNC rod particles were expected to function as carriers for these SO particles. As shown in the TEM pictures in Fig. 1(a), CNC had a rod-like structure and the dispersion exhibited a colloidal behavior mainly due to the negative charges. The size of the CNC of about 3–8 nm in width and 60–180 nm in length was evident. In the preparation of CNC-dispersed SO, SO was well dispersed at molecular level under both high shear force and ultrasonic treatment.

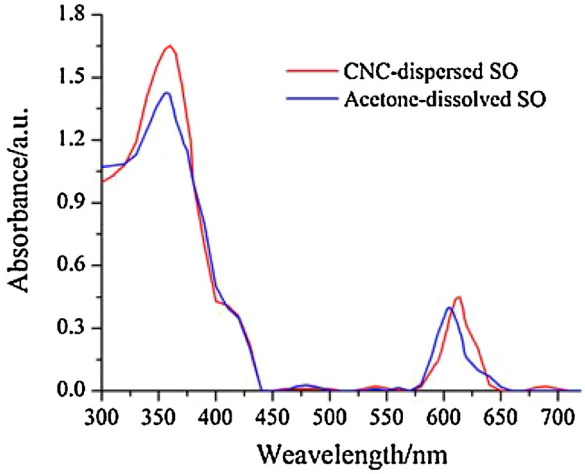

Fig. 2. UV–vis spectra of SO and CNC-dispersed SO (the SO concentration was 400 mg/l).

As shown in Fig. 1(b), the CNC rods adsorbed small particles, which were confirmed as SO, based on the nitrogen elemental mapping analysis. Thus, CNC was a good "adsorbent" for SO, and the SO particles were well dispersed and carried by the CNC rods. The attachment of the hydrophobic SO to the surface of hydrophilic CNC made it possible for hydrophobic compounds like SO to be used in an aqueous system. In this way, the use of CNC may have the potential of improving the SO photochromic efficiency. This possible enhancement in photochromic efficiency may be similar to the effect of cellulosic fibers on the brightening efficiency of optical brightening agents (OBAs) or fluorescent whitening agents (FWAs) (Zhang, Lei, Du, Li, & Wang, 2013), wherein a higher fluorescent brightening efficiency can be achievable by OBA absorption onto fibers.

3.2. Adsorption spectra of SO photochromic systems

The UV–vis spectra are shown in Fig. 2. There was a maximum absorption peak at 355 to 365 nm. According to a previous report by Larkowska, Wuebbenhorst, and Kucharski (2011), upon UV excitation, the spiro-carbon–oxygen (C—O) bond of the colorless closed-ring can break, and the subsequent isomerization can lead to the formation of colored ring-open isomers (merocyanine). The maximum absorption peak of merocyanine was in the range 600 to 615 nm. A noteworthy point is that the adsorption peaks were higher for the CNC-dispersed SO, and the presence of CNC resulted in the peak (merocyanine) shift from 605 to 613 nm.

Similar results were obtained when Feczkó, Varga, Kovács, Vidóczy, and Voncina (2011) prepared encapsulated SO using poly (methyl methacrylate) or ethyl cellulose. In their study, the absorptions of both poly (methyl methacrylate)-SO and ethyl-cellulose-SO nanoparticles were substantially higher than SO in the whole UV–vis range; the presence of poly (methyl methacrylate) or ethyl cellulose caused a red shift from 601 to 607 nm.

3.3. Photochromic efficiency of the CNC-dispersed SO

The photochromic efficiency of the CNC-dispersed SO was studied by impregnating it into paper strips. The color intensity of the paper can be described by the light absorption coefficient, which can be calculated from the diffusive reflectance data based on the well-known Kubelka–Munk theory. The results are shown in Table 1, which are the differential light absorption coefficients (Δk) of the paper strips before and after UV irradiation as a function of SO load ($\Delta k = k_{after} - k_{before}$). The results are given in terms of the red (Δk_X, λ_{max} = 595 nm), green (Δk_Y, λ_{max} = 557 nm) and blue (Δk_Z, λ_{max} = 455 nm) light ranges. It is evident that the CNC-dispersed SO treated paper had higher Δk than that treated with the acetone-dissolved SO, particularly Δk_Z. In addition, with the increase in SO load for both systems, the differential light absorption coefficients increased significantly.

