



Dielectric, viscoelastic and broad-line NMR study of konjac glucomannan films

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(Received 10 August 1990; revised version received 1 November 1990; accepted 6 November 1990)

Complex dielectric coefficients and elastic moduli of konjac glucomannan (KGM) were observed at 10 Hz in the temperature range from -180 to 150°C . Broad-line NMR measurements were also carried out over the same temperature range. Mechanical and dielectric loss peaks at -100°C were attributed to the rotational motion of hydroxymethyl group attached to the C-5 atom in glucose and mannose residues. The second moment of KGM decreased rapidly around temperatures at 0°C and at -60°C . These temperatures are higher than those found in amylose, pullulan and dextran indicating the movements of hydroxymethyl groups are hindered in KGM.

INTRODUCTION

The Japanese gel-like food 'konnyak', a gel of konjac glucomannan (KGM), is used frequently in traditional Japanese dishes. There have been a lot of investigations concerning the solution properties of KGM (Torigata *et al.*, 1952; Sugiyama *et al.*, 1972; Kishida *et al.*, 1978; Kohyama & Nishinari, 1990), the gelling mechanism of KGM (Maekaji, 1978), the chemical structure of KGM (Kato & Matsuda, 1969; Maeda *et al.*, 1980) and the crystalline structure of KGM (Chanzy *et al.*, 1982; Takahashi & Tanigaki, 1987). KGM is a polysaccharide whose main chain is composed of β -1,4 linked mannoses and glucoses (Kato & Matsuda, 1969). There are some branching points at the C-3 of the mannoses (Maeda *et al.*, 1980) (Fig. 1).

The widespread use of synthetic polymer films has caused serious pollution problems, and as a result, biodegradable films have attracted much attention. In the present work KGM films were prepared and the dielectric, viscoelastic and broad-line NMR measurements were carried out to elucidate the relationship between the chemical structure of KGM and its physico-chemical properties. We have already made viscoelastic, dielectric and broad-line NMR investigations on solid

amylose, pullulan and dextran (Nishihari & Fukada, 1980; Nishinari *et al.*, 1980; Nishihari & Tsutsumi, 1984; Nishinari *et al.*, 1985). The molecular motion of solid KGM is discussed in comparison with these polysaccharides.

EXPERIMENTAL

Material

KGM isolated from the tuber of *Amorphophallus konjac* K. Koch was kindly supplied by Dr Maekaji (Maekaji, 1974) (Hiroshima Food Research Institute). It was dispersed in water and reprecipitated by methanol. The ratio of D-mannose to D-glucose of this sample was determined at 63:37 by gas chromatographic analysis on acid hydrolysate of KGM, which agrees fairly well with previous reports (Kato & Matsuda, 1969; Maeda *et al.*, 1980). The content of acetyl groups must be negligible because the signal of the carbonyl carbon was not perceived at 180 ppm in the CP/MAS NMR spectrum (Fig. 2). KGM was dissolved in water and cast into a film of about $100\ \mu\text{m}$ thickness for dielectric, viscoelastic and NMR measurements.

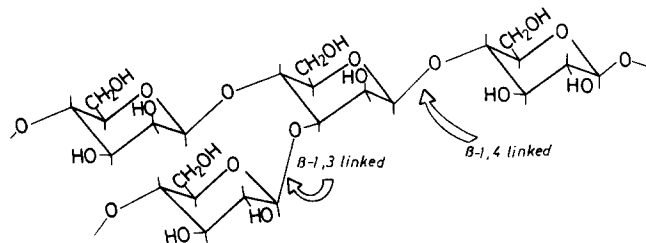


Fig. 1. Structure of konjac glucomannan.

Measurements

Dielectric studies

Electric fields of 10 Hz, and of 7 V were applied to the electrodes evaporated onto the film (1.0×2.0 cm). The film was dried in nitrogen gas by heating at 100, 120, 140, and 160°C for 40 min after reaching each temperature. The temperature was raised from the liquid nitrogen temperature at the rate of 2°C/min. The complex dielectric constants $\epsilon^* = \epsilon' - i\epsilon''$ were measured using a Rheograph-Solid from Toyo-Seiki-Seisakusho Ltd (Tokyo) by a conventional method described previously (Nishinari & Fukada, 1980).

