Effects of a Pretreatment with *N*-Methylmorpholine-*N*-Oxide on the Structures and Properties of Ramie

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ABSTRACT: To improve the dyeing properties of ramie, the ecofriendly organic solvent *N*-methylmorpholine-*N*-oxide (NMMO) was used to substitute sodium hydroxide as a ramie-fiber swelling solvent. Through padding and baking pretreatment, ramie fabric was modified by an NMMO aqueous solution. Ultraviolet–visible spectrophotometry, Fourier transform infrared spectroscopy, X-ray diffraction, and differential scanning calorimetry were used to investigate the effects of NMMO pretreatment on the structure of the ramie, whereas the color strength (K/S, where K is the light absorption coefficient and S is the scattering coefficient), adsorption isotherm, and dye uptake rate curve were measured to investigate the effects of NMMO pretreatment on the dyeing properties of the ramie. The results show that the ramie fiber experienced a limited and irreversible swelling because of the partial breakage of interhydrogen and intrahydrogen bonds of cellulose molecules in the amorphous area, but the crystal and chemical structure of the ramie fiber did not change obviously under the experimental conditions. The K/S value of the NMMO-modified ramie fabrics dyed with reactive dyes increased by about 100%, and the dye uptake increased by 27.88% compared to that of the raw sample, whereas the standard affinity and diffusion coefficient value of the reactive dyes on the NMMO-modified ramie fabric were higher than those of the raw ramie fabric. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2241–2250, 2010

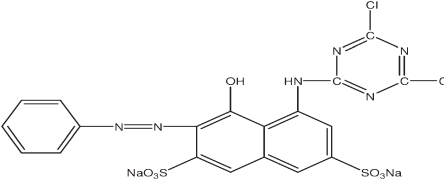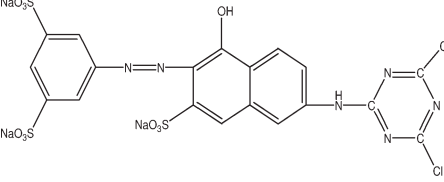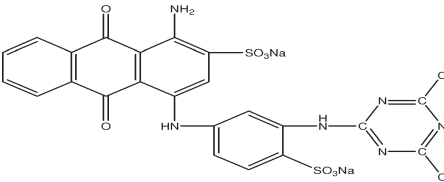**Key words:** dyes/pigments; modification; swelling

INTRODUCTION

Ramie is sometimes called *rhea* or *rhea grass,* and it is one of the oldest fiber crops, having been used for textile materials for at least 6000 years. Ramie is principally used for fabric production because of its excellent properties, including a high tensile strength, excellent thermal conductivity, coolness, ventilation function, moisture absorption, and antibacterial function.[1] The special molecular structure of ramie, including its high degree of polymerization, crystallinity, and orientation, results in some undesirable properties of in the ramie fiber and ramie fabric, such as poor elasticity, bad wrinkle recovery, itchiness, harsh handle, and dark and gloomy coloration. The disadvantages of ramie decrease its competitiveness in the high-grade-garment-fabric market greatly.[2] For a long time, to improve the dyeability of ramie fibers, some chemical methods, including mercerizing, cation modification,[3] liquid ammonia treatment,[4] copper ammonia solution modification,[5] acetylation modification,[6] and alkylation modification,[7] have been developed to modify the morphology and molecular structure of the ramie fiber, However, some problems needed to be solved when these methods were used.[8] Cation modification may bring with it the problem of level dyeing, liquid ammonia treatment is characterized by high cost, the copper ammonia solution is unstable and can produce ammonia gas easily, acetylation modification and alkylation modification result in the loss of some good characteristics of the original ramie, the mercerization of ramie fabric exhausts a large quantity of alkaline solution and extensive water for washing, and all of these processes bring with them the problem of environment pollution.

The toxicity of *N*-methylmorpholine-*N*-oxide (NMMO) is less than that of ethanol.[9] NMMO does not generate any potential pollution in the environment, and the NMMO solvent can be recovered almost completely.[10] NMMO as an ecofriendly organic solvent is widely used as a solvent for the direct dissolution of cellulose in industrial fiber making (the Lyocell process) and the modification of fibers. Some reports have indicated that cotton and wool fibers are swelled homogeneously in NMMO–water mixtures with water concentrations higher than 35%.[11] However, the substitution of sodium hydroxide with NMMO as a ramie swelling solvent to improve the dyeing properties of ramie has seldom been reported. In this study, ramie fabric was

TABLE I
Structures of the Dyes

Commercial name	CI generic name	Structure
Reactive Brilliant Red X-3B	CI reactive red 2	
Reactive Orange X-G	CI reactive orange 1	
Reactive Brilliant Blue X-BR	CI reactive blue 4	

modified through the padding of the NMMO solvent and baking pretreatment. The effects of NMMO pretreatment on the structure and dyeing properties of ramie were investigated through Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), color strength (K/S, where K is the light absorption coefficient and S is the scattering coefficient) measurement of a dyed ramie sample, thermodynamic parameter measurements, and diffusion coefficient (D) measurements of reactive dyes on the ramie fiber. The results show that it was possible to use NMMO to substitute for sodium hydroxide as a ramie fiber swelling solvent to improve the dyeing properties of the ramie under suitable treatment conditions.

