Softening of Wood Polymers Induced by Moisture Studied by Dynamic FTIR Spectroscopy

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ABSTRACT: The softening of the wood polymers is very important in the utilization of wood fiber products. To better to understand how the hemicelluloses interact with the other wood polymers in the fiber ultrastructure and contribute to the mechanical properties of the wood, their softening inside the cell wall of pulp fibers was studied by dynamic FTIR spectroscopy under humid conditions. The two hemicelluloses of spruce, glucomannan and xylan, exhibited different softening behaviors indicating a different organization of the two hemicelluloses inside the cell wall. Lignin in mechanical pulp showed a more viscoelastic behavior already under dry conditions than the polysaccharides of the cell wall. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2032–2040, 2004

Key words: biofibers; humidity; infrared spectroscopy; polysaccharides; viscoelastic properties

INTRODUCTION

The utilization of biofibers, such as wood fibers for paper production, demands a good characterization of the biopolymers building them up. The main biopolymers of wood fibers are two groups of polysaccharides, cellulose and hemicellulose (glucomannan and xylan for spruce fibers), and an aromatic polymer, lignin. All wood polymers are hygroscopic and the absorbed moisture has a profound influence on the properties of wood fibers, particularly their dimensions and mechanical properties. Because water acts as a plasticizer, the softening temperature of the wood polymers is drastically lowered even under humid conditions.[1] This effect is of particular relevance in the choice of temperature for the mechanical pulping process (lignin softening) or for the introduction of moisture and/or heat during calendering. The softening effect of moisture on the elastic modulus was determined for both paper[2] and extracted hemicelluloses[3] and lignin.[4] Close to the softening point of the polymers, they exhibit a clear viscoelasticity, so that mechanical spectroscopy provides a good tool for characterizing the influence on the softening behavior of the different components of the wood fiber.[5]

For a complicated biocomposite such as the wood fiber wall, the softening is difficult to interpret as the fine structure of the polymer blend is not fully known. For polymers that are distributed parallel to each other, the elastic modulus of a composite is determined mainly by the stiffest component. On the other hand, if the polymers are aligned in series in the loading direction, the elastic modulus is determined by the softest component. It is therefore important to understand not only the ultrastructural arrangement of the polymers within the wood fiber cell wall but also how each of them contributes to the mechanical properties of the cell wall composite.

Dynamic (or 2D) FTIR spectroscopy is a useful tool for polymer characterization.[6,7] This technique provides the elastic and viscous components of each molecular vibration and it therefore has a potential to reveal the behavior of individual components, and even molecular groups, in their contribution to the softening of a composite material. The dynamic behavior of the wood polymers under dry conditions (i.e., in the glassy state of the wood polymers) was studied earlier by using dynamic FTIR spectroscopy.[8–10]

In general, it is difficult to interpret IR spectra recorded under moist conditions because of the many broad absorption bands from water and to the changes occurring in these bands as moisture levels around the sample are changed. The problem can be overcome by a precise control of the environment around the sample. In the present study, a polymer stretcher was placed in a heated moisture chamber connected to an accurate humidity generator to perform dynamic FTIR experiments under humid conditions (i.e., under conditions where the hemicelluloses are softened).

TABLE I
Relative Carbohydrate Composition and Klason Lignin for the Different Pulp Samples

Sample	Glucose (%)	Xylose (%)	Arabinose (%)	Mannose (%)	Galactose (%)	Klason lignin (%)
Spruce holocellulose	71.4	8.4	1.2	17.4	1.6	0.3
Alkali-extracted spruce holocellulose	85.7	1.5	0.2	12.3	0.3	0
Birch kraft pulp	68.5	30.7	0.2	0.5	0.1	0.4
CTMP	66.5	9.6	2.1	18.0	3.8	25.9

EXPERIMENTAL

Materials

Thin sheets (20–25 g/m^2) of pulp fibers were used in the study to achieve good spectral performance in the transmission mode. Oriented sheets of four different pulps were made on a Formette Dynamique (French sheet-former) at a speed of rotation of 1400 rpm, giving sheets with the fibers oriented in the direction of rotation. Before sheet formation, the pulp was homogenized by pumping it several times through a slit in a laboratory homogenizer (Gaulin Corp., Everett, MA, USA). Four different pulps were studied: a chemi-thermomechanical pulp with both the lignin and the hemicelluloses preserved; a lignin-free holocellulose with a high concentration of both glucomannan and xylan; an alkali-extracted holocellulose with high glucomannan content; and a birch kraft pulp with high xylan content. The experimental conditions for preparation of the different pulps are given below and the carbohydrate compositions and lignin contents are listed in Table I.

