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The association of water to cellulose and hemicellulose in paper examined by FTIR spectroscopy

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Abstract—The nature of water sorption to different materials has always been a complex matter to address, partly due to the different possibilities of hydrogen-bond formation. For cellulosic materials this is extremely important for its product performance. In order to gain a deeper understanding of the moisture adsorption mechanisms of cellulose and hemicelluloses, the molecular interaction between moisture and paper and between moisture and some wood polymers was studied using FTIR spectroscopy under stable humid conditions. It was found that all the moisture-sorbing sites adsorbed moisture to the same relative degree, and that the rate of adsorption was the same for all these sites. It was also noticed that the moisture is adsorbed in the form of clusters. A direct relationship was found between the moisture weight gain and the increase in the absorbance peaks for humidities up to 50% relative humidity after which the moisture gain increased faster, a fact that still remains to be explained.
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1. Introduction

In hygroscopic materials like paper, the moisture sorption characteristics are of prime importance for the properties of the material under different environmental conditions. Sorption isotherms have earlier been analyzed in detail and adapted to theories of sorption mechanisms as a layered adsorption[1] or as cluster formation.[2–4] The idea that moisture is adsorbed to specific sites on the material has also been advocated by many researchers. In the wood fiber system, the potential adsorption sites are the hydroxyl groups and the carboxyl groups. For a number of hydrophilic materials, a limited number of 1.0–1.3 adsorbed water molecules per hydroxyl group at relative humidities somewhat below 100% has been well established.[5–8] In the case of lignocellulosic materials, it was shown that a specific adsorption to the hydroxyl groups of the different wood polymer components could well explain their sorption characteristics.[9,10] For a model system of partly carboxymethylated cellulose, the specificity of moisture adsorption to hydroxyl and carboxyl groups was demonstrated,[11] but few studies have been able to show the specific bonding of the water molecules to these adsorption sites.

In general, FTIR spectroscopy offers a potential for the assignment of absorbance bands to specific molecular structures. On the other hand, the presence of water in normal FTIR spectroscopy gives rise to broad, unresolved bands offering little precise information. The deconvolution of spectra taken on moistened samples has given some information regarding the assignment of the effects of water in the OH-valency region.[12] Some measurements involving the sealing of moist cellulose samples in order to obtain a general view of the effects of water sorption on the IR spectra have been performed.[13] The use of a specially designed humidity chamber, as discussed by Haxaire et al.,[14] makes it possible to take spectra under strictly controlled humidity conditions, and it is possible to obtain much improved spectra. In this paper measurements are reported where the adsorption characteristics of paper and some wood polymers have been examined by FTIR spectroscopy in humid atmospheres at different RH[†] levels.

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[†] RH = relative humidity.

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2. Materials and methods

2.1. Materials

A standard softwood kraft pulp was used to produce oriented sheets in a Formette Dynamic (1400 rpm) with a grammage of 30 g/m^2. The thickness was 68 μm.

A dissolving pulp from spruce provided by Borregaard with a cellulose content of 98% was used to make isotropic paper in a Finnish sheet former at a grammage of 25 g/m^2. The thickness was 38 μm.

Glucomannan extracted from *Amorphophallus konjac*, which contains only mannose and glucose, was cast into a film from an aqueous solution. The thickness was 42 μm.

2.2. Sorption measurements

Moisture sorption isotherms from the dry state to 90% RH (relative humidity) were obtained with DVS dynamic vapor sorption equipment from Surface Measurement Systems Ltd. (www.smsuk.co.uk). This device generates a moist atmosphere by mixing dry and saturated air streams. A microbalance registers the weight changes throughout the sorption process. The amount of water sorbed is given as the moisture ratio, that is, mass of water per mass of dry material.

2.3. FTIR spectroscopy equipment

Absorbance spectra in transmission in the IR region were recorded with a Bio-Rad FTS 6000 spectrometer (www.digilabglobal.com).