EXPERIMENTAL

Materials

The ramie fabric was supplied by Sichuan Textile Research Institute (Chengdu, China). The NMMO solution (60 wt % NMMO) was supplied by Sichuan Tianlong Chemical Co., Ltd. (Zigong, China). The anhydrous sodium sulfate (analytical reagent), sodium carbonate (analytical reagent), sodium hydroxide (analytical reagent), barium hydroxide (analytical reagent), and sodium chloride (analytical reagent)

were supplied by the Chengdu Kelong Chemical Reagent Factory (Chengdu, China). The commercial dyes CI reactive red 2, CI reactive orange 1, and CI reactive blue 4 were supplied by Zhejiang Longsheng Group Co., Ltd. (Shaoxing, China). The structures are shown in Table I.

Modification of the ramie fabric

The ramie fabric was soaked in a 40% NMMO aqueous solution with a bath ratio of 1:5 and heated in a water bath for 10 min at a temperature of 60°C. Then, it was passed double-dip/double-nip through the rolls at room temperature with a fabric liquid holdup of 80%; this was followed by baking for 5 min at a temperature of 130°C. After baking, the fabric was washed thoroughly with the dilute NMMO aqueous solution at 80°C and distilled water and finally dried at a temperature of 80°C.

Dyeing procedure

The ramie fabric, both modified or unmodified, was dyed with CI reactive red 2, CI reactive orange 1, and CI reactive blue 4 with a bath ratio of 1 : 30 at a temperature of 40°C. After dyeing for 5 min, anhydrous sodium sulfate (30 g/L) was put into the dye bath twice. After dyeing for 30 min, sodium

carbonate (15 g/L) was added to the bath to fix the dye onto the fabric. After 30 min, the dyed ramie fabric was washed thoroughly with distilled water and dried under ambient conditions.

Measurement of the adsorption isotherm

The dried fiber (400 mg) was immersed in a 250-mL conical flask filled with 200 mL of dyeing solution, and the dye concentrations were as follows: 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5, 25, 27.5, 30, and 32.5 g/L. Then, 4 g of sodium chloride was added to the conical flask. The conical flask was sealed and placed in a HZS-HA Super Thermostat water bath vibrator (Haerbing, China) and shaken for 6 h at different temperatures at 100 rpm. Then, the fiber was removed from the conical flask and thoroughly washed with 50 mL of distilled water. The washing solution was added to the dyeing solution, and the equilibrium concentration of the solution was measured at the maximum wavelength of reactive dye by a spectrophotometer. The adsorption isotherm was plotted with the value of the dye concentration on the fiber ($[D]_f$) as the value of the ordinate and the value of the dye concentration in the dyeing residual solution ($[D]_s$) as the value of the abscissa.

Measurement of the exhaustion curve

The dried fiber (400 mg) was immersed in a 250 mL conical flask filled with 200 mL of dyeing solution, and the dye concentration of the solution was 20 g/L. Then, 4 g of sodium chloride was added to the conical flask, and the fiber was dyed at a temperature of 35°C. The procedure of dyeing was as same as that of the previous test. The fiber was removed from the conical flask at different dyeing times and was thoroughly washed with 50 mL of distilled water. The washing solution was added to the dyeing solution, and the absorbance of the dyeing residual solution was measured at the maximum wavelength of the reactive dye by a spectrophotometer. The exhaustion curve was plotted with the dye uptake value as the value of the ordinate and the value of the dyeing time as the value of the abscissa.

Measurements of the dyeing properties and structural changes

The exhaustion and fixation of the dye were measured by the dye bath absorption spectra method.[12] The K/S value and color difference of the dyed fabric were measured with a Rite Color Premier 8200 benchtop spectrophotometer (X-Rite, Inc., Granville, MI) under the illuminant D_{65}.

The tensile strength and elongation at break of different samples were tested according to ISO/DIS 13934.1-94. The rubbing fastness and washing fastness of the ramie samples were tested according to ISO 105-X12 (1993) and ISO 150-C02 (1998), respectively.

Optical micrographs of cross sections of the ramie fibers were investigated with an Olympus CX31-P polarizing microscope (Tokyo, Japan) with a magnification of 400×.

IR spectra of the ramie fabrics were obtained with a Nicolet 200SXV FTIR spectrophotometer (Thermo Nicolet Corp., Madison, WI) by reflectance spectroscopy.

The XRD pattern of the ramie fiber was recorded on a X'Pert PRO X-ray diffractometer (PANalytical B.V., Almelo, Holland) between $2\theta = 5°$ and $2\theta = 50°$ at a scanning speed of 5°/min.

The thermal stability of the ramie fiber was measured in air by DSC with a CDR-4P caloric analysis instrument (Cary Precision Instruments, Shanghai, China). The following conditions were used: temperature range = 20–500°C, scanning rate = 10°C/min, differential thermal compensation range = 240 mW, and sampling temperature range = 0–500°C.

The accessibility analysis of the ramie fibers was evaluated by the barium number[13] and water retention value.[14] Before measurement, the ramie fibers were dipped in the NMMO solution with the concentration ranging from 10 to 50% for 10 min and then baked 5 min at 130°C.

