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The isolation and characterization of a water extract of konjac flour gum

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An aqueous extract from konjac flour was dried, milled and redispersed in water, prior to its characterization by viscometry and rheometry. The rate of change of relative viscosity with reciprocal absolute temperature was of a magnitude less than that of some other polar polysaccharides by a factor approximating 2. The volume-concentration relationship was non-linear in water, but linear in 0·04 M tartaric acid. The hydrophilicity of this extract in 0·04 M tartaric acid was only 0·68 g g^{-1} solute/100 g dispersion, much less than that of many of the commonly used polysaccharides. The intrinsic viscosity was 1320 ml g^{-1}, among the highest of the polysaccharides. Considering the relatively low water affinity, the high viscosity of the konjac extract was attributed mostly to solute-solute interaction, rather than to hydration, at functional use-levels. The dried, redispersed extract was characterized in both steady and dynamic shear by the Carreau and Cross equations, and by the Cox-Merz rule. Deviation from the Cox-Merz rule was attributed to molecular associations of time scales longer than non-specific physical entanglements.

INTRODUCTION

Konjac flour is the milled form of mature tubers of *Amorphophallus konjac*, containing approximately 85% high molecular weight (MW, in excess of 10^6 Daltons), water-soluble glucomannan in β-1,4-linkages, as in cellulose, in the ratio 1·6:1 (glucose:mannose). The flour is touted for its ability to create highly viscous systems in synergism with κ-carrageenans, for example, far greater than its glycomannan counterparts, the commonly used guar and locust bean gums (FMC, 1989). High viscosity in a dispersion can result from either solute–solvent or solute–solute interaction, depending on the 'goodness' of the solvent and/or on concentration of the solute (Isono & Nagasawa, 1980). In this paper, we show that konjac gum, by itself, is capable of large Newtonian-viscosity increases in the concentration range of hundredths to tenths of a percent, where its volume expansion (radius of gyration) should be largest.

It is generally believed that the konjac mannan structure contains some degree of methylation of acid groups (Nishinari *et al.*, 1992), and that it can exist in two forms, viz. a soluble and an insoluble form. In the opinion of Torigata (1952), deesterification resulted in insolubility and/or gelation.

The rheology of many food-gum dispersions has been reviewed by several authors (Morris *et al.*, 1981; Launay *et al.*, 1986; da Silva & Rao, 1992) who have generally recognized in the shear-rate interval an initial, zero-shear viscosity, followed by a power law viscosity, and finally an infinite-shear viscosity region. Often, due to a limited rheometric capability, data are obtained only over the zero-shear viscosity and the power law viscosity regions.

Rheological models such as those of Carreau (eqn (1)) and Cross (eqn (2)) (da Silva *et al.*, 1993) describe viscosity-shear rate data in the zero-shear (plateau) and power law regions; they also can provide reliable estimates of the zero-shear viscosity (η_0, Pa s) and the time constants of flow (Ross-Murphy, 1984; da Silva *et al.*, 1993). The importance of reliably determining η_0 is in its relationship to intrinsic viscosity ($[\eta]$), and hence to an accurate determination of molecular weights (Morris, 1990).

The Carreau and Cross models are, respectively,

$$\eta_a = \frac{\eta_0}{[1 + (\lambda_c \dot{\gamma})^2]^N} \tag{1}$$

$$\eta_a = \frac{\eta_0}{[1 + (\tau \dot{\gamma})^m]} \tag{2}$$

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where $\dot{\gamma}$ is the shear rate (s^{-1}), η_a is the apparent viscosity (Pa s) at concentration c, and λ_c (s), N, τ (s^m) and m are constants.

The product of $[\eta]$ and c (defined as the coil overlap parameter) of several random coil polymers was found to follow a common curve that could be divided into two regions (Morris *et al.*, 1981), viz. a region of dilute dispersion where the viscosity dependence on concentration follows a 1·4 power, and a region of concentrated dispersion where the viscosity dependence on concentration follows a 3·3 power. The transition from the dilute to the concentrated region occurred at $c[\eta] \approx 4$. However, a few biopolymers such as guar gum and locust bean gum were found to deviate from the above observation (Morris *et al.*, 1981; Robinson *et al.*, 1982). In these exceptions, the concentrated region began at $c[\eta] \approx 2{\cdot}5$, and the viscosity showed a higher dependence on c, i.e. a slope greater than 3·3. These deviations were attributed to specific intermolecular associations (hyperentanglements) between regular and rigid chain sequences in addition to the simple process of interpenetration.

