

# Preparation of Cellulose Sulphate and Evaluation of its Properties

Xu Huang\*, Wei-Dong Zhang

*Dyeing and Chemical Department, Nantong Dyeing and Chemical Department,  
No.105, East of Qing Nian Road, Nan Tong, Jiang Su Province, 226007, P.R. China.*

**Abstract:** This paper reports the reaction of cotton cellulose with sulphamic acid using pad bake process. FT-IR and FT-Raman were used to analyse the intermediate products formed during this study. The self-crosslinking of the modified cotton fibre has special characteristics including good dye ability in case of ammonia or ethanolamine initiated crosslinking. Peroxide should react with the modified fibre to give peroxy cellulose. The self bleaching and anti-bacterial qualities of this reacted cellulose are worthy of investigation.

**Keywords:** Cotton cellulose, sulphamic acid, self-crosslinking, self bleaching; anti-bacterial.

## 1. Introduction

### 1.1 Source of cellulose

Cellulose is the most abundant of all naturally occurring organic polymers, thousands of millions of tones being produced by photosynthesis annually throughout the world [1]. Although exploited for several millennia in the forms of cotton, flax and other textile fibres, and in the form of wood for papermaking and constructional purposes, our knowledge of its chemistry is comparatively less and studied recently. It was first recognized in 1838 as the common structural material among many of the higher land plants by Payen, who invented the name cellulose [2]. However, it was not until the 1930s that its constitution as a linear high polymer of anhydroglucose units was unequivocally established [3,4].

### 1.2 Crosslinking of cellulose

Cellulose can be crosslinked by any reagent containing at least two functional groups capable of reacting with hydroxyl groups. Modified cellulose containing other functional groups also form crosslinking [5].

Cellulose can be esterified with most inorganic and organic acids by methods analogous to those used for simple alcohols. Many of the products have practical applications.

### 1.3 FTIR and FT Raman spectroscopy

FTIR is the oldest and most developed of the above methods. It involves light absorption by fundamental vibrations; FTIR spectra have narrow line widths and

rich spectral detail, such that different molecules have distinguishable “fingerprints.” FTIR instrumentation is highly refined due to its widespread use, and interferometers possess excellent wavelength precision and stability. Although FTIR absorption is both popular and powerful, it does have some limitations that are fundamental to the wavelength range involved.

Raman spectra can be acquired noninvasively, and sampling can be simple and fast. Like FTIR, Raman scattering probes fundamental vibrations with high spectral resolution but in this case is sensitive to groups sharing polarization. Although the selection rules differ for FTIR and Raman, the information is similar and both are amendable to spectral libraries and fingerprinting. In addition, Raman has some added features based on resonance and/or surface enhancement, polarization measurements, and compatibility with aqueous samples [6,7].

### 1.4 Aims of this research work

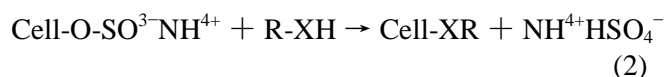
Cotton cellulose will be carefully dried and then reacted with a DMF solution of sulphamic acid at circa 80°C, the following Eq.1 is expected:



According to the degree of substitution, different properties can be expected, at a high level of substitution the cellulose may well dissolve in water and at lower levels the substrate may exhibit reactive properties (even self-crosslinking under alkaline conditions).

Reactivity of the substrate with appropriate nucleophiles may be summarized as Eq.2:

\*Corresponding author's email: huangxu31@126.com  
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## 2. Experimental

### 2.1 Preparation of sulphate fibre

Padding was carried out on a two-bowl laboratory pad-mangle set to give a nip expression of 100%. Baking of the treated fiber was carried out in a laboratory forced draught oven.

The pad liquor contained sulphamic acid ( $150\text{g dm}^{-3}$ ), and urea ( $150\text{g dm}^{-3}$ ), this liquor was padded onto the cotton (15.0g), the cotton was then dried at room temperature and baked for 5 minutes at  $150\text{ }^\circ\text{C}$ . The treated cotton was washed in tap water to remove un-reacted acid and residual urea [8].

### 2.2 Application of modified fibre

#### 2.2.1 Self-crosslinking investigation

##### 2.2.1.1 Reaction with sodium carbonate and sodium phosphate

The pad liquor contained sodium carbonate ( $30\text{g dm}^{-3}$ ), this liquor was padded onto the treated cotton (5.0g), the cotton was then dried at room temperature and baked for 5 minutes at  $150\text{ }^\circ\text{C}$  to fix the resist. The treated cotton was washed in tap water and then dried.