The sample was mounted in a temperature-controlled chamber with zinc selenide glasses (www.appl-tech.com) placed in the beam path in order to make it possible to change the atmosphere around the sample. Air with a controlled temperature and relative humidity was circulated through this chamber throughout the IR measurements. The atmosphere was generated by mixing dry air and moisture-saturated air in a VTI RH-200 apparatus (www.vticorp.com). Measurements were made in the range from 0% to 80% RH at a temperature of 30 °C.

In order to maintain a constant low load to counteract the expansion or contraction of the sample with changes in moisture content, the position of the clamps holding the sample could be adjusted either manually or in a closed loop connection monitoring the load on the sample (www.appl-tech.com).

Spectra with nonpolarized light were recorded in the wavenumber range from 500 to 4000 cm^{-1} by an MCT detector cooled with liquid nitrogen. The resolution of the spectra was 4 cm^{-1}. Background spectra were taken in the empty chamber with the same atmosphere as that used in the sorption experiment, in order to make it possible to compensate for the moisture in the air around the tested samples.

2.4. Spectral measurements

Spectra of moist air were collected at 30 °C in equilibrium at 0–80% RH for each 10% RH. Spectra of the kraft paper at equilibrium with the surrounding atmosphere were obtained after conditioning for 60 min at each relative humidity.

In kinetic spectroscopic tests performed at 30 °C during the sorption of moisture, the IR spectra were recorded every 0.3 s. Mean spectra were calculated for 30-s periods. Before the start of each test, the sample was allowed to equilibrate at the starting climate, 0% RH, for more than 1 h. The trial commenced with a 1-min collection of spectra at the starting humidity of 0% RH, after which the climate in the measuring chamber was changed to 80% RH. The expansion of the sample with increasing moisture content was adjusted so that a constant load was maintained on the sample either automatically by a step motor or manually. The load applied was small, and it was assumed not to affect the sorption process.

2.5. Spectral treatments

The spectra were baseline corrected to 0 at 1845 and 3739 cm^{-1} and normalized to 1 at 1160 cm^{-1}, the major absorbance peak reflecting the carbohydrate backbone.[15,16] The amount of moisture successively adsorbed by the sample was detected as the difference between the measured spectrum and the spectrum taken at an atmosphere of 0% RH. In order to quantify the amount of water adsorbed, the peak heights for each characteristic band was used noticing that the band widths were constant for all the RH levels studied.

3. Results and discussion

3.1. Samples in equilibrium with humid air

Figure 1 shows the spectra of a moist paper together with the difference spectrum between the wet and dry state reflecting the adsorbed water in the paper material. For comparison, spectra for water in the liquid (reproduced by permission from Spectraonline http://spectra.galactic.com/Spectraonline) and vapor phase is also shown. The IR spectrum of the moisture present in air at 70% RH showed a multitude of peaks at wavenumbers between 1100 and 1900 cm^{-1} as well as between 3500 and 4000 cm^{-1}, as was also reported by Grdadolnik and Maréchal.[17] These absorbance peaks were subtracted from the moisture adsorbed in the paper by the background spectra used.