At least two critical concentrations related to space occupancy have been determined within the transition region for several food hydrocolloids, viz. proteins (Lefebvre, 1982), xanthan gum (Launay *et al.*, 1984), and cellulose derivatives (Castelain *et al.*, 1986). It is also known that the Cox–Merz rule (eqn (3)), relating steady (η) and dynamic (η^*) shear viscosity, is followed by guar and other gums (Mills & Kokini, 1984), but not by others. The reasons for this non-compliance have been given as aggregation (e.g. pectins) and hyperentanglements (e.g. locust bean gum) (da Silva *et al.*, 1993).

$$\eta^*(\omega) = \eta(\dot{\gamma})\big|_{\omega=\dot{\gamma}} \quad (3)$$

The objective of this research was to characterize konjac glucomannan primarily on the basis of its steady and dynamic shear properties.

MATERIALS AND METHODS

Materials

Nutricol (Tradename, FMC, 1989) konjac flour was agitated in distilled water at 0·6% (w/v) for 1·5 h in a temperature-regulated shaker, held at approximately 70°C. The supernatant liquid was then decanted and centrifuged at 8000–9000 rev min^{-1} for 10 min. Ethanol (95%) at three times the volume of the supernatant liquid was added to the supernatant liquid, and the precipitate was separated, washed with 95% ethanol, and dried at 105°C to constant weight. The dried matter was milled to pass a 40 mesh sieve. The milled extract was stored over concentrated H_2SO_4, until ready for use.

Methods

Preparation of dispersions

The dried, milled extract was dispersed in water, and in 0·04 M tartaric acid solution (TA) to various concentrations. The weighed solute was first deposited in 100-ml volumetric flasks or 250-ml Erlenmeyer flasks, then 90 ml water or TA was added with stirring and mild heat. After cooling to room temperature (25°C), the final volume (100 ml) or weight (100 g) was obtained with water or TA.

Detection of cellulose

A film of the dried, milled extract, 8 μm thick, determined by a digital caliper, was prepared by drying approximately 10 ml of the dispersion (0·2% (w/v)) over the central area of a 100 mm-diameter watch glass and prying the residue with the tip of a spatula. This was tested for cellulose by the chlorozinciodine method (Greenish, 1923).

Infrared spectroscopy

0·2% and 0·4% (w/v) dispersions of the dried, milled extracts were made. To the 0·4% dispersion was added an equal amount of phthalate/HCl buffer (pH 2·80), and the dispersion was held for 1 h. The acid-treated dispersion was precipitated with ethanol, as previously described. The precipitate was dried and redispersed in water at 0·2% (w/v). Samples of these 0·2% dispersions were dried to a thin film, 8 μm thick, and held in a H_2SO_4 desiccator for 24 h. An infrared spectrum was obtained on this film, using a Perkin-Elmer model 267 infrared spectrophotometer (Perkin-Elmer Corporation, Norwalk, CT).

Hydrophilicity

The dried, milled extract was dispersed in water and in TA to concentrations between 0·063 g and 0·500 g 100 g^{-1} dispersion. The dispersions were degassed in a vacuum oven at 70°C, cooled, then centrifuged at 5000 rev min^{-1} for 10 min. Density (d) was measured with a 25 ml pycnometer. Samples (10 ml) of the dispersions were dried to constant weight, and, using this weight, after correcting for blanks, the actual weight/weight (C') or weight/volume (C) concentration was determined. The volume (V) was calculated from the density equation, $d = w/V$, where w was the corresponding weight of dispersion. V versus C' graphs were plotted, and the slope of the line was determined by a computer method of least squares.

Intrinsic viscosity

The dried, milled extract (0·069 g 100 ml^{-1}) was dispersed in water by magnetic stirring, without heating, overnight, then centrifuged at 5000 rev min^{-1} for 10 min. From this centrifuged, stock dispersion, 10 ml aliquots were dried to constant weight, so that C could be accurately calculated. Dilutions between 0·017 g 100 ml^{-1} and 0·046 g 100 ml^{-1} were made in a Cannon-Ubbelohde dilution viscometer (Cannon Instrument Co., State College, PA) immersed in a 28°C water bath. $[\eta]$ was determined from viscosity-number measurements (η_{sp}/C) versus C.

