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Low temperature bleaching of cellulose fabric with (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride as novel cationic activator for H_2O_2 bleaching

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ABSTRACT

The bleaching of cotton fabrics with hydrogen peroxide requires high temperature at a high pH value. A large amount of energy is consumed and the aggressive treatment conditions frequently damage the cellulose macromolecular chain. In this paper, novel cationic activator for H_2O_2 bleaching, (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride (TBCC), was synthesized and characterized by elemental analysis, FT-IR and ^1H NMR. Low temperature bleaching technique and surface morphology of cellulose fabric with TBCC were discussed. The desized and scoured cotton cellulose fabric could be bleached at low temperature 60 °C, using TBCC as active bleaching agent for H_2O_2. The whiteness index and wettability of the cotton fabric bleached at low temperature were similar with those of the cotton fabric bleached with the traditional high temperature method. Cotton cellulose fabric was not damaged at low temperature bleaching. It has potential application in cleaner production of cellulose materials.

1. Introduction

Cotton cellulose has excellent properties such as higher water absorbency and moisture, being comfortable to wear and easily to dye. For these reasons, the apparel industry is predominantly cotton based, and the share of cotton in total fiber consumption is about 50% (Fahmy, Aboshosha, & Ibrahim, 2009; Hebeish et al., 2009; Hou, Wang, & Yu, 2009; Hou, Zhou, & Wang, 2009; Shafie, Fouda, & Hashem, 2009; Wei, Cheng, Hou, & Sun, 2008; Xie, Wang, & Xu, 2009). Cotton is composed almost entirely of cellulose (90–96% based on weight of fibers). The impurities in cotton fiber range from 4% to 10% (Hashem, El-Bisi, Sharaf, & Refaie, 2009). The yellowish or brown coloration of the cotton fiber is related to the protoplasmic residues of protein and the flavones pigments of cotton flowers. Apart from these, the loom-state fabric is also contaminated with size, processing lubricant, such as machine oils, tars, and greases from harvesting, ginning, spinning and weaving. Prior to the dyeing and other finishing processes, non-cellulose substances have to be removed and natural pigments discolored.

Conventional processes of removing size and non-cellulose substances from cotton fabrics are called alkaline desizing and scouring, respectively. With these processes, pigments and seed coat fragments are not removed and that is why scouring is almost always followed by bleaching in order to discolor residual substances (Ibrahim, El-Hossamy, Hashem, Refai, & Eid, 2008). Hydrogen peroxide is a well-known environmentally safe bleaching agent for cotton fabrics. However, bleaching of cotton fabrics with hydrogen peroxide requires alkaline medium (normally NaOH), stabilizer and either high temperatures or long time. A large amount of energy in this process is consumed and the aggressive treatment conditions frequently damage the fiber cellulose chain (Presa & Tavcer, 2008). Meantime, a large amount of water is required for washing the residual un-decomposed hydrogen peroxide and the residual alkali.

Some attempts have been made to investigate new compounds as activator for H_2O_2 bleaching in order to reduce bleaching temperature. Hydrogen peroxide can bleach cotton cellulose fabrics using bleach activators at the low temperature conditions. Tetraacetylethylenediamine (TAED) and nonanoyloxybenzene sulphonate (NOBS) are well known as activator for H_2O_2. TAED or NOBS activating hydrogen peroxide system can improve bleaching effectiveness under mild conditions. In fact, bleach activators are peracid precursors, which generate peracids in situ in an alkaline hydrogen peroxide solution. The peracids are safe and efficient bleaching agent at mild condition. However, TAED is not soluble in water. NOBS is anionic compound with long alkyl chain, which has the poor water solubility. It limits their applications in the textile bleaching field because of the poor water solubility (Shafie et al., 2009). Recent research has shown that cationic compounds have potential application in bleaching of cotton cellulose

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fabrics. When the cotton fabrics are modified with cationic groups, the cationic group on the cationized cotton serves a dual function in the bleaching bath; the first is built-in catalyst for the bleaching process and the second is powerful alkali site necessary for activation of hydrogen peroxide bleaching bath instead of NaOH (Shafie et al., 2009). However, the reports of cationic compounds as activator for H_2O_2 bleaching are scarce.

