Influence of Water on Structure and Mechanical Properties of Regenerated Cellulose Studied by an Organized Combination of Infrared Spectra, X-ray Diffraction, and Dynamic Viscoelastic Data Measured as Functions of Temperature and Humidity

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ABSTRACT: An intimate relation between structure and mechanical properties of regenerated cellulose (Rayon, Benberg, etc.) has been investigated by measuring the humidity and temperature dependencies of infrared spectra, X-ray diffraction, and dynamic viscoelastic properties. At first the dynamic viscoelastic property and the infrared spectra were measured simultaneously during the increasing relative humidity at a constant rate (2% relative humidity/min) at room temperature. The Young's modulus was found to decrease remarkably around 40% relative humidity, where the content of the absorbed water increased largely as evaluated by the infrared spectral data. The water was considered to play a role as a plasticizer. Second, the temperature dependence of dynamic viscoelastic property was measured for the regenerated cellulose in a wide temperature region under the atmospheric environment. When the sample was heated from −150 °C, the anomalous phenomena could be observed in the temperature region of ca. −40 °C to room temperature: the Young's modulus was diverged, and the intensity and peak position of the X-ray reflections were shifted and the infrared absorbance of the water molecule increased. When the liquid paraffin was pasted on the surface of the cellulose sample, such anomalous phenomena were not observed. The temperature region of these anomalous changes was found to correspond to the region where the absorbed water molecules changed the aggregation state drastically from solid ice to liquid water. In other words, the change in the aggregation state of the absorbed water is considered to affect the mechanical behavior of the regeneated cellulose quite seriously.

Introduction

As reported in the previous papers,[1−4] we developed the new system of the simultaneous measurement of the infrared spectra and the dynamic viscoelastic properties of synthetic polymers under the control of relative humidity as a linear function of time. This system was found to be very useful for the investigation of the intimate relationship between structure and mechanical property of polymer materials. In particular, the system can change the relative humidity linearly with time, making it possible to measure the structure and the property as a function of humidity in a mode just similar to the thermal analysis using the DSC apparatus. This technique was applied to the several polymer samples such as poly(vinyl alcohol) (PVA), nylon 6, nylon 66, and poly(ethylene terephthalate) (PET). An influence of absorbed water molecules was found to be remarkably large for nylons and PVA and even for PET. For example, the dynamic viscoelastic properties of a dried nylon 6 film were measured continuously by increasing the relative humidity of the sample chamber linearly with time. The real part of Young's modulus E' decreased largely around the relative humidity of 40%, where the imaginary part of the modulus E'' and the tangent delta were found to show the peak. At the same time the elongation of the sample was found to develop in this humidity region. This slight extension of the sample length was induced by the absorbed water as a plasticizer under a static tensile force applied to the sample so as to avoid the slackening of the film. The simultaneously measured infrared spectra told us about the change of water content in the sample and the changes in the hydrogen bonds between polymers and between polymer and water. Around 40% relative humidity the water content increased appreciably, which affected largely the structure and mechanical properties of the nylon 6 film. The similar phenomena were observed also for nylon 66, PVA, and PET. In the case of PET, the content of the absorbed water was quite small, but the infrared spectrometer could detect this small amount of water.

In this way this system was found to be very useful for the investigation of an intimate relation between the structure and mechanical property of polymer in a convenient way as a function of humidity (and temperature). This system was applied also to the regenerated cellulose. The humidity was found to affect remarkably the mechanical properties of cellulose, the behavior of which was quite similar to those detected for the above-mentioned polymers. The influence of moisture on the mechanical properties of cellulose was well-known already,[5−10] but it must be emphasized that the structure change and the mechanical changes could be measured simultaneously for the cellulose sample. In addition to these measurements, the temperature dependence of dynamic viscoelastic properties was inves-

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Table 1. Characterization of Regenerated Cellulose Fibers

sample	cross-sectional area (mm^2)	crystallinity (%)	deg of chain orientation (%)
Rayon	0.0058	15.5	86.9
Benberg	0.0057	30.7	91.2
Newcell	0.0051	32.2	92.9

tigated for this polymer under an atmospheric environment. The result was quite curious. The Young's modulus and the sample length changed abnormally in the vicinity of −40 °C. The effect of humidity and temperature on the mechanical property of the regenerated cellulose has been studied extensively so far,[5−13] but such a curious phenomenon was found for the first time by carrying out the measurement using the newly developed system. The details of the experimental results will be reported in the present paper. The origin of this phenomenon will be discussed in association with the experimental data of infrared spectra and X-ray diffraction.

