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Modification of cellulose with reactive polyhedral oligomeric silsesquioxane and nano-crosslinking effect on color properties of dyed cellulose materials

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ABSTRACT

Reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol (R-POSS) as crosslinking agent has potential application in improving physical properties of nano-cellulose materials. The effect of nano-crosslinking with R-POSS on color properties of dyed cellulose materials was investigated by *K/S*, CIE-LAB, and SEM. Physical properties and color fastness of nano-cellulose fabrics were discussed. The results show that the crease recovery angles of three color samples (yellow, red, and blue) crosslinked with R-POSS significantly increased. The elastic recovery property of crosslinked samples containing R-POSS got obvious improvement. *K/S* values of three color samples containing R-POSS decreased. Wet rubbing fastness, washing fastness, and perspiration fastness of three color samples containing POSS slightly increased. The cellulose fibers crosslinked with R-POSS imparted transparent and smooth surface.

1. Introduction

Cellulose fiber is one of the excellent natural biomaterials. Nano-technology can improve mechanical, optical and thermal properties of cellulose-based composite materials (Fahmy, Aboshosha, & Ibrahim, 2009; Hou, Zhou, & Wang, 2009; Kulpinski, 2005; Wei, Cheng, Hou, & Sun, 2008). These composite materials are biocompatible, biodegradable and possess low toxicity in biomedical field (Fina, Tabuani, Frache, & Camino, 2005; Hou, Wang, & Wu, 2008; Musyanovych, Wienke, Mailander, Walther, & Landfester, 2008). However, high even dispersion system at the nanometer scale in the cellulose host matrix is very difficult to produce by traditional techniques. Recently, the sol–gel method has definitely proved its exceptional potential by providing a possibility of synthesizing a significant number of new nanomaterials (He, Wan, & Xu, 2007; Chen, Wang, & Chiu, 2008; Samuneva et al., 2008; Xie, Yu, & Shi, 2009). Polyhedral oligomeric silsesquioxane (POSS) can serve as model nanofillers. POSS has a nanometer-sized confine structure with a cubic silica core and can be functionalized with a variety of organic compounds (Choi, Harcup, Yee, Zhu, & Laine, 2001; Fu et al., 2001; Seckin, Koytepe, & Ibrahim, 2008; Hou, Wang, & Yu, 2009). Reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol (R-POSS) is one of POSS derivatives as candidates to modify cellulose. It is attractive staring monomer and has corner-capping framework of condensed POSS trisilanols (Feher, Soulivong, & Eklund, 1998; Feher & Wyndham, 1998; Janowski & Pielichowski, 2008; Xie, Zhang, & Yu, 2009).

The crosslinking with reactive polyhedral oligomeric silsesquioxane (R-POSS) is an important method to prepare nano-cellulose. R-POSS possesses a nano-sized inorganic core and reactive organic corner with multi-*N*-methylol groups. The structure of R-POSS containing multi-*N*-methylol groups is shown in Scheme 1.

After cellulose fabrics are treated with crosslinking monomer containing POSS nano-particles, physical properties and morphology will be changed. R-POSS can be used for cellulose fabric improving its shape memory performance. Sometimes, cellulose samples as color matrix have been dyed with reactive dyes. However, the nano-crosslinking can affect color properties of cellulose samples dyed with the reactive dyes (Jeon, Mather, & Haddad, 2000; Hou & Sun, 2009; Xie, Hou, & Zhang, 2009).

In this paper, the cellulose fabrics are dyed with reactive dyes and then reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol is used for dyed cellulose fabrics to prepare color nano-cellulose. The effect of nano-crosslinking with R-POSS on color properties of dyed cellulose materials is investigated. Color fastness and physical properties of dyed nano-cellulose samples are also discussed.

2. Experimental

2.1. Materials

R-POSS containing multi-*N*-methylol was obtained from National Engineering Research Center for Dyeing and Finishing of

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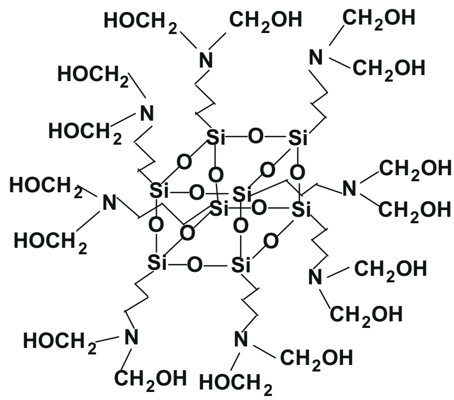


Scheme 1. Chemical structure of R-POSS containing multi-*N*-methylol groups.

