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Study on the performance of ramie fiber modified with ethylenediamine

Zhao-Tie Liu [a,*], Yani Yang [a], Lili Zhang [a], Ping Sun [a], Zhong-Wen Liu [a], Jian Lu [a], Heping Xiong [b], Yuande Peng [b], Shouwei Tang [b]

[a] *Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education, School of Chemistry & Materials Science, Xi'an 710062, PR China*

[b] *Institute of Bast Fiber Crops, Chinese Academy of Agricultural Sciences, Changsha 410205, PR China*

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Abstract

The chelate molecule, ethylenediamine, was incorporated onto the surface of ramie fiber via sequential reactions of the hydroxyl groups on ramie fiber with epichlorohydrin followed by the chelating agent. The performance of the modified material (CelNH) was characterized by Fourier transform infrared spectroscopy (FI-IR), X-ray diffraction (XRD), scanning electron micrographs (SEM), thermogravimetry analysis (TGA), UV–Vis, and elemental analysis. Results show that the excellent characteristics of the raw fiber were still remained after modification although the crystallinity of the modified fiber decreased. The modification parameters were optimized as the concentration of ethylenediamine of 0.75 mol/l, the temperature of 50 °C, and the reaction time of 5 h. Meanwhile, the dye of C.I. reactive red 2 was used to study the dyeability of the raw and the modified fibers. The color strength and the dye uptake of the modified fiber increased obviously with an increase in the nitrogen contents in CelNH. The color strength and the dye uptake of the modified fiber can be controlled by changing the extent of surface modification of raw ramie fiber.

Keywords: Ramie fiber; Ethylenediamine; Epichlorohydrin; Dyeing; Surface modification

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1. Introduction

Ramie, also called China grass (*Boehmeria nivea* (L.) Gaud.), is a hardy perennial herbaceous plant of the Urticaceae family. Today, it is mainly planted in China and other Asian countries including Philippines, India, South Korea, and Thailand (Liu, Liang, Zhang, Huang, & Zhang, 2001). Besides some impurities called gum such as hemicellulose (13.1–16.7%), pectin (1.9%), and wax (0.3%), ramie is mainly composed of cellulose (68.6–76.2%) (Goda, Sreekala, Gomes, Kaji, & Ohgi, 2006). Ramie fiber, stripped from stem bast of the plant, is characterized by its high tensile strength, excellent thermal conductivity, coolness, ventilation function, moisture absorption, antibacterial function, and so on when it is used as a textile material.

In a molecular-structure level, it is clear that the native cellulose is a linear macromolecule formed by β-*d* anhydroglucose units linked together by 1,4-glucosidic bonds. If the supramolecular structure is concerned, cellulose is composed of a partial crystalline phase where the cellulose chains are firmly tied through hydrogen bonds, an interfacial region next to the lateral faces of the crystallites, and an amorphous region where chain segments are believed to be randomly oriented. The morphological complexity in the supramolecular structure of cellulose has decisive consequences for its surface activity in sorption, swelling, reactivity, dyeing uniformity, and tinctorial capacity (Hinterstoisser, Åkerholm, & Salmén, 2003; Sasaki, Adschiri, & Arai, 2003; Yamaki et al., 2005). Taking the process of dyeing as an example, dye molecules are fully accessible to the amorphous regions of cellulose. In the case of the crystalline phase of cellulose, however, dye molecules are

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* Corresponding author. Tel./fax: +86 29 8530 3682.
E-mail address: ztliu@snnu.edu.cn (Z.-T. Liu).

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limited to be its surface because that hydrogen bond is formed in the inner part of crystalline region, which prevents the entering of dye molecules (Prado, Yamaki, Atvars, Zimerman, & Weiss, 2000; Talhavini, Atvars, Schurr, & Weiss, 1998; Vigil, Bravo, Baselga, Yamaki, & Atvars, 2003). Thus, modification is required in order to improve the dyeability of ramie fiber (Song & Shen, 1998; Liu et al., 2006). Generally, there are three methods to modify ramie fiber, i.e., mechanical, chemical, and biological methods. The mechanical method has very limited effect on improving the dyeability of the fiber. The application of the biological method is hindered by lacking of a suitable enzyme with high efficiency and low cost. In the case of chemical methods, not only the surface property but also the bulk performance of ramie fiber can be efficiently and conveniently modified by choosing proper chemicals. Therefore, it has been applied extensively. At present, several chemical methods, e.g., acetylation and alkylation, have been developed for the modification of cellulose-based materials (Hill, Abdul Khalil, & Hale Mike, 1998; Petru, Gray, & Bemiller, 1995; Samios, Dart, & Dawkins, 1997). If these kinds of modifications are applied for the modification of ramie fiber, the property of ramie fiber do change, but the dyeability of fiber cannot be increased in a sufficient level. Thus, in order to improve the dyeability of ramie fiber, it is necessary to introduce reactive groups onto the fiber.

