

# Molecular Mechanisms Involved in Creep Phenomena of Paper

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**ABSTRACT:** The phenomenon of mechanosorptive creep (i.e., the increasing creep occurring in some hygroscopic materials subjected to moisture cycling) was studied for paper from a molecular point of view. Paper was tested in creep at different loading levels in a constant high humidity of 90% relative humidity (RH) and in a cyclic climate between 30 and 90% RH. Throughout the creep tests, spectra from the mid- and near-IR, as well as dynamic mechanical data, were recorded to determine molecular changes occurring with time. In tensile stress scans the instantaneous, dynamic elastic modulus was found to increase. It is suggested that this increase was due to orientation of the cellulose molecules, which was detected as changes in the mid-IR spectra at  $1160\text{ cm}^{-1}$  assigned to the  $\text{C}_1\text{—O—C}_4$  stretching. During creep in constant and cyclic humidity, the modulus was found to increase with time, more so for the cyclic humidity. Changes in the mid-IR spectra at  $1184$  and  $1030\text{ cm}^{-1}$ , which is assigned to  $\text{CH}_2$ ,  $\text{CH}$ , and  $\text{C—O}$ , may indicate sliding between the cellulose chains. The near-IR measurements mainly showed differences in the moisture content. In stress scans the moisture content increased with increasing tensile load. In creep at constant 90% RH, the moisture content was also found to increase in a manner similar to the stress scan. In the cyclic humidity with a conditioning time of 70 min at 90% RH the moisture content decreased successively with increasing numbers of cycles. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1590–1595, 2001

**Key words:** mechanosorption; creep; spectroscopy; paper; humidity

## INTRODUCTION

The accelerated creep that occurs in paper materials subjected to cyclic changes in the environment is of substantial commercial importance, because of the damage occurring when boxes collapse in warehouses and the consequent need to increase the thickness of the packaging material used. This problem of mechanosorptive creep (i.e., the increasing creep occurring in some hygroscopic materials subjected to moisture cycling)

has been studied extensively ever since it was discovered in the late 1950s,<sup>1</sup> but there is still a discussion as to whether or not molecular mechanisms are involved.

Whenever a material is deformed, the molecules are subjected to forces and deformed accordingly. In crystalline materials, the straining may be observed in X-ray diffraction measurements, which provide an estimate of the elastic modulus of the crystals<sup>2</sup> (i.e., a reversible deformation). In an amorphous polymeric material, large strains leading to a flow of the material permanently orient the polymeric chains in the direction of the stress. Thus, changes occurring at the molecular level are directly coupled to the external load.

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When any polymeric material is kept at conditions not far below the temperature of its glass transition, noticeable physical aging occurs.<sup>3</sup> The phenomenon was well demonstrated for paper by Padanyi who showed that over a 10-day period a newly deaged sample might show an increase in stiffness of more than 10%.<sup>4</sup> It was also demonstrated that this aging process may be accompanied by changes in molecular properties recorded by near-IR (NIR) spectroscopy.<sup>5</sup>

When a hygroscopic material like wood or paper is strained, changes in the moisture content occur, an increase under tensile stresses and a decrease under compressive stresses.<sup>6,7</sup> However, in another experiment when paper was subjected to a changing relative humidity (RH), no significant increase in moisture content could be observed in specimens under tensile stress compared to unloaded specimens.<sup>8</sup>

Okushima and Robertson noticed that the "local" deloading elastic modulus calculated from the initial slope of the deloading curve in a stress-strain experiment increases with the degree of strain up to about 40% of the breaking strain.<sup>9</sup> It is also found that the dynamic elastic modulus recorded at different static strain levels increases with increasing strain, the increase in elastic modulus being higher with higher RH.<sup>10</sup> In creep experiments under both constant and changing humidity an increase in the elastic modulus, measured under dynamic conditions as  $E'$ , was observed in both paper and polyamide.<sup>11</sup> A similar increase in the deloading elastic modulus during creep occurs in Kevlar, and Ericksen suggested that this is related to a change in the crystalline orientation under an applied load.<sup>12</sup> In creep experiments on wood fibers Byrd<sup>13</sup> noticed a decrease in the fibril angle under constant creep but an increase in the fibril angle in creep under cyclic climatic conditions. Cyclic loading of single fibers also resulted in an increase in the deloading modulus with each cycle, a fact attributed to a decrease in the fibrillar orientation.<sup>14</sup>

