Experimental Influences on the Casson-Viscosity resp. the Casson Yield Point at Chocolate Tests

After introduction of the OICCC standard at the latest rheological tests are a must in the quality assurance of the chocolate industry. They include measurements at different shear rates up to 60 s^{-1} to be performed after a defined pre-treatment of the chocolate. With the computerized rheometers available today the measuring conditions and procedures can be preset so that most of them can be worked off automatically on the push of a button. This will reduce the time effort for routine tests drastically and the gained work capacity can be used otherwise. However, even when working accurately and, on the first glance, always the same pre-treatment of the samples the results can differ considerably especially in comparison with tests performed by someone else and with different instruments. Some of these measurement-related aspects should be introduced and explained. However, the dependence of the flow properties of chocolate on their composition will not be discussed here (see [1],[2]).

HISTORY

From the rheological point of view chocolate is not an easy fluid: it is a suspension of cocoa, sugar and solid milk particles in a continuous fat phase. The mix of the substances and their interactions are strongly dependent of the production and pre-treatment. The yield point of chocolate e.g. increases with longer tempering time since the cocoa butter is already partly crystallizing (i.e. physical networks are forming which have to be broken off before a possible shearing). In order to obtain comparable results special attention has to be paid to the correct reproducibility of the pre-treatment of the sample (there are tolerances even within the OICCC standard which can have their effects on the results, e.g. the cool-down/tempering times when filling the chocolate into the rheometer). The differences occurring at thixotropic chocolate

are especially dramatic: Here, the viscosity depends on the stirring time (shearing time). However, allowing sufficient time for pre-shearing can eliminate errors (the necessary time can be determined by test with a constant shear rate). Fig. 1 shows two successively recorded flow curves of a sample of a nougat creme available on the market (measuring time 3 min each) which also had a different history. A slight decrease of the viscosity can be detected which can be the result of the small thixotropy but also of sedimentation or homogenizing effects by shearing.

TEMPERATURE

The flow behavior of a substance is strongly influenced by the temperature due to a change of its inter- and intramolecular interactions. This dependence is very distinct especially at high-viscous substances (5-10% per 1°K are nothing unusual). The viscosity decreases at increasing temperatures (see Fig. 2). The "Casson yield point" can differ according to the composition of the chocolate (at milk chocolate it is usually increasing with temperature, at dark chocolate with lecithin additions it can stay constant or even decrease slightly to increase again at even higher temperatures). As a consequence from this dependence it is important to hold the temperature constant (the OICCC proposes ± 0.1°C). The absolute temperature should be controlled with a calibrated thermometer.
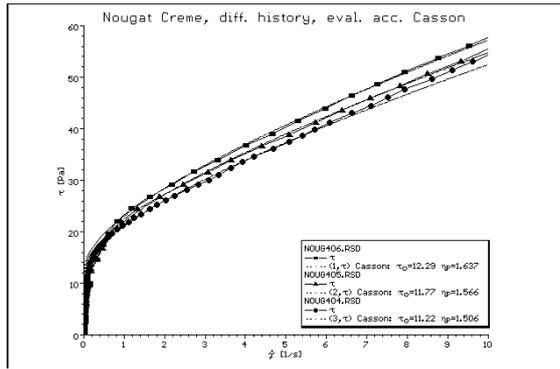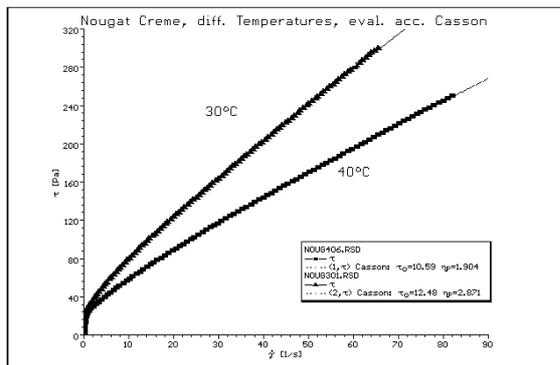
Fig. 1

Fig. 2

MEASURING TIME

Today, the automated rheometers allow the recording of complete flow curves instead of only a few points at different shear rates. Here, the measuring time for such a ramp can be selected as desired. When presetting very short measuring times the measured viscosity is sometimes (apparently) a little lower. The reason is the relation inertia of the sensor system to viscosity of the substance: at a preset shear rate the system needs a certain time to reach an equilibrium. Is this time too short the reaction is somewhat "delayed", i.e. the measured shear stress is based on a lower shear rate than preset by the viscometer. Since the viscosity is calculated from the measured shear stress divided by the actual shear rate the resulting value is lower than the real one. Fig. 3 shows two flow curves recorded after a pre-shearing of 3 min. with different ramp times (120 s resp. 500 s) preset. Although the resulting errors are not very large this effect should be taken into consideration when

defining measuring regulations by allowing sufficient time settings (at least 3 min./ramp, according to the shear rate range).

