

SHEAR FLOW AND LARGE AMPLITUDE OSCILLATION SHEAR STUDY OF SOLUTIONS OF AGGREGATING MICELLAR CASEIN PARTICLES

ANNE PITKOWSKI, TACO NICOLAI*, DOMINIQUE DURAND

Polymères, Colloïdes, Interfaces, UMR-CNRS, Université du Maine, 72085 le Mans Cedex 9, France

* Email: taco.nicolai@univ-lemans.fr

Fax: x33.2.43833558

Received: 8.6.2007, Final version: 1.10.2007

ABSTRACT:

Small micellar casein particles were formed in aqueous solutions of native casein after addition of polyphosphate. These so-called submicelles aggregated and gelled with a rate that increased with increasing temperature. The evolution of the viscosity during this process was determined at constant shear rate or shear stress. When applying a small shear stress the viscosity increased strongly until the shear rate became immeasurably slow, but when the applied shear stress exceeded a critical value (σ_c) the aggregates broke up and the viscosity reached a maximum. At longer times the viscosity decreased rapidly at first, followed by a very slow decrease. σ_c was independent of the shear rate and heating temperature, but increased strongly with increasing casein concentration. At constant shear rate the stress remained close to σ_c , but fluctuated irregularly. After cessation of shear flow, gels were formed rapidly. Oscillation shear measurements for $\sigma > \sigma_c$ showed a strongly non-linear response at the time of maximum viscosity.

ZUSAMMENFASSUNG:

Die Zugabe von Polyphosphaten in eine wässrige Lösung von nativen Kaseinproteinen führt zur Bildung von kleinen mizellaren Kaseinpartikeln. Diese sogenannten Submizellen aggregieren und gelieren in linearer Abhängigkeit mit der Temperatur. Die Viskositätsentwicklung während dieses Prozesses wurde unter konstanter Schubspannung und unter konstanter Schergeschwindigkeit untersucht. Unter geringer Schubspannungsbelastung steigt die Viskosität stark an, bis die Rotationsgeschwindigkeit unmessbar klein wird. Wenn allerdings die Schubspannung einen bestimmten Wert überschritten hat, werden die Aggregate aufgebrochen, und die Viskosität erreicht dann einen endlich hohen Wert. Über die Zeit nimmt die Viskosität erst rasch, dann geringfügig ab. Die kritische Schubspannung ist unabhängig von der Scherrate und der Aufheiztemperatur, steigt jedoch stark mit der Kaseinkonzentration an. Bei konstanter Scherrate bleibt die Schubspannung im Bereich des kritischen Wertes, schwankt jedoch unregelmäßig. Nach Abschaltung der Scherung werden die Gele schnell gebildet. Oszillationsversuche zeigen für Schubspannungen überhalb des kritischen Werts eine starke nicht-lineare Antwortfunktion, wenn der maximale Viskositätswert erreicht ist.

RÉSUMÉ:

Par addition de polyphosphates aux solutions aqueuses de caséines natives, des petites particules de caséines micellaires sont formées. Celles-ci, usuellement appelées submicelles, s'agrègent et gélifient avec une vitesse qui croît avec une augmentation de la température. L'évolution de la viscosité durant ce processus a été suivie pour une vitesse ou une contrainte de cisaillement constante. Par application d'une faible contrainte de cisaillement, la viscosité augmente fortement jusqu'à ce que la vitesse de cisaillement devienne trop faible pour être mesurable, mais lorsque la contrainte de cisaillement appliquée dépasse une valeur critique (σ_c), les agrégats se cassent et la viscosité atteint un maximum. Pour des temps plus longs, la viscosité décroît tout d'abord rapidement, puis cette décroissance devient très lente. σ_c est indépendant de la vitesse de cisaillement et de la température de chauffage, mais augmente fortement avec l'accroissement de la concentration en caséines. Pour une vitesse de cisaillement constante, la contrainte reste proche de σ_c , mais fluctue de façon irrégulière. Après cessation de l'écoulement de cisaillement, des gels se forment rapidement. Des mesures de cisaillement en régime oscillant pour $\sigma > \sigma_c$ montrent une réponse fortement non linéaire au temps associé à la viscosité maximale.