Spruce holocellulose

All lignin was selectively removed from spruce (*Picea abies*) chips by sodium chlorite extraction in an acetate buffer at 50°C.

Alkali-extracted spruce holocellulose

Most of the xylan was removed from the above spruce holocellulose by extraction with a 6.5% potassium hydroxide solution for 2 h at room temperature.

Birch kraft pulp

An unbleached industrially processed (at about 170°C) birch (*Betula verrucosa*) kraft pulp was cooked to Kappa No. 15.

CTMP

An unbleached industrially made (refined at about 120–150°C) chemi-thermomechanical pulp (CTMP) of spruce (*P. abies*) with a lignin content of 26% was used.

Before sheet forming, the pulp was fractionated in a Bauer McNett to remove middle lamella fragments, ray cells, etc., and to retain only the fiber fraction (16–30 mesh).

Dynamic FTIR measurements

All spectra were recorded on a FTS 6000 FTIR spectrometer (Digilab, Randolph, MA, USA) by using a liquid-nitrogen-cooled MCT (Mercury Cadmium Telluride) detector. During the dynamic FTIR measurements, small samples of the oriented pulp sheets were dynamically strained in the fiber direction and the IR responses were monitored as a phase lag with respect to the external perturbation. The experimental setup can be seen in Figure 1. Because the phase of the external perturbation in relation to the interferometer steps was known, digital signal processing made it possible to extract the dynamic changes in the IR transmission spectrum of the sample from the detector signal. These transmission changes were divided into two orthogonal spectra: the in-phase spectrum representing immediate changes or elastic responses (0° phase loss angle) and the out-of-phase spectrum representing the time-delayed changes or viscous responses (90° phase loss angle) using the Win-IR Pro 3.2 software (Digilab, Randolph, MA, USA).

The amplitude of the applied sinusoidal strain was <0.3% of the sample length and the frequency was 16 Hz. The incident IR radiation was polarized with a KRS5 wire grid polarizer at either 0° or 90° in relation to the stretching direction. The interferometer was run
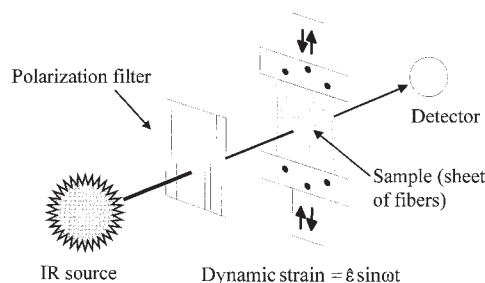

Figure 1 Experimental setup of a dynamic FTIR experiment with mechanical strain perturbation.

in a step-scan mode with a scanning speed of 0.5 Hz and a phase modulation of 400 Hz. The interferograms obtained were Fourier transformed and a triangular apodization function[11] was applied. The resulting in-phase and out-of-phase spectra were normalized with respect to the static spectrum and thereafter baseline corrected at 2200 cm^{-1}.

The spectra measured under dry conditions were obtained by using a Polymer Modulator (PM-100, Manning Applied Technologies Inc., Troy, ID, USA) mounted directly in the sample compartment of the spectrometer. The dynamic spectra of the holocellulose and the birch kraft pulp were published earlier[8,9] and are here shown as reference to the spectra obtained under humid conditions.

The dynamic FTIR experiments under humid conditions were made with the samples mounted in a specially constructed Polymer Modulator (PM-100) mounted inside a Temperature Control System (TC-100; Manning Applied Technologies Inc.), capable of keeping the system at 40°C during the measurements. A Relative Humidity Generator (RH-200; VTI Corp., Hialeah, FL, USA) was connected to the TC-100 and supplied it continuously during the measurements with air of 40°C and 90% relative humidity (RH). All connections and tubes were heated with ribbon heaters to avoid condensation anywhere in the system. The samples were prestretched in the fiber direction and allowed to relax and condition for more than 1 h under the experimental conditions before the measurement was started. One scan with a resolution of 8 cm^{-1} was performed for each measurement.

The dynamic spectra shown in this article are mean spectra of three measurements. Before averaging, the dynamic spectra were normalized as follows. The spectral data from each measurement were divided into one phase spectrum (phase delay of each absorption band) and one magnitude spectrum (the amount of induced absorption change for each absorption band). All magnitude spectra were then normalized to 1.0 at about 1165 cm^{-1}, the C—O—C asymmetric bridge stretching being most sensitive to load for a wood cellulose fiber material,[12] and new in-phase and out-of-phase spectra were calculated from these. These normalized in-phase and out-of-phase spectra were then used to calculate the mean dynamic spectra for each experiment.

