Dynamic viscoelasticity and structural changes of regenerated cellulose during water sorption

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The dynamic viscoelasticity of regenerated cellulose was studied as a function of relative humidity (r.h.). At 50 and 80°C the dyanamic modulus E' decreased rapidly at about 70–80% r.h. and a steplike change in E' was observed at 50–60% r.h. Simultaneously, a peak in tan δ appeared at about 90–95% r.h. and a shoulder was observed at about 50–60% r.h. From the X-ray analysis and nuclear magnetic resonance study, the steplike change in E' and the shoulder in tan δ at about 50–60% r.h. may be caused by crystal growth accompanied by molecular rearrangement due to sorbed water. The significant drop of E' and the tan δ peak at 90–95% r.h. may be due to the onset of micro-Brownian motion in the plasticized chain molecules.

(Keywords: regenerated cellulose; dynamic viscoelasticity; moisture dispersion; sorption isotherm; glass transition concentration; nuclear magnetic resonance)

INTRODUCTION

Hydrophilic polymers such as cellulose and its derivatives are widely used in textiles, packaging, food, medical and related industries, etc. They are used frequently under wet conditions. The behaviour of sorbed water in hydrophilic polymers has been classified into three regions[1-4]:

Region I. A few water molecules are absorbed on hydrophilic groups, such as hydroxy groups, and a monolayer of water molecules is formed. The molecular motion of water in this region is strongly restricted by hydrophilic groups and the correlation time τ_c has been calculated[2] as 10^{-5}–10^{-7} s.

Region II. A multilayer of water molecules is formed around hydrophilic polymers. In this region, water breaks intra- or intermolecular hydrogen bonds in the amorphous phase. The τ_c value of water is of the order of 10^{-7}–10^{-9} s and the molecular motion of water may be affected by the water around hydrophilic groups. Sorbed water in this region is classified as bound water[4].

Region III. Water molecules are absorbed in polymers as bulk water or free water. The molecular motion of water cannot be restricted by polymer molecules and τ_c is calculated[2] as 10^{-9}–10^{-12} s. In this region, hydrophilic polymers are plasticized by water and the molecular motion of polymers is activated. The water content needed to form free water depends on the kind of hydrophilic group, the number of hydrophilic groups per mole of polymer, the molecular weight and the crystallinity of the polymer.

Water sorption behaviour of hydrophilic semicrystalline polymers is usually explained on the basis of the two-phase model (crystalline and amorphous phases), i.e. water is absorbed uniformly in the amorphous phase. However, it is reported that some semicrystalline polymers such as polyamide[5], poly(vinyl alcohol)[6] and polypropylene[7] have an intermediate phase between amorphous and crystalline phases. Polymer molecules in the intermediate phase are believed to be packed densely but not to form the crystalline region. Water sorption for such polymers first occurs in the randomly oriented region where the intermolecular force may be weak and proceeds to the highly oriented intermediate phase[5,6]. Sorbed water on semicrystalline polymers sometimes causes structural change[5]. The intermediate phase may also be produced in regenerated cellulose, when it is converted from natural cellulose[8]. Since cellulose molecules form strong intra- and intermolecular hydrogen bonds, the structural change caused by sorbed water can occur in the amorphous or intermediate phases.

The dynamic viscoelastic properties of water-sorbed hydrophilic polymers have generally been measured as a function of temperature (temperature dispersion). In this case, a shift of glass transition to a lower temperature[9,10] or the appearance of β-relaxation caused by the interaction between water and hydrophilic group[10,11] can be observed. The micro-Brownian motion of polymers can usually be observed as the glass transition in the temperature dispersion. However, in the case of hydrophilic polymers, this motion also occurs during water sorption or desorption processes. This can be observed by measuring the dynamic viscoelastic properties as a function of relative humidity (r.h.) at a constant temperature. We have already investigated the dynamic viscoelasticity of lignosulphonates as a function of r.h.[12,13] A transition corresponding to the primary relaxation (T_g) in the temperature dispersion was observed during water sorption. This transition was found to be dependent on molecular weight[12] and counter-ions[13]. As mentioned above, regenerated cellulose has an intermediate phase[8] and a structural change may occur during the process of water sorption.

