Studies on Preparation and Emulsifying Properties of Guar Galactomannan Ester of Palmitic Acid

CHANGMING DONG, BINGSHOU TIAN

Department of Chemistry, Wuhan University, Hubei, China 430072

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ABSTRACT: Various degrees of palmitoylated guar galactomannan (PGGM) are prepared by a heterogeneous method. Both differential thermal analysis and X-ray diffraction spectra show substituted palmitoyl chains played a role in the new crystallization and the molecular aggregated structure of GGM was changed. Furthermore, the emulsifying properties of both water-soluble and oil-soluble PGGM were investigated in detail. It is demonstrated that PGGM has good emulsifying activity, even in high salt concentration or in acidic pH. In addition, the emulsifying properties of water-soluble PGGM–protein mixture was also studied systematically. It is proven that water-soluble PGGM is a kind of good oil in water (o/w) emulsion stabilizer. With water-soluble PGGM–casein mixture (0.1 wt %) as emulsifier, clove oil–water (v : v, 1 : 9) emulsion had good stability within 4 weeks at room temperature, and the breakage of emulsion was not brought about. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 639–645, 1999

Key words: palmitoylated guar galactomannan; polysaccharide emulsifier; polysaccharide stabilizer; emulsifying property

INTRODUCTION

Guar galactomannan (GGM) is the main ingredient of guar gum. In the 1980s, McCleary and colleagues[1,2] and Robinson and colleagues[3] made detailed research about the structure and property of GGM. Because GGM is easily soluble in water and usually does not form gel, it is conveniently refined from guar gum. Using GGM as the only emulsifier, Reichman and colleagues[4] prepared nonviscous oil in water (o/w) food model emulsion. Akio and colleagues[5] reported that GGM–protein mixture or conjugate was a kind of good macromolecular emulsifier in the food industry.

Recently, natural polysaccharides were used as emulsifiers and stabilizers in food,[6,7] pharmaceutical,[8,9] detergent,[10,11] and fuel[12,13] industries because they have good emulsifying property, being active in low concentrations ($\sim$ 0.01–0.1%), nontoxicity, antioxygenic activity,[14] and biodegradability. Landoll[15] prepared water-soluble polysaccharide surfactant by addition of long-chain *n*-alkyl epoxides to nonionic cellulose ether. Tian and colleagues[16] reported oil-soluble nonionic polysaccharide emulsifier in 1998. In this article we prepared two kinds of nonionic polysaccharide emulsifiers (water-soluble and oil-soluble) by a heterogeneous method. It was proven that PGGM is a kind of good o/w emulsifier and stabilizer, being active in low concentrations (0.02 or 0.1%), and that water-soluble PGGM–casein mixture will be used as an efficient macromolecular emulsifier in food, pharmaceutical, and cosmetic industries.

Correspondence to: B. Tian.

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EXPERIMENTAL

Materials

All reagents used were Analar grade. Purified GGM was refined from commercial guar gum.

Preparation of Sample

Purified GGM (3.0 g) was soaked in pyridine (30 mL) for 16 h at 80°C, after which pyridine was evaporated under reduced pressure. Purified GGM then was immersed again in toluene (25 mL) and pyridine (3 mL) for 12 h at 80°C. The mixture was cooled in an ice–salt bath, and palmitoyl chloride (1.70 mL) was added slowly with constant stirring; it was then cooled again for 0.5 h. The reaction was conducted in a thermostated bath at 80 ± 2°C for 3.5 h after which it was filtered and washed with acetone-distilled water (v : v, 1 : 1) for several times and then extracted with acetone. The sample was soluble in water and the oil-soluble PGGM was prepared according to the added amount.

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.

X-ray Diffraction Spectra

A Rigaku D/max-ra X-ray diffractometer (Cuk_{α}, 40 kV) was used to obtain the crystallogram.

Degree of Substitution

Degree of substitution (DS) was measured by the saponification method.

Measurement of Emulsifying Property

Emulsifying activity was determined by means of optical density measurement of the test liquid. To prepare emulsion, 0.5 mL of clove oil and 4.5 mL of sample solution were ultrasonically emulsified with a 25-W ultrasonic generator for 3 min. The absorbance of emulsion then was determined at 560 or 500 nm. The emulsifying activity was determined from the absorbance measured immediately after emulsion formation, and the emulsion stability was estimated by measuring the half-time of the turbidity of the emulsion. The o/w emulsion was identified by dye check under a microscope and was determined by the conductivity method.

