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Dielectric and Viscoelastic Properties of Cellulose Derivatives

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ABSTRACT

Complex dielectric and elastic coefficients of hydroxyethyl cellulose and hydroxypropyl cellulose with various average numbers of substituents per anhydroglucose unit were observed at 10 Hz at various moisture levels as a function of temperature, from the liquid nitrogen temperature to 150°C, when examining the structure and molecular motion in the solid state and the effect of water on it. The origins of the mechanical and dielectric loss peaks appearing at −130°C and −50°C, and the mechanical loss peak found at room temperature, are discussed.

INTRODUCTION

Dielectric and viscoelastic studies have proved to be useful for clarifying the effect of different modes of linkages on the molecular motion in solid polysaccharides, cellulose (Zelenev & Glazkov, 1972, Kimura *et al.*, 1974; Bradley & Carr, 1976; Kimura & Nakano, 1976; Norimoto, 1976; Crofton & Pethrick, 1982), amylose (Bradley & Carr, 1976; Nishinari & Fukada, 1980; Nishinari *et al.*, 1983), pullulan (Nishinari *et al.*, 1983–84, 1985) and dextran (Nishinari *et al.*, 1985). Molecular motions in cellulose derivatives, hydroxyethyl cellulose (HEC) and hydroxypropyl cellulose (HPC) may be influenced by the number of substituents, and this must affect the dielectric and viscoelastic coeffi-

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cients. In the present work dielectric and viscoelastic properties were observed at 10 Hz as a function of temperature from the liquid nitrogen temperature to 150°C for hydroxyethyl cellulose and hydroxypropyl cellulose in the solid state with various average numbers of substituents per anhydroglucose unit.

EXPERIMENTAL

Materials

The same samples of HEC and HPC of various average numbers of substituents per anhydroglucose unit (M.S.) used in a previous study (Nishinari *et al.*, to be published) were used in this work. HEC and HPC were dissolved in distilled water and cast into a film of 200 μm thickness on a teflon plate. Gold was evaporated onto the central area, 5×5 mm^2, of both surfaces of these films to serve as electrodes for dielectric measurement. Films of these polymers were cut into rectangular pieces, 2 mm × 20 mm, for viscoelastic measurement. The amount and position of substituents introduced in each glucosidic residue was evaluated by a gas chromatography-mass spectrometry (GC/MS) method to be described elsewhere (Nishinari *et al.*, to be published).

Measurements

A piezotron (Toyo Seiki Seisakusho Ltd) was used for the measurement of the temperature-dependence of the dielectric and viscoelastic coefficients. In dielectric measurements, a sinusoidal electric field of 10 Hz was applied to the electrodes on the film, and the induced electric polarization was amplified by a charge amplifier and fed to the operational circuit. In viscoelastic measurements the sinusoidal strain and stress at both ends of the film were detected by nonbonded strain gauges. In both dielectric and viscoelastic measurements, the operational circuit calculated immediately the real and imaginary parts of the complex response function from the two inputs: electric field and polarization in the dielectric measurement, strain and stress in the viscoelastic measurement. The temperature was raised from −180°C at a rate of 2°C/min in a dried nitrogen gas flow. The real and imaginary parts, ε' and ε'', of the complex dielectric coefficient ε^*, and the real and imaginary parts c' and c'' of the complex Young's modulus c^*, were plotted on a two-pen X-Y recorder as a function of temperature.

RESULTS AND DISCUSSION

The temperature dependence of the real and imaginary part of the dielectric coefficients ε' and ε'' for HEC films is shown in Figs 1 and 2. The imaginary part ε'' of an HEC film showed a peak at − 130°C, and this peak was more pronounced in a dried film than in a humid film (Fig. 2). This is attributed to the stabilization of crystalline structures in the presence of small amounts of water molecules. The peak is associated with the rotational motion of CH_2OR, where $R = H$ or $-(CH_2CH_2O)_m-H$ ($m = 1,2,\ldots$), attached to the C_5 carbons and/or $-(CH_2CH_2O)_m-H$ groups substituted on the 2nd and/or 3rd hydroxyl groups in the glucose residues. A shoulder on ε'' is observed at about − 50°C for a humid film (broken line). This shoulder became smaller when the film specimen was dried at higher temperatures in dried nitrogen gas and can therefore be attributed to the motion of bound water. The steep rise in ε' and ε'' with increasing temperature at about 0°C for HEC of M.S. = 1·7 M and at about − 20°C for HEC of M.S. = 2·5 M in the highly dehydrated state is due to DC conduction. At higher moisture levels, ε' and ε'' begins to increase at lower temperatures.

