Characterisation of the Structure and Flow Behaviour of Model Chocolate Systems by Means of NMR and Rheology

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Abstract:
In order to characterise the structure and flow behaviour of model chocolate systems Nuclear Magnetic Resonance (NMR) and rheometry were used to determine the T_1 - and T_2 - NMR relaxation times and their corresponding flow functions. T_1 and T_2 characterise the molecular mobility of fluids and correlate with both the zero-shear-rate and infinity viscosity of various chocolate model systems (determined with rotational rheometry and capillary rheometry). Based on this correlation, NMR provides the possibility to determine characteristic viscosities of chocolate masses by means of NMR-relaxation experiments. The viscosities of chocolate masses are important process parameters, as they are used for quality control of the production process. An online process viscosimetry via T_2 relaxation would allow the installation of an efficient process control and, thus, a process automation. This NMR application with comparatively short measuring times is especially interesting for disperse systems where the use of conventional rheometric techniques may cause large errors. The only prerequisite for the measurement of the viscosities using NMR is a previous calibration. This was performed with the help of rotational and capillary rheometry. The NMR self-diffusion experiments are especially appropriate to characterise the influence of emulsifiers on the structure and the flow behaviour of chocolate masses.

Zusammenfassung:
Die Struktur und das rheologische Verhalten von Modellschokolade wurde mit Nuclear Magnetic Resonance (NMR) und rheometrischen Methoden, d. h. über den Zusammenhang der T_1 - und T_2 - NMR Relaxationszeiten und der entsprechenden Fließkurven, untersucht. Die beiden Relaxationszeiten T_1 and T_2 charakterisieren die molekulare Mobilität der Flüssigkeit und können mit der Nullviskosität und der Viskosität bei hohen Scherraten für verschiedene Schokoladensysteme (bestimmt mit Rotations- und Kapillarrheometrie) korreliert werden. Basierend auf diese Verknüpfung können NMR-Messung zur Bestimmung charakteristischer Viskositätswerte von Schokoladenmassen angewendet werden. Diese Werte sind wichtige Prozessparameter, da sie direkt eine Qualitätskontrolle der Produktionsprozesse zulassen. Die Online-Viskosimetrie über die T_2 Relaxationzeit erlaubt somit eine effiziente Prozesskontrolle und Prozessautomation. Ein weiterer Vorteil der NMR-Methode liegt im Vergleich zur konventionellen Rheometrie in der relativ kurzen Messzeit. Für hochkonzentrierte Schokoladenmassen können somit einige signifikante Fehlerquellen reduziert werden. Die NMR-Diffusionsexperimente können zudem genutzt werden, um den Einfluss von Emulgatoren auf die Struktur und das Fließverhalten der Schokoladenmassen zu untersuchen.

Résumé:
Afin de caractériser la structure et le comportement en écoulement de systèmes modèles de chocolat, La Résonance Magnétique Nucléaire (RMN) ainsi que la rhéométrie ont été utilisées pour la détermination des temps de relaxation RMN T_1 et T_2 et leurs fonctions d'écoulement correspondantes. T_1 et T_2 caractérisent la mobilité moléculaire des fluides et sont corrélés avec la viscosité statique de même que la viscosité infinie (déterminées par rhéométrie en rotation et par rhéométrie capillaire) de systèmes modèles de chocolat variés. A partir de cette corrélation, la RMN fournit la possibilité de déterminer les viscosités caractéristiques de paquets de chocolat au moyen des expériences de relaxation RMN. Les viscosités des paquets de chocolat sont des paramètres de mise en œuvre importants, puisqu'ils sont utilisés pour le contrôle de la qualité durant la production. Un procédé de viscosimétrie "on-line" par l'intermédiaire de la relaxation T_2 pourrait permettre l'installation d'un procédé de contrôle efficace et donc d'un procédé d'automatisation. Cette application de la RMN avec comparativement des temps de mesure courts est spécialement intéressante pour les systèmes dispersés où l'utilisation de techniques de rhéométrie conventionnelle peut être à l'origine de grandes erreurs. L'unique condition pour la mesure des viscosités par RMN est une calibration préliminaire. Cette dernière a été effectuée à l'aide de la rhéométrie en rotation et capillaire. Les expériences de diffusion RMN sont particulièrement appropriées pour caractériser l'influence des émulsifiants sur la structure et le comportement en écoulement des paquets de chocolat.

Key words: Suspension, chocolate, emulsifier, viscosity, flow behaviour, NMR, process and quality control, process viscosimetry

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1 INTRODUCTION

Chocolate is, like many other food products, a complex multi-phase system containing (i) cocoa butter and milk fat as solidified continuous phase, (ii) sugar, cocoa and milk solids and possibly further solid (fat-insoluble) ingredients as disperse phase and (iii) as minor component surface-active agents in order to modify the interactions between the ingredients. The non-fat solid concentration varies from 55 to 73 %w/w total solids (40 - 60 %v/v) [1, 2]. At room temperature 80 to 90 %w/w of the continuous fat phase are solidified and crystalline.

At low shear rates chocolate masses, like many suspensions, show high viscosities (upper Newtonian plateau η_0), which decrease for rising shear rates and finally lead to the so-called lower Newtonian plateau η_∞. The change of the viscosity for increasing shear rate is correlated with structural modifications. At higher shear rates agglomerates break up, entrapped liquid fat is released, and the viscosity decreases, which are typical effects of conching [3]. It is, furthermore, imaginable that the simultaneous crushing of agglomerates and of primary particles causes an increase of the viscosity due to the immobilisation of fluid-molecules at the evolving solid surfaces [4]. In order to optimise the manufacturing process and formulation and to minimise costs, it is necessary to control and manipulate the chocolate rheology [5]. Besides the relevance of the rheological parameters characteristic for (i) the structure of the chocolate masses and (ii) the design of the involved apparatus and processes (mixing, moulding and conching), the flow behaviour is considered as (iii) a mark of quality for many food systems (production, i.e. quality control, and consumers, i.e. sensorial behaviour). This explains the efforts to use appropriate rheometric techniques as online-process viscosimetry and, based on this, process automation [5 - 8]. In spite of its great importance, the determination of the viscosity (usually by rotational rheometry [3]) is still problematic for many multi-phase systems [9, 10]. Monitoring the viscosity or secondary related parameters (yield stress, solid concentration, molecular mass) enables a more efficient quality and process control of many unit operations via an analysis in real-time [11].

Bloembergen et al. [12] found for simple Newtonian pure fluids (e. g. water, glycerine) theoretically and experimentally a correlation between the relaxation times T_1 and T_2, and the dynamic viscosity η, independent of temperature and pressure. A similar correlation also exists for solutions (aqueous sugar solutions, fruit juices, beer and wine) [13], suspensions (silicone oil/glass sphere, mashes) [9]. Due to scale effects only suspensions whose largest particles or agglomerates are at least an order of magnitude smaller than characteristic lengths of the measuring geometry can be tested in conventional rheometers. This could be problematic for conventional rheometric techniques due to flow-induced agglomeration of solid particles (sugar, milk powder, cocoa mass) during production processes. The aim of this study is to test if the correlation found by Bloembergen et al. [12] can be applied to chocolate suspensions to determine characteristic viscosities of suspensions via the usually faster T_2 experiments.