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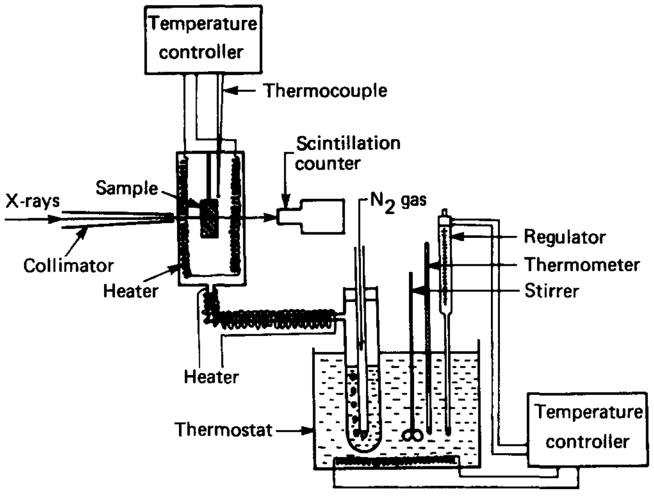

Figure 1 Apparatus for X-ray analysis of regenerated cellulose during water sorption at 80°C

In this paper, the dynamic viscoelastic properties of regenerated cellulose are measured isothermally as a function of r.h., and the structural change caused by sorbed water is studied.

EXPERIMENTAL

Cellophane of thickness 18 μm was used as a regenerated cellulose sample, which was supplied by Daicel Chemical Industries Ltd. The cellophane contains no additives and orientation is uniaxial with a birefringence index of $\Delta n = 8.6 \times 10^{-4}$. The crystallinity of the cellophane was estimated to be ~48% from the integrated intensities of the corrected X-ray diffraction curves of cellophane and amorphous cellulose in the region of $2\theta = 7$–$45°$.

The dynamic viscoelasticity of cellophane during water sorption was measured using a Rheovibron DDV-IIC (Orientec Co. Ltd) connected to a moisture generator, which has been described previously[12]. R.h. was controlled from 16 to 100% r.h. at 30°C, and from 5 to 100% r.h. at 50 and 80°C. The dynamic modulus E' and $\tan\delta$ were measured as a function of r.h. at 110 Hz.

The X-ray diffraction of cellophane during water sorption was measured using an apparatus as shown in *Figure 1*. The moisture generator was connected to the sample holder of an X-ray diffractometer (Rigaku Denki Co. Ltd). By controlling a thermostat at the dew point temperature, saturated vapour was sent to the sample holder maintained at 80°C. R.h. could be changed from 5 to 100% r.h. at 80°C. The X-ray diffraction patterns obtained with Cu Kα radiation at 30 kV and 30 mA were recorded with a scintillation counter. Since the (1 0 1) plane of cellophane is oriented parallel to the film surface, X-ray diffraction was measured from the edge of the sample. Corrections for air scattering, water scattering, incoherent scattering, absorption and polarization were made for the X-ray diffractograms obtained. To prepare the sample for X-ray diffractometry, the cellophane film was cut into strips about 1 mm wide and 10 mm long, and placed on top of each other to a thickness of ~2 mm.

The nuclear magnetic resonance (n.m.r.) of cellophane was measured with a Nicolet NT-200WB Fourier-transform n.m.r. spectrometer. The longitudinal and transverse relaxation times (T_1 and T_2) of ^{1}H were measured as a function of water content at 25°C. The T_1 value was measured by the 180°–τ–90° pulse sequence at 200 MHz. The T_2 value was obtained by the Meiboom–Gill variant of the Carr–Purcell method and by the solid echo method.

RESULTS AND DISCUSSION

Figure 2 shows sorption isotherms of cellophane at 30, 50 and 80°C, and a desorption isotherm at 30°C. The sorption isotherms of cellophane are typical sigmoidal curves. The temperature dependence of sorption isotherms indicates the exothermic sorption process: namely, the water regain at higher temperatures is lower than that at lower temperatures. Hysteresis is observed at 30°C as can be seen in *Figure 2*. One reason for the hysteresis in the case of polyamide or cellulose is that hydrogen bonds are broken during the absorption and the number of free hydrophilic groups increases in the desorption process[14].