Apparent activation energy of viscous flow

The dried, milled extract was dispersed in water overnight and made to a concentration of 0·054 g 100 ml^{-1}, then centrifuged. Single-point viscosity (relative viscosity, η') was measured with a Cannon-Fenske routine viscometer (Cannon Instrument Co., State College, PA), immersed in a water bath initially set at 60°C, then successfully lowered to 50°, 42° and 34°C. Log η' versus the reciprocal absolute temperature (T^{-1}) was plotted, and the activation energy of viscous flow (E) was calculated from the slope of log η' versus T^{-1}.

Stability

The dried, milled extract was dispersed in water, and in phthalate/HCl buffer containing 0·005% sodium azide to a concentration of 0·10 g 100 ml^{-1} dispersion. Specific viscosity, (η_{sp}), was measured daily, and η_{sp} versus time (in days) was plotted.

Rheometry

Steady and dynamic shear data on the dispersions (0·3–1·49%) were obtained at 25°C with a cone (2°, 4 cm dia.)-plate system of the Carri-Med CSL 100 rheometer (Carri-Med Americas, Valley View, OH). Dynamic shear data were obtained for concentrations between 0·74% and 1·49% over 0·6–6·3 rad s^{-1}. $\dot{\gamma}$, η_a and dynamic shear properties — storage modulus (G', Pa), loss modulus (G'', Pa), and dynamic viscosity (η^*, Pa s) — were calculated with the use of software (version 5·0) supplied by the manufacturer.

RESULTS AND DISCUSSION

Konjac glucomannan was separated from the cellulose fraction in konjac flour, in order to ensure that a cellulose–glucomannan interaction or synergism was not responsible for the results. Sodium azide was added for its anti-microbial function. The rheology of gum dispersions is important in assessing the thickening properties of gums. Thus, it would be desirable to have at hand rheology data of konjac gum dispersions in both steady and dynamic shear.

Detection of cellulose

The film of the milled extract prepared for the cellulose detection test was not stained blue or violet. This was an indication that cellulose was not isolated with the konjac glucomannan.

Infrared spectroscopy

The infrared spectrum of the acid-treated film (Fig. 1) was identical to that of the water extract, which is an indication of the acid-stability of konjac gum. Inasmuch as cellulose (i.e. β-1,4-glucopyranosyl linkages) in crystalline form exhibits a series of sharp bands in the 7·0–9·5 μm region (O'Connor *et al.*, 1957), the periodicity of the bands in the film in the 7·0–9·5 μm region may be construed as a tendency of β-1,4-glucopyranosyl copolymer blocks in the konjac mannan molecule to orient themselves in crystal-like form. This interpretation is consistent with the high viscosity obtained at very low concentrations of the glucomannan.

Apparent activation energy of viscous flow

E for the 0·054% konjac mannan was calculated from the slope of log η' versus T^{-1} to be 1·01 kcal mol^{-1} (Fig. 2). It is apparent that a small change in temperature

