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Carbohydrate Polymers 58 (2004) 417–420
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Characterization of cotton fabric scouring by FT-IR ATR spectroscopy

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Received 21 June 2004; revised 29 July 2004; accepted 9 August 2004
Available online 9 September 2004

Abstract

FT-IR attenuated total reflectance (ATR) spectroscopy has been used for the fast characterization of cotton fabric scouring process. The greige and the scoured cotton fabrics showed very similar FT-IR spectrum in transmission mode because the bulk composition of the fabrics are similar. However, FT-IR ATR spectroscopy can provide information about the surface of a fabric. By examination of C–H stretching region at 2800–3000 cm^{-1}, the amount of waxes left on the fabric can be estimated. The presence of pectins and/or waxes can also be probed by observation of carbonyl peak induced by the HCl vapor treatment on the fabric. Based on these changes of FT-IR ATR spectra, the scouring process has been characterized.

Keywords: FT-IR ATR; Scouring; Cotton; Wax; Pectin

1. Introduction

Cotton fiber is mainly composed of cellulose with some noncellulosic components surrounding the cellulose core. These noncellulosic components are waxes, pectins, and proteins and are mainly found in the cuticle layer and the primary wall which are the outermost layers of the cotton fiber (Nevell & Zeronian, 1985). Scouring process of the greige cotton fabric removes these impurities for better bleaching and dyeing. Commonly used alkaline scouring removes waxes, pectins and other impurities from the cotton fabric by treating the fabric in hot sodium hydroxide solution (Ellis, 1995; Freytag & Donze, 1983; Vigo, 1994). Various enzymatic scouring processes have also been developed to reduce the environmental burdens (Achwal, 1993; Finch & Roberts, 1985; Hartzell & Hsieh, 1998; Li & Hardin, 1997). The impurities removed from the cotton fiber have been characterized. In most cases, they isolate the removed impurities to identify which impurities are removed from the greige (Peters, 1967). However, not many methods have been reported to characterize the scoured fabric for remaining waxes and other impurities. Waxes and pectins left on the fabric were detected with some color forming reagent (Peters, 1967). These methods are only qualitative and not exact.

We would introduce very simple and fast method to measure the impurities left on fabric by FT-IR attenuated total reflectance (ATR) spectroscopy. This is a surface sensitive technique which has penetration depth of a few micrometers (Smith, 1996). Since the waxes and other impurities of cellulose are located in outermost layer of cotton fibers, this technique would be very useful to characterize small amount of these impurities. FT-IR spectroscopy has been used before to characterize the cotton fiber. Chen and Jakes (2002) studied the effect of pressing on IR spectra of single cotton fibers. Gilbert, Kokot, and Meyer (1993) used diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) and chemometrics to study cotton fabrics. Our method can provide information about impurities of cotton fibers very fast and efficiently without any treatment of samples or manipulation of results.

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0144-8617/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2004.08.005

2. Materials and methods

Knitted greige cotton fabric was obtained from Woo Sung Fabric Company. Alkaline scoured fabric was obtained by treating greige fabric in 2% aqueous sodium hydroxide solution for two hours at 95 °C. Sodium hydroxide, hydrochloric acid (35%) and ammonium hydroxide (28–30% in water) was purchased from Aldrich and used without further purification.

Thermo Nicolet Nexus FTIR spectrophotometer equipped with a liquid nitrogen cooled MCT-A detector was used. Transmission mode spectra (32 scans, 4 cm^{-1} resolution) were measured with KBr pellets of finely cut and ground fabrics. FT-IR ATR spectra (216 scans, 4 cm^{-1} resolution) were collected with a MIRacle, single reflection horizontal ATR accessory (PIKE instruments) having a diamond ATR crystal fixed at incident angle of 45°. A 10 mm × 10 mm piece of each fabric were mounted on top of ATR crystal and pressed gently by a pre-mounted sample clamp. ATR effect and atmospheric contributions from carbon dioxide and water vapor were corrected by the Omnic software.

3. Results and discussion

3.1. FT-IR transmittance spectra of cotton fabrics

As we can see from the chemical structures of cellulose, pectin, and waxes (Fig. 1), cellulose and pectins are carbohydrate polymers. Pectins in the greige cotton fabrics