RESULTS AND DISCUSSION

Characterization of Product

The infrared spectra of purified GGM and palmitoylated GGM (PGGM) are shown in Figure 1. The PGGM shows the appearance of new peaks at 1750 and 720 cm^{-1}, C═O of O-acylation, and $-(-CH_2-)_n$ ($n \geq 4$) in palmitic group, respectively.

Differential thermal analysis thermographs for PGGM samples B and C, along with the purified GGM sample A are shown in Figure 2. Sample C reserved the former crystalline state of purified GGM and produced a new one, whereas sample B did not give the same new crystalline state. This indicates that substituted palmitoyl chains played a role in the new crystallization and the molecular aggregated structure of GGM was changed.

The X-ray diffraction spectra for purified GGM sample A and PGGM sample B are shown in Figure 3. Sample B gave a narrow and strong diffraction peak, whereas sample A produced a wide and weak one. This also indicates that the substituted palmitoyl chains changed the molecular aggregated structure of GGM.

Emulsifying Properties

Figure 4 shows the effect of its concentration on the emulsifying activity of water-soluble PGGM. It is seen that water-soluble PGGM gave excellent emulsifying activity when its concentration was equal to 0.02 wt %. Thus, we investigated in detail the emulsifying properties of PGGM with the concentration of 0.02%.

Figure 5 shows the emulsifying property of water-soluble PGGM. The emulsifying activity of water-soluble PGGM was 0.575 at pH 7.0; when the water phase contained 10% NaCl, it was 0.285 and decreased by 50.4%; it was 0.400 and decreased by 30.4% when the water phase contained 1% citric acid (pH 2.3). This indicates that water-soluble PGGM had good emulsifying activity, even in high salt concentration or in acidic pH.