RESULTS AND DISCUSSION

Effect of the NMMO pretreatment on the dyeing properties of the ramie

Dye uptake and fixation of the reactive dye

The dye uptake and fixation rate curves of the reactive dye on the raw and modified ramie fabrics are shown in Figure 1. As shown in the curves in the figure, the dye uptake and fixation rate of the reactive dye on the NMMO-modified fabric were higher than those of the reactive dye on the raw ramie fabric. After the pretreatment with the NMMO aqueous solution, the hydrogen bond of the intercellulose or intracellulose molecules in the amorphous region of the ramie fiber was broken, and more hydroxyl groups, which could react with the reactive dye, were exposed under the strong swelling action of NMMO on the ramie fiber. The increase in dye accessibility and reactive groups of the modified ramie due to the opening of the ramie fiber structure led to increases in the dye uptake and fixation rate. Also, the dye uptake and fixation rate of CI reactive blue 4, with an anthraquinone structure, increased much less than that of dyes with azo structures, such as CI reactive red 2 and CI reactive orange 1.

K/S value

As shown by the data in Figure 1(d), after modification with the NMMO aqueous solution, the K/S
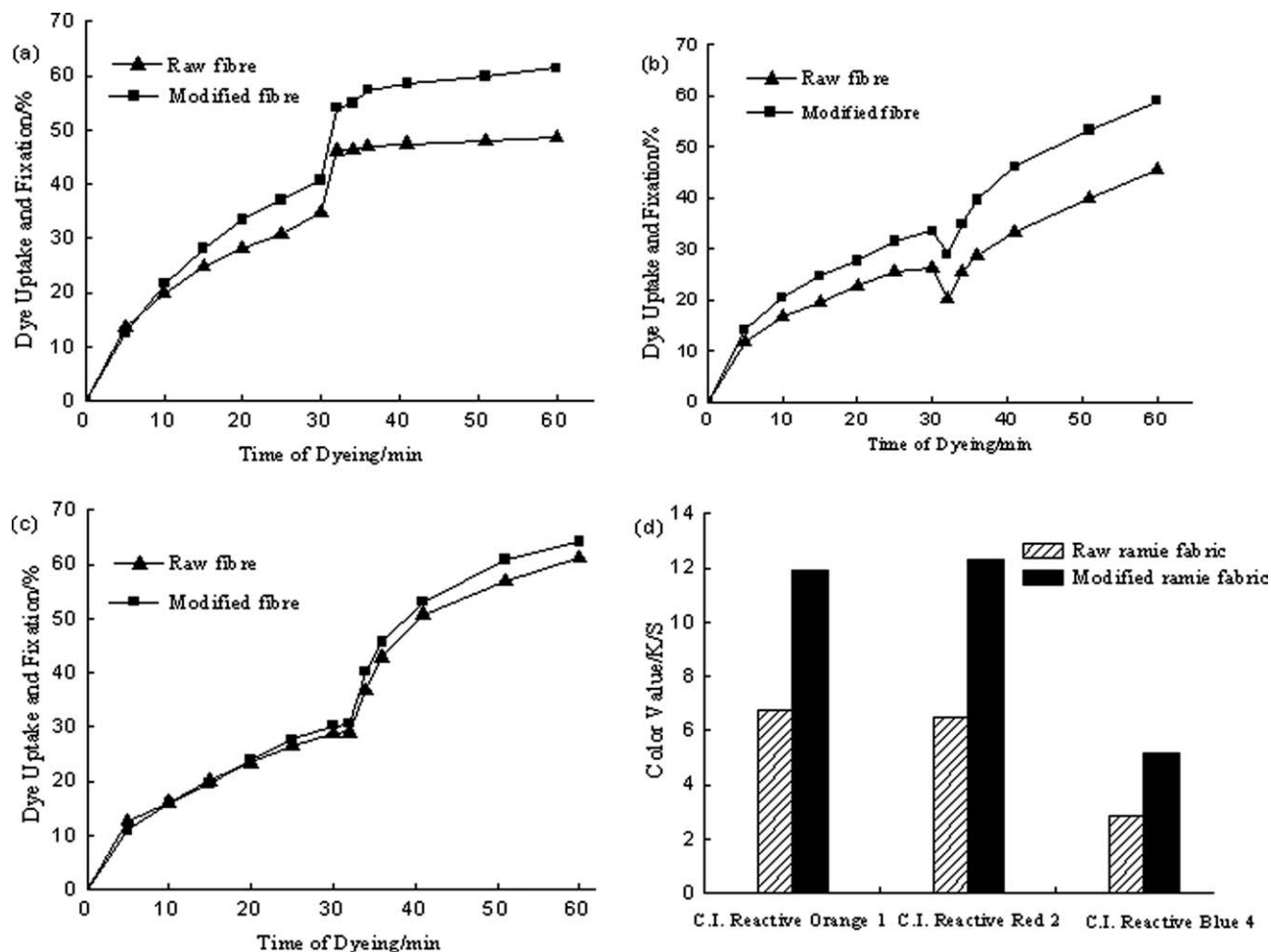
Figure 1   (a–c) Dye uptake and fixation of the reactive dyes (CI reactive red 2, CI reactive orange 1, and CI reactive blue 4, respectively) and (d) K/S values of the dyed ramie samples.

value of the ramie fabric increased by about 100%. This seemed to indicate that the increase of the K/S value of the ramie fabric was caused not only by the opening of the ramie fiber structure but also by the increase in the light reflection of the swelled ramie fiber.[8] The modification of the ramie fabric improved the surface color depth of the ramie fabric significantly and saved the dosage of the dye; this was beneficial to the reduction of the dyeing cost and discharge capacity of the dyeing effluent.

Color difference

The data listed in Table II are the color differences between the raw and modified ramie fabrics dyed with reactive dye. The lightness difference between the modified and raw ramie fabrics after dyeing was less than 0, whereas the chroma difference was more than 0, which indicated that the color of the modified ramie fabric was deeper and brighter than that of the raw ramie fabric after dyeing and that the problem of dull coloration for dyed ramie fabrics was improved by NMMO pretreatment.