Figure 3 shows the dynamic viscoelasticity of cellophane as a function of r.h. at 30, 50 and 80°C. At 30°C, E' decreases steadily with increasing r.h. At 50 and 80°C, it decreases significantly at 60–80% r.h. A steplike change in E' can be observed at about 60% r.h. at 50°C and at 50% r.h. at 80°C. The $\tan\delta$ value increases with r.h. At 50 and 80°C, $\tan\delta$ increases markedly at about 70–80% r.h. A peak is observed at 95% r.h. at 50°C and at 90% r.h. at 80°C. The water content at which the peak appears can be estimated as 24–26 wt % from the sorption isotherm given in *Figure 2*. This peak appears in the region II where sorbed water exists as freezing bound water[8].

Figure 4 shows the change in T_1 and T_2 as a function of water content W_c. Relaxation time T_1 has a minimum at $W_c = 0.2$–0.25, while T_2 increases steeply with water content. Child[15] observed the minimum in the T_1 *versus* water regain curve and the steep increase in T_2 over the same regain for various celluloses. Froix[16] also found the T_1 minimum at $W_c = 0.1$ at room temperature for cotton linters. Child[15] concluded that at regain values larger than that at the T_1 minimum, chain motion of cellulose increases because water molecules diffuse through the system and break intermolecular hydrogen bonds. According to our recent study[8], sorbed water in

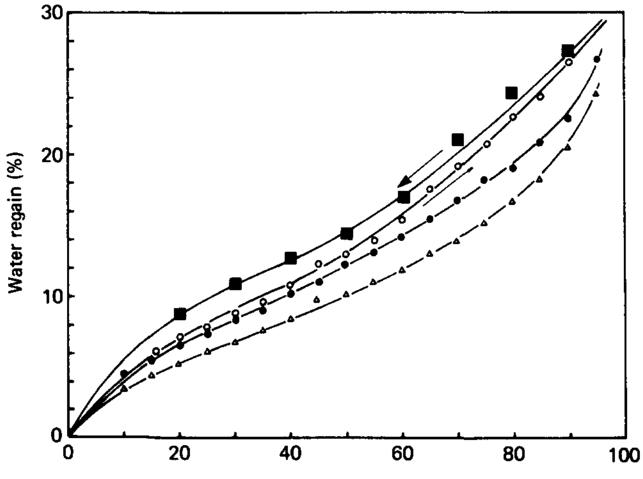

Figure 2 Sorption isotherms of regenerated cellulose at 30°C (○), 50°C (●) and 80°C (△), and a desorption isotherm at 30°C (■)