The ethylenediamine, a cheap industrial agent, has been used extensively. The method for chelating cotton fiber with ethylenediamine has already been developed by de la Orden and Urreaga. The modified material can chelate various metal ions, so it can be applied in the environmental protection (da Silva Filho, de Melo, & Airoldi, 2006; de la Orden & Urreaga, 2006; Torres, Faria, & Prado, 2006). However, in these methods, a high cost and toxic crosslinking agent such as $POCl_3$ is used (Torres et al., 2006). Moreover, the strength of ramie fiber is reduced such that the excellent characters of ramie fiber as a textile material are disappeared. In this paper, a crosslinking agent of epichlorohydrin with the characteristics of cheapness, wide availability, and less toxic than $POCl_3$ is applied for anchoring ethylenediamine onto ramie fiber. The hydroxyl groups in ramie fiber are transformed into reactive intermediate ether groups, and then ethylenediamine is grafted on to the fiber by reacting with the ether group. After modification, the fiber has similar characters with wool and a significantly improved dye uptake as a result that the molecules of the reactive dye can combine with the amine groups by covalent bonds.

2. Experimental

2.1. Materials

The ramie fiber obtained from the Institute of Bast Fiber Crops, Chinese Academy of Agriculture Sciences (CAAS), was used without further treatment. The ethylenediamine, epichlorohydrin, sodium hydroxide, sodium bicarbonate, and sodium chloride were provided by the Xi'an Chemical Co. Ltd. The commercial dye of C.I. reactive red 2 (the structure is shown in Fig. 1) was supplied by the Qin Long Co. Ltd., China.

2.2. Modification of ramie fibber

The treatment of ramie fiber in an alkaline solution called mercerization was carried out for 3 h at a room temperature, followed by extensive washing with water until free of any detergents. Then the mercerized fiber (1 g) was put in a round-bottomed flask equipped with a magnetic stirring bar. After this, a mixture of epichlorohydrin (3 mL), 5% alkaline solution (50 mL), and anhydrous ethanol (3 mL) was added into the flask. The reaction was carried out at 50 °C for 5 h under stirring. After reaction, the product was washed with water and anhydrous ethanol by turns until the pH of 7, and finally dried at 60 °C.

The treated fiber (1 g) was immersed in a mixture of ethylenediamine (0.25–1.75 mol/l), and a desired amount of sodium bicarbonate as a catalyst (10 g/l) was added under continuous stirring. After reaction, the product was washed with water and anhydrous ethanol by turns until the pH of 7, and dried at 60 °C. Finally, white cellulosic ether was obtained.

2.3. Dyeing procedure

The ramie fiber either modified or unmodified was dyed with C.I. reactive red 2 at a liquor of 1:20 using a cold pad-batch process. 0.5 g fiber was soaked in a dyeing bath composed of 0.1% aqueous solution of the dye. The temperature of dyeing bath was gradually raised to 30 °C over 10 min, and the sodium chloride was added to accelerate dyeing. After the sample was kept in the dye bath for 30 min, sodium bicarbonate was added to the mixture. After 30 min, the dyed ramie fiber was squeezed, rinsed thoroughly with water and dried at 60 °C.

