

## Solution property of low molar mass Konjac mannan

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Konjac mannan (KM) is a water soluble glucomannan with high molar mass. KM aqueous solution shows extremely high viscosity. KM can be depolymerized by high energy irradiation. Molar mass of irradiated KM decreased with increase of absorbed dose. The viscosity of KM aqueous solutions decreased with decreasing molar mass. The aqueous solution of KM with molar mass more than  $5 \times 10^5$  Da showed pseudo-plastic fluid behavior even at low concentration and at 50 °C. KM solution changed to Newtonian fluid with decreasing molar mass at low concentration. KM with molar mass less than  $2.3 \times 10^5$  Da was Newtonian fluid in semi-dilute region. The critical concentration at the overlap limit of KM solution increased with decreasing molar mass. The overlapping and entanglement of KM with high molar mass occur at lower concentration compared to those of KM with low molar mass.

Key words: Konjac mannan, low molar mass, viscosity, rheology, critical concentration

### 1. INTRODUCTION

Konjac mannan (KM) is a neutral glucomannan derived from tubers of *Amorphophallus Konjac C. Koch*, having a  $\beta$ -1,4 linked  $\beta$ -D-glucose (G) and  $\beta$ -D-mannose (M) backbone approximately in the ratio of 1:1.6. KM has side chains and the branching positions are considered to be the C3 of G and M. An acetyl group is attached to ca.13 sugar residues [1]. Deacetylation occurs in the presence of alkali and a non-thermoreversible elastic gel is formed [2]. KM aqueous solution shows extremely high viscosity. Polysaccharides undergo depolymerization by various methods:  $\gamma$ -irradiation [3,4], ultrasonic irradiation[3], chemical [5] and enzymatic hydrolyses [6].

From our previous study[7, 8], the  $\gamma$ -irradiation led to chain scission of KM, but introduced no significant new chemical groups into the structure, apart from a small increase in content of carbonyl groups. The intrinsic viscosity, molar mass and radius of gyration decreased rapidly with increasing dose up to 10 kGy and then at a slower rate. The Mark-Houwink-Sakurada equation for the KM gave  $[\eta] = 5.30 \times 10^{-4} M^{0.78}$ .

Here, the molar mass of irradiated KM was determined by size exclusion chromatography (SEC) and viscosity of the low molar mass KM was measured. The effect of molar mass of KM on fluid behavior was investigated. The critical concentration of the overlap limit of KM solution was also discussed.

### 2. MATERIAL AND METHODS

#### 2.1. Material

Commercial konjac flour (Akagi Ohodama species) was supplied by Ogino Shoten Co. Ltd. The flour was purified by washing with aqueous ethanol solution several times before use.

#### 2.2. $\gamma$ -Rays irradiation

The purified KM was irradiated with  $^{60}\text{Co}$   $\gamma$ -radiation under reduced pressure (below  $10^{-3}$  Torr) at room temperature. The absorbed dose was varied from 1 to 10kGy and the dose rate were in the range of 0.5 to 3.33 kGy/h.

#### 2.3. Molar mass measurement

Molar mass of KM was determined by a size exclusion chromatograph (Prominence series, Shimadzu) which was connected to a SEC column of TSK-GEL GMPW<sub>XL</sub> (TOSOH) and a differential refractive index (RI) detector. Eluent was 0.2 M sodium nitrate aqueous solution at 0.6 mL/min. A standard material used is KM with known molar masses which were determined by a SEC equipped with a multiangle static light-scattering (MALS) detector [7,8].

#### 2.4. Rheological measurement

The irradiated KM was dissolved in 0.05% NaN<sub>3</sub> aqueous solution and centrifuged to remove cell wall debris before measurements. Viscosity of the KM solution was measured using a RV-II Rotation Viscometer (Brookfield).