Furthermore, in order to minimise the risk of production disturbances (varying raw materials or composition) it would be very helpful to quantify the effect of variations of the ingredients plus their physical/chemical status (e.g. aggregated/dispersed). Therefore, NMR diffusion measurements, in addition to T_1 and T_2, were performed. NMR diffusion measurements enable one to study the structural parameters of disperse systems by using diffusing molecules as a probe of the accessible spatial compartments in structured materials. In addition, the structural influence of surface active agents (emulsifiers), which are often used to modify the flow behaviour of chocolate suspensions and to increase the sugar volume concentration at simultaneous lower viscosities, is studied.

2 FLOW BEHAVIOUR

As mentioned above chocolate masses are suspensions in the melted state with a complex chemical composition [2 - 4, 9 14 - 27]. Due to molecular groups in solid cocoa particles, which are less polar than those in sugar, cocoa butter molecules stick preferentially to the solid surface of the cocoa particles, thus increasing the rheologically effective volume of the cocoa particles [28]. The extension of the corresponding solvating envelopes, containing molecules of the fat phase, are different due to the polar properties of the present solid surfaces. It is, furthermore,

Table 1: Components of continuous and disperse phase.

Continuous phase	Disperse phase
AkomedR	sucrose
Emulsifiers: soya lecithin, sunflower lecithin, ammonium phosphatide (NY) and polyglycerol polyricinoleic acid (PGPR)	skimmed milk powder

assumed that sugar particles tend to build up three-dimensional network structures due to their hydrophilic sites, even at low solid volume contents. As a consequence of the strong interactions between the sugar particles and the simultaneous weak interaction between sugar and the fat phase a yield stress of the corresponding suspension can be observed [28]. The physical state of the interacting surfaces, the moisture, temperature and, furthermore, the type of emulsifier and its concentration have a great influence on the flow behaviour. Even low amounts of surface-active agents or surfactants, often erroneously called emulsifiers in food technology, lead to a significant decrease of the viscosity. At sufficiently high emulsifier concentrations an increase of the yield stress may be induced. Emulsifiers are used in the chocolate production for the following reasons:

- The re-agglomeration of sugar particles (e. g. conching process) is reduced. The emulsifier molecules solvate the hydrophilic sugar so that lipophilic cocoa butter is immobilised to the solid surface of sugar. Thus, the increased distance between sugar particles causes a reduction of the mutual interaction. This is a prerequisite for an optimal sensorial behaviour (particle sizes < 20-25 mm) and a reduced viscosity and yield stress [27, 29].
- The fat content is reduced at constant viscosity [30].
- Emulsifiers are applied as antibloom agents in chocolate and compound coatings via a reduced crystallisation rate of cocoa butter or other fat-types [30 - 32]. Fat bloom is a complex combination of melting, resolification, migration and uncontrolled crystallisation causing discoloration and bloom.
- The chocolate becomes tolerant towards variations of moisture and temperature [2].

Addition of 0.1 - 0.3 % soy lecithin reduces the viscosity by a factor of 10 and also the yield value by a factor 2-3 [2]. Ammonium phosphatide (YN) is even more effective up to 0.5 %. Above this concentration YN continues to decrease the plastic viscosity of chocolate masses, but does not affect the yield stress. For the yield stress there is no optimum dosage of YN. Polyglycerol polyricinoleic acid (PGPR) reduces the moisture absorption in chocolate and yield stress in chocolate. Below 0.3 % this emulsifier shows only a slight decreasing effect on chocolate viscosity, but a large effect on yield stress. For 0.5-1.0 % PGPR the yield stress approaches zero. PGPR is used in place of lecithin for reduced yield stress [5].

Emulsifiers are present not only at the interfaces between hydrophilic and lipophilic sites. At sufficient concentrations, depending on the emulsifier and specific surface of sugar, emulsifier molecules might be (i) dissolved in the fat phase or formed into (ii) emulsifiermicelles and (iii) a bilayer of emulsifier around the sugar particles causing higher viscosities. Thus, the emulsifier increases the rheologically effective volume of sugar particles and simultaneously hydrophobises them. Colloidal structures formed by lecithin in the fat phase are assumed to exist in cocoa butter in the present of 0.8 % soy lecithin [33]. These structures are presumably destroyed at higher shear rates releasing the formerly retained fluid fat.

Fat bloom was studied by Nuclear Magnetic Resonance Imaging (MRI) to visualise the migration of liquid triacylglycerol in chocolate confectionery [33]. The higher the temperature, the higher is the total migration of liquified cocoa butter towards the surface, where a recrystallisation as bloom can occur [34]. Thus, bloom can be detected, before the migrated butter components have recrystallised at the outer surface of the confectionery. MRI provides, therefore, a rapid test for the study of bloom and optimisation of the formulation, production and storage process. In the following the effect of emulsifiers on the texture, the corresponding T_1 and T_2, the self-diffusion coefficients D_S and flow behaviour is studied. Especially the possibilities of D_S, less sophisticated than MRI, to study effects of the recipe on the evolution of fat bloom are shown.

Component	Mass / g	% w/w	% v/v
AkomedR (A)			
AkomedR	111.60	100.00	-
AkomedR + lecithin (AL)			
AkomedR	111.60	100.00	-
lecithin	1.06	0.95	-
AkomedR + sucrose mix A (ASA)			
AkomedR	111.60		44.00
sucrose	238.40		56.00
D(v, 0.9) =11.89 µm % w/w	143.04	0.6 . 56.00	
D(v, 0.9) = 33.85 µm % w/w	95.36	0.4 . 56.00	
lecithin	0	0	0
AkomedR + sucrose mix B (ASB)			
AkomedR	111.60		44.00
sucrose	238.40		56.00
D(v, 0.9) = 11.89 µm % w/w	95.36	0.4 . 56.00	
D(v, 0.9) = 33.85 µm % w/w	143.04	0.6 . 56.00	
lecithin	0	0	0
AkomedR + sucrose Mix A + lecithin (ASAL)			
AkomedR	111.60		44.00
sucrose	238.40		56.00
D(v, 0.9) = 11.89 µm % w/w	143.04	0.6 . 56.00	
D(v, 0.9) = 33.85 µm % w/w	95.36	0.4 . 56.00	
lecithin	3.33	0	0.95
AkomedR + sucrose mix B + lecithin (ASBL)			
AkomedR	111.60		44.00
sucrose	238.40		56.00
D(v, 0.9) = 11.89 µm % w/w	95.36	0.4 . 56.00	
D(v, 0.9) = 33.85 µm % w/w	143.04	0.6 . 56.00	
lecithin	3.33	3.33	0.95
AkomedR + skimmed milk powder + lecithin (AML)			
AkomedR	111.60	68.11	0.30
skimmed milk powder	238.40	31.89	0.70
lecithin	3.33	0.95	
AkomedR + sucrose mix B + skimmed milk powder + lecithin (ASBML)			
AkomedR	111.60	31.89	0.35
skimmed milk powder	65.43	18.69	0.33
ground sucrose mix B	172.97	49.42	0.32
lecithin	3.33	0.95	
AkomedR + sucrose mix B + skimmed milk powder + defatted cocoa powder + lecithin (ASBMCL)			
AkomedR	111.60	31.89	0.27
skimmed milk powder	60.15	17.18	0.42
sucrose mix B	159.00	45.43	0.23
cocoa powder	19.25	5.50	0.07
lecithin	3.33	0.95	

Table 2: Formulation of the studied samples.

