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ORIGINAL PAPER

Dyeing performances of ramie fabrics modified with an amino-terminated aliphatic hyperbranched polymer

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Abstract An amino-terminated aliphatic hyperbranched polymer (HBP-NH_2) was used to modify ramie fabric. The molecular weight of HBP-NH_2 was established by GPC. HBP-NH_2 structure might represent as $BA_4BA_3BA_3$ (third generation). The total amine value, secondary amine value and primary amine value of HBP-NH_2 were 291.59, 210.14 and 81.45 mg/g respectively with hydrochloric acid—ethanol titration method. The unmodified and modified ramie fabrics were characterized by XRD and FE-SEM. XRD results showed a transformation of crystalline structure from ramie cellulose I to cellulose II allomorph during mercerization and epichlorohydrin modification, and the crystalline structure of cellulose II maintained with obvious crystallinity index increase after HBP-NH_2 modification. Nitrogen content of HBP-NH_2 modified fabrics were 1.25–2.61 %. Cationization degree (D_C) of HBP-NH_2 modified ramie fabrics were 4.41–9.40 %. C.I. Reactive Red 2 was applied to study the dyeing performance of modified fabrics. The modification parameters were optimized as 50 °C for 5 h when the concentration of HBP-NH_2 was 8 g/L. K/S value and dye uptake of modified fabric was 23.64 and 85.6 % respectively under optimal modification conditions. The washing, rubbing and light fastness of modified ramie fabrics were acceptable. The tensile strength and tear strength of HBP-NH_2 modified ramie fabrics were lower than those of unmodified fabrics. The warp, weft of tensile and tear strength retention of modified fabrics were between 85.23 and 87.50 %. The HBP-NH_2 modification mechanism and dyeing mechanism on ramie fabric were suggested.

Keywords Amino-terminated aliphatic hyperbranched polymer · Ramie fabric · Modification · Amine value · Color strength · Reactive dyeing

Abbreviations

HBP-NH_2	Amino-terminated aliphatic hyperbranched polymer
GPC	Gel permeation chromatography
D_C	Cationization degree
XRD	X-ray diffraction

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FT-IR	Fourier transform infrared spectrometer
FE-SEM	Field emission scanning electron micrograph

Introduction

Ramie fabric, mainly composed of cellulose, has such attractive features as high air permeability, excellent thermal insulation, favorable hygroscopicity, and good antibacterial properties, etc. (Pandey 2007). Concerning the supramolecular structure, ramie cellulose is composed of a partial crystalline phase where cellulose chains are firmly tied with hydrogen bonds, and an amorphous region where chain segments are believed to be randomly oriented. The morphological complexity in supramolecular structure of cellulose has decisive consequences on its surface activity in sorption swelling, reactivity, dyeing uniformity, and dye uptake (Junghans et al. 2006; Xie et al. 2005). However, because of its high degree of polymerization, orientation and crystallinity, normally dyed ramie fabric has relatively low dye uptake, low dye permeability, and low color strength. Therefore, it is necessary to modify the surface properties of ramie fabrics (Nam and Netravali 2006).

Moreover, with increasing awareness of environmental protection and ever more stringent regulations, the traditional textile industry is continuously looking for cleaner production process to replace the existing traditional dyeing method (Liu et al. 2006). Generally, three methods such as mechanical, chemical, and biological methods are used to modify ramie fabrics for environmentally benign dyeing process (Liu et al. 2006; Choi and Lee 2012).

To increase the affinity between dye molecules and ramie fabric to increase the dye uptake and color strength, several chemical methods, e.g., alkali (also named mercerization), silane, peroxide, ethylenediamine, supercritical fluid carbon dioxide (SCF_{CO2}) and 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTAC) have been applied for ramie fiber modification (Choi and Lee 2012; Kalia et al. 2009; Liu et al. 2006; Orden and Urreaga 2006; Liu et al. 2007; Liu et al. 2008). However, for above-mentioned chemical methods, there exist such dunmodifiedbacks as volatility, toxicity, formation of byproducts, harsh conditions, insufficient reactive sites (or reactivity), fabric yellowing and cumbersome process. Also, the dyeability and dye uptake (or color strength) of fabrics cannot be increased in a sufficient level. Thus, in order to improve the dyeability and dye uptake (or color strength) of ramie fabrics, it is necessary to introduce a modification agent with more reactive groups onto the fabrics.

In recent years, hyperbranched polymer, with novel three dimensional dentritic structure, high density of functional terminal groups, low viscosity, and interchain entanglement, exhibits broad perspective applications in additives, macromolecular building blocks, and heavy metal ions adsorption (Gao and Yan 2004; Ma et al. 2009; Rehim et al. 2010; Ibrahim et al. 2010; Li et al. 2011; Ibrahim et al. 2012). Amino-terminated hyperbranched polymer, as one of the most important hyperbranched polymers, has excellent characteristics, such as low viscosity, containing large number of reactive imino groups and terminal primary amino groups, and good solubility. Up to know, only limited literatures concerning amino-terminated hyperbranched polymer were reported to modified cellulose (including cotton cellulose and ramie cellulose) for better dyeing performances (Zhang et al. 2007; Ibrahim et al. 2012; Wang et al. 2014). A water-soluble amino-terminated hyperbranched polymer from methyl acrylate and diethylene triamine by melt polycondensation was used to modify cotton fabric and the performances (including salt-free dyeing, antimicrobial activities and anti ultraviolet properties) of modified cotton fabric were thoroughly studied (Zhang et al. 2007; Zhang et al. 2008a, b). An amino-terminated hyperbranched polymer, synthesized from diethyl malonate, methyl acrylate, and diethylenetriamine, was used for the salt-free dyeing of ramie cellulose (Wang et al. 2014).

In this paper, with our continuous work on the modification of ramie fabric for excellent dyeing performance (Zhuang et al. 2014; Wang et al. 2014), an amino-terminated aliphatic hyperbranched polymer ($HBP-NH_2$), synthesized from diethyl malonate, methyl acrylate and diethylenetriamine by two step procedure, was used to modify ramie fabric. The molecular weight of $HBP-NH_2$ was determined using GPC. Total amine value, secondary amine value and primary amine value of $HBP-NH_2$ was measured using hydrochloric acid–ethanol titration method. The unmodified and modified ramie fabrics were characterized by XRD and FE-SEM. Using K/S value and dye uptake as criterion, C.I. Reactive Red 2 was applied to study the dyeing performance of the unmodified and modified fabrics. The modification parameters were optimized. Cationization degree (D_C) of HBP-NH_2 onto ramie fabrics was determined by the nitrogen content of HBP-NH_2 modified ramie fabric. The washing, rubbing and light fastness of modified ramie fabrics were also tested. The mechanical strength (including tensile strength and tear strength) of unmodified and modified ramie fabrics were tested. The HBP-NH_2 modification mechanism and dyeing mechanism on ramie fabric were analyzed.

