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Synthesis and application of the cationic modifier on the ramie fiber

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ABSTRACT

A new cationic modifier was synthesized using trialkylamine and epoxy chloropropane, it was used to modify surface's morphologies of the ramie fiber. The modified ramie fiber was characterized by FT-IR spectroscopy and scanning electron microscope (SEM). Then modified ramie fiber was dyed with reactive dye and dye behaviour of the modified ramie fiber was measured. Results shown that the dye uptake of the modified ramie fiber can be controlled by changing the cationic modifier content. K/S value, the colour fastness and the dye uptake of the modified ramie fiber were greatly improved.

KEYWORDS

Ramie fiber;
Cationic modifier;
Reactive dye;
Dye uptake;
Colour fastness.

INTRODUCTION

The ramie fiber is an important textile[1-2] with good properties, such as high tensile strength, excellent thermalconductivity, coolness, ventilation function, moisture absorption, antibacterial function, and so on. The native cellulose is a linear macromolecule formed by β-D glucose units linked together by 1,4-glucosidicbonds. The ramie fiber is composed of a partial crystalline phase where the cellulose chains are firmly tied through hydrogen bond, an interfacial region next to the lateral faces of the crystallites, and an amorphous region where chain segments are believed to be randomly oriented. Experiments shown that the high crystallinity and orientation of the ramie fiber results in the comfortlessness on dress because of the scratchiness of ramie fiber[3-5], it also affected the dye uptake of reactive dye on the ramie fiber, dye uptake is not high in general.

In order to increase acting force of the dyes on the ramie fiber cellulose, moderate electrolyte such as NaCl and Na_2SO_4 was added in dye liquor to reduce repulsive force of the negative charge on the ramie fiber's surface[6]. However, add electrolyte to the dye liquor would increase the acidity of dye liquor and produce a new pollution to environment. Therefore, improvement of dyeing was studied for the ramie fiber in neutrality solution without electrolyte.

In order to improve the dyeability and some property of the ramie fiber, chemical methods were introduce into modification[7-12] of ramie fiber. Not only the surface properties but also the bulk performance of the ramie fiber, can be modified by choosing proper chemicals. A method for chelating cotton fiber with ethylenediamine was developed by D.L.Orden[13], Z.T.Liu and Y.Yang[14] has used ethylenediamine on the ramie fiber, for example.

Thus, in order to improve the dyeability of the ramie fiber efficiently, it is necessary to introduce reactive groups on the ramie fiber. In this paper, a new cationic modifier was synthesized using trialkylamine and epoxy chloropropane. The cationic modifier was used to modify ramie fibers, relationship between the modified condition and the modified effect of the ramie fiber were studied.

2. EXPERIMENTAL

2.1. Instruments and reagents

Trialkylamine, sulfuric acid, epoxy chloropropane, acetic acid, ethanol (Analytical reagent, China). 36s ramie fiber textile (China). reactive red X-6BN, reactive yellow X-4NR, reactive black X-BN (Technically pure,China).

IR analyses of the modified ramie fiber and the unmodified ramie fiber were carried out using a Fouriertransform infrared spectroscopy (FI-IR). Surface structure of the ramie fiber was analyzed with a scanning electron microscope (SEM, S-570, Japan). Colour fastness of the ramie fiber was measured by the GB 3920-83 textile and Y571B dry friction fastness. The K/S values of the ramie fiber were measured by SCT(Dataflash 100, U.S.). The dye uptake of the ramie fiber, the absorbency of the original dye liquor and the residual solution after dyeing were measured with UV–754 spectrometer.

2.2. Synthesis methods of the cationic modifier

0.50 mol trialkylamine and 60 mL deionized water were added to a 250 mL three-necked flask equipped with a spherical condenser and an agitator£¬0.1 mol.L^{-1} sulfuric acid and 0.1 mol.L^{-1} epoxy chloropropane were slowly added into the three-necked flask for a period of 0.5 h. The mixture was stirred for 3 h at 50-55^{0}C, one kind of slight yellow product was formed, then the residuals in the product were removed under vacuum at 50^{0}C. The cationic modifier was obtained.

2.3. Modified method of ramie fiber

The ramie fiber was added in a solution with appropriate amount of the cationic modifier, soaked for 60 minutes at a optimal temperature, then washed with water and 0.05mol·L^{-1} acetic acid solution, respectively.

