Viscosity of Weak Whey Protein Gels

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ABSTRACT

Viscosity behaviour of the membrane separated whey protein concentrates and the weak whey protein gels, produced by the chemically induced whey protein aggregation, are compared. Viscosity and the thixotropic loop width for the latter are greater than those for the former. The critical non-Newtonian protein concentration for membrane concentrates is 2.3 times that for gels, whilst the k_s value, characterizing the concentration dependence at the flow curve exponent for gels is 1.9 times that for concentrates. These distinctions reveal further possibilities to control the rheology behaviour of the whey protein concentrates via the method of their production. On the other hand, they confirm the formation of the weak protein gel by the sulphydryl group/disulphide bond interchange reaction during the thermally or the chemically induced whey protein aggregation.

Key Words: viscosity, whey protein aggregation, weak whey protein gel, thixotropy, shear rate

INTRODUCTION

Whey proteins are composed of a group of globular proteins, consisting of β-lactoglobulin (mol. weight, M = 18.3 kDa, isoelectric point, Ip = 5.3−5.5, fraction of total protein, PF = 50%), α-lactalbumin (M = 14 kDa, Ip = 4.2−4.5, PF = 12%), immunoglobulines (M = 15−1000 kDa, Ip = 5.5−8.3, PF = 10%), bovine serum albumin (M = 69 kDa, Ip = 5.1, PF = 5%) and proteasc-peptones (M = 4.1−40.8 kDa, Ip = 5.1, PF = 23%) [1]. The high nutritional value of the whey protein concentrates (WPC) [2−3], their food applications [4] and their important role in controlling the food product texture [5] stimulate intensive research and development into the WPC production and properties [6,7]. Available statistical data demonstrate a dramatic increase in WPC manufacture during the last 5−10 years. Most of the WPC is manufactured by industrial-scale ultrafiltration and diafiltration [8]. Though the mechanism of whey protein aggregation (WPA) is presently unclear [9], this process can also be used for a WPC production. There are two more methods for WPC production using WPA, by thermally induced [10,11] and chemically induced [12] WPA. Weak whey protein gels (WWPG) are obtained by these methods [13]. The protein aggregation as a result of the interchain crosslinking reaction [7,20] increases the protein molecular weight and considerably changes the viscosity and rheology behaviour of the produced WWPG. Understanding the flow behaviour of WPC is important for both new milk product development (included whey proteins), where viscosity is a major determinant of a texture, and for manufacturing process control, where such knowledge dictates the choice of pumps, heat exchangers, and mixing systems [14]. Recently the viscosity of membrane produced WPC has been reported [15], and in the present work it is compared with that of WWPG.

Along with the above mentioned manufacturing application, this comparison is of scientific importance with the introduction of the concept of the fractal structure in WPA [16]. The WWPG flow curves are analyzed via the Schurz scaling relationships [17] in terms of shear rate dependent whey protein aggregation-deaggregation equilibrium [18].

EXPERIMENTAL

Cheese whey with 0.68% w/w protein, 3.92% w/w lactose, 0.34% w/w non-protein nitrogen compounds and pH = 6.8 was used in this work. The whey samples were heated for 48 hours at 65 °C and the aggregated whey proteins were separated by their centrifugation for 30 min at 1.8×10^4 g after a sample cooling. The protein content in the dried sample at 30 °C for 3 days WWPG was 83.7% w/w. The same separation procedures were also used for the preparation of WWPG with roughly the same protein content by the recently suggested chemically induced WPA at 22 °C, normal atmosphere and pH = 6.7 [12].

WWPG samples for viscosity measurements were prepared by mixing a pre-weighed WWPG quantity with double-distilled water using the magnetic stirrer. Obtained WWPG samples were stored at 6 °C prior to testing for 20 hours.

Rheotest-2 viscometre (Germany) with a built-up microprocessor was used to determine the WWPG apparent viscosity (η), shear rate ($\dot{\gamma}$) and shear stress (τ) as a function of gel concentration and shearing time.

For relatively short ranges in $\dot{\gamma}$, used in this work, the Ostwald-de Waele power law:

$$\tau = \phi\, \dot{\gamma}^n \text{ or } \eta = \phi\, \dot{\gamma}^{n-1} \qquad (1)$$

should still hold (n is a dimensionless constant indicating the deviation of the fluid rheological behaviour from the Newtonian one; $\eta = \phi$ for Newtonian flow when n = 1) [17]. So, n values were calculated from the slopes of the flow curves (log η − log $\dot{\gamma}$). It proved the linear Schurz relationship between n^{-1} and gel concentration (c). For $\dot{\gamma}$ = constant:

$$n^{-1} = 1 + k_s c \qquad (2)$$

where k_s is a constant [19].

