

Benzylated Modification and Dyeing of Ramie Fiber in Supercritical Carbon Dioxide

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ABSTRACT: The effects of pretreatment conditions, including the addition of a phase-transfer catalyst, on the benzylation of ramie fiber were investigated in this study. Raw and benzylated ramie fibers were dyed in supercritical carbon dioxide, and the color strength (K/S) of the ramie fiber was measured by ultraviolet–visible spectroscopy. An obviously improved dyeing capability of the benzylated ramie fiber, that is, a better level-dyeing property and a higher K/S , was achieved. Moreover, the color strength of the ramie fiber, indexed as the value of K/S ,

increased significantly with the degree of substitution of the benzylated ramie fiber. The raw and modified ramie fibers were characterized with Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, and differential scanning calorimetry. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1872–1878, 2008

Key words: biofibers; degree of polymerization (DP); dyes/pigments; modification; morphology

INTRODUCTION

Cellulose is a very important natural macromolecular compound that exists in all kinds of plant organisms and biomembranes. Plants, which are the sole source of natural cellulose in the world, can produce hundreds of millions of tons of cellulose by photosynthesis every year.^{1–3} Ramie, which is composed mainly of cellulose, is an age-old graceful textile material and has a century-long growing history in China. The output of ramie fiber in China has accounted for the majority of the total yields in the world.⁴

Being a nascent bast fiber, ramie fiber has many unique properties, including a high Young's modulus, a high degree of the polymerization, and a high intensity of its single fiber.^{5–7} Therefore, it bears the advantages of cool, high-air pervious, good antibacterial, and mothproof properties. However, because of its high crystallinity and high degree of orientation, it has some disadvantages in the fabrication process, such as poor spinnability, easy corrugation, and poor dyeing capability. Moreover, it causes disgusting feelings of stinging or itching when it is

used as a textile and in contact with the skin.⁸ The elimination of stinging or itching feelings can mainly be realized through chemical modification of the ramie fiber. If one considers the improvement of other properties, such as the low dyeing capability, the fabric features of modified ramie fiber can be adjusted to those of the blended fibers. In this aspect, considerable attention has been paid to the modification of ramie fibers in recent years.

The molecular chains of ramie fibers are analogous to those of the other celluloses; that is, three active hydroxyl groups in every glucose cycle form intramolecular and intermolecular hydrogen bonds. The crystallinity and the degree of orientation in ramie fibers are much higher than those of other cellulose fibers, such as cotton and paper fibers. Thus, ramie fiber must be pretreated before its modification. Although many methods for the pretreatment of ramie fiber have been proposed,^{9–12} the alkali pretreatment called *mercerization* has been commonly used and has been proven effective.

To improve the spinning properties of ramie fiber, some methods for its modification have been developed, for example, sulfonation,¹³ cyanoethylation,¹⁴ and ion liquid modification.¹⁵ A higher dyeing efficiency was achieved for ramie fiber after cationic modification.¹⁶ For cotton fiber, benzoyl chloride modification and dyeing of modified cotton fiber in supercritical carbon dioxide (scCO_2) have been reported.¹⁷

In the past two decades, supercritical fluids (SCFs) have been used in different applications ranging

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Figure 1 Structure of DR 74.

from classical extraction¹⁸ to sophisticated industrial processes. The use of SCFs as solvents in the dyeing process has attracted considerable attention in recent years. Because the traditional dyeing processes in the water solution gave birth to environmental problems, an alternative dyeing process in SCFs has been proposed and applied for the dyeing of polyester fibers with disperse dyes.¹⁹ The advantages of SCF dyeing are both economic and ecological. Although a number of substances can be used as SCFs, carbon dioxide has been studied widely. Besides its low critical parameters (critical pressure (T_c) = 31°C and critical pressure (P_c) = 7.39 MPa), this particular SCF also has low cost, high purity, low toxicity, non-flammability, and recoverability. Thus, environmental pollution can be eliminated by the use of CO₂ as a SCF. Gebert et al.²⁰ showed that the dyeing of natural fibers in scCO₂ is possible, and many works have been done on the dyeing of both synthetic fibers and natural fibers in recent years.^{16,21}

In our previous study,²¹ the dyeing of ramie fiber with a disperse dye was investigated in scCO₂. To improve the modification efficiency, in this study, ramie fiber was modified with benzyl chloride, and the effects of the modification conditions, including the addition of a phase-transfer catalyst (PTC), on the degree of substitution (DS) of the benzylated ramie fiber were investigated. The benzylated ramie fiber was dyed with a disperse dye in scCO₂ for the evaluation of the efficiency of the modification. The addition of a PTC significantly increased the DS of the benzylated ramie fiber and led to improved dyeing capabilities.