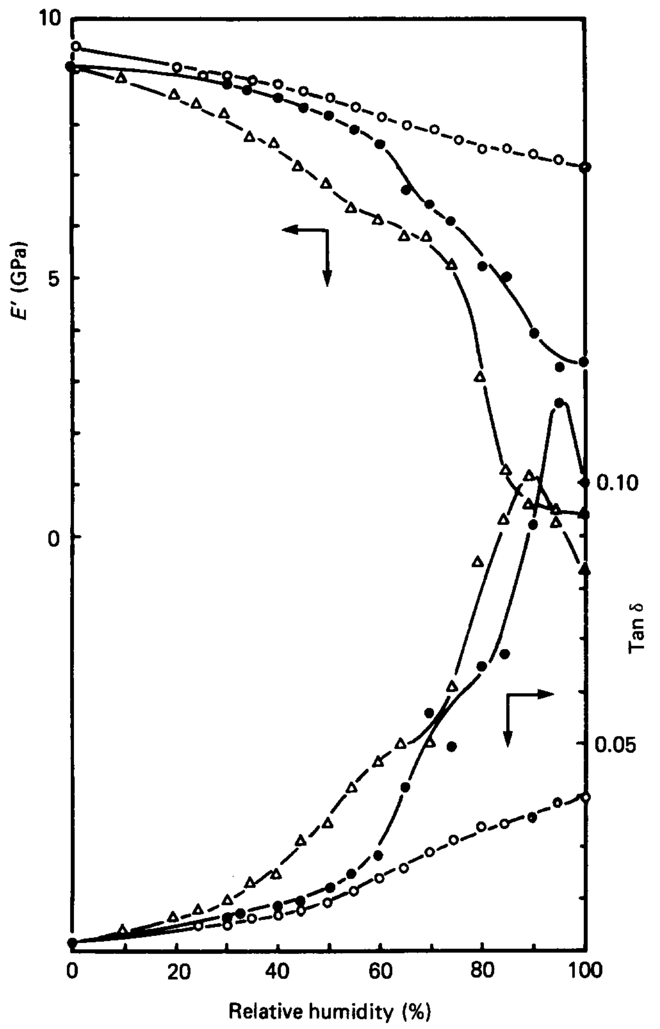

Figure 3 Dynamic viscoelasticity of regenerated cellulose as a function of relative humidity at 30°C (○), 50°C (●) and 80°C (△)

regenerated cellulose has been classified into three kinds of water, i.e. non-freezing bound water, freezing bound water and free water. D.s.c. studies showed that non-freezing water existed when W_c was lower than 0.25. Therefore, the T_1 minimum observed at $W_c = 0.25$ in *Figure 4* may appear corresponding to the boundary between non-freezing bound water and freezing bound water. If an approximation of the single-correlation-time model can be applied in the W_c range lower than 0.25 as well as in the previous report[17], τ_c can be calculated as follows: $\tau_c = 1.5 \times 10^{-7}$ s at $W_c = 0.15$ and $\tau_c = 1.0 \times 10^{-7}$ s at $W_c = 0.2$. This suggests that non-freezing water molecules are almost in the state of a non-rigid solid.

Accordingly the peak in tan δ curve at 50 and 80°C in *Figure 3* may be caused by the plasticization effect of sorbed water in region II. Micro-Brownian motion of cellulose molecules may occur due to sorbed water at ~95% r.h. at 50°C and at 90% r.h. at 80°C. However, plasticization by sorbed water at 30°C is not enough for micro-Brownian motion to occur in chain molecules. Lewis and Tobin measured the dynamic viscoelasticity of poly(methyl methacrylate)–benzene[18] and polystyrene–benzene[19] systems as a function of solvent concentration. A significant drop in the modulus and a peak in the logarithmic decrement were observed during the desorption process of solvents. They named this transition the glass transition concentration C_g by analogy with the glass transition temperature T_g in the temperature dispersion. The steep change in E' and the peak in tan δ at 50 and 80°C as shown in *Figure 3* correspond to the C_g.

As can be seen in *Figure 3*, the steplike change in E' and the shoulder in tan δ are observed at about 50–60% r.h. at 50 and 80°C. This behaviour seems to be related to the structural change of cellulose II during the water sorption process. *Figure 5* shows the X-ray diffractograms of the edge view of cellophane during water sorption at 80°C. When the cellulose absorbs water, the peak from (1 0 1) spacing that appears at $2\theta = 12°$ shifts to a small angle, while peaks from $(1 0 \bar{1})$ at 20° and (0 0 2) at 21° shift to a wide angle. This means that water diffuses into the crystalline region of cellulose II and the shape of the crystal lattice may be changed. Diffusion of water into the crystal structure has been reported for some polymers such as poly(vinyl alcohol)[20], polyamide[21] and cellulose II[22–24]. Ishikawa *et al.* found that the crystal lattice constant of the *a* and *c* axes for poly(vinyl alcohol)[20] and polyamide[21] were changed by diffusion of water into the crystals. Sakurada and Fuchino reported that water could diffuse into the crystal lattice of cellulose II[22] and that the (1 0 1) spacing increased by 0.3 Å[23]. Hermans and Weidinger[24] also reported that there was an increase in the (1 0 1) spacing of 0.4 Å by penetration of water between the lamella of the crystallites of cellulose II. In the present study, the increase in (1 0 1) spacing is found to be about 0.2 Å. Other spacings, $(1 0 \bar{1})$ and (0 0 2), decrease slightly during water sorption.