Calculation of mean phase loss angle

One measure of the viscoelasticity of a material is its phase loss angle, where 0° represents a completely elastic material and 90° represents a totally viscous material. This property is usually determined by mechanical spectroscopy. It is also possible to obtain this kind of information for each single molecular vibration with dynamic FTIR spectroscopy.[6] In this article,

the absolute values of the in-phase and out-of-phase spectra were used to calculate the angle by using the equation: phase loss angle $= \arctan(I_{\text{out-of-phase}}/I_{\text{in-phase}})$, where $I_{\text{out-of-phase}}$ is the absolute value of the intensity of the out-of-phase spectrum and $I_{\text{in-phase}}$ is the absolute value of the intensity of the in-phase spectrum. The mean phase loss angle from the 1150- to 1520-cm^{-1} region was calculated for each measurement.

RESULTS

The wood polymer interactions within two spruce holocelluloses, one birch kraft pulp and one CTMP, have here been investigated by using dynamic FTIR spectroscopy under both dry and humid conditions. The studies under humid conditions and at an elevated temperature were performed to investigate the effect of hemicellulose softening on the polymer interactions.

Dynamic spectra of wood pulp fiber sheets strained in the fiber direction and recorded at 0° polarization (parallel to the straining direction as well as the fiber direction) have been shown to be dominated by signals originating from the straining of cellulose.[9,10] This is an effect of the organization of the fiber cell wall where the cellulose is arranged in fibrils oriented preferentially parallel to the fiber axis and is therefore the main load-bearing element in the fiber direction. Dynamic spectra of such fiber sheets recorded at 90° polarization are more influenced by changes occurring perpendicular to the straining/fiber direction and thus provide more information about the matrix material of hemicelluloses and lignin.

Figure 2 presents the dynamic spectra at 0° polarization of the spruce holocellulose for the two different conditions, 0% RH, 25°C and 90% RH, 40°C. The elastic response clearly dominated the spectrum under both dry and humid conditions, which was not unexpected because the spectra mainly show responses from cellulose and because cellulose due to its high crystallinity is still in its glassy state under these conditions. Similar spectral results were obtained for the other pulps tested, although the calculated mean phase loss angle, Table II, was higher at the humid climate than at the dry climate for both the spruce holocelluloses and the CTMP. This increase in phase angle probably comes from hemicelluloses in less oriented fibers.

Figures 3-6 show the dynamic spectra at 90° polarization in the two different climates for all four pulps studied. In the case of the spruce holocellulose (Fig. 3), there was small increase in the viscous component in the spectra measured under humid conditions, especially in the low-wavenumber region. This indicates that the polymers (i.e., the molecular groups absorbing in this wavenumber region) were closer to their
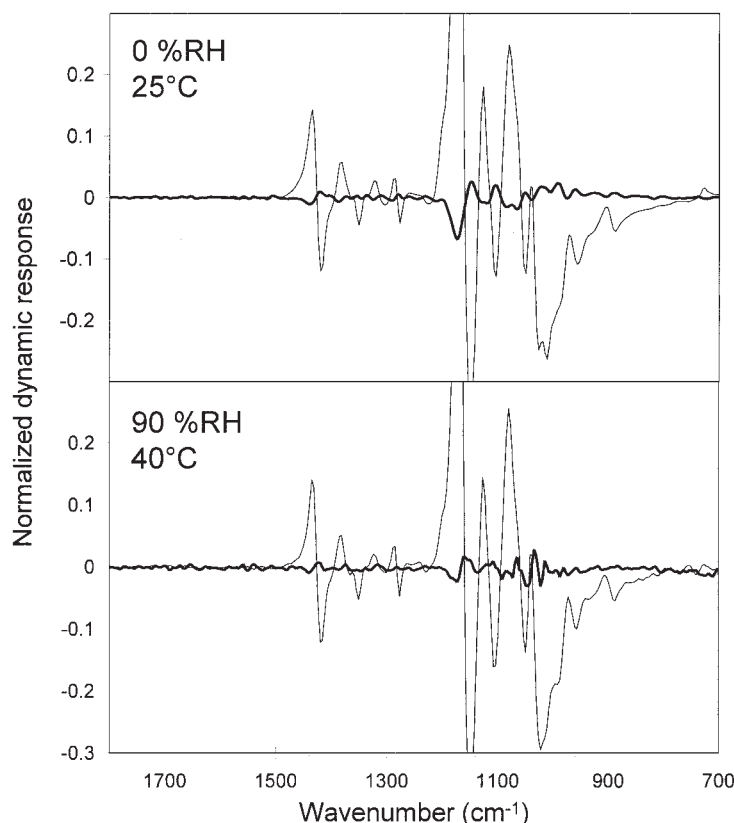
Figure 2 Dynamic FTIR spectra of spruce holocellulose recorded at 0° polarization; thin line = in-phase spectrum (elastic response) and thick line = out-of-phase spectrum (viscous response). The upper spectra were recorded at 0% RH, 25°C and the lower spectra were recorded at 90% RH, 40°C.