The pad liquor was changed to contain sodium phosphate ( $30\text{g dm}^{-3}$ ) then the same process was repeated.

##### 2.2.1.2 Reaction with ammonia and ethanolamine

Treated cotton (5.0g) was immersed in ammonia (100ml,  $20\text{g dm}^{-3}$ ) in a sealed tube for 1 hour at  $60\text{ }^\circ\text{C}$  and then dried at room temperature.

Treated cotton (5.0g) was immersed in ethanolamine (100ml,  $5\text{g dm}^{-3}$ ) then the same process was repeated.

#### 2.2.2 Bleach activation study

A tea-bag was immersed into distilled water for 3 hours. Untreated cotton 5.0g and treated cotton 5.0g were put into the cold tea solution at room temperature for ten minutes and then dried at room temperature.

Bleach liquor contained hydrogen peroxide (35%,  $1.5\text{g dm}^{-3}$ ) and sodium carbonate ( $5\text{g dm}^{-3}$ ) in distilled

water (150ml). The untreated and sulphamic acid treated samples were monitored for 15 minutes at  $40\text{ }^\circ\text{C}$ . The process was repeated with the corresponding tea-stained samples immersed in the tea solution for 3 hours.

### 2.3 Analysis of fiber

#### 2.3.1 FT-IR & FT-Raman analysis

FTIR analyses of all intermediate products prepared during this study were carried out using the Perkin-Elmer Spectrum Spotlight 1740 Fourier Transform Infrared Spectrometer. Samples were prepared by mixing 1mg of sample in 200mg of potassium bromide.

The standard data collection parameters used was as follows:

- Resolution:  $4\text{cm}^{-1}$
- Detector: DTGS
- No. of Scans: 100 (Diamond); 16 (KBr)
- Scan Range:  $4000 - 400\text{cm}^{-1}$
- Gain: 1
- Mirror Velocity: Normal

FT-Raman analyses of all intermediate products prepared during this study were carried out using the Perkin-Elmer 2000R Fourier Transform Raman Spectrometer.

The standard data collection parameters used was as follows:

- Resolution:  $4\text{cm}^{-1}$
- Detector: High sensitivity InGaAs detector
- No. of Scans: 100
- Scan Range:  $3500 - 200\text{cm}^{-1}$
- Laser: Nd:YAG laser with 200mW of laser power

## 3. Results and discussion

### 3.1 FT-IR analysis

Chemical changes in the fiber samples following treatment were monitored by FT-IR spectroscopy.

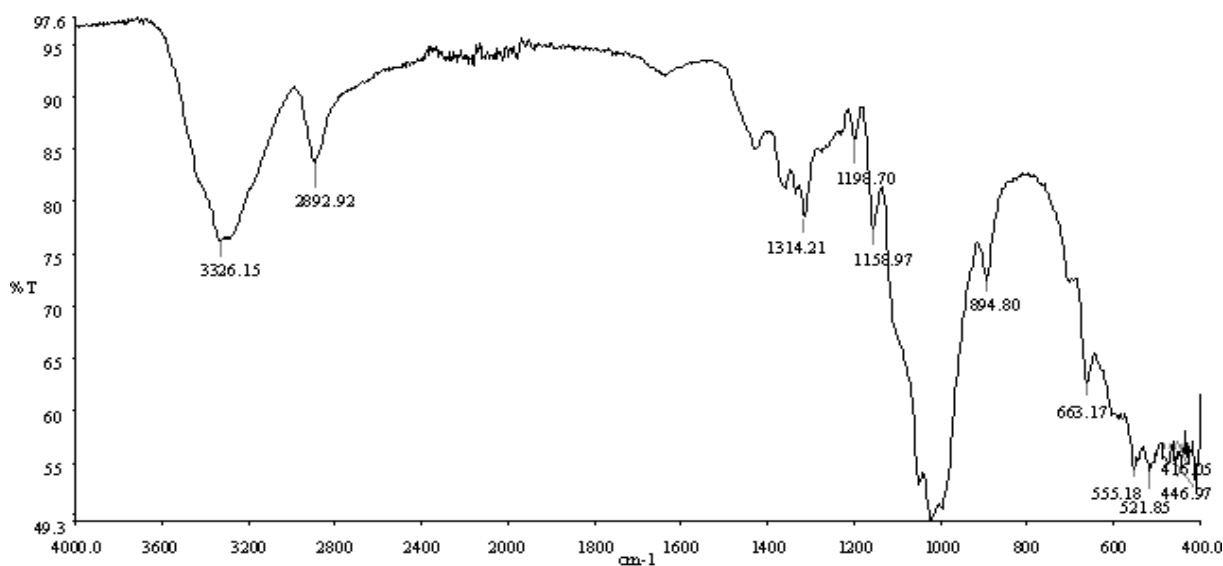


Figure 1 The FT-IR spectrum of untreated cotton.

