DC Electrical Conductivity of Cellulose

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ABSTRACT: DC electrical conductivity was measured from room temperature to about 230°C for Cellulose I and Cellulose II. The conductivity *vs.* temperature curve showed a break at about 150°C for Cell I and at about 80°C for Cell II. The break points corresponded to those observed previously in the spacing *vs.* temperature curves. These phenomena may possibly be associated with the second order transition at which the restricted motion of chain segments in the crystals begins to acquire high mobility. The conductivity in the fiber axis direction was approximately ten times as large as that in the perpendicular direction.
    KEY WORDS   Cellulose I / Cellulose II / Transition Point / DC Electrical Conductivity /

In a previous paper,[1] it was found for Cell I (Cellulose I) and Cell II (Cellulose II) that the temperature coefficients of the spacings and intensities of X-ray reflections change discontinuously at 150°C for Cell I and at 100°C for Cell II. This suggests that these crystals undergo second order transitions at these temperatures. The present work was undertaken to confirm this, by measuring the dc electrical conductivity from room temperature to about 230°C for both Cell I and Cell II. Furthermore, the anisotropy of the dc electrical conductivity was studied in the directions of intermolecular and intramolecular hydrogen (chain direction) bonds to observe the effects of hydrogen bonds on the electrical conductivity.

EXPERIMENTAL

The samples of Cell I were prepared from softwood tsuga (*Tsuga sieboldii* CARR) and hardwood kaba (*Betula tauschii* KOIDZ), both of which showed clear X-ray meridional reflections. The crystallinities of the untreated samples were almost the same. The samples of Cell II were prepared by measerizing tsuga and kaba with 30% NaOH for 240 h followed by regeneration by washing with cold water. The degree of transformation from Cell I into Cell II was 0.9—1.0, when estimated by Ranby's equation.[2] All the samples were treated with 4 N-HCl at 100°C for 2—10 h to remove any lignin and hemicellulose in the wood.

The sample was parallelpiped in form (10 mm × 10 mm × 15 mm). The arrangement of electrodes and the direction of electric current is illustrated in Figure 1. Stainless steel was used as the electrodes. Silver conducting paste (du Pont Electro-Chemicals Department No. 5504) was spread on both sides of the sample and heated at 200°C for 70 min in order to insure closer contact between the stainless steel and wood.

DC electrical conductivity was measured with the dc amplifier shown in Figure 2. The maximum applied voltage was 300 V and the standard resistance, 1 kΩ. Prior to each measurement, the specimen was dried at 100°C for about 2 h under a pressure of 10^{-3} torr.

RESULTS AND DISCUSSION

The temperature dependence of the dc electrical conductivity σ of Cell I (tsuga) hydrolyzed with 4 N-HCl at 100°C for various hours is shown in Figure 3. Figure 3A is for the fiber direction and Figure 3B, for the direction perpendicular to it. Breaks are seen at temperatures of about 150°C in both directions, and the temperature of the break point decreases slightly as the hydrolysis reaction proceeds. Figure 4 shows the relationship between electrical conduc-
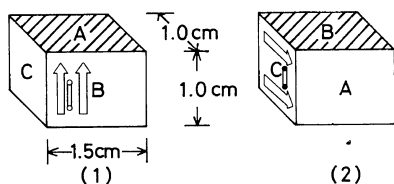
Figure 1. Arrangement of electrodes for measurement of conductivity in the (1) fiber direction and (2) tangential direction: A, cross face; B, radial face; C, tangential face; ▨, electrode; ⇒, fiber axis; ⊂⇒⊐, intramolecular hydrogen bond; ●━▶, intermolecular hydrogen bond.
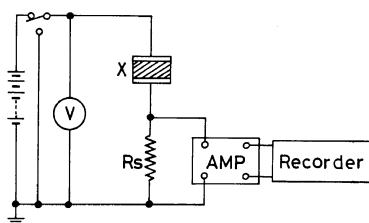

Figure 2. Schematic diagram of the apparatus for measuring time-dependent conductivity in a d.c. field: V, voltmeter; X, sample; Rs, standard resistance.

tivity and temperature for Cell I (tsuga) and Cell II (tsuga), each hydrolyzed with 4 N-HCl at 100°C for 6 h. The break point for Cell II is located in the vicinity of 80°C.