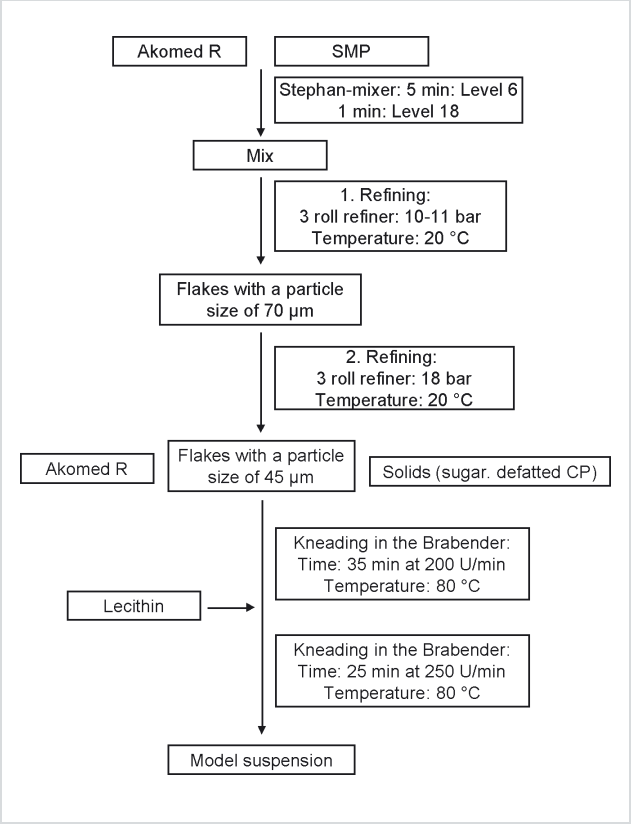


Fig. 1 (above): Flow diagram for the preparation of ASBMCL.

Table 3 (right): Moisture content (owen seasand method: 104°C, 2 h, 5 g sample mixed with 25 g of dried seasand) and solid concentration (Table 2).

Samples	Moisture / %	Solid volume concentration cV,S / % (v/v)
A	0.3	0
AL	0.3	0
ASA	0.3	56.0
ASB	0.3	56.0
ASAL	0.1	56.0
ASBL	0.1	56.0
AML	1.9	76.99
ASBML	1.2	64.82
AMSBCL	0.4	72.61

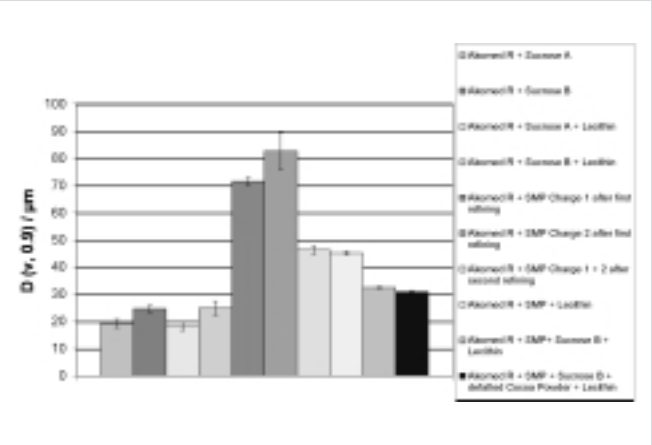
3 MATERIALS

The materials are selected to develop step by step the complex system of real chocolate suspensions. The suspensions are composed of the triglyceride blend AkomedR (Karlshamns BV, Zaandijk, Netherlands) being the liquid continuous fat phase with addition of sugar, milk powder and cocoa powder (disperse phases), with or without lecithin (Table 1). The advantage of these model suspensions is that they are liquid at room temperature due to AkomedR. AkomedR is a special medium-chain triglyceride known as caprylic/capric triglyceride (slip melting point < 0°C, cloud point < -5°C).

A native soybean lecithin, TOPCITHIN 50 Taylor (Lucas Meyer, Zaandam, Netherlands), is used as emulsifier common in the chocolate industry. Lecithin is a mixture of neutral lipids (triglycerides, sterols, fatty acids) and polar lipids (phospholipids, sugar- or glycolipids). The used agent contains 65 % w/w acetone-insoluble phosphatides (polar lipids). The residue is mostly soy oil. Phosphatides without soya oil are unstable [35]. Lecithin is lipophilic and used as w/o emulsifier [36]. For self-diffusion measurements liquid emulsifiers like soybean lecithin, sunflower lecithin, YN and PGPR are used. Sunflower lecithin (Solec Z, Quest Int., Zwijndrecht, Netherlands) has a viscosity of 12.5 Pa·s [37]. YN (E442, Palsgaard® NexusA/S, Juelsminde, Denmark) is based on partially hardened rapeseed oil and has a melting point of 35°C (Parlsgaard) [38]. PGPR (E476, Wol 1403, QuestInt., Zwijndrecht, Netherlands) is a mixture of partial esters of polyglycerol (predominantly di-, tri- and tetraglycerol) with linearly interesterified castor oil fatty acids.

Sugar is the major ingredient, with up to 70 % w/w of the solid fraction. Two batches of standard crystal sugar (Nordzucker AG, Uelzen, Germany) with D(v, 0.9) = 11.89 μm and 33.85 μm were used. Furthermore, a commercial, spray-dried skimmed milk powder (SMP) (Omira, Oberland Milchverwertung GmbH, Ravensburg, Germany) was applied (average fat content < 1 %). Defatted cocoa powder was dry milled to a particle size of D(v, 0.9) = 18.37 μm. The model suspensions are described in Table 2. All samples were mixed with a Brabender lab kneader (Duisburg, Germany). The complete flow diagram for the most complex sample ASBMCL (Table 2) is presented in Fig. 1. The composition and production are comparable to that of real chocolate masses. The samples were filled into NMR tubes immediately after the production and stored at -20°C.

The moisture content of the samples was determined using an owen seasand method at 104°C for 2 h. This method records the free water, but not crystal water of lactose-monohydrate. The moisture content is below 0.5 %, except for AkomedR plus skimmed milk powder with lecithin (AML) with a higher moisture content (Table 3). AML contains highly amorphous spray-dried skimmed milk powder and a high amount of free water. Hence this sample has a higher water absorption capacity than AMSBCL (Table 2). The particle-size distribution of the solid particles was determined using stray light (Master-Sizer Micro, Malvern Instruments GmbH, Herrenberg, Germany). The amount of 0.16 g sample was mixed with 20 ml AkomedR, treated with ultrasound (5 min) and analysed immediately in order to avoid sedimentation (Fig. 2).