### 3. RESULT AND DISCUSSION

#### 3.1 Molar mass of irradiated Konjac mannan

SEC chromatograms of the irradiated KM are shown in Fig.1. The chromatogram shifted to lower molar mass with absorbed dose, but the width of peak hardly changed. It is inferred that the decrease of molar mass is caused by the main chain scission of KM induced by the irradiation. The weight average molar mass (M<sub>w</sub>) was determined and plotted against the absorbed dose in Fig.2. The M<sub>w</sub> of original KM was  $11.0 \times 10^5$  Da. The M<sub>w</sub> decreased significantly with increase of absorbed

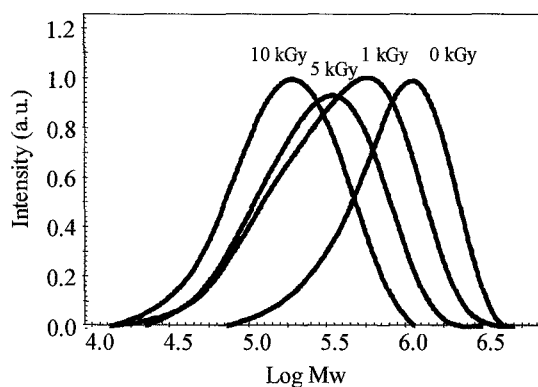
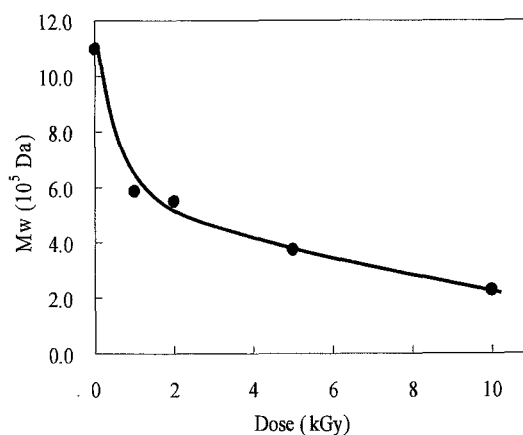
Fig.1 Molar mass distribution of  $\gamma$ -irradiated KM.

Fig.2 Relationship between Mw and absorbed dose for irradiated KM.

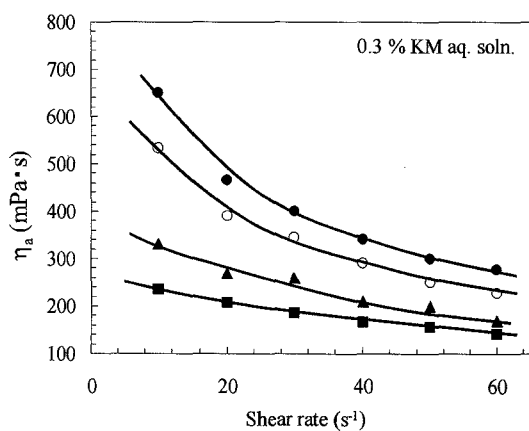


Fig.3 Apparent viscosity vs. shear rate of 0.3% KM aqueous solution for various temperature. ●, 20 °C; ○, 25 °C; ▲, 40 °C; ■, 50 °C.

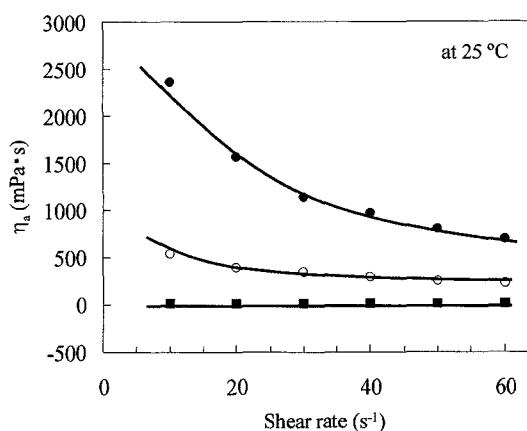


Fig.4 Apparent viscosity vs. shear rate of KM aqueous solution with different concentration at 25 °C. ●, 0.5%; ○, 0.3%; ■, 0.1%.

dose up to 2 kGy and then decreased gradually. The Mw of 10 kGy irradiated KM was  $2.3 \times 10^5$  Da.

