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Thermally Stimulated Current of Tsuga (*Tsuga sieboldii* CARR) in Cellulose I

Masae TAKAHASHI and Haruko TAKENAKA

Faculty of Home Economics, Japan Women's University, 2–8–1 Mejirodai, Bunkyo-ku, Tokyo 112, Japan

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ABSTRACT: Thermally stimulated current (TSC) of tsuga (*Tsuga sieboldii* CARR) in Cellulose I has been measured for the fiber and tangential directions in the temperature range from -20°C to 200°C. Three peaks A, B, and C for the fiber direction are observed at about 30°C, about 85°C and about 160°C, respectively. The peaks A and B appear for the tangential direction. The TSC currents I_{max} of the peaks A and B are proportional to the thickness of the sample, and increase with the polarizing field in the relation of the sine-hyperbolic equation. The peaks A and B are considered to be due to ionic space-charge polarization caused by the migration of mobile ions between neighbour-sites and next neighbour-sites of the long period with hopping.

KEY WORDS Cellulose I / Thermally Stimulated Current / Mobile Ion / Space-Charge Polarization /

In a previous paper,[1] it was found that the conductivity *vs.* temperature curve showed a break at about 150°C for Cellulose I (Cell I) and at about 80°C for Cellulose II (Cell II) in accordance with the spacing *vs.* temperature curve.[2] These breaks are possibly associated with the second order transition.

To study on the transition and the molecular motion in more detail, it is useful to observe the thermally stimulated current (TSC) which has been shown to be sensitive for the carrier detrapping process. An activation energy from the TSC shows an apparent trap depth modified by molecular motions.[3]

In this paper, thermally stimulated current of tsuga (*Tsuga sieboldii* CARR) in Cell I is reported, and furthermore, in order to clear the molecular motion of cellulose, some attempts to assign each peak in TSC spectra are undertaken.

EXPERIMENTAL

The sample of Cell I was prepared from soft wood tsuga, which showed clear X-ray meridional reflections as shown in Figure 1. The crystallinities of the samples were almost the same.

The sample was parallelpiped in form having a thickness of 10, 5, and 2.5 mm and a area of electrode side of 10 mm × 15 mm. The arrangement of electrodes and the direction of electric current is illustrated in Figure 2. Stainless steel was used as the electrodes. Silver conducting paste (du Pont Electro-Chemicals Department No.5504) was spread on both sides of sample and heated at 200°C for 70 min in order to insure closer contact between the stainless steel and wood. Experimental block diagram is shown in Figure 3. Before each measurement, the specimen was dried at 100°C for about 2 h under a pressure of 10^{-6} Torr. A measuring process of TSC was as follows. A polarizing electric field E_p was applied to a sample at a polarizing temperature T_p for a polarizing time t_p. Then the sample was cooled by the vapor of the liquid nitrogen to a low temperature (-20°C) with

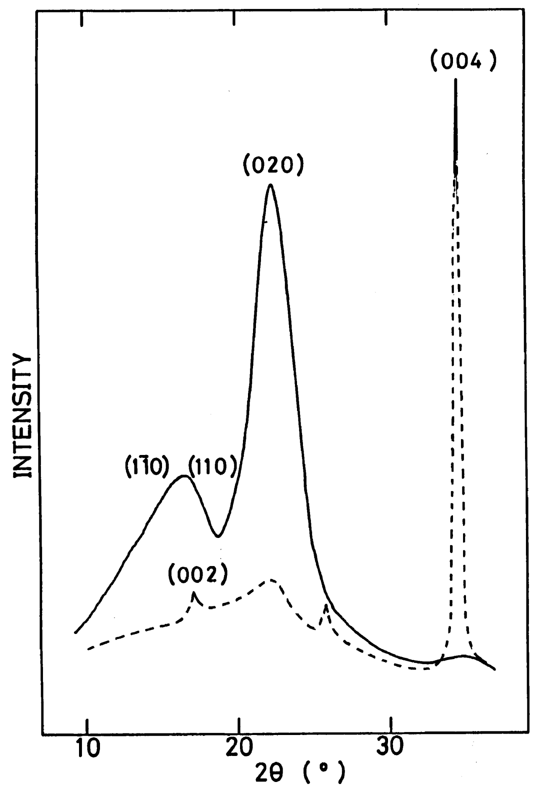

Figure 1. X-Ray diffractogram of *tsuga* (Cell I): ——, equatorial pattern; ----, meridional pattern.