Textiles, Shanghai, China. The reactive dyes, Reactive Yellow B-4RFN (C.I. Reactive Yellow 145), Reactive Red B-3BF (C.I. Reactive Red 250) and Reactive Blue B-RN (C.I. Reactive Blue 221) were obtained from Shanghai Matex Chemical Company, Shanghai. Scoured and bleached cellulose fabric (cotton fiber) was obtained from Shumei Textile Company, Shaoxing, China. Other chemicals were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Dyeing of cellulose fabrics

The cellulose fabrics were dyed in PYROTEC-2000 dyeing machine (Roaches International Ltd., UK) with a liquor ratio of 1:15, sodium sulphate (50 g/l) and sodium carbonate (10 g/l). Fabrics were immersed in the dye bath at room temperature and the temperature was increased to 60 °C at a rate of 1 °C/min. Dyeing was carried out at this temperature for 60 min. After dyeing, the dyed samples were rinsed in hot water and soaped in a solution of a nonionic surfactant (OP-10, 1.0 g/l) at 85 °C for 15 min at liquor ratio 1:15. The fabrics were removed, rinsed thoroughly in hot tap water until the rinsing water was clear and air-dried.

2.3. Nano-crosslinking of cellulose fabric with reactive polyhedral oligomeric silsesquioxanes (R-POSS)

R-POSS was diluted with distilled water to certain concentration solution (1.6% and 2.4% w/w, respectively). Citric acid (0.1%, w/w) and 1.5% (w/w) $MgCl_2{\cdot}6H_2O$ as catalysts were used in the crosslinking reaction. The mixtures were sufficiently mixed by stirring at room temperature. Two concentration solutions, 1.6% and 2.4% w/w, were called RP-1 and RP-2, respectively.

Dyed cellulose fabrics were padded with the RP-1 or RP-2 to give 80% wet pick-up, respectively. The dry temperature and time were 95 °C and 3 min, respectively. After drying, the fabrics were cured for 1.5 min at 160 °C. The POSS crosslinking nano-cellulose samples were obtained. They were named as Y-CRP-1, Y-CRP-2 (yellow samples), R-CRP-1, R-CRP-2 (red samples), and B-CRP-1, B-CRP-2 (blue samples) according to the color of sample and the concentration of R-POSS, respectively. For comparison, the dyed samples without the R-POSS were cured under the same condition.

2.4. Color data analysis

The color yields (*K*/*S*) of the dyed fabrics were determined by a Datacolor SP600+ spectrophotometer (Datacolor, USA). The tristimulus values of the dyed samples were measured in the visible spectrum region 360–700 nm and the reflectance at the wavelength of maximum absorption (λ_{max}) was used to calculate the color yield of dyed fabrics by the Kubelka–Munk equation (Eq. (1)):

$$K/S = \frac{(1-R)^2}{2R} \tag{1}$$

where *K* is the absorption coefficient of the substrate, *S* is the scattering coefficient of the substrate and *R* is the reflectance of the dyed fabric.

2.5. Measurements

Dry crease recovery angle (CRA) was determined according to AATCC 66-1998. The samples were conditioned at 20 °C and 65% relative humidity for at least 24 h before testing. Tensile strength of the crosslinked sample was tested according to ISO 13934.1-94.

Color fastnesses of the dyed samples were determined according to the respective ISO standards: fastness to washing, ISO 105-C03: 1989; fastness to rubbing, ISO 105-X12: 1993; fastness to perspiration, ISO 105-E04: 1994.

For SEM analysis, the samples were sputtered with gold and then examined with a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

3. Results and discussion

3.1. Nano-crosslinking reaction of cellulose samples with R-POSS

The reactive dyes, yellow B-4RFN, red B-3BF and blue B-RN were used for cellulose fabrics. Cellulose fabrics were dyed with the reactive dyes, 2% (o.w.f.). R-POSS has a lot of high-reactive *N*-methylol ($-CH_2OH$) to react with cellulose fiber and form network structure. The crosslinking reaction of cellulose and R-POSS is shown in Scheme 2.