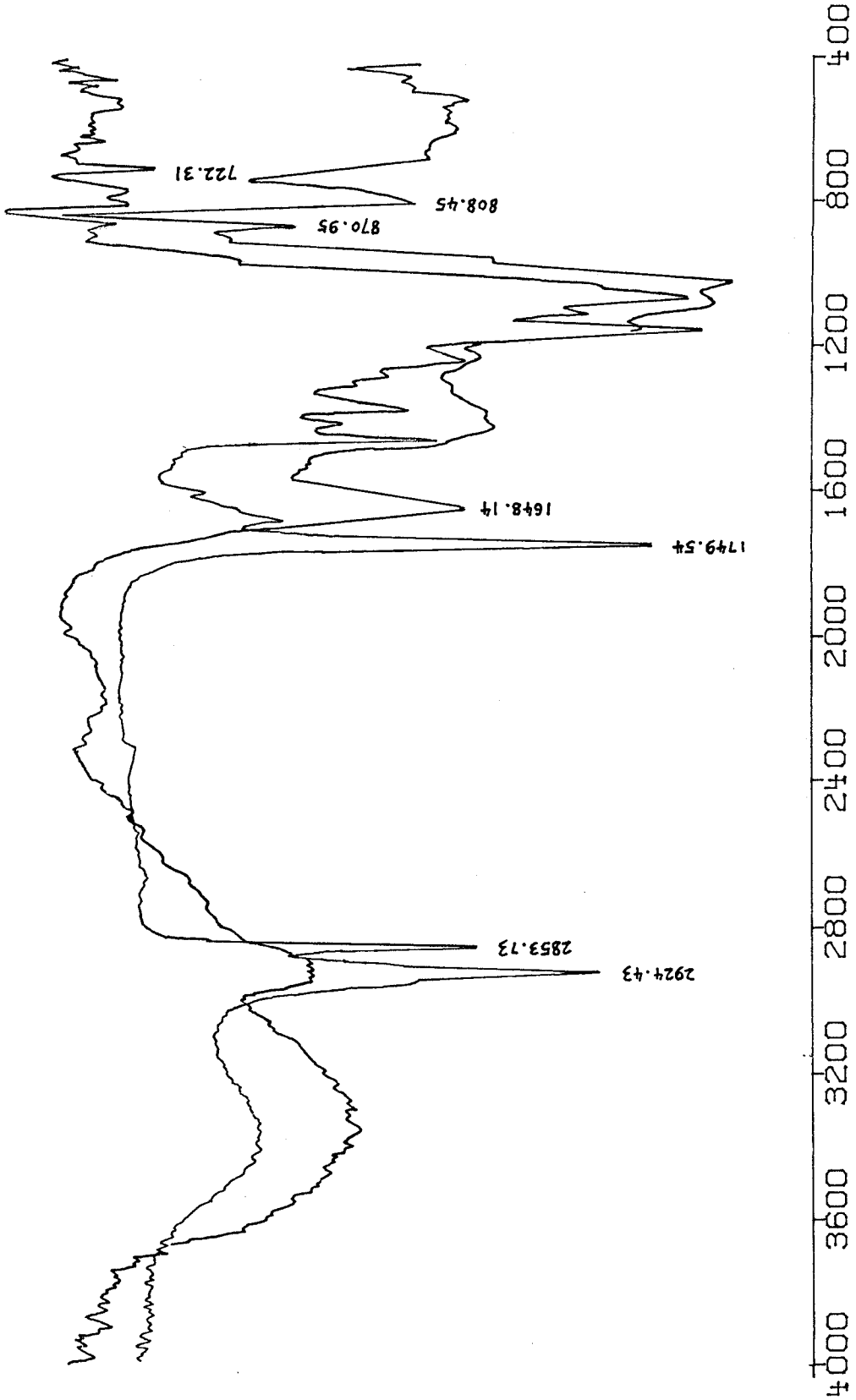

Figure 1 Fourier transform infrared spectra of samples GGM and PGGM.

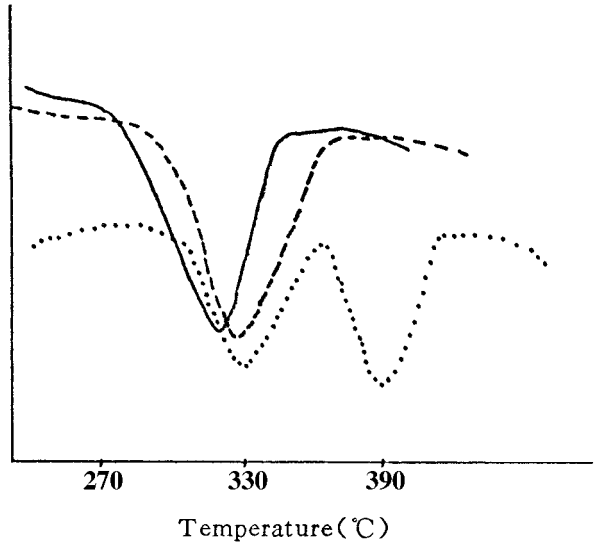

Figure 2 Differential thermal analysis thermographs of samples GGM and PGGM [——, GGM; – –, PGGM (DS = 0.24); · · ·, PGGM (DS = 2.68)].

Figure 6 shows the emulsifying property of oil-soluble PGGM. The emulsifying activity of oil-soluble PGGM was 0.310 at pH 7.0; when the water phase contained 10% NaCl, it was 0.190 and decreased by 38.7%; it was 0.290 and decreased by 6.5% at pH 2.3. The above shows that oil-soluble PGGM had better salt-it and acid-resistant properties than water-soluble PGGM and that the latter had better emulsifying activity than the former.

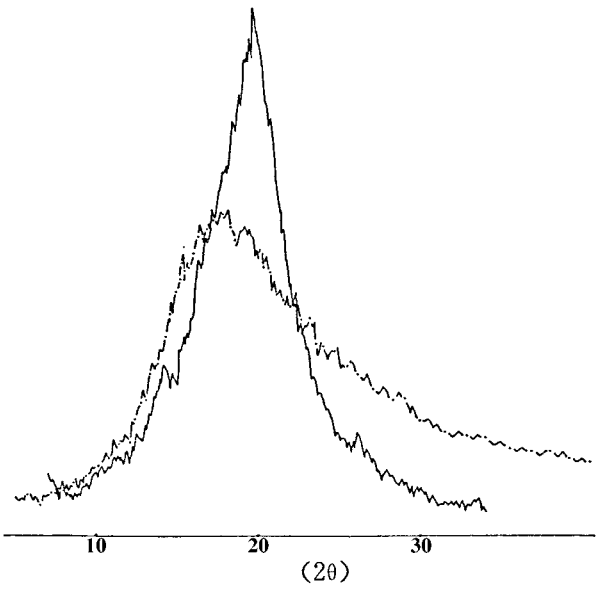

Figure 3 X-ray diffraction spectra of samples GGM and PGGM [— · —, GGM; ——, PGGM (DS = 2.68)].

