Flow behaviour of gellan sol with selected cations

Shipra Sharma · Suwendu Bhattacharya

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Abstract An understanding of the flow behaviour of the sols before gel formation is important for developing nutrient enriched gels. The influence of cations like CaCl_2 (0.05 and 0.1 %, w/w) and FeSO_4 (0.05 and 0.1 %, w/w) on the rheological properties of 1 % gellan sol (w/w) prior to gelling was investigated. The apparent viscosity, reported at a shear-rate of 100 s^{-1} , indicated that the gellan dispersion without any cation possessed lower values compared to other samples containing different cations. The Cross model provided the best fit ($0.97 \leq r \leq 0.99$, $p \leq 0.01$) compared to moderate fitting to power law model ($0.94 \leq r \leq 0.98$). Among the different Cross model parameters, the zero-shear viscosity (η_0) increased with the addition of CaCl_2 and FeSO_4 , and with an increase in their concentrations. Zero-shear viscosity values were 0.46 Pas for gellan sol, 0.79 Pas for gellan with 0.05 % (w/w) CaCl_2 , 1.41 Pas for gellan with 0.1 % CaCl_2 , 3.85 Pas for gellan with 0.05 % FeSO_4 and 4.33 Pas for gellan with 0.1 % FeSO_4 . An increase in cation concentration from 0.05 to 0.10 % (w/w) marginally increased the relaxation time (λ) values indicating the development of more solid characteristics in the sol.

Key words Gellan gum · Sol · Rheology · Model

Introduction

The importance of rheological characterisation lies in the development of processes and products, design of flow systems, scale-up and modelling in addition to understanding the behaviour during transportation, flow and deformation (Skendi et al. 2010). For a flowable liquid food like a hydrocolloid dispersion, the

generation of a wide range of data on shear-rate/shear-stress/apparent viscosity helps to understand the behaviour of material that are useful for many practical applications including relating with sensory attributes.

Several hydrocolloid based food gels are gaining popularity as attractive confectionery foods (Saha and Bhattacharya 2010a, b). These specialty gels offer specific advantages including attractive appearance and texture, and the enjoyment during chewing (Tiwari et al. 2012). However, the judicious selection of hydrocolloid and other additives, and adjustment of appropriate gel forming conditions like temperature, pH, concentration and time are equally important to obtain a hydrocolloid based gel with desired objective and subjective attributes (Tiwari and Bhattacharya 2014).

Several hydrocolloids are used in the food system. Among these hydrocolloids used in food formulations, gellan gum possesses several advantages including developing a product with sparkling clarity (Lau et al. 2000). It is an anionic polysaccharide produced by *Sphingomonas elodea*, previously referred to as *Pseudomonas elodea*. Commercially it is manufactured by the fermentation process (Sworn 2009). This polysaccharide is widely used in the food and biotechnology industries (Tapia et al. 2007) because it forms a relatively heat and acid resistant gel compared to other polysaccharide gels. The precise gelation properties depend crucially on the cation present (Morris et al. 2012). Gellan gum also possesses several advantages like easy and quick setting characteristics to offer a highly transparent gel. The multi-component or mixed gels containing gellan can combine with another hydrocolloid to offer special features which may not be possible when using one individual gelling agent. Tang et al (1996) have determined the textural attributes of gellan gels formed with mono- and divalent cations.

Binary gels using a mixture of gellan and other hydrocolloids have been reported; Bayarri et al. (2002) have reported

S. Sharma · S. Bhattacharya (✉)
Food Engineering Department, Central Food Technological
Research Institute, Mysore 570020, India
e-mail: suwendu@cftri.res.in

that the concentration of gellan gum has a pronounced effect on textural properties of the formed gel. (Rodríguez-Hernández et al. 2003) have determined the viscoelastic (oscillation properties) characteristics of gellan sols at low concentrations (0.005–0.05 %). They have observed that the reinforcement of the network structures occurs with an increase in gellan concentration which finally results in more elastic gels well evidenced through the rheology of the systems.

Divalent cations are more effective gel formers than monovalent cations (Tang et al. 1994). Marginally soluble calcium salts such as calcium sulphate, calcium chloride and calcium citrate have been reported to form crosslink in gels (Harding et al. 2011). The experiments by Miyoshi et al. (1994) have suggested that gellan gum dispersions with sufficient divalent cations form firm gels on cooling below the gel setting temperature. This behaviour is markedly different from that of thermoreversible gels formed by gellan gum alone or in the presence of monovalent cations. In this context, it may be possible to use divalent iron and calcium sources to be used along with gellan such that the developed gels may serve as a good source of these nutrients. Hence, scope exists to develop divalent ion incorporated gellan gels wherein the characterisation of the sol is mandatory to understand its flow behaviour. The usefulness of such studies lies in the selection and design of flow system for handling gellan sols prior to the preparation of health benefiting gels.

