

Preparation of Konjac Glucomannan Ester of Palmitic Acid and Its Emulsification

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ABSTRACT: Various degrees of palmitoylated konjac glucomannan (PKGM) are prepared by a heterogeneous method. Differential thermal analysis thermographs show PKGM having 0.51 degrees of substitution (DS) gave a new crystalline peak at higher temperature. With the increase of DS, the former crystalline state of konjac glucomannan will disappear; PKGM only shows the new crystalline state. Furthermore, the effect of the DS of PKGM on its emulsifying ability has been investigated in the water in oil and oil in water systems. It is demonstrated that it is a kind of good water in oil emulsifier, with the DS ranged between 1.00 and 1.70, whereas $DS < 0.50$. It is a kind of good oil in water emulsifier and an interesting phenomenon appears in the water in oil system. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1035–1038, 1998

Key words: heterogeneous method; palmitoylated konjac glucomannan; polysaccharide emulsifier; emulsifying ability

INTRODUCTION

Konjac glucomannan (KGM) is the main ingredient of konjac. In Japan, America, and China, the applied research of KGM has made important progresses in pharmaceutical, food, chemical engineering, and fabric aspects. Shimahara and colleagues,¹ Maeda and colleagues,² and Takahashi and colleagues³ have made detailed research about the structure and property of KGM. Because purified KGM was easily soluble in water, but insoluble in organic solvents such as *N,N*-dimethylformamide or dimethylsulfoxide,² we have prepared KGM esters of palmitic acid by a heterogeneous method reported by Fujii and colleagues.⁴ This was based on similar work on chitosan⁵ and cellulose.⁶

Recently, polysaccharides as raw materials for the detergent industry^{7,8} and as emulsion stabilizer^{9,10} in food have been reported. In 1992, Alain and colleagues¹¹ reported polyose and fatty acid

complex, with high fatty acid content used as emulsifying or moisturizing agent. Moreover, extracellular polysaccharide biosurfactant is also exploited.¹² Palmitoylated KGM (PKGM) has the characteristics of both surfactant and polymer, and it is proved that it is a kind of water in oil (w/o) and oil in water (o/w) emulsifier, being active in low concentrations (0.1–0.01%). Thus, we predict it will be used as an efficient emulsifier.

EXPERIMENTAL

Materials

All reagents used were Analar grade. Purified KGM was refined from commercial konjac flour.

Preparation of the Sample

Purified KGM (1.50 g) was soaked in pyridine (20 mL) for 24 h at 60°C, after which pyridine was evaporated under reduced pressure. Purified KGM was then immersed again in benzene (20 mL) and pyridine (6 mL) for 18 h at 60°C. The

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Table I Experimental Data for DS of PKGM and Its Optical Density^a

DS	0.51	0.99	1.47	2.00	2.34	2.72
OD ^b	-0.325 ^d	0.485	0.670	-0.130 ^d	-0.325 ^d	-0.425 ^d
OD ^c	0.350	0.055	-0.060 ^d	0.050	0.165	-0.040 ^d

^a Optical density (OD) value represents emulsifying ability.

^b w/o system.

^c o/w system.

^d Negative value of optical density was used only if the transmittance of the system containing PKGM was more than that of blank.

mixture was cooled in an ice-salt bath, and palmitoyl chloride was added slowly with constant stirring; then, it was again cooled for 0.5 h. The reaction was conducted in a thermostated bath at $70 \pm 2^\circ\text{C}$ for 4.5 h after which it was poured into hydrochloric acid (pH 4) for 10 h, then extracted with distilled water. The sample was dried and extracted with acetone. Various degrees of PKGM were prepared according to the added amount. We found it was ineffective for different periods of time according to the degree of substitution (DS) desired.⁶

Infrared Spectra

Infrared spectra of samples dispersed in KBr were obtained using a NICOLET 170SX Fourier transform infrared spectrophotometer.

Differential Thermal Analysis

A Shimadzu DT-30B differential calorimeter was used to record the thermographs under nitrogen.