Figure 6 shows the change in the intensity and halfwidth of the (1 0 1) diffraction peak. The intensity from (1 0 1) spacing initially increases with r.h., and after reaching a maximum at about 80% r.h., it decreases with

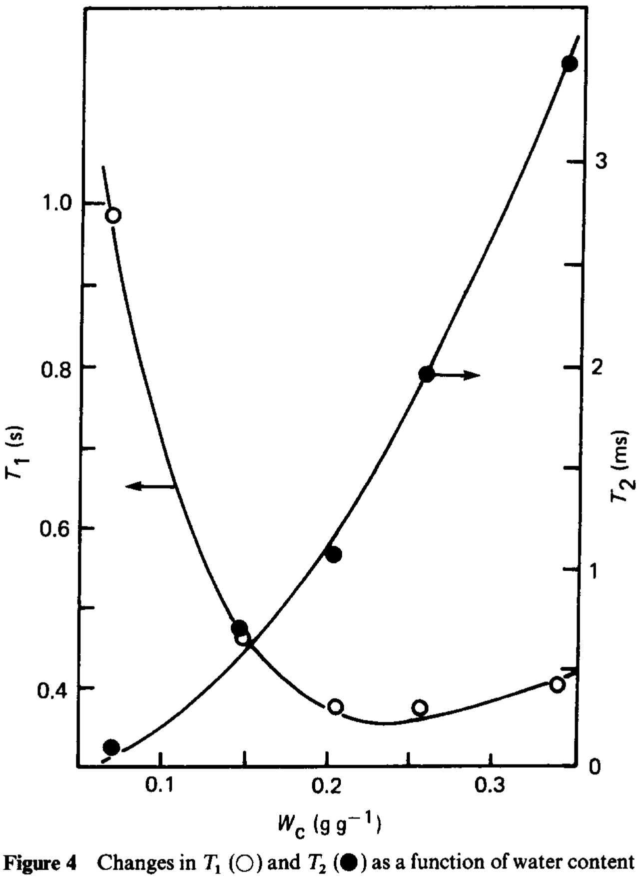

Figure 4 Changes in T_1 (○) and T_2 (●) as a function of water content

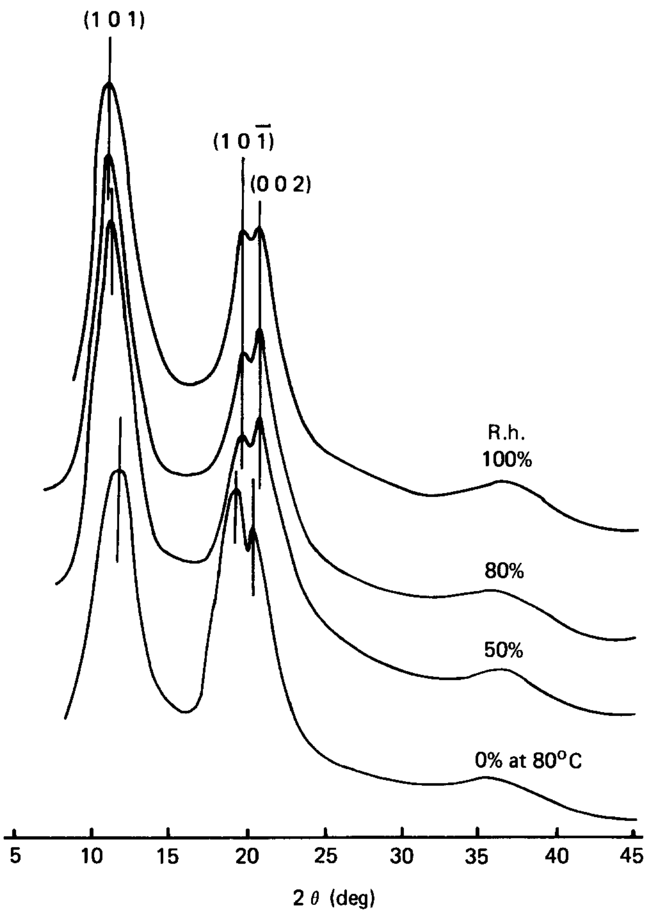

Figure 5 X-ray diffractograms of regenerated cellulose during water sorption at 80°C