EVALUATION

The Casson equation which is frequently used for the evaluation of chocolate tests is not undisputed among experts. Nevertheless, the results often correspond with the practical experiences. It may become difficult if comparisons have to be performed between different production plants. Fig. 4 shows the influence of the selected regression range on the result: Evaluating the complete shear rate range (regression 1) will lead to a considerably higher Casson-viscosity and a lower Casson yield point than the evaluation of a slightly smaller range from $0.2\ s^{-1}$ to the max. shear rate (regression 2).
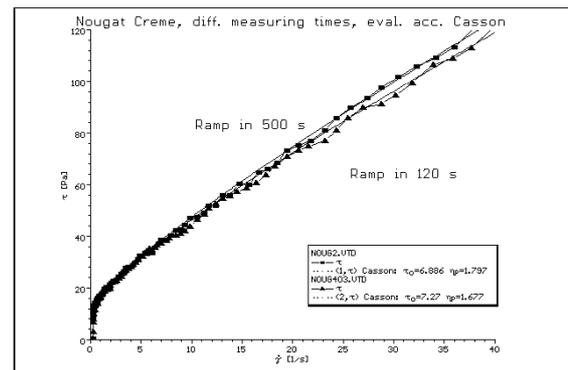

Fig. 3

The results show that the Casson equation is not suitable for the determination of the flow properties in the range of small shear rates (see also [3]). This is the reason why for regression results always the ranges have to be indicated from which they were gained. he differences become even more significant if the Casson equation is not used for evaluation. Leaving the mere production or quality assurance and entering research and development criteria it is vital to investigate the flow behavior of the chocolates especially at very low shear rates also in the transition range between solid and liquid behavior. Very sensitive shear stress controlled instruments like the HAAKE rheometers RheoStress® allow the presetting of

very small forces and measuring the resulting deformation of the substance resp. the shear rate. Below the yield point the substance will react like a solid (elasticity), i.e. the applied force will lead to a deformation of the sample but not to a steady state flow. Above the yield point the structures of the sample are destroyed and the substance will start to flow. Fig. 5 shows the measuring data from a flow curve recorded with a stress controlled instrument where the deformation is plotted as function of the shear stress. The yield point will be found at abt. 20 Pa (the Casson yield point was determined with abt. 12.5 Pa). Above this value the range of the steady state flow begins. At lower shear stresses, however, a slope of almost 1 can be recognized in the double logarithmic diagram which is typical for a solid (the deformation is proportional to the applied force, the Hook spring law is valid). The transition can be seen at a shear rate of abt. 0.1 s^{-1} which is indicated by Tscheuschner as typical for chocolate. The complete flow curves are usually not evaluated with the Casson equation in such cases but with formulas especially designed for such applications ([4],[5]).

INSTRUMENT

One has to be especially careful when comparing the results obtained with different instruments. Fig. 6 shows measuring curves once recorded with the deformation controlled Viscotester VT550 with cylindrical rotor MV1 and once with the stress controlled rheometer RheoStress ® with plate-plate geometry. This diagram can be considered as summary of the preceding paragraphs. The comparability of such data results from the error ranges of both measuring instruments and therefore is higher than the reproducibility of measurements performed with one instrument (which is abt. 1 to 2% when using rotational viscometers with DIN measuring units). Besides this, all subjects already mentioned have to be watched closely: Different measuring geometries can cause different histories (different sample preparation – caused by the different geometries in the example), the temperature

can differ even when the same temperature is displayed on the instruments (in this example the real temperature difference was abt. 0.4°C) and should be checked at least once with a calibrated thermometer and corrected if necessary; the operating softwares available today usually allow such an "offset". Also of importance is the same measuring time (ensured in this example) and the identical evaluation of the curves (also ensured in this example).
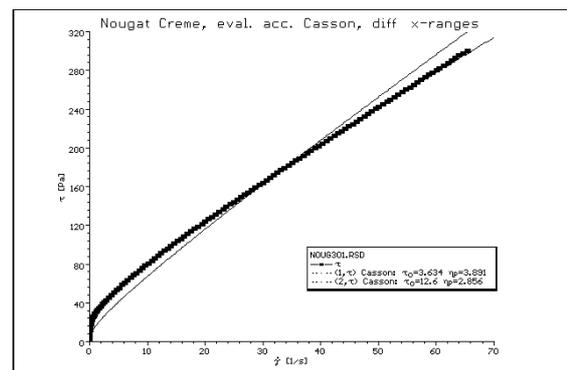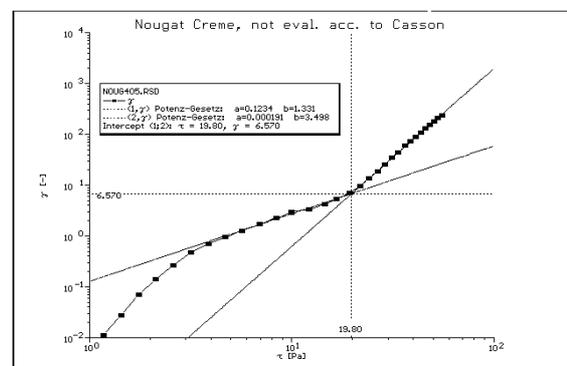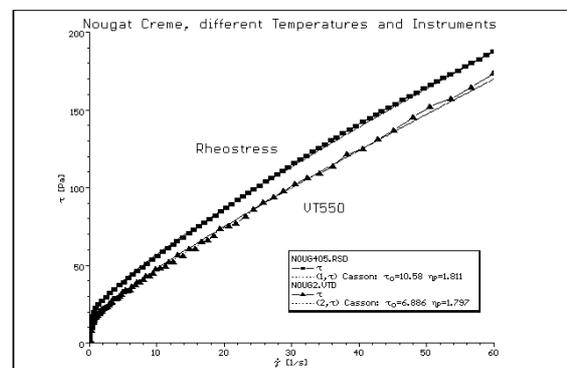

Fig. 4

Fig. 5

Fig. 6

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