Color fastness

The data in Table III show that the washing fastness of the ramie fabrics modified by the NMMO aqueous solution was similar with that of the raw ramie sample and the wet rubbing fastness of the modified sample was a little bit inferior to that of raw ramie sample after dyeing. This might be explained by the facts that the modified ramie fiber was easily swollen by water under the wet rubbing fastness measurement conditions and the dye molecule easily transferred from inside of the fiber to the surface under the action of friction force. Therefore, it is necessary

TABLE II
Colorimetric Data for the Dyed Ramie Fabric

Sample	DE	DL	DC	DH	DA	DB
CI reactive orange 1	7.474	−5.318	5.251	−0.019	2.280	4.731
CI reactive red 2	9.315	−6.543	3.170	5.823	2.395	6.183
CI reactive blue 4	8.635	−8.348	1.516	1.602	1.384	1.717

DA = red/green difference; DB = yellow/blue difference; DC = chroma difference; DE = color difference; DH = hue difference; DL = lightness difference.

TABLE III
Fastness Properties of the Dyed Ramie Fabric

| | | Washing fastness | | Rubbing fastness | | | |
| | | | | Warp direction | | Weft direction | |
Sample		Fading fastness	Staining fastness	Dry	Wet	Dry	Wet
CI reactive orange 1	Unmodified	4–5	4–5	4–5	4	4	4
	Modified	4–5	4–5	4	3–4	3–4	3–4
CI reactive red 2	Unmodified	4–5	4–5	4–5	4	4–5	3–4
	Modified	4–5	4–5	4–5	3–4	4–5	3
CI reactive blue 4	Unmodified	4–5	4–5	4–5	4	4–5	4–5
	Modified	4–5	4–5	4	4	4	4

to carry out a fixation treatment to improve the wet rubbing fastness of modified ramie fabrics.[15]

Tensile properties

The tensile data of the raw and modified ramie fabrics are listed in Table IV. The tensile strength of the modified fabric decreased with increasing baking time and increasing NMMO concentration because the breaking degree of hydrogen bonds broken in the amorphous region of the ramie fiber increased and the crystallinity of the ramie fiber decreased with increasing baking time and NMMO concentration. The elongation of the modified ramie fiber increased compared to that of the raw ramie fiber, which was attributed to the disorientation of cellulose macromolecules during NMMO aqueous solution swelling treatment.[16] So the dyeing properties and mechanical performance of the modified ramie fabric should be comprehensively considered when the optimum conditions of NMMO aqueous solution pretreatment are determined.

Thermodynamic parameters of dyeing and D values of the dye

Thermodynamic parameters

The standard affinity ($-\Delta\mu^0$) of a dye is a basic thermodynamic parameter. This parameter is defined as a negative difference between the chemical potential of the dye on the fiber and the chemical potential of the dye in the dyeing solution. This value is the measurement of the tendency for a dye moving from its standard state in solution to its standard state as a fiber.[17] The absorption isotherms of CI reactive red 2 on the ramie fiber at different temperatures are shown by the curves in Figure 2.

The adsorption isotherms of CI reactive red 2 on the raw ramie fiber and NMMO-modified ramie fiber at 35 and 60°C were found to obey the Freundlich adsorption isotherm. Thus, $-\Delta\mu^0$ (kJ/mol) of CI

reactive red 2 on the ramie fiber was calculated as follows:[18]

$$-\Delta\mu^0 = -(\mu_f^0 - \mu_s^0) = RT \ln\frac{a_f}{a_s}$$

$$= RT \ln\frac{[D^{z-}]_f[Na^+]_f^z}{V^{Z+1}} - RT \ln[D^{z-}]_s[Na^+]_s^z \quad (1)$$

$$[Na^+]_f = [D^{z-}]_f\left\{\frac{z}{2}\left(\frac{z^2}{4} + \frac{[Na^+]_s[Cl^-]_s V^2}{[D^{z-}]_f^2}\right)^{\frac{1}{2}}\right\}$$

where μ_f^0 is the standard chemical potential of the dye in the fiber, μ_s^0 is the standard chemical potential of the dye in the solution, R is the gas constant (1.9872 cal mol^{-1} K^{-1}), T is the absolute temperature (K), $[D^{z-}]_f$ is the dye concentration in the fiber (mol/kg), $[D^{z-}]_s$ is the dye concentration in the solution (mol/L), $[Na^+]_f$ is the concentration of sodium cations in the fiber (mol/kg), $[Na^+]_s$ is the concentration of sodium cations in the solution (mol/L), a_f is the dye activity in the fiber (mol/kg), a_s is the dye activity in the solution (mol/L), $[Cl^-]_s$ is the concentration of chloride anion in the solution (mol/L), V is the internal volume of cellulose (0.30 dm^3/kg), and Z is the charge number of dye anion.