2.4. Dyeing of the ramie fiber

The modified ramie fiber was dyed with 3%(wt.%) reactive dye liquor, (The fabric and the dye liquor ratio of are 1 to 20). The temperature of dye liquor was gradually raised to 40^{0}C over 10 min. After dyeing, the dyed ramie fiber was squeezed, rinsed thoroughly with water and dried at 60^{0}C. But 0.05mol·L^{-1} sodium phosphate solution was add in dye liquor during dyeing of the unmodified ramie fiber.

3. RESULTS AND DISCUSSIONS

3.1. Structural characterization of the ramie fiber

1. FT-IR analysis

Infrared spectrum of the ramie fiber exhibited O–H stretching absorption around 3210-3650cm^{-1}, C–H stretching absorption around 2890-2990cm^{-1}, and C–O–C stretching absorption around 1100-1230 cm^{-1}. These absorptions are consistent with those of the typical cellulose backbone[14]. After modification with the cationic modifier, the peak intensity of the modified ramie fiber at 3360 and 2940 cm^{-1} increased slightly, which is attributed to the introduction of the alkyl, the epoxy groups and amine groups.

2. SEM analysis

The surface's morphologies of the ramie fiber are shown in figure 1 (unmodified) and figure 2 (modified). The unmodified ramie fiber has a smooth and compact surface, but the surface of the modified ramie fiber is uneven, the original smooth surface of ramie fiber turned the strip shape or filiform.

Ramie fibers usually have a high crystallinity and rough surface[2]. Because, the cationic modifier contains the epoxy groups and amine groups, surface's

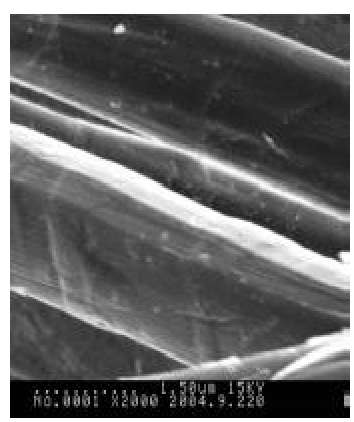

Figure 1 : Scanning electron microscopy photo of the the unmodified ramie fiber

morphologies of the ramie fiber can be improved through forming the ether bond between the hydroxyl groups of the ramie fiber and the epoxy groups of the cationic modifier. At first, modification of the ramie fiber in the presence of cationic modifier is a swelling process, then is grafting process of cationic modifier on the ramie fiber cellulose. Among swelling process, the capillaries walls of the ramie fiber were extented, the surface's morphologies of the ramie fiber were improved through swelling, resulted in the surface area of the ramie fiber (including internal surface) and molecular linkage spacing was increased, then it would reduce the hydrogen bond intensity and even break the crystal lattice of the ramie fiber. Some groups was wrapped up in the ramie fiber can appearence through swelling, increased the response active spot of the ramie fiber, it is advantageous to form the ether bond between the hydroxyl groups of the ramie fiber and the epoxy groups of the cationic modifier, the ether groups are reactive intermediate of the ramie fiber for dyeing.

Softness of the ramie fiber can be improved through destruction of the ramie fiber crystal lattice in the cationic modifier. So that the cationic modifier can improve the response performance and softness of the ramie fiber cellulose.