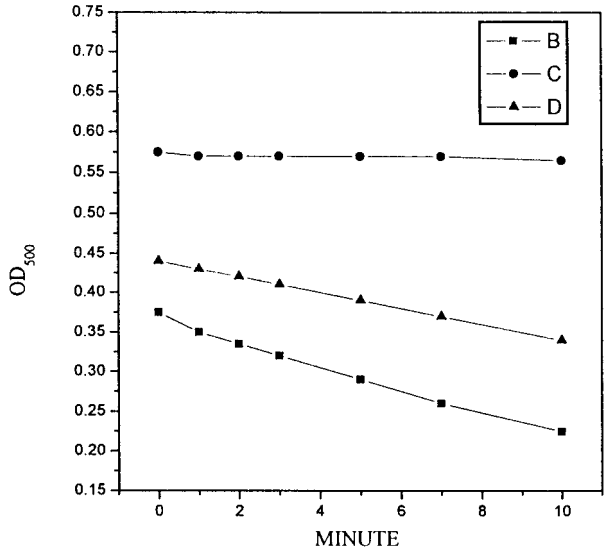

Figure 4 The emulsifying activity of water-soluble PGGM as a function of its concentration.

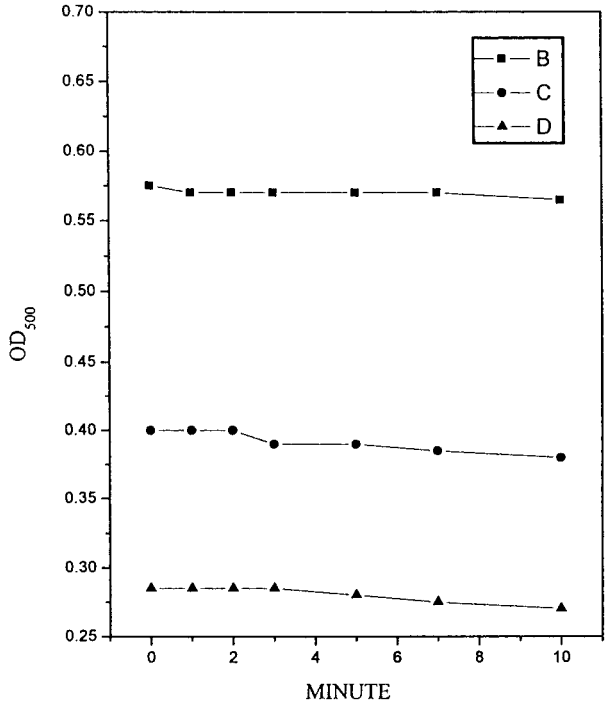

Figure 5 The emulsifying property of PGGM (DS = 0.24) (B, 0.02% PGGM, pH 7.0; C, 0.02% PGGM, pH 2.3; D, 0.02% PGGM, with 10% NaCl contained in the water phase).

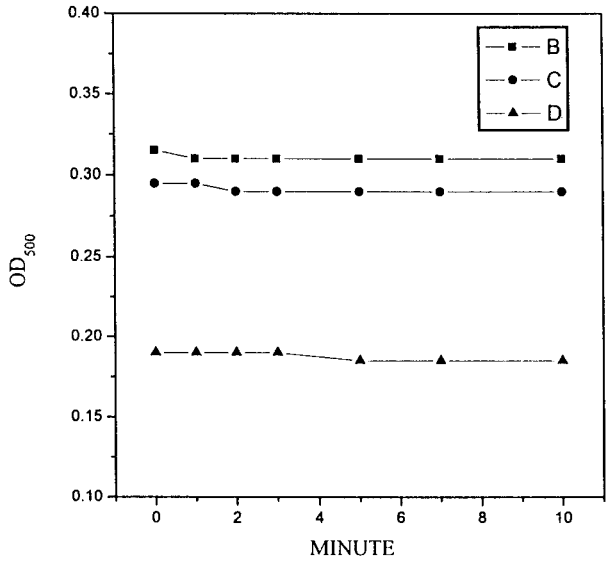

Figure 6 The emulsifying property of PGGM (DS = 2.68) (B, 0.02% PGGM, pH 7.0; C, 0.02% PGGM, pH 2.3; D, 0.02% PGGM, with 10% NaCl contained in the water phase).