TABLE IV
Tensile Strength and Elongation of the Ramie Fabric

| Sample | Tensile strength (N) | | Elongation at break (%) | |
	Warp	Weft	Warp	Weft
Unmodified	381	529	12.19	6.82
Modified I[a]	331	528	17.5	10.2
Modified II[b]	297	464	17.4	8.75

[a] The pretreatment consisted of dipping for 5 min in a 30% NMMO solution and baking for 2 min at 130°C.
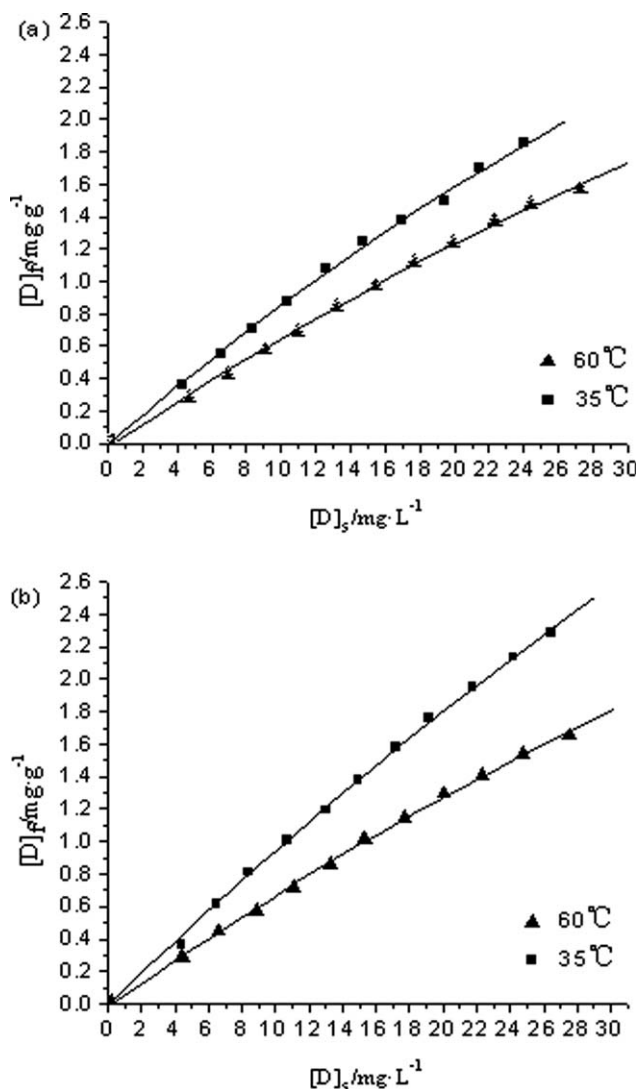[b] The pretreatment consisted of dipping for 10 min in a 40% NMMO solution and baking for 5 min at 130°C.

Figure 2 Adsorption isotherms of CI reactive red 2 on (a) the raw ramie fiber and (b) the NMMO-modified ramie fiber.

The enthalpy change [ΔH^0 (kJ/mol)] in the adsorption process was obtained from the relationship between $\Delta\mu^0/T$ and $1/T$, as shown as eq. (2).

$$\Delta H^0 = \frac{\partial(\Delta\mu^0/T)}{\partial(1/T)} \Delta H^0 = \frac{T_2\Delta\mu_1^0 - T_1\Delta\mu_2^0}{T_2 - T_1} \quad (2)$$

where $-\Delta\mu_1^0$ and $-\Delta\mu_2^0$ are the standard affinities (kJ/mol) and T_1 and T_2 are the absolute temperatures (K).

The entropy change [ΔS^0 (J K^{-1} mol^{-1})] was calculated as follows:

$$-\Delta\mu^0 = \Delta H^0 - T\Delta S^0 \quad (3)$$

where ΔH^0 is the heat of dyeing (kJ/mol).

The adsorption of a dye on a fiber is normally an exothermic reaction process, and the amount of exo-

thermic energy depends on the dyeing conditions, such as the dyeing media and the type of fiber and dye. ΔH^0 of dyeing is considered as the measurement of the adsorption strength of a dye with a fiber. Meanwhile, ΔS^0 of dyeing represents the entropy difference of a dye molecule transferring from a dyeing bath onto a fiber.[19] ΔS^0 shows a negative value in most dyeing processes because adsorbed dye becomes more restrained within fibers than in a dyeing bath. Therefore, the value of ΔS^0 can be regarded as a measurement of the immobility of dyes within fibers.

The $-\Delta\mu^0$, ΔH^0, and ΔS^0 values of CI reactive red 2 on the raw ramie fiber and the NMMO-modified ramie fiber are shown in Table V. $-\Delta\mu^0$ of CI reactive red 2 of the NMMO-modified fibers was a little higher than that of the raw ramie fibers, which indicated that the dye had a higher tendency to move from the dyeing bath to the NMMO-modified fiber than to the raw ramie fiber. The decrease in the dyeing enthalpy showed that the adsorption strength between the dye and the NMMO-modified ramie fiber decreased, which would be beneficial to the uniform dyeing of the ramie fabric. The decrease in the dyeing enthalpy and entropy indicated that the color fastness of the ramie fiber decreased after modification by NMMO.

D values of the dye

A dyeing process involves three continuous steps. The first step is the diffusion of the dye from aqueous dye bath onto the fiber. The second step is the adsorption of dye onto the outer layer of the fiber. The last step is the diffusion of dye into the fiber inside from the adsorbed surface. The diffusion of the dye within the fiber is the key process affecting the dyeing rate.

As shown in Figure 3, the dye uptake rate was higher in the modified ramie fiber than in the raw ramie fiber. The dye uptake rate increased with increasing dyeing time before 150 min; then, the dye uptake rate increased slowly until dyeing equilibrium.

