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Flow Properties of Concentrated Solutions of Casein Glycomacropeptide*

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Abstract: The shear stress/shear rate relations of 2.5, 5.0, 7.5 and 10% solutions of a commercial preparation of casein glycomacropeptide (80% GMP) were measured at 25, 35, 45, 55 and 65°C, respectively. The corresponding viscosities for the GMP solutions were calculated from these relations. Changes in apparent viscosity in relation to temperature suggest the formation of polymeric forms at $\geq 45^\circ\text{C}$. The shear stress/shear rate relations were found to fit the Hershey-Burkley model with correlation coefficients close to unity. Calculating the yield stress suggested that it was affected markedly by the concentration and temperature. At 25°C, the apparent viscosity of 5% GMP solution decreased with the increase of pH from 3.4 to 8. At 45°C, GMP solutions exhibited higher viscosities than at 25°C and pH 3.4 and 5 but lower at pH 8, suggesting the formation of high molecular weight polymers. The shear stress/shear rate relations for the 2.5 and 7.5 GMP solutions at 25°C increased slightly to a maximum when 0.1-0.15% CaCl_2 were added and to a maximum when 0.15-0.20% CaCl_2 when measurements were carried out at 45°C.

Key words: Casein glycomacropeptide, flow properties, shear stress, shear rate, yield stress, viscosity

Introduction

The growing demand for palatable and nutritious foods has placed heavy emphasis on the need for proteins with functional properties that match the specific needs for the desired food. Such approach requires deep knowledge on the functional properties of the used ingredients particularly proteins.

During the last two decades extensive research has been undertaken to explore the functional properties of milk proteins particularly whey protein preparations. This has been the subject of several reviews (Kinsella, 1984; Harper, 1991) for whey protein preparations and for casein glycomacropeptide (Abd El-Salam *et al.*, 1996).

The flow properties of concentrated solutions of proteins used as ingredients in formulated foods determine the rheological properties of these foods and the proper conditions for their processing. However, no cited literature dealt with these properties for casein glycomacropeptide (GMP).

The present research describes the results of the flow properties of GMP solutions as affected by concentration, temperature and addition of CaCl_2 .

Materials and Methods

Materials

Casein glycomacropeptide (GMP). The GMP was a commercial product (Lactoprodan® CGMP-10) obtained as a gift from Arla Foods Ingredients (Viby, Denmark). It had $85 \pm 2\%$

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protein, 2% lactose, 0.5% fat, 6.5% ash, 5.5% moisture, 80% GMP and 4.2% sialic acids (data of the supplier).

Calcium chloride, Sodium azide A.R. (Merck, Darmstadt, Germany)

Methods

Measurement of Flow Properties

The flow properties of GMP solutions were measured using coaxial cylinder viscometer (Bohlin V88, Sweden) attached to a work station loaded with soft ware V88 viscometry programme. The system (C30 finite s) was filled with the GMP solution, equilibrated at the measuring temperature for 15 min and measurement of shear stress was carried out in the up and down mode at shear rates ranging from 125 1/s to 1054 1/s. The viscosity was calculated simultaneously from these relations.

Experiments

Ten, 7.5, 5 and 2.5% solutions of GMP were prepared in distilled water. Sodium azide was added at the rate of 0.02% as preservative. The shear stress of the prepared solutions were measured at 25, 35, 45, 55 and 65°C, respectively.

Five percent solution of GMP was prepared and adjusted at pH 3.4, 5.0 and 8.0 using 1N HCl or NaOH. The shear stress and viscosity of the prepared solutions were measured at 25 and 45°C, respectively.

GMP solutions (2.5 and 7.5%) were prepared and CaCl₂ was added to each at the ratios of 0.05, 0.1, 0.15, 0.2.0 and 0.25%, respectively. The shear stress and viscosity of the prepared solutions were measured at 25 and 45°C.

Results and Discussion

Flow Properties of GMP Solutions

Effect of Concentration and Temperature

Figure 1 to 5 show the shear stress as a function of shear rate for 2.5, 5.0, 7.5 and 10.0% GMP solutions at 25, 35, 45, 55 and 65°C, respectively. The up and down mode measurements showed very small hysteresis loop.

