SFG ANALYSIS OF CELLULOSE POLYMORPHS IN BLEACHED, MERCERIZED, AND L-NH_3 TREATED COTTON FABRICS

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Abstract

Sum frequency generation (SFG) is a non-linear spectroscopy which can take place only in a system lacking inversion symmetry. When a noncentrosymmetric medium material through which electromagnetic waves propagate is irradiated with high-intensity laser pulses with two different frequencies, a new photon can be emitted whose frequency is the sum of two input frequencies. The noncentrosymmetry constraint of the SFG process makes the vibration modes with a net polar ordering in the cellulose crystal to be active in SFG vibration spectroscopy. The packing of cellulose chains by hydrogen bonding is different in cellulose polymorphs (I, II, III), which is very sensitive in SFG. In this study, we report the detection and propose a method to quantify cellulose polymorphs in cotton fabrics treated with bleaching, mercerizing, and liquid-NH_3 processes. The fabric treatments are reviewed, and SFG analysis is shown in comparison to X-ray diffraction (XRD) data.

Extension to Abstract

In the textile industry, cotton fabrics are processed with sodium hydroxide and liquid ammonia to improve their physical properties such as luster, dyeability and mechanical strength. During these treatments, these properties are enhanced by slightly changing the native crystal structure, cellulose I_β (Wakida et al., 2000). Strong alkali treatment (mercerization) can convert the cellulose I_β into cellulose II, and liquid ammonia can change cellulose I_β to cellulose III. It is often desirable to treat the cotton fabrics with both methods consecutively, which results in a mixture of three allomorphs (I_β, II, III), to achieve the best fabric product. To assess the fabrics properties, identifying the crystal forms and quantifying the allomorphs in the processed cotton is crucial. Here, we have used XRD and SFG to analyze twill cotton fiber that has been mercerized and treated with liquid ammonia consecutively.

Treatments of cotton fabrics

The fabric used for this study was 100% cotton twill (270 g/m^2) fabric that had been commercially woven at a US mill. This fabric was subjected to various treatments in order to generate different forms of crystalline cotton cellulose. The bleached-only cotton was obtained by processing the twill fabric on a jig in Cotton Incorporated's pilot laboratory. The fabric was enzyme desized to remove starch, scoured to remove waxes, and bleached with a hydrogen peroxide formulation to remove the colored impurities. These processes were designed to remove the impurities from the cotton fabric while maintaining its natural crystalline structure as cellulose I. The mercerized cotton fabric was processed in a commercial textile mill. Desizing, scouring, and bleaching were performed using continuous open-width processing equipment. Mercerizing was performed with sodium hydroxide under tension. The bleached-only fabric and the mercerized fabric were taken to Lafer SpA in Prato, Italy, for liquid ammonia treatment on the new Permafix machine. The treated fabrics were provided to the Pennsylvania State University for sum frequency generation (SFG) analyses. The same fabrics were analyzed with X-ray diffractometry (XRD) at Tulane University.

SFG and XRD analysis

XRD is commonly used to study the cellulose structure. Based on the intensity of the diffracted beams and the angle (2θ) at which the diffraction occurs, the crystal structure of cellulose can be obtained. Each cellulose crystal forms (allomorphs) have characteristic peaks. Cellulose I_β has diffraction peaks at $2\theta = 14.7^o$, 16.4^o and 22.6^o. A very weak peak at $2\theta = 20.6^o$ is often noticed. Cellulose II shows peaks at $2\theta = 12.2^o$, 19.9^o and 21.8^o. Cellulose III has peaks at $2\theta = 11.7^o$ and 20.7^o (Tripp et al., 1972; Liang, 1972). However, the quantification of allomorphs by XRD

method is often not straightforward (Barnette et al., 2012). There are three commonly used methods to determine crystallinity; each method provides a different result for identical cellulose samples (Park et al., 2010). Also, the XRD resolution of small cellulose crystal size (5nm) in cotton is not adequate for structural study (Park et al., 2010).

Recently, SFG vibrational spectroscopy has been shown to selectively detect the crystalline cellulose structure and quantify the crystal amount present in lignocelluloses (Barnette et al., 2011; Barnette et al., 2012). SFG does not suffer from spectral interferences from amorphous cellulose and non-cellulosic polysaccharides due to its unique selection rules, which are only met by crystalline cellulose. SFG has also been shown to be sensitive to cellulose allomorphs with unique peaks in the C-H vibrational stretch region (Lee et al., submitted). Pure cellulose I_β crystal shows typically peaks at 2944cm^{-1} (exocyclic CH_2 asymmetric vibration of the glucopyranose ring) and 3320cm^{-1} (intra-chain O-H hydrogen-bond along the cellulose chain). The CH_2 peak shifts to 2964cm^{-1} and the OH peaks are hard to detect in pure cellulose II prepared from Avicel (100% cellulose isolated from wood by acid hydrolysis). Cellulose III prepared from Avicel shows the same CH_2 peak as in cellulose type II (2964cm^{-1}) and a sharp OH peak at 3484cm^{-1} which is almost twice as intense as the CH_2 peak. Based on these vibrational peak positions and peak intensity ratios of each cellulose allomorph, we have identified the allomorphs present in a mercerized and liquid-ammonia-treated cotton fabric. Quantification can be also done after constructing a calibration curve for each individual allomorph, which has been shown previously for cellulose I_β (Barnette et al., 2012).