2.4. Characterization

The amount of ethylenediamine grafted on ramie fiber was calculated based on the nitrogen content, determined

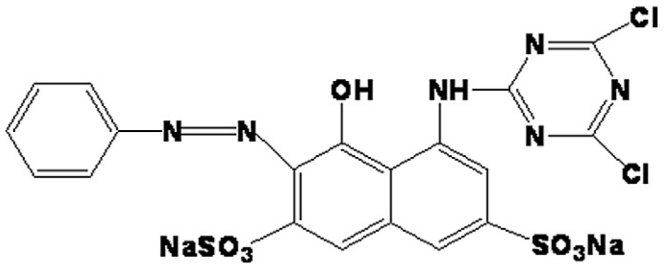


Fig. 1. The dye structure of C.I. reactive red 2.

by an elemental analyzer (Germany Elementar Analysensysteme GmbH, Vario EL III). IR analyses were carried out using an FT-IR spectrometer (Brucher Co. Ltd., EQUINOX55). About 2 mg of fiber was mixed with 200 mg of spectroscopic grade KBr, and the FT-IR spectra were recorded with a detector at 4 cm^{-1} resolution and 32 scans per sample. XRD was measured by a D/Max2000PC Rigaku wide angle X-ray diffractometer (WAXD) at a scan speed of 5° min^{-1}. For SEM analysis, ramie fiber was shadowed with gold and then examined with a Philips-FEI Model Quanta 2000 field emission scanning electron microscopy (FESEM), which was operated at 20 kV. Differential scanning calorimetry (DSC) measurements and thermogravimetric analysis (TGA) were performed using a Thermoanalyzer System, model Q600SDT (TA Co. Ltd.). About 5 mg of samples, placed in a DSC pan, were heated from −10 to 550 °C at a scanning rate of 10 °C min^{-1} under nitrogen atmosphere. The color strength and the dye uptake were measured with UV–Vis-NIR spectrometer (model Lambd 950, Perkin–Elmer Co. Ltd., USA). The color strength expressed as K/S is calculated from the reflectance values R using the Kubelka–Munk Eq. (1):

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

where R is the observed reflectance, K is the absorption coefficient, and S is the scattering coefficient.

The absorbency of the original dye solution and the residual solution was measured, and the dye uptake is calculated according to the Eq. (2).

$$E = (1 - A_1/A_0) \times 100\%, \tag{2}$$

where E is the dye uptake, A_0 is the absorbency of the original dye solution, A_1 is the absorbency of the residual solution after dyeing (Liu, Zhang, & Wang, 2005; Sabaa & Mokhtar, 2002).

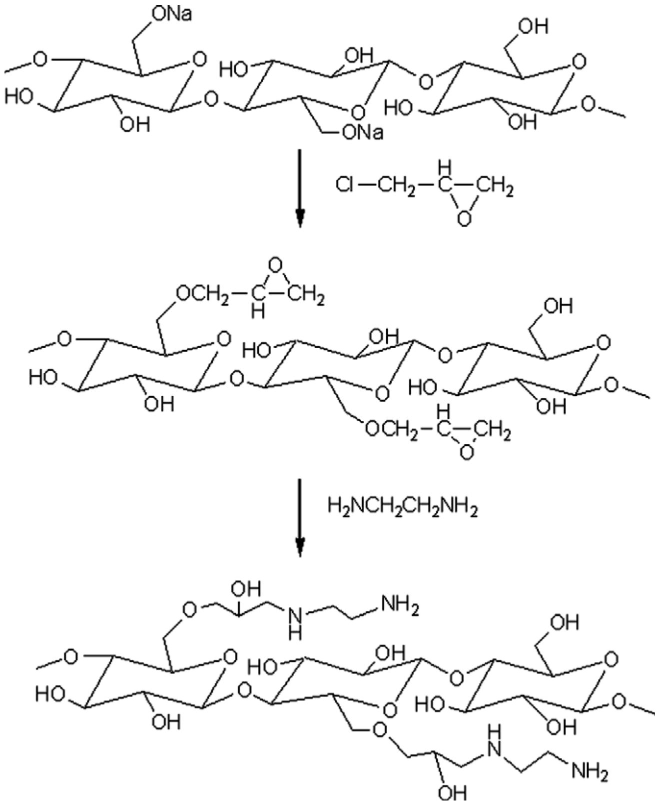
3. Results and discussion

3.1. The mechanism

The inter-reactive activities of ethylenediamine with the mercerized cellulose are poor, thus epichlorohydrin as a crosslinking agent was used to produce a cellulosic ether to improve the reactivity. Under the catalysis of alkali, cellulosic ether can be efficiently reacted with ethylenediamine, and a new material (CelNH) was formed (Lian, 2005). The reaction equations are shown as Scheme 1. To determine the optimal conditions for the grafting of ethylenediamine, effects of the concentration of ethylenediamine, temperature, and reaction time on the nitrogen content in CelNH were investigated and discussed as follows.