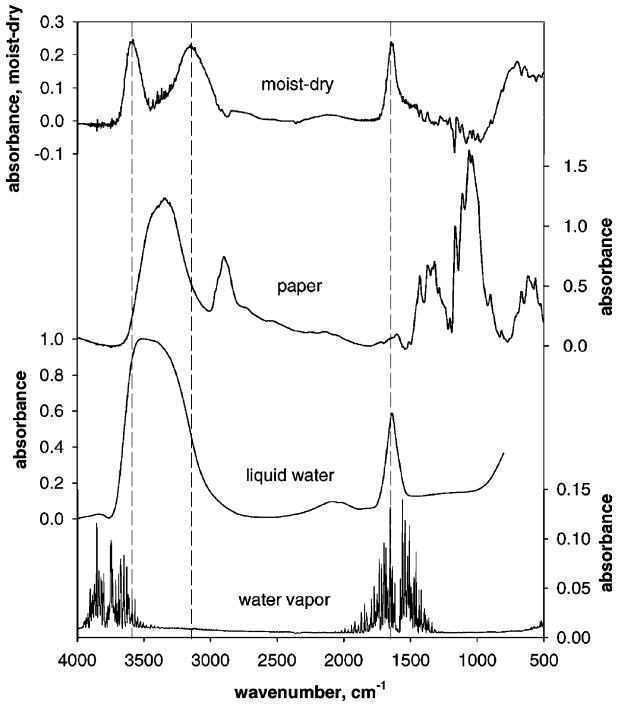

Figure 1. Difference spectrum, moist – dry, for a kraft paper together with the spectrum for the same kraft paper at 80% RH, 30 °C. The spectrum for liquid water is replotted by permission from http://spectra.galactic.com/Spectraonline, and a spectrum of water vapor at 70% RH is included for comparison.

There is a considerable degree of resemblance between the absorbance peaks for liquid water and the differential peaks representing the adsorbed water in the moist paper material; that is, at 2100, 1650, and 700 cm^{-1}. The peak at approximately 700 cm^{-1} has been assigned to the out-of-plane vibrations of O–H groups[15] or to rotational vibrations of the whole H_2O molecule,[17] while the peak at 1650 cm^{-1} has been assigned to the H–O–H angle vibration[14] and that at 2100 cm^{-1} to vibrations from the scission and rocking of water.[18]

The peak at 3600 cm^{-1} in the differential spectrum corresponds to the shoulder of the large OH peak of the water originating from stretching bands belonging to OH groups engaged in hydrogen bonding.[17] On the other hand, the peak at 3200 cm^{-1} in the differential spectrum does not obviously correspond to any peak in the spectrum of free liquid water. This latter peak has also been identified by deconvolution of spectra of cellulose I after humidification.[12]

Figure 2 shows the development of the spectra associated with the sorption of moisture in the kraft paper with increasing RH, calculated as the difference between a moist and a dry paper spectra. The sample was allowed to equilibrate for 1 h at each RH in steps of 10% RH from 0% up to 80% RH. For clarity, only the spectra taken at 10%, 40%, and 80% RH are shown in the figure. All the observed peaks associated with moisture were found to increase with increasing RH.

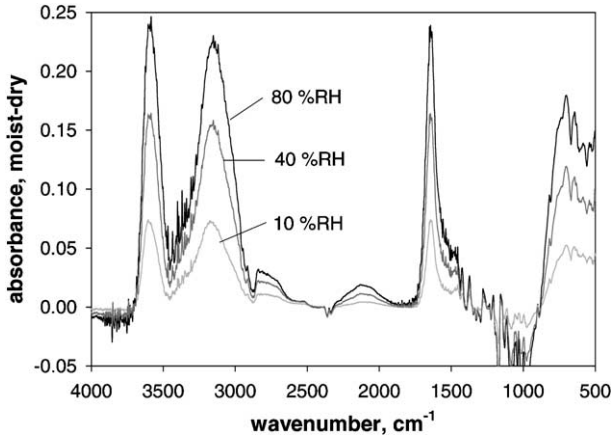

Figure 2. The development of the spectra associated with the sorption of moisture in kraft paper calculated as the difference between the humid and dry spectra of the paper.

The peak at 3200 cm^{-1} may be associated with strongly bound water,[13,19] that is, water bound directly by hydrogen bonds to the OH groups of the cellulose and the hemicelluloses, and this would explain why no such peak is observed for free water. The peak at 3600 cm^{-1} is associated with more loosely bound water,[13,19] that is, water indirectly bonded to the OH groups via another water molecule. These water molecules can thus be said to make up a cluster of water, and they may therefore also be found at the shoulder in the spectrum of free water. An association to 'free' hydroxyl groups has also been suggested as a result of curve-fitting methods by Kondo.[20] The remaining peaks, that is, those at 2100, 1650, and 700 cm^{-1} are all associated with water itself, and their origin has been discussed earlier.