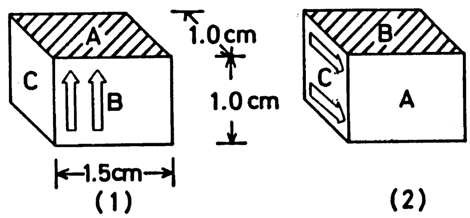

Figure 2. Arrangement of electrodes for measurement of TSC in the (1) fiber direction and (2) tangential direction: A, cross face; B, radial face; C, tangential face; ▨, electrode; ⇨, fiber axis.

applying field E_p. From this temperature, the sample was heated at a constant rate β from $-20°C$ to 200°C, and the current, *i.e.*, TSC was measured in the short circuit condition.

RESULTS AND DISCUSSION

Figure 4 shows TSC for fiber direction with various T_p and with constant E_p ($56\,kV\,m^{-1}$), t_p (1 min) and β ($0.23 \sim 0.25\,K\,s^{-1}$). Main peaks are observed at about 30°C and about 85°C in every curves, and about 160°C in two curves. They are indicated A, B, and C, respectively. The response signals correspond to the peaks A and B could not detect by X-ray study of thermal expansion and by measurement of the dc electrical conductivity. The peaks A, B, and C are observed in the opposite direction of the polarizing field, so they are due to de-polarization. The peaks A and B were observed in TSC spectra for tangential direction, but no curves showed peak C. Then, the peaks A and B observed for both directions have been examined quantitatively.

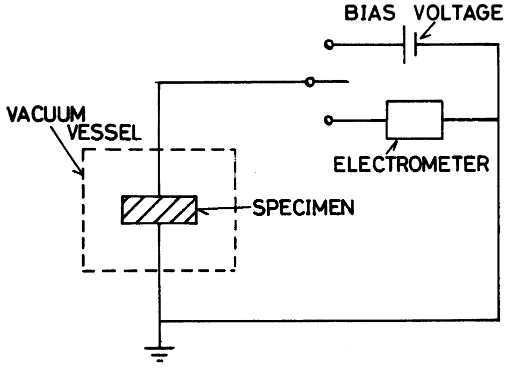

Figure 3. Schematic diagram of TSC measurement.

The dependence of TSC maximum currents I_{max} of peaks A and B on the polarizing field E_p for both directions is shown in Figure 5 (I) and (II). It is difficult to decide that the voltage-current curves of peaks A and B in both directions show linear relation or nonlinear relation.

If the peaks A and B are due to dipolar polarization, I_{max} has to be proportional to E_p and to be independent on a thickness of the sample.[4] If these peaks are due to ionic space-charge polarization caused by the migration of mobile ions within polymer over macroscopic distance, I_{max} has to be expressed in sine-hyperbolic relation with E_p and to be dependent on a thickness of

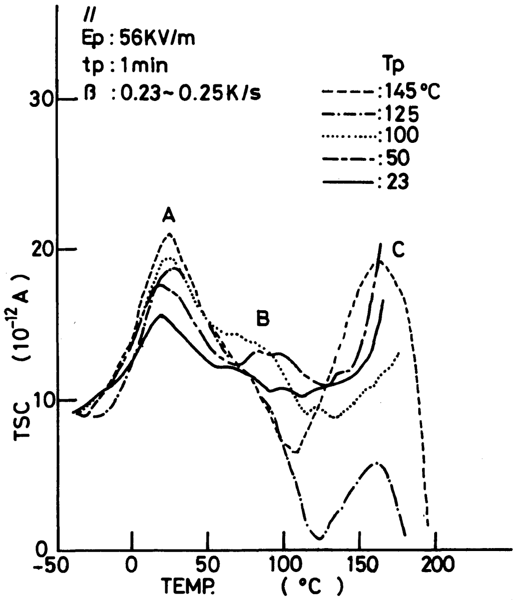

Figure 4. TSC for various polarizing temperature T_p in fiber direction: A, A peak; B, B peak; C, C peak.