The emulsion stability curve is given in Figure 7. It is seen that the emulsion remained relatively stable for the initial 0.5 h and then the optical density of the emulsion dropped sharply and the halftime of the emulsion was about 1.5 h. This was different from that of polysaccharide biosurfactant RAG-1 emulsion.[17]

The emulsifying properties of the water-soluble PGGM–protein mixture (wt/wt, 1 : 1) were investigated systematically using protein, ovalbumin

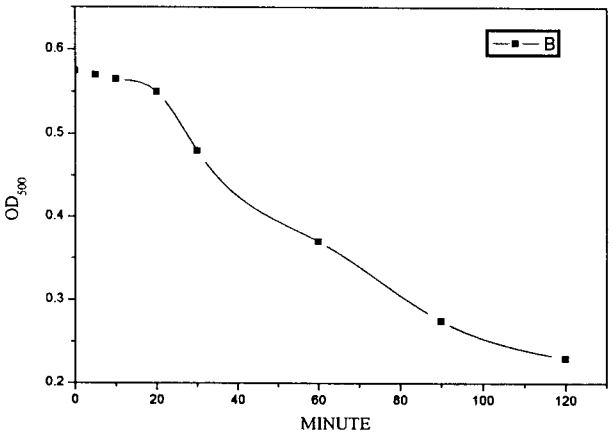

Figure 7 Stability of PGGM-induced emulsion (B, 0.02% PGGM, pH 7.0).

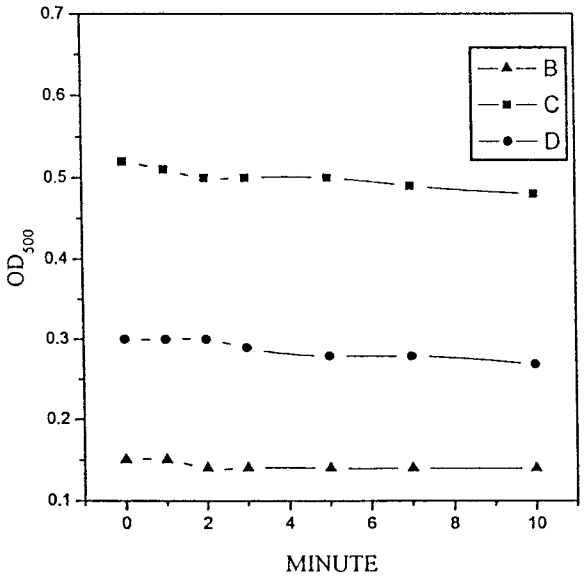

Figure 8 The emulsifying property of OVA–PGGM mixture (B, 0.1% OVA–PGGM, pH 7.4; C, 0.1% OVA–PGGM, pH 2.3; D, 0.1% OVA, pH 2.3).

(OVA), bovine serum albumin (BSA), lysozyme, and casein. Figure 8 shows the emulsifying property of OVA–PGGM mixture. The emulsifying activity of the mixture was 0.150 at pH 7.4; when the water phase contained 1% citric acid (pH 2.3), it was 0.220 and increased by 73.3%. This indicates that water-soluble PGGM improved the emulsifying activity of OVA, especially in acidic pH. It was possible that the folding structure of OVA was stretched at pH 2.3 because of the static repelling force and the strong interaction was produced between OVA and water-soluble PGGM.

Figure 9 shows the emulsifying property of BSA–PGGM mixture. The emulsifying activity of the mixture was 0.250 at pH 7.4 and it was 0.260 and increased by 288.9% at pH 2.3. This indicates that water-soluble PGGM had improved dramatically the emulsifying activity of BSA in acidic pH.

The emulsifying property of the lysozyme–PGGM mixture is shown in Figure 10. The emulsifying activity of the mixture was 0.260 at pH 7.4 and it diminished slightly at pH 2.3, but the emulsifying activity of lysozyme was enhanced by 0.210. The above indicates that water-soluble PGGM could not improve the emulsifying activity of lysozyme in acidic pH.

The emulsifying property of the casein–PGGM mixture is shown in Figure 11. The emulsifying activity of the mixture was 0.830 at pH 7.4 and it diminished by 15.7 or 17.5% when the water