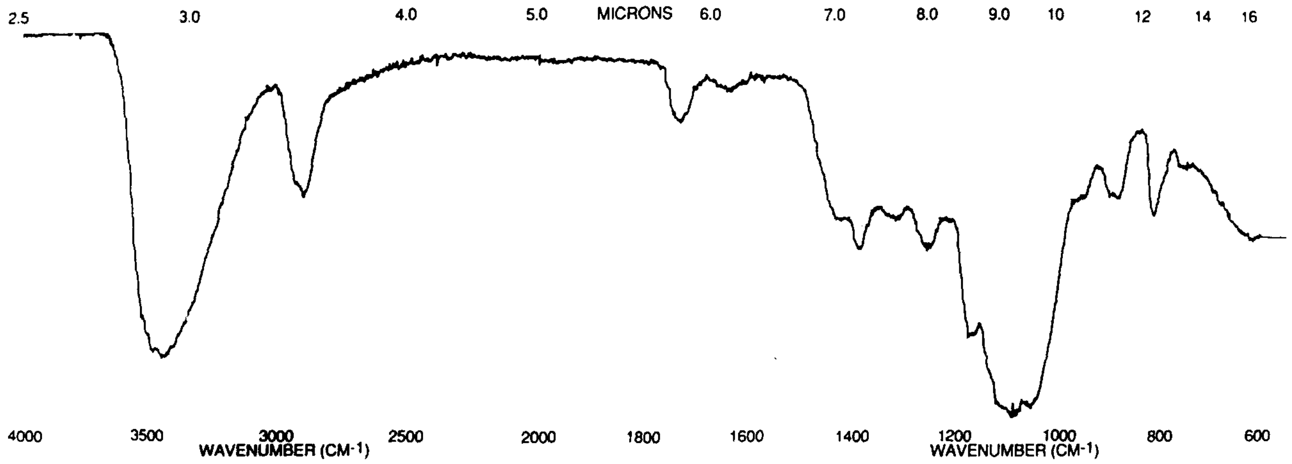

Fig. 1. Infrared spectrum of an acid-treated konjac, zerogel film, 8 μm thick.

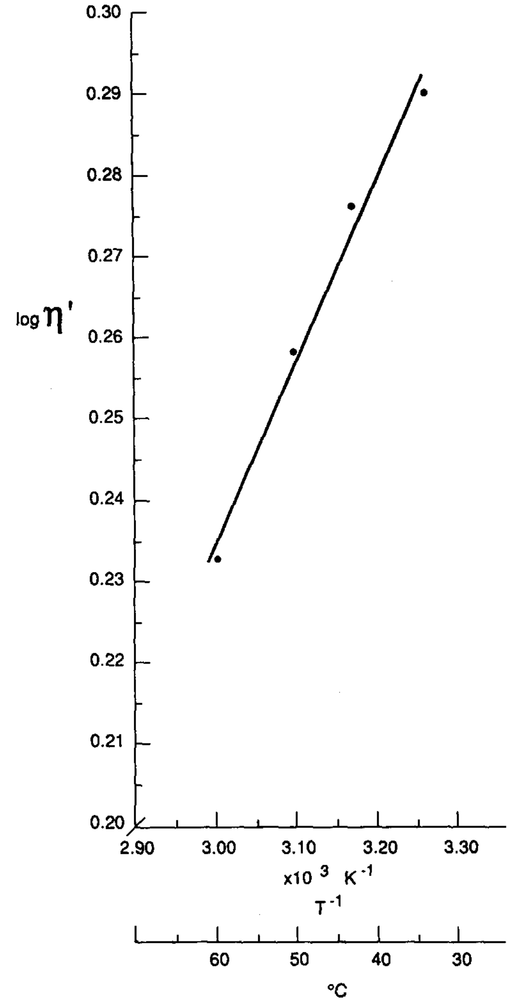

Fig. 2. Log η' versus T^{-1} of a 0·054% dried, milled konjac extract, redispersed in water.