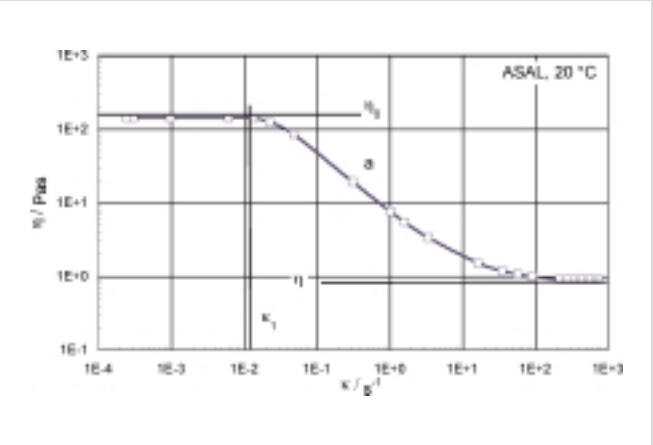


Fig. 2 (left): Particles size D(v, 0.9) for the studied samples (Table 2).

Fig. 3 (right): Exemplary fit (Eq.4) of the shear-thinning behaviour of ASAL (20°C).

4 METHODS

4.1 NMR

In order to limit the extension of the present work the basic ideas of NMR are not treated [38 - 40]. NMR is based on the fact that nuclei possess further characteristics besides the mass and charge. One of them is the magnetic moment (spin) of specific isotopes (e. g. 1H, 19F). If such a material is brought into an external magnetic field, the spins usually have different energy levels. By means of various techniques the thermal equilibrium can be disturbed. Information concerning the composition, the structure and the state of motion can be derived from the subsequent relaxation and the corresponding relaxation times T_1 and T_2. T_1 and T_2 are measures of the interaction of a spin with its surroundings and the mobility of a spin, respectively. As such, it is possible to distinguish between free fluid that does not interact with the solid particles or dissolved molecules and immobilised fluid (chemically/physically bound). T_2 experiments are usually preferred to T_1 experiments (not shown) due to the shorter measuring time and the higher sensitivity of T_2 experiments to the presence of various phases in a system. For the T_2 relaxation the envelope curve of the echoes can be described, due to the present phases, as

$$U(t) = a + p_{2,1} e^{-\left(t/2T_{2,1}\right)^2} + \sum_i p_{2\,i} e^{-\left(t/T_{2\,1}\right)} \quad (1)$$

with $\Sigma_i p_{2,i} = 1$, a as zero drift, $p_{1,i}$ and $T_{1,i}$ as fraction and average T_2 relaxation time of the spins in the solid state, $p_{2,i}$ and $T_{2,i}$ as fractions and average T_2 relaxation times of the spins in fluid states for i > 1; $T_{2,1} < T_{2,2} < T_{2,3} < \ldots$ A mean T_2 relaxation time can be defined as T_{2m}

$$T_{2m} = \sum_i p_{2,i} T_{2,i} \quad (2)$$

A low-resolution NMR spectrometer, MINISPECmq20 (Bruker BioSpin GmbH, Rheinstetten, Germany), was used. The resonance frequency of ^{1}H is 20 MHz. For the T_2 experiments a combination of FID [40] (scanning time distance: 5.2.10^{-4} ms) and subsequently a CPMG [40] sequence (duration (90° - 180°) τ: 0.2 ms, 19600 pulses) was applied. Thus, the influence of field inhomogeneities and diffusion or chemical exchange on the relaxation are minimised and in spite of the high scanning rate comparably long total measuring times (~ 8 s) can be achieved.

NMR diffusion measurements allow (i) the quantification of the molecular mobility of the diffusing substances/molecules in homogeneous and disperse systems and (ii), derived from this, the characterisation of the solid matrix probed by the diffusion behaviour of the corresponding solvents. It is possible to determine D_S as a function of the effective diffusion time Δ and to calculate the mean distance travelled by the diffusing molecules during Δ [41]. I_g is the signal in a PGTSE (pulsed field gradient stimulated echo) experiment, with applied gradient magnetic field g, I_0 is the corresponding signal without gradient. The ratio of I_g and I_0 is given by

$$-\frac{I_g}{I_0} = e^{-\gamma^2\delta^2 g^2 (\Delta - 1/3\,\delta) D_S} \quad (3)$$

where γ is the gyromagnetic ratio, δ the gradient-pulse duration, g the magnitude of the gradient amplitude and Δ the duration between two gradient pulses (diffusion time)

4.2 RHEOLOGICAL EXPERIMENTS

The rheological measurements were performed in a rotational rheometer (BohlinCV120, Bohlin-Instruments, Pforzheim, Germany), at constant stress without preconditioning in order to treat the rheological samples in the same way as in the NMR measurements (twice at 5, 20, 40 and 70°C).

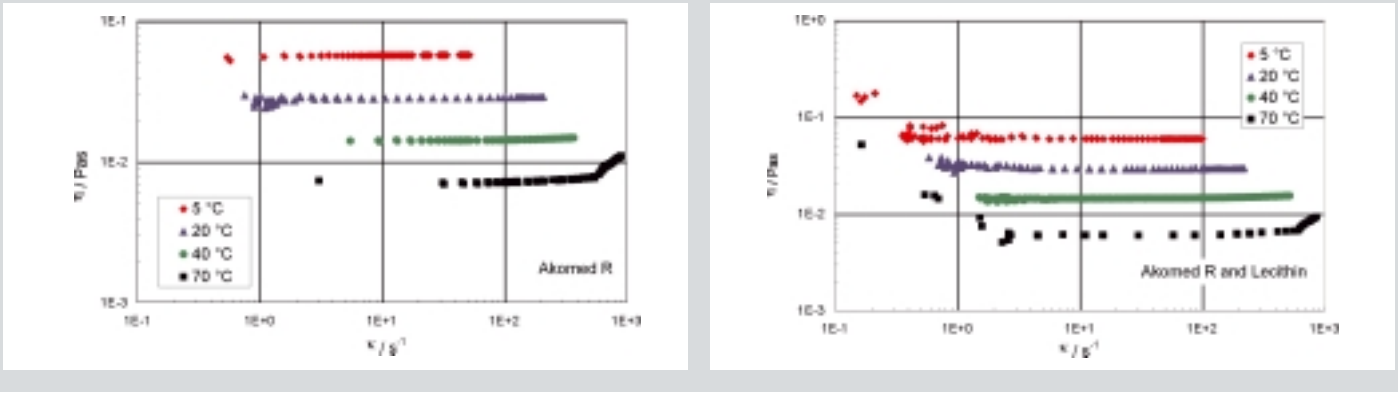


Fig. 4 (above): Viscosity functions of AkomedR and AkomedR with lecithin (0.95 %w/w).