From Figure 1 the strong diffuse band  $3326\text{ cm}^{-1}$  and the weak band  $2892\text{ cm}^{-1}$  can be attributed to stretching vibration of hydroxyl groups, including hydrogen bonds, and of  $\text{CH}_2$  and  $\text{CH}$  groups respectively [9]. The band  $1314\text{ cm}^{-1}$  is the deformation vibration frequencies of  $\text{C-OH}$  and  $\text{CH}$  groups. The strong

absorption band in the  $1000\text{-}1200\text{ cm}^{-1}$  regions is mainly attributed to the stretching vibrations of  $\text{C-O}$ .

The Eq.3 of cellulose and sulphamic acid is:

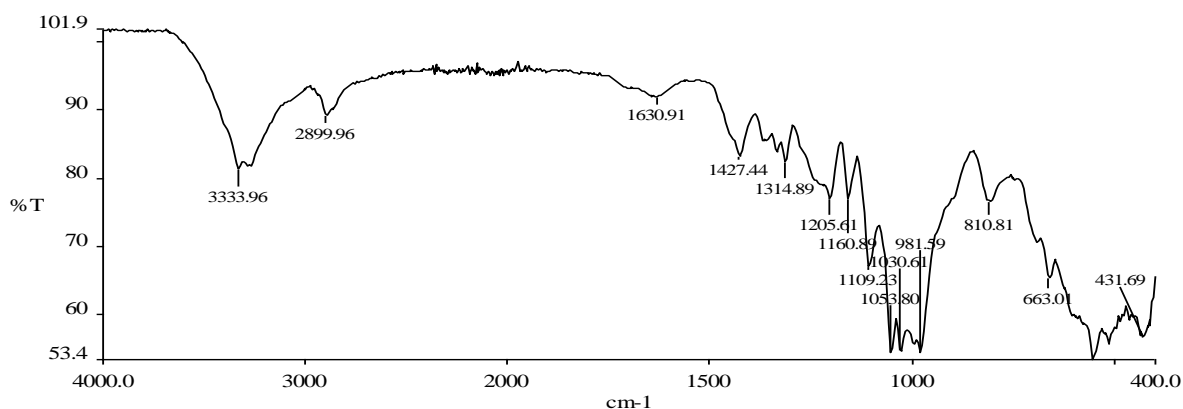


Figure 2 The FT-IR spectrum of cotton treated by pad-bake process.

From Figure 2 the bands at  $1205\text{ cm}^{-1}$  and  $1053\text{ cm}^{-1}$  correspond to  $-\text{OSO}_3^-$ . Sulphate ions ( $-\text{SO}_4^{2-}$ ) have a very strong band at  $1109\text{ cm}^{-1}$ . The new band at  $810\text{ cm}^{-1}$  could be attributed to acid sulphate  $-\text{HSO}_4^-$ .

The pad-bake method gave the intensity banded  $-\text{OSO}_3^-$  vibration, which implies this was a very efficient procedure.

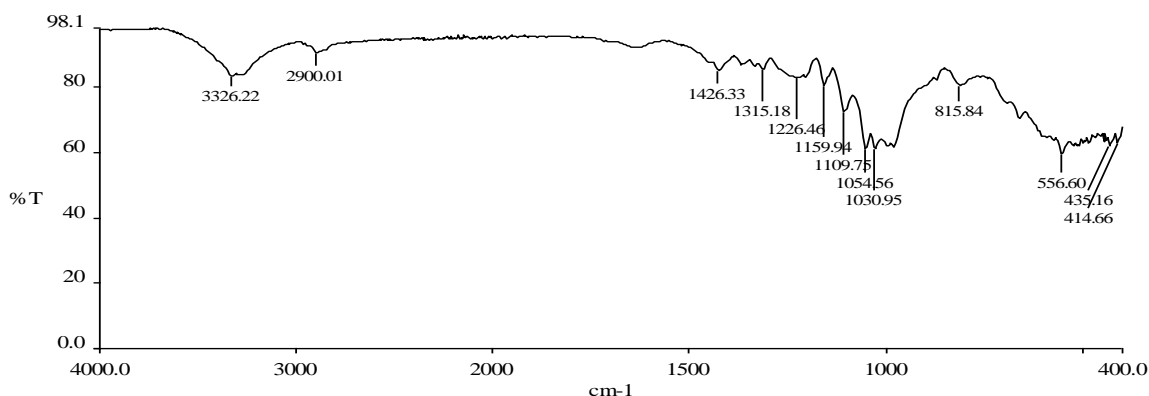


Figure 3 The FT-IR spectrum of self-crosslinking reaction with sodium carbonate of treated cotton.

