

Modification of lipophilic suspension rheology by lecithins and lecithin fractions

Gunther Arnold¹, Yvonne Schneider¹, Salvadora Ortega², Steve Eglin¹ and Harald Rohm¹

¹Institute of Food Technology and Bioprocess Engineering, Technische Universität Dresden, Germany

²Department of Chemical Engineering, University of Murcia, Campus de Espinardo, Spain

ABSTRACT

Herschel-Bulkley model parameters extracted from stress ramp measurements, and apparent viscosity at selected shear rates were used to compare the impact of lecithin of different origin and phosphatidyl choline concentrate on the rheological behaviour of dark chocolate. While slight differences in the composition did not affect the impact of the lecithin, the single phospholipid fraction caused deviating results.

INTRODUCTION

Lecithin, a by-product of oil processing containing phospholipids and glycolipids, is widely used in the confectionary industry, especially to influence the rheological behaviour of chocolate.

Molten dark chocolate is a suspension consisting of sugar and cocoa solids dispersed in a liquid phase of cocoa butter. The addition of lecithin results in a reduction of viscosity and yield stress which is generally explained by the adsorption of surface active compounds at the solid-liquid interface, thus causing a reduction of particle interactions^{1,2}.

As that offers advantages for processing steps such as pumping, dosing, coating and moulding, the impact of soybean lecithin in different chocolates has been extensively investigated. Apart from the influence of moisture, particle size distribution of the disperse phase and chocolate composition^{3,4}

it was also the specific impact compared to alternative surfactants like polyglycerol polyricinoleate or ammonium salts of phosphatidic acid which were considered⁵⁻⁹.

Generally these investigations have been carried out by adding a defined amount of lecithin while its composition considered in detail. However, as lecithin is a natural product, its composition is usually influenced by origin and processing^{10,11}. Hence the total amount and the fractions of amphiphilic substances in a technical grade lecithin may vary so that different surfactants are difficult to compare.

Aim of this study was to investigate the rheology of molten chocolate as influenced by lecithin of different origin which exhibit variations in absolute and relative composition of its main phospholipids, namely phosphatidyl choline (PC), phosphatidyl inositol (PI), phosphatidyl ethanolamine (PE) and phosphatidic acid (PA). A further approach was to compare the behaviour of technical grade lecithin with that of a single phospholipid fraction, a phosphatidyl choline concentrate. To increase the understanding of influencing factors, the amount of added lecithin was calculated on the basis of the phospholipids content.

MATERIALS AND METHODS

Lecithin-free dark chocolate was supplied by KVB (Berlin, Germany) and

Barry Callebaut (Lebbeke-Wieze, Belgium) and used as reference suspension. Soybean, rapeseed and sunflower lecithin was supplied by European Lecithins GmbH Co. & KG (Hamburg, Germany), and phosphatidyl choline concentrate was provided by PHOSPHOLIPID GmbH (Cologne, Germany). Phospholipids in the lecithins were characterized by ^{31}P NMR. After dissolving a sample aliquot as well as triphenyl phosphate in deuteriochloroform/methanol (2+2; v+v) and after addition of EDTA-caesium carbonate, the sample was mixed and separated. Part of the heavier fraction was used for analysis.

For rheological measurements a specific amount of lecithin or phosphatidyl choline concentrate was dispersed in cocoa butter and added to the chocolate. While the total amount of surfactant was calculated on the basis of the phospholipid content, the quantity of cocoa butter in the system was adjusted to 34 % (comparison of different technical grade lecithin) and 36 % (comparison of lecithin and phosphatidyl choline concentrate) fat in the chocolate. The suspensions were homogenized using a laboratory stirrer (IKA-Werke, Germany) at 1000 rpm for 60 min and stored overnight at 50 °C.

The rheological experiments were performed using a MCR 300 rheometer (Anton Paar GmbH, Ostfildern, Germany). After transferring the sample into the CC 27 concentric cylinder system and adjusting to 40 °C, it was pre-sheared at 900 Pa for 60 s. The flow characteristics were then determined at a shear stress range from 900 to 0.1 Pa at 40 °C. Herschel-Bulkley model parameters extracted from stress ramp measurements, and apparent viscosity at selected shear rates (40 s^{-1} , 5 s^{-1}) were used to determine the impact of the surfactants.

RESULTS AND DISCUSSION

As shown in Table 1, ^{31}P NMR exhibited similar total amounts of phospholipids for sunflower and rapeseed lecithin, whereas

soybean lecithin showed a slightly lower amount. Rapeseed and soybean lecithin exhibited a similar relation between main phospholipids while the relation between PE and the hydrophilic fractions (PC, PI and PA) was lower for sunflower lecithin.