Viscoelasticity

The complex viscoelastic constants $c^* = c' + ic''$ at 10 Hz were determined by detecting the sinusoidal strain and stress at both ends of the film (0.15×1.8 cm). The heating rate and drying conditions were the same as in dielectric measurements.

NMR

The powdered sample was put in a glass tube, which was evacuated at 120°C for 1 h, and sealed. Broad-line ^1H -NMR derivative spectra were measured by means of a continuous wave method with a JEOL-JNM-W-40

spectrometer operated at 40 MHz as a function of temperature from -150 to 100°C , and the second moments were calculated from the spectra. The field modulation frequency was 35 Hz, and in most cases the amplitude was kept low enough to neglect the modulation broadening. A radio frequency field below the limit of saturation was chosen by comparing the curves at different power levels.

RESULTS AND DISCUSSION

Dielectric studies

Figure 3 shows the real and imaginary part of the dielectric coefficient ϵ' and ϵ'' for the glucomannan film as a function of temperature for various moisture levels. At low temperatures, ϵ' is almost independent of moisture levels. The real part, ϵ' , increases gradually with increasing temperature, while the imaginary part, ϵ'' , of glucomannan film heated at 100°C for 40 min (solid curve) shows a large peak at about -50°C . This peak became smaller and shifted to higher temperatures with decreasing moisture level. The peak disappeared when the film was further dried at 160°C , therefore, it is considered to be due to the presence of water.

When the film was dried further at 120°C for 40 min, a new peak of ϵ'' appeared at about -100°C . The intensity of this peak increased with decreasing moisture level. This peak was attributed to the rotational motion of hydroxymethyl group attached to the C-5 atom in glucose and mannose residues.

The dielectric relaxation strength $\Delta\epsilon$ was determined from the difference between the asymptote at the lower temperatures and ϵ' of thoroughly dried sample at the higher temperature. The $\Delta\epsilon$ (c. 2.2) of KGM is smaller

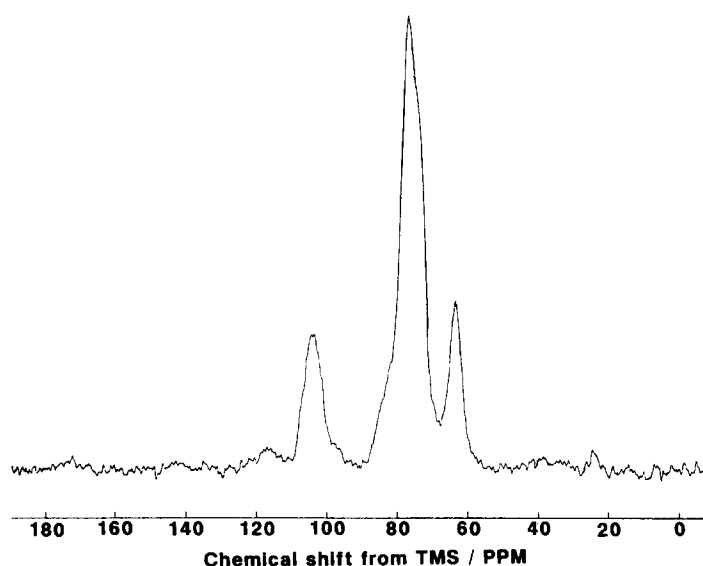


Fig. 2. ^{13}C CP/MAS NMR spectrum of konjac glucomannan: 100 MHz, 30°C .