According to the equation of Hill[20]

$$\frac{C_t}{C_\infty} = 1 - \sum \frac{4}{a_n^2}\exp\left(-\frac{Da_n^2 t}{a^2}\right) \quad (4)$$

TABLE V
Thermodynamic Parameters of CI Reactive Red 2 on the Ramie Fiber

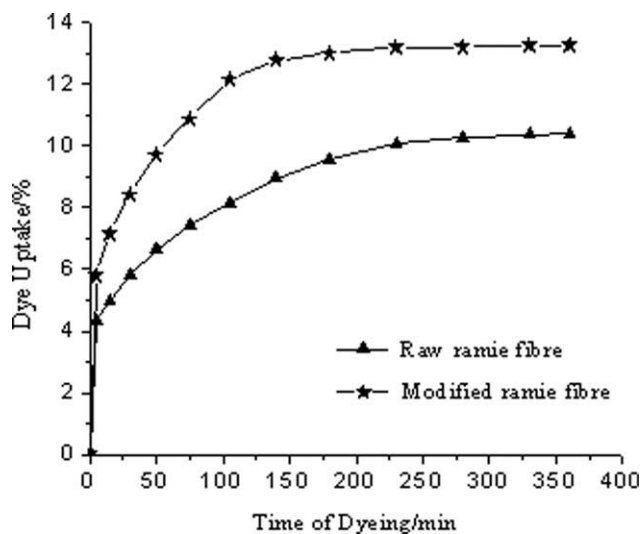| Sample	$-\Delta\mu^0$ (kJ/mol)		$-\Delta H^0$ (kJ/mol)	$-\Delta S^0$ (J K^{-1} mol^{-1})
	35°C	60°C		
Raw fiber	14.152	13.565	21.384	23.480
Modified fiber	15.019	14.636	19.738	16.222

Figure 3 Exhaustion curves of CI reactive red 2 on the ramie fiber.

where C_t is the ratio of the dye uptake at time t, C_∞ is the ratio of the dye uptake at equilibrium, a_n is the positive root of the Bessel function of the zero order, and a is the radius of the fiber (cm). D is calculated here as the apparent diffusion coefficient. If the dyeing time is short, eq. (4) can be rewritten as follows:

$$\frac{C_t}{C_\infty} = \frac{4}{\pi^{1/2}}\left(\frac{Dt}{a^2}\right)^{1/2} - \frac{Dt}{a^2} - \frac{1}{3\pi^{1/2}}\left(\frac{Dt}{a^2}\right)^{3/2} + \dots \quad (5)$$

$Dt/a^2 \ll 1$ leads to eq. (6).

$$\frac{C_t}{C_\infty} = 4\sqrt{\frac{Dt}{\pi a^2}} \quad (6)$$

The values of D at different dyeing times calculated by eq. (6) are shown in Table VI. The D values of the reactive dye on the NMMO-modified ramie fiber were higher than that of the reactive dye on the raw ramie fiber at all dyeing times, which indicated that the breakage of hydrogen bonds of the intercellulose or intracellulose molecules in the amorphous region of the ramie fiber after the NMMO swelling treatment led to the open of fiber structure and decreased the diffusion resisting force of the dye in the ramie fiber.[21]

Effect of the NMMO pretreatment on the structure of ramie

The barium number and water retention value were used to indicate the amorphous region and accessibility change of the fiber. The results reveal that the barium number and water retention value increased sharply with increasing concentration of NMMO

TABLE VI
D Values of CI Reactive Red 2 on the Ramie Fiber

Dyeing time (min)	D ($\times 10^{-14}$ m^2/s)	
	Raw ramie fiber	Modified ramie fiber
5	2.117	2.629
15	1.093	1.883
30	0.756	1.317
50	0.585	1.036
75	0.497	0.855
105	0.425	0.764
140	0.390	0.635
180	0.342	0.509
230	0.292	0.417
280	0.257	0.341
330	0.220	0.292
360	0.201	0.267

because, with increasing NMMO concentration, the quantity of hydrogen bonds broken in the amorphous region of the ramie fiber increased, and the swelling degree of the ramie fiber increased (Fig. 4). Compared with mercerization, the barium number
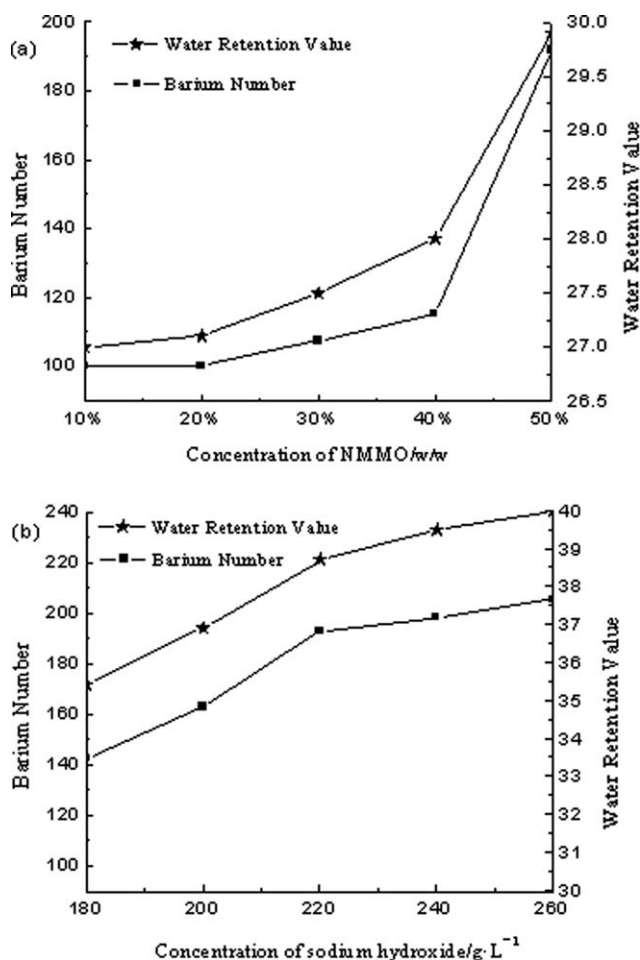