For a given SO load, the Δk was much higher for paper treated with the CNC-dispersed SO than that treated with the acetone-dissolved SO (see Table 1). 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 1.00 mg/g. Interestingly, the use of CNC-dispersed SO, instead of the acetone-dissolved SO, could result in about 50% reduction of the SO dosage. Therefore, the use of CNC as carriers can significantly improve the photochromic efficiency of SO in paper.

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

Fig. 3 shows the color development of the SO-impregnated paper strips exposed to 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 for both CNC-dispersed SO and acetone-dissolved SO treated paper samples, the light absorption in blue, red, and green ranges had a rapid increase initially, and then reached a plateau. Compared with the results of latex-dispersed SO coloration efficiency (Sun et al., 2013), the CNC rods were less effective partly because the π–π chemical interaction between the latex and SO was absent in the CNC-dispersed SO system.

As soon as the UV irradiation was stopped, the paper color started to fade away. Noticeably, the de-coloration of the CNC-dispersed SO treated paper was faster than that for the acetone-dissolved SO treated paper (Fig. 4). The half-life-times of de-coloration for the CNC-dispersed SO treated paper and acetone-dissolved SO treated paper were about 5 and 20 s, respectively.

Table 1
Effect of SO load in paper on the change of the light absorption coefficient (Δk) in red, green, and blue light ranges upon UV irradiation*.

SO load in the paper (mg/g paper)	Δk_Z (blue light) (m^2/kg)		Δk_Y (green light) (m^2/kg)		Δk_X (red light) (m^2/kg)	
	Acetone-dissolved SO	CNC-dispersed SO	Acetone-dissolved SO	CNC-dispersed SO	Acetone-dissolved SO	CNC-dispersed SO
0.5	0.55	0.83	0.62	0.85	0.92	1.22
0.75	0.63	0.99	0.76	1.28	1.08	1.71
1	0.71	1.06	0.93	1.6	1.23	2.02
1.25	0.82	1.27	1.01	2.15	1.47	2.55
1.5	0.93	1.41	1.19	2.44	1.62	3.11
1.75	1.01	1.53	1.26	2.93	1.82	3.62
2	1.13	1.72	1.45	3.32	1.98	4.05

* Irradiation time of 5 min; UV lamps parameter: 360 nm of the nominal wavelength and UV lamps intensity of 2.7 mW/cm^2.