3.1.1. Effect of the concentration of ethylenediamine

By keeping a constant concentration of sodium bicarbonate (10 g/l), the grafting of ethylenediamine onto ramie fiber was studied at 50 °C for 5 h with different concentrations of ethylenediamine ranging from 0.25 to 1.75 mol/l. The results of Fig. 2 reveal that the nitrogen content contributed from amine groups in CelNH increased sharply with the increase of the concentration of ethylenediamine until 0.75 mol/l. Then it was leveled off when the concentration of ethylenediamine was above 0.75 mol/l. This can be easily explained based on the available epoxy groups



Scheme 1. The reaction procedure for the modification of ramie fiber.

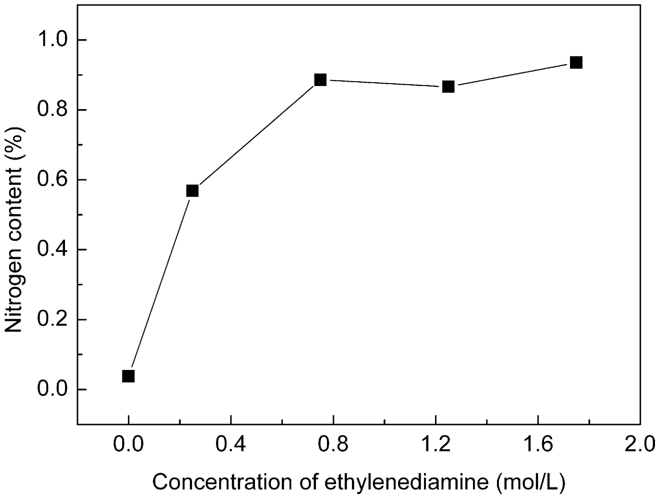


Fig. 2. The effect of the concentration of ethylenediamine on the nitrogen content of CelNH.

of CelNH. At a lower concentration of ethylenediamine, the increase in the concentration of ethylenediamine results in the increase of the extent of modification, and correspondingly the increase of the nitrogen content of CelNH. However, at higher concentrations of ethylenediamine (above 0.75 mol/l), the accessible epoxy groups of CelNH were used up for reacting with ethylenediamine, leading to an almost constant nitrogen content of CelNH.

3.1.2. Effect of temperature

The effect of temperature on the grafting behavior of ethylenediamine onto ramie fiber was studied by varying reaction temperature from 10 to 90 °C at a constant concentration of ethylenediamine (0.75 mol/l), sodium bicarbonate (10 g/l), and reaction time of 5 h. From Fig. 3, it can be seen that the nitrogen content of CelNH increased with the increase of temperatures until the temperature of 50 °C. However, the nitrogen content of CelNH decreased slightly when the temperature was above 70 °C. This may be due to that the epoxy groups were slightly hydrolyzed at higher temperatures leading to the slight decrease in nitrogen content of CelNH.

3.1.3. Effect of reaction time

The effect of reaction time on the extent of modification was studied at the concentration of ethylenediamine of 0.75 mol/l and sodium bicarbonate of 10 g/l at 50 °C . As shown in Fig. 4, after reaction for 5 h, the nitrogen content of CelNH was kept basically at a constant value within the experimental errors. This is straightforward that the degree of modification is determined by the amount of the active groups of cellulosic ether, so far as the reaction equilibrium was achieved, the nitrogen content of CelNH will not increase any more by extending reaction time.

From the above results, the optimal conditions for the preparation of CelNH are the concentration of ethylenediamine of 0.75 mol/l, the temperature of 50 °C, and the reaction time of 5 h.