EXPERIMENTAL

Materials

The ramie fiber was obtained from the Institute of Bast Fiber Crops, Chinese Academy of Agriculture Sciences (Changsha, China). The PTC was cetyl trimethyl ammonium bromide (CTAB), which was purchased from the Tianjin Kermel Chemical Tech Co., Ltd. (Tianjin, China). Benzyl chloride was purchased from Shanghai San'aisi Chemical Co., Ltd. (Shanghai, China). Sodium hydroxide, toluene, and sodium chloride were provided by Xi'an Chemical Co., Ltd. (Xi'an, China). C. I. Disperse Red 74 {DR 74; C₂₂H₂₅N₅O₇, N-[5-(2-acetoxy) ethyl] amino-2-[(4-nitrophenyl) azo] phenyl} was obtained from the Xi'an Qinlong Co., Ltd. (Xi'an, China). The molecular

structure of DR 74 is illustrated in Figure 1. The CO₂ (99.99%) was supplied by the Xi'an Yatai Co., Ltd. (Xi'an, China).

Dyeing apparatus

The experimental apparatus is shown in Figure 2. The liquefied CO₂ from a cylinder passed through a cooling unit was introduced into a high-pressure syringe (model 260D, ISCO, Lincoln, NE) and eventually flowed into the dyeing autoclave. The dyeing autoclave (Weihai Chemical Device Co., Ltd., Weihai, China), modified by our research team as schematized in Figure 2, was a stainless steel autoclave of 500 cm³ equipped with a stainless steel screw tube, a pressure-sealed magnetic stirrer, and a quick-release cap. The apparatus was pressure-tested for use up to 20 MPa at 400°C. The vessel was heated with a heating jacket, and the temperature, indicated by a thermocouple, was controlled by a temperature controller.

Characterization methods

Fourier transform infrared (FTIR) spectroscopy was carried out in the IR region with an FTIR spectrometer (Bruker Co., Ltd., Madison, WI, EQUINOX 55). The spectra were recorded at 4-cm⁻¹ resolution, and 32 scans were recorded for each sample. X-ray diffraction (XRD) was measured by a D/Max 2000PC Rigaku (Tokyo, Japan) wide-angle X-ray diffractometer at a scanning speed of 8° (2θ)/min. For scanning electron microscopy (SEM) analysis, the ramie fibers were shadowed with gold and then examined on a field-emission scanning electron microscope (Philips FEI, Eindhoven, Netherlands model Quanta 200),

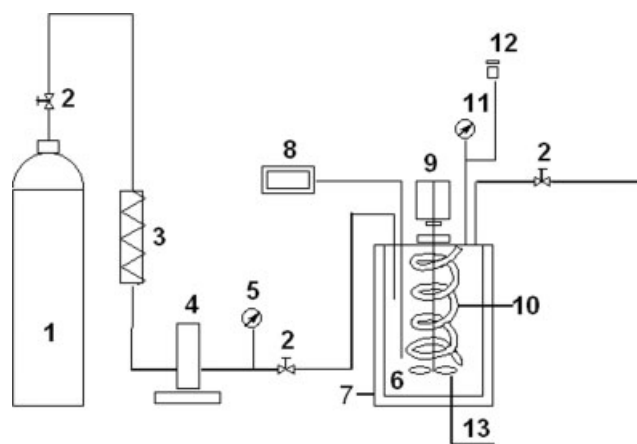


Figure 2 Experimental apparatus: (1) CO₂ cylinder, (2) shut-off valve, (3) cooling unit, (4) high-pressure syringe, (5) pressure gauge, (6) dyeing vessel, (7) heating jacket, (8) temperature controller, (9) magnetic rotor, (10) screw tube, (11) pressure gauge, (12) quick release cap, and (13) magnetic stirrer.

which was operated at 20 kV. Thermogravimetric analysis and differential scanning calorimetry (DSC) were performed with a thermoanalyzer system (model Q600SDT, TA Co., Ltd., New Castle, DE). Samples of about 5 mg, placed on a DSC pan, were heated from 50 to 500°C at a temperature ramp of 10°C/min under nitrogen. The color strength (K/S) and the dye uptake were determined by a Lamda 950 spectrophotometer (PerkinElmer Co., Ltd., Waltham, MA).