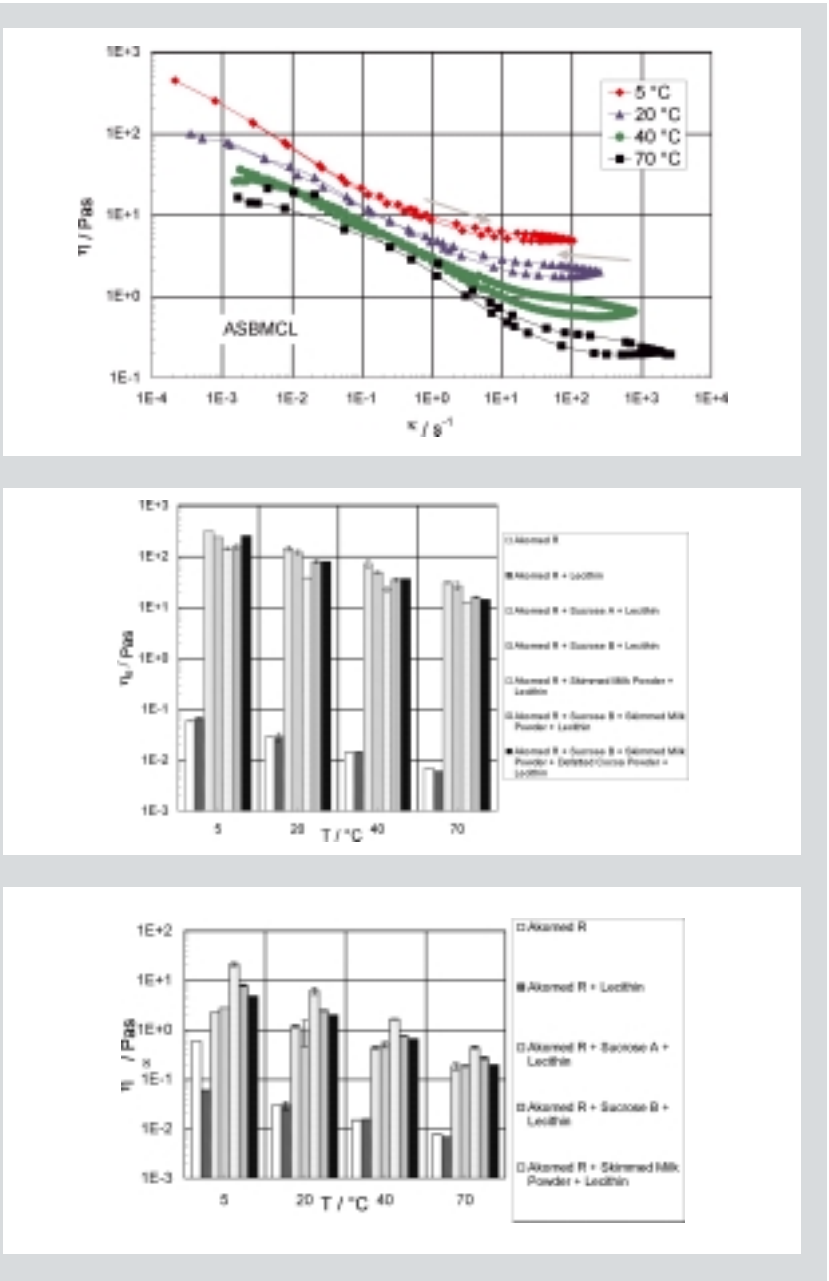


Fig. 5 (above): Temperature dependence of viscosity functions of ASBMCL ($c_{v,s}$=72.6 %v/v); rotational rheometer. At high shear rates the upper curve represents the up- and the lower curve the down-curve.

Fig. 6: η_0 (a – middle) and η_∞ (b – below) of the samples, rotational rheometer (cup-and-bob).

The measuring system was a Couette geometry (inner diameter: 25 mm, width of the gap: 2 mm, height: 25 mm). The samples were defrosted and filled without stirring into the bob for tempering 30 min prior the measurement. The cone also was tempered in the heating chamber or refrigerator. Hence the samples showed the required measuring temperature and were treated in the same manner as the filled NMR tubes. The samples were sheared for a defined time at constant shear stress. The resulting up-down curves give the viscosities at different applied shear stresses. The raw data were corrected according to Rabinowitsch-Weissenberg. Viscosities η_0 and η_∞ were determined by fitting the experimental data (TableCurve™, SPSSInc., Chicago) using the modified Carreau model [42]

$$c = \frac{\eta_0 - \eta_\infty}{[1+(\kappa/\kappa_1)^a]^{0.5}} + \eta_\infty \qquad (4)$$

where κ is the shear rate and a, κ_1 are fitting parameters. κ_1 represents the shear rate where the non-Newtonian flow behaviour starts. The parameter a is a measure of the slope in the non-Newtonian region (Fig. 3).

4.3 LIGHT MICROSCOPY

Light microscopy (Axioplan2: ZeissGmbH Oberkochen, Germany) was used to study the influence of emulsifiers on the inner structure of chocolate-model suspensions. The corresponding samples are diluted with glycerine.

5 RESULTS AND DISCUSSION

5.1 RHEOLOGY

Motivated by the varying temperatures in process units and during storage and distribution, the viscosity functions of the samples (Table 2) are studied for 5, 20, 40 and 70°C. These measuring temperatures can also be realised in the measuring volume of the NMR device. Fig. 4 shows the viscosity functions of pure AkomedR

and AkomedR with lecithin (0.95 %). For high shear rates κ no significant effect of the added lecithin on the viscosity can be observed. At sufficiently low shear rates (dependent on the temperature), however, shear-thinning behaviour for AkomedR plus lecithin is observable, as it was found for cocoa butter plus soya lecithin [25].

The viscosity functions of the other studied samples (Table 2) show qualitatively the same dependence on the shear rate and the temperature like the chocolate-similar mixture ASBMCL (Fig. 5). The shear stress was stepwise increased and reduced. At high shear rates the upper curve represents the up-curve and the lower curve the down-curve. The experimentally found up- and down-curves show that the viscosity functions can be fitted adequately by Eq. 4, but reveal the dependence of the flow behaviour on the pretreatment/-history of the suspensions. The derived viscosities η_0 and η_∞ (Fig. 6) of the samples (Table 2) decrease with the temperature. The viscosities η_0 (Fig. 6a) of ASAL are higher than those of ASBL due to the smaller particle size and hence the higher specific surface of the sugar mix A. This, however, does not hold for η_∞ of the samples ASAL and ASBL (Fig. 6b), where the infinite viscosities are approximately identical within the measuring accuracy. The behaviour of η_0 and η_∞ is also not identical for the more complex samples. AML, for example, has the lowest viscosity η_0 (apart from AkomedR and AkomedR plus lecithin) and the highest η_∞, with the highest solid volume concentration $c_{v,s}$ = 76.99 % (Table 3). The viscosity η_∞ increases with the solid volume concentration (Table 3), in accordance with known formulae concerning the viscosity of suspensions as a function of the solid volume concentration. The behaviour of η_0 for AML is, however, surprising. The different types of solid particles (SMP, sugar, defatted cocoa powder) behave obviously differently in a rheological point of view, presumably due to the (i) different polarity at the solid surfaces and the resulting "hydration shells" of fat molecules, (ii) different particles sizes combined with different specific solid surfaces, fluid absorption and (iii) the composition (protein, emulsifier). Due to the different amount of immobilised fluid molecules by the solid materials it is problematic to develop a comparably simple phenomenological relation for chocolate masses between the viscosity and

Fig. 7: AkomedR with sucrose (ASB) and AkomedR with sucrose and lecithin (ASBL).