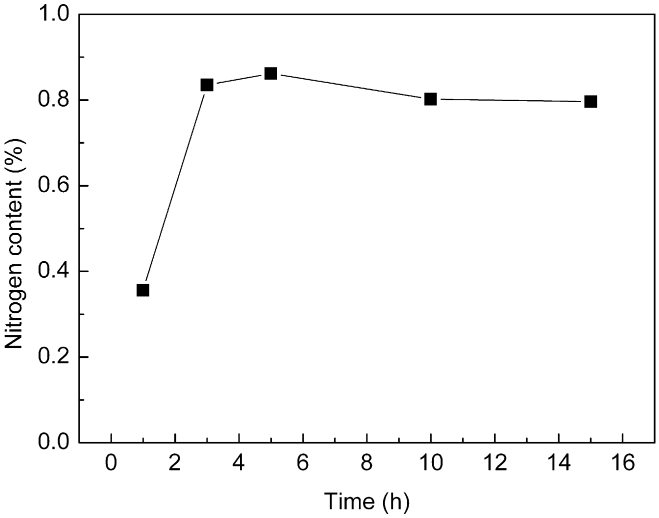


Fig. 4. The effect of reaction time on the nitrogen content of the CelNH.

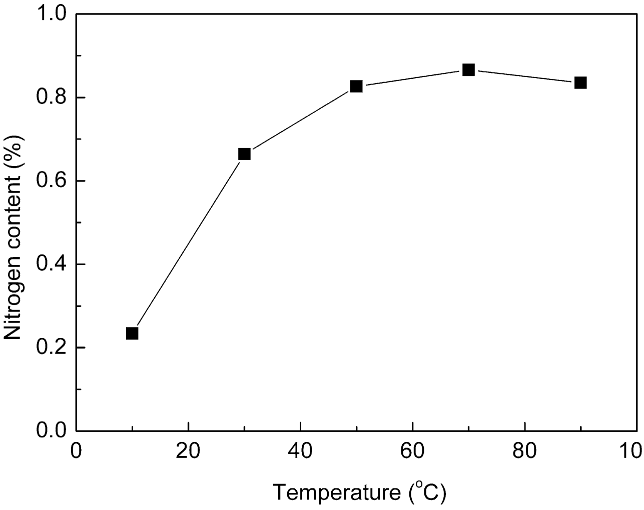


Fig. 3. The effect of reaction temperature on the nitrogen content of the CelNH.

3.2. FT-IR analysis

The IR spectra of the raw and the modified ramie fibers are shown in Fig. 5. The spectrum of the raw fiber exhibited O–H stretching absorption around 3449 cm^{-1}, C–H stretching absorption around 2900–3000 cm^{-1}, and C–O–C stretching absorption around 1061 and 1104 cm^{-1}. These absorptions are consistent with those of the typical cellulose backbone (Zhang, Price, & Daly, 2006). In the case of the mercerized fiber, almost the same absorption peaks to those of the raw fiber were observed (Fig. 5b). After modification with epichlorohydrin, the peak intensity at 2920 and 1060 cm^{-1} increased obviously, which is attributed to the introduction of the $-\mathrm{CH}_2$ groups. For the

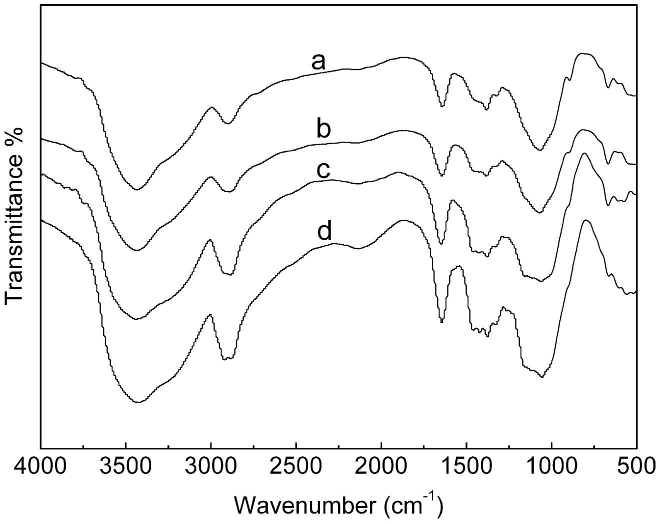


Fig. 5. FT-IR spectra of (a) ramie fiber, (b) the mercerized fiber, (c) the epichlorohydrin modified fiber, and (d) the CelNH.

CelNH, the peak intensity at 2920 and 1060 cm^{-1} increased furthermore as a result of the large quantity of –NH$_2$ and –CH$_2$ groups.