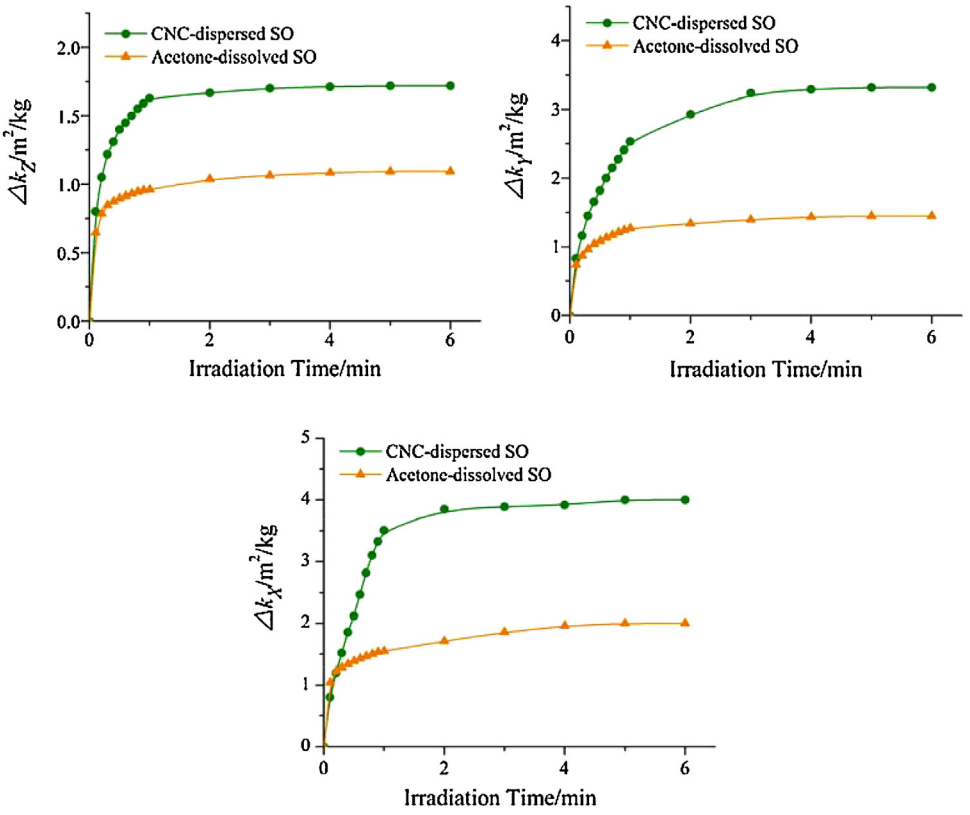

Fig. 3. UV irradiation of paper samples: comparison of CNC-dispersed SO and acetone-dissolved SO. The color changes are more pronounced in the CNC-dispersed system than that in the acetone-dissolved SO system. (SO load of 2 mg SO/g paper in all cases; UV lamps parameter: 360 nm of the nominal wavelength and UV lamps intensity of 2.7 mW/cm^2).

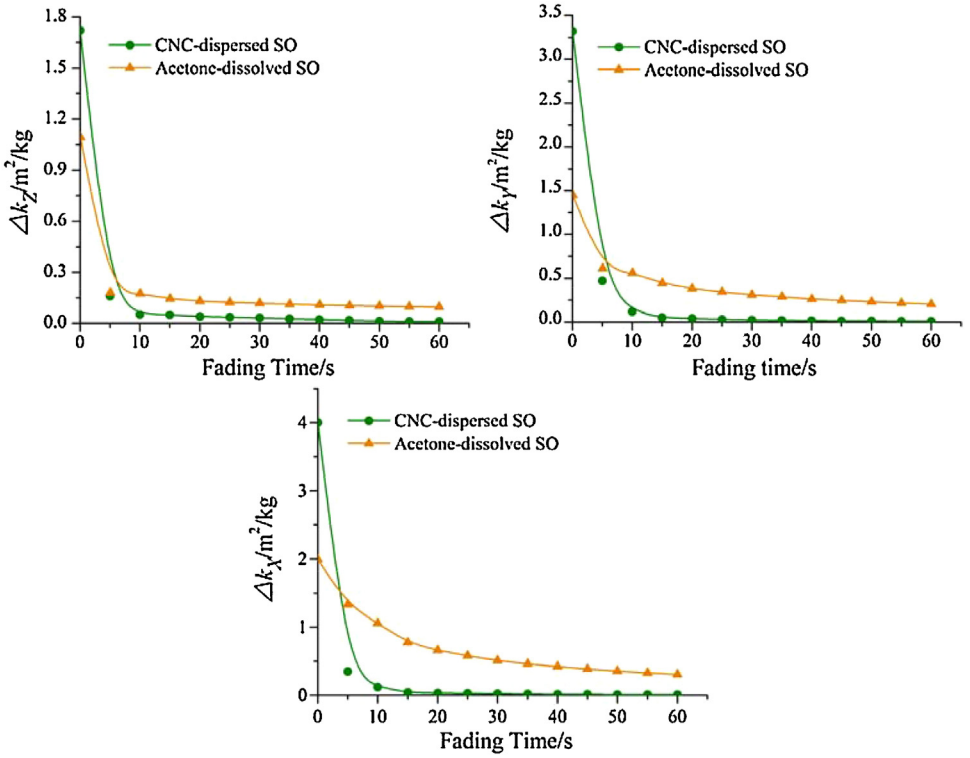

Fig. 4. Comparison of de-coloration of paper samples after the completion of UV irradiation: CNC-dispersed SO versus acetone-dissolved SO. The de-coloration process was much faster for the CNC-dispersed SO system than that for the acetone-dissolved SO system (SO load of 2 mg SO/g paper in all cases; irradiation time of 5 min; UV lamps parameters: 360 nm of the nominal wavelength and UV lamps intensity of 2.7 mW/cm^2).