In this work, (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride as novel cationic activator for H_2O_2 bleaching was synthesized and characterized. The molecule of TBCC not only had cationic groups, which catalyzed for the hydrogen peroxide bleaching process, but also had peracid precursor groups, which generated peracids in situ in an alkaline hydrogen peroxide solution. Low temperature bleaching technique for cellulose fabric with TBCC was discussed.

2. Experimental

2.1. Materials

Greige 100% woven cotton fabric was obtained from Zhengzhou No. 4 Cotton Textile Co., Ltd., Zhengzhou, China. The fabric had the following specification: plain weave, 27.8 tex × 27.8 tex, warp 236 yarn/10 cm, weft 236 yarn/10 cm. The warps of the fabric were sized with oxidized starch-based sizing agent.

Enzymes, Desizyme 2000L (amylase), Scourzyme L (pectinase), Cellusoft CR (cellulase), were obtained from Novozymes China, Beijing, China. Hydrogen peroxide (30%), sodium hydroxide, sodium silicate, potassium permanganate, 4-(chloromethyl) benzoyl chloride, toluene, caprolactam, triethylamine, acetonitrile, acetone, chloroform, all being AR, were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Non-ionic dispersing agent (JFC) was obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Synthesis of the cationic bleach activator

2.2.1. Synthesis of 4-(chloromethyl) benzoyl caprolactam

4-(Chloromethyl) benzoyl chloride (0.1 mol) was slowly added to the blends of caprolactam (0.11 mol), toluene 50 ml, and triethylamine (0.1 mol) at room temperature. The reaction mixture was heated to 110 °C for 1 h. The reaction mixture was stirred for 6 h at 110 °C. The reaction process was monitored by thin layer chromatography (TLC) using acetone: toluene in the ratio 1:20 as the fluent. The mixture was cooled to room temperature. The solid formed was filtered off to give crude. The purification was achieved by recrystallization with chloroform and gave white solid.

2.2.2. Synthesis of N-[4-(triethylammoniomethyl) benzoyl] caprolactam chloride

4-(Chloromethyl) benzoyl caprolactam (0.1 mol) was slowly added to a solution of trietheylamine (0.15 mol) and acetonitrile (25 g). The reaction mixture was heated to 90 °C and stirred for 4 h. The mixture was cooled to room temperature and dropped into acetone (100 ml). The solid form was filtered off to give crude. The purification for N-[4-(triethylammoniomethyl) benzoyl] caprolactam chloride (TBCC) was achieved by recrystallization with chloroform and gave white solid.

2.3. Desizing and scouring

Desizing and scouring of greige cotton fabric was carried out using impregnation technique. Cotton fabric was treated with an aqueous solution containing Desizyme 2000L 1.5 g/L, Scourzyme L 1.0 g/L, Cellusoft CR 0.8 g/L and JFC 1 g/L using material to liquor ratio 1:20 at 55 °C, pH 7 for 60 min. The sample was washed several times with boiling water then washed with cold water and finally dried at ambient conditions. The whiteness index of desized and scoured cotton fabric with enzyme technique was 16.254.

2.4. Bleaching

The bleaching process was performed using the exhaustion method. In this technique, desized and scoured cotton fabrics were treated with an aqueous solution containing different concentrations of N-[4-(triethylammoniomethyl) benzoyl] caprolactam chloride (TBCC) (0–12 g/L), hydrogen peroxide (H_2O_2) (0.5–4 g/L), sodium hydroxide (0–4 g/L). A material to liquor ratio of 1:20 was used. The bleaching process was performed at 60 °C for 60 min. The bleached sample was washed three times with hot water (80 °C) then three times with cold water and finally dried at ambient conditions.

The traditional bleaching method was performed at hydrogen peroxide (H_2O_2, 30%) (2 g/L), sodium hydroxide (2 g/L), sodium silicate (2 g/L), liquor ratio of 1:20, at 98 °C for 60 min.