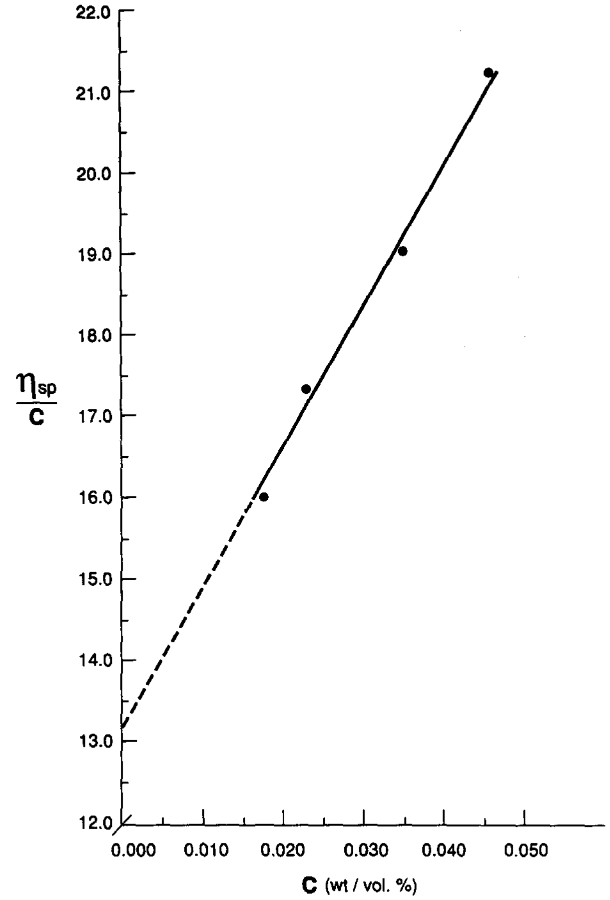

Fig. 3. Viscosity number (η_{sp}/C, ml g^{-1}) versus concentration (C, g ml^{-1}) for dried, milled konjac extract, redispersed in water. $[\eta]$ = 1320 ml g^{-1}.

of the konjac dispersion resulted in a large change in η'; this is an indication that the physical state of the dispersed konjac mannan in the very dilute regime is quite susceptible to temperature (Severs, 1962).

Intrinsic viscosity

$[\eta]$ from capillary viscometry of the dried, milled extract was 1320 ml g^{-1} (Fig. 3), among the highest of the polysaccharides (Blanshard & Mitchell, 1979), in agreement with data of Kishida *et al.* (1978). Viscosity is a combined function of many factors (Carpenter & Westerman, 1975). The low hydrophilicity of the konjac water extract therefore led to the supposition that the high viscosity of the konjac glucomannan dispersions was a function of the molecular weight (reported to be in the order of 10^6 Daltons) and of the frictional coefficient, rather than of hydration.

Hydrophilicity

The hydrophilicity of a polysaccharide has been quantitatively defined as the increase in weight (or volume) of 'colloidally bound' water, *vis-à-vis* free water, in 100 g dispersion, with increasing 1-g additions of polysaccharide (Walter & Talomie, 1990). The volume of the konjac dispersion was non-linear in water between 0·05 and 0·15%, and appeared to reach a maximum above approximately 0·20% concentration. In 0·04 M TA, the relationship was linear, and the hydrophilicity approximated 0·68 g/g solute/100 g dispersion (Fig. 4). For some other comparable polysaccharides, the hydrophilicity range in TA was 1·2–9·8 g/g solute/100 g dispersion (Walter & Talomie, 1990). The generally lower volumes of konjac mannan in TA than in water suggested that the dispersed macromolecules behaved as polysaccharide polyanions (Walter & Talomie, 1990). Given what is known about the effect of cations on polyanions, i.e. they decrease the molecular volume by decreasing the effective ionization (Tanaka, 1981; Ohmine & Tanaka, 1982), it is a reasonable conclusion that konjac mannan experiences its greatest volume expansion in water (greatest hydration) in the vicinity of 0·20% concentration. Inasmuch as the volume was constant above approximately 0·20%, and since there is a frictional as well as a dimensional component to viscosity (Carpenter

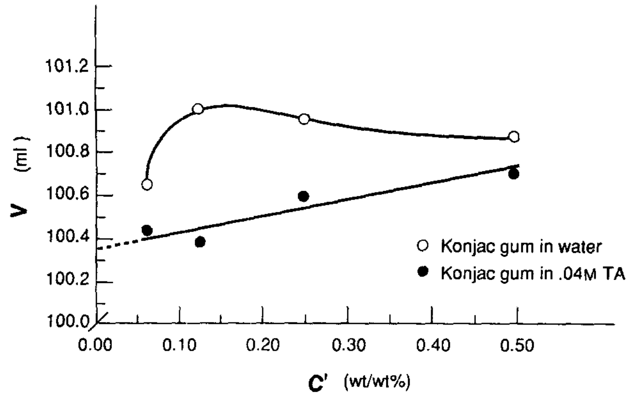

Fig. 4. Volume (V) as a function of concentration (C', g g^{-1}) for dried, milled konjac extract, redispersed in water and in 0·04 M tartaric acid. In TA, $V = 100{\cdot}37 + 0{\cdot}69\,C'$.

& Westerman, 1975), it is also a reasonable conclusion that the high viscosity of aqueous konjac dispersions (Fig. 3) is a property of solute-solute interaction, rather than of hydration.

Stability

There was a 7·6% reduction in η_{sp} in water, and a 2·5% reduction in TA of the viscosity number, over a 4-day interval (Fig. 5). The greater stability in TA compares with pectin in a hydrophobic medium (Walter & Sherman, 1983).