Experimental

Materials

Plain woven 100 % ramie fabric (260 g/m^2), was supplied by Huayu Co., Ltd. (Zhejiang, China). All the fabrics were bleached and scoured. Cibacron Red C-R (C.I. Reactive Red 2), shown in Fig. 1, was obtained from Ciba Dyestuffs Co. Ltd., and was used as received.

Diethyl malonate, methyl acrylate, tetrabutylammonium bromide, diethylenetriamine, epichlorohydrin, sodium hydroxide, sodium bicarbonate, and sodium chloride were provided by Shanghai Chemical Co. Ltd. Amino-terminated hyperbranched polymer (HBP-NH_2), shown in Fig. 2, was synthesized according to literatures (Wang et al. 2009; Wang et al. 2014).

Preparation of HBP-NH_2

Michael bis-adducts of 3,3-diethyl-1,5-dimethyl pentane-1,3,3,5-tetra carboxylate was prepared according to literature (Wang et al. 2009; Wang et al. 2014) with anhydrous potassium carbonate as the base and tetrabutylammonium bromide(TBAB) as the phase transfer catalyst.

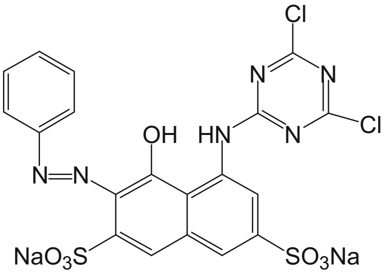

Fig. 1 Chemical structure of C.I. Reactive Red 2

Diethylene triamine (90 mL, 0.84 mol) was added into a 1L four-neck round-bottomed glass flask. Then above prepared tetracarboxylic ester (66 g, 0.2 mol) in methanol (200 mL) was added dropwisely into the flask. The mixture was stirred for 3 h at 45 °C, distilled using automatic rotary vacuum evaporator (Shanghai Yarong Company, China). The temperature was slowly raised to 70 °C and react for 4 h under low pressure to remove the methanol and ethanol, until the yellow viscous liquid, HBP-NH_2 was obtained (Wang et al. 2014).

Amine values of HBP-NH_2

Total amine value, secondary amine value and primary amine value of HBP-NH_2 were measured using hydrochloric acid–ethanol titration method.

Determination of total amine value (A_T)

About 1.0 g of HBP-NH_2 was added in a 250 mL conical flask, and 50 mL ethanol was added to dissolve HBP-NH_2. The ethanol solution was refluxed 1 min to remove free amine, and cooled to room temperature, then 3 drops bromophenol blue was added to the mixture. Calibrated hydrochloric acid solution was used to titrate the mixture. The consumption volume of hydrochloric acid was recorded when the titration solution changed from blue to yellow. The total amine value (A_T, mg/g) of HBP-NH_2 was calculated as following Eq. (1):

$$A_T = \frac{56.1 \times C \times V}{m} \quad (1)$$

where 56.1 is the molecular weight of KOH, C refers to the molar concentration of hydrochloric acid (mol/L); V refers to the volume of hydrochloric acid solution (L); m refers to the weight of HBP-NH_2 (g).

Determination of secondary amine value (As)

About 1.0 g of HBP-NH_2 was added into a 250 mL conical flask, and 50 mL chloroform-ethanol (1:1) was added to dissolve HBP-NH_2. The mixture was refluxed 1 min to remove free amine, and cooled to room temperature. Then 3 mL of salicylaldehyde was

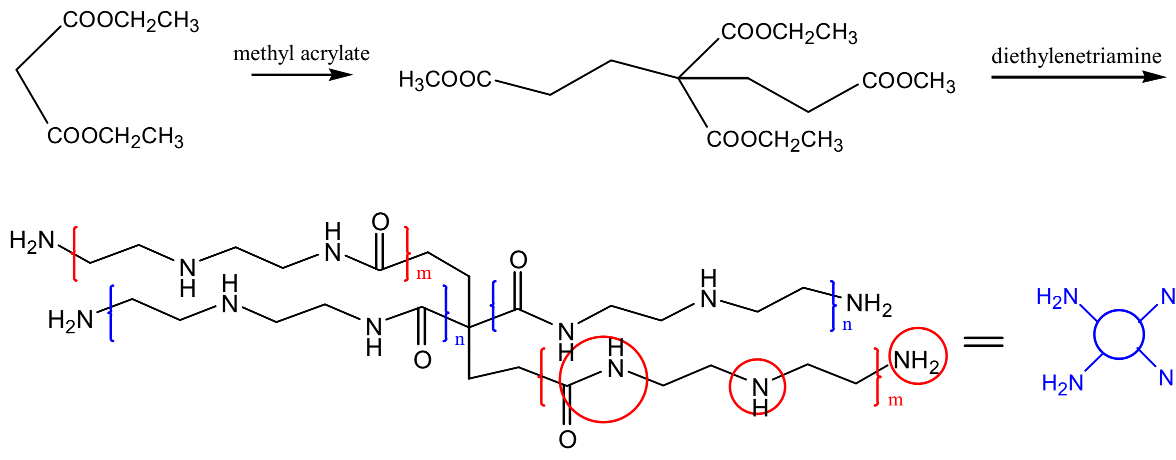

Fig. 2 Possible structure of HBP-NH_2

added to the mixture, 30 min later, then 3 drops bromophenol blue was added to the mixture. Salicylaldehyde will react with primary amine to generate Schiff base, while secondary amine won't react. So the secondary amine value can be determined by hydrochloric acid titration method. Calibrated hydrochloric acid solution was used to titrate the mixture. The consumption volume of hydrochloric acid was recorded when the titration solution changed from blue to yellow. The secondary amine value (A_S, mg/g) of HBP-NH_2 was calculated as following:

$$A_s = \frac{56.1 \times C_1 \times V_1}{m_1} \quad (2)$$

where C_1 refers to the molar concentration of hydrochloric acid (mol/L); V_1 refers to the volume of hydrochloric acid solution (L); m_1 refers to the weight of HBP-NH_2 (g).

Determination of primary amine value (A_P)

The primary amine value (A_P) was calculated as following Eq. (3):

$$A_p = A_T - A_S \quad (3)$$

where A_T refers to the total amine value and A_S is the secondary amine value.

The amine value experiments were conducted three times to check the reproducibility, and the mean values were considered as the experimental values.