2.5. Measurement

FT-IR spectrum of the synthesized sample was measured by a OMNI Sampler of the Nexus-670 FT-IR-Raman spectrometer (Nicolet Analytical Instruments, Madison, WI). H NMR spectrum was recorded on a Bruker AV 400 (Bruker Co., Faellanden, Switzerland). Element analysis was measured with Vario ELIII, Elmentar, Germany. For SEM analysis, the samples were sputtered with gold and then examined with a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

The degree of sample whiteness expressed as whiteness index was measured on Color-Eye 7000A spectrophotometer (Gretag Macbeth, USA) by using the CIE method according to ISO 105-J02: 1997(E) standard. The damage of fabric was determined by measuring the tensile strength according to ISO 13934.1, 1994 by Hounsfield Test Equipment H5KS.

Wettability was monitored. Three specimens in one group were tested. The length of specimen was 300 mm and the width was 50 mm. Three specimens in one group were hanged. The bottoms of samples were immersed in the stilled water at room temperature. After 30 min, the length of specimens with water was measured. The mean value of three specimens was calculated.

Decomposition rate of H_2O_2 (DR) was determined with the standard solution of potassium permanganate and calculated by Eq. (1).

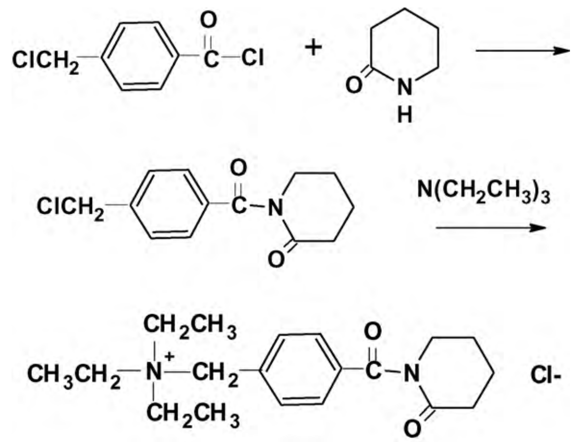
$$DR = \frac{V_0 - V_1}{V_0} \tag{1}$$

where V_0 is the volume of the standard solution of potassium permanganate consumed by 5 mL bleaching bath before bleaching and V_1 is the volume of the standard solution of potassium permanganate consumed by 5 mL bleaching bath after bleaching.

3. Results and discussion

3.1. Synthesis of (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride

The synthesis of (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride (TBCC) was divided into two steps. First, 4-(chloromethyl)benzoyl caprolactam was synthesized by the reaction of 4-(chloromethyl)benzoyl chloride and caprolactam with toluene as solvent. Second, TBCC was finally synthesized by the reaction of 4-(chloromethyl)benzoyl caprolactam and triethylamine with acetonitrile as solvent. The reaction is shown in Scheme 1.



Scheme 1. Synthesis reaction of (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride.

N-[4-(Triethylammoniomethyl) benzoyl] caprolactam chloride was achieved by recrystallization with chloroform. Yield is 67.31%. Elemental analysis found for $C_{19}H_{29}O_2N_2Cl$ (calc.): C 64.15% (64.68%); H 8.934% (8.23%); N 7.46% (7.94%). IR (KBr, cm^{-1}): 2986, 2933, 2863(–CH_3, –CH_2–,); 1702, 1669 (C=O), 1472, 1454 (Ar–). In order to reconfirm chemical structure of TBCC, ^1H NMR spectrum was determined. ^1H NMR spectrum of TBCC is shown in Fig. 1. ^1H NMR (D_2O, ppm): 1.27 (m, 9H, CH_3), 1.71 (m, 4H, CH_2), 2.65 (m, 2H, CH_2), 3.14 (m, 6H, CH_2), 3.90 (m, 2H, CH_2), 4.35(m, 2H, N^+–CH_2–Ar), 7.46-7.55(m, 4H, Ar–H).

3.2. Low temperature bleaching of cotton cellulose fabrics with TBCC

In the bleaching process of cotton fabrics, hydrogen peroxide liberates perhydroxyl anion (HOO^-) in alkali condition. HOO^- as nucleophilic substitution reacts with (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride and cationic benzoyl hydroperoxide is obtained. The mechanism of catalyst is shown in Scheme 2. Compared with hydrogen peroxide, the activity of cationic benzoyl hydroperoxide as oxidant is higher. Furthermore, benzoyl hydroperoxide for its cationic property is easy to combine with cotton fabric having negative charge and reacts with colored impurities in cotton. So, hydrogen peroxide can bleach cotton fabric at low temperature using TBCC as bleach activator.