From Figure 3 the pH value of sodium carbonate (30gl<sup>-1</sup>) is found to be 10.5. The band at 1205 cm<sup>-1</sup> markedly reduced, indication that -OSO<sub>3</sub><sup>-</sup> has been replaced.

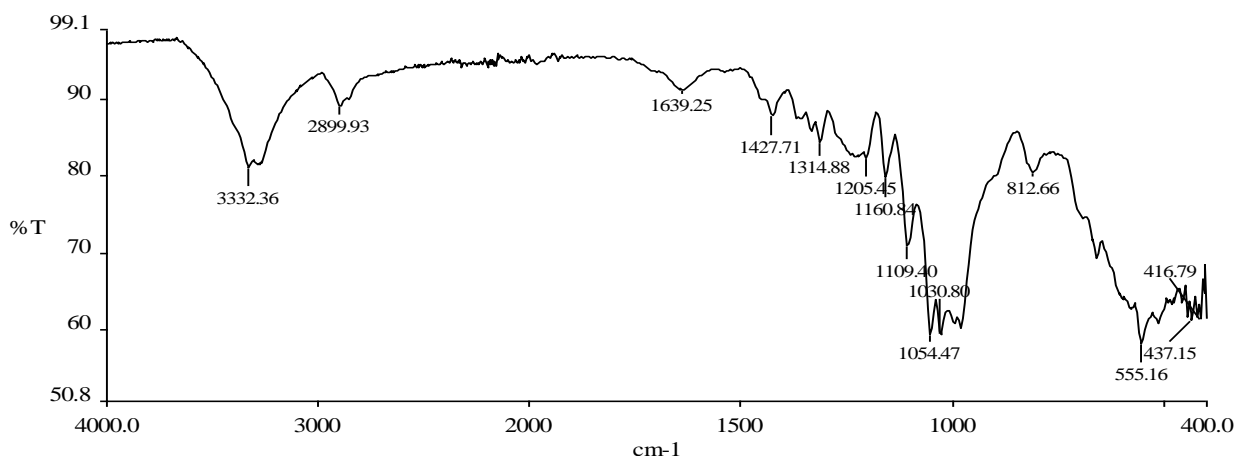


Figure 4 The FT-IR spectrum of self-crosslinking reaction with sodium phosphate of treated cotton.

From Figure 4 the pH value of sodium phosphate (30gl<sup>-1</sup>) is found to be 11.5, it is higher than sodium carbonate but the FTIR spectrum indicated little change.

Eq.4:



The proposed self-crosslinking reaction is shown in

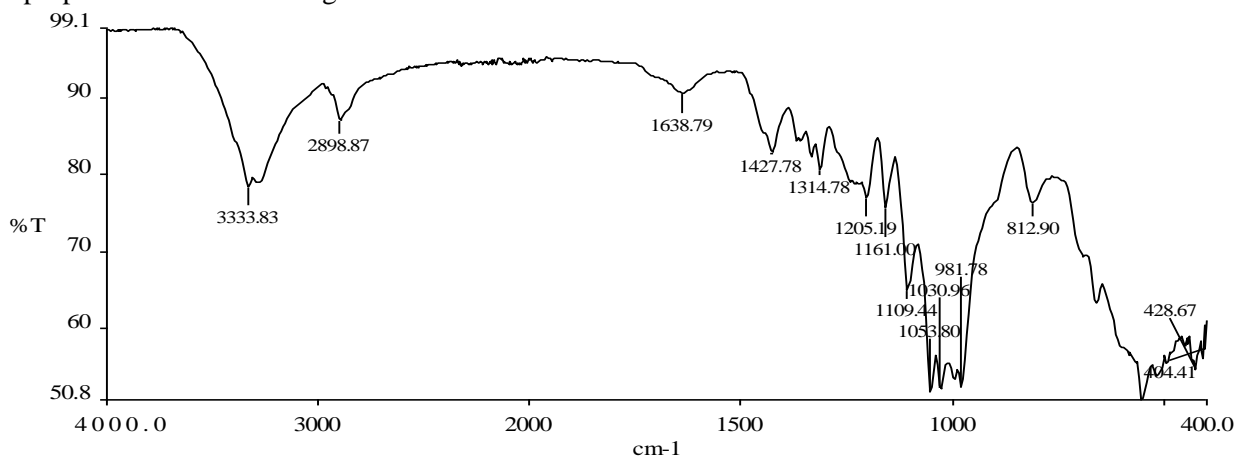
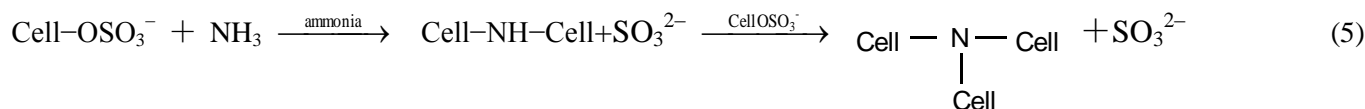