The break points found here correspond to those previously observed in the crystal spacing *vs.* temperature curves.[1] The apparent activation energy ΔH^* was estimated from Figures 3 and 4, with the results shown in Table I. The activation energy ΔH^* of Cell I is constant for samples hydrolyzed for more than 2 h. Cell II gives similar values for ΔH^*. The dissociation energies can be calculated by substituting these activation energies into Murphy's equation,[3] *i.e.*,

$$\sigma = \sigma_{01} \exp\left[-(\tfrac{1}{2}W_d + W_a)/RT\right]$$
$$+ \sigma_{02} \exp\left(-W_a/RT\right)$$

where W_d is the energy for dissociation into ion pairs and W_a is the activation energy for the mobility of these ions. The calculated dissociation energies of 1.2—1.4 eV are smaller than 1.72 eV estimated for the activation energy for thermal decomposition.[3,4] Therefore, it is unlikely that the marked increase in dc conductivity above the break
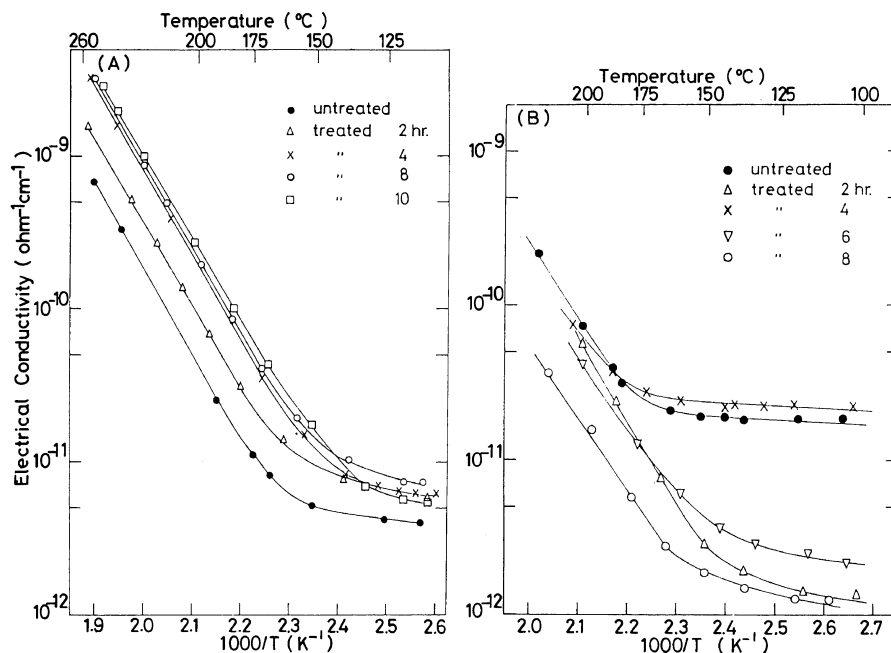
Figure 3. Temperature dependence of the d.c. conductivity for Cell I (tsuga) hydrolyzed with 4 N-HCl at 100°C for indicated hours: A, fiber direction; B, tangential direction.
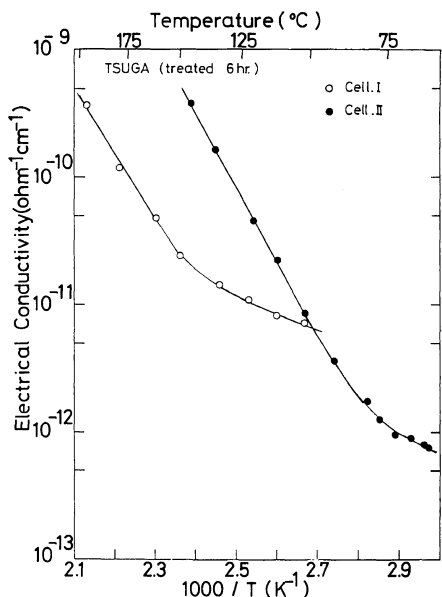
Figure 4. Temperature dependence of the d.c. conductivity for Cell I and Cell II in the fiber direction.

Table I. Values of apparent activation energy ΔH^* of Cell I

Sample	$\Delta H^*/eV$ (above break point)		$\Delta H^*/eV$ (below break point)	
	$\parallel$[a]	$\perp$[b]	$\parallel$	$\perp$
Tsuga	1.1	1.0	0.5	0.3
Kaba	1.2	1.0	0.4	0.3

[a] Fiber direction.
[b] Perpendicular direction.

point is due to an increase in the number of charge carriers caused by decomposition.

It has been found[5,6] that the temperature coefficient of the electrical conductivity of polymers increases suddenly at the glass transition temperature T_g. This phenomenon can be interpreted qualitatively as resulting from a remarkable increase in the mobility of the current carriers due to activated segmental motion of the amorphous chains. In our case, however, the break points of 150 and 80°C were far below the T_g of cellulose (>240°C).[7,8] It has been proposed[9] that cellulose has another second order transition at about 113°C and this may be attributed to enhanced thermal motion caused by
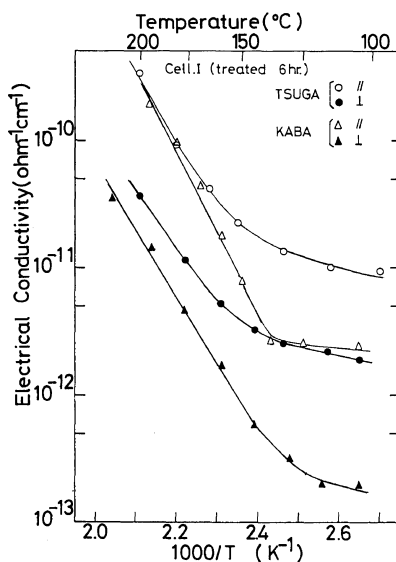

