Fixation of Chitosan on Cross-Linked Cellulose Fabrics with Polycarboxylic Acids

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Abstract: Fixation of chitosan on cellulosic fabrics with using a cross-linking reaction of polycarboxylic acid has been investigated. Cotton fabrics that was cross-linked with polycarboxylic acid such as citric acid (CA) and butanetetracarboxylic acid (BTCA) showed to have appreciable amount of free carboxylic acid residues on the fabric that came from the polycarboxylic acid without participating the cross-linking reaction. Chitosan could be fixed on the fabric with good fastness to acid washing by padding and following curing process. Relatively high wrinkle recovery characteristics of the cross-linked and chitosan fixed fabric was obtained. The fixation of the chitosan on cotton fabric could also be done by the simpler process that consists of padding of mixture of polycarboxylic acid and chitosan onto untreated cotton fabric followed by high-temperature curing. With this process, simultaneous chitosan fixation could be achieved with the cross-linking reaction of polycarboxylic acid with cotton substrate. Intermolecular ester linkage formation by the polycarboxylic acid was suggested by the FTIR measurements.

1. Introduction

Polycarboxylic acids have been used successfully in durable press (DP) finishing of cotton fabrics in order to realize a smooth-drying appearance without ironing after laundering. Since Gagliardi and Shippee [1] first introduced the polycarboxylic acid class as non-formaldehyde cellulose crosslinking agents for DP cottons, the application of polycarboxylic acid has been developed for DP finishing of cotton fabrics [2-8].

On the other hand, chitosan, whose applications have been widely studied in the medical field, is expected as one of textile finishing reagents because of its aggregation and antibacterial nature. Chitosan is one of the most interesting natural compounds in textile finishing process as well. Recently, several researchers have reported its application on cotton fabric [9-12].

Here, we consider the novel method for the fixation of chitosan on cellulosic fabrics by using of polycarboxylic acid. The aims of the fixation of chitosan on cellulosic fabrics are improvement of dyeability and assignment of an antibacterial property. In the previous paper, we reported that UV photo-oxidized cotton fabric could effectively absorbed chitosan [12]. Carboxylic group formed by the UV light irradiation on cotton fabric seemed to act an important role for the fixing chitosan on the substrate. From the results, it can be expected that if one can introduce carboxylic groups by anyhow on the cellulosic fabric the fixation of chitosan can well be done on the cellulosic fabrics without using any artificial chemicals. One of the possible ways to introduce carboxylic groups on the cellulosic substrate is to treat with polycarboxylic acid such as citric acid (CA) and butanetetracarboxylic acid (BTCA) by a cross-linking reaction as a wrinkle resistance treatment. Yang reported the ester cross-linking and its mechanism between cotton cellulose and polycarboxylic acids using Fourier transform infrared (FTIR) spectroscopy [13-15]. The cross-linking reaction of the polycarboxylic acids with cellulosic substrate produces carboxylic residues that are not esterified with cellulose.
[13]. The carboxylic groups remaining on the cellulosic substrate may act as fixation sites for chitosan that are similar to that of the photo-oxidized cellulosic substrate as mentioned above. We used FTIR spectroscopy to study the esterification reactions of polycarboxylic acids with cellulose and chitosan. In addition, washing fastness and wrinkle resistance of cross-linked cellulose fabric was also investigated.

2. Experimental

2.1 Materials

Fabrics used as substrates were cotton broad cloth (40 count, warp 130 /inch, welt 70 / inch). They were washed before and after the cross-linking reaction with distilled water at boil for 30 minutes. Citric acid (CA) and butanetetracarboxylic acid (BTCA) used as the cross-linking agents and sodium phosphinate monohydrate (NaH₂PO₂.H₂O) used as a catalyst for the cross-linking reaction of the polycarboxylic acids were reagent grade chemicals. Chitosan (Sigma Chemicals Co. Ltd.) used in this study was of 89% deacetylated derivative from crab shell chitin.

2.2 Method

2.2.1 Cross-link reaction of cotton fabric with polycarboxylic acids

Cross-link reaction was carried out on a laboratory scale. 6% w/w of aqueous CA or BTCA solution that contains the same amount of sodium phosphinate monohydrate to the polycarboxylic acid was applied on the cotton fabric at 80% pick up and dried under the atmospheric condition. The fabric was then cured at 170 ℃ for 90 seconds in a convection oven and washed 3 times for 5 minutes with distilled water at boil and dried. The amount of CA or BTCA introduced on the fabric was evaluated by the weight increase of the treated fabric weighted with a high temperature electronic balance.

2.2.2 Chitosan treatment

Chitosan was dissolved in 0.7% aqueous acetic acid solution to be concentration of 0.5% w/w. Fabric with or without cross-link reaction was dipped in the chitosan solution and was nipped with a laboratory mangle to be ca. 120% wet add-on. The chitosan-padded fabric was dried under the atmospheric condition and cured at 170 ℃ for 90 seconds in a convection oven. The cured fabric was then washed with 0.7% boiling acetic acid solution to remove unfixed chitosan for 1 hour and dried.