Experimental Section

Samples. Regenerated cellulose fibers, Rayon, Benberg, and Newcell were supplied by Asahi Chemical Industry Co. Ltd., Japan.[12] Some characterization results of these fibers are shown in Table 1. The film samples of ca. 7 μm thickness were also used in the measurement, which was prepared by casting from the viscose solution. The samples were washed by a mixed solvent of acetone and chloroform (1:2 molar ratio) for 1 day at room temperature in order to take away the oily components attached on the surface of the samples. The samples were dried up by heating at 120 °C for 12 h and stored in a desiccator.

Simultaneous Measurement of Dynamic Viscoelastic Property and Infrared Spectra. The infrared spectra and the dynamic viscoelastic property of these samples were measured by using the system described above. As shown in Figure 1, this system was consisted of the dynamic viscoelastometer and the Fourier transform infrared spectrometer. The used dynamic viscoelastometer was a DVA-300 developed by IT Keisoku Seigyo (Measurement-Control) Co. Ltd., Japan. The heating and cooling rates were controlled linearly with time at the rate of 5 °C/min. The relative humidity was also controlled as a linear function of time at a constant temperature: the humidity-increasing rate was 2%/min. The frequency of the tensile strain applied to the sample was 10 Hz. The infrared spectra were measured by using a rapid-scan-type Fourier transform infrared spectrometer FTS-60A/896 of Bio Rad Co. Ltd. The infrared beam was taken out of the spectrometer by inserting a flat mirror in the light pass. This infrared beam was focused to the sample position by a parabolic mirror. The infrared beam entered a small hole of the sample chamber of the viscometer and passed through the sample and was detected by an MCT (mercury cadmium telluride) detector positioned at the back of the dynamic viscoelastometer. The infrared spectrum was measured for 16 s in a rapid-scanning mode at every 5% of relative humidity. The resolution power of the spectrometer was 2 cm^{-1}.

The temperature dependence of the X-ray diffraction was measured by using a cryostat (Rigaku Denki Co. Ltd., Japan) in the range of −150 °C to room temperature. The X-ray diffraction profile was measured by using a Rigaku Denki RAD-ROC diffractometer with the graphite-monochromatized Cu−Kα line (λ = 1.541 78 Å) as an incident X-ray beam.

Results and Discussion

Humidity Dependence of Dynamic Viscoelastic Properties. The Young's modulus and the infrared spectra were measured for the Benberg film of 7 μm thickness by changing the relative humidity at the rate of 2%/min at 35 °C. The results are shown in Figure 2.

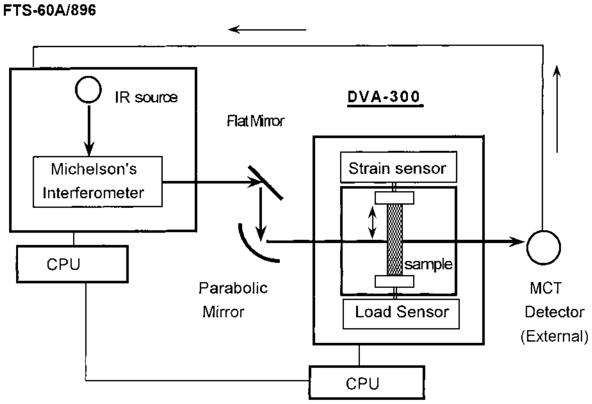

Figure 1. Schematic diagram of simultaneous measurement system of infrared spectra and dynamic viscoelastic property of polymers under the control of humidity and temperature as functions of time.