Mercerization and crosslink of ramie fabrics

Ramie fabric (5 g), dried for 24 h at 60 °C before use, was put into a four-mouth flask equipped with a magnetic stirring bar. And a mixture of 15 % sodium hydroxide (60 mL) and epichlorohydrin (6 mL) was added. The mercerization and crosslinking were conducted at 50 °C for 5 h. Then the treated ramie fabric was washed with deionized water until pH was 7.0, then dried at 60 °C for further treatment.

Modification of ramie fabrics with HBP-NH_2

The above mentioned mercerized and crosslinked ramie fabrics were padded with HBP-NH_2 solution (2–12 g/L) and sodium bicarbonate (10 g/L) at specific reacting temperature(10–90 °C) and reacting time(1–9 h) using a laboratory padder (P-AO padder, Ningbo textile instrument factory, China) at 100 % wet pick-up. The padded fabrics were dried at 80 °C for 5 min and then cured in a Mini dryer (Rapid XC-32, Xiamen Rapid Co., Ltd.) at 140 °C for 5 min. The treated ramie fabrics were rinsed thoroughly in hot water for 5 min to remove unfixed materials and air-dried at room temperature for at least 12 h.

Dyeing procedure

Figure 3 showed the dyeing process for ramie fabrics. Unmodified ramie fabric and modified ramie fabrics were dyed with C.I. Reactive Red 2 (2 % owf) at a bath ratio of 1:40. The fabric (1 g) was soaked and stirred in the dyebath for 30 min at 40 °C. Then, the dyebath temperature was raised to 90 °C at a rate of 2 °C/min, 30 min later, sodium chloride was added to accelerate the dyeing process. The temperature of dyebath was kept at 90 °C for another 30 min, then sodium bicarbonate was added and continued dyeing for another 30 min. Finally, the ramie fabric was washed thoroughly with deionized water. At last, the dyed ramie fabric was dried at 60 °C.

Gel permeation chromatography (GPC) and viscosity of $HBP\text{-}NH_2$

The viscosity of $HBP\text{-}NH_2$ was determined using NDJ-7 rotational viscometer at 25 °C (Shanghai Tianping Instrument Co. Ltd., China). Gel permeation chromatography (GPC) of $HBP\text{-}NH_2$ was carried out on Agilent 1200 series, with column (TSKgel G3000PWXL column (7.8 × 300 mm, Tosoh, Japan) using 0.3 M Na_2SO_4 (pH was adjusted to 4.0 with acetic acid) as the eluent at a flow rate of 0.5 mL/min. The effluent was monitored by ultraviolet detector at 215 nm. The molecular weights were calculated based on polyethylene glycol standard.

Cationization degree of $HBP\text{-}NH_2$ onto ramie fabrics

The modification of ramie fabric with $HBP\text{-}NH_2$ can be evaluated by the degree of cationization (D_C). D_C was calculated based on the following Eq. (4) (Liu et al. 2007; Liu et al. 2008; Wang et al. 2009).

$$D_c = 3.857 \times \frac{N}{W} \times 100\,\% \tag{4}$$

where N is the nitrogen content of $HBP\text{-}NH_2$ modified ramie fabric, and W is the weight of the ramie fabric used. The nitrogen contents of unmodified ramie fabric and the $HBP\text{-}NH_2$ modified ramie fabric were determined by Flash EA-1112A Elemental analyzer instrument (Thermo Finnigan, Italy).

XRD of ramie fabrics

XRD patterns of unmodified ramie fabric and modified ramie fabrics were recorded from $2\theta = 10°$ to $60°$ with Bruker D8 Advance XRD diffractometer (Bruker Co. Ltd., Germany) equipped with a graphite monochromator and Cu Kα radiation at $\lambda = 0.154$ nm (50 kV, 40 mA). For each sample, approximately 0.1 g ramie cellulose powder was compressed into specimen holder (26 × 26 mm).

Diffraction profiles of the samples were fitted with MDI Jade 5.0 software using separate diffraction peaks and subsequent integration was performed on each peak. The crystallinity index (CI) of samples was determined by the peak separation program of MDI Jade 5.0 software following the equation (Wang et al. 2007; Wong et al. 2009):

$$CI = \frac{A_{crystal}}{A_{total}} \times 100 \tag{5}$$

where, $A_{crystal}$ is the sum of the areas under the crystalline diffraction peaks and A_{total} represents the total area under the diffraction curve $2\theta = 10°–60°$.

The crystallite size of each sample, ω (nm), was calculated by the Scherrer equation (Liu et al. 2010; Han et al. 2013):

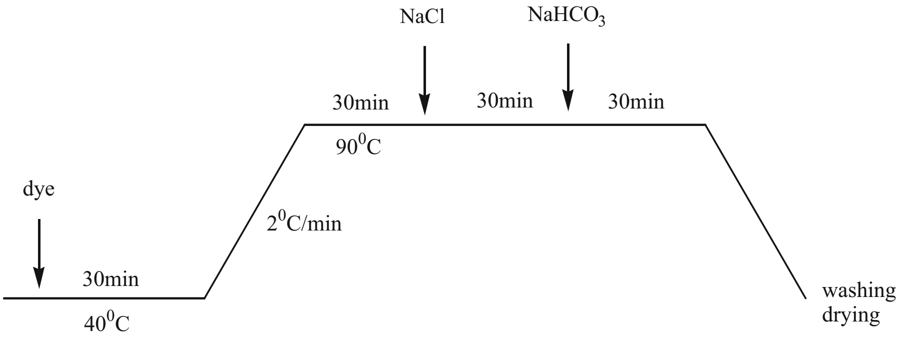

Fig. 3 Schematic of dyeing process of ramie fabrics

$$\omega = \frac{K\lambda}{\beta \cos \theta} \quad (6)$$

where θ is the diffraction angle, K = 0.94 (correction factor), λ = 0.154 nm and β is the peak width in radians at half maximum height (peak FWHM).

FE-SEM of ramie fabrics

FE-SEM photomicrographs of unmodified and modified ramie fabrics were recorded with Ultra 55 field emission scanning electron microscope (Carl Zeiss SMT Pte Ltd., Germany) at an accelerating voltage of 20 kV. The free surfaces were coated with thin layers of gold before observation.

Measurement of K/S value and dye uptake

The color strength (K/S value) was measured by computer-assisted predicting instrument, Datacolor 600 (Datacolor Co. Ltd., USA). The dye uptake (E) in ramie fabrics was calculated with Eq. (7) basing on the absorbance of the dyebath at λ = 540 nm with 752 s spectrophotometer (Lengguang Tech Co., Ltd., Shanghai):

$$\mathrm{E} = \left(\frac{A_0 - A_1}{A_0}\right) \times 100\,\% \quad (7)$$

where E is dye uptake, A_0 is absorbency of original dyebath, A_1 is absorbency of residual dyebath.