Rheometry

Steady shear data

Newtonian behavior was observed in dispersions up to concentrations below about 0·3 g 100 ml^{-1}. From the steady shear data with concentrations 0·3–1·49 g 100 ml^{-1}, the constants in the Cross and the Carreau models (eqns (1) and (2)) were determined, using a non-linear parameter estimation program (GENSTAT, Numerical Algorithms Group, Oxford, UK). Both models were satisfactory for the most part in describing the data that covered the zero-shear and the power law regions. The Carreau model did not follow well the shear rate–apparent viscosity data at high shear rates. Figures 6 and 7 show the experimental results compared with predictions from the two models. The Cross model followed well the shear rate–apparent viscosity data. Magnitudes of the constants of the two flow models are presented in Table 1. The time constants of the dispersions were functions of concentration (Fig. 8), as observed previously for locust bean gum dispersions (da Silva *et al.*, 1993).

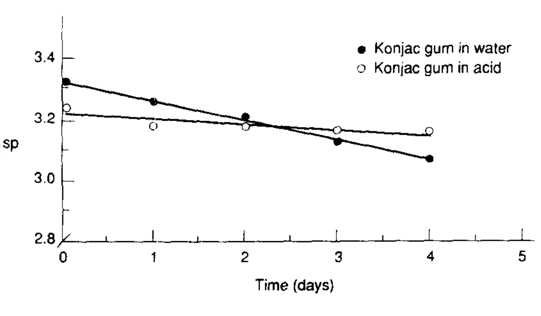

Fig. 5. Specific viscosity (η_{sp}) as a function of time (days) for a 0·10% (w/v) dried, milled konjac extract, redispersed in water and in phthlate/HCl buffer (pH 2·80).

The plot, ln ($c[\eta]$)–ln (η_{sp}) (Fig. 9), based on (η_0) for non-Newtonian dispersions calculated from eqns (1) and (2), shows separate linearity for the dilute and the concentrated regimes that are characteristic of many polymer dispersions. The respective slopes (β) were 1·66 and 3·98. $\beta = 3{\cdot}98$ in the concentrated regime is similar to that observed for locust bean (da Silva *et al.*, 1993) and guar gum dispersions (Robinson *et al.*, 1982). β of this magnitude can be attributed to hyperentanglements (Morris *et al.*, 1981).

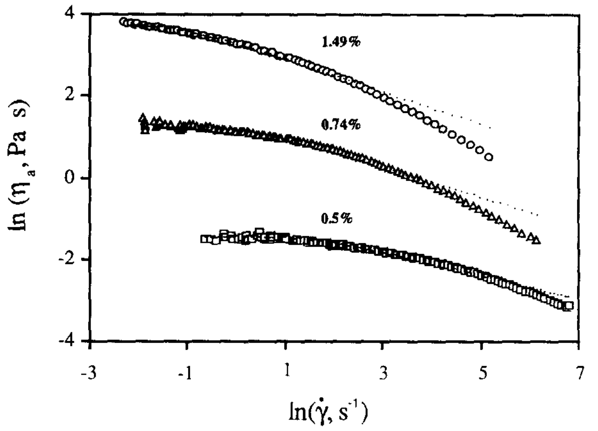

Fig. 6. Ln shear rate ($\dot{\gamma}$, s^{-1})–ln apparent viscosity (η_a, Pa s) plots of 0·5%, 0·74% and 1·49% konjac extract dispersions. Dotted line (·····) represents calculated values according to the Carreau model.

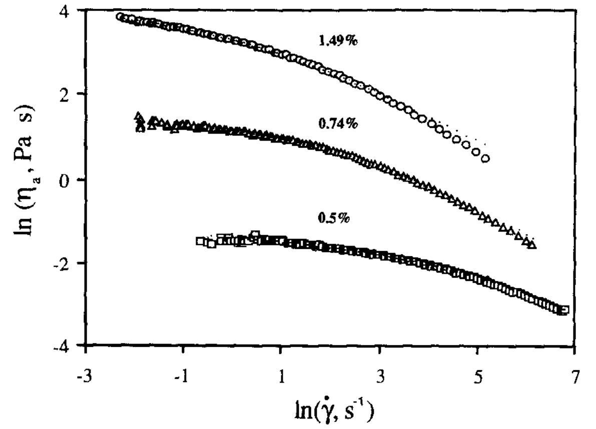

Fig. 7. Ln shear rate ($\dot{\gamma}$, s^{-1})–ln apparent viscosity (η_a, Pa s) plots of 0·5%, 0·74% and 1·49% konjac extract dispersions. Dotted line (·····) represents calculated values according to the Cross model.