Tab 1. Phospholipid compositions of phosphatidyl choline concentrate (PC) and lecithins of soybean (SO), rapeseed (RS) and sunflower (SF)

| Phospholipid | Phospholipid composition (g/100g) | | | |
|---|-----------------------------------|----------------|----------------|----------------|
| | SO | RS | SF | PC |
| PC ¹ | 12.63 ±0.21 | 14.71 ±0.13 | 16.73 ±0.20 | 94.83 ±0.20 |
| PI | 9.53 ±0.14 | 10.37 ±0.07 | 14.14 ±0.05 | - |
| PE | 8.74 ±0.08 | 9.12 ±0.09 | 7.46 ±0.08 | - |
| PA | 4.75 ±0.07 | 5.16 ±0.03 | 3.07 ±0.04 | - |
| Others (lysophospholipids, PE derivatives and others) | | | | |
| Total | 42.03 ±0.60 | 45.01 ±0.37 | 44.89 ±0.17 | 96.53 ±0.07 |

¹ PC, phosphatidyl choline; PI, phosphatidyl inositol; PE, phosphatidyl ethanolamine; PA, phosphatidic acid.

Generally, the addition of lecithin resulted in a specific reduction of the rheological parameters of chocolate. Figure 1 depicts the effect of technical grade lecithin on the Herschel-Bulkley yield stress of a dark chocolate. The addition resulted in a significant and continuous reduction of the yield stress until a minimum (approximately 50 % of the reference) at a phospholipid concentration (C_{PI}) of 0.2 % was reached. A further addition up to 0.5 % caused a subsequent yield stress increase to about 80 % of the initial value. Lecithin was also responsible for a decrease of apparent viscosity (shear rate: 40 s^{-1}). The reduction of about 50 % was similar to that of yield stress but, for $C_{\text{PI}} \geq 0.2\%$, it remained constant. This is in accordance with previous work on soybean lecithin.

Technical grade lecithin did not show significant differences when incorporated at similar phospholipid concentrations in

chocolate. This leads to the assumption that small differences in phospholipid composition do not affect the rheological behaviour of chocolate to a large extent.

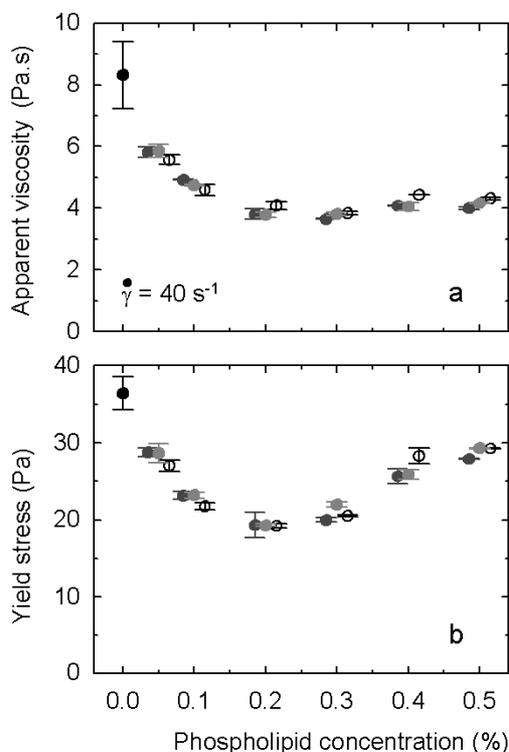


Fig 1. Apparent viscosity (a) and yield stress (b) of dark chocolate as affected by phospholipid source and concentration: without surfactant (●) rapeseed (●), soy (●), sunflower (○). Markers of rapeseed and sunflower lecithin are shifted along the x-axis ($\pm 0.015 \%$)

In additional investigations the impact of technical grade soybean lecithin was compared with that of phosphatidyl choline concentrate (Fig 2). Again, soybean lecithin resulted in a yield stress reduction at low concentration (minimum was 70 % of the reference value) and a subsequent increase for $C_{PI} > 0.2 \%$. At a $C_{PI} = 0.4 \%$ the yield stress is equal to that of the reference. When using phosphatidyl choline concentrate, however, yield stress remained constant for $C_{PI} > 0.2 \%$. Nevertheless, the phospholipid fraction seems to be not as effective in

reducing the yield stress at low concentrations as technical grade lecithin.