Pretreatment and modification of ramie fiber

The pretreatment was carried out by the immersion of ramie fiber in a solution of 18 wt % sodium hydroxide (80 mL) for 4 h at a room temperature.

The modification of the pretreated ramie fiber (1.0 g) was carried out in a rockered flask. Predetermined amounts of sodium hydroxide solution (15 mL), CTAB, benzyl chloride, and toluene were put into the rockered flask, and then, the mixture was heated to the desired temperatures. After the reaction, the benzylated ramie fiber was washed alternately by anhydrous ethanol and distilled water to remove residues of the reactants and impurities and was then filtered decompressedly. The benzylated ramie fiber was obtained after washing with distilled water, filtration, and drying at 60°C for 6 h.

Dyeing procedure in $scCO_2$

The ramie fiber (0.5 g) was wrapped around a stainless steel mesh tube, and then, the tube was loaded into the high-pressure reaction autoclave. DR 74 (0.0025 g) and acetone (2.5 mL) were added into the autoclave. After that, the autoclave was sealed and heated to the desired temperature of 120°C. At the same time, carbon dioxide was pumped into the autoclave by a high-pressure syringe until the pressure in the autoclave reached 18 MPa. After 3 h of reaction, the sample was collected carefully and washed with a soap lotion for the dye-fastness testing.

Calculation of DS

For the calculation of DS, both the raw ramie fiber and the benzylated ramie fiber were dried until they reached a constant weight, and the weight gain of the ramie fiber after benzylation (WPG) was measured, as given in eq. (1):²²

$$\text{WPG (\%)} = \frac{W_{\text{product}} - W_{\text{reactant}}}{W_{\text{reactant}}} \times 100\% \quad (1)$$

where W_{product} is the mass of the benzylated ramie fiber and W_{reactant} is the mass of the raw ramie fiber.

There are three active hydroxyls in every glucose ring in the cellulose chain [Fig. 3(a)]. The benzylated

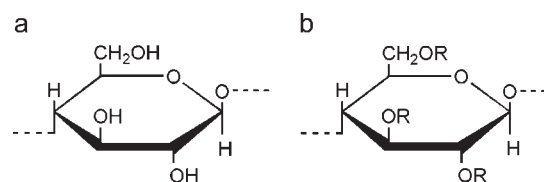


Figure 3 Molecular structures of (a) ramie cellulose and (b) benzylated ramie cellulose ($R = C_6H_5-CH_2-$).

ramie fiber was the product of the hydrogen in hydroxyls of the cellulose substituted by the benzyl group in benzyl chloride [Fig. 3(b)]. Thus, the theoretical maximum DS of the benzylated ramie fiber was 3. After simple mathematics, the DS of the benzylated ramie fiber could be calculated on the basis of the measured WPG by the following formula:

$$\text{DS} = [162.08 \times \text{WPG (\%)}] / 90.12 \quad (2)$$

where 90.12 is the molecular weight of the benzyl group and 162.08 is the molecular weight of the glucose ring in the ramie fiber.

K/S

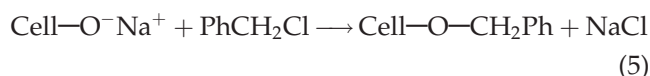
To check the fixation of the dye on the benzylated ramie fiber and to assess the quality of the dyeing in $scCO_2$, the method reported in ref. ²³ was used. The dyed material was subjected to the test with a 5-g/L soap solution at 50°C for 45 min. The ratio of color on the benzylated ramie fiber was determined by the measurement of K/S (krnax) before and after washing. The reflectivity (R_∞) of the dyed benzylated ramie fiber was measured with the Lamda 950 spectrophotometer, and K/S was calculated with the Kubelka–Munk (KM) equation, as shown next:

$$K/S = (1 - R_\infty)^2 / 2R_\infty \quad (3)$$

R_∞ is the value that a colored sample approaches to the infinite thickness. During calculation, the reflectivity at the maximal wavelength is usually adopted as R_∞ .

RESULTS AND DISCUSSION

The benzylation of ramie fiber is a typical reaction of the Williamson nucleophilic substitution:



where the hydroxyl groups of ramie fiber are denoted by Cell–OH.