3.3. XRD analysis

The XRD patterns of the raw and the modified fibers are shown in Fig. 6. The raw fiber (Fig. 6a) showed the characteristic crystalline form of cellulose I as reported in the references (Ishikawa, Kuga, & Okano, 1998; Liu et al., 2007; Wada, Heux, & Sugiyama, 2004; Yin et al., 2007). For the mercerized fiber, the diffractions at 2θ of 11.7°, 19.9°, and 21.6° were observed, which are attributed to the typical cellulose II crystalline form. Thus, the crystal structure of ramie fiber was changed (from cellulose I to cellulose II) during mercerization. Moreover, in comparison with the raw fiber, the peak intensity of the mercerized fiber declined markedly indicating the decrease in crystallinity. After reaction with epicholorodrin, the crystal structure of cellulose II was still reserved although its peak intensity further decreased. However, the CelNH with XRD diffractions at 8.34° and 20.12° showed different crystal structure from either of cellulose I or II. The interplanar distances of the new crystal planes (8.34° and 20.12°) were wider than those of cellulose I and II, which can be attributed to an increase in the intermolecular distance between the cellulose chains.

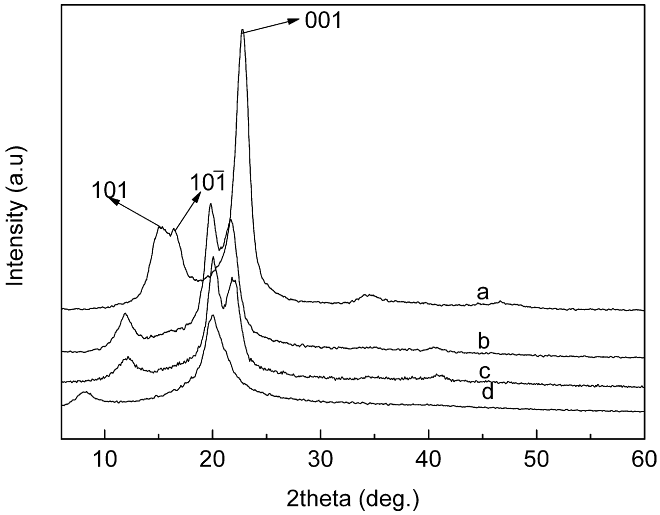


Fig. 6. XRD patterns of (a) ramie fiber, (b) the mercerized fiber, (c) the epichlorohydrin modified fiber, and (d) the CelNH.

3.4. SEM analysis

The surface morphology of the raw and modified fibers is shown in Fig. 7. The raw fiber has a very smooth and compact surface, and some knurls are observable along the vertical section (Fig. 7a). The surface of the mercerized fiber is quite similar to that of the raw fiber. However, after reaction with epicholorodrin and ethylenediamine, some silk-like materials can be seen on the surface of the fibers. Thus, there is only a little effect either of mercerization or modification with epicholorodrin and ethylenediamine on the surface morphology of ramie fiber observed by SEM.

3.5. TGA analysis

The TGA results of the raw and the modified ramie fibers are shown in Fig. 8. In the case of the raw fiber (Fig. 8a), after initial loss of moisture and desorption of gases at about 100–120 °C, a major decomposition occurred from 285 to 405 °C. For the mercerized fiber, the decomposition pattern was very similar to that of the raw fiber although its initial weight loss increased slightly. When the fiber modified with epicholorodrin and/or ethylenediamine, the starting decomposition temperature decreased obviously, indicating a decreased thermal stability. On the one hand, this may be due to the easy degradation nature of the grafted molecules, i.e., epicholorodrin and ethylenediamine. It has been reported that the thermal

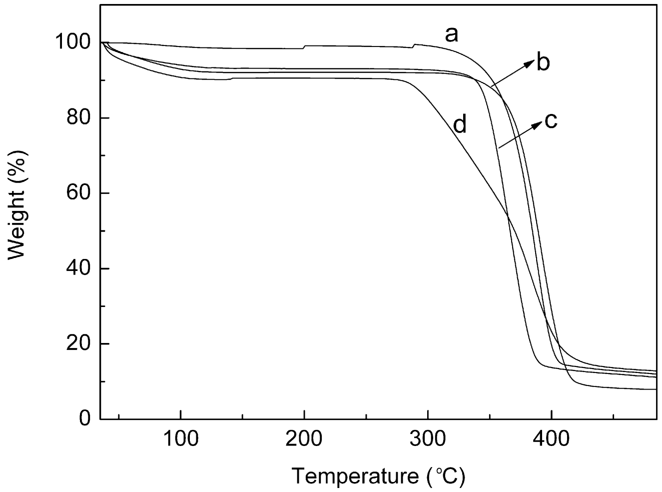


Fig. 8. TGA thermograms of (a) ramie fiber, (b) the mercerized fiber, (c) the epichlorohydrin modified fiber, and (d) the CelNH.