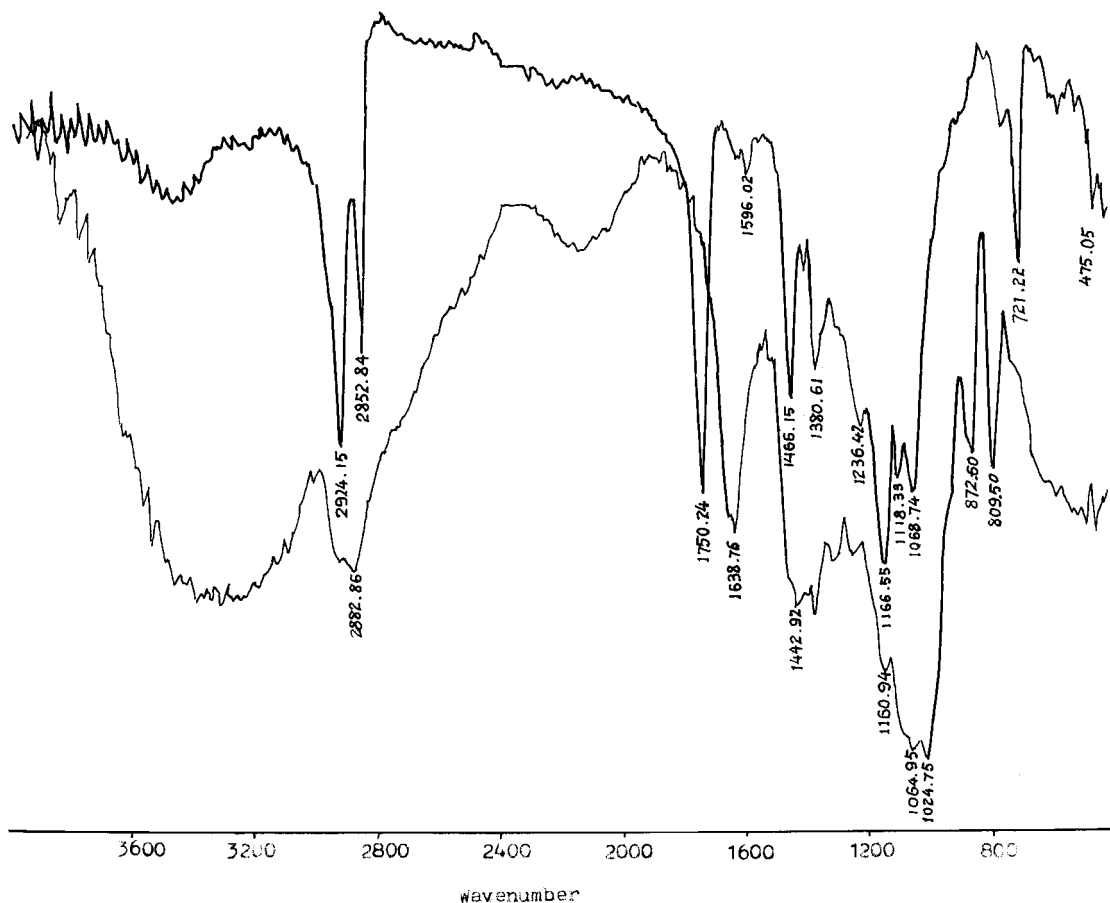


Figure 1 Fourier transform infrared spectra for PKGM and KGM.

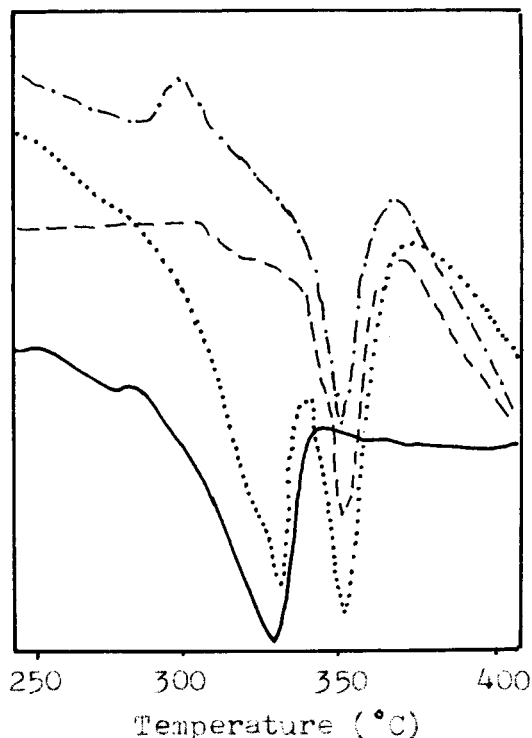


Figure 2 Differential thermal analysis thermographs of PKGM samples B (·····), C (---), D (-·-·-), and KGM sample A (—).

X-Ray Diffraction Spectra

A Rigaku D/max-ra X-ray diffractometer ($\text{CuK}\alpha$, 40 kV) was used to obtain the crystallogram.

Degree of Substitution

DS was measured by the saponification method.

W/O and O/W Systems

The w/o and o/w systems contained 4 mL benzene solution (concentration of PKGM: 2 mg mL^{-1}) and 1 mL distilled water, 1 mL benzene solution, and 4 mL distilled water, respectively. They were obtained by using a 25 W ultrasonic generator for 5 min of ultrasonic emulsification. The w/o and o/w systems were identified by dye check under a microscope and determined by the conductivity method.

Emulsifying Ability

Emulsifying ability was determined by means of optical density measurements of the test liquids at 620 nm .¹³ Those results were presented in Table I.

RESULTS AND DISCUSSION

Characterization of the Product

The infrared spectra of purified KGM and PKGM are shown in Figure 1. PKGM shows the appearance of new peaks at 1750 cm^{-1} and 720 cm^{-1} , $\text{C}=\text{O}$ of *O*-acylation and $-(\text{CH}_2)-$ ($n \geq 4$), respectively.