softening point and thus showed a more time-dependent response. Because the spectra recorded at 90° polarization are more indicative of the response of the

TABLE II
Mean Phase Loss Angles for Different Pulps under Different Climates, Determined from the Absolute Values of the Two Orthogonal Components of the Dynamic FTIR Spectra

Sample	0% RH, 25°C	90% RH, 40°C
0° Polarization		
Spruce holocellulose	14 (3)	20 (4)
Alkali-extracted spruce holocellulose	15 (7)	21 (1)
Birch kraft pulp	11 (2)	12 (2)
Chemithermomechanical pulp	13 (1)	25 (1)
90° Polarization		
Spruce holocellulose	17 (1)	29 (6)
Alkali-extracted spruce holocellulose	27 (7)	28 (4)
Birch kraft pulp	23 (2)	24 (2)
Chemithermomechanical pulp	26 (5)	36 (1)

The phase loss angles are calculated for the 1150–1520 cm^{-1} wavenumber range. Standard deviations of three measurements are given in parentheses.

matrix material, the increased viscoelasticity should probably be attributed to the hemicelluloses within the fiber material. A high viscous response was mainly seen for the characteristic peaks of glucomannan[8] at about 810 and 870 cm^{-1} and in the area between 1040 and 1080 cm^{-1} as well as, to some extent, at some higher wavenumbers. In the 1040- to 1080-cm^{-1} region characteristic peaks of galactose, the side groups of glucomannan have been reported.[13,14] There are, however, also several strong cellulose bands in this region, related to highly coupled motions dominated by CC and CO stretching motions with small contribution from HCC, HCO, and skeletal atom bending.[15] A PLS data analysis of alkali-extracted holocelluloses[8] showed that both xylan and glucomannan contribute strongly to the absorption in this area. Although a softening of both the xylan and the glucomannan is probable under the high humidity conditions used,[3,16] there were no viscous signals from the characteristic xylan vibrations at 1600 and 1730 cm^{-1}. These signals originate, however, from side groups in the polymer chain and may not be affected to the same extent as the main chain when the fibers are subjected to loading.

The region between 1150 and 1270 cm^{-1} contains both skeletal stretching vibrations and methine bend-
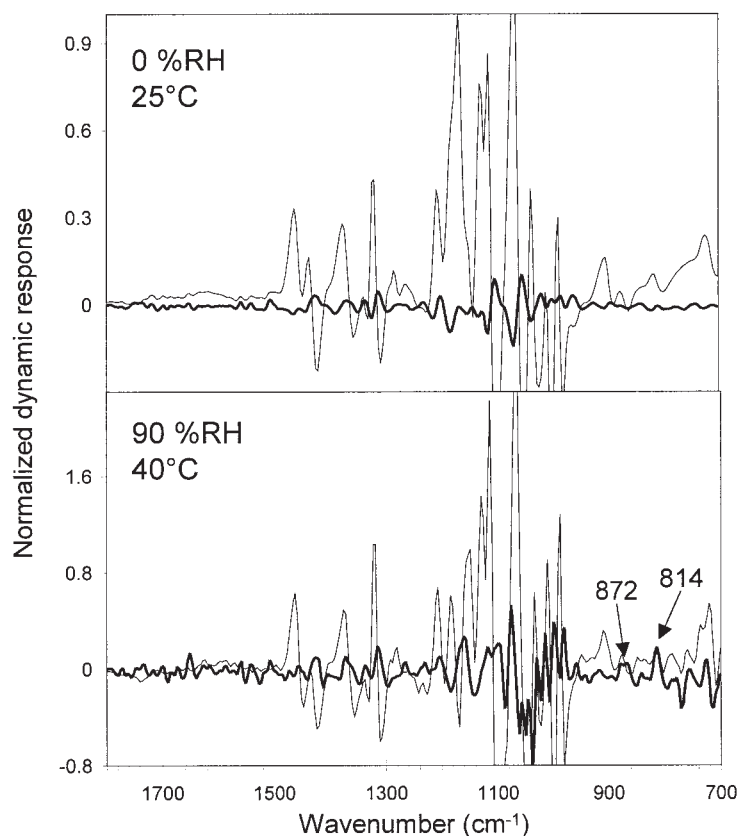
Figure 3 Dynamic FTIR spectra of spruce holocellulose recorded at 90° polarization; thin line = in-phase spectrum (elastic response) and thick line = out-of-phase spectrum (viscous response). The upper spectra were recorded at 0% RH, 25°C and the lower spectra were recorded at 90% RH, 40°C.