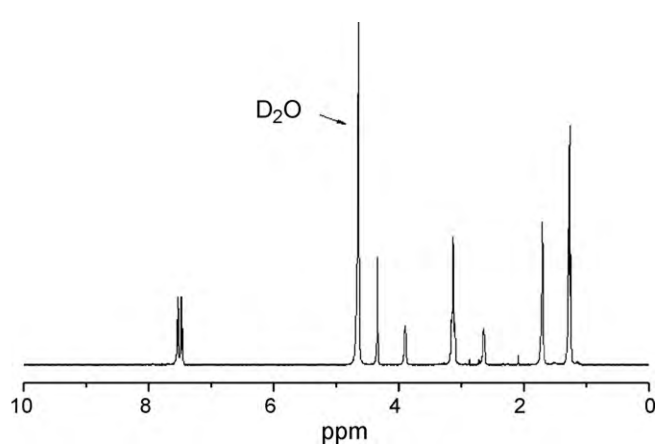
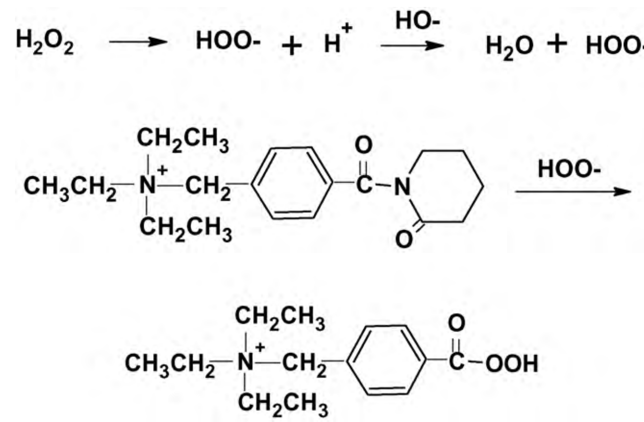


Fig. 1. ^1H NMR spectrum of (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride.



Scheme 2. Mechanism of TBCC bleaching for cellulose.

The effects of TBCC, hydrogen peroxide, sodium hydroxide on bleaching properties were investigated. Whiteness and decomposition rate of H_2O_2 were two important parameters.The fabrics were monitored for whiteness index and decomposition rate of H_2O_2 during the exhaust bleaching.

3.2.1. Effect of TBCC concentration

The desized and scoured cotton fabric was bleached at different conditions. In order to investigate the effect of TBCC concentration on the whiteness index, the samples were bleached with hydrogen peroxide (30%), 2 g/L, sodium hydroxide, 2 g/L, liquor ratio 1:20, at 60 °C for 60 min. The results are shown in Table 1. It indicates that the fabrics could be bleached with hydrogen peroxide at low temperature 60 °C, using TBCC as bleach activator. The decomposition rate of hydrogen peroxide gradually increased with increasing the concentration of TBCC from 0 g/L to 12 g/L. At low concentrations of TBCC from 0 g/L to 6 g/L, the whiteness index of bleached fabric was gradually improved with increasing the amount of TBCC, because much more cationic benzoyl hydroperoxide as effective bleach component was obtained. At high concentrations of TBCC from 6 g/L to 12 g/L, the whiteness index of bleached fabric did not get further improvement with increasing the amount of TBCC.

3.2.2. Effect of hydrogen peroxide concentration

Hydrogen peroxide is main component in bleaching system and plays an important role in fabric bleaching. To investigate the effect of the concentration of hydrogen peroxide on the bleaching property, the samples were bleached with TBCC, 6 g/L, sodium hydroxide, 2 g/L, liquor ratio 1:20, at 60 °C for 60 min. The results are presented in Table 2. The decomposition rate of hydrogen peroxide gradually decreased with increasing the concentration of hydrogen peroxide. The whiteness index of bleached fabrics was increased with increasing the concentration of hydrogen peroxide, from 0.5 g/L to 2 g/L. However, when the concentration of hydrogen peroxide was further increased, the whiteness index did not get improvement. The suitable concentration of hydrogen peroxide was 2 g/L in TBCC low temperature bleaching system.