Differential thermal analysis thermographs for PKGM samples B–D, along with the purified KGM sample A, are shown in Figure 2. Sample B reserved the former crystalline state of purified KGM and produced a new one, whereas sample D gave only the same new crystalline state that existed in samples B and C. This indicates that, with the increase of DS, the former crystalline state of purified KGM would be completely destroyed. Furthermore, it is interesting that the new crystalline state exists at higher temperature. The high substituted chitosan⁵ ester of long fatty acid did not give a new crystalline state, but the former crystalline state diverted to a lower temperature. This indicates that the crystalline state of purified KGM was easily destroyed and KGM was less thermally stable than PKGM. The molecular skeleton of purified KGM was more flexible than that of chitosan.

The X-ray diffraction spectra for PKGM samples C and D, along with purified KGM sample A, are shown in Figure 3. It was calculated that *d* values for samples A, C, and D are 4.62 \AA , 4.43 \AA , and 4.38 \AA , respectively. [Bragg equation: d

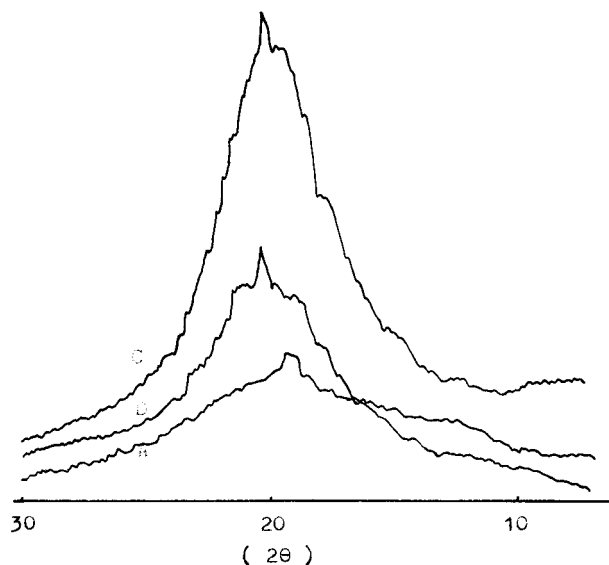


Figure 3 X-ray diffraction spectra for PKGM samples C and D, and KGM sample A.

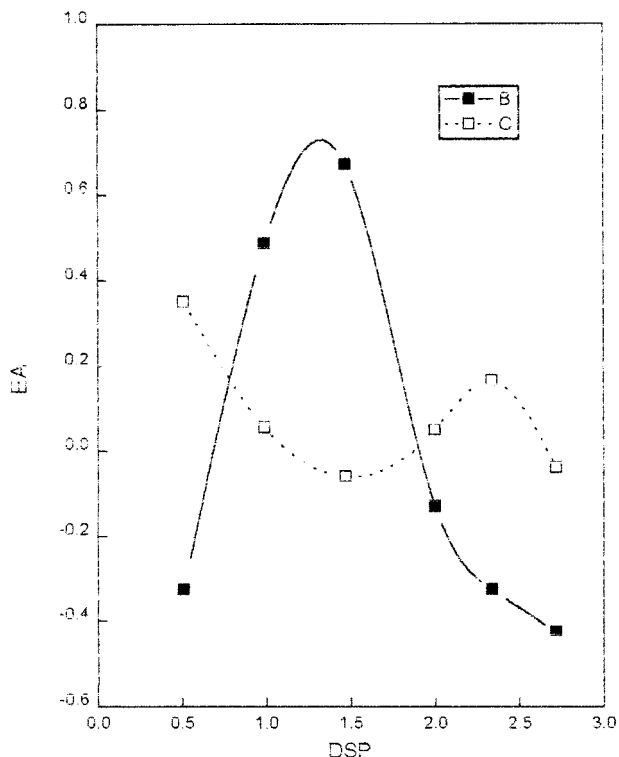


Figure 4 Relationship of emulsifying ability and DS of PKGM in w/o and o/w systems. EA, emulsifying ability; DSP, DS of PKGM; B, w/o; C, o/w.

$= \lambda / (2 \sin \theta)$.] Because of the decrease of d value, the crystalline state of PKGM would be closer than that of purified KGM, and it appeared at a higher temperature. This result is in agreement with that of differential thermal analysis.

From Figure 4, two observations can be made: (1) with DS ranging between 1.00 and 1.70, the emulsifying ability was beyond 0.50 and stable w/o emulsion can be formed; and (2) for DS < 0.50, the emulsifying ability was beyond 0.40 and stable o/w emulsion can be formed. It was possible that a strong interaction was produced between PKGM and the interface of oil droplet for

the former, whereas for the latter—because of the strong hydrophilic characteristics of PKGM—strong interaction was produced between PKGM and the interface of the water droplet. This explanation was based on the model¹⁴ of strong interaction between the polymer and liquid droplet. However, an exciting phenomenon appears in Figure 4. It was with some hydrophilic characteristics of PKGM and the palmitoyl chains that gave an orderly state and accumulated in the oil–water interface that resulted in maximal peak. This opinion was also elucidated by differential thermal analysis and X-ray diffraction analysis.

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