At 25°C positive relations were found between the GMP concentration and shear stress and viscosity (Fig. 1). These positive relations also apply for GMP solutions up to 7.5% at all measuring temperatures. The 10% GMP solution showed anomalous behaviour as it showed less viscosity than 7.5% GMP solution at 35 and 45°C, respectively (Fig. 2 and 3) and less viscosity than the 5 and 7.5% GMP solutions at 55 and 65°C, respectively (Fig. 4 and 5). A visual protein precipitate was formed in the 10% GMP solutions at temperature $\geq 45^\circ\text{C}$. This would explain the low viscosity of 10% GMP at $\geq 45^\circ\text{C}$ due the decreased concentration of the remaining protein in solution. The formation of protein aggregates at such low temperature can not be expected from a hydrophilic and relatively low molecular weight protein which is free from cysteine residues. Also, GMP carries a negative charge at the pH of this solution (6.8) which would not allow for electrostatic interaction. This suggests that the carbohydrate moiety of the GMP may play a role in the formation of GMP protein aggregates at this low temperature. Previous studies (Nakano and Ozimak, 1998) showed that GMP to occur as an aggregate of 3 monomers. The observed protein aggregates may be an initial step for gelation and that the GMP concentration was not sufficient to form a gel. Whey protein solutions fail to form gels below 8% (Harper, 1991) which may explain the present finding.