The amount of chitosan fixed on the fabric was determined by the analytical procedure established by Tsuji using nitrous acid and 3-methyl-3-benzothiazolone hydrazone hydrochloride (MBTH) [17, 18]. This method is based on the colorant formation reaction between chitosan, NaNO₂ and MBTH in the presence of FeCl₂. The amount of the colorant formed by the reaction, which is proportional to the amount of D-glucosamine unit in the sample, was determined spectrophotometrically at 653 nm.

2.2.3 Wrinkle recovery measurements

Conditioned wrinkle recovery angle of the cross-linked and chitosan treated fabric was evaluated as an warp and filling value by a Monsanto tester (ASTM D 1295-60T) under the condition of 25℃ and 65% humidity.

2.2.4 FTIR spectroscopy

IR spectra were recorded on Nicolet FTIR Protege 460 using KBr pellet technique and the attenuated total reflectance (ATR) technique on a germanium crystal cell with incident angle of 30°. 100 scans was carried out for each ATR measurement.

3. Results and Discussion

3.1 Amount of carboxylic group introduced on the cross-linked fabric

The amount of carboxylic group introduced on the fabric by the cross-linking reaction with the polycarboxylic acids (CA and BTCA) was determined by NaOH titration and plotted in Figure 1 in owf (on the weight of fiber or fabric) scale against the amount of the polycarboxylic acids padded on the fabric. Figure 1 shows that remarkable amount of free carboxylic group can be determined on the cross-linked fabric with increasing the polycarboxylic acids padded on the fabric. Figure 1 shows that remarkable amount of free carboxylic group can be determined on the cross-linked fabric with increasing the polycarboxylic acid introduced on the fabric. This indicates that sufficient amount of free carboxylic group that does not participate in the cross-linking reaction with the cotton substrates is left on the cotton substrate, which can be expected to be utilized as a fixing site for chitosan.

3.2 Fixation of chitosan on the cross-linked cotton fabric

The amount of chitosan fixed on the cross-linked fabric was determined and plotted in Figure 2 in owf
Fig. 1 Amount of carboxyl residue fixed on a cotton fabric against a concentration of the fixed polycarboxylic acid

![Graph showing carboxyl residue fixed on a cotton fabric against concentration of polycarboxylic acid.](image)

Fig. 2 Amount of chitosan fixed on a cotton fabric against a concentration of the fixed polycarboxylic acid

![Graph showing chitosan fixed on a cotton fabric against concentration of polycarboxylic acid.](image)

scale against the amount of polycarboxylic acids introduced on the cotton fabric. It is of interesting, as shown in Figure 2, that the amount of chitosan fixed on the cross-linked fabric increases linearly with increasing the amount of polycarboxylic acid introduced on the fabric as a cross-linking agent. Chitosan applied on the fabric seems to be fixed by an esterification or amide formation reaction with the free carboxylic group that was introduced on the cotton fabric by the cross-linking reaction. The ability for fixation of chitosan is more effective in the case of the fabric that was cross-linked with CA than in the case of with BTCA. This result indicates that the more active carboxylic group that participates in the fixing reaction with chitosan is present in the case of CA rather than in the case of with BTCA. The less activity of BTCA for chitosan fixation on cotton fabric might be caused by a steric hindrance of the free carboxylic group in BTCA molecule, although the amount of the free carboxylic group of BTCA introduced on the cotton fabric seemed to be similar to that of CA as shown in Figure 1.

3.3 Wrinkle recovery of the cross-linked fabrics

Figure 3 shows wrinkle recovery angle of cotton fabrics treated with polycarboxylic acid. The polycarboxylic acid-treated cotton fabrics (c, e) have large wrinkle recovery angles comparing with that of untreated cotton fabric (a). The wrinkle recovery angles of the polycarboxylic acid-treated cotton fabric were slightly decreased after chitosan fixation (d, f). These wrinkle recovery angles (d, f), however, are still keeping appreciably higher values than that of untreated cotton fabric. From these results, it can be concluded that polycarboxylic acids-treated cotton fabrics have good wrinkle recovery characteristics even after the chitosan fixation.

3.4 Fastness property of the fixed chitosan to washing

Fastness of the fixed chitosan to washing was evaluated by a washing test with 0.7% aqueous acetic acid solution at boiling temperature as a washing test.

![Graph showing wrinkle recovery angle of cotton fabrics treated with chitosan.](image)
solution. In Figure 4, amount of residual chitosan on the fabric after the each washing test was plotted in owf scale against the washing time. The chitosan fixed cotton fabrics were prepared by padding 0.6%owf chitosan onto cotton fabrics that were previously processed with or without CA cross-linking reaction. After the chitosan add on, the fabrics were cured and pre-washed for 1 hour with 0.7% aqueous acetic acid solution at boiling temperature in order to remove unfixed chitosan from the fabrics.