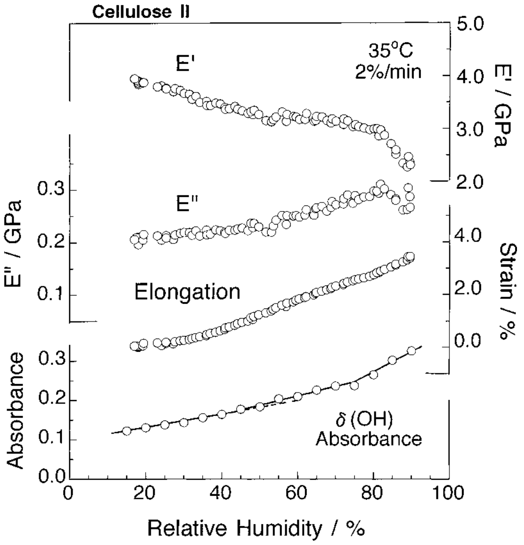

Figure 2. Relative humidity dependence of the dynamic viscoelastic property of regenerated cellulose film measured at 35 °C at the increasing rate of 2% RH/min. The infrared absorbance of OH stretching band is also plotted for comparison.

The real part E' of the Young's modulus decreased gradually with increasing humidity. Around 40% relative humidity, the E' showed a deflection point and changed more slowly. Above 80% relative humidity, the E' decreased again steeply. These changes were several times smaller than those detected for PVA and nylons. The imaginary part E'' of the modulus changed also with humidity but was difficult to detect the peaks corresponding to the changes in the E' (except for the region of 80% relative humidity) because the E'' itself was small. The sample was elongated slightly by increasing humidity because the small static weight was applied to the sample (the static force about 2 times larger than the dynamic force, e.g., 20 g for a bundle of fiber of 0.006 mm^2 cross-sectional area) in order to keep the sample from slackening during the measurement. The slope of this elongation changed around 40% relative humidity, corresponding to the deflection point of E'. Figure 3 shows the infrared spectra measured at the same time with the above-mentioned dynamic viscoelastic measurement. By increasing the relative humidity, the band at 1640 cm^{-1}, which is assigned to the OH bending mode of the absorbed water molecule as well as that of the cellulose OH groups, increased the intensity gradually.

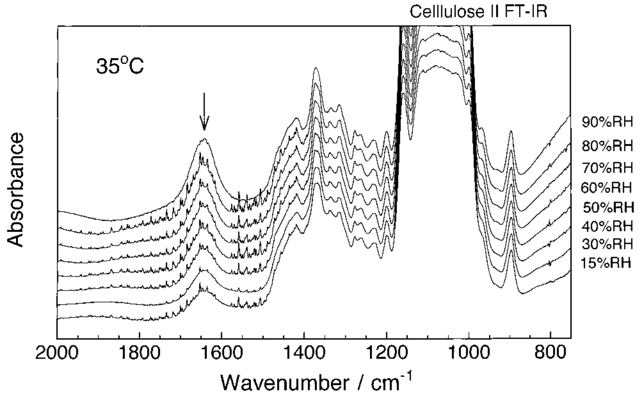

Figure 3. Relative humidity dependence of infrared spectra of regenerated cellulose film measured simultaneously with the dynamic viscoelastic property shown in Figure 2.

The similar change could be detected in the frequency region of 3500 cm^{-1}, OH stretching mode region. This region is quite important in the discussion of aggregation state of absorbed water,[14,15] but the evaluation of the intensity was not made in this study because the band intensity was saturated. The integrated intensity of the 1640 cm^{-1} band was plotted against humidity as shown in Figure 2. The band intensity increased gradually and changed the slope around 40% and 80% relative humidity, corresponding well to the dynamic viscoelastic data. This correspondence indicates clearly that the mechanical properties such as the Young's modulus and sample length were affected by increasing an amount of absorbed water molecules. The water molecules are considered to play a role as a kind of plasticizer making the film softer. It is said that water is difficult to penetrate into the crystalline region of cellulose but can enter only the amorphous region at room temperature.[16−19] Therefore, the absorbed water is considered to change the mechanical behavior of the amorphous region. In the vicinity of the relative humidity 70−80%, the infrared bands at 1278, 1268, 1370, 968, and 930 cm^{-1} and so on were found to increase their intensities. These bands are assigned to the vibrational modes associated with the hydroxyl groups of the cellulose chains. Therefore, we might speculate some change in structure or the change in the interaction between polymer and water by absorbing water molecules, although the details are not known at the present stage.