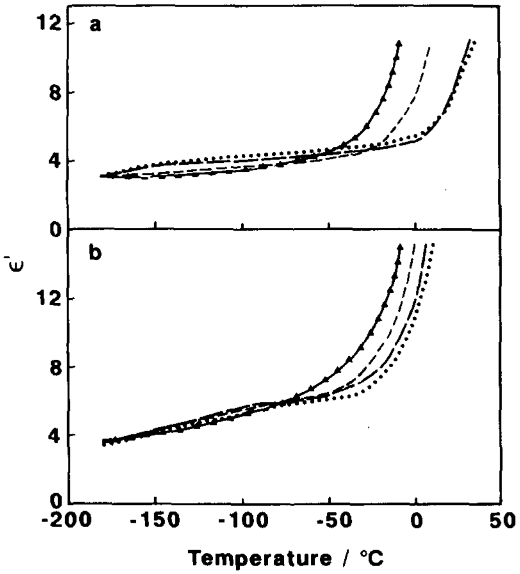

Fig. 1. Temperature dependence of the dielectric coefficient ε' for HEC of different M.S. at various moisture levels achieved by heating. (a) M.S. = 1·7 M; (b) M.S. = 2·5 M. —▲—▲—▲— heated at 40°C for 40 min; ----- heated at 80°C for 40 min; — — — heated at 120°C for 40 min; ····· heated at 150°C for 40 min.

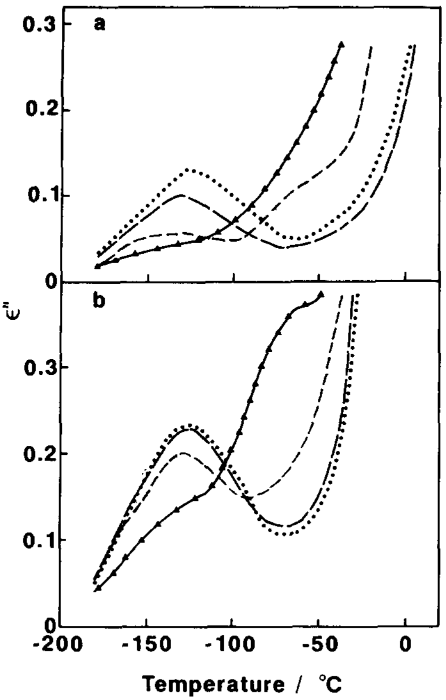

Fig. 2. Temperature dependence of the dielectric loss ε'' for HEC of different M.S. at various moisture levels achieved by heating. (a) M.S. = 1·7 M; (b) M.S. = 2·5 M. Symbols have the same meaning as in Fig. 1.

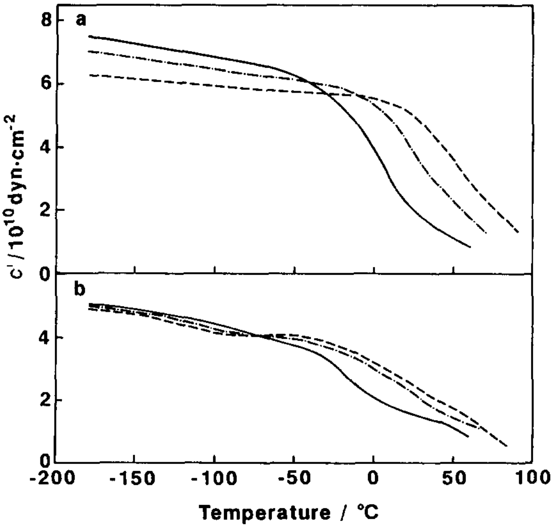

Fig. 3. Temperature dependence of the storage modulus c' for HEC of different M.S. at various moisture levels achieved by heating. (a) M.S. = 1·7 M; (b) M.S. = 2·5 M. —— non-dried; —·—·— heated at 60°C for 40 min; ---- heated at 80°C for 40 min.

The temperature dependence of the real and imaginary part of the complex Young's modulus c' and c'' for HEC films is shown in Figs 3 and 4. The value of c'' showed three peaks: at -130°C, at $-80 \sim -60$°C, and at $0 \sim 50$°C (Fig. 4). The peak at -130°C was attributed to the rotational motion of CH_2OR, where R = H or $—(CH_2CH_2O)_m—H$ ($m = 1, 2, \ldots$), attached to the C_5 carbon and/or $—(C_2H_4O)_m—H$ groups substituted on the 2nd and/or 3rd hydroxyl groups. As mentioned above, a peak at -130°C was also observed for the dielectric measurements. The peak at the temperatures from -80 to -60°C was attributed to the commencement of the motion of frozen bound water, which was observed as a shoulder at the same temperature range for the dielectric measurements. The peak at the temperature range from 0 to 50°C was attributed to the melting of ice; this was not observed for the dielectric measurements because it was hidden by the steep rise of the signal. In this temperature range, c' began to decrease rapidly, and the