### 3.2 Viscosity of Konjac mannan aqueous solution

The apparent viscosity ( $\eta_a$ ) of 0.3 % KM aqueous solution was measured using the rotation viscometer. Fig.3 shows the relationships between  $\eta_a$  and shear rate at various temperatures. At 20 °C, the  $\eta_a$  decreased drastically with decrease of the shear rate, which is the feature of pseudo-plastic fluids. The  $\eta_a$  decreased with elevating temperature. However, KM solution at 50 °C still showed pseudo-plastic fluids behavior.

Fig.4 shows the effect of KM concentration on the  $\eta_a$  at 25 °C. The  $\eta_a$  of 0.5% KM solution was extremely high at low shear rate and the value decreased remarkably with decrease of the concentration. For 0.3%KM solution, the  $\eta_a$  showed relatively high value (550 mPa · s) at low shear rate and then decreased with increasing shear rate. The value of  $\eta_a$  changed to 220 mPa · s at the shear rate of 60 sec<sup>-1</sup>. The  $\eta_a$  of 0.1% KM solution

showed quite small value (14 mPa · s) at shear rate of 10 sec<sup>-1</sup> and decreased slightly with increasing the shear rate. The solution property of KM gets closer to Newtonian fluids behavior at low concentration region.

### 3.3 Viscosity of low molar mass Konjac mannan aqueous solution

Fig.5 shows the relationships between the  $\eta_a$  and the shear rate for 0.3% KM aqueous solutions with various Mw at 25°C. Comparing to the original KM, the  $\eta_a$  of  $5.9 \times 10^5$  Da KM decreased slightly with decrease of the shear rate. For  $2.3 \times 10^5$  Da KM, the  $\eta_a$  showed a constant value regardless of the shear rate.

The zero shear viscosity ( $\eta_0$ ) of KM solution was determined by extrapolation of the  $\eta_a$  value to shear rate of zero. Fig.6 shows the relationships between the  $\eta_0$  and measurement temperature for 0.3% KM aqueous solutions with various Mw. The  $\eta_0$  decreased exponentially with increasing the measurement temperature and with decreasing the Mw. The decrement

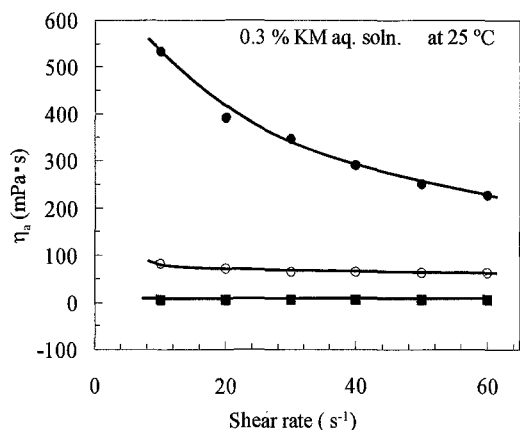


Fig.5 Apparent viscosity vs. shear rate of 0.3% low molar mass KM aqueous solution at 25 °C. ●, 11.0 x 10<sup>5</sup> Da; ○, 5.9 x 10<sup>5</sup> Da; ■, 2.3 x 10<sup>5</sup> Da.

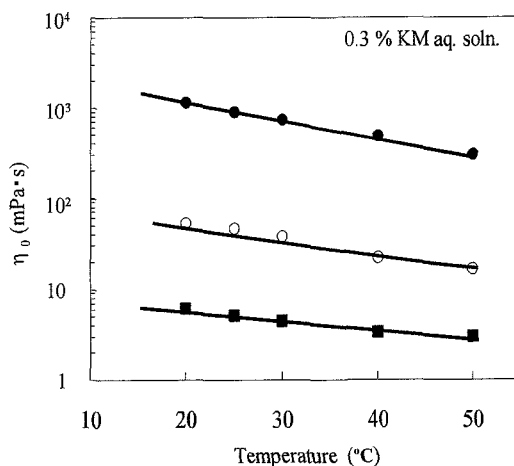


Fig.6 Dependence of zero shear viscosity on temperature for 0.3% low molar mass KM aqueous solution. ●, 11.0 x 10<sup>5</sup> Da; ○, 5.5 x 10<sup>5</sup> Da; ■, 2.3 x 10<sup>5</sup> Da.