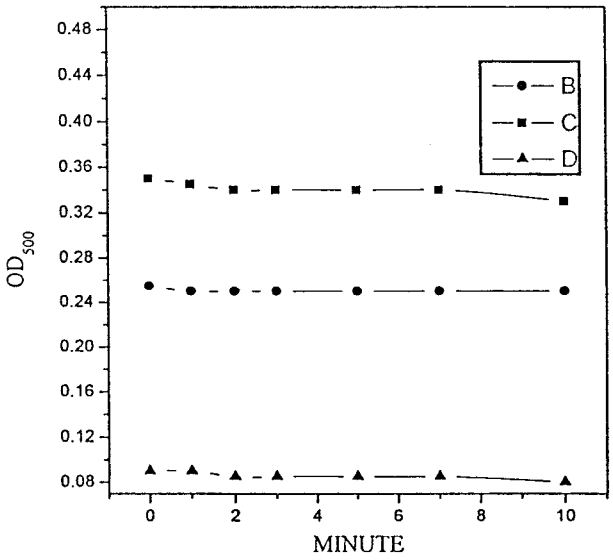

Figure 9 The emulsifying property of BSA–PGGM mixture (B, 0.1% BSA–PGGM, pH 7.4; C, 0.1% BSA–PGGM, pH 2.3; D, 0.1% BSA, pH 2.3).

phase contained either 1% citric acid or 10% NaCl. The above shows that water-soluble PGGM dramatically enhanced the emulsifying activity of casein, even in high salt concentration or in acidic pH. This may be caused by the fact that the strong interaction was brought about between casein and PGGM because of the unfolding structure of casein. Thus, the cooperative effect of the casein–PGGM complex improved the emulsifying activity of casein. Meanwhile, with the water-soluble PGGM–casein mixture (0.1%) as emulsifier, clove oil–water (v : v, 1 : 9) emulsion had good stability within 4 weeks at room temperature, and the breakage of emulsion was not brought about.

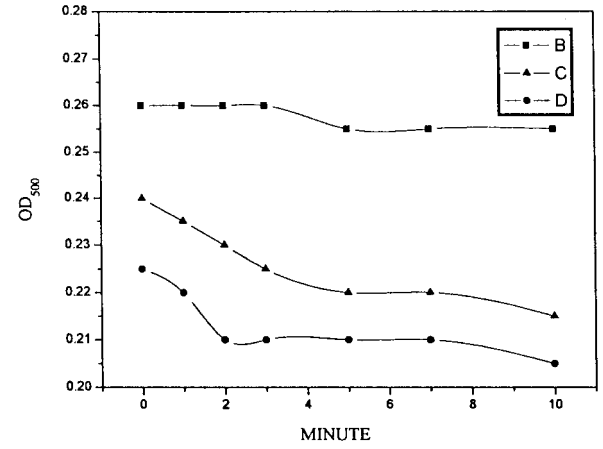

Figure 10 The emulsifying property of lysozyme–PGGM mixture (B, 0.1% lysozyme–PGGM, pH 7.4; C, 0.1% lysozyme–PGGM, pH 2.3; D, 0.1% lysozyme, pH 2.3).

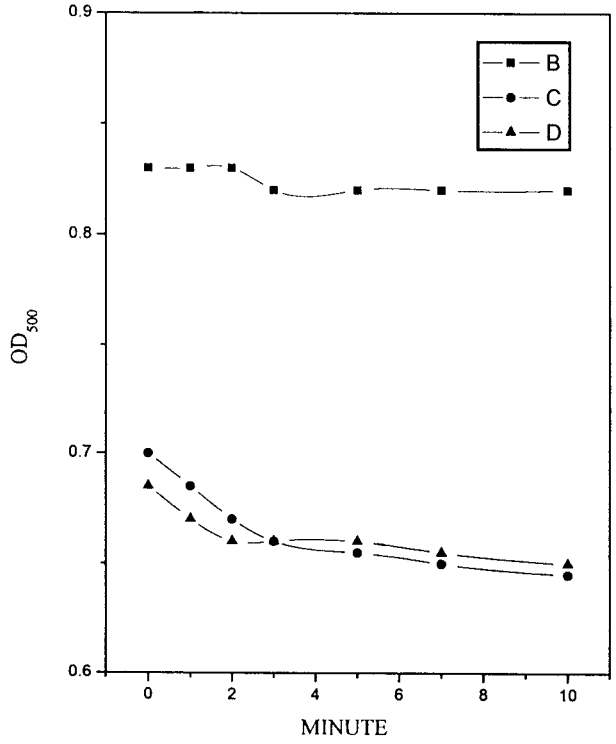

Figure 11 The emulsifying property of casein–PGGM mixture (B, 0.1% casein–PGGM, pH 7.4; C, 0.1% casein–PGGM, pH 2.3; D, 0.1% casein–PGGM, with 10% NaCl contained in the water phase).

In conclusion, the water-soluble PGGM–casein mixture can be used as a kind of prospective macromolecular emulsifier in food, pharmaceutical, and cosmetic industries.

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