The changes occurring in material properties under creep during cyclic humidity changes are much debated. Many of the early studies indicated a loss of rigidity during the transient moisture changes<sup>1</sup> and/or an increase in the mechanical damping,<sup>15</sup> which suggested an increase in molecular mobility. Also, NMR studies on cotton and keratin fibers under sorption conditions indicated such an increase in molecular mobility.<sup>16</sup> On the other hand, a more extensive analysis of the dynamic mechanical behavior during chang-

ing humidity conditions suggested that at least the anomalous behavior in mechanical damping during the moisture transient can be explained as an artifact caused by the measuring technique.<sup>11</sup>

In order to investigate the molecular mechanisms involved in mechanosorptive creep, an investigation was set up to compare the mechanical changes of paper under loading with changes occurring at a molecular level. Deformation and changes in the elastic modulus and mid-IR and NIR spectra were studied for papers strained under different conditions. It is well known that the orientation of the polymer chains in a material may be studied with polarized IR spectroscopy, and this is also so for the wood polymers.<sup>17</sup> Thus, changes on the macroscopic level may be coupled with changes in molecular orientation.

## EXPERIMENTAL

### Materials

The paper used in these studies was made from unbleached kraft pulp from the Norway spruce (*Picea abies*) and was formed in a Formette Dynamique apparatus, which gives an oriented sheet. The grammage was 15 g/m<sup>2</sup> to allow for mid-IR measurements in transmission.

### Methods

The elastic modulus was measured in tension with a Perkin-Elmer DMA7e dynamic mechanical analyzer. Strips were cut in the direction of the fiber orientation with a width of 5 mm and mounted in the DMA7e with a length of 12.5 mm. A sinusoidal load of a constant amplitude of approximately 0.5 MPa at a frequency of 1 Hz was superimposed on the static load to determine the instantaneous, dynamic elastic modulus measured as  $E'$ . In this setup the dynamic elastic modulus was monitored during straining or creep experiments under constant, as well as changing, humidity. NIR spectra were also recorded in all these measurements.

Stress scans were performed at 90% RH by increasing the static stress in steps of 0.04 MPa and recording the dynamic elastic modulus after 15 s of creep.

The creep under constant 90% RH was monitored under different static stresses for 18 h. Samples were conditioned for 4 h at 90% RH under a small static stress of 0.4 MPa before a

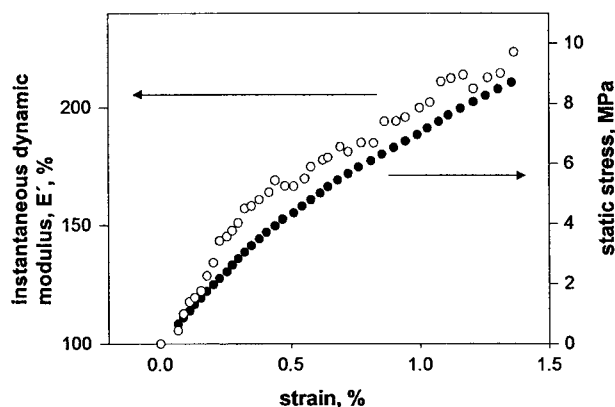
stress of 2.2, 3.5, or 6.1 MPa was applied. The breaking stress at 90% RH for the paper was approximately 18 MPa. The creep stresses were chosen to cover the range from viscoelastic to plastic deformation of the material without breaking it.

Creep under cyclic humidity was started in the same manner as the creep under constant humidity. After 60 min at 90% RH under the applied static load, the humidity cycling between 90 and 30% RH at intervals of 70 min was started.