To check the effect of absorbed water on the mechanical property, liquid paraffin was pasted on the surface of the film. In Figure 4 are compared the humidity dependencies of the dynamic viscoelastic properties of the Benberg films with and without liquid paraffin. By pasting paraffin, the change of E' was clearly depressed: almost no decrement of E' was detected in the humidity region of 10−40% and around 80%. The sample length was also found to show smaller extension even when the humidity was increased up to 90%. At the same time, the infrared band at 1645 cm^{-1} originating from the absorbed water showed smaller increase than the case of the cleaned film without any contamination of oil. Therefore, by comparing the results of two types of the films with and without paraffin pasted, we can definitely clarify the role of the absorbed water on the mechanical properties of regenerated cellulose sample.

Temperature Dependence of Dynamic Viscoelastic Property. The dynamic viscoelastic properties were measured for the cellulose fibers starting from −150 °C.

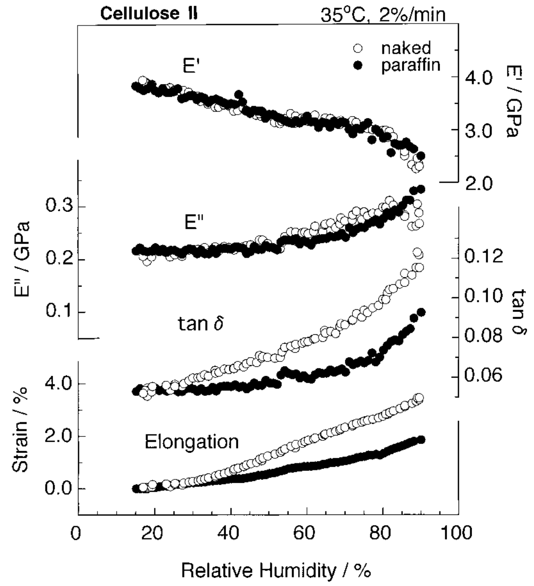

Figure 4. Comparison of relative humidity dependence of the dynamic viscoelastic property of regenerated cellulose film with and without liquid paraffin pasted on the surfaces.

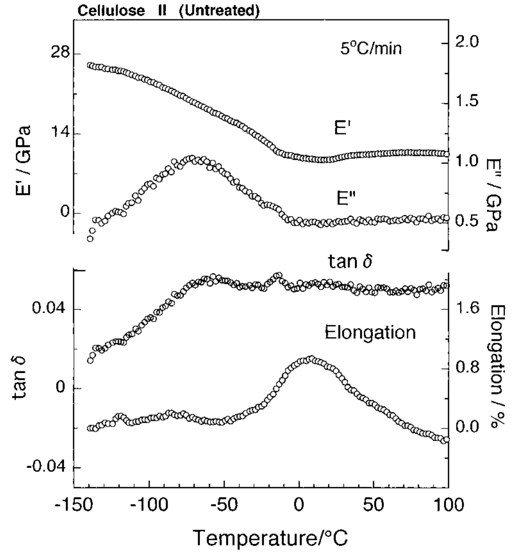

Figure 5. Temperature dependence of the dynamic viscoelastic property of the original regenerated cellulose fiber measured under the atmospheric environment.

Figure 5 shows an example of the result measured for Rayon fiber which was the original fiber and was not washed by solvents to take away oil on the surface. The E' showed some deflection points around −80, −50, +190 °C, etc., and the E'' showed the peaks correspondingly.[11−13] The E' changed, though more slightly, in the vicinity of −40, +20 °C and so on. The corresponding peaks of E'' could not be specified clearly because they were small and broad peaks. The sample length was found to change in these temperature regions, in particular in the region of −40 to +20 °C. These changes in E', E'', and sample length were detected in a similar way for all the kinds of cellulose fibers, Benberg, Rayon, and Newcell, although slight differences could be observed among them: for example, Newcell sample did not show the E'' peak around +190 °C, and the extension of the sample length was also smaller compared with the other fibers. They might come from the differences in the degree of chain orientation and the degree of crystallinity as listed in Table 1.

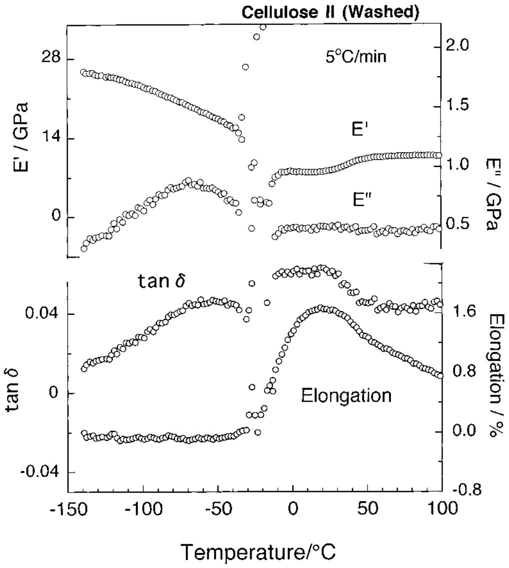

Figure 6. Temperature dependence of the dynamic viscoelastic property of the cleaned regenerated cellulose fiber measured under the atmospheric environment.