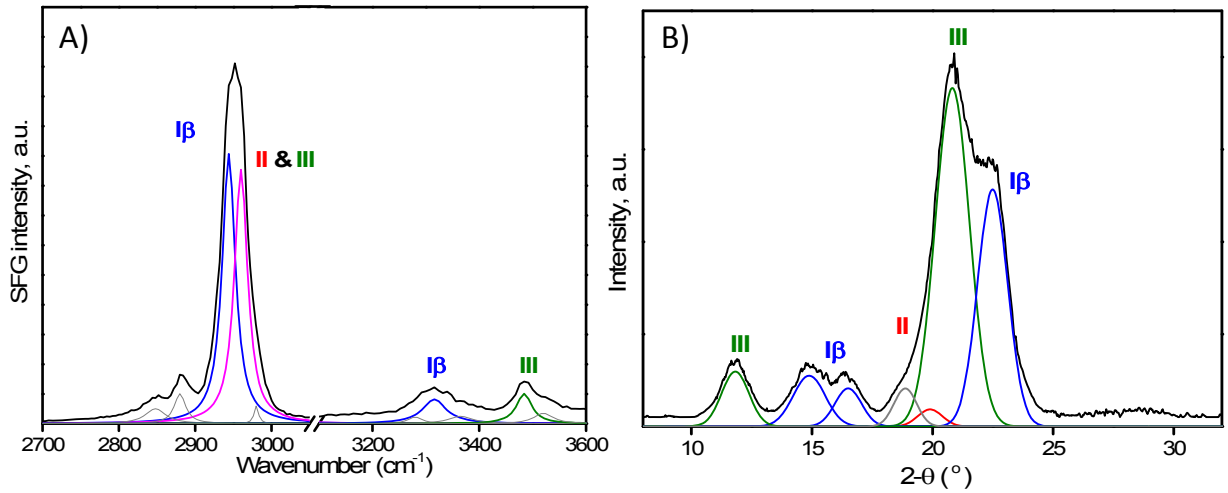

Figure 1. A) SFG spectra and, B) XRD diffractogram of twill cotton fabric bleached, mercerized and treated with liquid ammonia. Each plot shows allomorph type next to the fitted peaks representing the distinct cellulose allomorph.

Figure 1 shows the XRD diffractogram and SFG spectrum of twill cotton that has been bleached, mercerized and treated with liquid ammonia. The SFG spectrum is deconvoluted using the Lorentzian peak shape; XRD diffractogram is fitted with the Gaussian peak shape. The fitted peaks are marked with different colors for three allomorphs (Iβ, II, and III). In XRD, peaks unique to cellulose I and cellulose III are readily observed (Figure 1B), but the cellulose II peak (shown in red) is too small to be noticed.

In comparison, SFG shows peaks unique to all three allomorphs (Figure 1A). Specifically, SFG shows a major peak at 2964cm^{-1}. This peak is present in both reference cellulose II and III. However, the ratio of the peaks unique to reference cellulose III (2964cm^{-1}/3484cm^{-1}) is not the same in processed twill cotton. This could mean that the cellulose II and III in processed cotton may have different crystalline ordering compared to reference Avicel cellulose III. Hence, using the peak intensity ratio of 2964cm^{-1}/3484cm^{-1} from reference cellulose III, we can deconvolute 2964cm^{-1} peak further to separate the cellulose II and III. The manual deconvolution of SFG peaks shows that SFG can be more sensitive than XRD in identifying the cellulose allomorphs. Previously, cellulose I_β in lignocellulosic biomass has been quantified based on the SFG peak intensity at 2944cm^{-1}, which showed a non-linear relationship between SFG intensity and the mass fraction of cellulose in sample (Barnette et al., 2012). The SFG peak intensity of pure type II and type III can be also correlated to their mass fraction by carefully constructing

a calibration curve. However, the quantification with XRD can be ambiguous due to several popularly used methods providing different values for an identical cellulose sample and the limitations inherent to the crystallographic process.

Conclusion

We showed that SFG can clearly detect type II cellulose in mercerized + liquid ammonia treated cotton fabrics, but it is hard to decipher from XRD. Allomorphs could be quantified from SFG measurements after careful construction of calibration curve relating peak intensity to mass fraction of the allomorphs. SFG is a powerful technique to assess the structural changes in textile fibers and can be further developed as a quantitative tool to examine fiber properties in textile industries.

References

Barnette, A. L.; Bradley, L. C.; Veres, B. D.; Schreiner, E. P.; Park, Y. B.; Park, J.; Park, S.; Kim, S. H., 2011. Selective detection of crystalline cellulose in plant cell walls with sum-frequency-generation (SFG) vibration spectroscopy. Biomacromolecules. 12, 2434-2439.

Barnette, A. L.; Lee, C. M.; Bradley, L. C.; Schreiner, E. P.; Park, Y. B.; Shin, H.; Cosgrove, D. J.; Park, S.; Kim, S. H., 2012**.** Quantification of crystalline cellulose in lignocellulosic biomass using sum frequency generation (SFG) vibration spectroscopy and comparison with other analytical methods. Carbohydrate polymers. 89:3, 802-809.

Lee, C. M.; Mittal. A, Barnette, L.; Kafle, K.; Park, Y.B.; Shin, H.; Johnson, D.K.; Park, S.; Kim. S., 2013. Cellulose Polymorphism Study with Sum-Frequency-Generation (SFG) Vibration Spectroscopy: Determination of Exocyclic CH2OH Conformation and Chain Orientation. Manuscript submitted for publication.

Liang, C. Y. 1972. In Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose; O'Connor, R. T. Ed., Marcell Dekker Inc.: New York; p 59

Tripp, V. W.; Conrad, C. M. 1972. In Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose; O'Connor; R. T. Ed. Marcell Dekker Inc.: New York, NY; p 339

Wakida, T., Kida, K., Lee, M., Bae, S., Yoshioka, H., & Yanai, Y. 2000. Dyeing and mechanical properties of cotton fabrics treated with sodium hydroxide/liquid ammonia and liquid ammonia/sodium hydroxide. Textile Research Journal. 70:4. 328-332.