After the dyed cellulose samples were crosslinked with R-POSS, physical properties of cellulose hybrids containing R-POSS were measured. Crease recovery angle and tensile strength of nano-cellulose fabrics are summarized in Table 1. The results show that the crease recovery angles of three color samples crosslinked with R-POSS significantly increased. Moreover, with increasing R-POSS concentration, the crease recovery angles of the crosslinked fabrics further increased. The tensile strength of crosslinked cellulose samples noticeably decreased. It shows that elastic recovery property of crosslinked nano-cellulose samples got significant improvement. This is demonstrated that cellulose fiber and R-POSS formed covalent bonds by crosslinking reaction. The decrease of tensile strength and the increase of crease recovery angles were that the slippage between the cellulose macromolecules was inhibited because of the crosslinking reaction. In the crosslinking reaction, POSS particles were dispersed in the cellulose host matrix, bonding to cellulose through covalent bonds.

3.2. Effect of nano-crosslinking with R-POSS on K/S of dyed cellulose materials

After dyed cellulose samples are crosslinked with R-POSS, the effects of nano-crosslinking on *K*/*S* are shown in Figs. 1–3. As can be seen in Figs. 1–3, *K*/*S* values of three color samples (yellow, read, and blue) crosslinked with R-POSS obviously decreased. It may be attributed to the transparent films formed by R-POSS on the dyed cellulose samples. However, *K*/*S* values of yellow Y-CRP-2 and blue B-CRP-2 samples were higher than those of yellow Y-CRP-1 and blue B-CRP-1, respectively. It may be transparent film formed on the dyed cellulose becoming thick with increasing R-POSS concentration.

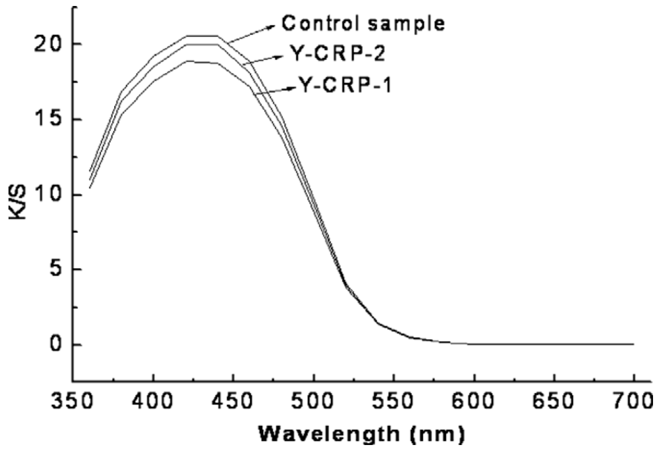


Fig. 1. *K/S* curves of yellow cellulose samples.

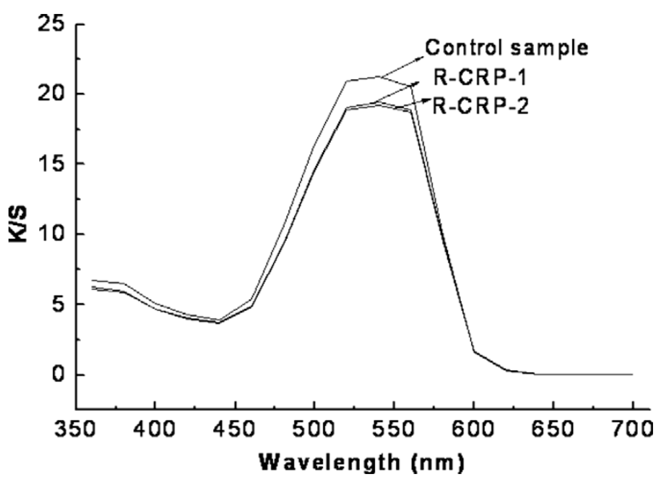


Fig. 2. *K/S* curves of red cellulose samples.