Table 1
Effect of TBCC concentration on bleaching properties.

TBCC (g/L)	Whiteness index	DR of H_2O_2 (%)
0	55.833	40.85
2	62.386	46.38
4	68.888	51.06
6	71.844	57.02
8	72.086	60.04
10	72.557	62.13
12	72.553	68.09

Table 2
Effect of hydrogen peroxide concentration on bleaching properties.

H_2O_2 (g/L)	Whiteness index	DR of H_2O_2 (%)
0.5	57.457	63.29
1.0	66.189	52.83
2.0	69.938	51.96
3.0	70.328	49.68
4.0	70.274	45.54

Table 3
Effect of sodium hydroxide concentration on bleaching properties.

NaOH (g/L)	Whiteness index	DR of H_2O_2 (%)
0	28.978	27.55
1	64.585	43.80
2	68.300	49.75
3	66.934	46.40
4	66.663	41.37

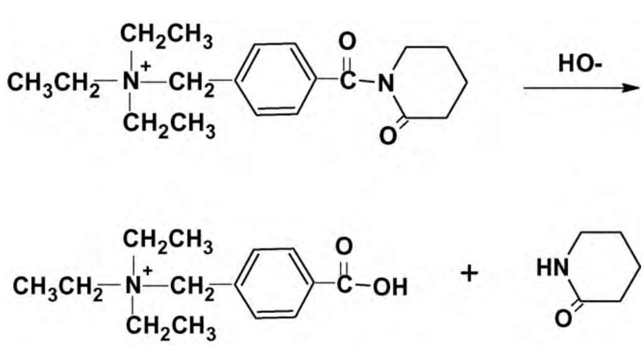
3.2.3. Effect of sodium hydroxide concentration

Effect of sodium hydroxide concentration on the bleaching property was also discussed. The cotton fabrics were bleached with hydrogen peroxide (30%), 2.0 g/L, TBCC, 6 g/L, liquor ratio 1:20, at 60 °C for 60 min. Results obtained are set out in Table 3. The results of Table 3 show that increasing NaOH concentration from 0 g/L to 2 g/L was accompanied by increasing in whiteness index of the bleached cotton fabric from 28.978 to 68.300. However, when NaOH concentration was further increased, the whiteness index of the bleached fabric decreased. It can be seen that the liberation of HOO^- anion at higher sodium hydroxide concentration was so rapid that it became unstable with the formation of oxygen gas which had no bleaching property. At same time, TBCC could be hydrolyzed and produced the unbleachable compound (shown in Scheme 3) leading to lower whiteness index.

3.3. Effect of low temperature bleach on physical properties

The traditional bleaching method was performed with hydrogen peroxide at high temperature 98 °C and might affect the physical property of cotton fabric. In this work, the cotton fabric was bleached with hydrogen peroxide bleaching system, TBCC as active bleaching agent at low temperature 60 °C. The whiteness index, wettability and warp tensile strength of fabrics were measured. The physical properties of cotton fabrics bleached with the traditional method or the low temperature method are presented in Table 4.

Compared with greige cotton fabric (whiteness index 9.351, wettability 0.1 cm), the whiteness index of the desized and scoured fabric with enzymes was slightly improved and the wettability of it was significantly improved. And they were further improved and reached the similar values after the low temperature or traditional



Scheme 3. Hydrolysis of TBCC.

Table 4
Physical properties of bleached cotton fabrics.

	Control sample	Low temperature bleach	Traditional bleach
Whiteness index	16.254	71.342	73.602
Wettability (cm)	8.3	9.7	10.0
Tensile strength (N)	494.1	493.1	364.2

bleaching. However, the tensile strength of the fabric bleached at low temperature was similar with that of the control sample (desized and scoured fabric), and the tensile strength of the fabric bleached with the traditional method obviously decreased. It indicates that compared with the low temperature bleach, the fabric