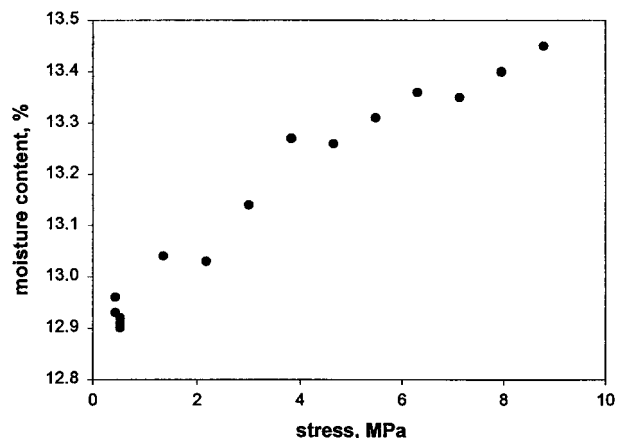
NIR spectra were recorded in diffuse reflectance by a Galileo fiber probe connected to a Bio-Rad FTS 6000 spectrometer. The probe was placed facing the paper surface at a distance of less than 0.5 mm. Spectra were recorded at wave numbers in the interval of 4000–7000  $\text{cm}^{-1}$ .

The moisture contents of the samples were determined from the NIR spectra using a multivariate model. Spectra from paper samples at eleven different relative humidities between 0 and 90% RH were recorded. The spectral variations were correlated to the moisture contents determined at the same humidities with a Perkin Elmer TGA, thermogravimetric analyser. In the NIR-spectra, the baseline was corrected to a straight line intercepting the spectrum at wave numbers of 4491 and 5701  $\text{cm}^{-1}$ . The calibration model for the moisture content was based on the peaks between 4506 and 5406  $\text{cm}^{-1}$ .

Mid-IR spectra were recorded in transmission by a Bio-Rad FTS 6000 spectrometer in the wavelength range of 400–4000  $\text{cm}^{-1}$ . The irradiating beam was polarized parallel to the load direction of the sample. Measurements were made under dry conditions with dry nitrogen as the purge gas.



**Figure 1** The stress and instantaneous dynamic elastic modulus relative to that at 0% strain as a function of strain from a stress scan at 90% RH.



**Figure 2** The moisture content determined from NIR spectra as a function of stress at 90% RH. The samples were preconditioned at 90% RH prior to the test.

Spectra were recorded on samples with a width of 10 mm and clamped with a span of 15 mm. Samples were loaded either progressively in a stress scan or held under a constant load in the creep experiments. The samples under creep load were subjected to cyclic changes in humidity using an external humidity chamber with 90% RH and the dry climate in the spectrometer where the spectra were recorded.

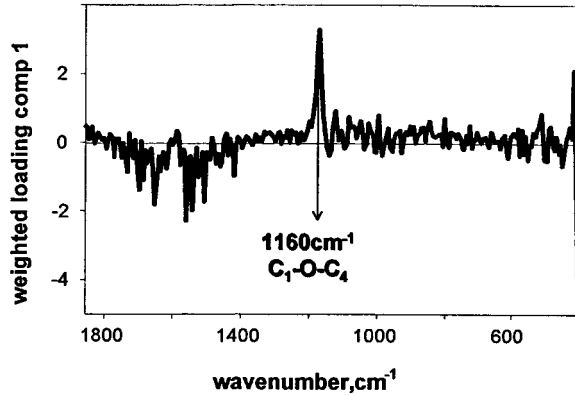
For the mechanical and NIR experiments, the RH was regulated by a humidity generator (VTI RH-200) that produced moist air at a flow rate of 70–100 mL/min and at RHs of 30 and 90%.