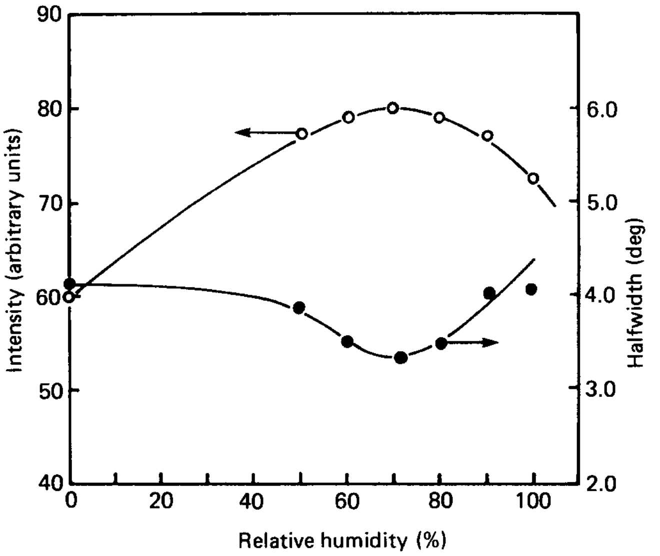

Figure 6 Changes in the intensity (○) and halfwidth (●) of the (1 0 1) diffraction peak during water sorption at 80°C

r.h. The halfwidth of the (1 0 1) peak decreases with r.h., and after having a minimum at about 70% r.h. it increases. Plasticization by sorbed water leads to molecular rearrangement and formation of hydrogen bonds. According to the Scherrer equation[25], crystallite size is inversely proportional to the halfwidth of the diffraction peak. The crystallite size of cellulose II may increase during water sorption up to about 70% r.h. It has been reported that crystallization of amorphous cellulose was accelerated by sorbed water and an increase in the modulus was observed above 52% r.h. at 20°C[26]. In the case of cellulose I, it was found that the size of the crystallites increased with water content[27]. As can be seen in *Figure 6*, the decrease in the intensity and the increase in the halfwidth are observed above 90% r.h. Recently it has been found that the X-ray diffraction peak from (1 0 1) plane has decreased at $W_c = 0.25$ and the peaks from (0 0 2) and (1 0 1̄) planes have decreased above $W_c = 0.75$[8]. It has been concluded that the crystallinity of cellulose II was decreased by sorbed water, which broke the hydrogen bonding in the crystalline region of cellulose II. In the present case, *Figure 6* may also indicate the decrease in crystallinity during water sorption above 90% r.h. ($W_c \geq 0.24$ converted from *Figure 2*). However, a more detailed study may be required to explain the decrease in crystallinity caused by sorbed water.

Consequently, as shown in *Figure 3*, the steplike change in E' and the shoulder in $\tan\delta$ curve at 50–60% r.h. at 50°C and 80°C may be due to crystallization accompanied by molecular rearrangement during water sorption. The steplike change in E' may be the result of overlap of the decrease in E' caused by plasticization and the increase in E' caused by crystallization. The significant decrease in E' and the large peak in $\tan\delta$ at 90–95% r.h. may be attributed to the onset of micro-Bronian motion in the amorphous phase during water sorption.

SUMMARY

The dynamic viscoelasticity of regenerated cellulose was measured as a function of relative humidity (r.h.) at 30, 50 and 80°C. At 30°C the dynamic modulus E' decreased monotonically and $\tan\delta$ increased with r.h. At 50 and 80°C, E' decreased rapidly at about 70–80% r.h., and a steplike change in E' was observed at 50–60% r.h. Simultaneously, a peak in $\tan\delta$ appeared at about 90–95% r.h., and a shoulder was observed at about 50–60% r.h. From the X-ray analysis, the steplike change in E' and the shoulder in $\tan\delta$ at about 50–60% r.h. may be caused by crystallization accompanied by molecular rearrangement due to sorbed water. The significant drop of E' and the $\tan\delta$ peak at 90–95% r.h. may be due to the glass transition concentration C_g (onset of micro-Brownian motion in the plasticized chain molecules during the water sorption process).

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