TABLE I
Effect of the Amount of CTAB on DS of the Benzylated Ramie Fiber

CTAB (g)	DS
0.00	0.32
0.01	0.43
0.02	0.79
0.04	1.13
0.06	0.88

The reaction mixture contained 15 mL of 10 mol/L NaOH, 10 mL of benzyl chloride, and 10 mL of toluene. The reaction was carried out at 125°C for 6 h.

The benzylation of ramie fiber is a three-phase reaction, which is composed of solid, water, and oil. It is common sense that the reaction will be more effective if a suitable PTC is applied. In this study, CTAB was used as a PTC to improve the reaction efficiency, and the effect of CTAB was investigated under different conditions. Before modification, the ramie fiber was immersed in a sodium hydroxide solution at a room temperature for 4 h; this is called *mercerization*. During mercerization, the ramie fiber swelled, which was favorable for the subsequent modification.

Effect of mercerization on DS

For the mercerization of ramie fiber, it has been reported that the concentration of sodium hydroxide and time are optimized at 18 wt % sodium hydroxide and 4 h, respectively.²⁴ In this study, the same conditions were adopted but with different procedures in the succeeding modification; that is, after mercerization, one sample was directly subjected to benzylation without washing, and the other sample was benzylated after washing with distilled water until it was neutral. The DS of the sample with washing after mercerization (1.83) was much higher than that of the one without washing after mercerization (0.27). This indicated that a thorough washing after mercerization was an essential step for a higher DS.

Effect of PTC addition on DS

Table I shows the relationship between the amounts of PTC added and the DS of the benzylated ramie fiber. As shown by the results in Table I, the DS of the benzylated ramie fiber was only 0.32 when there was no PTC added. The DS of the benzylated ramie fiber reached 1.13 when the amount of PTC was 0.04 g, which indicates that the benzylation of ramie fiber was obviously improved with the addition of the PTC. However, the DS of the benzylated ramie

fiber decreased to 0.88 when the amount of PTC was further increased to 0.06 g.

The reason may be as follows. With the addition of CTAB as a PTC, the hydrated sodium ion near the reactive hydroxyl groups in the ramie fiber was replaced by the CTAB ion, which led to a higher DS. With the increase of the amount of CTAB added, more hydrated sodium ions were replaced by the CTAB ion; thus, the DS of the benzylated ramie fiber increased. When all of the hydrated sodium ions around the active center were completely replaced and the CTAB reached saturation, the DS of benzylated ramie fiber reached the maximum value. If the amount of CTAB was further increased, DS decreased because the nucleophilic capability of the active center decreased.

IR spectroscopy

As shown by the FTIR spectra in Figure 4, the chemical structures of the benzylated ramie fiber and the benzylated ramie fiber after dyeing were obviously changed from that of the raw ramie fiber. The diversification of the IR pattern and the peak position of the benzylated ramie fiber extremely resembled benzylated wood.² The peaks at 1957, 1877, and 1813 cm^{-1} were assigned to the outside surface bending vibrations of the C—H bond. The characteristic absorption peak of the C—H bond stretching vibration appeared at 3029 cm^{-1} .

As a result of the esterification of the hydroxyl group in the raw ramie fiber, the vibrating absorption of the benzylated ramie fiber at about 3428 cm^{-1} was weakened. Moreover, two new peaks assigned to the single-substitution absorption of the aryl ring appeared at 742 and 693 cm^{-1} , and the

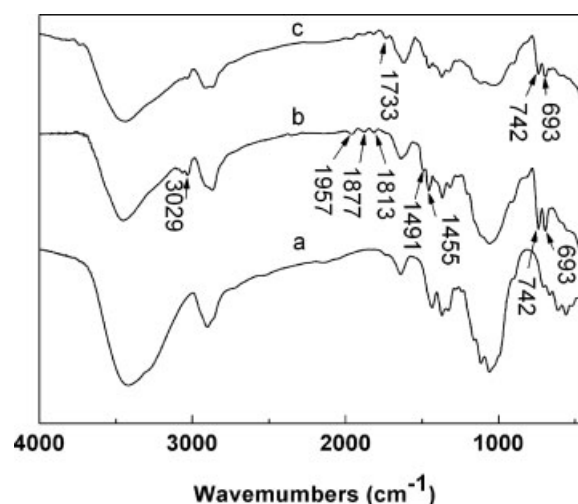


Figure 4 IR spectra of the (a) raw ramie fiber, (b) benzylated ramie fiber, and (c) benzylated ramie fiber after dyeing.