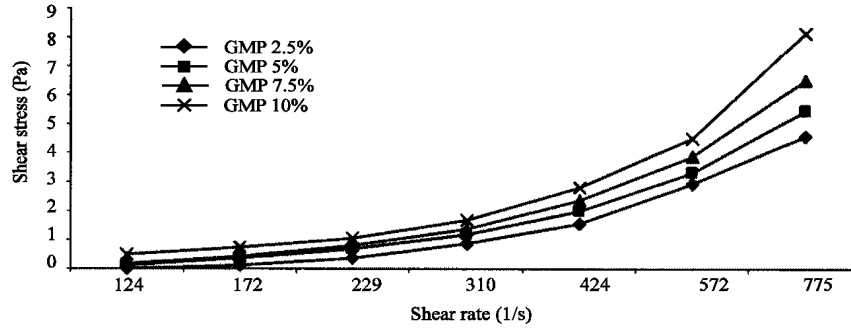


Fig. 1: Flow curves of GMP solutions of different concentrations at 25°C

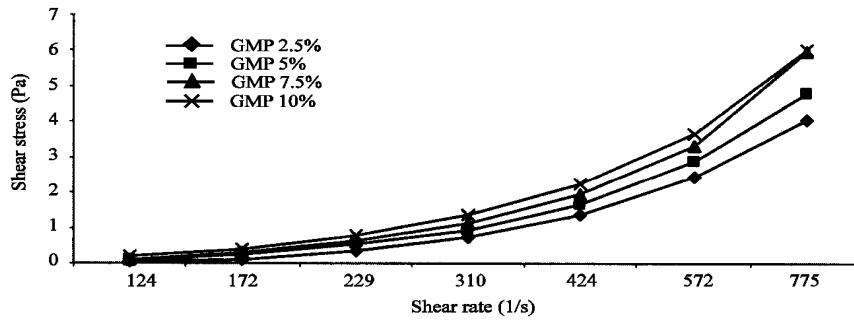


Fig. 2: Flow curves of GMP solutions of different concentrations at 35°C

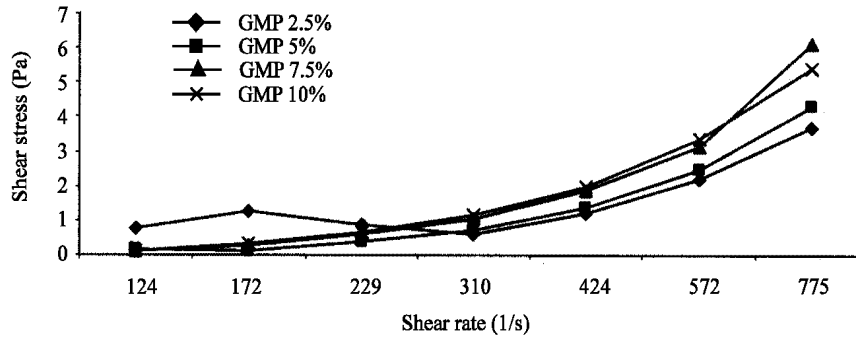


Fig. 3: Flow curves of GMP solutions of different concentrations at 45°C

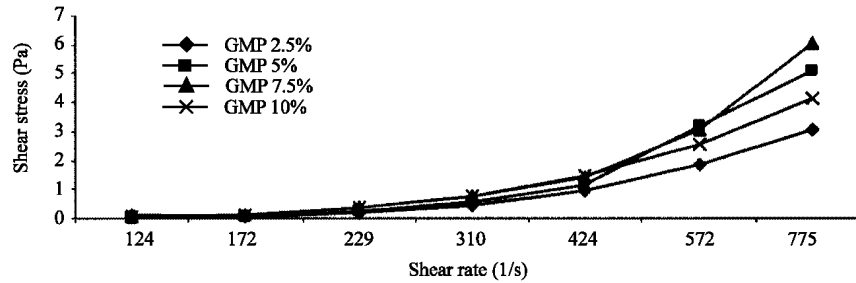


Fig. 4: Flow curves of GMP solutions of different concentrations at 55°C

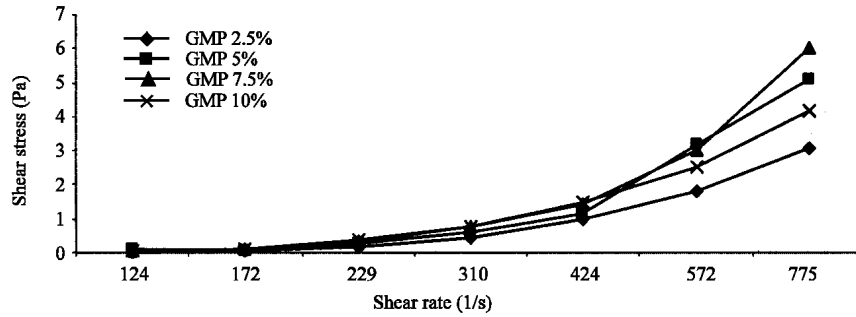


Fig. 5: Flow curves of GMP solutions of different concentrations at 65°C

Table 1: Yield stress (Pa) for GMP solutions of different concentrations and at different temperatures

Temperature (°C)	2.5% GMP	5.0% GMP	7.5% GMP	10% GMP
25	0.089	0.369	0.380	0.438
35	0.126	0.392	0.423	0.216
45	0.471	0.368	0.220	0.220
55	0.121	0.538	0.216	0.070
65	0.109	0.840	0.313	0.049

It is of interest to note that the viscosity of 5 and 7.5% solutions increased at 55 and 65°C, respectively, which may suggest the formation of aggregates of higher viscosity at these temperatures, but not to the stage of the formation of visible precipitate.

The shear stress/shear rate relations of all solutions and at the different temperatures follow the Hershel Bukly model with correlation coefficients close to unity. The yield stress of these relations was calculated as shown in Table 1.

At 25°C the 2.5% GMP solution was found to exhibit the lowest while the 10% GMP solution exhibited the highest yield stress. As the temperature increased, such relation was not apparent. Thus the 2.5% GMP solution showed a maximum yield stress at 45°C and decreased thereafter, whereas the yield stress of 5% GMP solution increased to a maximum at 65°C. The highest yield stress for 7.5% GMP solution was apparent at 35°C, while the yield stress of the 10% GMP solution decreased continuously as the temperature increased. This would coincide with the possible maximum formation of soluble GMP aggregates.