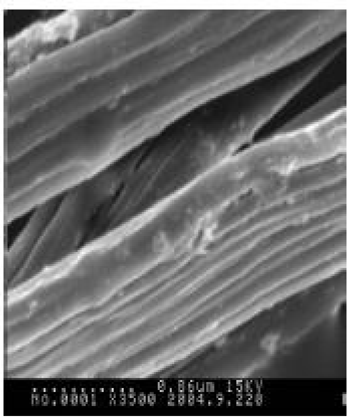

Figure 2 : Scanning electron microscopy photo of the modified ramie fiber

3.2. Effect of cationic modifier content to ramie fiber

The effect of the cationic modifier to the ramie fiber was tested at an optimal temperature for 60 min with different cationic modifier content, ranging from 0.1% to 0.5 %(wt.%). Experimental results as shown in **TABLE** 1. Results indicate, when the cationic modifier content from 0.1% to 0.35%(wt.%), the K/S values and the dye uptake of the modified ramie fiber increased almost linearly with the increase of the cationic modifier content, then it is about the same with the further increase in the cationic modifier content above 0.35%(wt.%). Colour fastness of the modified ramie fiber is about the similar at cationic modifier content from 0.1% to 0.5%(wt.%). The relationship between the cationic modifier content and the dye uptake of the modified ramie fiber can be explained with the epoxy group and amine group of the cationic modifier. The hydroxyl groups of the ramie fiber can be combined with the epoxy group of the cationic modifier, they were transformed into reactive intermediate ether groups, then the acidic groups of the reactive dye can combine with the amine group of the cationic modifier by ionic bond, this chemical interactions is advantageous in enhances the dye uptake of the ramie fiber, so the dye uptake of the modified ramie fiber was increased. When the cationic modifier content is below 0.35%(wt.%), increase of cationic modifier content provide more epoxy groups and amine groups, therefore result in an increase of the dye uptake of the modified ramie fiber. However, when

TABLE 1: K/S values, dye uptake and colour fastness of the modified ramie fiber with the cationic modifier content

Content of the modifier	Reactive red X-6BN			Reactive yellow X-4NR			Reactive black X-BN		
	K/S values	Dye uptakes	Colour fastness	K/S values	Dye uptakes	Colour fastness	K/S values	Dye uptakes	Colour fastness
0.1%	10.05	43.51%	3-4	9.36	42.96%	3-4	10.59	47.81%	4
0.15%	11.25	50.35%	3-4	11.08	49.01%	3-4	12.92	54.65%	4
0.20%	13.93	57.74%	3-4	13.11	54.03%	3-4	14.21	61.45%	4
0.25%	14.85	61.53%	3-4	14.27	57.72%	3-4	15.13	64.74%	4
0.30%	15.78	63.85%	3-4	15.23	59.67%	3-4	16.61	67.56%	4
0.35%	15.91	65.71%	3-4	15.25	61.21%	3-4	16.62	69.61%	4
0.40%	15.92	65.79%	3-4	15.24	61.40%	3-4	16.64	69.96%	4
0.45%	15.90	65.87%	3-4	15.27	61.51%	3-4	16.65	70.12%	4
0.50%	15.91	65.92%	3-4	15.25	61.49%	3-4	16.65	70.16%	4

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TABLE 2: K/S values of the modified ramie fiber and unmodified ramie fiber

Dye	Modified ramie fiber	Unmodified ramie fiber
Reactive red X-6BN	15.91	9.67
Reactive yellow X-4NR	15.25	9.02
Reactive black X-BN	16.62	10.06

TABLE 3: Dye uptakes of the modified ramie fiber and unmodified ramie fiber

Dye	Modified ramie fiber	Unmodified ramie fiber
Reactive red X-6BN	65.71%	45.2%
Reactive yellow X-4NR	61.21%	44.1%
Reactive black X-BN	69. 65%	49.7%

TABLE 4: Colour fastness of the modified ramie fiber and unmodified ramie fiber

Dye	Modified ramie fiber		Unmodified ramie fiber	
	Fastness to crocking	Fastness to soaping	Fastness to crocking	Fastness to soaping
Reactive red X-6BN	4	4	4	3-4
Reactive yellow X-4NR	4	4	4	3-4
Reactive black X-BN	5	4	4-5	3-4

TABLE 5: The absorbency of the residual solution after dyeing

Dye	Modified ramie fiber (0.35% the cationic modifier)	Unmodified ramie fiber
Reactive red X-6BN	0.102	0.198
Reactive yellow X-4NR	0.112	0.211
Reactive black X-BN	0.097	0.187

cationic modifier content above 0.35%(wt.%), the epoxy groups of the cationic modifier are excess in the ramie fiber, so that K/S values and the dye uptake of the modified ramie fiber are close to the similar level.