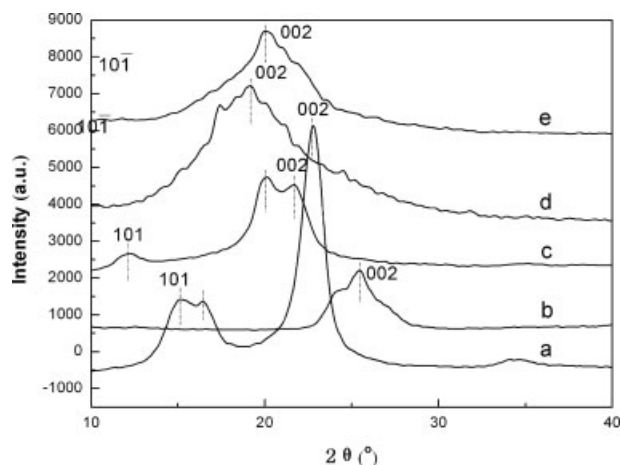


Figure 5 XRD patterns of the (a) raw ramie fiber, (b) mercerized ramie fiber, (c) benzylated ramie fiber, and (d) benzylated ramie fiber after dyeing.

absorptions of aryl rings were clearly observed at 1615, 1491, and 1455 cm^{-1} . In addition, with the increase of DS, the absorption of the hydroxyl bond obviously decreased, and the peak of C—H stretching vibrations appearing at 3029 cm^{-1} was clearly augmented (not given in Fig. 4). These IR results strongly indicate that ramie fiber was successfully benzylated under the conditions used.

For the ramie fiber after dyeing [Fig. 4(c)], a new peak at 1733 cm^{-1} , assigned to the absorption of the carbonyl groups in the DR 74 molecule, was clearly observed, whereas it was absent for either of the raw fiber or the benzylated fiber, which suggests that the dye molecules were attached to the fiber.

Crystal structure of the fibers

The XRD patterns of the raw ramie fiber, mercerized ramie fiber, benzylated ramie fiber, and benzylated ramie fiber after dyeing are shown in Figure 5(a–d). The XRD pattern of the raw ramie fiber matched well with that of the well-crystallized cellulose I. After mercerization, the crystal structure of the raw ramie fiber was transformed into cellulose II; the possible reason for this is discussed in our previous

article.²¹ In the case of the benzylated ramie fiber, the XRD pattern was different from that of either cellulose I or cellulose II, which suggests that ramie fiber was successfully benzylated. This was consistent with the IR results. In addition, not only was the peak intensity obviously decreased, but also the peak width was significantly increased. These changes caused by benzylation were very similar to those of cellulose shaped into balls.²⁵ The XRD pattern of the dyed ramie fiber was quite similar to that of the benzylated fiber without dyeing, which indicated that the dye molecules attached on the fiber had very limited effects on the crystal structure of the benzylated ramie fiber.

Morphologies of different fibers

SEM photographs of different ramie fibers are shown in Figure 6. For the raw ramie fiber, its surface was relatively smooth. Although the surface of the mercerized ramie fiber was still smooth, some changes were observed, which were caused by the swelling effect during mercerization. However, after benzylation, the surface of the ramie fiber became very coarse and rough, and some patches were clearly observed, which looked like a corroded surface. These corruptions may have formed large quantities of pores or channels in the fiber, which promoted dyeing efficiency. After dyeing, the surface texture of the benzylated ramie fiber became very rough and chapped, and CO_2 molecules getting into the pores of fibers enhanced the further swelling of the fiber, which was beneficial to the disperse dye entrapped in the pores of the fiber.²⁶

DSC and thermogravimetric measurements

The DSC curve illustrated the change in heat flow, and the DSC base line indicated the alteration of the specific heat capacity of the materials. The procedure for DSC analysis was as follows. To eliminate the influence of the physically adsorbed water in the sample, the temperature was increased to 145.9°C and maintained for 30 min. After that, the tempera-