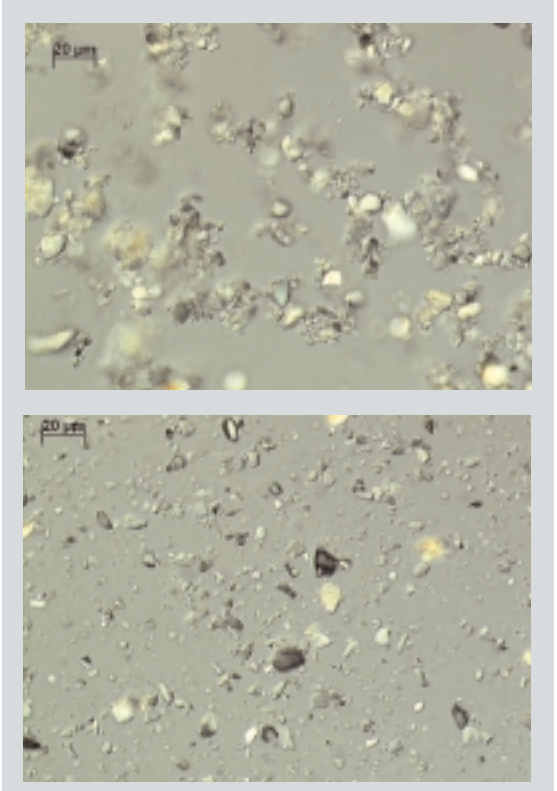
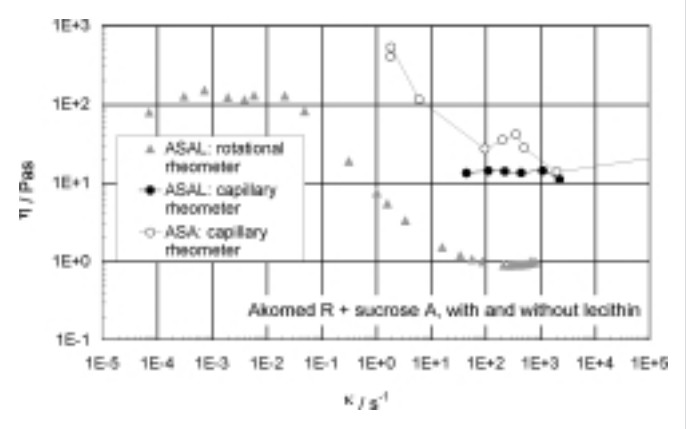


Fig. 8: Light microscopy of (a – above) ASB and (b – below) ASBL.



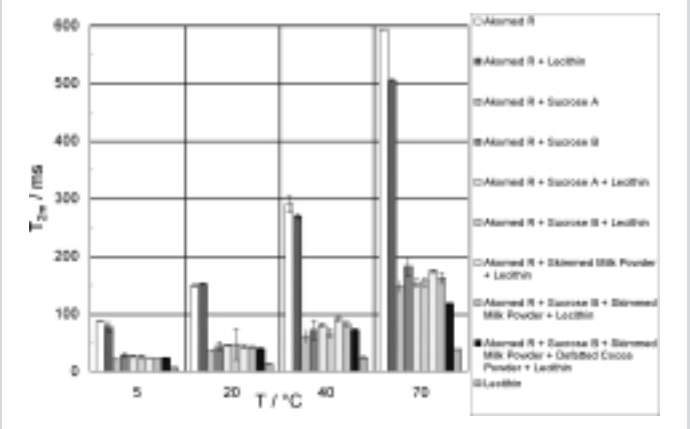


Fig. 9 (left): Viscosity functions of ASA and ASAL (20°C): (i) capillary rheometer: diameter of channel 15.0 mm, round nozzle: D = 2.0 mm. ASA: lengths L = 10.0, 20.0 mm, ASAL: lengths L = 20.0, 30.0 mm. (ii) ASAL: rotational rheometer.

Fig. 10 (right): T_{2m} of the samples (Table 2).

the effective volume fraction of the solids. These interpretation-difficulties possibly induced by the different polarities of the solid-surfaces might be responsible for the monotonous decrease of the viscosity η_0 with the calculated solid volume concentration of the chocolate masses. The two viscosities η_0 and η_∞ seem, nevertheless, appropriate to characterise and quantify the influence of the composition (type and concentration) of the model suspensions on the flow behaviour.

The samples ASA and ASB cannot be tested in a conventional rotational rheometer due to their solid-like deformation behaviour (sugar: 56 %v/v). ASB behaves like a wet bulk solid revealing a yield stress, it sticks onto a spoon and has an optically disperse, coarse appearance (Fig. 7 left). ASBL, however, is an optically homogeneous, smooth suspension (Fig. 7 right). By light microscopy the "inner" explanation for the completely different rheological behaviour of ASB and ASBL becomes obvious. In ASB agglomerates of approximately 60 mm form a coarse-stranded network structure (Fig. 8a). This solid matrix obviously causes the solid-character of ASB. In ASBL, however, neither network structures nor agglomerates are observable (Fig. 8b). In the sugar - AkomedR systems the emulsifier lecithin seems to break-up the whole network structure plus the sugar agglomerates producing isolated primary particles of sugar. Molecules of the fluid fat phase, which might be retained inside of the agglomerates, are released by the emulsifier. This process, combined with the destruction of the solidnetwork, fluidises the mixture. In order to quantify the flow behaviour of the pure sugar - AkomedR systems and to study the effect of the lecithin on the flow behaviour, ASA and ASAL were studied by capillary rheometry. The averaged measuring values and apparent viscosity functions have been corrected with Bagley and Rabinowitsch - Weissenberg (Fig. 9). The viscosity of ASA is, as expected, for all realised shear rates higher than that of ASAL. The capillary rheometer allows one to quantify the influence of the measuring method (capillary/rotational rheometer) on the derived viscosity functions. The viscosities determined by the capillary rheometry are more than one order higher than those of the rotational rheometry.

5.2 NMR

5.2.1 Relaxation Experiments

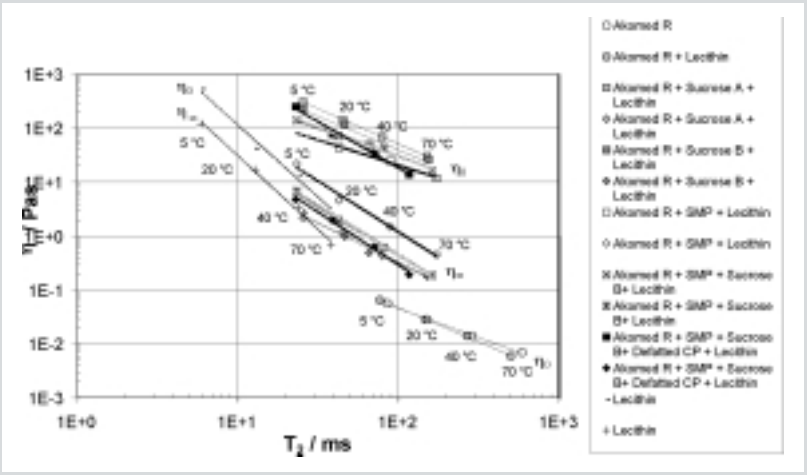
Fig. 10 shows the average T_{2m} (Table 2) as a function of the temperature. T_{2m} of all samples increases with the temperature according to the enhanced molecular mobility. Thus, T_{2m} of pure AkomedR is for all temperatures higher (or equal) than T_{2m} of AkomedR plus lecithin. This is a hint that lecithin modifies the structure causing a reduced mobility of T_{2m} for AkomedR. The addition of solid particles (sugar, skimmed milk powder, defatted cocoa powder) reduces the corresponding T_{2m} to approx. a fourth of the relaxation times of AkomedR or AkomedR plus lecithin. (i) Interactions between solid particles and AkomedR and (ii) steric spatial inhibition, simply due to the existence of solid surfaces, combined with (iii) modifications of the original molecular order are responsible for the lower T_{2m} of the tested suspensions. Another remarkable observation, furthermore, is that T_{2m} of ASA is for all temperatures consistently lower than those of ASB. This is presumably due to the higher specific solid surface of ASA which has a significantly smaller mean particle-size diameter than ASB. The behaviour of ASAL and ASBL is different from that of ASA and ASB for the studied temperatures. T_{2m} of ASAL is higher or equal than that of ASBL. Lecithin presumably exists in chocolate masses in other states besides molecularly dissolved lecithin molecules or colloidal structures, combined with different interactions between the corresponding lecithin and the present sugar solid surface. Although the total solid volume concentration (Table 3) of AML (77 %)

