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 alcolols. 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℃, the following Eq.1 is expected:

$$\text{Cell-OH}+NH_2SO_3H \rightarrow \text{Cell-O-}SO^{3-}NH^{4+} \quad (1)$$

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

$$Cell\text{-}O\text{-}SO^{3-}NH^{4+} + R\text{-}XH \rightarrow Cell\text{-}XR + NH^{4+}HSO_4^- \quad (2)$$

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 (150g dm^{-3}), and urea (150g 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 ℃. 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 (30g 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 ℃ to fix the resist. The treated cotton was washed in tap water and then dried.

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

2.2.1.2 Reaction with amonia and ethanolamine

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

Treated cotton (5.0g) was immersed in ethanolamine (100ml, 5g 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%, 1.5g dm^{-3}) and sodium carbonate (5g dm^{-3}) in distilled water (150ml). The untreated and sulphamic acid treated samples were monitored for 15 minutes at 40 ℃. 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: 4cm^{-1}
- Detector: DTGS
- No. of Scans: 100 (Diamond); 16 (KBr)
- Scan Range: 4000 – 400cm^{-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: 4cm^{-1}
- Detector: High sensitivity InGaAs detector
- No. of Scans: 100
- Scan Range: 3500 – 200cm^{-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.