Fastness test

Washing fastness tests were performed according to GB/T 3921-2008 (Textiles-Tests for color fastness—color fastness to washing with soap or soap and soda) using the SW-12D washing fastness tester (Ningbo Textile Instrument Factory, China). Rubbing fastness tests were performed according to GB/T 3920-2008 (Textiles-Tests for color fastness-color fastness to rubbing) using the Y571A rubbing fastness tester (Ningbo textile instrument factory, China). Light fastness tests were performed according to GB/T 8427-2008 (Textiles-Tests for color fastness-Color fastness to artificial light: Xenon arc fading lamp test) using YG(B)611-IV colour fastness to sunlight and weather tester (Wenzhou Darong Textile Instrument Factory, China).

The samples were balanced at 20 °C for 24 h under 60 % RH (relative humidity) before test. All tests were done five times and the average value was taken as final results.

Mechanical test

The mechanical strength (including tensile strength and tear strength) of unmodified and modified ramie fabrics were determined with YG(B)026G-50 electronic fiber strength tester (Wenzhou Darong Textile Instrument Factory, China) according to GB/T 3923.1-2013(Textiles-Tensile properties of fabrics-Part 1: Determination of maximum force and elongation at maximum force using the strip method). Test conditions are as follows: initial distance between clamps was 100 mm, stretching speed was 20 mm/min and pretension was 0.1 N.

The strength retention (R_S) was calculated as following Eq. (8):

$$R_S = \frac{S_1}{S_0} \quad (8)$$

S_0 was the tensile or tear strength of unmodified ramie fabrics. S_1 was the tensile or tear strength of modified ramie fabrics. Each sample was tested five times and the average value was used.

Results and discussion

Gel permeation chromatography (GPC) and viscosity of HBP-NH_2

From the GPC results (Fig. 4), the number average (M_n) molecular weight of HBP-NH_2 was estimated about 1,468 g/mol. The viscosity of HBP-NH_2 was about 1,800 mpa.s at 25 °C.

As shown in Fig. 2, if we denoted diethylenetriamine as group A, tetracarboxylic ester as group B, the prepared HBP-NH_2 structure might represent as $BA_4BA_3BA_3$ (third generation).

Amine values of HBP-NH_2

As discussed above, the prepared HBP-NH_2 structure might represent as $BA_4BA_3BA_3$ (third generation), so there were 30 total amine group, 22 secondary amine group and 8 primary amine group in HBP-NH_2.

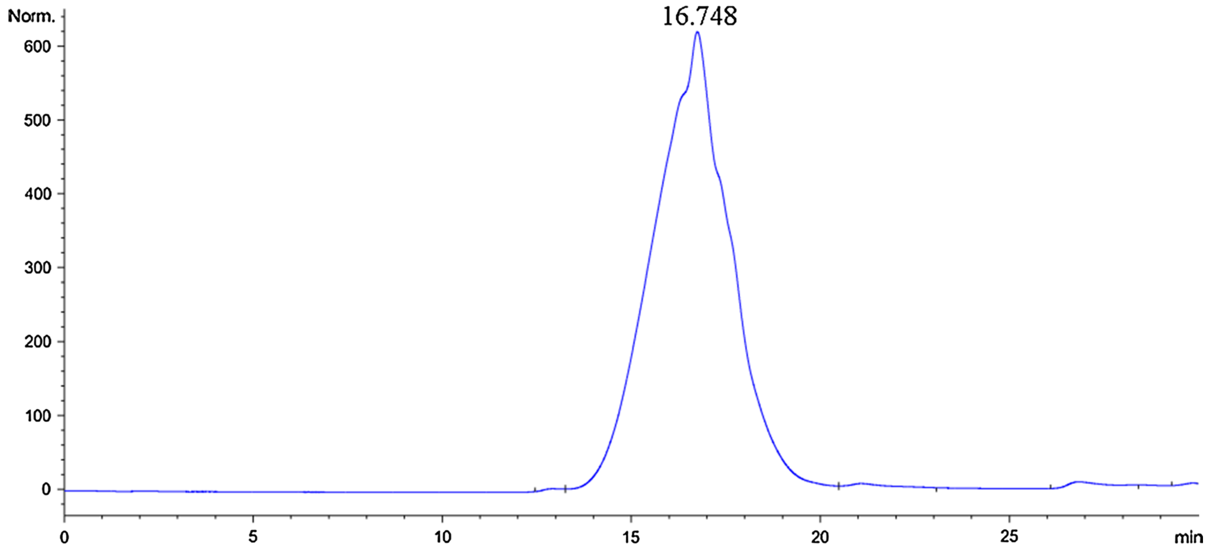

Fig. 4 GPC curve of HBP-NH_2

Accordingly, the total amine value was 290 mg/g, the secondary amine value was 213 mg/g, and the primary amine value was 82 mg/g. Total amine value, secondary amine value and primary amine value of HBP-NH_2 were listed in Table 1. As shown in Table, the total amine value, secondary amine value and primary amine value of HBP-NH_2 were 291.59, 210.14 and 81.45 mg/g respectively, close to the calculated values, which further confirmed the structure of HBP-NH_2.

Optimization of the modification conditions

Effects of HBP-NH_2 concentration, reacting temperature and reaction time on the K/S value were discussed to get the optimal modification conditions. The results were shown in Fig. 5.

Table 1 Amine values of HBP-NH_2

Samples	A_T (mg/g)	A_S (mg/g)	A_P (mg/g)
1	291.49	209.64	81.85
2	287.57	207.83	79.74
3	295.71	212.95	82.76
Mean value	291.59	210.14	81.45

Molar concentration of hydrochloric acid was 0.2182 mol/L; HBP-NH_2 weight = 1.05 g

Effect of HBP-NH_2 concentration on K/S value

In order to investigate the effect of HBP-NH_2 concentration on K/S values, different concentration of HBP-NH_2 ranging from 2 to 12 g/L was used for modification process at 50 °C for 5 h respectively. The results shown in Fig. 5a revealed that K/S values increased significantly when HBP-NH_2 concentration increased from 2 to 8 g/L. K/S values were leveled off when HBP-NH_2 concentration was above 8 g/L. This can be explained that the color strength (K/S value) depended on the dye uptake, while the reaction between HBP-NH_2 modified ramie fabric and dye molecules affected the dye uptake. As we know, abundant amine groups of HBP-NH_2 will react with available epoxy groups of cellulose ether, which was crosslinked by epichlorohydrin (Liu et al. 2008). At a lower concentration of HBP-NH_2, the increase of HBP-NH_2 concentration leaded to the increase of modification extent, correspondingly the increase of K/S value. However, at a higher concentration of HBP-NH_2 (above 8 g/L), the accessible epoxy groups in ramie fabrics were almost used out for reacting with HBP-NH_2 to give an almost constant K/S value.