Effect of pH

The pH and temperature affected markedly the flow curve of the 5% GMP solution. At 25°C the GMP solution showed the highest shear stress at pH 3.4 followed by that at pH 5.0 and the lowest at pH 8.0 (Fig. 6). The density of the negative charge in the GMP molecule may be responsible for such behaviour as GMP has the highest negative charge at pH 8 and the least at pH 3.4. The increased repulsive forces brought by the negative charge would result in the observed low viscosity and shear stress of GMP at pH 8. As the temperature increased to 45°C, the shear stress and viscosity of GMP at pH 8 decreased, while it increased for GMP at pH 3.4 and particularly at pH 5 (Fig. 7). The increased temperature would enhance the aggregation of the GMP and that pH 5 seem to be optimum for the formation of these aggregates. The mechanism for the formation of the GMP aggregates seem to depend mainly on its carbohydrate moiety. The shear stress/shear rate relations of 5% GMP at the different pH and temperatures were found to fit the Hershel-Bukly model with very high correlation coefficients.

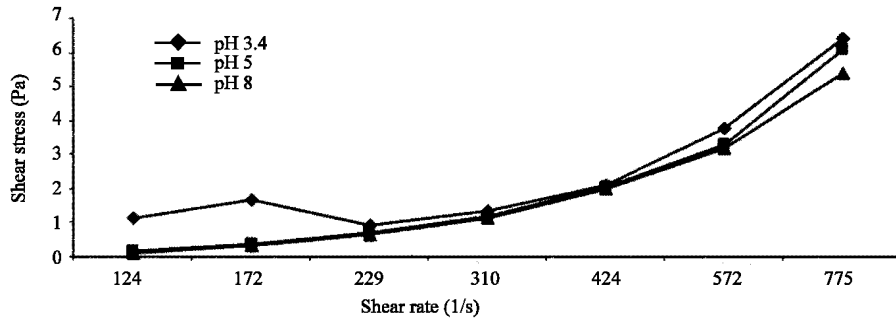


Fig. 6: Flow curves of 5% GMP solution of different pH values at 25°C