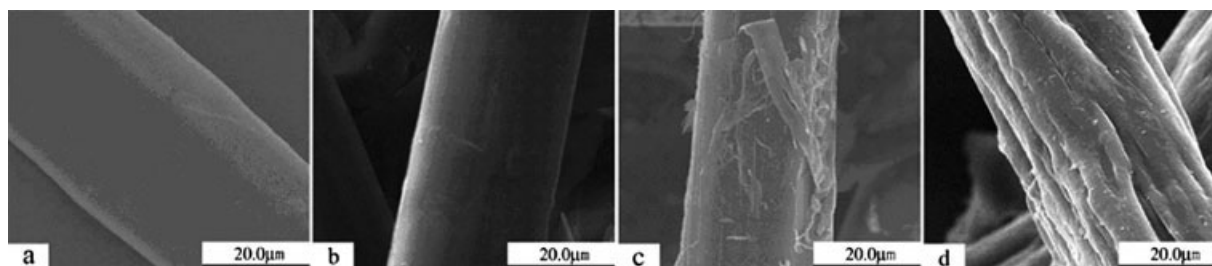


Figure 6 SEM photographs of the (a) raw ramie fiber, (b) mercerized ramie fiber, (c) benzylated ramie fiber, and (d) benzylated ramie fiber after dyeing.

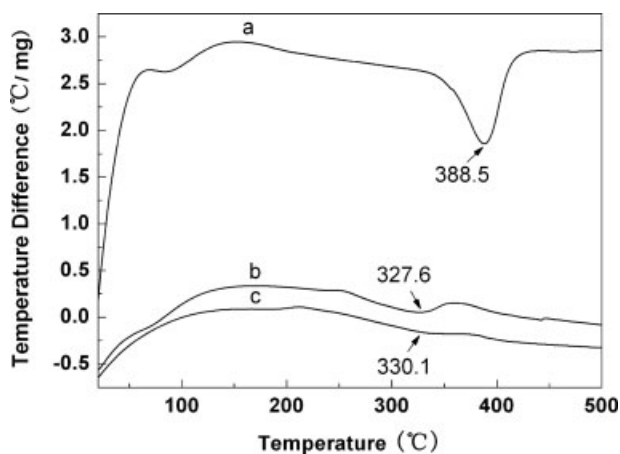


Figure 7 DSC curves of the (a) raw ramie fiber, (b) benzylated ramie fiber, and (c) benzylated ramie fiber after dyeing.

ture was decreased to room temperature. Finally, the temperature was increased to 500°C for DSC analysis. As shown in Figure 7, the process for the dehydration of the ramie fiber was quite complex and was ascribed to its high crystallinity. In the case of the raw ramie fiber, a strong endothermic peak was observed at temperatures from 18 to 64°C, probably because the ramie fiber still contained the adsorbed water. Moreover, at the glass temperature of 114°C, the raw ramie fiber was obviously deformed. The appearance of the glass temperature is one of the main characteristics of thermoplastic substances.²⁷ It implies that a part of the chains is in the amorphous zone, and the amorphous or semicrystal polymer begins to rupture at this temperature. In addition, ramie fiber had a clear exothermic peak at a peak maximum of 388.5°C, and the decomposition of the ramie fiber occurred at this temperature. For the benzylated ramie fiber, a strong endothermic peak at temperatures from 20 to 160°C [Fig. 7(b)] was also observed because of the water contained in the sample. The benzylated ramie fiber was completely decomposed at 327.6°C, as indicated by the small exothermic peak. If the benzylated ramie fiber after dyeing was considered, a quite similar DSC pattern was observed to that of the fiber without dyeing. The main difference was the slightly higher temperature for the complete decomposition of the benzylated ramie fiber after dyeing, that is, 327.6 versus 330°C. In summary, as a result of the difference in the molecular structure and the aggregation state of the ramie fibers, their thermal behaviors were different. After modification, the thermal stability of the ramie fiber was decreased. Dyeing had only a slight effect on the stability of the ramie fiber.

With increasing temperature, a fast deformation of the ramie fibers was experienced in the thermogravimetric (TG) analysis, which represented the pro-

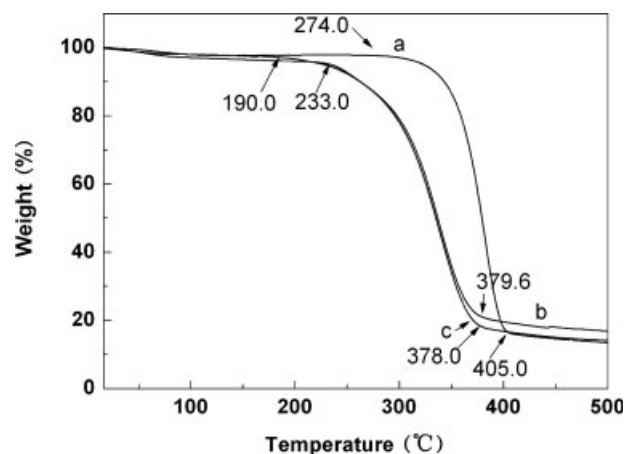


Figure 8 Thermogravimetric analysis curves of the (a) raw ramie fiber, (b) benzylated ramie fiber, and (c) benzylated ramie fiber after dyeing.

