

# Changes in NMR Characteristics of Cotton and Wool During Water Adsorption

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## Synopsis

NMR signals have been followed for cotton and wool materials during humidification of the fibers. It is shown that the adsorbed water is present in two main states of different mobilities and that the relative velocities for the penetration of the water to these different states can easily be followed. It has been observed that the amount of adsorbed water with low mobility, in the primary sites, grows more rapidly in cotton than in wool during the sorption. Overlap between the signal contributions from water with reduced mobility and from the polymer chains makes observations of the segmental mobility of the polymer chains difficult.

## INTRODUCTION

Attempts have been made earlier to use NMR for studies for the segmental mobility of cotton and wool during the sorption process.<sup>1</sup> Earlier measurements of wrinkle height have been interpreted from the assumption of large structural changes during the first period of the sorption process. The special properties during the sorption process are demonstrated very clearly from measurements of the dynamic rigidity modulus,<sup>2</sup> which passes through a marked minimum in the introductory phase of the sorption process. This has been attributed to transient stresses produced in the fibrous material during sorption and is assumed to be connected with breaking of intermolecular bonds in the vicinity of the front of the swollen fibrous phase. It has also been assumed that the fiber structure is to some extent affected by rupture of hydrogen bonds during the sorption process and that the structure thereafter once more is stabilized by rebuilding of the hydrogen bonds.<sup>3</sup> Finally, it has also been put forward that the temperature of the fibers is somewhat raised due to water uptake and that the resultant increase in segmental mobility could also explain the special properties during the sorption process.<sup>1</sup> As NMR allows direct observation of the segmental mobility, it can be assumed that direct investigations of the fibers during the sorption process could be done with the aid of this technique. The earlier NMR measurements<sup>1</sup> were planned to give information concerning these properties. From measurements with NMR on equilibrated wet samples of cellulose, it has been shown, however, that the adsorbed water gives rise to signal contributions with both very narrow and appreciable linewidths.<sup>5</sup> It is assumed here that the adsorbed water is present partly in primary adsorption sites attached to hydrophilic groups of the polymer and partly in a condensed phase, where it is in equilibrium with the surrounding atmosphere. The mobility of the protons is comparatively low at room temperature in the first case, and the resonance line arising from water in the primary adsorption sites has a linewidth which is of the same order of magnitude as that of the resonance line arising from

the protons of the cellulose. Thus, it is not possible to make direct observations of the mobilities of the polymer chains in the wet samples. The mobility of the protons in the condensed phase is, on the other hand, very high, and this part of the adsorbed water gives rise to a comparatively narrow line, which at room temperature is rather well resolved from the broad line. These conditions are also confirmed by the results obtained from measurements of the proton resonance during sorption of cotton and wool fibers.<sup>1</sup> In these experiments, a number of different spectra have been recorded in course of the sorption process using one and the same setting of the spectrometer. The signal intensities are thus proportional to the number of protons in the samples taking part in the resonance phenomenon at a specified value of the magnetic field. Definite conclusions can, therefore, be drawn from comparisons of the line intensities of spectra recorded at different times during the sorption process.

For the dry fibrous material, only a broad line is observed. The amplitude of the narrow-line component grows very rapidly during the sorption process, but a substantial growth of the amplitude of the broad line is also observed. The linewidth of the broad line, as determined by the peak-to-peak distance in the registered derivative curve, decreases to some extent at the same time. Changes in linewidth during adsorption can therefore not be taken as a measure of changes of segmental mobility only. Probably, it gives information mainly concerning the mobility of the adsorbed water on the primary sites. For textile fibers subjected to different chemical treatments, different linewidths are observed for the samples with the same water content, and thus it is probable that the relaxation of the adsorbed water on the primary sites is different in different samples. The proton mobility in the amorphous part is low at room temperature for the dry samples. The signal contribution from the amorphous part is of about the same width as that from the crystalline part. Increasing mobility of the polymer chains during the sorption process should in experiments of this type result in a distinct decrease of the signal amplitudes in the outermost parts of the spectra and in a corresponding increase in the central parts (Fig. 1). Due to the use of phase-sensitive detection, the relative changes in the registered spectra are always much larger in the central parts than in the outer parts. All effects in the central parts are, however, concealed by the signal contribution from the adsorbed water, which is the reason why information concerning the mobility of the polymer chains could only be obtained from the outermost parts of the spectra.