Figure 5 The FT-IR spectrum of self-crosslinking reaction with ammonia of treated cotton.

The self-crosslinking reaction with ammonia is shown in Eq.5:



From Figure 5 it can be concluded that almost every peak was similar to the ones occurred in case of sulphamic acid treated cotton; under the conditions

where little reaction of the ammoniac nucleophile with sulphated cellulose occurred.

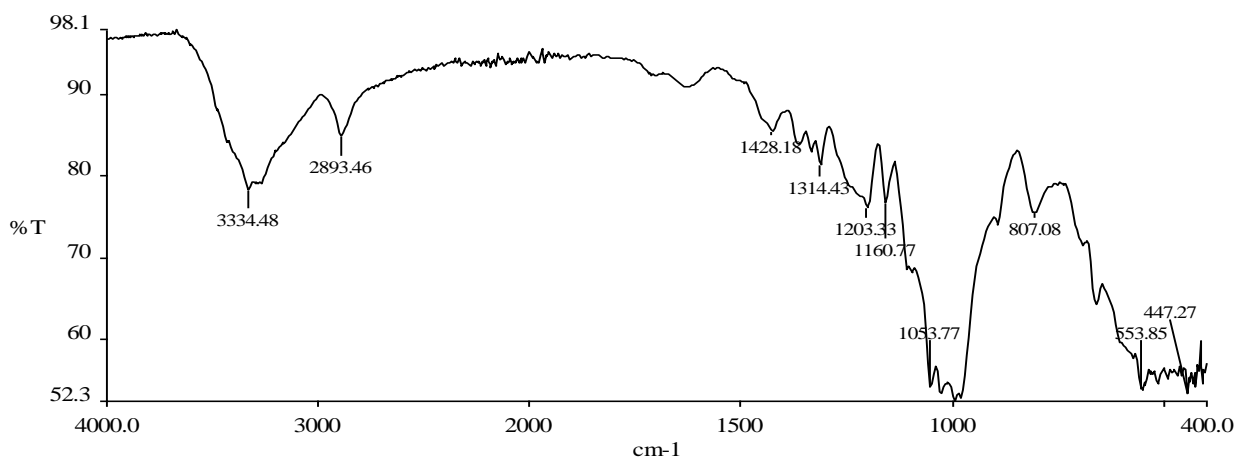
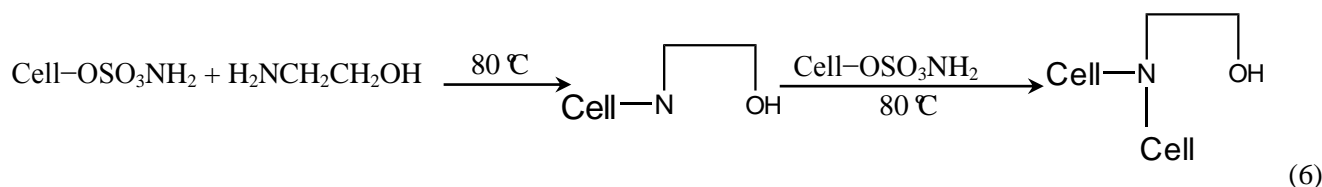


Figure 6 The FT-IR spectrum of self-crosslinking reaction with ethanolamine of treated cotton.

The self-crosslinking reaction with ethanolamine is shown in Eq.6:



From the Figure 6 the band at  $1109\text{ cm}^{-1}$  disappeared, and the band at  $1054\text{ cm}^{-1}$  was much diminished which proved that the sulphate group ( $-\text{OSO}_3^-$ ) has been displaced by the ethanolamine nucleophile.