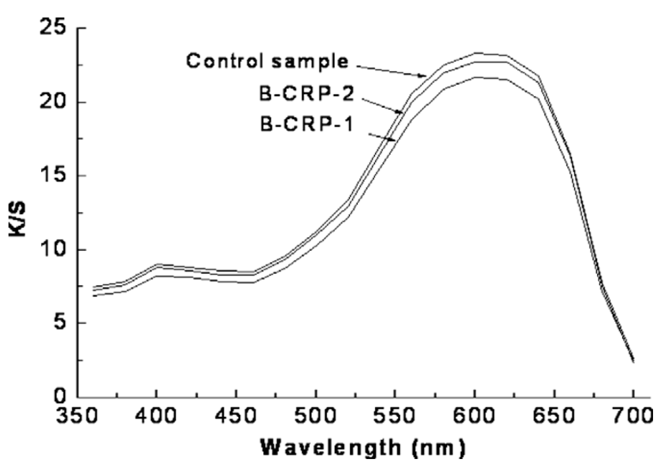
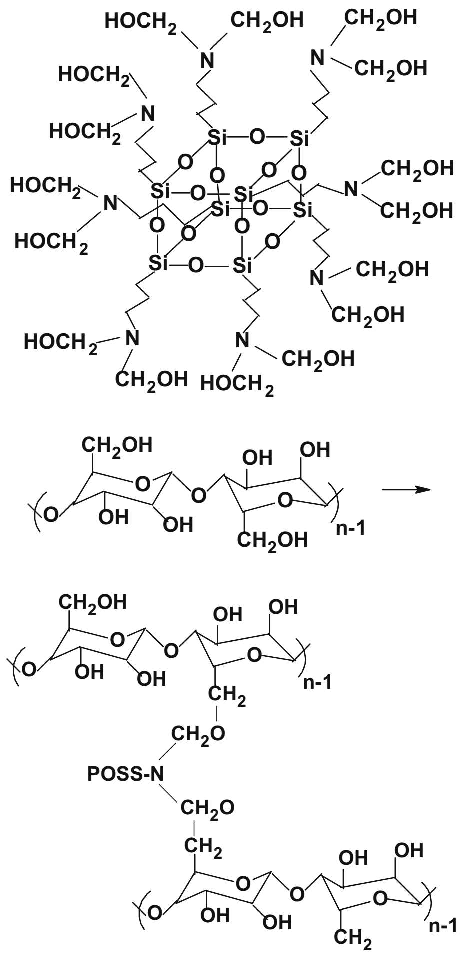


Fig. 3. *K/S* curves of blue cellulose samples.



Scheme 2. Crosslinking reaction of cellulose and R-POSS.

Table 1
Physical properties of color nano-celluloses containing R-POSS.

Samples		Crease recovery angle ($W + F$, °)	Tensile strength (N)	
			Warp	Weft
Yellow	Control	104.71	747.6	303.3
	CRP-1	156.62	635.8	236.8
	CRP-2	168.15	598.5	223.8
Red	Control	104.23	744.5	301.8
	CRP-1	158.14	637.2	239.1
	CRP-2	171.65	606.2	228.1
Blue	Control	103.45	749.4	305.2
	CRP-1	154.26	645.9	239.3
	CRP-2	179.15	581.7	222.5

In order to further observe surface morphology of color nano-cellulose crosslinked with R-POSS, SEM micrographs of the samples were measured. SEM micrographs of the control sample and yellow cellulose fiber crosslinked with 1.6% R-POSS (Y-SCR-1) are shown in Fig. 4. Compared with control cellulose fiber, the cellulose fiber modified with R-POSS imparted transparent and smooth surface.

3.3. Colorimetric data of three color nano-cellulose samples

The color data of the color nano-cellulose samples were determined by a Datacolor SP600$^+$ spectrophotometer. The tristimulus values *X*, *Y* and *Z* of the samples were measured and the color parameters *L*, *a*, *b*, were also calculated. The color differences (ΔE) were calculated using the measured values of CIE-LAB (Eq. (2)).

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{\frac{1}{2}} \quad (2)$$

ΔL, Δa and Δb are the difference in the color parameters of the dyed fabrics crosslinked without and with R-POSS.