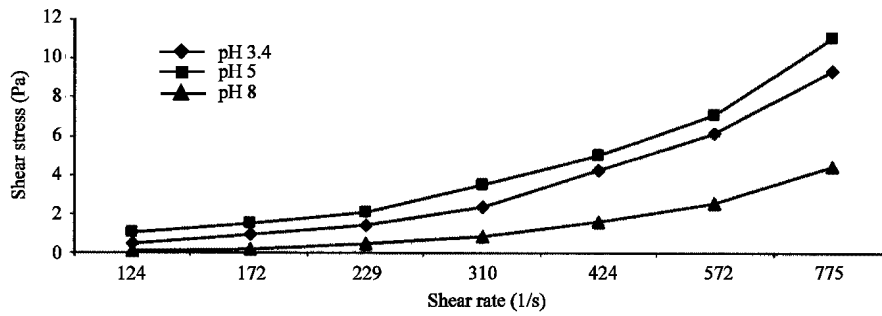


Fig. 7: Flow curves of 5% GMP solution of different pH values at 45°C

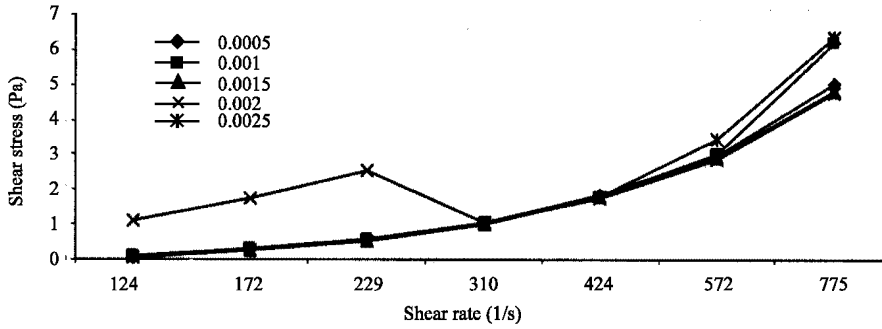


Fig. 8: Flow curve of 2.5% GMP solution containing different CaCl₂ at 25°C

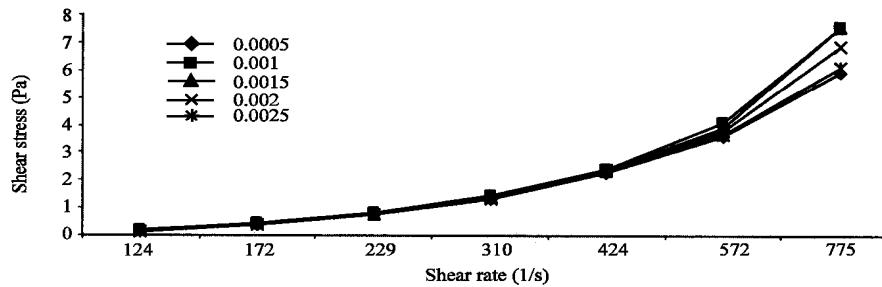


Fig. 9: Flow curve of 7.5% GMP solution containing different CaCl₂ at 25°C

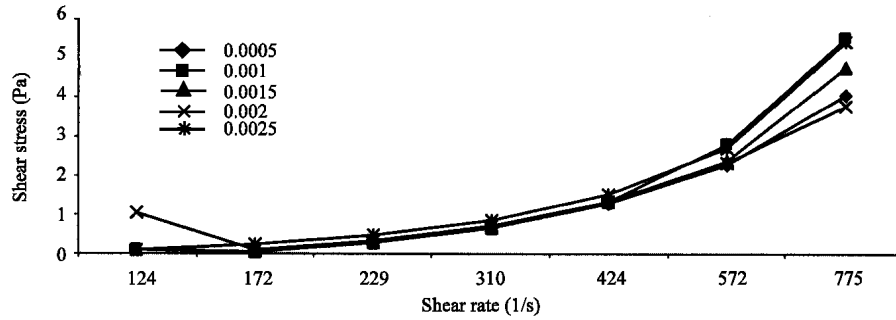


Fig. 10: Flow curve of 2.5% GMP solution containing different CaCl₂ at 45°C

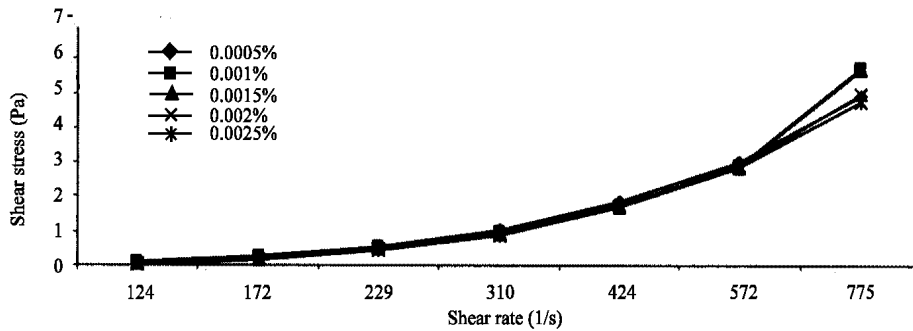


Fig. 11: Flow curve of 7.5% GMP solution containing different CaCl₂ at 45°C

Effect of Added Calcium Chloride

Addition of CaCl₂ had a very slight effect on the pH of the GMP solution being in the order of 0.01 unit/0.05% of added CaCl₂. Also, the effect of added calcium chloride on the flow curves of the GMP solutions was slight. Thus for 7.5% GMP solution it showed maximum viscosity at 25°C when 0.1 and 0.15% CaCl₂ were added and at 45°C when 0.15 and 0.2% CaCl₂ were added and then decreased with further increase in the added calcium chloride (Fig. 8-11). For the 2.5% GMP solution, the addition of 0.1% CaCl₂ brought the highest increase in viscosity at both 25 and 45°C (Fig. 8-11).

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