Effect of reacting temperature on K/S value

The effect of reacting temperature on K/S value was studied when the HBP-NH_2 concentration was 8 g/L,

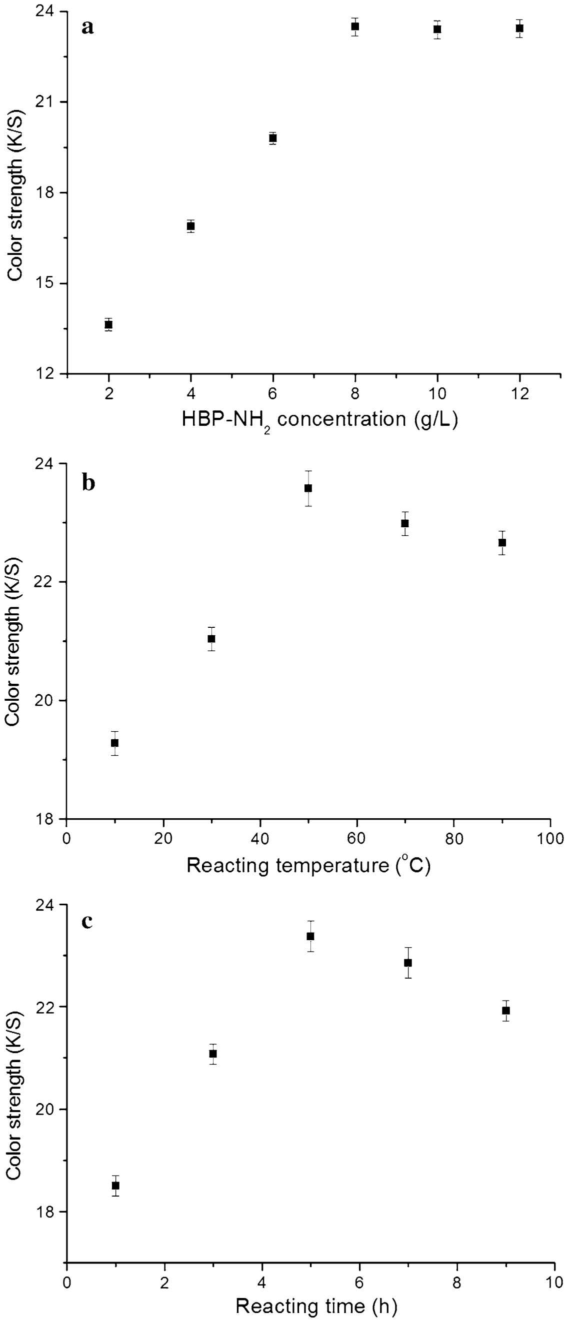

Fig. 5 Effect of modification conditions on color strength (K/S)

sodium bicarbonate was 10 g/L and reacting time was 5 h. As shown in Fig. 5b, when the temperature was below 50 °C, K/S value rose obviously with the increase of temperature until a maximum K/S value was obtained at 50 °C. After that, K/S value decreased with the increase of temperature. This may be explained that the amino groups in HBP-NH_2 hydrolyzed at higher temperature and partial hydrolysis of reactive dyes, which resulted in poor dye uptake and low K/S value.

Effect of reacting time on K/S value

The effect of reacting time on grafting behavior of HBP-NH_2 onto ramie fabric was studied by varying reacting time from 1 to 9 h at a constant HBP-NH_2 concentration (8 g/L), sodium bicarbonate (10 g/L), and reacting temperature (50 °C). From Fig. 5c, it could be seen that K/S value increased with the increase of reacting time until 5 h, after 5 h, however, K/S value declined slowly but within the experiment errors. This may be explained that the reacting equilibrium had been achieved in 5 h or the active sites in the ramie fabric were not sufficient, and with the increasing of reaction time, the K/S value will not increase any more, so the K/S value became stable.

Above results provided us with such optimal modification conditions for ramie fabric as the HBP-NH_2 concentration of 8 g/L, reacting temperature of 50 °C, and reaction time of 5 h.

Dyeing performance of modified ramie fabrics under optimal conditions

Under above mentioned optimal modification conditions (HBP-NH_2 concentration 8 g/L, 50 °C, 5 h), the unmodified and modified ramie fabrics were dyed with C.I. Reactive Red 2 (2 % owf, ratio 1:40) to evaluate their color strength (K/S) and dye uptake (E). The results were shown in Table 2. It was obvious that modification greatly influenced the color strength and dye uptake. The dye uptake and color strength of modified ramie fabric were 85.6 and 23.64 % respectively. The color strength of modified ramie fabric increased nearly four times than that of unmodified ramie fabric. This was derived from the abundant reactive imine and amino groups of HBP-NH_2 grafted onto the surface of ramie fabric, which could easily react with the active groups of reactive dye, thus the dye uptake and dyeing performance of modified ramie fabric were improved.

Cationization degree of HBP-NH_2 onto ramie fabrics

The elemental analysis of unmodified ramie fabric, HBP-NH_2 modified fabrics and the Dc of the HBP-

Table 2 Dyeing performance of modified ramie fabrics under optimal conditions

No.	A_0	A_1	E (%)	K/S
Unmodified fabric	0.873	0.648	25.8	8.71
Modified fabric	0.855	0.123	85.6	23.64

Reactive Red 2 (2 % owf), 1:40, HBP-NH_2 concentration 8 g/L, 50 °C, 5 h

NH_2 modified fabrics were shown in Table 3. In comparison with the unmodified ramie fabric, the contents of carbon and hydrogen decreased, while the nitrogen content of HBP-NH_2 modified fabric increased obviously (from 1.25 to 2.61 %) with the increase of HBP-NH_2 concentration (from 2 to 8 g/L), but the nitrogen contents were leveled off when HBP-NH_2 concentration was above 8 g/L, which is attributed to the grafting of the primary amine group onto the ramie fabric. Moreover, the D_C (cationization degree) values of the modified fabric increased sharply with nitrogen contents increase of the modified fabric. Comparing with literatures (Liu et al. 2007; Liu et al. 2008), the nitrogen content of HBP-NH_2 modified ramie fabrics (1.25–2.61 %) were much higher than those of 3-chloro -2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) modified ramie fabric (about 0.4–0.5 %) or ethylenediamine modified ramie fabrics (about 0.9–1.0 %), which ascribe to the abundant amine groups in HBP-NH_2. Moreover, the D_C (cationization degree) values of HBP-NH_2 modified ramie fabrics (4.41–9.40 %) were much higher than those CHPTAC modified ramie fabric (about 0.85–1.74 %).