Table 2
Fatigue resistance of the paper treated with the CNC-dispersed SO or acetone-dissolved SO during continuous UV irradiation in red, green, and blue light ranges[a].

Irradiation Time (h)	Δk_Z decrease ratio[b] (blue light)		Δk_Y decrease ratio[b] (green light)		Δk_X decrease ratio[b] (red light)	
	Acetone-dissolved SO	CNC-dispersed SO	Acetone-dissolved SO	CNC-dispersed SO	Acetone-dissolved SO	CNC-dispersed SO
0	0	0	0	0	0	0
0.5	0.136	0.062	0.116	0.056	0.102	0.039
1	0.241	0.095	0.221	0.078	0.197	0.06
2	0.345	0.117	0.326	0.096	0.292	0.072
4	0.450	0.136	0.431	0.11	0.388	0.081
6	0.557	0.151	0.536	0.123	0.483	0.092

[a] 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.
[b] Δk decrease ratio = $(\Delta k_{original} - \Delta k_T)/\Delta k_{original}$. Original stands for the original paper sample; T stands for the different irradiation time (h), T = 0, 0.5, 1, 2, 4, 6.

Table 3
Comparision of CNC-dispersed SO with PMMA-dispersed and EC-dispersed SO[a].

Category	Δk_Z after saturation (m^2/kg)	De-coloration Time (s) (Δk_Z reaches 0.02 m^2/kg)	Δk_Z decrease ratio[b] at irradiation time of 1 h
PMMA-SO	1.38	145	0.169
EC-SO	1.61	53	0.115
CNC-SO	1.72	40	0.117

[a] 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.
[b] Δk_Z decrease ratio = $(\Delta k_{original} - \Delta k_T)/\Delta k_{original}$. Original stands for the original paper sample; T stands for the irradiation time (h), T = 1.

3.5. Fatigue resistance

For fatigue resistance analysis, the paper samples were continuously exposed 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.

Under extended UV irradiation, the color intensity of both CNC-dispersed SO and the acetone-dissolved SO treated paper decreased (see Table 2). However, for the rate of decrease of rate of the Δk, CNC-dispersed SO treated paper was much lower than that of the acetone-dissolved SO treated paper. Thus, the use of CNC as carriers improved the fatigue resistance of SO. After a 6 h UV irradiation, the Δk decreased by about 52% for the acetone-dissolved SO sample; however, the decreased percentage was only about 9.2% for the paper treated with the CNC-dispersed SO. The role of CNC in improvement of fatigue resistance might be due to its electro-steric stabilizing effect in the system, which inhibited the oxidative-degradation of SO (Lucotti, Bertarelli, & Zerbi, 2004).

3.6. Comparison of CNC-dispersed SO with PMMA-SO and EC-SO

Poly (methyl methacrylate) (PMMA) and ethyl cellulose (EC) were used for dispersion of SO dye (Feczkó et al., 2011). In this study, CNC was compared with PMMA and EC, and the results are shown Table 3, which details the coloration, de-coloration and fatigue resistance efficiency. The experiments were carried out under otherwise the same conditions. It can be found that CNC-dispersed SO had higher coloration and de-coloration effect than EC- or PMMA-dispersed SO, which is the consequence of the better dispersion effect from CNC due to the unique nano-particle characteristics. The abundant hydroxyl groups could also contribute positively to the excellent dispersion function of CNC.

In addition, it can found that EC-dispersed SO had better performance than PMMA-dispersed SO. The above results are in good agreement with those in the literature (Feczkó et al., 2011).

4. Conclusions

Cellulose nanocrystals (CNC) are good carriers for hydrophobic compounds, such as spirooxazine (SO), which was supported by the TEM results. The adsorption of the SO dye onto CNC protected the SO dye against aggregation in the aqueous system. Subsequently, SO-induced photochromatism on cellulosic paper was investigated by using CNC-dispersed SO. The results showed that the CNC-dispersed SO exhibited higher photochromic efficiency than the control. In addition, the color stability and the fatigue resistance were improved in the presence of CNC.

The present results support the notion that CNC are versatile materials which can be applied in many different fields; in particular, CNC can be used as carriers for organic hydrophobic compounds so that they can be compatible with aqueous systems. We are presently engaging in further research that extends this applications.

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