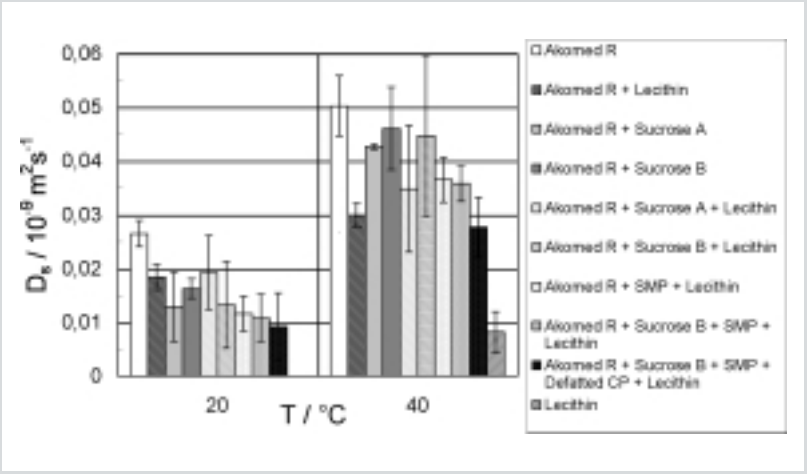
is higher than that of ASBML (65 %) and ASBMCL (73 %) (Table 2), T_{2m} of AML is higher than that of ASBML and ASBMCL. In addition to the volume concentration of the solid phase and the viscosity of the fluid phase, further variables (like interactions between the constituents and moisture-effects) have obviously to be taken into consideration.

Furthermore, T_2 experiments were used to quantify the macroscopically observable effect (Fig. 7) of lecithin with regard to the structure and flow behaviour of chocolate masses. There are, however, no significant differences detectable for ASA and ASAL, neither with regard to the relaxation times $T_{2,i}$ nor to the corresponding fractions $p_{2,i}$ (at all studied temperatures). This is a surprising result, which cannot be explained yet. The behaviour of the T_1 relaxation is qualitatively similar to that of T_2 and is, therefore, not shown here. In contrast to T_2 there are no great differences between the T_{1m} relaxation times of AkomedR and AkomedR plus lecithin on one side and the suspension-samples on the other side. This is not inconsistent, as T_1 and T_2 are completely independent physical quantities. T_1 is correlated with the energy of the spin system and T_2 with the entropy. For some samples and temperatures T_{1m} of suspension models are higher than that of AkomedR or AkomedR plus lecithin. The combination of T_{1m} and T_{2m} (Fig. 10) indicates the solid-behaviour of the suspensions [12].

5.2.2 CORRELATION OF NMR-RELAXATION AND RHEOLOGY

In Fig. 11 the dependence of the dynamic viscosity η (or the characteristic viscosities η_0 and η_∞, respectively) and the corresponding T_2 (or T_{2m}) relaxation times is shown in a double-logarithmic plot. The results for all samples are arranged on straight lines, approximately parallel to one another according to [12]. The slope of a simple Newtonian fluid is theoretically given by - 1, which is in very good approximation fulfilled by AkomedR and AkomedR plus lecithin both in the $T_{2\text{-}\eta}$ and $T_{1\text{-}\eta}$ (not shown) diagrams. The slopes of the other samples, which are all, apart from pure lecithin, real suspensions, differ from -1, thus indicating a more complex structure and flow behaviour. Lecithin shows the greatest deviations from Newtonian behaviour, thus revealing (with the help of the microscopic relaxation times) its complex structure.





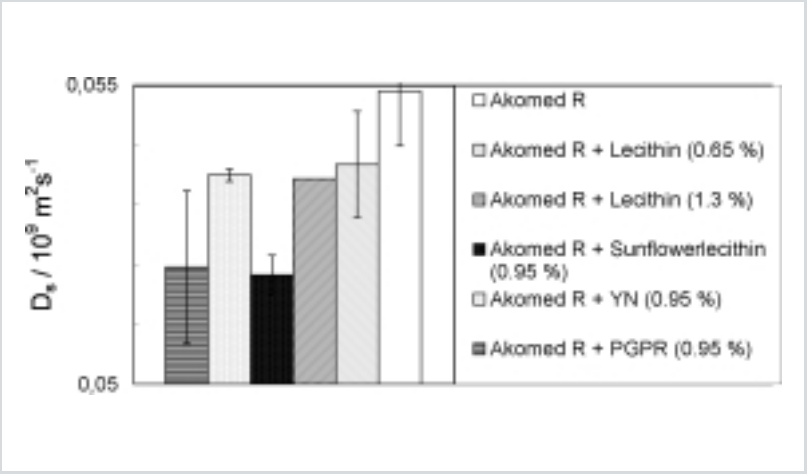


Fig. 11 (above): Correlation of the dynamic viscosities (η_0, η_∞) and the corresponding T_2 (Table 2). Fig. 12: (a – middle) D_S (Table 2). Δ = 7.503585 ms, δ = 0.5 ms, τ = 7.50295 ms, g = 1.96 Tesla/m. (b – below) D_S of AkomedR plus emulsifiers (40°C). Δ = 35 ms, δ = 2 ms, τ=49.9940 ms, g = 1.09025 Tesla/m.

The rheological and NMR experiments, nevertheless, correlate well with one another, providing an unambiguous relation between the relaxation times and viscosities. As a consequence, based on these correlations characteristic viscosities of model chocolate systems can be determined by T_1 and T_2 measurements (after calibration tests considering a sufficient range of the temperature, solid concentration and composition of the ingredients). T_2 measurements with measuring times of approximately 1 min are sufficiently fast compared to characteristic times of structural changes and the residence times of the chocolate masses in relevant process units. A sufficiently fast measuring method is, on one hand, appropriate and necessary for fundamental research, since single reaction steps can be detected and quantified. Thus, the required knowledge concerning the microstructure and microprocesses during chocolate production can be detected and observed in order to develop physically/chemically established, phenomenological constitutive laws for industrial applications. On the other hand, a process method would allow one to characterise initial and intermediate materials, to analyse structural changes or possible reactions and determine relevant reaction-kinetic parameters required for the design of the corresponding process units.