To assign spectral information to variations in the moisture, stress and creep time multivariate analysis was performed using Extract 3.0. Quantitative models were calculated from spectral data using partial least-squares regression (PLS).<sup>18</sup> The main feature of these multivariate models is their ability to calculate uncorrelated orthogonal regressors with the objective of maximizing the variance or covariance of the data set. In order to identify the spectral features corresponding to the variations in moisture content (stress and creep time), subspectra were obtained by plotting the loadings of the principal components for the spectral range measured.

## RESULTS AND DISCUSSION

### Creep at Increasing Stress

Figure 1 shows that the instantaneous dynamic elastic modulus in tension increases linearly with

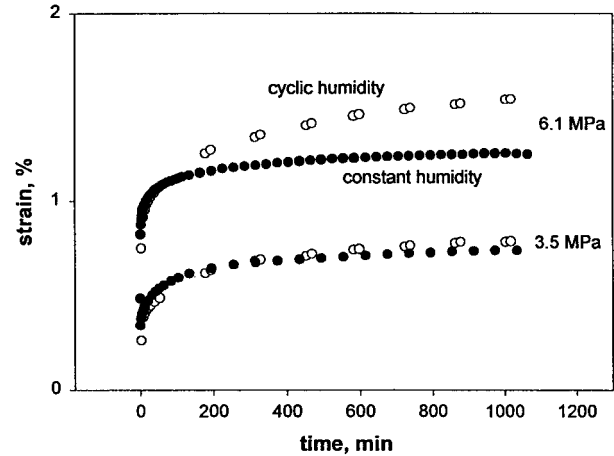


**Figure 3** The weighted loading for component 1 as a function of the wave number from a PLS analysis of mid-IR spectra versus stress from a stress scan in dry conditions.

increasing strain up to about 0.5%. At higher strains, the increase in modulus is less, presumably as an effect of plastic deformation. The increase in elastic modulus is in accordance with earlier observations of the deloading modulus<sup>9</sup> and the dynamic modulus of prestrained paper.<sup>10</sup>

It is evident in Figure 2 that the increase in tensile stress leads to an increase in moisture content in accordance with the observations of Kubát and Nyborg.<sup>6</sup> The amount of moisture sorbed by the material due to the stress is also similar to what was reported earlier. This can be interpreted as being due to an increase in the free volume with increasing tensile stress.

Figure 3 shows a loading spectrum from a PLS analysis based on mid-IR spectra with polarized light, which were taken successively under dry conditions during a stress scan up to a stress close to the breaking point of the sheet. The most pronounced peak covarying with the stress is the peak at  $1160\text{ cm}^{-1}$ , which is assigned to vibrations in the  $\text{C}_1\text{—O—C}_4$  bridge (the glucosidic linkage) in cellulose. Because the spectra are taken by polarized light, the  $\text{C}_1\text{—O—C}_4$  peak indicates an orientation of the cellulose chains during the deformation. This orientation may be an effect of orientation on the molecular, fibrillar, or fiber level. The orientation may also account for the increase in dynamic elastic modulus with increasing strain. This phenomenon, earlier referred to as strain hardening, is also accompanied by an increase in the internal stress level and Kubát et al. suggested<sup>10</sup> that it is a consequence of molecular orientation.