Table 3 Elemental analysis of unmodified ramie fabric and modified ramie fabrics, and cationization degree (D_c) of the HBP-NH_2 modified fabrics

	C (%)	H (%)	N (%)	D_c (%)
Unmodified ramie fabric	47.58	7.69	0.05	–
Modified fabric-2	42.35	6.95	1.25	4.41
Modified fabric-4	42.05	6.85	1.76	6.28
Modified fabric-6	41.94	6.79	2.39	8.60
Modified fabric-8	41.87	6.74	2.59	9.33
Modified fabric-10	41.78	6.71	2.61	9.40
Modified fabric-12	41.71	6.67	2.60	9.37

Modified fabric-2, -4, -6, -8, -10 and -12 were ramie fabrics modified with different HBP-NH_2 concentrations of 2, 4, 6, 8, 10 and 12 g/L respectively, sodium bicarbonate 10 g/L, at 50 °C for 5 h; the weight of the ramie fabrics were 1.05 g

XRD analysis of ramie fabrics

XRD patterns of unmodified ramie fabric, mercerized and epichlorohydrin modified ramie fabric and HBP-NH_2 modified ramie fabric at 2θ of 10°–60° were shown in Fig. 6. The diffraction peaks at 14.84° (1 1 0), 16.38° (1 1 0), 22.68° (2 0 0) and 34.20° (0 0 4) (as shown in Fig. 6a), were typical characteristic of "cellulose I crystal" (French and Santiago Cintrón. 2013; French. 2014, Wang et al. 2014). The high intensity of diffraction peak at 22.68° suggested the highly crystalline structure of unmodified ramie fabric. After mercerization and epichlorohydrin modification, the diffraction peaks at 20.22° (1 1 0), 22.28° (0 2 0) and 34.34° (0 0 4) (shown in Fig. 6b) were associated with the typical peaks of cellulose II allomorph (Liu et al. 2007; French and Santiago Cintrón. 2013; Han et al. 2013; French. 2014; Wang et al. 2014). This suggests that a transformation

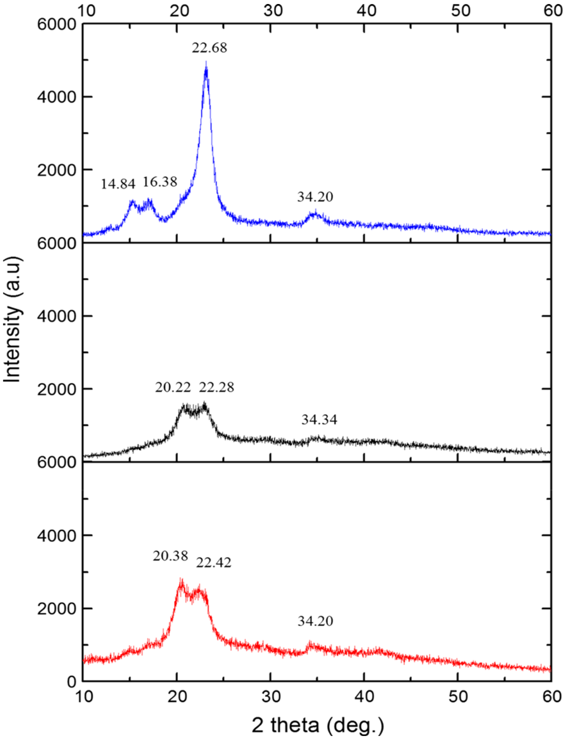

Fig. 6 XRD patterns of unmodified ramie fabric and modified ramie fabrics

of crystalline structure from cellulose I to cellulose II allomorph during mercerization and epichlorohydrin modification. The (1 1 0) peak at $2\theta = 14.84°$ and (1 1 0) peak at $2\theta = 16.38°$ completely disappeared. The HBP-NH_2 modified ramie fabric also showed the characteristic XRD pattern of cellulose II ($2\theta = 20.38°$, 22.42° and 34.20°, as shown in Fig. 6c), suggesting that the HBP-NH_2 modification has no effect on the crystallite structure of the mercerized fabric.

Using MDI Jade 5.0 software and Eq. (5), the CI of unmodified ramie fabric, mercerized and epichlorohydrin modified ramie fabric and HBP-NH_2 modified ramie fabric were calculated as 85.2, 50.2 and 64.7 % respectively. The CI of mercerized and epichlorohydrin modified ramie fabric decreased sharply, while the CI of HBP-NH_2 modified ramie fabric was higher than that of mercerized and epichlorohydrin modified ramie fabric. This is probably caused by three dimensional dendritic structure, low viscosity, good solubility, rich imino groups and terminal primary amino groups of HBP-NH_2. When HBP-NH_2 is applied for the modification of ramie fabric, HBP-NH_2 can easily penetrate into the ramie fabrics and form abundant hydrogen bonds and Van der Waals force with cellulose groups (Wong et al. 2009; Zhang et al. 2008a, b; Wang et al. 2014).

The crystallite size of untreated ramie fabric, mercerized and epichlorohydrin modified ramie fabric and HBP-NH_2 modified ramie fabric were calculated using MDI Jade 5.0 software and Scherrer Eq. (6), 5.8, 3.1 and 3.6 nm respectively.

XRD suggested a transformation of crystalline structure from ramie cellulose I to cellulose II allomorph during mercerization and epichlorohydrin modification, and the crystalline structure of cellulose II was retained with obvious CI increase after HBP-NH_2 modification.

The crystalline structure change from ramie cellulose I to cellulose II allomorph was favorable for reactive dyeing process. Highly crystalline phase was destroyed to form randomly oriented amorphous region with hydrogen bonds disruption. Thus the reactive dyes molecules could easily penetrate into the inner part of ramie cellulose, and combine with the abundant reactive imine and amino groups of HBP-NH_2. Accordingly, the dye uptake (K/S values) and dyeing performance of modified ramie fabric were improved.

FE-SEM analysis of ramie fabrics

The surface morphology (magnification, 2,000×) of the unmodified ramie fabric and modified ramie fabrics were shown in Fig. 7. Figure 7a showed that the surface of unmodified ramie fabric was relatively smooth and appeared a layered structure (Liu et al. 2008). After reacting with epichlorohydrin, the surface became smoother because of the mercerization function of alkaline solution and epichlorohydrin cross linking (Fig. 7b). When ramie fabric was modified with HBP-NH_2, a very rough surface partly covered with polymer-like granules was observed (Fig. 7c), which suggested that HBP-NH_2 was grafted onto the surface of ramie fabric.