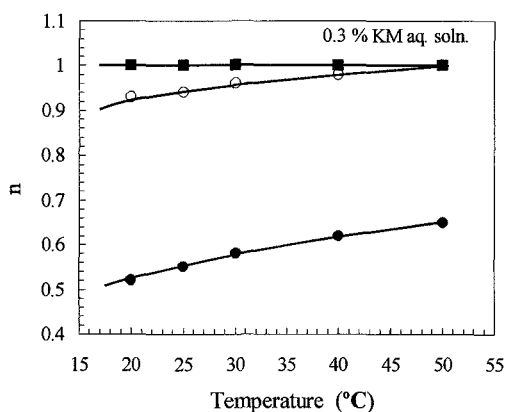


Fig.7 Relationships between flow behavior index and measurement temperature of low molar mass KM aqueous solution. ●, 11.0 x 10<sup>5</sup> Da; ○, 5.5 x 10<sup>5</sup> Da; ■, 2.3 x 10<sup>5</sup> Da.

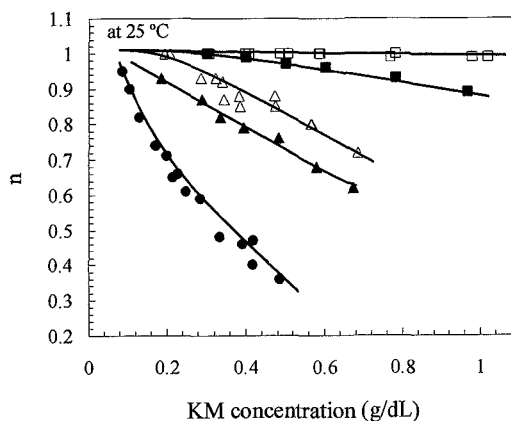


Fig.8 Flow behavior index of low molar mass KM aqueous solution. ●, 11.0 x 10<sup>5</sup> Da; ▲, 5.9 x 10<sup>5</sup> Da; △, 5.5 x 10<sup>5</sup> Da; ■, 3.7 x 10<sup>5</sup> Da; □, 2.3 x 10<sup>5</sup> Da.

of the  $\eta_0$  became small for KM with low Mw.

The flow behavior index ( $n$ ) is expressed by the following power law [9],

$$\eta_a = K S^{n-1} \quad (1)$$

,where  $\eta_a$  is the apparent viscosity,  $S$  is the share rate,  $K$  is a consistency index. When the  $n$  value is unity, the solution is Newtonian fluid.

Fig.7 shows the relationships between the flow behavior index and measurement temperature for 0.3% KM aqueous solutions. The flow behavior index of the original KM was remarkably smaller than that of KM with low Mw. The flow behavior index approached to 1 with increasing temperature for KM with Mw of 5.9 x

10<sup>5</sup> Da. The flow behavior index of KM with 2.3 x 10<sup>5</sup> Da was 1 regardless of the temperature.

Fig.8 shows the relationships between the flow behavior index and the concentration of KM solution with various Mw at 25°C. The value of flow behavior index for the 2.3 x 10<sup>5</sup> Da KM was 1 regardless of the solution concentration. This means that the 2.3 x 10<sup>5</sup> Da KM kept Newtonian fluids behavior even at 1%, i.e., semi-dilute region. Though the 3.8 x 10<sup>5</sup> Da KM solution was Newtonian fluid in dilute region, it changed to non-Newtonian fluid in semi-dilute region. In the case of KM with Mw more than 5.5 x 10<sup>5</sup> Da, the value of flow behavior index decreased with increase of the solution concentration, especially for the original KM (Mw = 11.0 x 10<sup>5</sup> Da). The KM solution with high Mw