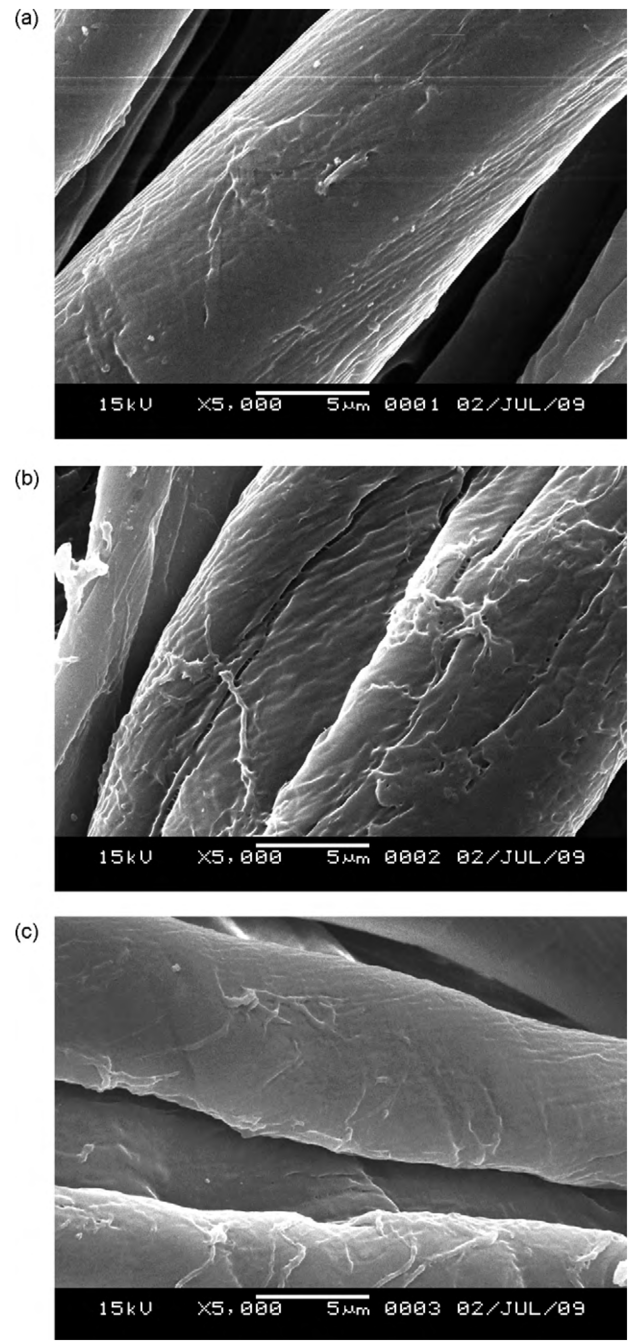


Fig. 2. SEM of cotton fibers (a, SEM of the control sample; b, SEM of the cotton fiber bleached with traditional method; c, SEM of the cotton fiber bleached at low temperature).

was damaged during the traditional bleaching process. This would be further confirmed by scanning electron microscopy.

3.4. Surface morphology of bleached cotton fiber

SEM analysis was used to characterize any changes in the surface morphology of the fibers as a result of the treatments applied, such as the appearance of pitting, cracking, and crazing. To investigate the surface morphological changes of cotton fibers before and after bleaching, representative SEM micrographs, taken at a magnification of ×5000, of the cotton fibers unbleached, bleached with the traditional method or with the low temperature bleaching method are shown in Fig. 2. Compared with the unbleached cotton fiber, there were obvious pitting, cracking, and crazing on the SEM of the cotton fiber bleached with the traditional method. However, there were no pitting, cracking, and crazing on the SEM of the cotton fiber bleached at low temperature. It further demonstrates that the cotton fiber bleached with the traditional method was damaged at some extent and the cotton fiber bleached at low temperature was not damaged.

4. Conclusions

(N-[4-Triethylammoniomethyl]-benzoyl) caprolactam chloride (TBCC) as novel activator for H_2O_2 bleaching was synthesized. The cotton fabric could be bleached with hydrogen peroxide at low temperature 60 °C, using TBCC. TBCC as active bleaching agent had excellent catalyzing properties. The whiteness index and wettability of the cotton fabric bleached at low temperature were similar with those of the cotton fabric bleached with the traditional method. SEM of the cotton fibers show that the cotton fiber bleached with the traditional method was damaged and the cotton fiber bleached at low temperature was not damaged. Low temperature bleaching of cotton fabric with (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride as novel cationic activator for H_2O_2 bleaching could save a large amount of energy.

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