The comparison of reactions shown in Figure 5 and Figure 6 imply that the stronger nucleophile and higher temperature made the reaction easier.

### 3.2 FT-Raman analysis

Chemical changes in the fiber samples following treatment were monitored by FT-Raman spectroscopy.

From Figure 7 the strong diffuse band  $2894\text{ cm}^{-1}$  and the weaker band  $3339\text{ cm}^{-1}$  can be attributed to stretching vibration of hydroxyl groups, including hydrogen bonds, and of  $\text{CH}_2$  and  $\text{CH}$  groups respectively [9]. The bands between  $1300\text{-}1400\text{ cm}^{-1}$  are the deformation vibration frequencies of  $\text{C-OH}$  and

$\text{CH}$  groups. The strong absorption band in the  $1000\text{-}1200\text{ cm}^{-1}$  regions was mainly attributed to the stretching vibrations of  $\text{C-O-C}$  (ether residues).

Comparing Figure 7 and Figure 8, a new peak at  $1061\text{ cm}^{-1}$  corresponds to  $\text{SO}_2$  stretching.

From Figure 9 the peaks at  $1061\text{ cm}^{-1}$ ,  $747\text{ cm}^{-1}$ ,  $650\text{ cm}^{-1}$  correspond to  $\text{SO}_2$  disappearance. There are new peaks at  $1070\text{ cm}^{-1}$ ,  $608\text{ cm}^{-1}$ ,  $912\text{ cm}^{-1}$ .

From Figure 10 it can be seen that the peaks at  $747\text{ cm}^{-1}$ ,  $650\text{ cm}^{-1}$  correspond to  $\text{SO}_2$  disappearance. There are new bands at  $912\text{ cm}^{-1}$ ,  $1070\text{ cm}^{-1}$ .

Figure 11 illustrates the bands between  $410\text{-}310\text{ cm}^{-1}$  that correspond to CNC skeletal vibration. The peak at  $829\text{ cm}^{-1}$  correspond to  $\text{NH}_2$  wagging vibrates of  $-\text{CH}_2\text{NH}_2$ . The bands at  $747\text{ cm}^{-1}$ ,  $650\text{ cm}^{-1}$  correspond  $\text{SO}_2$  disappearance. There are new peaks at  $829\text{ cm}^{-1}$  and  $608\text{ cm}^{-1}$ .

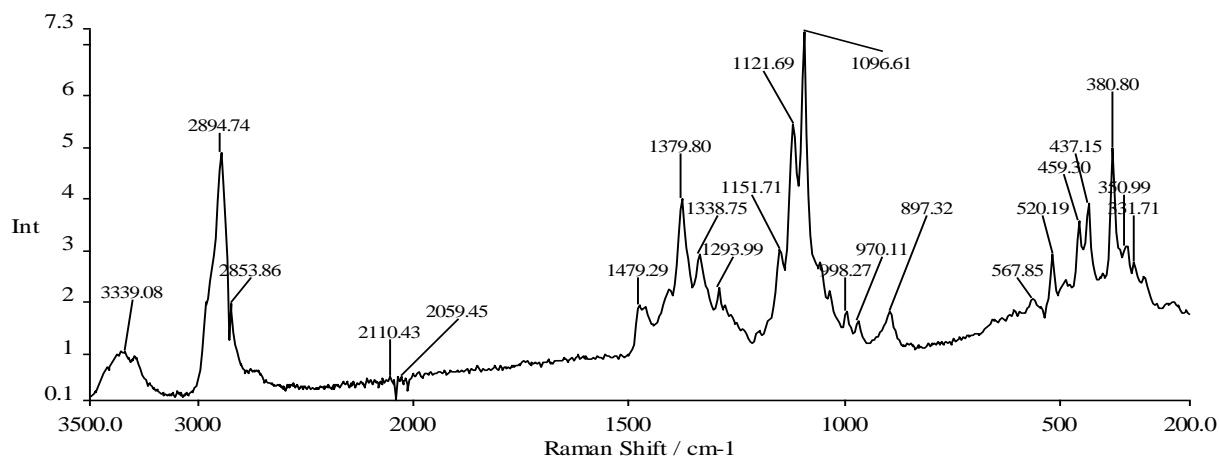


Figure 7 The FT-Raman spectrum of untreated cotton.