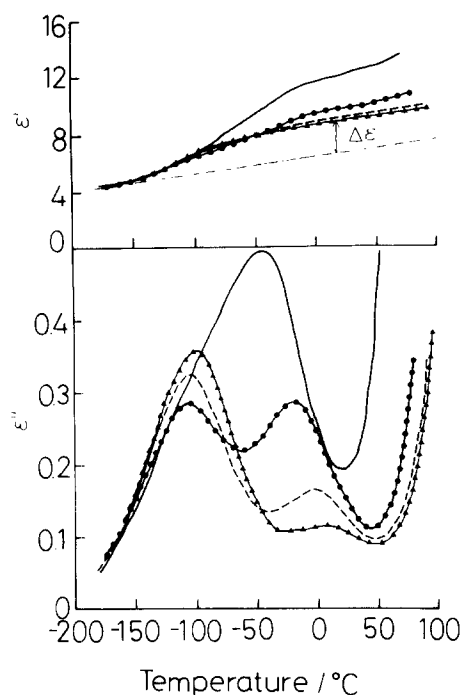


Fig. 3. Temperature dependence of the dielectric coefficients ϵ' and ϵ'' for various moisture levels: (—) heated at 100°C; (—●—●—●) heated at 120°C; (---) heated at 140°C; (—▲—▲—▲) heated at 160°C. Heating time: 40 min. The asymptote at the lower temperature in the upper graph is drawn to estimate the dielectric relaxation strength.

than that of amylose (3.0) (Nishinari & Fukada, 1980) but larger than that of pullulan (1.5) (Nishinari *et al.*, 1980) or that of dextran (0.83) (Nishinari *et al.*, 1985). It is considered that the magnitude of $\Delta\epsilon$ is mainly determined by the rotational motion of hydroxymethyl groups because the sample has no acetyl group. The number of hydroxymethyl groups in KGM and in amylose is considered the same, while the number in pullulan is about two thirds of that. Dextran has very few hydroxymethyl groups. Therefore, the order of magnitude of the dielectric relaxation strength for these three polysaccharides, amylose, pullulan and dextran, can be understood in terms of the amount of this group as discussed previously (Nishinari *et al.*, 1985) (Table 1). From these experimental results, the rotational motion

of the hydroxymethyl groups in KGM is slightly hindered in comparison to the motion of the hydroxymethyl groups in amylose.

Viscoelasticity

The temperature dependence of the viscoelastic constants of KGM is shown in Fig. 4. The real part decreased monotonically with increasing temperature. The value of c'' for non-dried sample showed a large peak at about -50°C , and this peak decreased in height when it was dried just as for the dielectric results. For dry KGM, a peak appeared at about -100°C , and it is attributed to the rotation of hydroxymethyl groups attached to the C-5 atom in mannose and glucose residues. Kimura *et al.* (1974) also found a mechanical loss peak at -100°C for pine glucomannan using a torsion pendulum method, and attributed it to the rotational motion of hydroxymethyl groups. As the

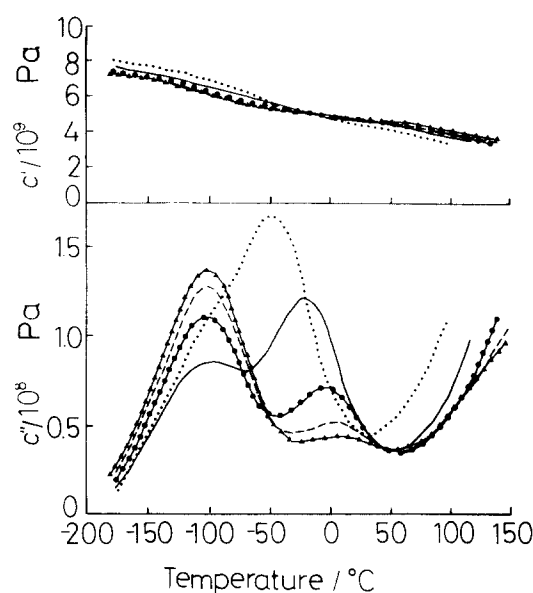


Fig. 4. Temperature dependence of the elastic coefficients c' and c'' at various moisture levels: (.....) non-dried; (—) heated at 100°C; (—●—●—●) heated at 120°C; (---) heated at 140°C; (—▲—▲—▲) heated at 160°C. Heating time: 40 min.