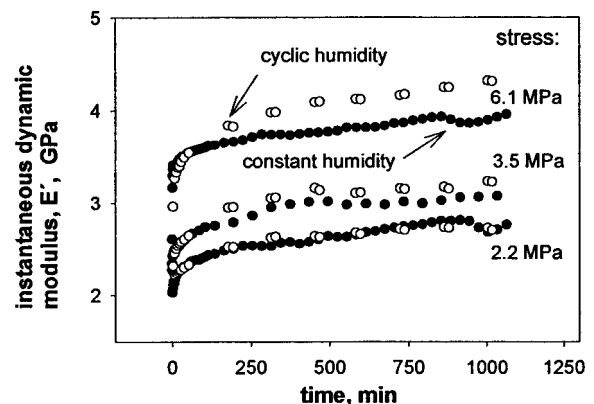


**Figure 4** The creep deformation at constant 90% RH and cyclic 90/30% RH conditions at two different stress levels.

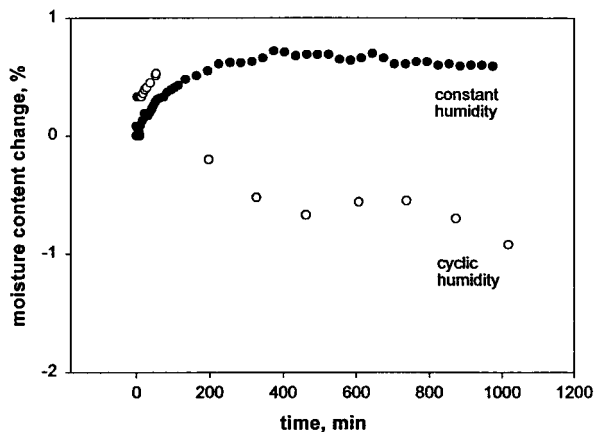
### Creep at Constant Stress

In Figure 4 the tensile creep deformations at constant and cyclic humidity are compared at different stress levels. Obviously, a mechanosorptive creep occurs (i.e., a greater creep during cyclic humidity than at constant humidity). This tendency increases with increasing stress levels. At the lowest stress level of 2.2 MPa no difference was observed, which is not shown in the figure.

Figure 5 contains a comparison of the instantaneous dynamic elastic moduli for creep during constant and cyclic humidity for different stress levels. Here the elastic modulus increases with time for all measurements, the increase being



**Figure 5** The instantaneous dynamic elastic modulus in creep experiments at constant 90% RH and cyclic 90/30% RH conditions at three different stress levels. The breaking stress for this paper is approximately 18 MPa at 90% RH.

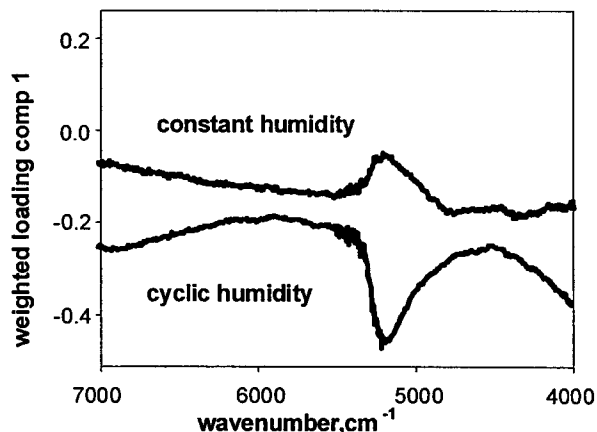


**Figure 6** The change in the moisture content calculated from NIR spectra during creep at constant 90% RH and cyclic 90/30% RH conditions under a load of 6.1 MPa.

somewhat larger under higher stress. Under cyclic humidity conditions the increase is larger than under constant humidity creep. The increase in modulus follows a trend similar to that of the increase in strain. This may indicate that it is the straining of the paper that is responsible for the increase in modulus in the same way as in a stress scan.

During constant creep the moisture content increases with time (Fig. 6), similar to the behavior for a stress scan, which could be characterized as a cumulative creep experiment. Almost all the moisture change may be associated with the application of the load, while very little happens during prolonged periods. For the samples subjected to cyclic humidity creep, the moisture content first increases during the first 90% RH period, which is similar to a constant creep. Thereafter, with each progressive cycle the moisture content decreases. To some extent this is a reflection of a similar decrease in the moisture content during the drying phase where the moisture content has not reached equilibrium during the 70 min. Under cyclic humidity conditions considerably longer times are necessary to reach equilibrium, a fact that could explain the difference in the results previously mentioned.