KEY WORDS: casein, submicelle, viscosity, gel, shear flow, large amplitude oscillation

© Appl. Rheol. 18 (2008) 23050-1 – 23050-7

This is an extract of the complete reprint-pdf, available at the Applied Rheology website

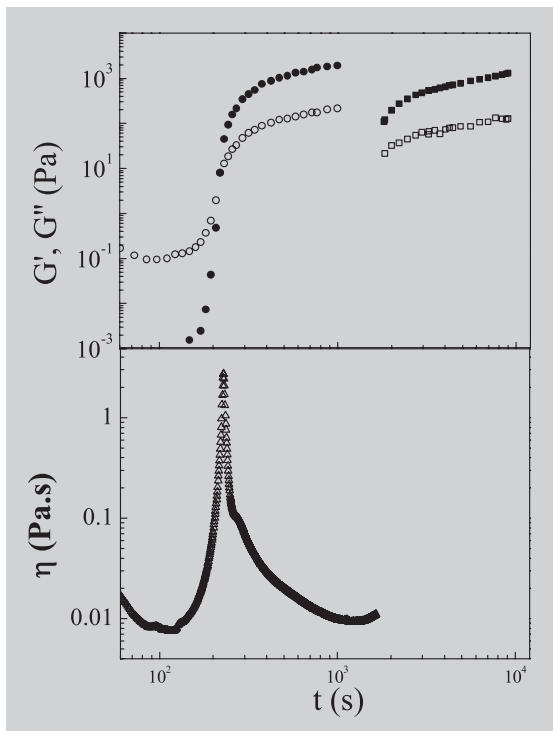
<http://www.appliedrheology.org>

23050-1

Applied Rheology
Volume 18 · Issue 2

This is an extract of the complete reprint-pdf, available at the Applied Rheology website

<http://www.appliedrheology.org>



The increase of G' was slower if the temperature was decreased after cessation of the shear flow and it was hardly visible at 20°C for the duration of the experiment, see Figure 7. The reason is that the rate of bond formation decreases strongly with decreasing temperature [6]. The gels obtained after recovery at 80°C are almost indistinguishable from gels obtained at rest if the shear flow was stopped soon after t_g . However, a difference between the gels formed at rest and after recovery appeared when the time at which the shear flow was stopped was much larger than t_g , probably due to slow densification of the aggregates under shear flow as mentioned above.

The concentration, temperature and pH dependence of the gelation process were discussed in [6]. It was shown that the concentration and the temperature dependences of the gel time were independent and could be described by the following equation:

$$t_g(s) = 8.5 \cdot 10^{-8} C^{-1.7} \exp\left(\frac{90}{RT}\right) \quad (1)$$

with RT the kinetic energy in kJ/mol and C the casein concentration in g/L. This expression described the observed values of t_g within the experimental error over a wide range of concentrations (10–180 g/L) and temperatures (20–90°C).

As shown above, the strong increase of the viscosity occurred close to t_g . We confirmed this correspondence for a range of concentrations and temperatures. Figure 8 shows the viscosity at constant shear rate of 10 s⁻¹ as a function of

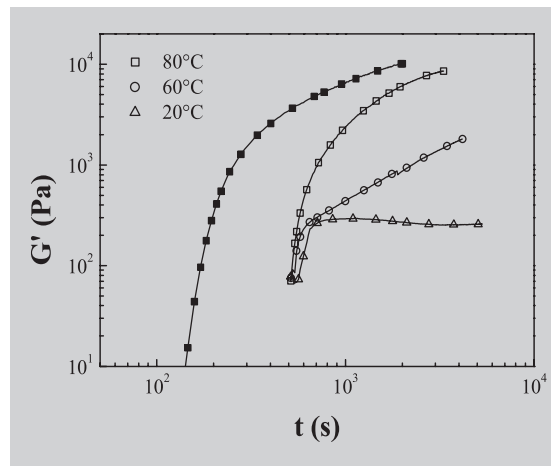


Figure 6 (left): Comparison of the time dependence of the storage (●) and loss (○) shear moduli of an unperturbed submicelle solution at 120 g/L heated at 90°C, with that of the same system (squares) after cessation of shear flow at $t = 1.8 \cdot 10^3$ s. The viscosity during the period of shear flow at a constant shear stress of 20 Pa is shown in the bottom figure.