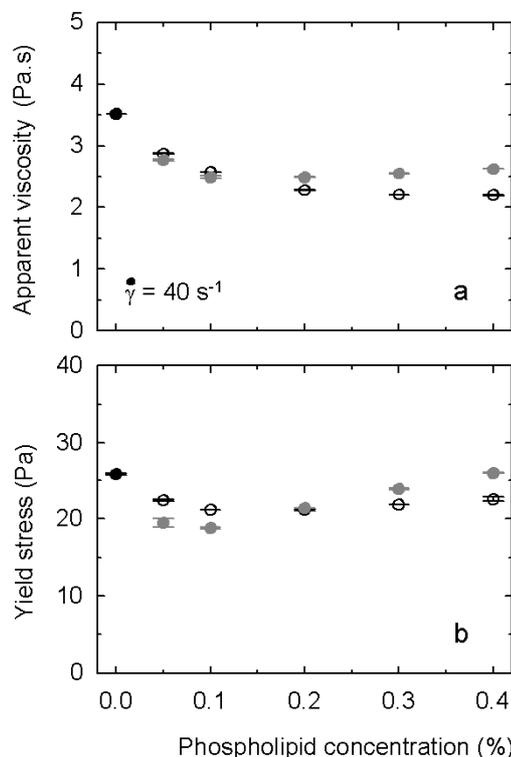


Fig 2. Apparent viscosity (a) and yield stress (b) of dark chocolate (●) affected by soy (●) and phosphatidyl choline concentrate (○).

Differences in the impact of the surfactants are also evident for apparent viscosity. Soybean lecithin reduced that parameter to approximately 70 % of the reference (for $C_{PI} = 0.1 \%$) and did not cause any further changes at higher concentrations from 0.1 % - 0.4 %. However, the reduction of apparent viscosity by using PC concentrate was more pronounced (minimum: 60 % of reference at $C_{PI} = 0.4$).

The results demonstrate the specific impact of a phospholipid fraction as compared to the influence of technical grade lecithin. Furthermore it has to be pointed out that the total amount of surface active components has to be taken into account for comparing influences of different lecithin preparations on the rheological behaviour of chocolate.

ACKNOWLEDGMENTS

Special thanks to European Lecithins GmbH Co. & KG, Hamburg, Germany and PHOSPHOLIPID GmbH, Cologne, Germany for providing the technical grade lecithins and the phosphatidylcholine concentrate.

REFERENCES

1. Beckett, S.T. (2009), "Chocolate flow properties", In: Industrial chocolate manufacture and use (ed. Beckett, S.T.), *Blackwell Publishing Ltd*. Oxford, pp. 224-246.
2. Afoakwa, E.O. (2010), "Chocolate science and technology", *Wiley-Blackwell*, Oxford, pp. 101-154.
3. Afoakwa, E.O., Paterson, A., and Fowler, M. (2008), "Effects of particle size distribution and composition on rheological properties of dark chocolate", *Eur. Food Res. Technol.*, **226**, 1259-1268.
4. Sokmen, A. and Gunes, G. (2006), "Influence of some bulk sweeteners on the rheological properties of chocolate", *LWT*, **39**, 1053-1058.
5. Aguilar, C.A. and Ziegler, G.R. (1995), "Viscosity of molten milk chocolate with lactose from spray-dried whole milk powders", *J. Food Sci.*, **60**, 120-124.
6. Vernier, F.C. (1997), "Influence of emulsifiers on the rheology of chocolate and suspensions of cocoa or sugar particles in oil", Ph.D.-thesis, Reading.
7. Hugelshofer, D., Windhab, E.J. and Wang, J. (2000), "Surface excess of emulsifiers and rheological properties of a concentrated food model suspension", *Proceedings ISFRS*, **2**, 344-348.
8. Schantz, B. and Rohm, H. (2005), "Influence of lecithin-PGPR blends on the rheological properties of chocolate", *LWT*, **38**, 41-45.
9. Karnjanolarn, R. and McCarthy, K.L. (2006), "Rheology of different formulations of milk chocolate and the effect on coating thickness" *J. Texture Stud.*, **37**, 668-680.
10. Nieuwenhuyzen, W.V. and Tomás, M.C. (2008), "Update on vegetable lecithin and phospholipid technologies", *Eur. J. Lipid Sci. Technol.*, **110**, 472-486.
11. Schneider, M. (2008), "Major sources composition and processing", In: Phospholipid Technology and Applications (ed. Gunstone, F.D). *The oily press. Bridgewater*, England, pp. 21-40