RESULTS AND DISCUSSION

Flow Curves

In Figure 1 the flow curves for various gel concentrations are shown. As it is known [13], there are in principle three different types of flow curves, characterizing high molecular weight polymer solutions (s-type flow curves), weak

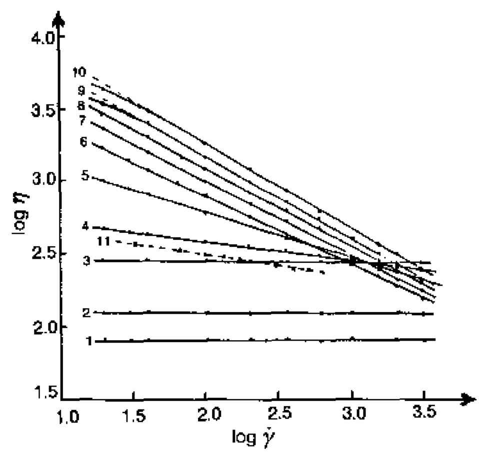

Figure 1. Flow curves of the weak whey protein gels (curves 1−10), produced by chemically induced whey protein aggregation (T=22 °C; pH = 6.7) and membrane separated whey protein concentrate (curve 11) at T=22 °C and pH = 6.5 [15]. The protein concentrations are: (1) 2.5, (2) 5.0, (3) 10.0 , (4) 15.0 , (5) 20.0, (6) 30.0, (7) 35.0, (8 and 11) 40.0, (9) 45.0, and (10) 55.0%, w/w.

particle networks with a yield stress (hyperbolical type flow curves) and weak particle networks without a yield stress (straight flow lines). The presented flow curves (Figure 1) display the investigated whey protein aggregates, obtained by a chemically induced aggregation, could be considered as networks without any yield stress. A short deviation from straight line for flow curves at c = 45.0% w/w and c = 55.0% w/w and at the least $\dot{\gamma}$ values also indicates the partly polymer nature of this type WPC. It is important to note that such deviation is absent in the flow curves for WPC obtained from membrane separated whey proteins [15]. For a comparison, one of the flow curves for this type WPC is also shown in Figure 1. However, more considerable distinctions between these two types WPC are shown in Figure 2. From the data presented in this figure, it is clear that in this case Schurz relationship (2) allows us to determine the critical gel concentration (c_{cr}), bounding the Newtonian (n=1) from the non-Newtonian (n≠1) rheology behaviour. For the membrane separated WPC, c_{cr} = 26.2% w/w as shown in Figure 2 (curve 1) and it is determined from the results presented in [15]. This is 2.3 times that of the investigated in this work for WWPG (c_{cr} = 11.5% w/w), produced by chemically induced WPA. This considerable distinction could be explained by molecular weight increase during this aggregation. The formation of intermolecular disulphide bridge bonds as a result of a thermal or chemically induced sulphydryl group/disulphide bond interchange reaction [20] causes both the protein molecular weight increase and rheological behaviour, typical for weak bonded particle networks. As a result of this k_s value (inclination of the lines in Figure 2) increases also from 2.5 × 10^{-2} per wt% for the membrane separated WPC to 4.8 × 10^{-2} per wt% for the investigated WWPG. In general, the comparison of the viscosity behaviour of these two types of WPC shows the increase of viscosity and k_s value and the shift of a non-Newtonian flow to less protein concentrations for WWPG.

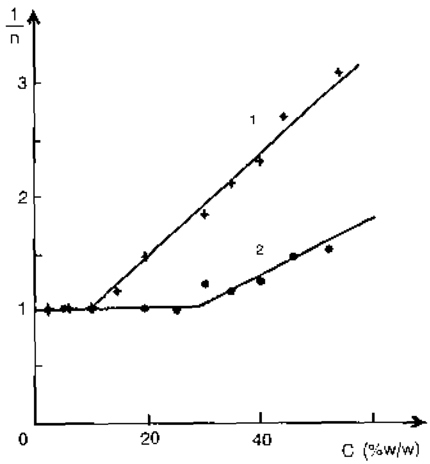

Figure 2. Dependence of the slopes (n) of flow curves on the protein concentration (c) at 22 °C and shear rate $\dot{\gamma}$ = 500 s^{-1} for weak whey protein gels, produced by: (+) chemically induced protein aggregation at pH = 6.7, and (•) membrane separated whey protein concentrate at pH = 6.5 [15].