Figure 4 Barium number and water retention values of the ramie fiber swollen by (a) NMMO and (b) a sodium hydroxide solution.
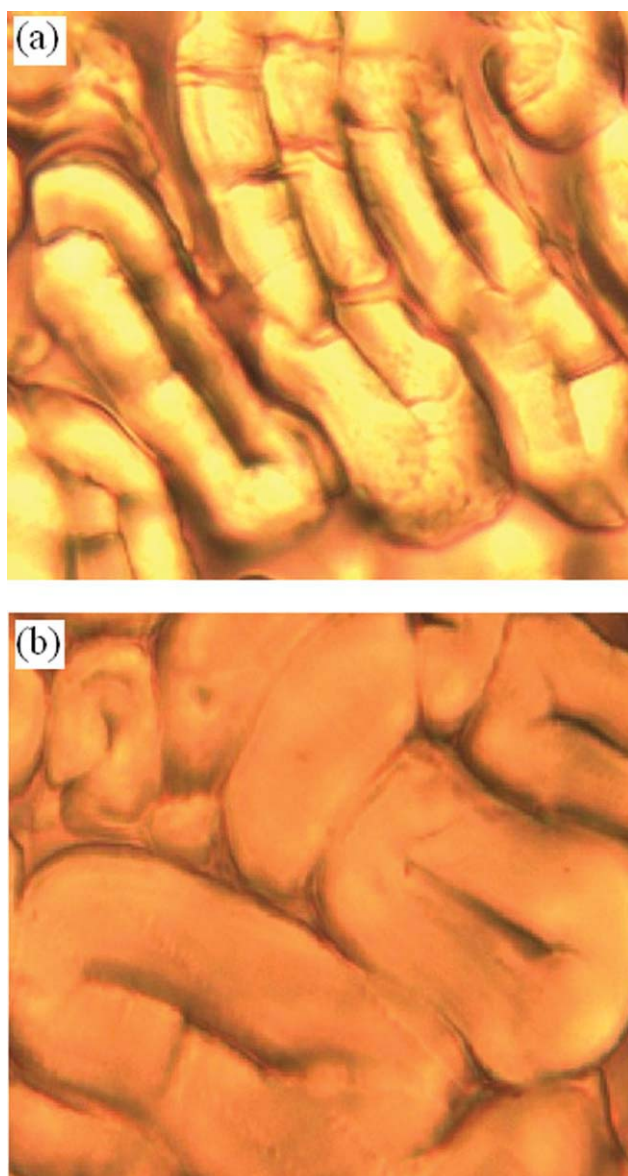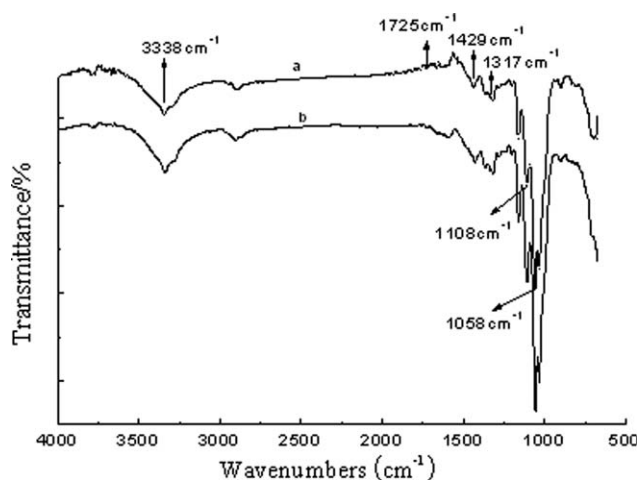
Figure 6 FTIR spectra of (a) the raw ramie fiber and (b) the NMMO-modified ramie fiber.

the shorter diameter of the cross section was about 2.30. After it was swollen by the NMMO aqueous solution, the ramie fiber thickness of the cell wall and cross-section diameter increased, and the ratio of the radial diameter to the crosswise diameter of the ramie fiber cross section decreased to 1.75, which was equivalent to that of the ramie sample mercerized by the 200 g/L sodium hydroxide solution.