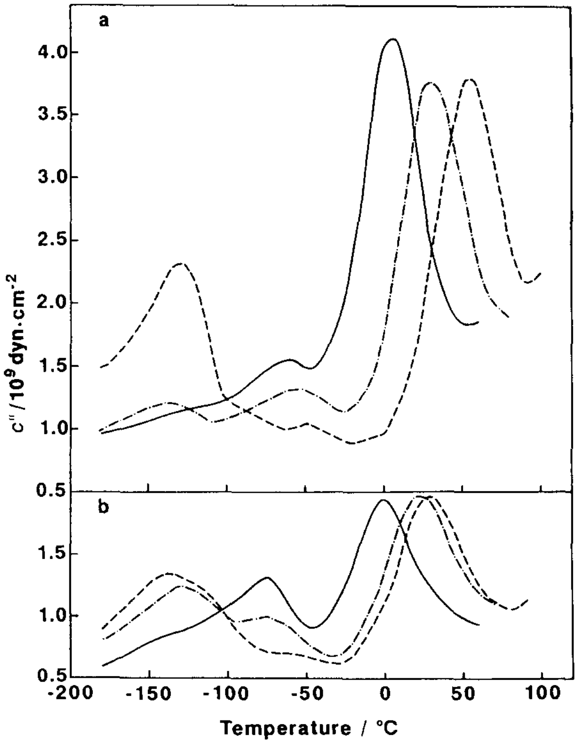

Fig. 4. Temperature dependence of the loss modulus c'' for HEC of different M.S. at various moisture levels achieved by heating. (a) M.S. = 1·7 M; (b) M.S. = 2·5 M. Symbols have the same meaning as in Fig. 3.

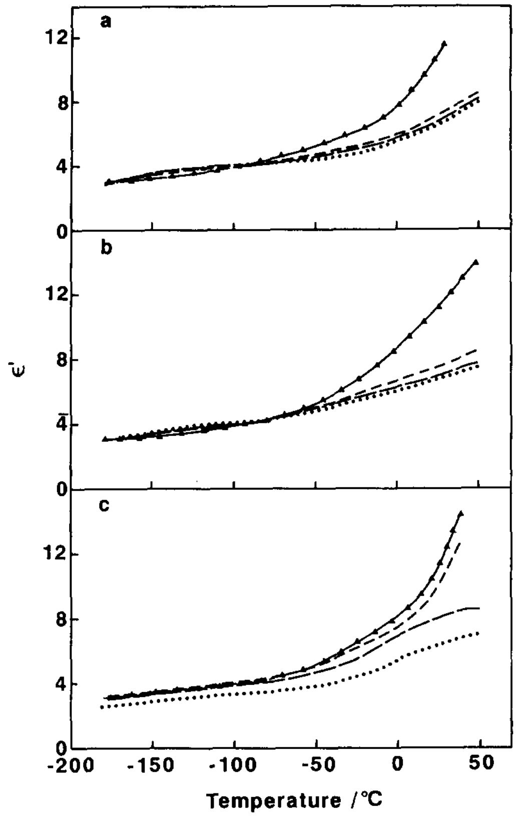

Fig. 5. Temperature dependence of the dielectric coefficient ε' for HPC of different M.S. at various moisture levels achieved by heating. (a) M.S. = 2·4 M; (b) M.S. = 3·0 M; (c) M.S. = 4·1 M. Symbols have the same meaning as in Fig. 1.

value of c' for a humid film became smaller than that for a dehydrated film. This can be explained by the plasticizing effect of water molecules over this temperature range. Since the specimen examined in this work was dried at 60°C or 80°C for 40 min and then cooled rapidly to liquid nitrogen temperature, it will not contain much water. The glass transition temperature of cellulose has been reported to be about 230°C (Back & Didricksson, 1969). Therefore, even if a very small amount of water molecules depresses the glass transition temperature, it must appear at higher temperature than 50°C. At lower temperatures the value of c' for humid HEC films is larger than that of dried films. This is also due to the structural stabilization by water molecules, and hindrance of the rotational motion of CH_2OR, where $R = H$ or $-(CH_2CH_2O)_m-H$

($m = 1,2,\ldots$), attached to the C_5 carbons and/or —$(CH_2CH_2O)_m$—H groups substituted on the 2nd and/or 3rd hydroxyl groups. This corresponds well to the observation that the peak of ε'' and of c'' at about − 130°C is more pronounced in a dried film than in a humid film. Similar behaviour has been found for amylose and pullulan (Nishinari *et al.*, 1983, 1983-84, 1985). This structural stabilization by a small amount of water has been found also in cellulose I (Hatakeyama & Hatakeyama, 1985), amylose (Nishinari & Fukada, 1980; Nishinari *et al.*, 1983) and collagen (Andronikashvili *et al.*, 1976).