cesses of thermal softening and fusion. As shown in Figure 8(a), softening and fusion of the raw ramie fiber started at about 274°C and was completed at about 405°C. The softening temperatures of the ramie fibers after modification and dyeing were at 233 and 190°C, respectively, and their temperatures for complete fusion were at 379.6 and 378.0°C, respectively. This indicated that the thermal stability of the ramie fiber after benzylation and dyeing was basically the same. When curves (b) and (c) are compared with curve (a) in Figure 8, it is clear that the benzylation decreased the softening and fusion temperatures, which suggests that the thermoplastic properties of the benzylated ramie fiber increased. Moreover, dyeing had only a small effect on the thermal properties of the ramie fiber, which was consistent with the DSC results.

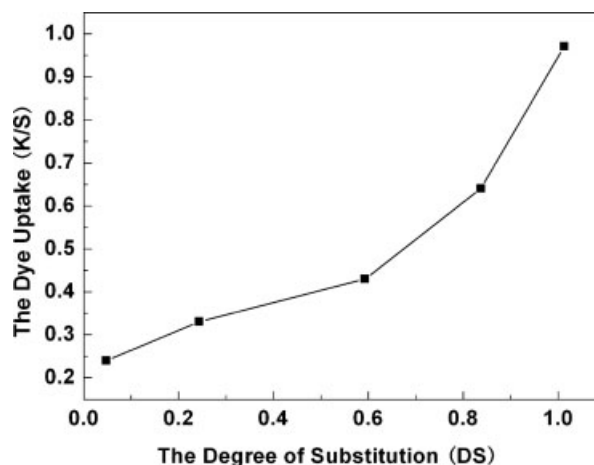


Figure 9 Relationship between DS of the benzylated ramie fiber and K/S (the lowest K/S was 14.8; the highest K/S was 27.7).

Effect of DS on *K/S*

Figure 9 shows the relationship between DS of the benzylated ramie fiber and *K/S*. A low DS of the fiber always caused a lower *K/S*, and the *K/S* values increased continuously when the DS was increased from 0.05 to 1.13. The reason may be explained as follows. Both the disperse dye and the benzyl groups were hydrophobic. The reaction of the hydroxyl groups in the ramie fiber with hydrophobic benzyl groups not only reduced the crystallinity of the fiber, which was favorable to the diffusion of the dye molecules, but also increased the hydrophobicity of the fiber, which strengthened the affinity between the benzylated ramie fiber and the dye molecule. Consequently, *K/S* increased with increasing DS value. Therefore, because both the dye molecule and the benzyl group were hydrophobic, the benzylation of the ramie fiber increased its hydrophobicity, which led to the increase in *K/S*.

CONCLUSIONS

Pretreatment with sodium hydroxide, benzylation modification catalyzed by CTAB as a PTC, and dyeing of the ramie fibers in scCO₂ were investigated, and the following conclusions were drawn:

1. Under the conditions used, the characterization results show that the hydroxyl groups in the ramie fiber were successfully reacted with benzyl chloride. To achieve a higher DS of the benzylated ramie fiber, a thorough washing after mercerization is an essential step.
2. CTAB as a PTC was effective in catalyzing the benzylation of the ramie fiber, and DS of the benzylated ramie fiber increased significantly when the PTC concentration was lower. Moreover, there existed an optimal value for the addition of the PTC, and this was reasonably explained.
3. The benzylated ramie fiber was dyed with a disperse dye in scCO₂, and a better dye efficiency was obtained as indicated by the higher *K/S* values. Furthermore, the color strength, indexed as *K/S*, was almost doubled when the DS of the benzylated ramie fiber was increased from 0.04 to 1.01.

4. The dyeing efficiency of the ramie fiber in scCO₂ was obviously improved through the modification of benzyl chloride, which was explained as the increase in the hydrophobicity of the benzylated ramie fiber.

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