Table 1. Dielectric and viscoelastic characteristics of various polysaccharides in solid state

Sample	Temperature of max ϵ'' ($^\circ\text{C}$)	$\Delta\epsilon$	Temperature of max c'' ($^\circ\text{C}$)	$c'/10^9$ Pa at -150°C
Amylose ^a	-75	3.0	-75	8.4
Pullulan ^b	-90	1.5	-100	7.8
Dextran ^c	-120	0.83		
Konjac glucomannan	-100	2.2	-100	7.2

^aNishinari & Fukada (1980).

^bNishinari *et al.* (1980).

^cNishinari *et al.* (1985).

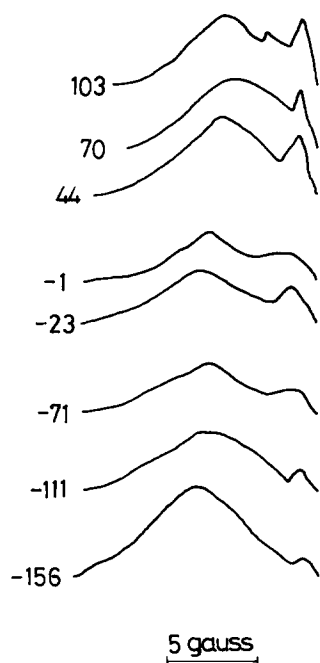


Fig. 5. Derivative spectra of solid konjac glucomannan at various temperatures. Figures at the left of each curve represent the temperature in °C.

moisture content decreases, the value of c' became larger at temperatures below about -20°C , but it became smaller at higher temperatures. The water plays a role of plasticizer at temperatures higher than the ambient temperature.

NMR

The observed derivative spectra of KGM at various temperatures are shown in Fig. 5. The narrow component

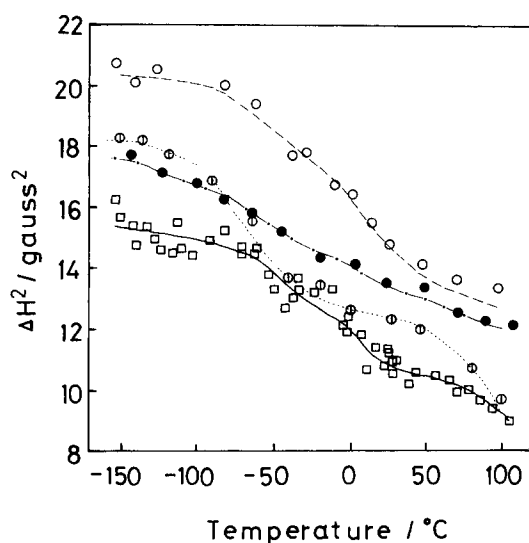


Fig. 6. Temperature dependence of the second moment of various polysaccharides in the solid state. (□ —) Konjac glucomannan; (○ ---) amylose; (○ ·····) pullulan; (● - · - ·) dextran.

appeared superimposed on the broad one at all the temperatures, and in addition to this the other narrow component appeared at higher temperatures. The narrow component which appeared in amylose, pullulan, and dextran, was attributed to a small amount of water since specimens left in air showed a steep rise in the narrow component (Nishinari & Tsutsumi, 1984). However, the narrow component in the spectra of glucomannan was not influenced so much by the drying conditions. It must be attributed to other factors than the presence of water, but the reason is not clear at present.

Second moments of KGM together with those of amylose, pullulan and dextran are shown in Fig. 6 as a function of temperature. The second moment of KGM at lower temperatures is smaller than that of the other three polysaccharides, amylose, pullulan and dextran. The second moment decreased rapidly at about 0 and -60°C . The temperatures at which the second moment decreases rapidly are higher than those in the other polysaccharides. This suggests that the movements of hydroxymethyl groups of KGM are slightly hindered in comparison with the other three polysaccharides. Further investigations are urgently required in order to clarify whether this is due to the different modes of α or β glucosidic linkages or due to the presence of branching or for other reasons.

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