Figures 5 and 6 show the temperature dependence of the real and imaginary part of the dielectric coefficient for HPC of different M.S. The imaginary part ε'' of an HPC film showed a peak at about − 130°C (Fig. 6). This peak is considered to be caused by the rotational motion of CH_2OR, where R = H or —$(CH_2CH_2O)_m$—H ($m = 1,2,\ldots$), attached to

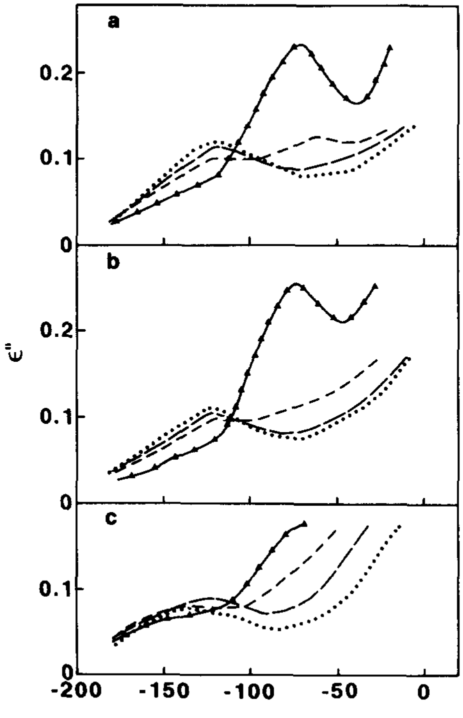

Fig. 6. Temperature dependence of the dielectric loss ε'' for HPC of different M.S. at various moisture levels achieved by heating. (a) M.S. = 2·4 M; (b) M.S. = 3·0 M; (c) M.S. = 4·1 M. Symbols have the same meaning as in Fig. 1.

the C_5 carbons and/or —$(CH_2CH_2O)_m$—H groups substituted on the 2nd and/or 3rd hydroxyl groups. Since the peak temperature is shifted to lower temperatures, and the peak height decreased with increasing M.S., this peak must be caused mainly by hydroxymethyl groups. The number of hydroxymethyl groups decreases with increasing M.S. as shown by gas chromatography–mass spectrometry (GC/MS) (Nishinari *et al.*, to be published). Thus, the peak height must decrease with increasing M.S. We suggest the reason why the peak temperature is shifted to lower temperatures is as follows. The crystallinity will decrease with increasing M.S., and hence the value of *c*′ will decrease with increasing M.S. as shown in Fig. 7. It may also be the case that the increased steric hindrance due to the increased M.S. would give rise to increased free volume allowing increased hydroxymethyl group mobility. These interpretations will be explored in the future. In this situation, the mobility of hydroxymethyl groups increased, and therefore the peak temperature shifted to lower temperatures. A peak or a shoulder in ε'' at about −50°C for a slightly humid film of HPC (—▲—▲—▲— and ---- in Fig. 6) is attributed to

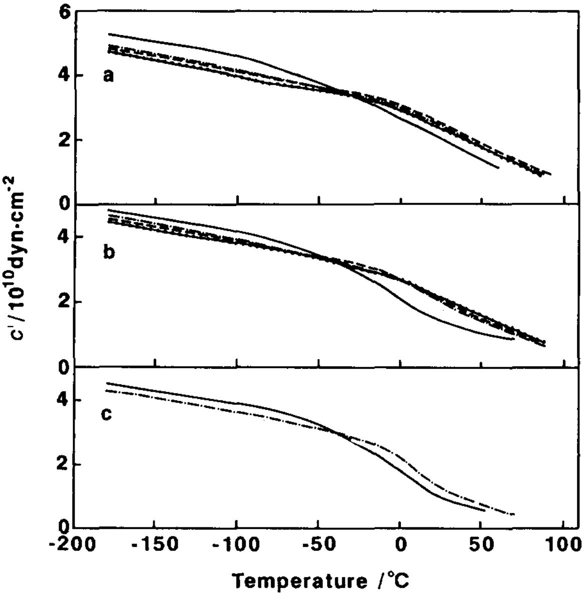

Fig. 7. Temperature dependence of the storage modulus *c*′ for HPC of different M.S. at various moisture levels achieved by heating. (a) M.S. = 2·4 M; (b) M.S. = 3·0 M; (c) M.S. = 4·1 M. —— heated at 100°C for 40 min. Other symbols have the same meaning as in Fig. 3.

commencement of motion of frozen bound water, because as in the case of HEC it disappeared completely on dehydration (····· in Fig. 6).