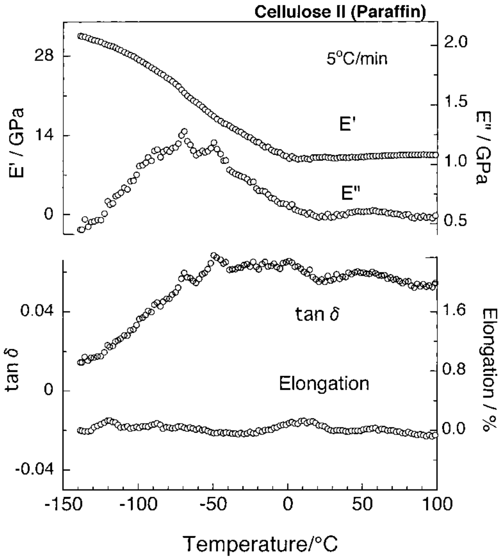

Figure 8. Temperature dependence of the dynamic viscoelastic property of the cleaned regenerated cellulose fiber with liquid paraffin pasted on the surfaces.

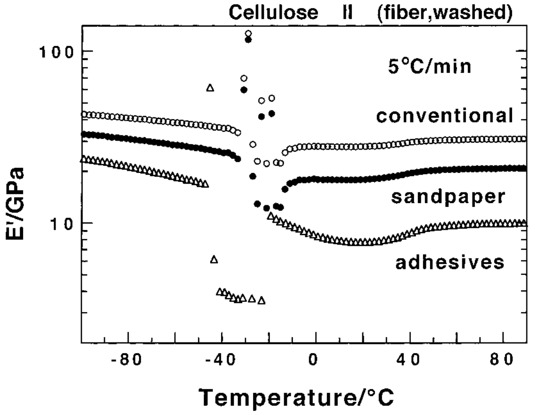

Figure 7. Temperature dependence of E' measured for the cleaned regenerated cellulose samples fixed to the metal holders by using sandpaper or adhesives. The "conventional" indicates the result obtained by the usual fixing method. The vertical axes of these curves are shifted arbitrarily in order to make the comparison easier.

Now we will see the temperature dependence of the dynamic viscoelastic properties measured for the Rayon fiber which was washed by acetone/chloroform mixing solvents. As shown in Figure 6, most of the data were essentially the same with those of the original sample except for the temperature region of −50 to −20 °C, where the E', E'', and the sample length showed the abnormal changes. For example, E' and E'' showed a random divergence and could not be measured exactly. The sample length showed also such an anomalous phenomenon. The similar phenomenon was observed also the washed Benberg and Newcell fibers. At first we doubted the slippage of the sample from the metal holder. Then, by using the sandpaper or even the adhesives, the sample was fixed more tightly between a pair of the metal plates of the holder. But any change in the abnormal phenomenon could not be detected as shown in Figure 7. Because the temperature region of −40 °C corresponds to the melting point of the ice water in the sample, we speculated this abnormal might come from the effect of the water molecules which show the remarkable change in the aggregation state. Then we pasted the liquid paraffin on the surface of the sample and measured the dynamic viscoelastic property again under the same conditions. The result is reproduced in Figure 8. Almost no abnormal divergence was detected, indicating the remarkably large effect of water invaded into the sample.