ing and is sensitive to the orientation of the glycosidic linkage.[15] This region of the holocellulose spectra in Figure 3 was also affected by the change in climate, but here it was mainly the in-phase spectrum that showed changes. The positive peak at 1169 cm^{-1} in the in-phase spectrum recorded under dry conditions was split into three peaks under humid conditions: one positive peak at 1150 cm^{-1}, one negative peak at 1169 cm^{-1}, and one positive peak at 1184 cm^{-1}. This behavior was similar to the 0° polarization case. It may be that the softening of the hemicelluloses results in higher strains in the whole network and thus also in higher strains on the cellulose fibrils oriented perpendicular to the fiber orientation.

The degree of viscoelasticity, calculated as the mean phase loss angle, is given in Table II. For the holocellulose, the phase loss angle in the 90° polarization experiments clearly increased with increasing humidity as a result of softening. In contrast, the alkali-extracted spruce holocellulose showed no change in the mean phase loss angle as a result of the change in climate. This pulp had however a higher phase loss angle than the holocellulose already under dry conditions. From its spectra in Figure 4, it is clear that an increase in the viscous response in the 700- to 1100-

cm^{-1} region (region of glucomannan characteristic vibrations) occurs when moisture is introduced into the system. This region is not included in the mean phase loss angle calculation. The changes evident at ~ 1160 cm^{-1} in the in-phase spectrum for the holocellulose were not seen in the spectrum of the alkali-extracted holocellulose.

The dynamic measurements on the birch kraft pulp resulted in about the same mean phase loss angles as for the alkali-extracted holocellulose. The dynamic spectra of this pulp (Fig. 5), revealed no change in viscous component in the 700- to 1100-cm^{-1} region as a result of the change in climate. This is consistent with the very low amount of glucomannan in this pulp. At about 1630 cm^{-1}, a broad signal could be seen in the in-phase spectrum of the birch kraft pulp under humid conditions, but this signal was not present under dry conditions. In this area, molecularly adsorbed water absorbs IR radiation[17] and nearby, at about 1600 cm^{-1}, the carboxylate ion of xylan[18] has a high absorptivity.

Figure 6 shows the dynamic spectra at 90° polarization for the different climates, 0 and 90% RH, for the CTMP. A viscous response could be detected already in the dry state for lignin-characteristic vibrations as
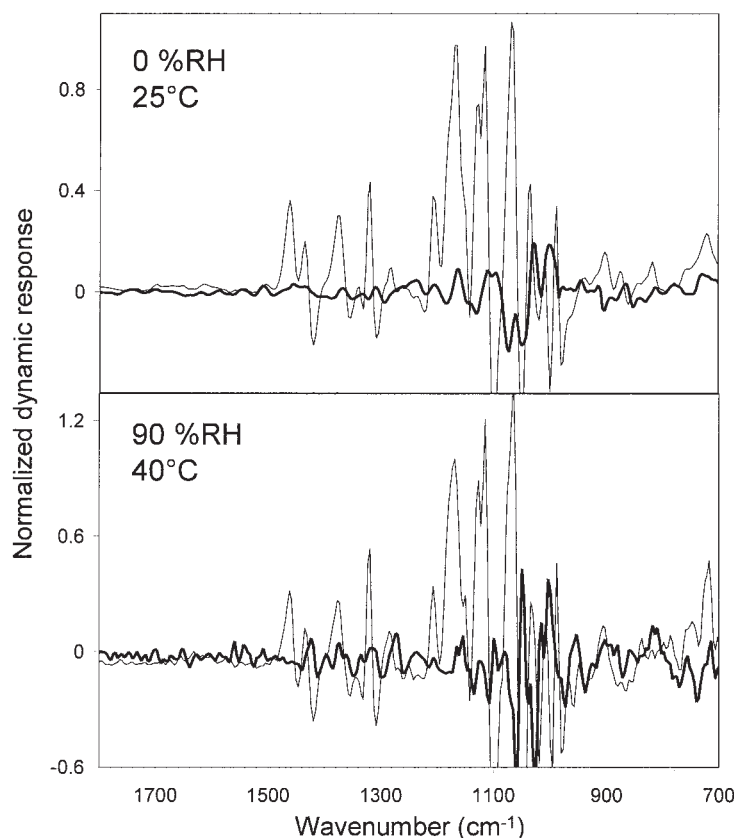
Figure 4 Dynamic FTIR spectra of alkali-extracted spruce holocellulose recorded at 90° polarization; thin line = in-phase spectrum (elastic response) and thick line = out-of-phase spectrum (viscous response). The upper spectra were recorded at 0% RH, 25°C and the lower spectra were recorded at 90% RH, 40°C.