## EXPERIMENTAL

A number of sorption experiments have been repeated for pure cotton and wool with the aid of the equipment used in the earlier work.<sup>1</sup> The most drastic changes in the mechanical properties are observed during the initial stages of the sorption process. Spectra have therefore been recorded with both fast and slow sweeps of the spectrometer. By use of the fastest sweeps, the first complete spectrum has been recorded 0.5 min after start of the humidification. The NMR spectra are, however, obtained with a higher accuracy by the use of slow sweeps, and a number of further measurements have therefore also been performed using sweep times between 3 and 15 min. Series of measurements have also been performed during water sorption of untreated cotton and wool at a constant value

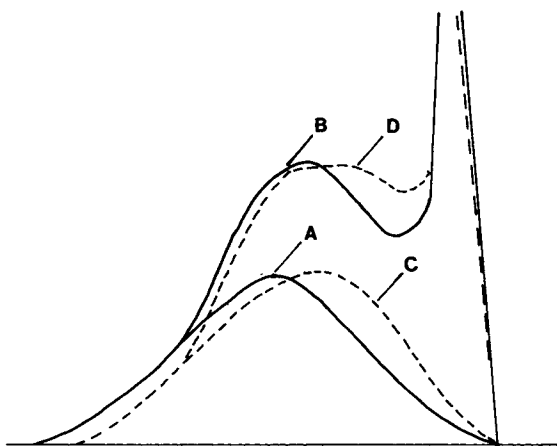


Fig. 1. Principal diagram showing half-derivative curves: curve A, spectrum of dry sample; curve B, spectrum of a wet sample (the difference between curves B and A can be supposed to represent the signal contribution from the adsorbed water); curve C, line shape of a polymer sample with increased segmental mobility; curve D, line shape of a wet sample with increased segmental mobility, constructed as the sum of curve C and the difference between curves B and A.

of the main magnetic field. The variation of the signal intensity with time is recorded in each experiment for one special value of the abscissa of the spectrum. The shapes of the different resonance lines appearing during the sorption process can then be constructed from a number of repeated experiments performed at different magnetic fields using different samples. Investigations of this type requires more extensive experimental work but allows registration of rapid events with the sensitivity achieved in normal NMR registrations using slow sweeps. The drawbacks of lower signal-to-noise level and lower reproducibility of the magnetic field which appear with the use of rapid sweeps are thereby eliminated.

When the samples reached equilibrium with the surrounding air of a given controlled relative humidity, the sample tubes were sealed. Spectra were thereafter registered up to two weeks after the sorption experiment, showing no important changes of the spectral shapes. In some cases the sorption process was interrupted before equilibrium had been reached. No important changes in the line shapes were observed after storing these samples for similar times. The amplitudes of the narrow and the broad lines vary appreciably with the regain of the samples, which makes possible an assignment of the lines to the different states of adsorbed water. NMR spectra for some samples of very high regain have therefore also been recorded. These samples had been prepared simply by addition of known amounts of water to dry samples of textile material.

## RESULTS AND DISCUSSION

The experiments show that the outermost parts of the spectra agree within the limits of the experimental accuracy between spectra recorded at different times during the sorption process. This agreement is also good between spectra of dry samples and samples of high regain. These effects are also clearly demonstrated by the spectra published earlier.<sup>1</sup> The experiments performed at

constant magnetic field show that the variations of the signal amplitudes in the outermost parts of the spectra are very small. No special changes are observed during the initial stages of the sorption process, which could be connected with the earlier measurements of dynamic rigidity modulus obtained by use of a torsion pendulum.

A very small effect could possibly be detected for untreated wool in the experiments at constant magnetic field and in experiments where the whole of the spectrum was recorded. The segmental mobility could thus to some degree be dependent on the moisture content in this material, but this effect does not seem to be present for the wool fibers subjected to chemical treatment. In the central parts of the spectra, the signal intensities only increase during the absorption. It appears that experiments in this field will primarily permit investigations of the kinetics of the sorption process.

In order to interpret the typical S-shaped adsorption isotherm for textile materials, it has since long been assumed that the water is adsorbed in two different positions.<sup>6</sup> The water is assumed to be present partly in primary adsorption sites attached to hydrophilic groups of the polymer material and partly as a condensed phase which is in equilibrium with the surrounding atmosphere. It has in later works been assumed that a series of different positions has to be regarded for the adsorbed water. We would like to assume that the signal contributions to the broad line originate from water in the primary positions and that the narrow line is due to the more mobile secondary water in the condensed phase. The amplitude of the broad line grows with increasing amount of adsorbed water mainly at low regains. This is in agreement with the original theory where the amount of water in the primary positions is limited by the number of hydrophilic groups in the polymer. The intensity of the narrow line, on the other hand, grows particularly rapidly with increase in adsorbed water at high regains, which is also the case for the condensed phase according to the original theory. The presence of water in two different positions with different degrees of mobility has recently been established also from dielectric measurements at high frequencies.<sup>7</sup>