At this stage we have to consider one important point. So far the temperature dispersion of the dynamic viscoelastic property of the regenerated cellulose had been measured by many people.[5,11−13] But they did not report any such abnormal phenomenon in their papers. Why is it so? To interpret this abnormal phenomenon, we have to understand the measurement system of the present viscoelastometer. Usually the measurement is made by applying a sinusoidal strain, and the tensile stress of the sample is detected in parallel. To keep the sample from slackening, a slight static tension is given along the deformation direction of the sample. If the sample is elongated at a moment by some reasons, the sample is slackened more or less. Correspondingly, the tensile stress becomes smaller. Then, by increasing the span of the metal holder, the slackening of the sample is recovered. If the slackening of the sample is small and only for a short time, the recovery of the original state may be made soon. Therefore, almost no abrupt change of the modulus will occur apparently. But, if the elongation of the sample occurs appreciably and continues for a long time, the recovery to the tensioned state will take longer time, during which the Young's modulus cannot be evaluated correctly, giving a divergence of the E' and E''. By controlling the static tensile stress constantly, this problem might be avoided, but the forced elongation (or contraction) of the sample length will change the condition and suppress the phenomenon intrinsic of the sample. In fact, we could control the system to keep the tensile stress almost constantly by adjusting the sample length quite frequently, and the curves of E' and E'' changed apparently smoothly. But, by carrying out this adjustment, we might cover the original phenomenon itself. In other words, we might say that the measurement condition of the present dynamic viscoelastometer worked as a sensitive detector of the change in the sample length. The observation of the divergence of the modulus is a reflection of some abnormal phenomenon occurring

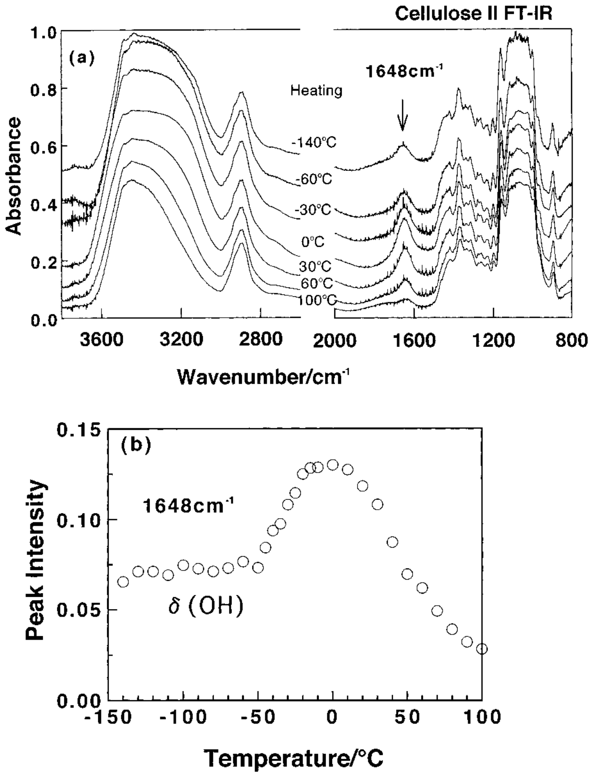

Figure 9. (a) Temperature dependence of infrared spectra of the cleaned regenerated cellulose film measured simultaneously with the dynamic viscoelastic property shown in Figure 6. (b) Temperature dependence of infrared absorbance of 1648 cm^{-1} OH bending band.

actually in the sample in the vicinity of −40 °C. This is supported by the observation made for the paraffin-coated sample. This sample did not show almost any abnormal divergence of the modulus, although the measurement condition (including the averaging process and so on) was almost perfectly the same. Besides, we have another experiment. The sample was dipped in water before the measurement, and the wet cloths were put outside the sample chamber. These processes were performed so that the water content in the sample increased more. This sample gave the extremely large change of the length in the temperature region of −40 °C to room temperature. In another experiment, we applied the very large static force (about 4 times larger than the usual cases) along the sample direction so that the sample could keep its length from any change such as slackening. As the result, no abnormal observation was made in the temperature region of −40 °C. Therefore, from all these experimental results, we may conclude confirmatively that the mechanical property of the sample changed too drastically in the temperature region of −40 °C, giving the abnormal curve in Figure 6.