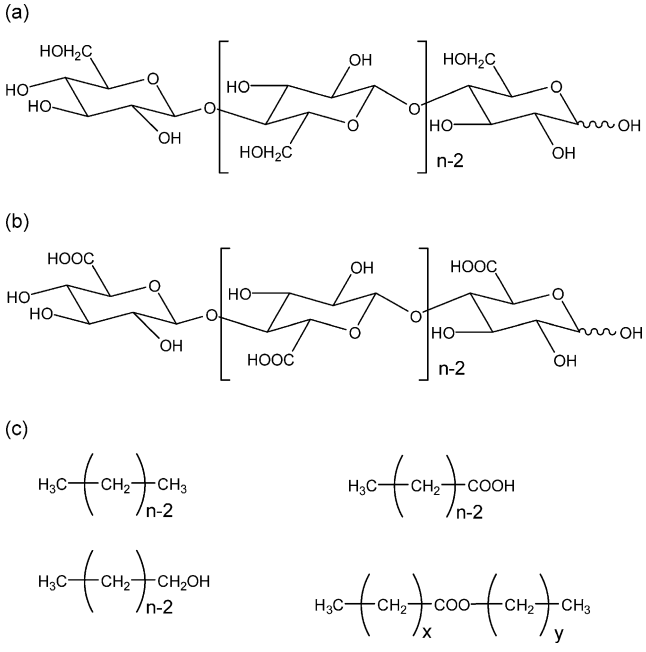

Fig. 1. Chemical structures of (a) cellulose, (b) pectin, and (c) waxes. For the pectin and the carboxylic acid form of waxes, only free acids structures are drawn. In natural state, they exist as mixtures of carboxylates, free acids, and methyl esters.

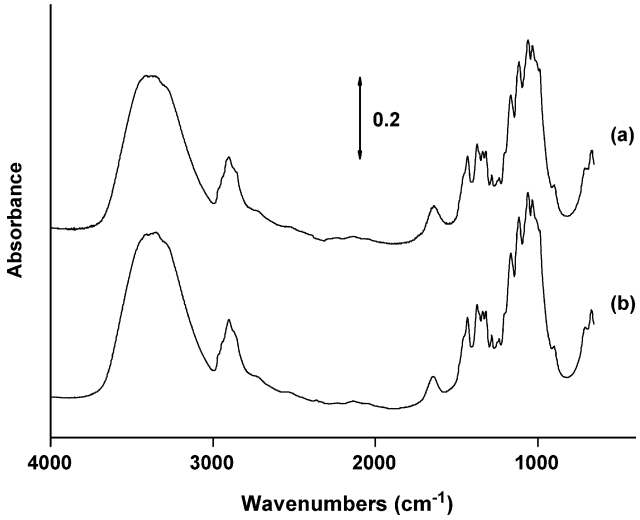

Fig. 2. FT-IR transmission spectra of (a) the greige cotton fabric and (b) the scoured cotton fabric. The spectra were taken with a KBr pellet of finely cut and ground fabric.

have been reported to have most of the carboxyl group methylated (Peters, 1967). Waxes are mixtures of hydrocarbons, alcohols, esters and free acids which have long alkyl chains.

Fig. 2 show the FT-IR spectra of the greige and the scoured cotton fabrics measured by transmission mode. The two spectra look basically same, and it is very hard to notice any differences between these two spectra. Since the spectra were taken with KBr pellets made of finely cut and ground fabrics, the spectra show the characteristic peaks of only cellulose which is the main component of cotton fiber. Although the greige fabric has the impurities such as waxes and pectins, the quantity of these impurities is too small to show up in the spectrum. We observed a broad peak centered 3300 cm^{-1} corresponding to O–H stretching. Also we observed broad peak at 3000–2800 cm^{-1} region for C–H stretching. Although cellulose has $–CH_2–$ groups in their structure, the peaks corresponding to the symmetric and asymmetric stretching modes have never been separated as sharp peaks. A peak around 1640 cm^{-1} is due to the adsorbed water molecules. Other peaks of these spectra and ATR spectra are assigned in Table 1 based on the references. (Chen & Jakes, 2002; Gilbert, Kokot, & Meyer, 1993; Roeges, 1994)

3.2. FT-IR ATR spectra of cotton fabrics

The FT-IR transmission spectra could not tell the differences of the greige and the scoured fabrics because it measured only bulk composition of fabrics. Waxes and pectins of noncellulosic components are located on the rim of cotton fibers. FT-IR ATR spectroscopy which is a surface sensitive technique can measure the presence of waxes and pectins semi-quantitatively. Fig. 3 shows the FT-IR ATR spectra of the greige (a and b) and the scoured cotton fabrics

Table 1
Infrared absorption frequencies of cellulose and other impurities

Experimental (cm^{-1})		Literature (cm^{-1})	Peak characteristics
Trans-mission	ATR		
3650–3100	3550–3100	3570–3200	H-bonded OH stretch
2980–2800	2980–2800	3000–2800	C–H stretching
	2918[a]		Asym. CH_2 stretch: long alkyl chain
	2849[a]		Sym. CH_2 stretch: long alkyl chain
	1750[a]		C=O stretch (after HCl vapor treatment)
1640	1644	1650–1633	Adsorbed H_2O
	1600[a]		Asym. carboxylate stretch
1433	1429	1430	CH wagging (in-plane bending)
1372	1368	1372	CH bending (deformation stretch)
1338	1337	1336	OH in-plane bending
1320	1316	1320	CH wagging
1281	1281	1282	CH deformation stretch
1238	1247	1236	OH in-plane bending
1203	1203	1204	OH in-plane bending
1169	1160	1178	Asym. Bridge C–O–C
1113	1108	1130	Asym. Bridge C–O–C
1061	1057	1092	Asym. In-plane ring stretch
1031	1030	1042	C–O stretch
992	1000	998–1002	C–O stretch
898	900	898	Asym. out-of-phase ring stretch: C_1–O–C_4; β glucosidic bond

[a] These peaks are from the impurities such as waxes and pectins.