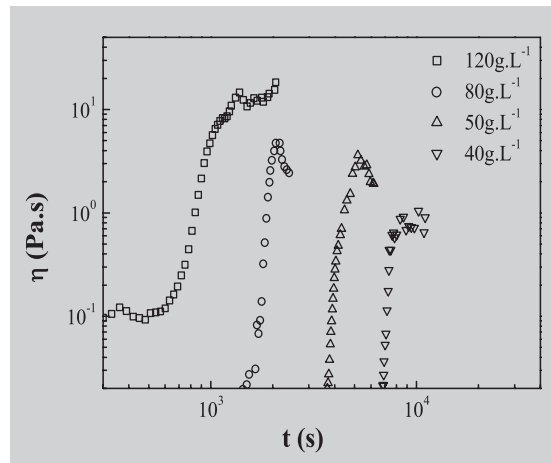


Figure 7 (right above): Recovery of the storage shear modulus following the cessation of shear flow of a submicelle solution at 120 g/L heated at 80°C during the shear flow. The temperature was lowered immediately after the shear flow was stopped to values indicated in the figure. For comparison the evolution of G' at 80°C in the absence of shear flow is also shown (filled symbols).

Figure 8 (right below): Time dependence of the viscosity for submicelle suspensions heated at 77°C for different concentrations indicated in the figure. The shear rate was 10 s⁻¹.

time during heating at 77°C for different casein concentrations. Increasing the casein concentration both accelerated the aggregation process and increased the maximum viscosity. We have verified for each concentration that the viscosity stopped increasing at a critical shear stress independent of the shear rate. Within the rather large scatter σ_c increased with the concentration as: $\sigma_c \approx C^3$, see Figure 9. The critical shear stress that the system could resist during the gelation process was much smaller than the elastic modulus of the gels. However, the concentration dependence of the latter was weaker: $G' \approx C^2$ as shown in [6].

Figure 10 shows the evolution of the viscosity at a shear rate of 10 s⁻¹ for a submicelle suspension with $C = 120$ g/L at different temperatures. At low temperatures the initial viscosity of the suspensions is much higher and one can clearly observe that the viscosity decreases first before increasing. This effect was also observed at room temperature where it occurs over a period of days [5]. It may be caused by reorganisation of the submicelles before they start to aggregate. Increasing the temperature accelerated the aggregation, but had no significant influence on σ_c . In fact, the values of σ_c shown in Figure 8 were obtained at several different temperatures, between 40 and 90°C.

Figure 9 (left): Concentration dependence of the critical shear stress for submicelle solutions. Results obtained at different temperatures between 40 and 90°C were the same within the experimental noise. The solid line has slope 3.

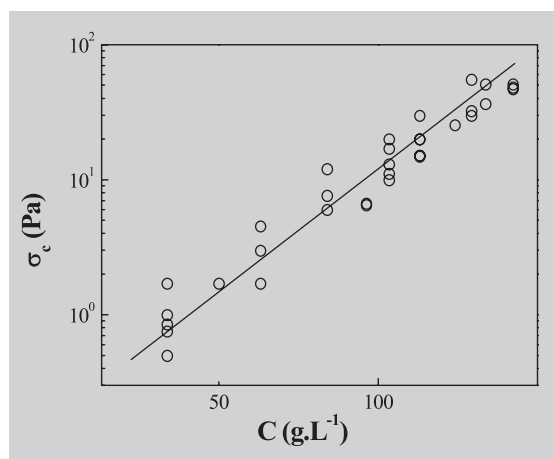
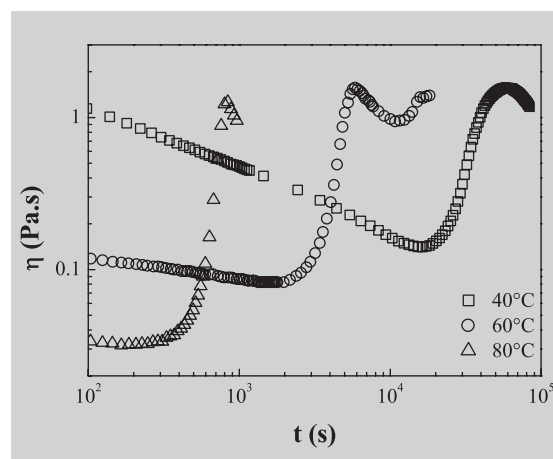


Figure 10: Time dependence of the viscosity for a submicelle suspension at 120 g/L heated at different temperatures indicated in the figure. The shear rate was 10 s⁻¹.