Figure 3 shows for comparison the spectra for the adsorbed water in different materials; kraft paper, cellulose as of dissolving pulp, and glucomannan film, calculated as difference spectra between dry and moist samples at 80% RH. The overall absorbance was highest

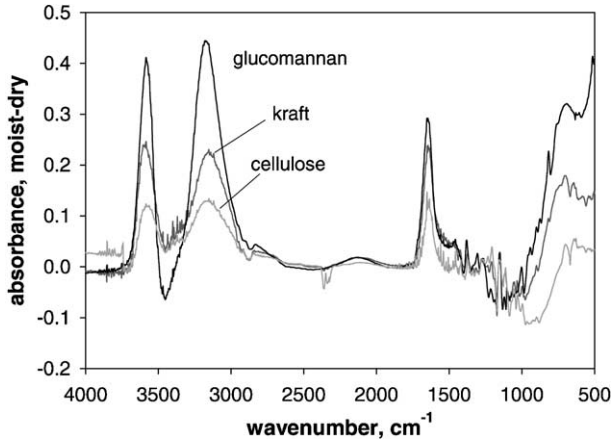

Figure 3. Spectra of absorbed moisture in sheets from kraft pulp, cellulose, and a film of glucomannan from *Amorphophallus konjac*.

in the glucomannan and lowest in the cellulose, with the peaks for the kraft paper at an intermediate level but closer to those of the cellulose in height. The difference in absorbance may be related to the amount of water adsorbed in the different materials. Cellulose is the most crystalline and sorbs the smallest amount of water, while the glucomannan is completely amorphous and sorbs the most. The negative peaks are probably related to insensitivity, due to too high an absorbance in these areas in the dry spectra.

In Figure 4, the changes occurring in the fingerprint region are more closely examined. Two positive peaks that depend on the moisture content are evident, that is, at 1430 and 1380 cm^{-1} as well as a splitting of the 1160 cm^{-1} peak into a negative one at 1174 cm^{-1} and a positive one at 1159 cm^{-1}. At 1425 cm^{-1}, vibrations are associated with COO groups,[15] and the 1430 cm^{-1} band is probably associated with the adsorption of water to such groups. There is currently no explanation of the band at 1380 cm^{-1}. The splitting of the 1160 cm^{-1} band is due to the shift of this peak, related to the vibrations of the glucosidic C–O–C bond as well as of the whole glucose ring. This is shown in Figure 5 where the absorbance spectra for the kraft paper under dry and humid conditions are compared. The adsorption of water probably affects the vibration of the O(3)H···O(5) hydrogen bond, which stiffens the cellulose chain and is important for the stress transfer along the chain.[16,21] A weakening of this hydrogen bond probably changes the vibrational energy of the whole cellulose chain, and thus affects the 1160 cm^{-1} band.

Figure 6 shows the development of the peak height as a function of RH, for the major peaks affected by moisture adsorption, together with the adsorption curve measured in the traditional way as grams of water per gram of dry paper. The increase in moisture uptake occurring above 60% RH was not evident to the same extent as an increase in the height of any of the absorbance peaks. Similar discrepancies between the weight gain due to absorbed water and the increase in absorbance peaks have been observed for other hygroscopic materials,[17,22] and they are also evident in other measurements on cellulosic materials[13] if these are compared with the general moisture isotherms for such materials. On the other hand, the data from those measurements[17,22] indicated a substantial increase in the absorbance peaks related to adsorbed water above 90% RH, much higher than the weight increase at those humidities. These anomalies still remain to be explained.

The relative adsorption characteristics for the different peaks in Figure 6 are compared with the adsorption up to 60% RH in Figure 7. Clearly the increase in the peak height for the different moisture absorbance peaks was very similar throughout this RH range, indicating that water was attached simultaneously to all the characteristic sorption sites. The increase in peak height for

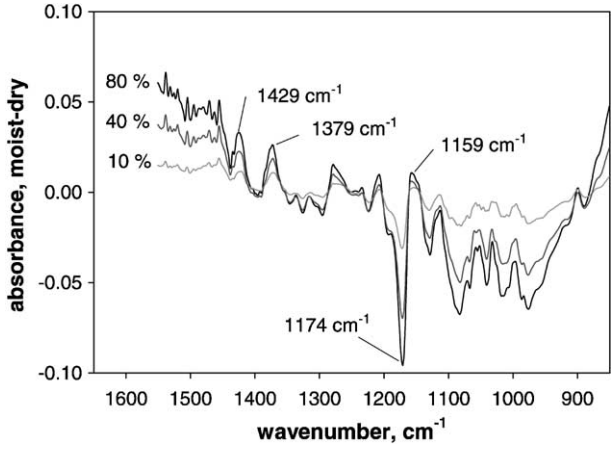

Figure 4. Difference spectra, moist – dry, for three different relative humidities for the kraft sample, illustrating the effect of moisture sorption on the spectra in the fingerprint region.