Table 1. Magnitudes of Bird-Carreau and Cross model parameters of Konjac dispersions

Concentration (%)	Bird-Carreau				Cross			
	η_0 (Pa s)	λ (s)	N	R^2	η_0 (Pa s)	τ (s^m)	m	R^2
0·30	0·079	0·12	0·13	1·00	0·11	0·26	0·42	1·00
0·50	0·24	0·19	0·14	1·00	0·27	0·13	0·54	1·00
0·74	3·57	0·81	0·18	0·99	4·04	0·29	0·64	1·00
0·87	4·02	0·58	0·18	1·00	4·74	0·27	0·63	1·00
1·00	4·39	1·43	0·15	0·98	5·20	0·44	0·53	1·00
1·26	17·56	2·11	0·19	0·97	21·43	0·69	0·61	1·00
1·49	43·78	3·46	0·20	0·95	56·86	1·11	0·59	0·99

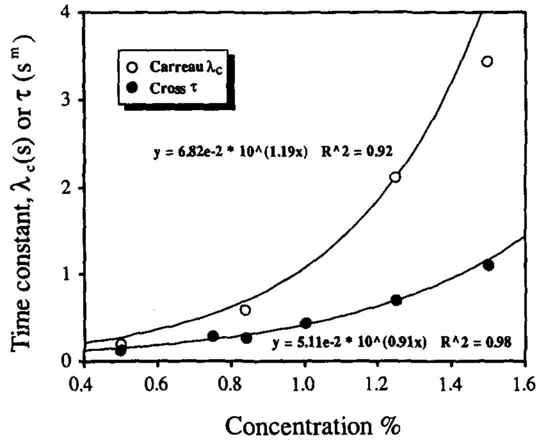

Fig. 8. Effect of concentration on time constants in Cross and Carreau models.

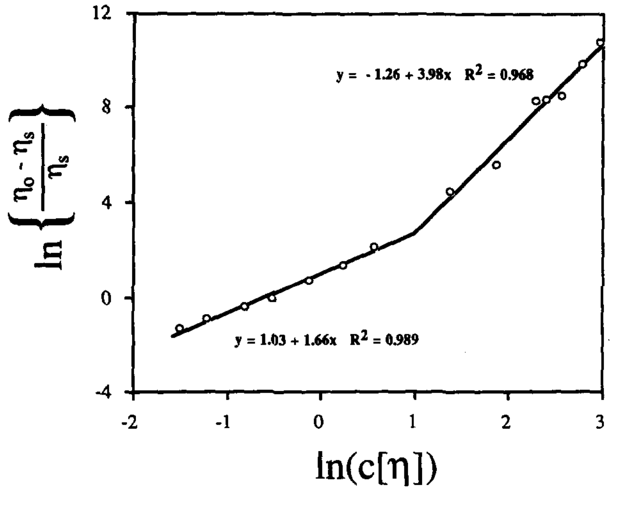

Fig. 9. Plot of ln ($c[\eta]$)-ln (η_{sp}) for dilute and concentrated regimes of konjac extract dispersions.

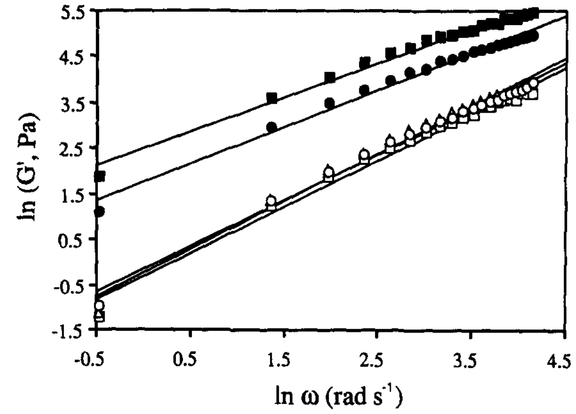

Fig. 10. Ln frequency (ω)-ln storage modulus (G', Pa) of konjac extract dispersions of concentration 0·74% (open squares), 0·87% (open triangles), 1·0% (open circles), 1·26% (filled circles) and 1·49% (filled squares).