the aromatic vibration at 1508 cm^{-1}. The more viscoelastic behavior of lignin compared to that of the polysaccharides within the cell wall was earlier discussed in relation to measurements on a thermomechanical pulp and could be related to lower secondary (β) transitions of the lignin.[10] The CTMP also showed a broad signal at about 1630 cm^{-1} in the in-phase spectrum recorded under humid conditions.

DISCUSSION

Viscoelastic polymers dissipate energy during deformation. This dissipation of energy (i.e., an increase in phase loss angle) reaches different maxima at different transitions in the polymer, where the glass transition leads to the most drastic changes in mechanical properties. These transitions are monitored by mechanical spectroscopy by measuring, for instance, the change in elastic modulus with changing temperature or humidity. With dynamic FTIR spectroscopy, an increase in damping is evident as an increase in the viscous (out-of-phase) spectral response. In this study, only two different climates were compared. To achieve a complete picture of the softening process inside the wood

cell wall, dynamic FTIR experiments ought to be performed at a variety of climates.

This analysis shows that an overall increase in the viscous component of the dynamic spectra occurs with increasing humidity both at 0° and 90° polarization. The mean phase loss angle was calculated for each pulp (Table II) to permit a comparison of their viscoelastic properties, but it should be kept in mind that these values were calculated only for a restricted region. They give no molecular information. To obtain such information, each pair of spectra has to be examined in detail.

The softening of lignin occurs at higher temperatures than were used in this study.[19] Due to its crosslinked structure, the glass transition temperature (T_g) of lignin can only be lowered to about 75°C by the absorption of moisture,[19] whereas the T_g of the hemicelluloses may be lowered to room temperature.[20] This means that the viscous response of the aromatic vibrations detected already in the dry state by dynamic FTIR spectroscopy (90°) must be attributed to the presence of a secondary (β) transition in the lignin. The small increase in viscosity as a result of the change in climate in the case of the lignin-rich CTMP (Table II
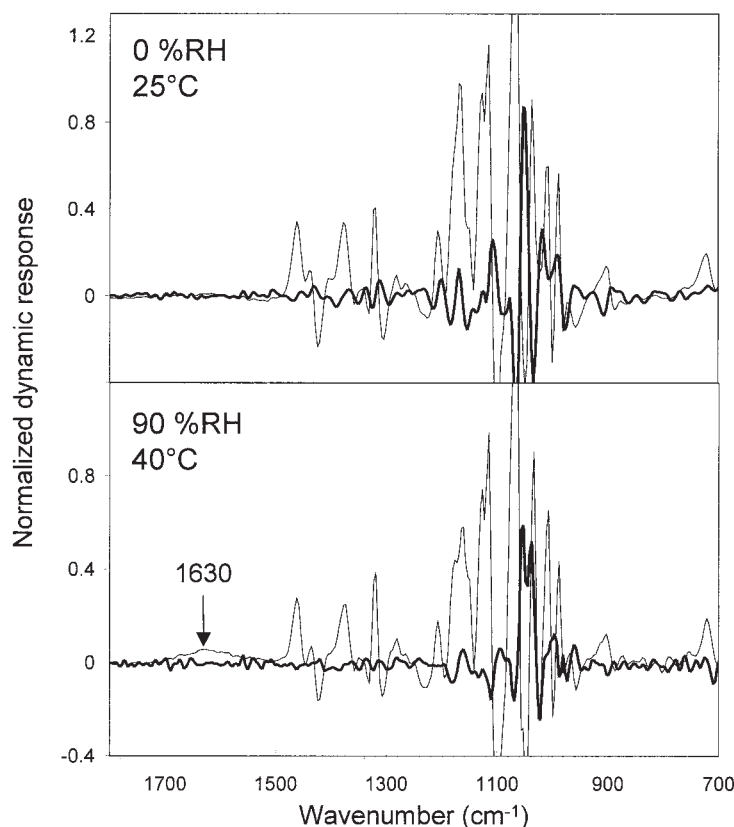
Figure 5 Dynamic FTIR spectra of a birch kraft pulp recorded at 90° polarization; thin line = in-phase spectrum (elastic response) and thick line = out-of-phase spectrum (viscous response). The upper spectra were recorded at 0% RH, 25°C and the lower spectra were recorded at 90% RH, 40°C.