As can be seen in Figure 4, initial amount of fixation of chitosan on the CA cross-linked fabric is appreciably high compared with that on the original fabric without CA cross-linking process. Amount of chitosan on the fabrics decreases with time of acid washing, especially at initial washing stage. However, the amount of the residual chitosan on the CA cross-linked fabric is approximately twice as much as that on the original fabric even if the fabric is washed in an acetic acid solution for 24 hours. This finding indicates that free carboxylic acid formed on the CA cross-linked fabric may act as an effective fixation site for chitosan. The washing fastness of chitosan on the fabric that was CA cross-linked and then chitosan padded in the absent of final curing process is appreciably poor compared with that on similar fabric in the presence of final curing process as shown in Figure 4. This fact indicates that final curing process would be necessary to obtain complete fixation of chitosan on the fabric. An esterification or amide formation reaction between the carboxylic group on the cotton fabric and chitosan would occur during the final curing process.

As described above, it can be concluded that a series of processes of cross-linking reaction with polycarboxylic acid, chitosan padding, and final curing process would be necessary to obtain fixation of chitosan on the cotton fabric. Here, one can expect that if suitable amount of chitosan may be mixed with polycarboxylic acid at the cross-linking reaction process, the fixation of chitosan on the cotton fabric may be achieved by one step process, i.e. padding of the mixture of polycarboxylic acid and chitosan followed by curing for cross-linking reaction.

Figure 5 shows the fastness to acid washing of the fixed chitosan on the fabric that was obtained by the one step process described above. The mixture of 6%w/w CA and 0.5%w/w chitosan was padded on cotton fabric and then cured once at 170°C for 90 seconds. After the curing process the fabric was pre-washed for 1 hour with 0.7% aqueous acetic acid solution at boiling temperature in order to remove unfixed chitosan from the fabrics.

As can be seen in Figure 5, amount and fastness of fixed chitosan on the cotton fabric obtained by padding of the mixture of CA and chitosan and followed by curing process is similar to the case of that obtained with step-by-step multiple process that consists of CA cross-linking reaction and chitosan fixation. The fixation and fastness of chitosan, on the other hand, obtained by padding of the mixture of CA and chitosan without curing process was remarkably poor, indicating that during curing process CA may be introduced by cross-linking reaction with cotton substrate and simultaneously chitosan may be fixed on the substrate by an esterification or amide formation reaction with free carboxylic acid formed on the substrate by the CA cross-linking reaction.

3.5 FTIR Spectroscopy of chitosan fix cotton fabric

In order to clarify the cross-linking reaction of polycarboxylic acid with cellulosic substrate, FTIR measurement was carried out. Figure 6 (a, c) shows the infrared spectra of cotton fabrics, on which
polycarboxylic acids, CA or BTCA, were applied, cured at 170°C for 90 seconds and then washed with aqueous acetic acid at 100°C for 1 hour. In this spectrum, absorption bands in the region of 1700-1750 cm⁻¹ due to carbonyl groups are observed. However, it is difficult to assign the absorption bands to the ester carbonyl group because the carbonyl band is usually overlapped by the free carboxyl band. On the other hand, the spectra of a cotton fabric that is not cured after introducing polycarboxylic acid does not show the absorption band in the region of 1700-1750 cm⁻¹ as shown in Figure 6 (b, d). The polycarboxylic acid introduced on the cotton fabric without curing might be entirely removed by the acid washing process. This result indicates that with the curing process chemical bonds which can be regarded as ester group between polycarboxylic acid and cotton substrate might be formed showing the IR absorption band in the region of 1700-1750 cm⁻¹. Several research workers have reached the similar conclusion through infrared spectroscopy analysis that polycarboxylic acids esterify cotton cellulose during a curing process [13-16].

Similarly, Figure 7 shows the infrared spectra of chitosan which was mixed with polycarboxylic acid, CA or BTCA, in a solution and dried at 170°C for 90 seconds. When the spectra of the dried mixture (a, d) are subtracted from the spectra of the cured one (b, e), as shown in the difference spectra (c, f), each distinct band at 1730 cm⁻¹ (c) and 1713 cm⁻¹ (d) can be assigned to the stretching modes of the ester carbonyl groups. These results are in accordance with an expectation that polycarboxylic acids esterify chitosan under the curing condition.

From the results of Figure 6 and Figure 7, polycarboxylic acids can be considered to connect with cotton cellulose, as well as with chitosan, with intermolecular ester linkage.

References

Fig. 7  Infrared spectra of the chitosan cured with 4.0% CA: (a) dried and cured at 170°C for 90 seconds, (b) dried at 50°C, (c) difference spectra, b-a, and 4.0% BTCA: (d) dried and cured at 170°C for 90 seconds, (e) dried at 50°C, (f) difference spectra, f-e