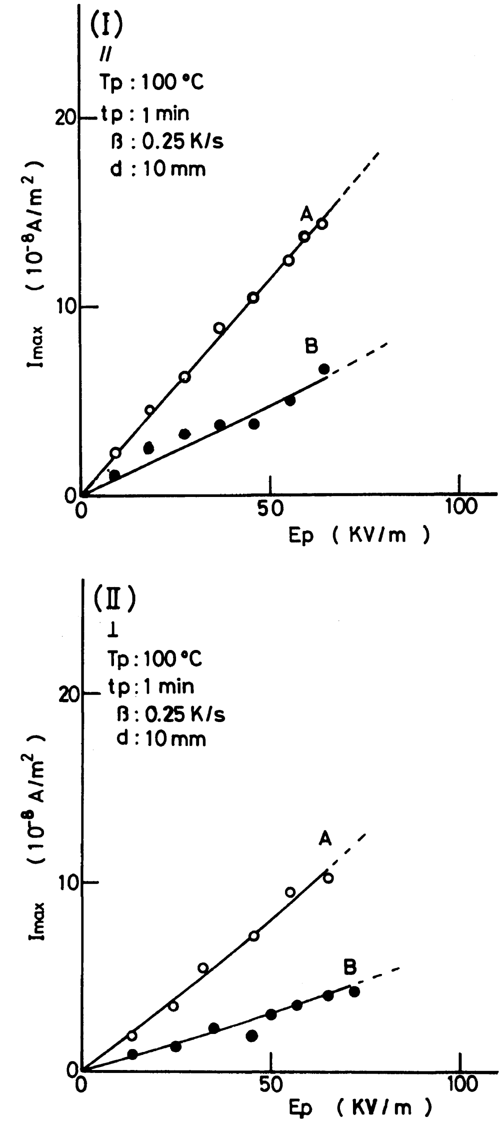

Figure 5. Voltage-current characteristics of peaks A and B in two directions: (I), fiber direction; (II), tangential direction.

the sample.[5] The dependence of TSC at peaks A and B on the thickness d under E_p of 55 kV m^{-1} and 110 kV m^{-1} is shown in Figure 6. The measurement was carried out only for the tangential direction, because, for the fiber direction, it was considered that silver conducting paste penetrated into sample and the sample thickness was affected by this penetration in the thin sample. I_{max} of peaks A and B are proportional to thickness under both polarizing fields. From the above result, these peaks are considered to be due to ionic space-charge polarization. The carrier in cellulose may be ion such as proton or proton-hole detected by Murphy.[9]

As the voltage-current characteristics in Figure 5 are regarded to be due to the hopping conduction of mobile ions, they are expressed in the sine-hyperbolic equation in the hopping conduction model,[5] *i.e.*,

$$i = i_o \sinh(eaE_p/2kT_p) \quad (1)$$

Here a is the hopping distance, i_o is the initial current density and k is Boltzmann's constant. Figure 7 (I) and (II) show the voltage-current characteristics of I_{max} at A peak for fiber and tangential directions, respectively. The dotted lines show the calculated curves which are obtained by substituting hopping distance $a = 4.5 \times 10^{-8}$ m and 3.2×10^{-8} m, and initial current density $i_o = 3.25 \times 10^{-6}$ A m^{-2} and 3.00×10^{-6} A m^{-2} into the equation (1), re-