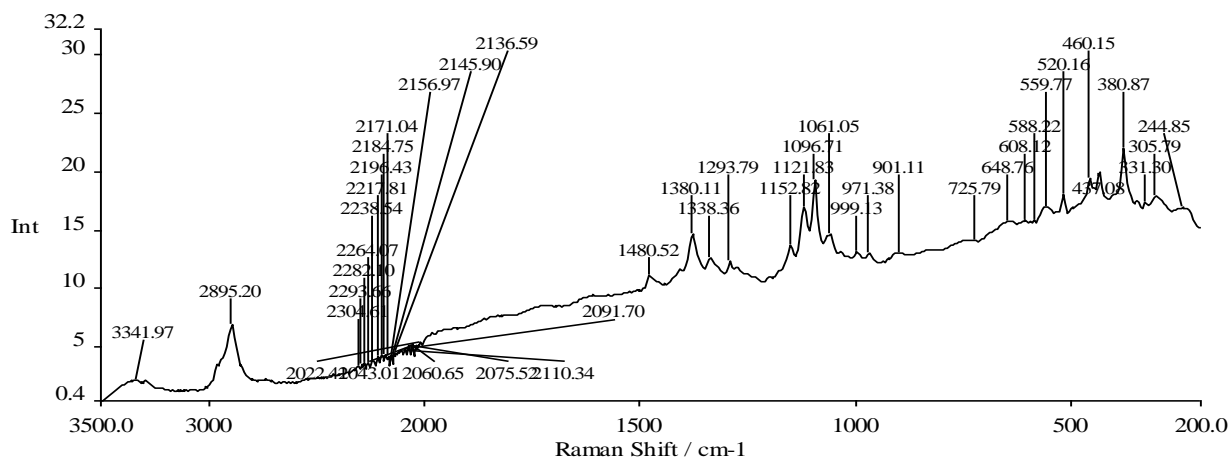


Figure 8 The FT-Raman spectrum of cotton treated by pad-bake process.

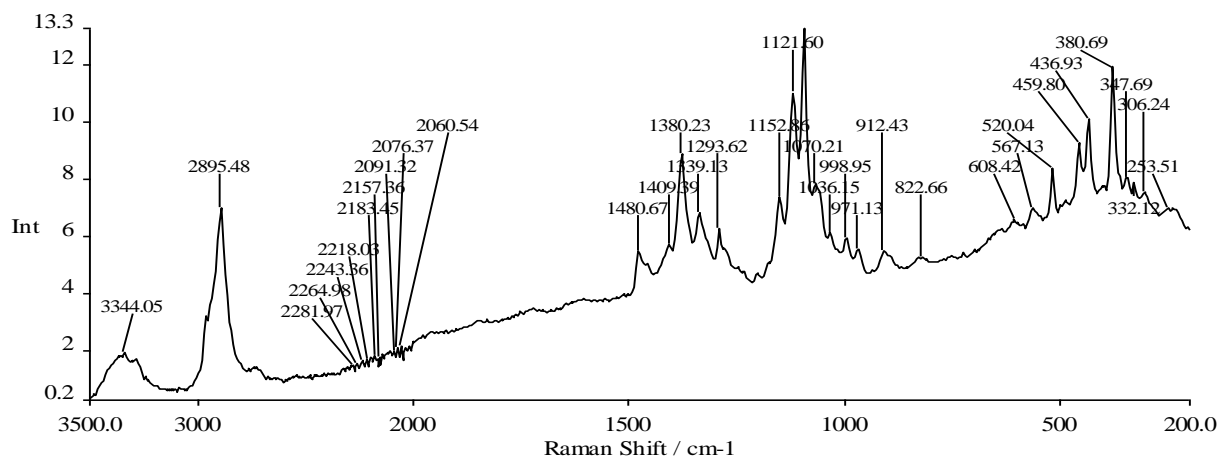


Figure 9 The FT-Raman spectrum of self-crosslinking reaction with sodium carbonate of treated cotton.