Fastness properties

The fastness properties (including washing fastness, rubbing fastness and light fastness) of unmodified ramie fabrics and HBP-NH_2 modified ramie fabrics (HBP-NH_2 concentration 8 g/L, 50 °C, 5 h) with C.I. Reactive red 2 (2 % owf, ratio 1:40) were shown in Table 4. Compared with the unmodified ramie fabrics, the HBP-NH_2 modified ramie fabrics had good washing fastness and rubbing fastness. Clearly, the washing fastness and rubbing fastness of reactive dye dyeing were maintained. Light fastness value of unmodified ramie fabric (grade 4–5) was higher than that of HBP-NH_2 modified ramie fabric (grade 4).

The washing fastness and rubbing fastness of HBP-NH_2 modified ramie fabrics with C.I. Reactive red 2 were higher than those of unmodified ramie fabrics. This was derived from the abundant reactive imine and amino groups of HBP-NH_2 grafted onto the surface of ramie fabric, which could easily react with the active groups of reactive dye. HBP-NH_2 modified ramie cellulose had large amounts of actively amide, amino and hydroxyl groups. These reactive groups would strongly attract anionic group (disulphonated anions) of reactive dyes, and combine with reactive dyes molecules.

Moreover, as shown in XRD test, during mercerizing, epichlorohydrin and HBP-NH_2 modification, the crystallinity intensities of mercerized and epichlorohydrin modified ramie fabric and HBP-NH_2 modified fabric obviously decreased. Thus the reactive dyes molecules could easily penetrate into the inner part of ramie cellulose, and combine with the abundant reactive imine and amino groups of HBP-NH_2.

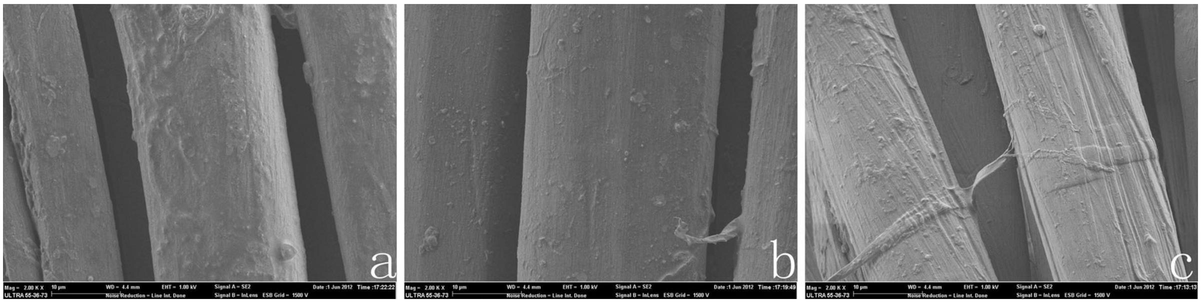

Fig. 7 FE-SEM images of unmodified ramie fabric and modified ramie fabrics

Table 4 Fastness properties of unmodified and modified ramie fabrics

Ramie fabrics	Light fastness	Rubbing fastness		Washing fastness	
		Dry	Wet	Fading	Staining
Unmodified	4–5	4–5	3–4	4–5	4
Modified	4	5	4	5	4–5

Reactive Red 2 (2 % owf), 1:40, $HBP\text{-}NH_2$ concentration 8 g/L, 50 °C, 5 h

The decrease of light fastness of $HBP\text{-}NH_2$ modified ramie fabrics mainly ascribed to the yellowing of free imine and amino groups from $HBP\text{-}NH_2$.

Mechanical properties

Under modification conditions ($HBP\text{-}NH_2$ concentration 8 g/L, 50 °C, 5 h), the unmodified and modified ramie fabrics were dyed with C.I. Reactive Red 2 (2 % owf, ratio 1:40) to evaluate their mechanical properties. Table 5 showed the tensile strength, tear strength and strength retention of unmodified ramie fabrics and $HBP\text{-}NH_2$ modified ramie fabrics. As shown in Table 5, the tensile strength and tear strength of $HBP\text{-}NH_2$ modified ramie fabrics were lower than those of unmodified fabrics. The warp, weft tensile strength retention was 85.97 and 87.02 % respectively. The warp, weft tear strength retention was 85.23 and 87.50 % respectively.

The transformation of crystalline structure from ramie cellulose I to cellulose II allomorph during modification may ascribe to the strength loss and higher dye fixation on fabrics may also have certain responsibility for the strength decrease.

Modification mechanism

The possible modification mechanism of $HBP\text{-}NH_2$ and ramie cellulose was shown in Fig. 8. The $HBP\text{-}NH_2$ modification of ramie fabric involved two steps: one was mercerization and epichlorohydrin crosslinking of ramie fabric, next step was the graft between $HBP\text{-}NH_2$ and epichlorohydrin crosslinked ramie cellulose.

As shown in Fig. 8, after mercerization with high concentration of sodium hydroxide, the high reactivity of hydroxyl group of ramie cellulose would form large amount of O^- anion (Kalia et al. 2009; Wang et al. 2014). Then O^- anion would react with epichlorohydrin to form intermediate under alkaline conditions, eliminating hydrogen chloride and H_2O (Liu et al. 2008; Wang et al. 2014). Large amount amino group of $HBP\text{-}NH_2$ would react with epoxy to get $HBP\text{-}NH_2$ modified ramie cellulose, elimination of H_2O molecular. Then ramie cellulose had large amounts of actively amide, amino and hydroxyl groups covalently bound to the $HBP\text{-}NH_2$ chains. These reactive groups would strongly attract anionic group (disulphonated anions) of reactive dyes, and eliminate hydrogen chloride between amino group and chloride atom of reactive dyes (Fig. 9).