The IR spectra of the raw and modified ramie fibers are shown in Figure 6. The spectrum of the raw fiber exhibited an O—H stretching absorption peak around 3338 cm^{-1}, a C—H stretching absorption peak around 2900–3000 cm^{-1}, and a C—O—C stretching absorption peak around 1058 and 1108 cm^{-1}. These absorption peaks were consistent with those of a typical cellulose macromolecule
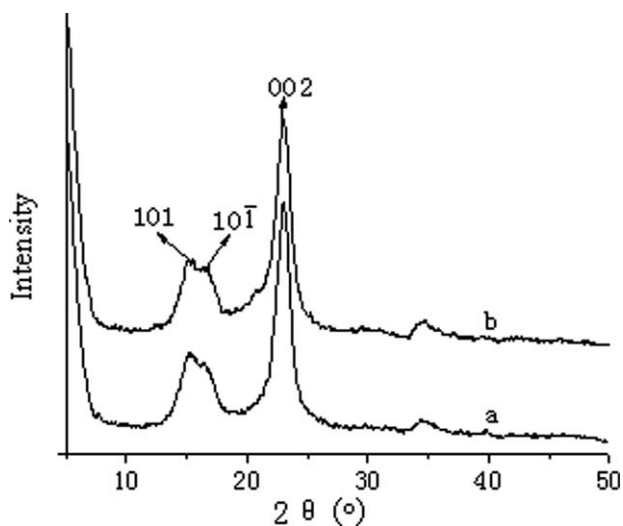
Figure 5 Optical micrographs of cross sections of (a) the raw ramie fiber and (b) the NMMO-modified ramie fiber with a magnification of 400×. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the ramie sample treated by the 50% NMMO aqueous solution was about 190, which was only equivalent to that of the ramie sample treated by a 220 g/L sodium hydroxide solution. The result indicates that the swelling action of the NMMO solution on the ramie fiber was lower than that of the sodium hydroxide solution on the ramie fiber under the experimental conditions.

Optical micrographs of the cross sections of the ramie fibers are presented in Figure 5. The cross section of the raw ramie fiber had an irregular oval with a cell cavity morphological structure, as shown as in Figure 5, and its ratio of the longer diameter to

Figure 7 XRD patterns of (a) the raw ramie fiber and (b) the NMMO-modified ramie fiber.
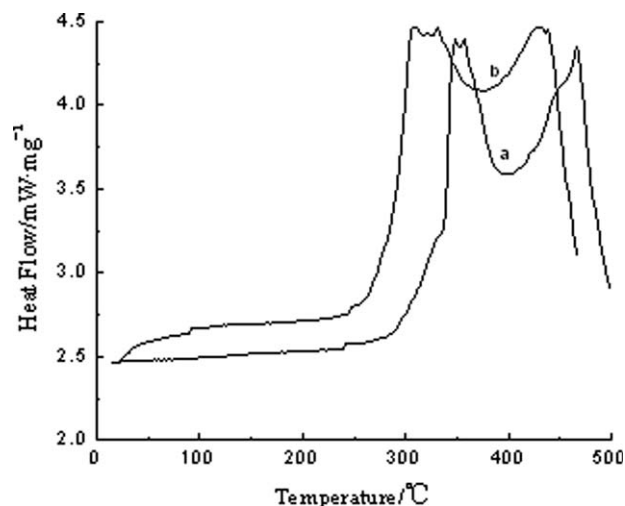
Figure 8 DSC thermograms of (a) the raw ramie fiber and (b) the NMMO-modified ramie fiber.

backbone.[22] Compared with the spectrum of the raw ramie fiber, the IR spectrum of the modified ramie fiber was without significant changes; this indicated that the chemical structure of the ramie cellulose macromolecule backbone did not change under the experimental conditions.

The peaks of 2θ at 15.1, 16.5, and 22.9° appearing in Figure 7(a) indicated that the type of crystals of the raw ramie fiber was consistent with cellulose I, as reported in ref. 23. The peaks of 2θ at 15.0, 16.3, and 22.9°, shown in Figure 7(b), suggested that the crystal structure of the ramie fiber modified by the NMMO aqueous solution did not change obviously under the experimental conditions, but compared with that of the raw fiber, the decline of the 2θ peak intensity at 22.9° indicated that the crystallinity of the modified ramie decreased to some degree.

The DSC plot of the raw ramie fiber contained two exothermic peaks at 354 and 470°C and an endothermic peak at 397°C. The corresponding DSC plot for the modified ramie fiber contained two exothermic peaks around 300 and 440°C and an endothermic peak at 370°C (Fig. 8).

The exothermic peaks of the ramie fiber were associated with the decomposition processes of cellulose fibers during heating. The exothermic peak at 354°C on the DSC curve of the raw ramie fiber was caused by the decomposition of cellulose macromolecules into laevoglucose at that temperature; then, the laevoglucose decomposed into coke and smaller molecules, whereas the exothermic peak at 470°C on the DSC curve of the raw ramie fiber showed that the coke was oxidized further into CO_2 or secondary coke under high temperatures.

The exothermic peaks on the DSC curve of the modified ramie fiber moved ahead to around 300

and 440°C, and the decomposition temperature of the modified ramie fiber decreased significantly compared with that of the raw ramie fiber, which indicated that the ramie fiber easily suffered thermal degradation, and then, its thermal property deteriorated after the fiber was modified by NMMO because of the breakage of hydrogen bonds and the decrease in crystallinity of the modified ramie fiber.

CONCLUSIONS

A modification process for ramie fiber with the environmentally friendly NMMO solution as a cellulose fiber expansion agent and as a substitute for the traditional sodium hydroxide solution was developed in this study. After modification by the NMMO solution, the crystallinity of the ramie fiber decreased and the accessibility of the ramie fiber increased to some degree, whereas the chemical structure of the ramie cellulose macromolecular backbone and the crystal structure of the ramie fiber did not change significantly.

When the modified ramie fabric was dyed with reactive dye, the dye uptake and K/S value of the modified samples improved compared to those of the raw samples. $-\Delta\mu^0$ and D of the reactive dye of the NMMO-modified fiber were higher than those of the raw ramie fiber. NMMO as a low-toxic solvent can be used to substitute for sodium hydroxide to improve the dyeing properties of ramie fiber under suitable treatment conditions.

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