Thixotropy Behaviour

Two different thixotropic hysteresis loops WPC are shown in Figure 3; for the membrane separated WPC (curve 2) [15] and for the WWPG

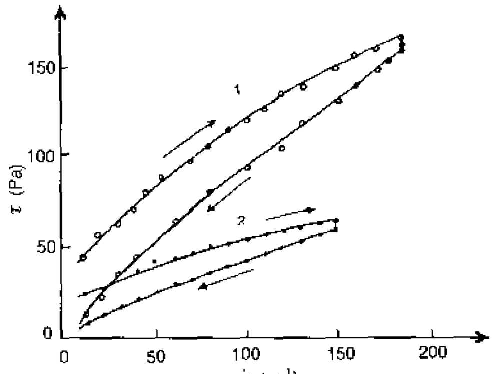

Figure 3. Thixotropy loops for a weak whey protein gel, produced by chemically induced whey protein aggregation (loop 1) at 22 °C, c = 40.0% w/w, pH = 6.7 and membrane separated whey protein concentrate (loop 2) at 20 °C, c=40.0% w/w, pH=6.5 [15].

investigated here (curve 1). As could be expected, the width of the loop as a measure of the thixotropy is higher for WWPG than that for the membrane separated WPC. This distinction could be explained again with a weak crosslinking between the whey protein macromolecules caused by chemically induced, in this case, the intermolecular disulphide bond formation. As a result of this, τ values at constant $\dot{\gamma}$ are larger for WWPG than those for the membrane separated WPC (Figure 3). It is known [17] that the discussed thixotropy loops for a representation of the thixotropic effect is not very convenient as it does not allow the effects of the shear rate and of the time to be separated. A rather convenient way to overcome this is the use of a plot of viscosity vs the product $\dot{\gamma} \times \tau$ with t (time) as a parameter (Figure 4). In this plot the measured curves give viscosity values at constant time. Constant shear rates are presented by straight lines through the origin. The convenience of this plot is that any required viscosity value corresponds to certain value of t and $\dot{\gamma}$ which can be determined by interpolation. Unfortunately the necessary experimental data [15] for a similar representation of the thixotropic effect of the membrane produced WPC are not available.

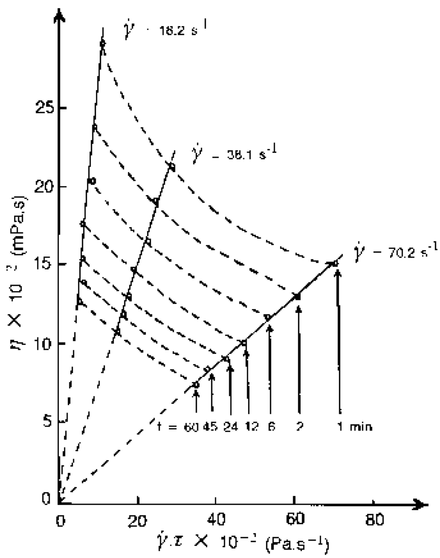

Figure 4. Viscosity of the weak whey protein gel, produced by chemically induced whey protein aggregation as a function of both shear rate ($\dot{\gamma}$) and shearing time (t) at 22 °C, pH = 6.5 and c = 40.0% w/w.

CONCLUSION

Several distinctions between the rheological behaviour of WPC, produced by a membrane whey protein separation concentrate and the chemically induced WPA (WWPG) are established here: a deviation of the WWPG flow curves from linearity at higher protein concentrations and lower $\dot{\gamma}$ values, larger k_s values and more considerable thixotropic effect for WWPG than that for a membrane separation whey protein concentrate and a shift of the critical protein concentration for a non-Newtonian flow behaviour. In this manner, proving the dependence of the WPC flow behaviour on the WPC formation method, and further possibilities for a control of this behaviour is revealed. On the other hand, the distinctions pointed out above can be explained by taking account of the protein aggregate molecular weight increase. This explanation is in accordance with the suggested mechanism for thermally induced or chemically induced WPA by the sulphydryl group/ disulphide bond interchange reaction. So, it is right to consider the obtained protein aggregate as a weak gel or a living polymer which are under intensive study in recent years [18].

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NOMENCLATURE

c concentration (wt %).

η apparent viscosity (mPa.s).

$\dot{\gamma}$ shear rate (s^{-1}).
τ shear stress (Pa or mPa).
k_s Schurz equation constant (1/wt%).

SYMBOLS

WPA whey protein aggregation due to the thermally or special chemically induced interaction between the protein macromolecules.
WPC whey protein concentrate, produced from the whey by the water separation.
WWPG weak whey protein gel-WPC with the partially crosslinked protein macromolecules as a result of the protein aggregation.

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