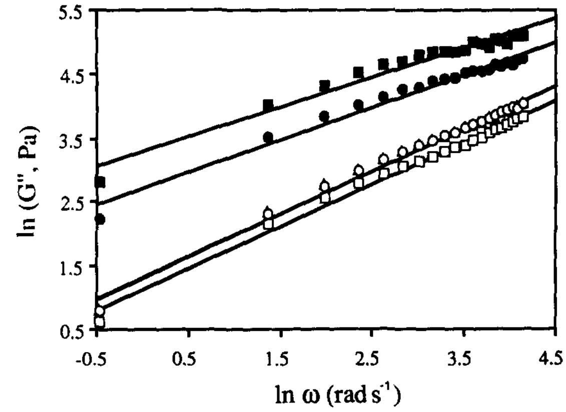

Fig. 11. Ln frequency (ω)-ln loss modulus (G'', Pa) of konjac extract dispersions; symbols defined in Fig. 10.

Dynamic shear data

Ln-ln plots of angular frequency (ω) against G', G'' and η^* showed the characteristics of many concentrated solutions, in that G' and G'' increased with increase in Hz values, while η^* decreased (Figs 10–12) (Ross-Murphy, 1984). All three parameters increased with increasing concentration. However, the increase was small over the concentration range 0·74–1·0%. There was a relatively large increase in the three parameters when concentration was increased from 1·0 to 1·26%. For the 0·3% and 0·5% concentrations, negative values of G'', not herein reported, were obtained at low frequencies.

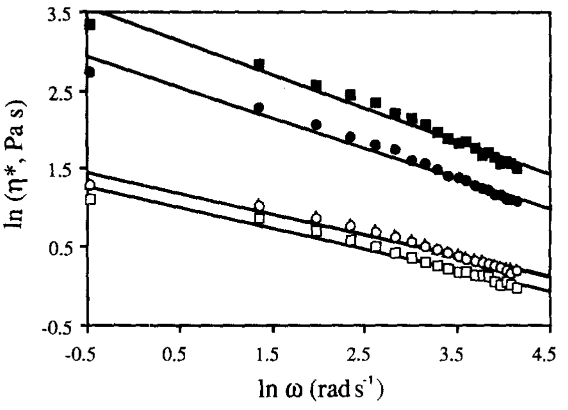

Fig. 12. Ln frequency (ω)-ln complex dynamic viscosity (η^*, Pa s) of konjac extract dispersions; symbols defined in Fig. 10.

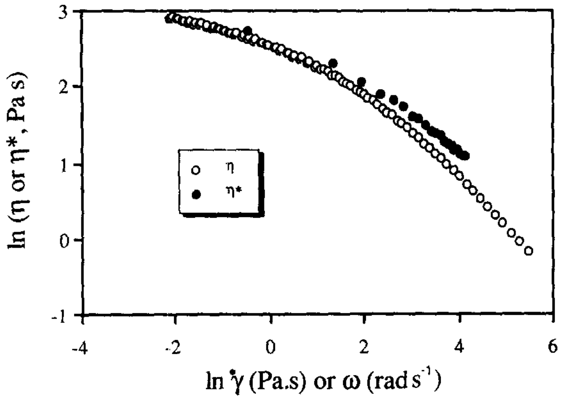

Fig. 13. Cox-Merz plot of 1·26% konjac extract dispersion.

Applicability of Cox-Merz relationship

The 0·74% and 0·87% dispersions showed reasonable agreement with the Cox-Merz rule. However, the 1·26% and 1·49% concentrations (Fig. 13) showed deviations in that η^* was higher than η, especially at high values of $\omega/\dot{\gamma}$. If specific molecular associations of longer time scale than non-specific physical entanglements (Morris *et al.*, 1981; Robinson *et al.*, 1982) are indeed responsible for the deviations, Fig. 13 illustrates a greater severity at the higher values of $\omega/\dot{\gamma}$.

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