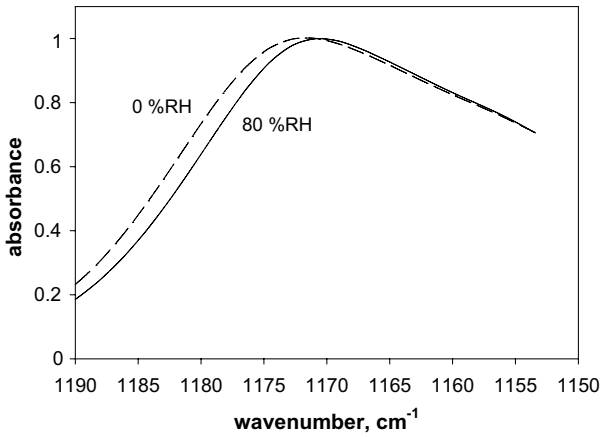

Figure 5. Spectra of the kraft paper at 0% and 80% RH in the region of the 1160 cm^{-1} band. A shift to lower wavenumbers occurred at the higher humidity.

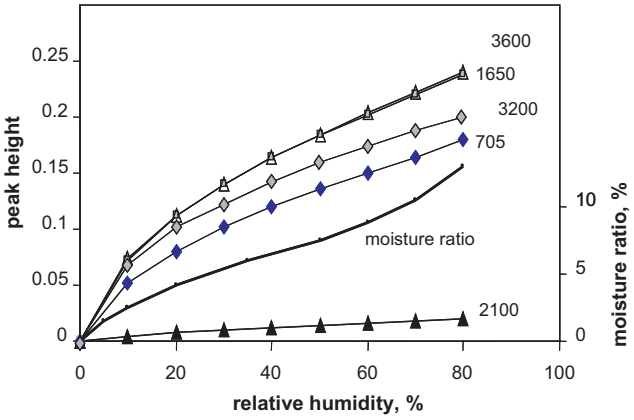

Figure 6. Peak height for the major peaks associated with moisture sorption taken from difference spectra, moist – dry, at equilibrium at the different relative humidities for the kraft paper.

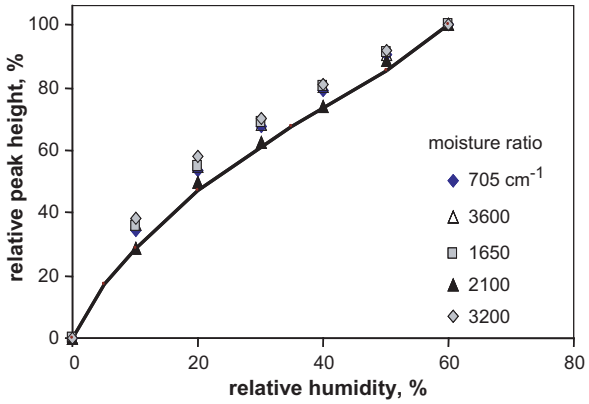

Figure 7. Relative peak height for the major peaks associated with moisture sorption taken at equilibrium at the different relative humidities from differential spectra, moist – dry, for the kraft paper together with the relative moisture gain.

the 1430 and at 1380 cm^{-1} peaks (not shown) followed exactly the same behavior. Although the moisture sorption curve normalized to the amount at 60% RH was somewhat lower than the increase in relative peak height between 0% and 60% RH, it is clear that up to 50% RH the increase in peak height was a linear function of the moisture weight gain. The same behavior has been observed for the effect of moisture sorption on the spectra of a hyaluron polysaccharide.[22]