The narrow- and broad-line components could rather well be resolved for the wet samples. The line intensities can therefore be used as a measure of the amounts of water in the mobile and less mobile sites. The results are summarized in Figure 2. It appears here that the intensity of the broad-line component for cotton grows very rapidly, while the increase of the narrow-line component occurs rather slowly. However, in the case of wool fibers, the rate of increase in the intensities of both the narrow and the broad lines are slow. The comparatively fast penetration of water to the primary positions in cotton as compared to wool may be explained from their different chemical and morphologic structure. The hydrogen bonds, which are the dominating intermolecular bonds in cotton, can be supposed to undergo rapid rearrangements during the penetration of water. The disulfide bonds may reduce the accessibility of the penetrating water molecules to the hydrophilic sites in the wool fiber. The number of accessible primary sites is lower in cotton than in wool due to the higher degree of crystallinity in cotton. This fact may also explain why a faster saturation is observed here.

The experimental results presented here give no direct evidence for an increase in the segmental mobility during the sorption process. The possibility of an

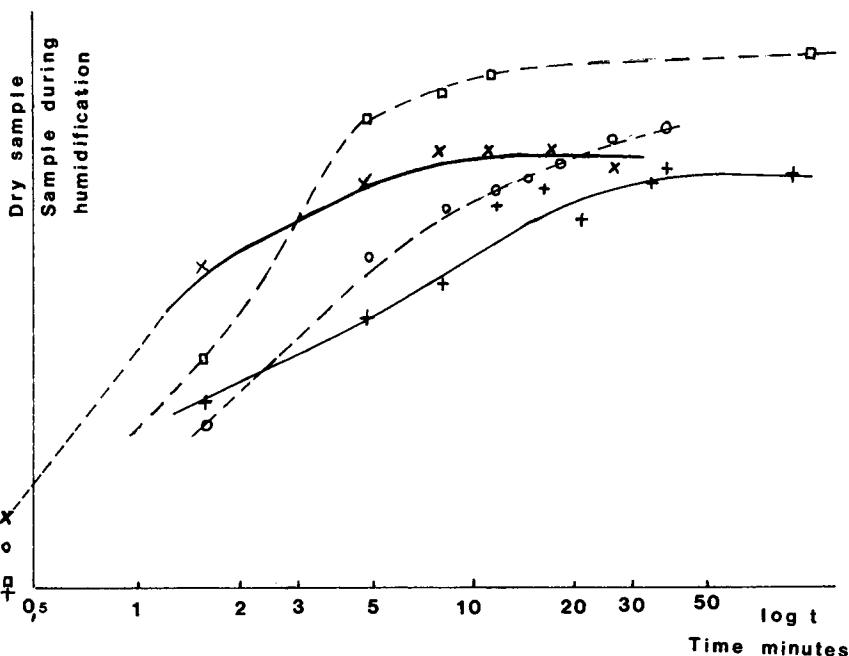


Fig. 2. Signal amplitudes of the narrow and broad line for untreated cotton and wool as a function of time by humidifying from 0% to  $50 \pm 1\%$  R.H. at  $25^\circ\text{C}$ . The signal amplitudes were measured simply as peak-to-peak heights between the minimum and maximum in the registered derivative curve. Arbitrary units were used, as no attempts to compare the amplitudes of the different lines has been made in this investigation: (—x—) cotton broad line; (- -o - -) cotton narrow line; (—+—) wool broad line; (- -□ - -) wool narrow line.

increase in the segmental mobility with increased regain can, however, not be excluded from the presented experiments. The decreased signal contribution from the polymer segments which should occur with increased regain should in such a case be compensated by a signal contribution arising from the primary adsorbed water. It can be concluded from the results that the mobility of the water in the primary sites increases during humidification. This increased mobility can possibly be due to an increased segmental mobility because of the close and direct bonding between this water and the receptive segments in the fibers.

It follows from these considerations that the effects that are observed by NMR cannot be related to the structural changes which are responsible for the marked minimum in the dynamic rigidity modulus. These structural changes may probably influence only a limited part of the fibrous material so that most polymer segments are not affected. Changes due to rearrangement of intermolecular hydrogen bonds supposedly occur only within a limited zone between the swollen and the unswollen parts of the textile fiber, and this model can thus very well be connected with the results of these NMR experiments. If a substantial heating of the textile material occurs during the condensation of water, it is possible that the heated fiber allows mechanical deformations to a higher degree because of a higher content of vacancies or because of changes of structure. It is not probable that the material is heated to such a degree that the mobility of the main part of the polymer segments is affected.

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