Conclusions

In this study, $HBP\text{-}NH_2$ was synthesized from diethyl malonate, methyl acrylate and diethylenetriamine by a

Table 5 Mechanical strength of unmodified and modified ramie fabrics

Ramie fabrics	Tensile strength (N)		Tear strength (N)	
	Warp	Weft	Warp	Weft
Unmodified	440.5	292.8	8.8	7.2
Modified	378.7	254.8	7.5	6.3
Strength retention (%)	85.97	87.02	85.23	87.50

Reactive Red 2 (2 % owf), 1:40, HBP-NH_2 concentration 8 g/L, 50 °C, 5 h

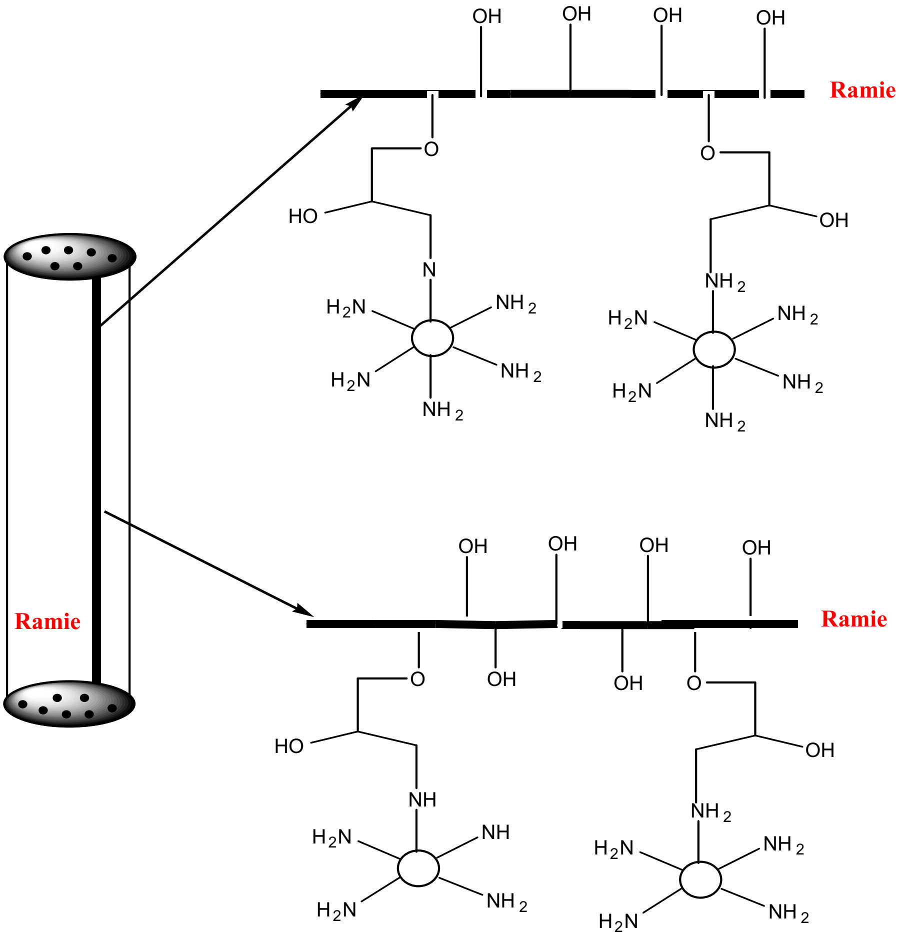

Fig. 8 Possible modification mechanism of HBP-NH_2 with ramie cellulose

two-step procedure. The molecular weight of HBP-NH_2 was determined using GPC. HBP-NH_2 structure might represent as $BA_4BA_3BA_3$ (third generation). Total amine value, secondary amine value and primary amine value of HBP-NH_2 were measured using hydrochloric acid–ethanol titration method. Total amine value, secondary amine value and primary amine value of HBP-NH_2 were 291.59, 210.14 and 81.45 mg/g respectively.

Then, a modification procedure for ramie fabric using HBP-NH_2 was developed. The unmodified ramie fabric and modified ramie fabrics were characterized by XRD and FE-SEM. FE-SEM results confirmed that HBP-NH_2 was successfully grafted

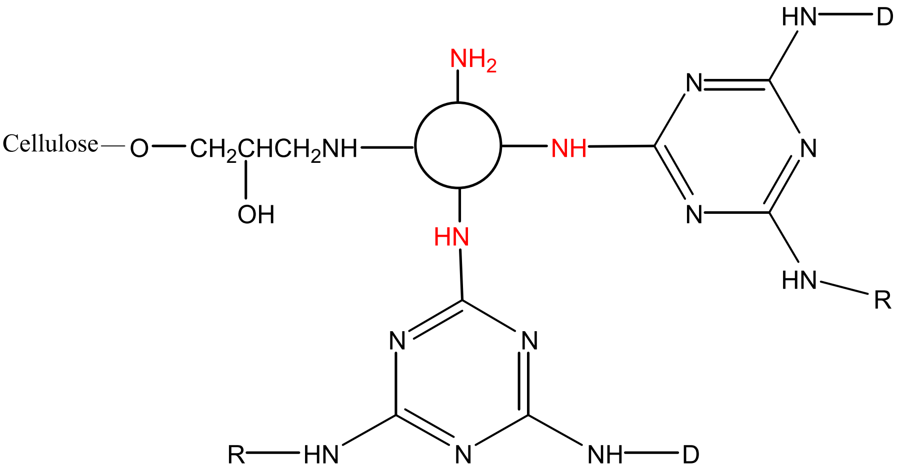

Fig. 9 Possible reaction between HBP-NH_2 modified ramie cellulose and reactive dye

onto the fabric surface. XRD results showed a transformation of crystalline structure from ramie cellulose I to cellulose II allomorph during mercerization and epichlorohydrin modification, and the crystalline structure of cellulose II maintained with obvious CI increase after HBP-NH_2 modification. Cationization degree of HBP-NH_2 onto ramie fabrics was determined by the nitrogen content of HBP-NH_2 modified ramie fabric. Nitrogen content of HBP-NH_2 modified fabric were 1.25–2.61 %, D_C values of HBP-NH_2 modified ramie fabrics were 4.41–9.40 %.

Using K/S value and dye uptake as criterion, C.I. Reactive Red 2 was applied to study the dyeing performance of modified fabrics. The optimized modification was carried out at 50 °C for 5 h when the concentration of HBP-NH_2 was 8 g/L. K/S value and dye uptake of modified fabric was 23.64 and 85.6 % respectively under optimal modification conditions, which were much higher than those of the unmodified one. The washing, rubbing and light fastness of HBP-NH_2 modified ramie fabrics were also good compared with those obtained by conventional dyeing. The tensile strength and tear strength of HBP-NH_2 modified ramie fabrics were lower than those of unmodified fabrics. The warp, weft of tensile and tear strength retention of modified fabrics were between 85.23 and 87.50 %. The HBP-NH_2 modification mechanism and dyeing mechanism on ramie fabric were suggested.

Therefore, this HBP-NH_2 modification procedure of ramie fabric could be used to improve the utilization of dyes, increase the dyeing color strength, and reduce pollution, which showed prospective application for ramie fabric treatment.

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