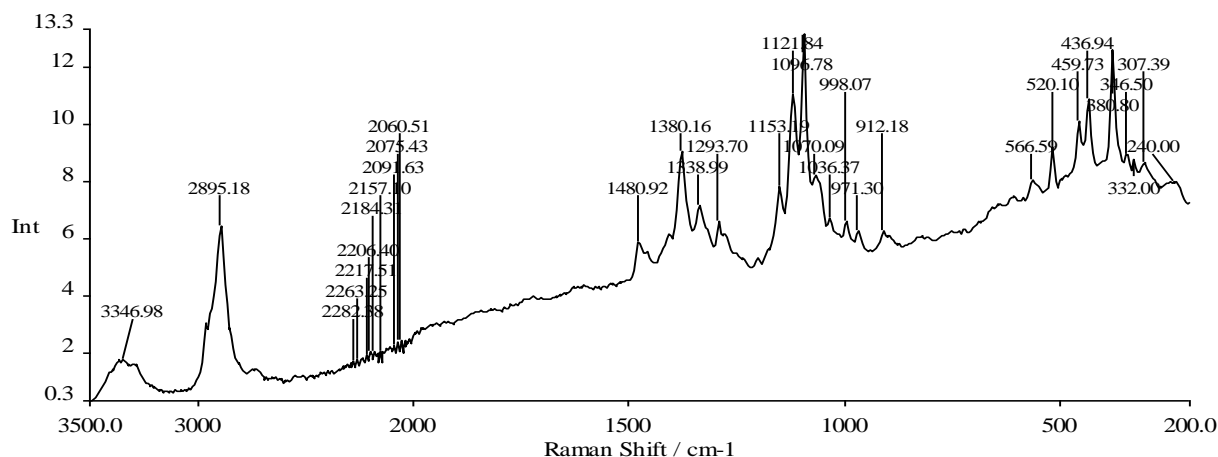


Figure 10 The FT-Raman spectrum of self-crosslinking reaction with sodium phosphate of treated cotton.

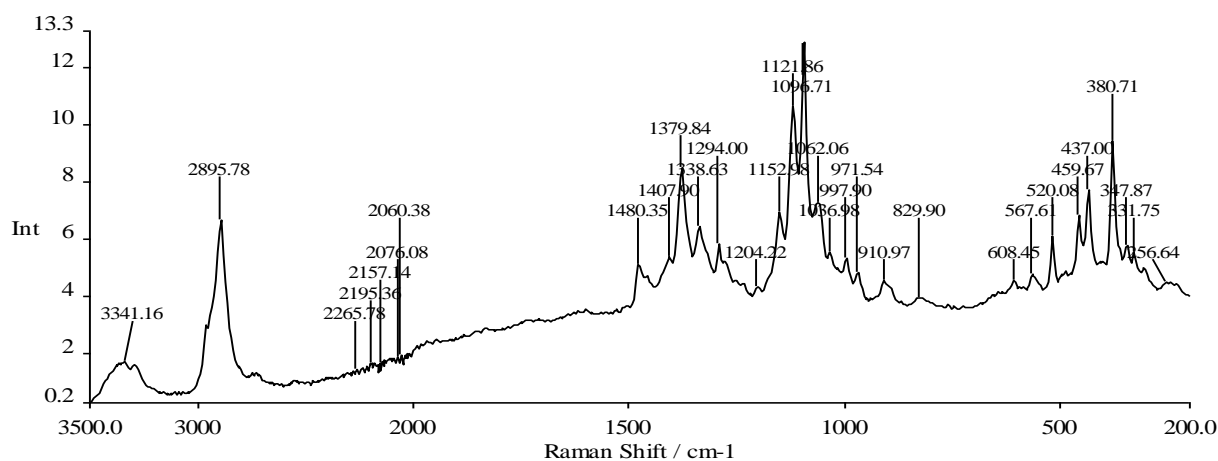


Figure 11 The FT-Raman spectrum of self-crosslinking reaction with ammonia of pad-bake treated cotton.

### 3.3 Bleach results

All natural fibers are coloured and the colouring matter confers a yellowish brown colour to the fibers. The purpose of bleaching is to destroy this coloured material and to confer a pure white appearance on the fibers. The colour of the two cottons proved that the modified fiber (Eq. 7) have better bleach properties than the untreated fiber (Eq. 8). It was easier to bleach.



When the time at which cotton was immersed in the cold tea solution was not enough the brown colour was not stable on the cottons. The colours that appeared on

both cottons returned to white immediately, so no effect occurred until the cotton had been immersed in tea solution for a longer time [10].

### 4. Further work

The preparation of cellulose sulphate is very easy. From the self-crosslinking reaction one can get a result that the higher temperature and stronger alkali makes the reaction easier. The self-crosslinking of modified fiber should have special characters including good dye ability in case of ammoniac or ethanolamine initiated crosslinking. Peroxide should react with the modified fiber to give peroxide cellulose. The analysis of self bleaching and anti-bacterial quality of this reacted cellulose is a worthwhile investigation.

In this experiment, FT-IR and FT-Raman were used

to analysis the data. They are sensitive to different characteristic group, so both were needed.

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