The pH dependence was studied for a submicelle suspension at 120 g/L heated at 90°C. The effect of varying the pH on the shear flow behaviour was similar to that shown in [6] for the storage shear modulus. The results were independent of the pH between pH 5.5 and pH 6.5. At lower or higher pH the aggregation rate increased and the critical stress decreased. Comparison with the corresponding values of G' , see Figure 12 in [6], showed that the dependence of σ_c on the pH was similar to that of the shear modulus.

5 CONCLUSION

In the absence of shear flow, casein submicelles formed a gel with a rate that increased strongly with increasing temperature. During continuous shear flow at constant stress a gel was formed only below a critical stress that increased strongly with increasing concentration, but that was weakly temperature dependent. If $\sigma > \sigma_c$ the shear rate reached a maximum as large aggregates broke up before they could form a percolating network. At constant shear rate the stress increased until it stagnated at a value close to σ_c independent of the shear rate. Imposed oscillatory stress with $\sigma_{max} > \sigma_c$ yielded a non-linear response close to the gel time that could be qualitatively understood by stress induced shear flow.

REFERENCES

- [1] D. G. Schmidt: Colloidal aspects of casein, Netherlands Milk and Dairy Journal 34 (1980) 42-64.
- [2] H. S. Rollema: Casein association and micelle formation, Advanced Dairy Chemistry 1 (1992) 111-140.
- [3] M. Panouillé, T. Nicolai, D. Durand: Heat induced aggregation and gelation of casein submicelles, International Dairy Journal 14 (2004) 297-303.
- [4] M. Panouillé, D. Durand, T. Nicolai, E. Larquet, N. Boisset: Aggregation and gelation of micellar

casein particles, Journal of Colloid and Interface Science 287 (2005) 85-93.

- [5] M. Panouillé, L. Benyahia, D. Durand, T. Nicolai: Dynamical mechanical properties of suspensions of micellar casein particles, Journal of Colloid and Interface Science 287 (2005) 468-475.
- [6] A. Pitkowski, T. Nicolai, D. Durand: Dynamical characterization of gelling micellar casein particles, J. Rheology 51 (2007) 971-986.
- [7] A. A. Potanin, N. B. Uriev: Microreological models of aggregated suspensions in shear flow, J. Coll. Int. Sci. 142 (1989) 385-395.
- [8] R. C. Sontag, W. B. Russel: Structure and break-up of flocs subjected to fluid stresses, J. Coll. Int. Sci. 113 (1986) 399-413.
- [9] P. Schuck, M. Piot, S. Mejean, Y. Le Graet, J. Fauquant, G. Brulé, J. L. Maubois: Déshydratation par atomisation de phosphocaseinate natif obtenu par microfiltration sur membrane, Lait 74 (1994) 375-388.
- [10] A. Pierre, J. Fauquant, Y. Le Graet, M. Piot, J. L. Maubois: Préparation de phosphocaseinate natif par microfiltration sur membrane, Lait 72 (1992) 461-473.
- [11] A. Oliva, M. Llabres, J. B. Farina: Comparative study of protein molecular weights by size-exclusion chromatography and laser-light scattering, Journal of Pharmaceutical and Biomedical Analysis 25 (2001) 833-841.
- [12] D. G. Schmidt, J. Koops, D. Westerbeek: Properties of artificial casein micelles. 1. Preparation, size distribution and composition, Netherlands Milk Dairy Journal 31 (1977) 328-341.
- [13] T. Serra, J. Colomer, X. Casamitjana: Aggregation and break-up particles in a shear flow, J. Coll. Int. Sci. 187 (1997) 466-473.
- [14] W. B. Russel, D. A. Saville, W. R. Schowalter: Colloidal Dispersions, Cambridge University Press, Cambridge (1989)
- [15] D. Chen, M. Doi: Simulation of aggregating colloids in shear flow. II, J. Chem. Phys. 91 (1989) 2656-2663.
- [16] T. Nicolai, L. Benyahia: Shear flow and large Strain oscillation of dense polymeric micelle suspension, Macromolecules 38 (2005) 9794-9802.