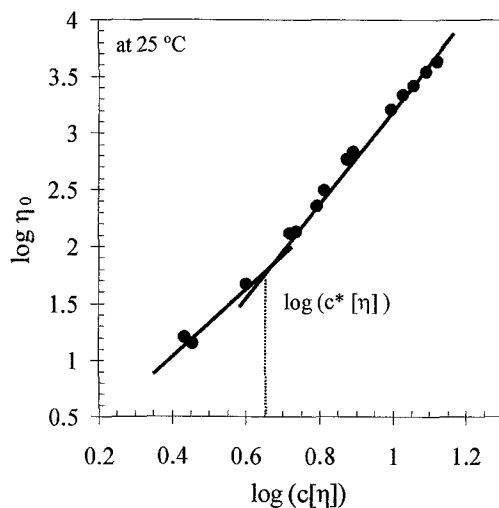


Fig.9 Determination of  $C^*$  from the variation in the zero shear viscosity.

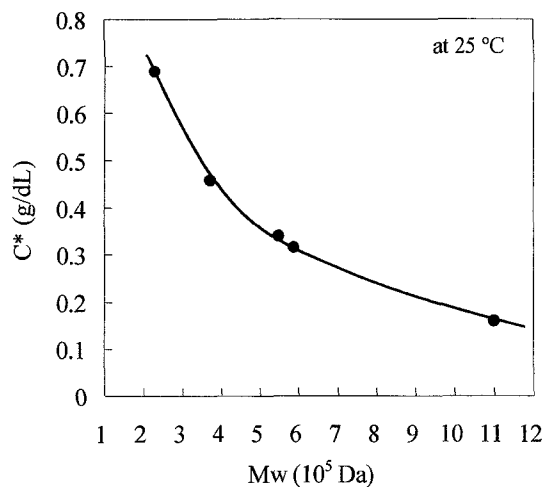


Fig.10 Relationship between  $C^*$  and molar mass of KM.

more than  $5.5 \times 10^5$  Da was non-Newtonian fluid even in the dilute region.

#### 3.4 Critical overlap concentration of Konjac mannan aqueous solution

From our previous study, the intrinsic viscosity ( $[\eta]$ ) of KM aqueous solution is 28.45 dL/g at 25 °C [7,8]. The zero shear viscosity of KM aqueous solution in the form of a double logarithmic plot against the coil overlap parameter ( $C[\eta]$ ) is shown in Fig.9. Two linear relationships between  $\log \eta_0$  and  $\log C[\eta]$  were observed. The polymer concentration at the intersection of two lines is defined as the critical overlap concentration ( $C^*$ ) [10-12]. The polymer chains are essentially free to move individually below  $C^*$  and start to overlap with each other and form a transient network structure above  $C^*$  [11]. The  $C^*$  of the original KM was 0.18 g/dL. The similar relationships were also observed for KM with low Mw.

The relationship between  $C^*$  and Mw of KM is shown in Fig 10. The  $C^*$  gradually increased with decrease of Mw until  $5 \times 10^5$  Da and then increased remarkably. Since the  $\alpha$  value of KM derived from the Mark-Houwink-Sakurada equation is 0.78 [7,8], KM chains are considered to be relatively stiff and extended. The radius of gyration ( $R_G$ ) of KM can be determined by the following equation [7,8],

$$R_G = 2.77 \times 10^{-2} Mw^{0.60} \quad (2)$$

The  $R_G$  of the original KM is 117 nm and decreases to 45 nm for KM with Mw of  $2.3 \times 10^5$  Da. It is inferred that the intermolecular interaction of KM with high Mw is stronger than that of KM with low Mw, at the same concentration. Accordingly, the overlapping and entanglement of KM with high Mw occur at lower concentration as compared to those of KM with low Mw.

#### 4. CONCLUSIONS

The Mw of irradiated KM decreased with increase of absorbed dose. The aqueous solution of KM with Mw more than  $5 \times 10^5$  Da showed pseudo-plastic fluids behavior even at low concentration and at 50 °C. At low concentration region, KM solution changed to Newtonian fluid with decreasing Mw. KM with Mw less than  $2.3 \times 10^5$  Da was Newtonian fluid at semi-dilute region.

The critical overlap concentration decreased with increasing Mw. The overlapping and entanglement of KM with high Mw occur at lower concentration as compare to those of KM with low Mw.

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