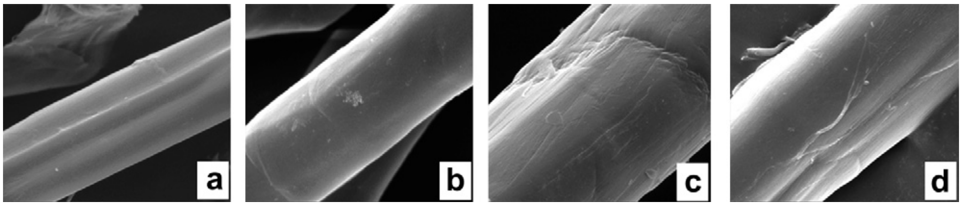


Fig. 7. SEM images of (Magnification, 3000×): (a) ramie fiber, (b) the mercerized fiber, (c) the epichlorohydrin modified fiber, and (d) the CelNH.

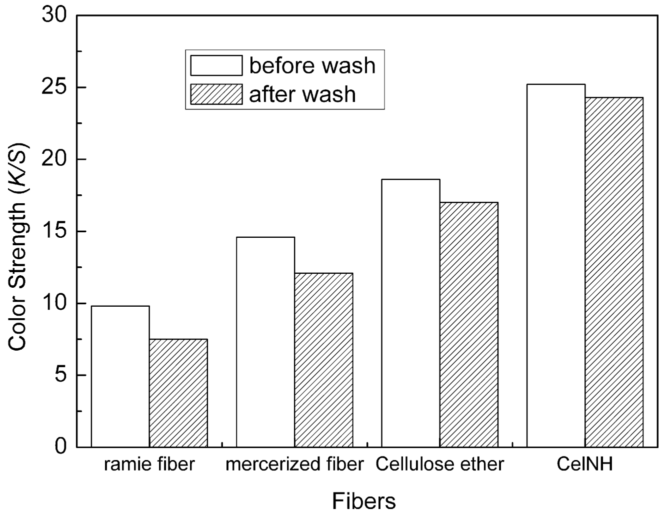


Fig. 9. The color strength (*K*/*S*) for the raw and modified fibers.