As already pointed out, this temperature region corresponds to the melting temperature of ice absorbed in a material. The change of the aggregation state of water molecules in the cellulose sample is considered to give the remarkable change in the mechanical behavior of the cellulose. This can be checked by analyzing the simultaneously measured infrared spectra as seen in Figure 9a. The temperature dependence of the absorbance of the OH bending band at 1648 cm^{-1} is shown in Figure 9b. In the low-temperature region the band intensity was low. Around −50 °C, the band intensity started to increase remarkably and showed the maximum around 0 °C and decreased as the temperature increased furthermore. The temperature region of this remarkable spectral change corresponds well to the above-mentioned abnormal phenomenon. The molar extinction coefficient of ice is much smaller than that of liquid water. Therefore, an increase of the infrared band intensity indicates the change of the aggregation state of the absorbed water from ice to liquid water. The intensity decrement in the region higher than room temperature is due to the evaporation of liquid water from the sample. We had another experimental data supporting this intimate relation between the melting of ice and the abnormal mechanical behavior of cellulose. Figure 10 shows the temperature dependence of the *E′* measured for the cleaned cellulose fiber. In the experiment of Figures 6−9, the sample was cooled to −150 °C at first and then was heated at a constant rate (5 °C/min). The absorbed water was considered to be frozen into ice by cooling the sample down to −150 °C. In Figure 10 the cooling was stopped at higher temperature before reaching −150 °C, and then the mechanical property was started to be measured by heating the sample from this temperature. When the lowest temperature was −140, −100, or −80 °C, the abnormal divergence was observed for this sample. But, when the lowest temperature was −50 °C, almost no abnomal phenomenon could be detected for *E′* under almost the same measurement conditions. The freezing point of water absorbed in the sample is −20 to −30 °C (for free water) and −30 to −50 °C (bound water).[6,7] Therefore, it is speculated that, in the case of −50 °C, the water molecules absorbed in the sample was not totally frozen to ice. Therefore, in the heating process from such a liquid state did not cause any drastic change of the mechanical behavior of the cellulose sample.

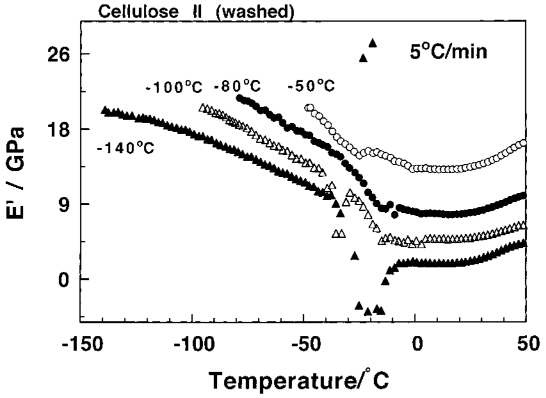

Figure 10. Temperature dependence of *E′* measured for the regenerated fibers which were cooled at first down to the temperatures indicated on each curve and then heated to higher temperature.

Temperature Dependence of X-ray Diffraction. In the previous section we pointed out that the melting of ice water absorbed in the cellulose fiber affected the mechanical behavior of the fiber dramatically in the temperature region of −40 °C. At the same time, we pointed out also that the water molecules may be absorbed mainly in the amorphous region. But we need still to check the effect of the water on the behavior of the crystalline region. Then the X-ray diffraction measurement was made in the same manner starting from −150 °C. The measured reflections were 004, 110, $1\bar{1}0$, and 020 where the *c* axis was taken in parallel to the chain axis.[20,21] A bundle of the regenerated cellulose

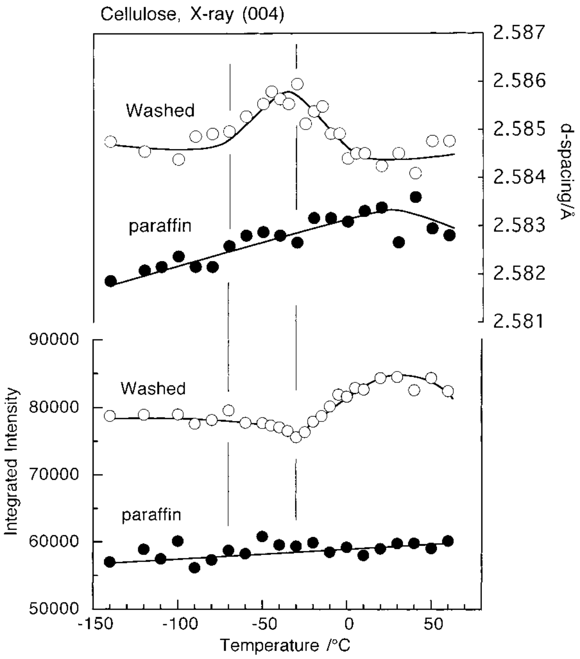

Figure 11. Temperature dependence of the lattice spacing and integrated intensity of the 004 reflection measured for the regenerated cellulose fibers with and without liquid paraffin coated on the surfaces.