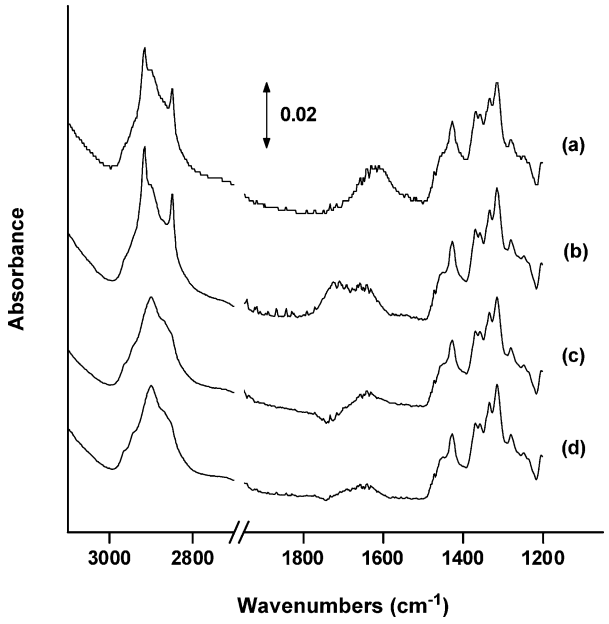

Fig. 3. FT-IR ATR spectra of (a) the greige cotton fabric, (b) the greige cotton fabric treated with HCl vapor, (c) the scoured cotton fabric, and (d) the scoured cotton fabric treated with HCl vapor.

(c and d). Fig. 3(c) is the spectrum of the scoured cotton fabric which showed typical characteristic peaks for pure cellulose. Broad C–H stretching band appears from 2800 to 3000 cm^{-1} region. Spectrum of the greige fabric in figure (a) shows extra peaks at 2918 and 2849 cm^{-1} corresponding to the asymmetric and the symmetric stretching of methylene (–CH_2–) groups in long alkyl chains. These peaks prove the presence of waxes. The other impurities such as pectins and proteins usually do not have these methylene groups of long alkyl chain. The intensities of methylene peaks at 2918 and 2849 cm^{-1} indicate the amount of waxes remained on the fabric.

Other information can be obtained in the region of 1600–1800 cm^{-1}. At first glance, not much difference can be seen in the region for the greige and the scoured fabrics shown in spectra (a) and (c) in Fig. 3. However, if the greige fabric was exposed to the HCl vapor for a few minutes, a new peak appeared at around 1750 cm^{-1}. These are from the protonation of carboxylate groups. If the carboxylate exist in ionized form (COO^-), it would show two peaks at 1600 and 1400 cm^{-1} for the asymmetric and the symmetric stretching of COO^- ion, respectively. In carboxylate ion the two C–O bond is identical with 1.5 bond order. If it is protonated, it would become –COOH in which double bond (C=O) and single bond (C–OH) are exist. The C=O stretching would show up at around 1750 cm^{-1}, and C–OH stretching at 1200 cm^{-1}. C–OH stretching would be buried in other C–O modes which cellulose has a lot. However, C=O stretching mode showed clearly in the spectrum. When we exposed the fabric of spectrum (b) into NH_3 vapor and took new spectrum of the fabric, the spectrum was almost identical to the spectrum of (a). This means that transformation between COO^- and COOH is reversible process. It also tells that the carboxylate responsible for this acid/base transformation exist as free carboxylate form not ester form. Previously, most carboxylate in the pectins of the greige cotton fabrics were reported to exist as methylated ester (Peters, 1967). However, if it is true, there should be some peaks at around 1750 cm^{-1} for C=O stretching mode of ester in the spectrum of greige fabric. As seen in Fig. 3(a), we cannot find any trace of peaks around there. The scoured fabric was free from this carboxylate. When we compared the spectrum (c) to the spectrum (d), the HCl vapor treatment of the scoured cotton fabric did not induce the appearance of C=O peak. Although we are not sure if these carboxylate are from waxes or pectins at this moment, we are sure that these are from the impurities of cotton fabric which normally removed during scouring.

Since scouring process removed two methylene peaks and induced carbonyl peak by HCl vapor treatment in the spectra of fabrics, the FT-IR ATR spectroscopy can be used as the characterization tool for scouring process. This method does not need any reagent except HCl or pretreatment of samples. More detailed work using different ATR crystals and different incident angles for the characterization of cotton fabrics are on the way.

Acknowledgements

This work was supported by a sabbatical leave of Chinkap Chung from Keimyung University.

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