Gelation of Konjac Glucomannan with Different Degree of Acetylation

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It is widely accepted that the 5-10 % acetyl substituted residues in glucomannan backbone of konjac glucomannan (KGM) confers water solubility on the glucomannan,[1] and the deacetylation generated by the addition of alkali is a crucial step leading to the gelation of KGM.[2] The role of acetyl groups is not fully elucidated possibly due to the difficulty in obtaining well-fractionated KGM samples and the very few acetyl groups in refined KGM. In the present case, acetylated KGM samples with different degree of acetylation (DA) were synthesized, and the rheological behavior in the gelation process of KGM samples on addition of Na_2CO_3 was investigated by dynamic viscoelastic measurements. Effect of DA on the gelation behavior for KGM was studied.

Inhomogeneous acetylation of KGM was carried out using acetic anhydride in the presence of pyridine as catalyst. DA of native and acetylated KGM samples was determined by a modified Eberstadt method including saponification and successive titration. A range of DA from 1.38~10.1 % of KGM samples was obtained by changing the acetylation temperature or amount of catalyst. Intrinsic viscosities of the samples in cadoxen at 25 ± 0.02 $^{\circ}$C were 557 for native KGM and 500 ± 20 $cm^3 \cdot g^{-1}$ for acetylated samples. It indicates that pyridine is a mild catalyst for the acetylation of KGM, where no obvious depolymerization was observed.

Winter and Chambon[3] criterion was used to determine the critical sol-gel transition points for gelation processes of all the samples. At a fixed alkaline concentration, the critical gelation time (t_{cr}) increased monotonically with increasing DA, and the plateau value of storage modulus (G'_{sat}) became larger with that. It was suggested that the relatively slow gelation rate of the KGM samples with higher DA was favorable for the improvement of elastic modulus, possibly due to the capability of homogeneous distribution of junction points during gelation at a slow gelation rate. However, if the effect of DA was taken into consideration, that is, at a fixed ratio of alkaline concentration (C_{Na}) to DA (C_{Na}/DA), the very close values of tcr and G'sat irrespective of DA was observed. The different DA dependence of gelation behaviors at a fixed alkaline concentration or at a fixed ratio of C_{Na}/DA suggested that the gelation process of the KGM samples were largely influenced by the deacetylation rate during gelation.

It was as expected that the critical gelation time and the saturated modulus of the KGM samples increased at higher temperature or higher KGM concentration. However, a rapid gelation rate resulted in a pronounced slippage during the initial gelation stage. The apparent activation energy (Ea) obtained from the Arrehenius representations of the temperature dependence of t_{cr} at a fixed ratio C_{Na}/DA were found to be independent of DA, and an average Ea of 110 $kJ \cdot mol^{-1}$ was observed. From the KGM concentration dependence of the G'_{sat} of native KGM obtained from the best fitting results by using first order kinetics model, a steep slope at lower polymer concentrations (0.87~1.28 %) and a gradual slope at higher concentrations (1.28~1.96 %) was observed.

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Role of Acetyl Groups in Gelation of Konjac Glucomannan

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Introduction

The Glucomannan backbone of konjac glucomannan (KGM) possesses 5-10 % acetyl substituted residues, [1] and it is widely accepted that the presence of this group confers water solubility on the glucomannan. The gelation mechanism of KGM is still under progress since the early studies of Maekaji, [2] which demonstrated that the deacetylation generated by the addition of alkali is a crucial step leading to the gelation. It has been reported that gelation of KGM may also occur under a high KGM concentration over 7 % [3]. Williams et al [4] suggested that the induction period following alkali addition observed in the time course of elastic modulus for KGM dispersion corresponds to both the aggregation kinetics of the deacetylated product and the deacetylation delay. The role of acetyl groups is not fully elucidated possibly due to the difficulty in obtaining well-fractionated KGM samples and the very few acetyl groups in refined KGM. In the present case, acetylation of KGM was carried out using pyridine as catalyst. The rheological behavior in the gelation process of KGM samples with different degree of acetylation (DA) on addition of Na2CO3 was investigated by dynamic viscoelastic measurements to make further insight into the effect of DA on the gelation behavior for KGM.

Results and Discussion

DA of native and acetylated KGM samples were determined by a modified Eberstadt method including saponification and successive titration. A range of DA from 1.38~10.1 % of KGM samples was obtained by changing the acetylation temperature or amount of catalyst (Table 1). Intrinsic viscosities of the samples in cadoxen at 25 ± 0.02 ^{o}C were 557 for native KGM and 500 ± 20 $cm^3 \cdot g^{-1}$ for acetylated samples (Table 1).

Table 1. Effect of the amount of pyridine and temperature on acetylation and the results of viscosity measurements of the products.