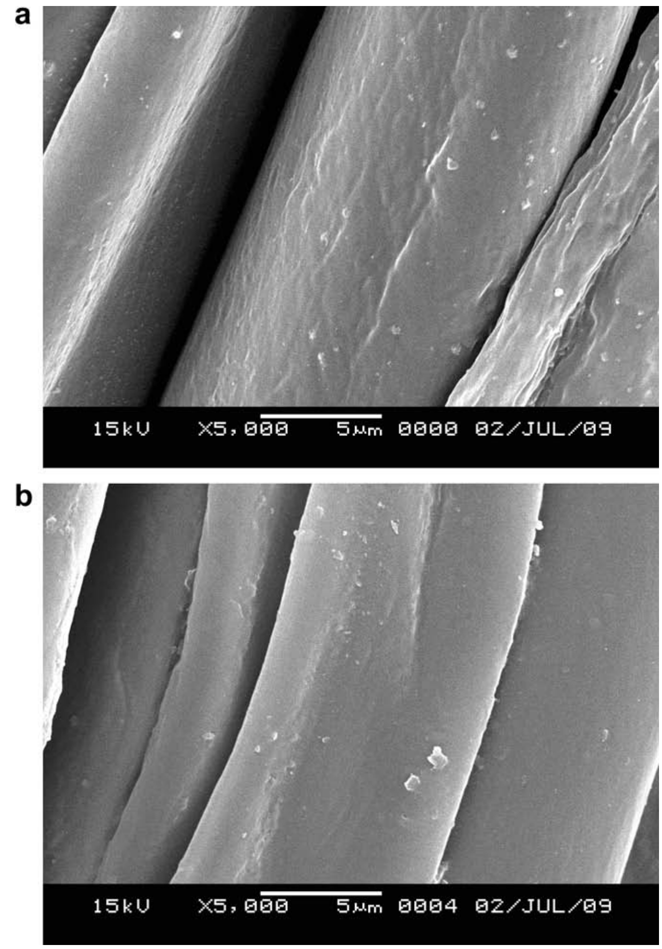


Fig. 4. SEM micrographs of control sample and Y-SCR-1. (a) Control sample. (b) Y-SCR-1 sample.

Colorimetric data of three color nano-cellulose samples are summarized in Table 2. The results in Table 2 show that all *L* values increased after three color samples were crosslinked with R-POSS. Meantime, with increasing R-POSS concentration, all *L* values were further improved. This means that the films formed with R-POSS were transparent and imparted good reflectance. The *a* values of three color fabrics decreased with increasing R-POSS concentrations, meaning the decrease in the red component instead of the green. The *b* values of three color fabrics also decreased, meaning the decrease in the blue component instead of the yellow.

The color differences (ΔE) of three color fabrics crosslinked with RP-2 were obvious. The color differences (ΔE) of the dyed nano-cellulose samples were in agreement with the changes of their color yields.

3.4. Effect of nano-crosslinking with R-POSS on fastness of dyed cellulose fabrics

The fastness properties of three color nano-cellulose fabrics were determined (shown in Table 3). The results show that wet rubbing fastness, washing fastness, and fastness to perspiration of all three color samples containing POSS slightly increased. It may be due to R-POSS forming net-crosslinking among dyes, cellulose and POSS. It could further improve crosslinking degree of cellulose and dyes. It was beneficial to improve fastness properties of dyed cellulose fabrics.

4. Conclusions

Reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol was used for three dyed cellulose fabrics to prepare color nano-cellulose. The crease recovery angles of three color samples crosslinked with R-POSS significantly increased. The tensile strength of crosslinked cellulose fabrics decreased. Elastic recovery properties of color samples containing R-POSS got significant improvement. The effect of nano-crosslinking with R-POSS on

Table 2
Colorimetric data of dyed cellulose fabrics crosslinked with R-POSS.

Samples	*L*	*a*	*b*	*c*	ΔL	Δa	Δb	Δc	ΔE
Control	66.12	40.08	81.59	90.91					
Y-CRP-1	66.26	39.77	81.20	90.43	0.14	−0.31	−0.39	−0.48	0.18
Y-CRP-2	66.32	39.54	80.22	89.45	0.20	−0.54	−1.37	−1.46	0.46
Control	37.76	59.40	6.13	59.72					
R-CRP-1	37.99	58.46	4.42	58.62	0.23	−0.94	−1.89	−1.10	1.06
R-CRP-2	37.86	58.35	4.45	58.53	0.10	−1.05	−1.68	−1.58	0.96
Control	19.94	−0.81	−12.84	12.86					
B-CRP-1	19.65	−0.86	−12.76	12.78	−0.29	−0.05	0.08	−0.08	0.25
B-CRP-2	20.62	−1.07	−13.07	13.11	0.68	−0.26	−0.23	0.25	0.66

Table 3
Fastness properties of dyed nano-cellulose fabrics.

Samples		Fastness to rubbing		Fastness to washing		Fastness to perspiration	
		Dry	Wet	SC	SW	SC	SW
Yellow	Control	4–5	3–4	4	3–4	4	3–4
	CRP-1	4–5	4	4	4	4	4
	CRP-2	4–5	4	4	4	4	4
Red	Control	4–5	3–4	4	3–4	4	3–4
	CRP-1	4–5	3–4	4	4	4	4
	CRP-2	4–5	4	4	4	4	4
Blue	Control	4–5	3–4	4	3–4	4	3–4
	CRP-1	4–5	4	4	3–4	4	3–4
	CRP-2	4–5	4	4	4	4	4

SC, staining on cotton; SW, staining on wool.

color properties of dyed cellulose materials was obvious. *K/S* values of three color samples crosslinked with R-POSS noticeably decreased. The nano-cellulose fiber containing R-POSS imparted transparent and smooth surface. Meantime, wet rubbing fastness, washing fastness, and fastness to perspiration of three color fabrics containing POSS slightly increased.

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