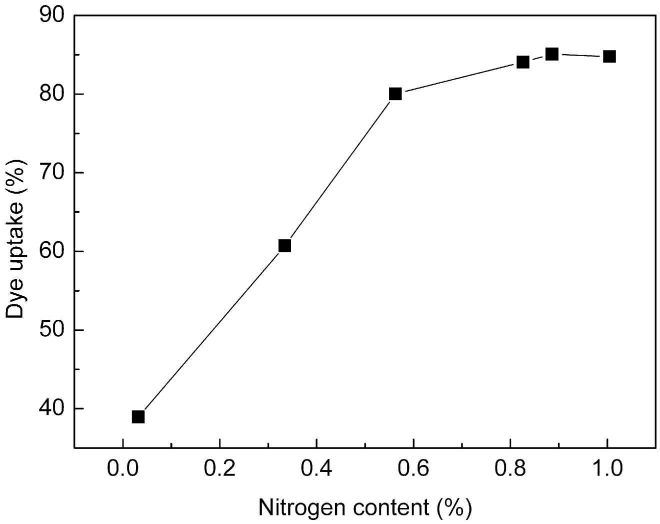


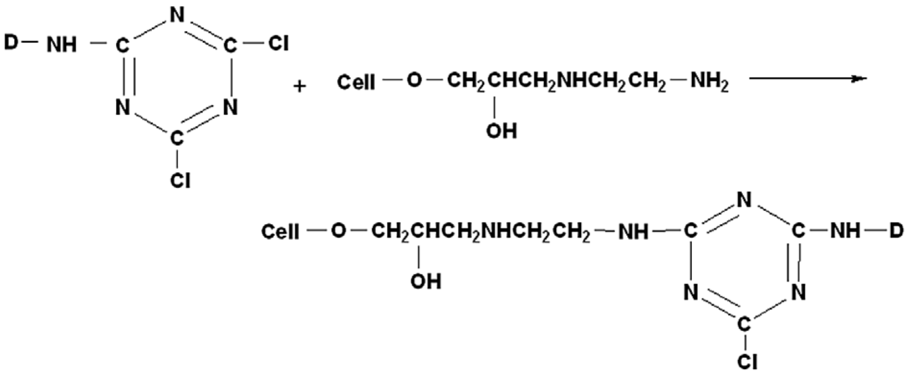
Fig. 10. The relation between the nitrogen content of CelNH and the dye uptake.

stability of cellulose and the modified cellulose depends on their crystallinity (Yin et al., 2007). Based on this fact, the lower stability of the modified ramie fiber may also be from the decreased crystallinity as shown in the XRD results.

3.6. Dyeing analysis

Generally, the fixing process of the dye to ramie fiber involves the transport of dye molecules from bulk solution across a porous surface layer within the fiber next to the solution, and then into the bulk fiber. The possible interactions between dye molecule and ramie fiber are electrostatic, van der Waals, and/or hydrogen bond (Tam et al., 1997; Yamaki et al., 2005). Reactive dyes are applied to cellulose using an alkaline solution. Hydroxide ions from the aqueous solution penetrate into the cellulose and the cellulosate ions thus formed proceed with a nucleophilic substitution or addition reaction with the reactive group of the dye molecule, which becomes covalently bonded to the polymer (Broadbent, Thérien, & Zhao, 1995). For the modified fiber, the reactive dye can react with the reactive groups of the CelNH, and the dyeability was improved.

The dyeability of the raw and modified fibers with the C.I. reactive red 2 was measured by color strength (*K*/*S* value) and dye uptake. As shown in Fig. 9, the raw fiber had a very low *K*/*S* value and a poor fastness to washing. For the mercerized fiber, the *K*/*S* value increased slightly. After modification with epichlorohydrin, the *K*/*S* value increased obviously. Among the fibers studied, the *K*/*S* value of CelNH was the highest (*K*/*S* about 25). This may be explained as follows. In the case of the raw fiber, dye molecules are combined mainly from physical adsorption or weak chemical interactions besides that a small quantity of dye molecules can combine with the raw fiber via covalent bond. As a result of swelling during mercerization, more sites for chemical and physical bonding of dye molecules are created, which results in the *K*/*S* value enhanced. After modification with epichlorohydrin, the reactive groups of ether can react with the dye molecule, so the color strength is enhanced. For the CelNH, many –NH groups are grafted on the fiber which have much higher reactivity and can react with dye molecules, and the color strength is enhanced further more. The reaction



Scheme 2. The reaction between modified fiber and reactive dye.

occurred between the CelNH and dye molecules is given below (see Scheme 2):

The relationship between the nitrogen content and the dye uptake of CelNH is illustrated in Fig. 10. At first, the dye uptake increased almost linearly with the increase of the nitrogen content when the nitrogen content is below 0.56%. The dye uptake increased slowly with the increase of the nitrogen content from 0.56% to 0.83%, and then it was leveled off with the further increase in nitrogen contents. The reason is from the limitation of the available –NH groups in CelNH as discussed previously. Thus, the color strength and the dye uptake of CelNH can be conveniently controlled by changing the modification degree of the fiber.

4. Conclusions

The chemical modification of ramie fiber with ethylenediamine was extensively studied using a crosslinking agent of epichlorohydrin under different conditions. The optimal conditions for the modification of ramie fiber were the concentration of ethylenediamine of 0.75 mol/l, the temperature of 50 °C, and the reaction time of 5 h. The characterization results show that the excellent characteristics of ramie fiber is still reserved after modification although the crystal structure of CelNH is different from either of cellulose I or cellulose II. The dyeability of the modified fiber expressed as K/S value and dye uptake was studied as a function of the nitrogen content in CelNH. Based on the analysis of the dyeing mechanism, it is proposed that the dye molecules were fixed on CelNH via covalent bonds and the dye uptake and the color strength of the modified fiber can be controlled by changing the degree of modification. Meanwhile, the two-step procedure using a less toxic and a cheap crosslinking agent has a potential industrial application.

Acknowledgments

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