and Fig. 6), is probably due to the small plasticizing effect that water has on the lignin component, but it may also be due to the plasticizing of the hemicelluloses.

It is difficult to interpret the significance of the broad dynamic in-phase signal with its maximum at 1630 cm^{-1} in the 90° polarized dynamic spectra recorded under humid conditions of the birch kraft pulp and the CTMP. These signals could originate from the xylan or from adsorbed water or, in the CTMP case, from the lignin. From the shape of the broad peak and the fact that earlier results obtained by mechanical spectroscopy indicated a softening of xylan inside the cell wall after the removal of lignin,[5] it is probable that these dynamic peaks have their origin in the xylan. Their appearance as an elastic (in-phase) rather than a viscous response was probably because the xylan had already passed its glass transition with its dissipation maximum under the moist conditions here employed. The xylan may have become rearranged in the structure to participate in the matrix response to the load.

Both the alkali-extracted and the nonextracted holocellulose showed similar increases in viscous signals at 90° polarization, probably attributed to the glucomannan, with changing climate. The viscous re-

sponses of the characteristic vibrations at 810 and 870 cm^{-1} reveal that the glucomannan is exhibiting a high damping. There were some differences between the in-phase spectra of the two holocelluloses between 1150 and 1300 cm^{-1}.

The holocellulose was only treated at a temperatures of 50°C, whereas both the birch kraft and the CTMP were subjected to temperatures >100°C. This could make a difference in the xylan arrangement, which was not detectable by dynamic FTIR spectroscopy under dry conditions but gave spectral differences between the holocellulose and the birch kraft and the CTMP under humid conditions.

In summary, at 40°C and 90% RH the spruce glucomannan was probably close to its glass transition, whereas both the birch and spruce (CTMP) xylan were already softened and in a more or less rubbery state. Studies on extracted hemicelluloses have indicated a somewhat lower and a greater drop in the elastic modulus during softening for xylan than for galactoglucomannan.[3,16] A later study on a commercial glucomannan without galactose groups showed an earlier softening of the glucomannan than of birch xylan, and in this case, the drop in elastic modulus was about the same for the two hemicelluloses.[21] These results indicate no great
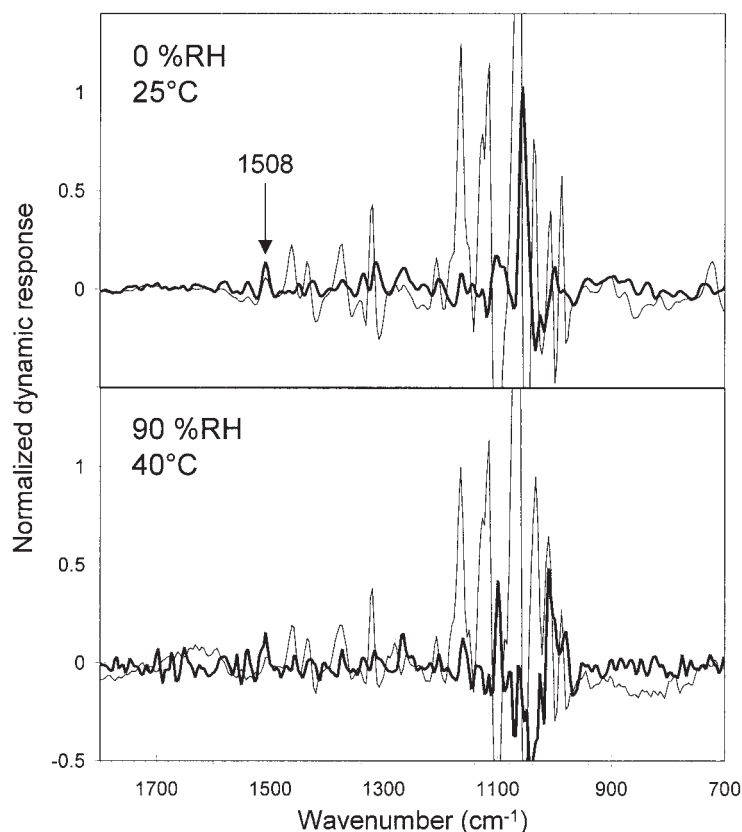
Figure 6 Dynamic FTIR spectra of CTMP recorded at 90° polarization; thin line = in-phase spectrum (elastic response) and thick line = out-of-phase spectrum (viscous response). The upper spectra were recorded at 0% RH, 25°C and the lower spectra were recorded at 90% RH, 40°C.