fibers was wound around the metal holder tightly, just like the case of tensile force applied to the sample in the dynamic viscoelastic measurement, and was inserted into the cryostat for the X-ray diffraction measurement. The sample was cooled to −150 °C, and the X-ray diffraction profiles were measured step by step at constant temperatures. The measurement of the 004 reflection was made in the transmission mode. For the measurement of the equatorial reflections, the reflection mode was used. Figure 11 shows the temperature dependence of the lattice spacing and the integrated intensity evaluated for the 004 reflection for both the samples with and without paraffin coated on the surface. In the temperature region of −40 °C, the lattice spacing was found to show abnormal increase. This abnormal maximum was not detected for the paraffin-coated sample. The scattering intensity also showed a large deviation from the flat line. As for the equatorial reflections, we could also observe the abnormal behavior for both the lattice spacing and the intensity.

As already stated, water is considered to enter mainly the amorphous region. But, as seen in Figure 11, the X-ray diffraction from the crystalline lattice showed an abnormal behavior. Therefore, we may assume that the water molecules can interact with the cellulose chains at the boundary between the crystalline and amorphous regions, for example, on the surface of the crystallite. The water molecules frozen on the surface of crystallites are melted and change into the liquid state around −40 °C, and this change on the surface affects the internal structure of the crystallite more or less. As a more concrete idea, which was pointed out by one of the reviewers for our original manuscript, we might speculate that the ice crystals are getting larger by annealing before melting and thus lead to internal stresses from the surfaces of the crystallites. This could explain why the change in the lattice spacing occurred only temporarily around −40 °C and went back to the original value at higher temperature. To check such a speculation, we need to study this anomalous phenomenon in more detail.

Conclusions

In the present paper we reported the usefulness of the system of simultaneous measurement of FTIR spectrometer and dynamic viscoelastometer for the study of the effect of absorbed water on the mechanical behavior of the regenerated cellulose sample under the systematically controlled humidity and temperature. In the first section the effect of humidity on the Young's modulus of the dried cellulose sample was measured at room temperature. A good correspondence could be detected between the decrease of the modulus and the increase of water content.

In the second part of this paper we described the abnormal mechanical behavior in the heating process of the cellulose sample with the cleaned surface. This abnormal phenomenon was related with the melting of ice water into liquid state. Besides, even the internal structure of the crystalline region was found to be affected more or less by this transition process, although the water molecules were considered to be difficult to invade into the crystalline region, and only the surface of crystallites might be affected by water. Our image of structural change is as follows. In the low-temperature region, the water molecules are frozen and trapped in the amorphous region and on the surface of the crystallites. By heating the sample up to −40 °C, the frozen water or ice crystal becomes larger by annealing before melting and then leads to the internal stresses to the crystal lattices, as detected by the X-ray diffraction measurement. Above the melting point, the crystal ice changes to liquid, as being detected as the intensity change of infrared band of the absorbed water. This liquid water is considered to play a role as a plasticizer, and the mechanical property and the mobility of the chain are affected largely and the sample length is changed (by a slightly applied static tensile force). In the present paper we did not classify the absorbed waters into the several types of groups such as tightly bound water, weakly bound water, and free water. It may be important to clarify the roles of these different types of water molecules in the change of the mechanical behavior of the cellulose sample through the quantitative analysis of the water band profiles in the infrared spectra.

In the temperature region of −80 to −50 °C, the regenerated cellulose shows two peaks as seen in Figures 5 and 6, which were assigned to the β relaxations or the molecular motions in the amorphous region.[12−14] The divergence in the −40 to −20 °C might be related with such a molecular motion in the amorphous region or on the surface of the crystallites and might not be related with the change in the aggregation state of water as mentioned above. But the similar phenomenon could be detected also for the other kinds of polymers such as nylon 6, PET, etc., which should show the molecular motions in the amorphous region in much higher temperature regions. Therefore, we might speculate that the dramatic change in the aggregation state of frozen water gives the remarkable influence on the structure (and motion) of the amorphous region of these polymers, which absorb water molecules to some extent. The details on the experimental data obtained for nylon 6, PET, and so on will be reported in a separate paper.

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