3.3. Dyeing analysis of reactive dyes with the modified ramie fiber

Experimental results (TABLE 1-5) shown that K/S values and dye uptake of the modified ramie fiber are greater than the unmodified ramie fiber in three different dye liquor: 1) reactive red X-6BN, 2) reactive yellow X-4NR, and 3) reactive black X-BN under the same conditions. TABLE 2 shows that K/S values of modified ramie fiber were about 1.5 to 1.6 times greater than that of the unmodified ramie fiber. TABLE 3 shows that dye uptake of the modified ramie fiber is about 1.4 to 1.5 times deeper than that of the unmodified ramie fiber. TABLE 4 shows that colour fastness of the modified ramie fiber also increased slightly. TABLE 5 revealed the absorbency of the residual solution after dyeing was greatly reduced. For comparison, parallel experiments shows that the residual dye of the modified ramie fiber in the dye liquor was about 20% to 50%(wt.%) lower than that of the unmodified ramie fiber. Experimental results demonstrated a potential reduction in the amount of materials needed and therefore a cost can be reduced in manufacturing.

Usually, there are an inherent attraction for one another between reactive dyes and the ramie fiber. Reactive dyes are attracted to the ramie fiber molecules through chemical interactions between the reactive dye molecules and the ramie fiber in the dyeing. In fact, dyeability of ramie fiber can be effected with substrate variation of the ramie fiber. The mature ramie fiber can have a major effect on dyeability. Characterical detects discover£¬due to the presence of small number immature ramie fibers range from the presence of clumps of white, unmodified ramie fibers to off shade materials resulting from differential dye uptake of the different reactive dyes in the dyeing. Since each individual secondary bond is relatively weak, multiple interactions are needed for a good bonding between a single reactive dye molecule and the ramie fiber molecules. Because the capillaries walls of the ramie fiber were extented through swelling of the cationic modifier, the active groups of the ramie fiber were further developed£¬the amine groups and the epoxy groups were further grafted on ramie fiber at the same time, the secondary wall in the mature or immature ramie fibers can be developed through modification of ramie fiber.

Generally, dyeing involves the transfer of dye molecules from bulk solution across a porous surface layer of the ramie fiber, then penetrate into the bulk fiber. In dyeing of the unmodified ramie fiber, most of dye molecules are physical adsorption or weak chemical interactions with ramie fiber. Only a portion of dye molecules can firmly link to ramie fiber through covalent bond. The possible interactions between dye molecules and the ramie fibers are through electrostatic force, van der waals or hydrogen bond.

But the ramie fiber molecules can induce the amine groups and the epoxy groups after the modification, some reactive sites for chemical and physical binding of ramie fiber molecules are created. In dyeing of the modified ramie fiber, dye molecules from the dye liquor penetrate into the cellulose, amine groups of the modified ramie fiber can be efficiently reacted with the reactive groups of the dye molecule, an ionic bond can form between the amine groups of modified ramie fiber and the acidic groups of reactive dye. These ionic bond is stronger than hydrogen bond or van der waals, therefore, grafting of the cationic modifier molecules on the ramie fiber is also hindered giving them the potential for better dyeability and colour fastness properties, reactive dyes which form ionic bond or covalent bonds with the modified ramie fibers. Results in the dyeability of the modified ramie fiber is improved, So that the K/S values and dye uptake of the modified ramie fiber increased significantly.

Since reactive dyes which form ionic bond or covalent bonds with the modified ramie fibers, the bond is very strong and resistant to cleavage, the colour fastness of the modified ramie fiber is enhanced. so that the modified ramie fibers have excellent washfasness.

The ramie fiber moisture absorption mainly occurs in the amorphous area. After the ramie fiber was modified, the crystal lattice of the ramie fiber cellulose would be destroyed. Crystallinity of the modified ramie fiber was reduced, moisture absorbability of the modified ramie fiber was improved through hydrogen bond between amine groups of the modified ramie fiber and water. Therefore, the moisture absorbability and softness of the modified ramie fiber is better than the unmodified ramie fiber.

4. CONCLUSIONS

A new cationic modifier was synthesized and used to modify ramie fiber. Results shown that the surface's morphologies of the modified ramie fiber have been changed by the cationic modifier. The dyeing of the modified ramie fiber was relatively simple. The K/S values, the colour fastness and the dye uptake of the modified ramie fiber increased significantly with an increase in the cationic modifier content. Parameters of the modification were optimized. The optimal cationic modifier content is about 0.35%(wt.%). The absorbency of the residual solution after dyeing was greatly reduced and softness of ramie fiber was improved.

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