Therefore, the objectives of the present investigation are to determine the effect of selected cations like calcium chloride and ferrous sulphate on the rheological status of gellan sol prior to gelling, and examining the suitability of flow models to characterise them.

Materials and Methods

Materials

Gellan gum (CleriGel, Himedia, Mumbai, India) was used as the gelling agent. The dispersion of 1 % gellan gum (dry solid basis, w/w) in glass distilled water was prepared (Saha and Bhattacharya 2010a) by hydrating the gum powder in a laboratory model magnetic stirrer for 15 min followed by heating in a water bath, maintained at a temperature of 90 °C for 20 min. Calcium sulphate and ferrous sulphate were procured from Himedia, Mumbai, India. The concentrations of 0.05 and 0.10 % (w/w) for CaSO_4 and FeSO_4 were adjusted by adding these solids only at the end of heating period of gellan gum followed by mixing well employing a mechanical stirrer. A concentration of 0.15 % (w/w) was difficult as gel formation started immediately on addition.

Methods

Flow behaviour

The prepared 1 % gellan gum (w/w) dispersions, as mentioned in the earlier section, were cooled to about 60 °C avoiding evaporation of water, and were subjected to flow measurement. A coaxial cylinder attachment was employed; the ratio of the outer diameter of a stationary cylinder to the diameter of the rotating bob was 1.085 wherein 9 ml of sample was used. A rheometer (Model # RS 6000, Haake Rheowin, Thermoscientific, Karlsruhe, Germany) was employed in the controlled stress (CS) mode while the shear-stress was increased progressively in a linear manner from 0.0001 to 30 Pa in a span of 100 s. A total of hundred data sets comprising shear-stress, shear-rate and apparent viscosity were recorded at a temperature of 60 °C. A circulating water bath, supplied by the rheometer manufacturer and coupled with the rheometer, was used to control the temperature of measurement by a deviation upto ± 0.1 °C. Apparent viscosity, calculated as the ratio of shear-stress and shear-rate, was reported at a shear-rate of 100 s^{-1} for comparison of results. The flow measurements were repeated for cation added gellan dispersions. Each measurement was replicated twice.

The time-independent flow behaviour data comprising shear-rate and shear-stress were subjected to fitting to the common rheological models like the power law and Cross models (Eq. 1) (Cross 1965; Foster and Wolf 2011).

$$\tau = \dot{\gamma} \left(\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \left((\lambda \dot{\gamma})^n \right)} \right) \quad (1)$$

Here, τ was the shear-stress (Pa), η_0 was the zero-shear viscosity (Pas), η_{∞} was the asymptotic value of viscosity at a very high shear-rate (Pas), $\dot{\gamma}$ was shear-rate (s^{-1}), λ was the relaxation time (s), and n was the dimensionless power index of Cross model. The values of η_{∞} were obtained from the experimental results corresponding to the equilibrium or residual apparent viscosities which were obtained at the end of the shearing period.

Statistical analysis

The statistical analysis of the samples included fitting of the shear-rate/shear-stress data to the power law and Cross equation using the method of nonlinear analysis. The constants of these equations were derived by employing the software provided by the rheometer manufacturer. The extent of fit of the power law and Cross models was judged by determining the correlation coefficient (r); the statistical significance of r values was judged at a probability (p) of 0.01.

Fig. 1 Sample graph showing apparent viscosity against shear-rate for 1 % gellan dispersion. The line shows the fitting of data employing Cross model

Results and discussion

Flow behaviour

The sample rheogram (plot of apparent viscosity against shear-rate) for 1 % gellan dispersion or sol (w/w) is shown in Fig. 1; it shows the non-Newtonian shear-thinning characteristics as there is a logarithmic linear decrease when the shear-rate is increased. The phenomenon of shear-thinning is