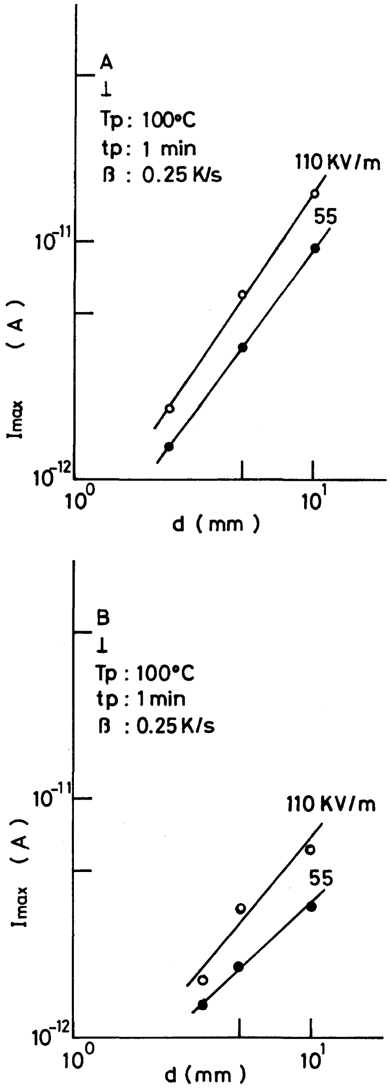

Figure 6. Relations between TSC maximum current I_{max} and thickness of samples in tangential direction: A, A peak; B, B peak.

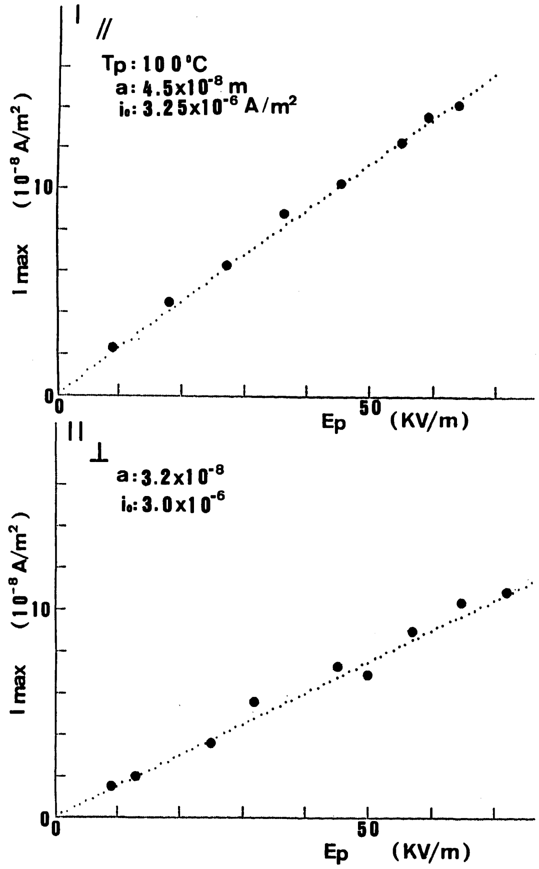

Figure 7. Voltage-current characteristics of A peak in two directions: I, fiber direction; II, tangential direction.

spectively. The results of B peaks obtained in the same way are shown in Figure 8 (I) and (II). a and i_0 are 1.0×10^{-7} m and 6.5×10^{-7} A m^{-2} for fiber direction, and 7.0×10^{-8} m and 5.5×10^{-7} A m^{-2} for tangential direction. A long hopping distance such as several hundreds angstrom has been also reported in another polymers.[10]

It has been reported that after hydrolysis, the modifications derived from native cellulose showed a levelling off degree of polymerization of about 80 and a meridional small-angle reflection corresponding to a long period of about 400 Å.[6] Then, the hopping distance for peak A in fiber direction is nearly equal to the long period which consists of two crystallite lengths.[6] The activation energies estimated from the initial rises of the peaks A and B in Figure 3 are about 0.45 eV and 0.75 eV, respectively. The activation energy of peak A is about twice the energy of the hydrogen bond. From the above results, it is considered that the peak A observed at about 30°C in fiber direction is due to ionic space-charge polarization caus-