difference in the glass transition position of the extracted hemicelluloses. However, in a biocomposite such as the wood cell wall, the native arrangement inside the cell wall has a great influence on the softening behavior of the polymers. Hence, the different softening behaviors of xylan and of glucomannan observed in this study indicate that the arrangement of the glucomannan inside the fiber wall prevents the glucomannan from softening to the same extent as the xylan.

CONCLUSION

The different softening behaviors of xylan and galactoglucomannan found in this study indicate a different organization of the two hemicelluloses inside the cell wall. The fact that no xylan softening was observed in the holocellulose, in contrast to the other pulps, could be a consequence of the different processing temperatures used.

The lignin shows a viscous response already in the dry state inside the cell wall and a slightly larger phase loss angle under humid conditions. These effects appear to be a consequence of a secondary (β) transition in the lignin polymer at low temperatures, because mechanical spectroscopy has not shown that lignin is softened under the conditions used in this study.

References

1. Salmén, L.; Hagen, R. in Handbook of Physical Testing of Paper; Mark, R. E.; Habeger, J. C. C.; Borchand, J.; Lyne, M. B., Eds.; Marcel Dekker: New York, 2001; pp. 77–113.
2. Salmén, N. L.; Back, E. L. Tappi J 1980, 63, 117.
3. Cousins, W. J. Wood Sci Technol 1978, 12, 161.
4. Cousins, W. J. Wood Sci Technol 1976, 10, 9.
5. Salmén, L.; Olsson, A.-M. J Pulp Pap Sci 1998, 24, 99.
6. Noda, I. Anal Chem 1994, 66, 1065.
7. Noda, I.; Dowrey, A. E.; Marcott, C. in Characterization of Polymers; Ishida, H., Ed.; Plenum: New York, 1987; pp. 33–59.
8. Åkerholm, M.; Salmén, L. Polymer 2001, 42, 963.
9. Åkerholm, M.; Salmén, L. J Pulp Pap Sci 2002, 28, 245.
10. Åkerholm, M.; Salmén, L. Holzforschung 2003, 57, 459.

11. Griffiths, P. R.; Haseth, J. A. D. Fourier Transform Infrared Spectroscopy; Wiley-Interscience: New York, 1986.
12. Hinterstoisser, B.; Åkerholm, M.; Salmén, L. Carbohydr Res 2001, 334, 27.
13. Wilson, R. H.; Smith, A. C.; Kacuráková, M.; Saunders, P. K.; Wellner, N.; Waldron, K. W. Plant Physiol 2000, 124, 397.
14. Bjarnestad, S. Characterization of the Carbohydrate Composition of Pulp Fibers; Lic. thesis, Royal Institute of Technology: Stockholm, 2002.
15. Wiley, J. H.; Atalla, R. H. Carbohydr Res 1987, 160, 113.
16. Olsson, A.-M.; Salmén. L. International Conference on Wood-Water Relations; Copenhagen, 1997; pp. 269–280.
17. Kalutskaya, E. P.; Gusev, S. S. Polym Sci USSR 1981, 22, 550.
18. Marchessault, R. H. Pure Appl Chem 1962, 5, 107.
19. Salmén, L. J Materials Sci 1984, 19, 3090.
20. Back, E. L.; Salmén, N. L. Tappi J 1982, 65, 107.
21. Olsson, A.-M.; Salmén, L. in Xylans, Mannans, and Other Hemicelluloses: Science and Technology; Gatenholm, P.; Tenkanen, M., Eds.; ACS Symp. Ser: Washington, DC, 2004, pp 184–197.