Figure 5. Temperature dependence of the d.c. conductivity for tsuga (Cell I) and kaba (Cell I) in two directions; //, fiber direction; $\perp$, tangential direction.
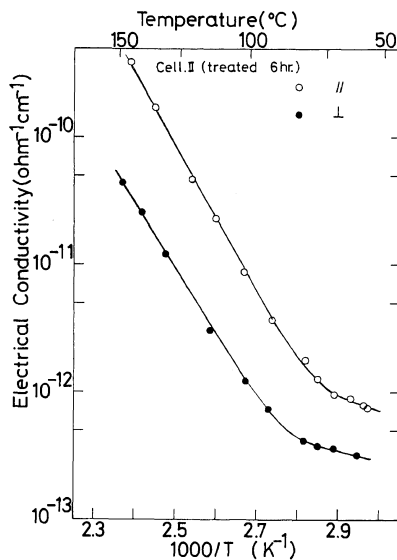

Figure 6. Temperature dependence of the d.c. conductivity for Cell II (tsuga) in two directions; //, fiber direction; $\perp$, tangential direction.

the breaking of weak hydrogen bonds. Therefore, the break points observed in the electrical conductivity curves may be considered as reflecting the second order transition of the crystal. It should be
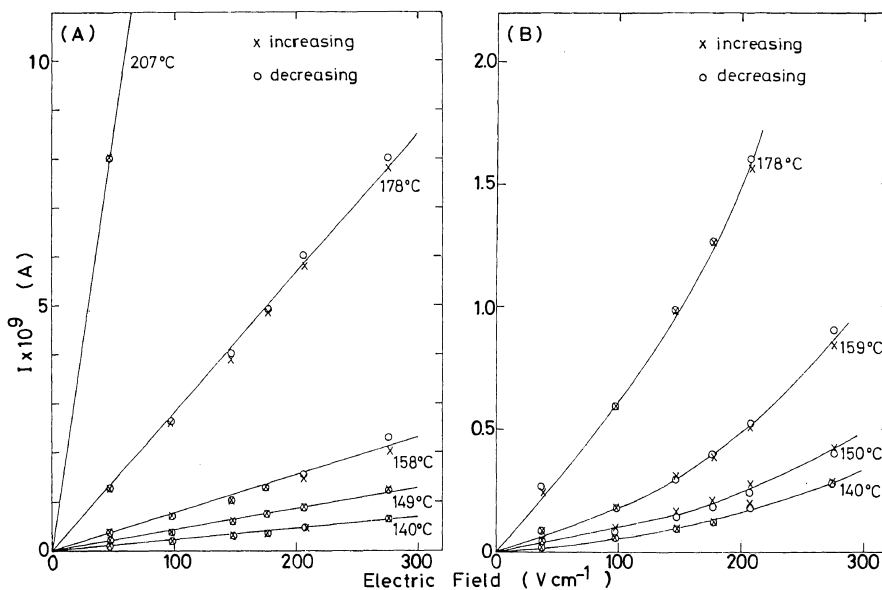
Figure 7. Voltage-current characteristics in Cell I (tsuga) in two directions: A, fiber direction; B, tangential direction.

noted that the transition point T_r for Cell II (80°C) is much lower than that for Cell I (150°C). The difference may be due to the greater flexibility of the Cell II chain. Therefore, the marked increase in electrical conductivity above T_r may be attributed mainly to an increase in the mobility of the current carriers.

Our interest was directed to the anisotropic dc electrical conductivities in the directions of intramolecular (fiber direction) and intermolecular hydrogen bonds (perpendicular direction). Figure 5 shows the values of σ in these two directions plotted against $1/T$ for Cell I (tsuga and kaba) treated with $4\,N$-HCl at 100°C for 6 h. The conductivity in the fiber direction is approximately ten times as large as that in the perpendicular direction. A similar result was obtained from the temperature dependence of σ for Cell II shown in Figure 6.

Figure 7 shows the voltage-current characteristics for these two directions of Cell I (tsuga) at various temperatures. Results similar to those in Figure 7 were obtained for Cell II. The voltage-current curves in the perpendicular direction show a non-linear relation in contrast to those in the fiber direction. This nonlinear effect may be due to a potential barrier which always exists in poly-

mers.[10,11] Thus, the electric current in the tangential direction is disturbed by the potential barrier more intensely than that in the fiber direction.

CONCLUSION

The dc electrical conductivity vs. temperature curve shows a break at about 150°C for Cell I and about 80°C for Cell II. The break points correspond to those observed in the spacing vs. temperature curves, implying that they are related to the second order transition of crystals above which the restricted segmental motion of the chain becomes free. The conductivity in the fiber direction was approximately ten times as large as that in the perpendicular direction.

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