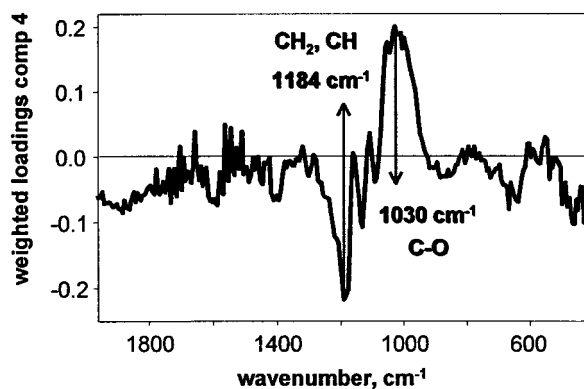
The NIR spectra of the paper exhibited a main covariation with time at about  $5150\text{ cm}^{-1}$ , which was associated with the adsorbed water. The change with time during creep experiments was examined by multivariate analysis of the PLS of the spectra versus the logarithmic creep time. In the load plots in Figure 7 most of the changes



**Figure 7** The weighted loadings for component 1 as a function of the wave number from PLS analysis of the time versus NIR spectra taken at 90% RH in creep tests with constant 90% RH and cyclic 90/30% RH.

during constant and cyclic humidity are associated with the change in moisture content (the peak at  $5150\text{ cm}^{-1}$ ). At creep under constant conditions the peak is positive, reflecting the increase in moisture content, whereas it is negative under cyclic humidity conditions. In the first PLS component, on average more than 97% of the variation of the spectral information explains about 90% of the variation in time.

Figure 8 shows the weighted loading of component 4 from the PLS analysis of mid-IR spectra versus the cycle number for papers under constant load and cyclic humidity conditions. The spectra were taken at the end of the drying period of each cycle. Two main features in the spectra can be noticed: a peak at about  $1030\text{ cm}^{-1}$  that is



**Figure 8** The weighted loading for component 4 as a function of the wave number from PLS analysis of mid-IR spectra taken in dry conditions versus the number of cycles in experiments with cyclic 90/30% RH.

assigned to CO stretching<sup>19</sup> and a peak at 1184  $\text{cm}^{-1}$  from rocking of  $\text{CH}_2$  or bending of CH bonds.<sup>20</sup> Thus, molecular changes other than the orientation of the cellulose occur during the cyclic creep. This mechanism could be sliding between the cellulose chains. No peak at 1160  $\text{cm}^{-1}$ , reflecting orientation of the cellulose molecule, is visible in Figure 8. This is due to the fact that all spectra were taken after the samples had been loaded.

When another set of spectra from unloaded samples were compared with spectra from creep under cyclic and constant humidity conditions after a deloading, the main difference was the peak at 1160  $\text{cm}^{-1}$ . Thus, the permanent strain remaining as a result of the applied load is also reflected in the permanent orientation of the cellulose molecules, which reflects the initial straining of the sample when a load is applied.

The analysis of the creep experiments thus indicates that the loading during creep under both constant and cyclic humidity results in an orientation of the cellulose chains in the direction of the straining. At creep in constant and cyclic humidity, the maintained load leads to additional deformations of the cellulose structure. Thus far, with mid-IR it was not possible to find any difference in the molecular changes between the two types of creep experiments.

## CONCLUSION

Paper samples adsorb moisture to a somewhat greater extent when subjected to tensile stress than under an unloaded equilibrium condition. Despite this, the instantaneous dynamic elastic modulus increases with stress, an effect presumably related to the orientation of the cellulose molecules. However, it should be remembered that the paper examined was very thin, which probably means that the effects seen are overemphasized compared to those in more compact, thicker paper structures.

During all types of tensile creep experiments the dynamic elastic modulus increased, an effect that may be related to the increase in orientation of the cellulose molecule due to the loading. Sliding between the cellulose chains may also occur during prolonged creep and eventually lead to failure. For creep at constant humidity an in-

crease in moisture content was detected as in the straining experiments. However, for samples subjected to cyclic humidity conditions, the moisture content after 70 min of absorption in 90% RH decreased with each cycle. Apparently, the conditioning of the samples was much slower than may normally be expected. Surprisingly, this nonequilibrium situation in the moisture content did not affect the dynamic elastic modulus, which attained its equilibrium value much faster.

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