Sample	Rs	Ac1	Ac2	Ac3	Ac4	Ac5	Ac6	Ac-D
Pyridine (mL)	/	0.5	1	1.5	2	2.5	2.5	10
Temp (^{o}C)	/	40	40	40	50	50	80	40
Time (h)	/	2	2	2	2	2	2	3
DA (%)	1.376	4.128	4.472	4.816	5.848	7.396	7.568	10.148
DS	0.05	0.16	0.18	0.19	0.23	0.30	0.31	0.42
$[\eta]$ ^{a} (cm^3 g^{-1})	557	493	520	486	500	524	487	480

Winter and Chambon [5] criterion was found to be effective to determine the critical sol-gel transition points for gelation processes of all the samples. The gelation processes of aqueous dispersions of the KGM samples were monitored by the change of tan δ with time at the frequency range of 1~64 $rad \cdot s^{-1}$. The critical gelation time (t_{cr}) for each sample corresponds to the point at which tan δ remains as a constant and is independent of frequency. (Figure 1) At a fixed alkaline concentration, t_{cr} increased monotonically with increasing DA, and the plateau value of storage modulus (G'_{sat}) became larger with that. It was suggested that the relatively slow gelation rate of the

KGM samples with higher DA was favorable for the improvement of elastic modulus, possibly due to the capability of homogeneous distribution of junction points during gelation at a slow gelation rate. However, if the effect of DA was taken into consideration, that is, at a fixed ratio of alkaline concentration (C_{Na}) to DA (C_{Na}/DA), the very close values of tcr and G'sat irrespective of DA was observed. The different DA dependence of gelation behaviors at a fixed alkaline concentration or at a fixed ratio of C_{Na}/DA suggested that the gelation process of the KGM samples were largely influenced by the deacetylation rate during gelation.

We also studied the effect of temperature and KGM concentration on the geation kinetics for the KGM samples. It was as expected that the critical gelation time and the saturated modulus of the KGM samples increased at higher temperature or higher KGM concentration. However, a rapid gelation rate resulted in a pronounced slippage during the initial gelation stage. The apparent activation energy (Ea) obtained from the Arrehenius representations of the temperature dependence of the critical gelation time at a fixed ratio C_{Na}/DA were found to be independent of DA, and an average Ea of 110± 1.1 kJ·mol^{-1} was observed. From the KGM concentration dependence of the saturated modulus of native KGM obtained from the best fitting results by using first order kinetics model, a steep slope at lower polymer concentrations (0.87~1.28 %) and a gradual slope at higher concentrations (1.28~1.96 %) was observed.

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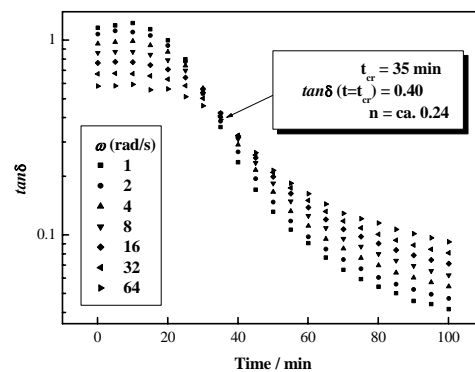
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Figure 1. tan δ as a function of time at different frequencies at 50 °C for 2.0 wt% Ac1 aqueous dispersion. The Na$_2$CO$_3$ concentration was 0.8 wt%.
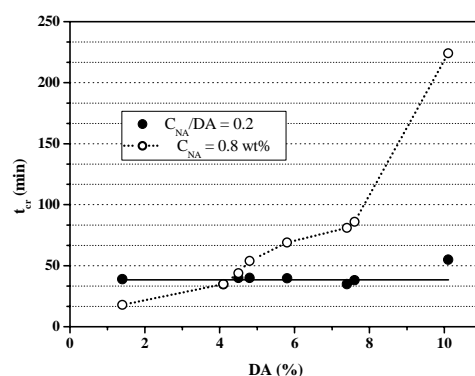

Figure 2. Plotted of t$_{cr}$ of the KGM samples as a function of DA in the case of C$_{Na}$ / DA as 0.2 and Na$_2$CO$_3$ concentration (C$_{Na}$) as 0.8 wt%, respectively.
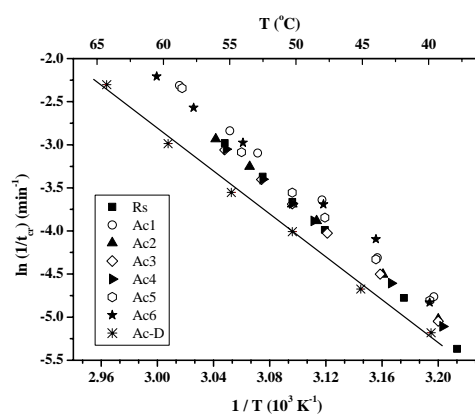

Figure 3. Arrehenius representations of the temperature dependence of t$_{cr}$ for 2 wt% KGM aqueous dispersions. The ratio C$_{Na}$ / DA was fixed to 0.2.