3.2. Measurements made with increasing air humidity

The dynamics of moisture adsorption was studied in kinetic experiments up to 10 min. The introduction of moisture into the measurement chamber was not immediate due to the volume of the measuring cell. To estimate the RH in the cell, the area under the spectra of the moist air was used. In Figure 8, the change in the relative humidity going from dry conditions to a relative

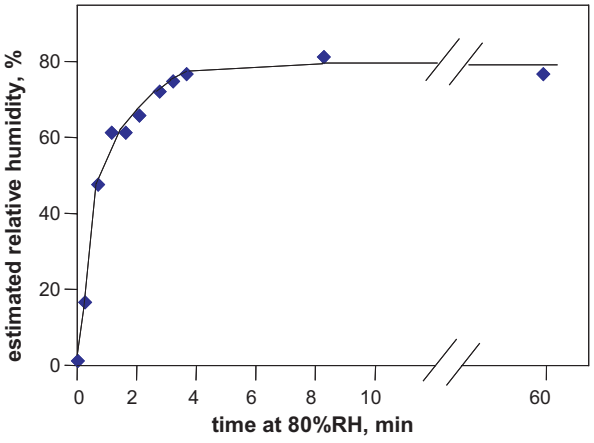

Figure 8. Development of the relative humidity in the empty measuring chamber, 0–80% RH.

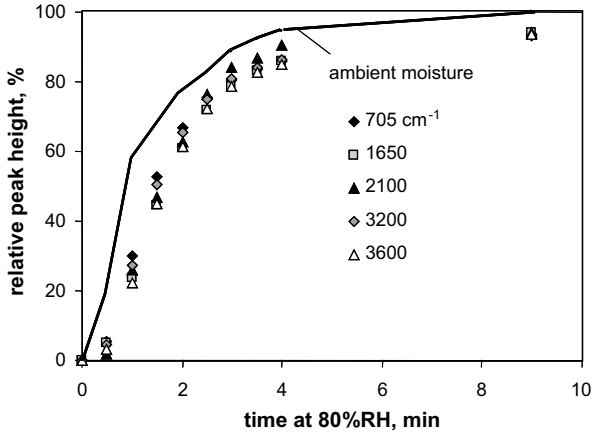

Figure 9. The relative peak heights during sorption from 0% to 80% RH in kraft pulp compared to uptake of moisture as a function of time.

humidity of 80% in the empty chamber is illustrated. The relative humidity at different times of humidification was estimated from the integrated spectra in relation to the area at equilibrium at 80% RH. A linear relationship was found between % RH at equilibrium and the total absorbance from moisture spectra in air. Obviously it took up to 10 min before the humidity in the chamber had fully reached the set RH. This time lag had to be taken into account when evaluating the sorption experiments.

The dynamic moisture adsorption in the kraft paper is illustrated in Figure 9, which shows the increase in the absorbance peaks associated with sorbed moisture going from dry conditions to 80% RH. The increases in peak height were found to be the same for all the different peaks and to follow the increase in RH in the measuring chamber. However the increase with time was somewhat slower than the increase in relative humidity of the chamber, which may not be surprising considering the amount of moisture that has to be delivered to the paper from the surrounding air. It can thus be concluded that, under dynamic sorption, all of the available hydrophilic groups of the paper adsorb water at a similar rate.

4. Conclusions

It is clear from these measurements of moisture sorption in cellulosic materials that the moisture is taken up by the material in a very uniform manner. Although the simultaneous development of the absorbance peaks for tightly and loosely bound water indicates a cluster type of water adsorption, these clusters seem to adhere equally to all types of sorption sites over the whole RH range studied. Different types of association of moisture to hydroxyl groups and to carboxylic acid groups were earlier demonstrated by NIR spectroscopy,[11] but

estimates of the sorption development of these groups as a function of RH appears to be similar on a relative basis at RH levels up to 80%.[9] At higher humidity, the moisture uptake around the carboxylic acid groups occurs much faster than that on the hydroxyl groups.[9] This may have some bearing on the discrepancy noticed between weight gain and the height of the absorbance peaks.

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