The temperature dependence of the real and imaginary part of the complex Young's modulus for HPC of different M.S. is shown in Figs 7 and 8. Here again, the imaginary part c'' showed a peak at about − 130°C (Fig. 8). The peak temperature shifted to lower temperatures, and the peak height decreased with increasing M.S. just as in the dielectric case (Fig. 6). The origin of this peak is thought to be a rotational motion of CH_2OR, where $R = H$ or $-(CH_2CH(CH_3)O)_m-H$ ($m = 1,2,\ldots$), attached to the C_5 carbons and/or $-(CH_2CH(CH_3)O)_m-H$ groups substituted on

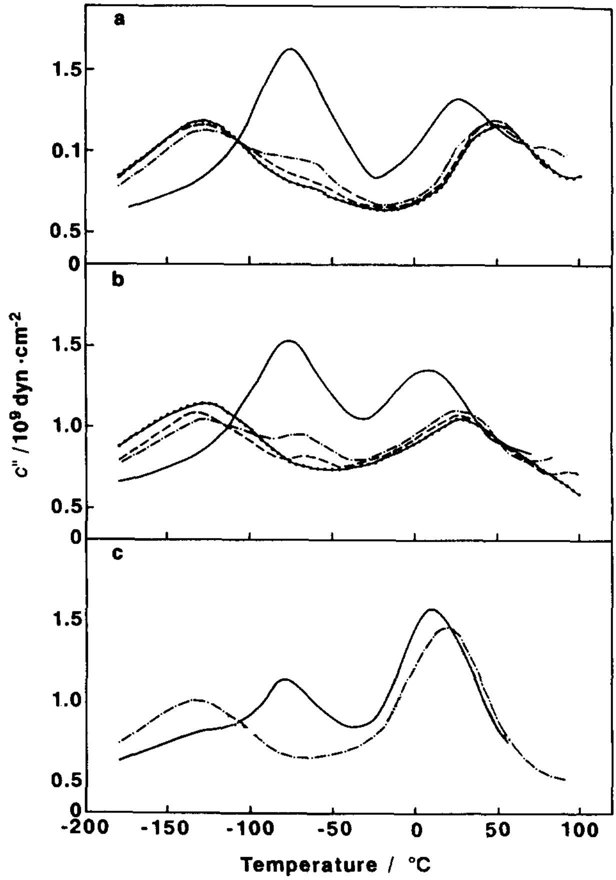

Fig. 8. Temperature dependence of the loss modulus c'' for HPC of different M.S. at various moisture levels achieved by heating. (a) M.S. = 2·4 M, (b) M.S. = 3·0 M; (c) M.S. = 4·1 M. —— heated at 100°C for 40 min. Other symbols have the same meaning as in Fig. 3.

the 2nd and/or 3rd hydroxyl groups. The behaviour of this peak could be understood in the same way as the dielectric case (Fig. 6).

The effect of water molecules on this peak in the dielectric loss (Fig. 6) and in the mechanical loss (Fig. 8) is the same as in the case of HEC (Figs 2 and 4).

A peak or a shoulder of c'' for a slightly humid film of HPC (—·—·— and ---- in Fig. 8(a), (b) and (c)) at a temperature around −70°C is attributed to the commencement of motion of frozen bound water. It disappeared completely on dehydration (—— in Fig. 8).

A peak in c'' for HPC films in the temperature range from 10 to 50°C is considered to be induced by the plasticizing effect of water molecules immediately following the melting of ice (Fig. 8). This peak is more pronounced in hydrated films than in dehydrated films. At the temperature range of this peak, c' decreased most steeply.

In the case of HEC, the peak in both the dielectric and mechanical loss at about −130°C was attributed to the rotational motion of both CH_2OR, where $R = H$ or $-(CH_2CH_2O)_m-H$ ($m = 1, 2, \ldots$), attached to the C_5 carbon and the $-(CH_2CH_2O)_m-H$ group substituted on the 2nd and/or 3rd hydroxyl groups in the case of HEC. For HPC, the peak was attributed mainly to a rotational motion of the hydroxymethyl group. $-(CH_2CH(CH_3)O_m-H$ groups are so bulky that they would not be able to move so easily.

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