often encountered in food systems which are believed to be due to disruption of the particles existing as agglomerates in the dispersions (Barnes 1997). Nickerson et al. (2003) have shown that the power-law model can adequately describe the flow behaviour and viscosity values at low to intermediate shear-rates for dilute gellan dispersions near the sol–gel transition. In the present investigation, the Cross model (Eq. 1) can provide an excellent fit ($0.97 \leq r \leq 0.99$, $p \leq 0.01$) (Fig. 1) compared to moderate fitting of power law model ($0.94 \leq r \leq 0.98$). An increase in the zero-shear viscosity (η_0) and the infinite-shear viscosity (η_∞) of the Cross model occurs with an increase in cation concentration (Fig. 2). The zero-shear viscosity reflects the undisturbed status of the sample and is important during storage; it indicates the rheological status at an extremely low shear-rate like that encountered during storage. An increase in the same means that the system is more stable during storage and does not flow easily. The infinite-shear viscosity occurs at high shear-rates and represents the rheological status of a sample that undergoes a high extent of disturbance such as spraying, mixing and pumping. However, the magnitudes of infinite-shear viscosity are much smaller than their corresponding zero-shear viscosity, and hence, this term can be neglected compared to η_0 (as shown in Eq 2). The power index of the Cross model (n) reflects the characteristic behaviour of a sample; a high value of n decreases the apparent viscosity of the system according to

Fig. 2 Effect of different cations on (A) apparent viscosity at a shear-rate of 100 s^{-1} , (B) zero-shear viscosity, (C) Cross power index, and (D) relaxation time of gellan dispersions. Same figure with different alphabets (a, b, c, d and e) indicate the values to be different at $p=0.01$

Eq. (2). In the range of the present experimental conditions, the n values are between 0.38 and 0.86.

$$\tau = \dot{\gamma} \left(\frac{\eta_0}{1 + ((\lambda \dot{\gamma})^n)} \right) \quad (2)$$

Effect of cations

The effect of cations on different parameters of flow behaviour is shown in Fig. 2. The apparent viscosity, reported at a shear-rate of 100 s^{-1} , indicates that the gellan sol without any cation possesses lower apparent viscosity compared to other samples containing different cations; the latter samples are not statistically different ($p \leq 0.01$) in their apparent viscosity values (Fig. 2A). Among the different Cross model parameters, the zero-shear viscosity (η_0) increases with the addition of CaCl_2 and FeSO_4 , and with an increase in their respective concentrations (Fig. 2B). The power index (n) of the Cross model is a dimensionless constant (Barnes 1997) which reflects the characteristics of the dispersions. An increase in n values is expected to decrease the apparent viscosity of the system. In the present study, it varies with the type and concentration of the cations (Fig. 2C). However, no clear trend in n values with cations is observed. It is possible that the method of non-linear analysis used in the present study (to calculate n values) is unable to determine the small changes occurring in the n values. The relaxation parameter (λ) is an indicative of the time taken for the material for relaxation to $1/e$ fraction of the initial stress. A low value means predominant liquid characteristics while a high value indicates solid behaviour; a liquid offers an instantaneous relaxation when allowed to relax and possesses a value close to zero. On the contrary, a solid sample takes a significant time for relaxation while viscoelastic samples offer intermediate values between an ideal liquid and ideal solid. An increase in cation concentration from 0.05 to 0.10 % (w/w) increases the λ values particularly for FeSO_4 sol samples meaning the development of more solid characteristics prior to gelling. The sol containing 0.10 % (w/w) FeSO_4 possesses the prominent solid characteristic as evidenced by the highest λ value of 0.183 (Fig. 2D).

It has been reported that calcium salts such as calcium sulphate, calcium chloride and calcium citrate try to form crosslink in gels (Harding et al. 2011). The formation of such crosslinks increases the viscosity of the system. A previous study by Miyoshi et al. (1994) suggests that gellan gum dispersions with sufficient divalent cations can form firm gels on cooling below the setting temperature. This behaviour is different from that of thermo-reversible gels formed by gellan gum alone or in the presence of monovalent cations. Miyoshi et al. (1996) has also indicated that the gelation properties of gellan sol depend crucially on the cation present. Sufficient

divalent cations are needed for gellan gum sol to form a firm gel by various junction zones with different thermal stabilities. In the present study, an increase in the concentration of cations increases the apparent viscosity of the sol system. Divalent cations promote the formation of more stable junction zones than monovalent cations (Morris et al. 2012). Sworn (2009) have mentioned that the setting temperature increases with increasing cation concentration. For example, the temperature increases from approximately 71°C to 80°C as the calcium concentration increases from 2 to 80 mM. A similar increase also occurs when sodium or potassium concentration is increased from 10 to 200 mM. High acyl gellan gum is capable of forming self supporting gels at concentrations above approximately 0.2 % gum.

Conclusions

Gellan dispersions behave as non-Newtonian fluids and exhibit shear-thinning characteristics. The presence of cations like CaCl_2 and FeSO_4 modifies the rheological status of sol prior to gelling. The Cross model is suitable to explain the relationship between shear-rate and shear-stress. The change in relaxation time of the dispersions depends on the level and type of cations.

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