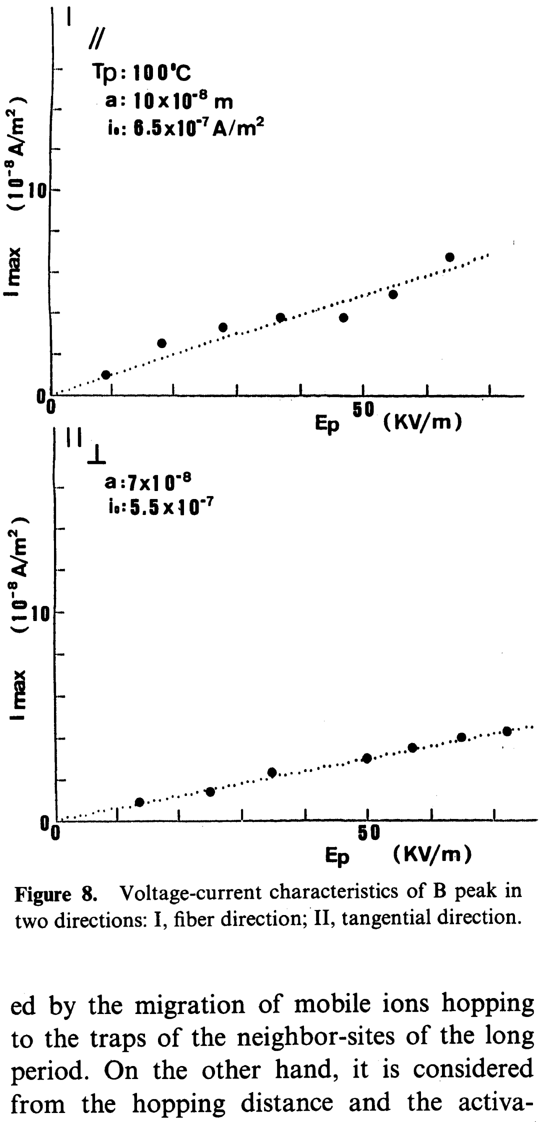

Figure 8. Voltage-current characteristics of B peak in two directions: I, fiber direction; II, tangential direction.

ed by the migration of mobile ions hopping to the traps of the neighbor-sites of the long period. On the other hand, it is considered from the hopping distance and the activation energy that the peak B observed at about 85°C in fiber direction is due to ionic space-charge polarization caused by the migration of mobile ions hopping to the traps of the next neighbor-sites of the long period.

In the tangential direction, the hopping distance for peak A is nearly equal to the long period of about 300 Å obtained by an equatorial small-angle scattering curve.[7] The long period is considered as the distance between microfibrils in width.[8] The activation energies of the peaks A and B estimated by the same method as in the fiber direction were about 0.5 eV and 0.8 eV, respectively. Then, from the same consideration as in the fiber direction the peaks A and B in tangential direction may be caused by the migration of mobile ions hopping to the traps of the neighbor and next neighbor microfibrils.

Furthermore, the peak C or the increase of TSC at 160°C may be related to the break observed in the conductivity *vs.* temperature curve and in the spacing *vs.* temperature curve.[1,2]

CONCLUSION

Thermally stimulated current spectra of *tsuga* in Cell I for the fiber and the tangential directions have been observed from −20°C to 200°C. Three peaks A, B, and C for the fiber direction are observed at about 30°C, about 85°C and about 160°C, respectively. These peaks appear in opposite direction of a polarizing field, so they are due to de-polarization. On the other hand, the peaks A and B appear for the tangential direction.

The TSC currents I_{max} of the peaks A and B are proportional to the thickness of the sample, and increase with the polarizing field E_p in the relation of the sine-hyperbolic equation.

From these results, the peaks A and B are considered to be due to ionic space-charge polarization caused by the migration of mobile ions between neighbor-sites and next neighbor-sites of the long period with hopping.

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