At present many laboratory methods with various measuring quantities, like rheometry and particle-size analysis, are applied for quality control in food technology. Due to time-consuming preparations and comparably long measuring times no process control can be realised. However, materials could be pumped through the NMR-spectrometer, for example through a split stream in a bypass. Thus, time-consuming laboratory methods could be partially substituted by process methods. The advantages are (a) a fast measuring method, (b) small sample quantities, (c) relatively low initial costs for Low Resolution NMR spectrometers, (d) prevention of phase-separation by the use of stirrers, and (e) the non-destructive and non-invasive character of NMR [9].

5.2.3 DIFFUSION EXPERIMENTS

The structural influence of ingredients (Table 2) and the temperature on D_S and, thus, the mobility of the fat phase was studied by self-diffusion experiments. According to the Einstein-Stokes equation, D_S is proportional to the reciprocal of the viscosity ($D_S \sim 1/\eta$). Diffusion processes play an important role in chocolate masses with respect to (i) migration of lipid components, moisture or flavour substances, (ii) fat- and sugar-crystallisation and, (iii) fat bloom combined with fat- and sugar-crystallisation.

D_S of the samples (Table 2) are shown in Fig. 12a. The obtained D_S are about one hundred times smaller than that of water at the same temperature. That is one of the reasons for the comparably high standard deviations. D_S increases for all samples with the temperature (20 and 40°C), for AkomedR and ASBMCL by a factor of approx. 2 and 3, respectively. D_S of pure AkomedR is 30 % (20°C) and 50 % (40°C) higher than that of AkomedR plus lecithin revealing the great impact of lecithin on D_S and hence the structure of AkomedR. In the same way, the addition of solid particles to AkomedR reduces D_S compared to AkomedR. There are, however, suspensions with D_S equal or higher than for AkomedR plus lecithin. This indicates that AkomedR molecules in these suspensions (averaged over the whole sample) have weaker interactions with lecithin and the solid phases than the AkomedR molecules in AkomedR plus lecithin.

D_S of ASA is smaller than that of ASB due to the smaller mean particle-size and hence the higher specific solid surface interacting with the AkomedR molecules. The addition of lecithin causes for ASAL an increase of D_S at 20°C and a decrease of D_S at 40°C compared to ASA. The corresponding interactions of AkomedR molecules with their surroundings might be strongly temperature-dependent. For ASB the addition of lecithin (ASBL) does not have any significant influence on the corresponding D_S. This is possibly due to the smaller specific surface compared to sample ASA and the same concentration of lecithin (higher surface-density). In order to quantify the influence of the type and concentration of an emulsifier on the structure of AkomedR-systems, AkomedR plus various emulsifiers as simplest mixtures were studied by self-diffusion experiments (Fig. 12b). It is obvious that D_S of the mixture can be controlled both by the choice of the emulsifier and the concentration (here only tested for lecithin) of the chosen emulsifier. This provides the possibility to reduce D_S of fat fractions in chocolate masses and to adapt the self-diffu-

sion of fat components to the required shelf-life, limited for example by fat bloom.

6 DISCUSSION AND CONCLUSIONS

The aim of these investigations was to study the structure and flow behaviour of suspensions which were generated in order to simulate the complex structure and rheology of chocolate masses by similar, but simpler formulations. The measuring methods are NMR, rheometry and light microscopy.

T_1 and T_2 experiments were applied to chocolate model systems in order to determine the mean relaxation times T_{1m} and T_{2m} (Fig. 10), the fractions $p_{2,i}$ (not shown) and the corresponding relaxation times (not shown) for the T_1 and T_2 relaxation. The addition of solids affects the T_1 relaxation time less than the T_2 relaxation time. This means that T_2 is, as expected, more sensitive in detecting several phases in suspensions than T_1. The dependence of the structure on the formulation, particlesize distribution and temperature can be quantified. The influence of lecithin, however, is only observable by a little shift of T_{2m}, compared to the corresponding systems without lecithin. It is surprising, that the obtained fractions and relaxation times of the present phases differ only marginally both with regard to the T_2 and T_1 relaxation in spite of the macroscopically completely different appearance (Fig. 7).

The flow behaviour was partly studied with conventional Couette rheometry (cup and bob) (Fig. 4 - 6) and partly with capillary rheometry (Fig. 9) for the high-viscous systems (ASA). By means of the capillary rheometer it is possible to quantify the effect of lecithin on the viscosity function, comparing ASA and ASAL with one another. The discrepancy between the results of the two measuring methods is not surprising regarding the complex composition of these solid-fluid systems. Capillary experiments offer the extension of the shear rates to higher values (about two orders of magnitude). Rotational rheometers, however, enable access to smaller shear rates, which are more than four orders below the available regime of the used capillary rheometer. To summarise the findings, the two types of shear rheometry have to be considered as complementary methods. Dependent on the process and material in question, capillary or rotational techniques have to be preferred.

The correlation of T_1 and T_2 (Fig. 6) with characteristic viscosities like η_0 and η_∞ provides the possibility to determine the characteristic viscosities by means of NMR. In comparison to rheometry, T_2 measurements, especially, have the following positive features: (i) time-saving. (ii) contact-free, non-invasive and non-destructive: Processes can be studied completely by NMR using one single sample, thus reducing systematic measuring errors (compositional or experimental variations). (iii) none or minor preparation required. (iv) real online measuring method (process rheometry) and applicable as process control.

In order to correlate T_2 relaxation times and characteristic viscosities previous calibration-tests are necessary. Thus, a partial substitution of conventional laboratory rheometry, which is not appropriate for online measurements, is possible. If the knowledge of the viscosity is not required for other purposes, the NMR data can directly be used for process control. Therefore, an independent determination of the viscosity becomes unnecessary.

Appropriate emulsifiers strongly modify the structure and flow-behaviour of chocolate masses (Fig. 7). Sugar-agglomerates forming a string-structure in AkomedR-sugar mixtures without lecithin (ASB) could be observed by light microscopy (Fig. 8a). Addition of lecithin destroys these agglomerates (Fig. 8b), which causes a decreased D_S, presumably due to the newly evolved solid-surfaces (Fig. 12a). By addition of solids to AkomedR D_S is also smaller than that of pure AkomedR. Addition of lecithin reduces D_S even in pure AkomedR, obviously caused by lecithin molecules in the AkomedR phase forming micellar structures (Fig. 12b). The effect of emulsifiers on the structure of AkomedR depends on the type and concentration of emulsifier applied. Self-diffusion measurements show that emulsifiers do not only influence interactions between ingredients, but also the order of the fluid phase.

It is plausible to assume that the decrease of D_S and the thus reduced migration of AkomedR, induced by emulsifiers, reduces the risk of fat bloom in confectionery products. Diffusion-measurements provide the possibility to determine the optimal emulsifier and concentration in order to reduce the self-diffusion of critical fat components. As experiments used to study fat

bloom usually last up to months, a comparably fast analysis method like the self-diffusion experiments would be helpful in order to determine reaction kinetic parameters, predict the shelf-life of a product and optimise process and storage conditions and formulation.

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