

What makes for smooth, creamy chocolate?

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Chocolatiers adjust properties of chocolate's ingredients to confect a treat that feels as good as it tastes.

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Many people, when describing what happens after they bite off a piece of chocolate, would say that the chocolate melts in their mouth, then they swirl it around with their tongue to best enjoy the sweet, creamy sensation. Food scientists might describe the process differently. They'd observe that the tongue induces a shear flow within the melted chocolate layer between tongue and palate. According to Newton's law, the shear stress τ applied by tongue is the product of chocolate's bulk shear viscosity η and the shear rate, which itself is approximately the ratio of the tongue's velocity to the thickness of the melted chocolate layer. Chocolate rheology, however, is non-Newtonian; the viscosity depends on shear rate, time, and temperature. What typical consumers consider "smooth and creamy" corresponds to a viscosity of 1.5–3.5 Pa·s (pascal-seconds), at a representative shear rate of 20/s and body temperature 37 °C.

The challenge to the chocolatier and food scientist is to understand how the microstructure of melted chocolate mirrors chocolate rheology. Melted chocolate contains sugar, cocoa, and milk powder particles dispersed within a Newtonian fat melt, typically cocoa butter. Those dispersed particles assume a number of forms: They might look like cubes, platelets, fibers, or coils. Added surfactants cover the interfaces between the suspended particles and the continuous fluid phase. When the melted chocolate is sheared, a number of mechanisms all operating at the same time can induce structure in the suspension. The figure illustrates those mechanisms: deformation, orientation, deagglomeration, and agglomeration. The first three mechanisms, loosely speaking, lead to a more uniformly structured suspension and so are called structuring effects.

The structuring effects are triggered when the shear stress exceeds a characteristic value τ_0 , called the yield value. Typically, τ_0 is in the range of 5–12 Pa. Once the yield value is surpassed, melted chocolate ceases to behave like a solid. With increasing shear stress, the structuring effects get further developed, and as a consequence, the viscosity decreases. At fixed shear stress, developing structure would also lead to a decrease in viscosity with time, until a shear-stress-specific equilibrium structure is reached. At a second characteristic shear stress τ_1 , the viscosity reaches its minimum value $\eta_{\min}$, which is typically about 0.5–2.0 Pa·s; the structuring is said to be "completed." As the shear stress increases beyond τ_1 , the viscosity remains constant until a new characteristic stress τ_2 is reached. Once τ_2 is exceeded, shear-induced structure collapse or "superstructuring" may

occur; one type of superstructure consists of agglomerated flocculated particles. As a consequence of those structural changes, the viscosity increases with shear stress or shear rate and with time. As yet another stress τ_3 is surpassed, any superstructure degrades, and viscosity once again falls with increased stress, shear rate, and time. If structure collapse or superstructuring doesn't occur, the high-shear viscosity keeps the value $\eta_{\min}$.

Surfactants such as lecithin affect interparticle interactions. Thus they help determine the characteristic stresses τ_0 and τ_1 .

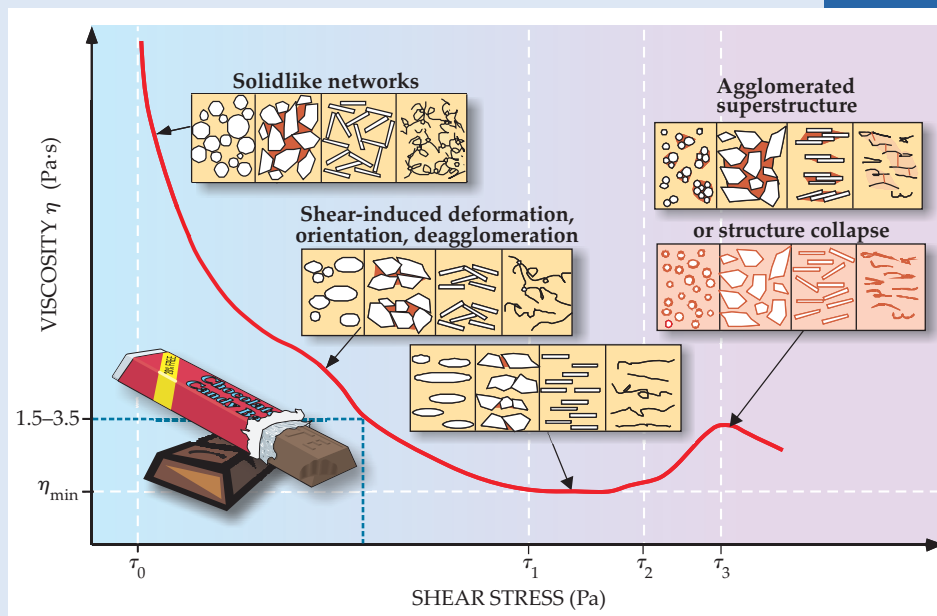
The fluid substrate

The structure of the particles suspended in chocolate, considered in and of itself, affects the rheology of chocolate. But those particles are suspended in a fluid with which they interact. The idea of fluid immobilization (FIM) allows one to describe the complex relationship between rheology and microstructure in chocolate. Specifically, FIM quantitatively describes how the suspended solids' concentration, size, and shape affect the shear viscosity of chocolate. In essence, FIM postulates that changes in the solids' properties lead to concomitant changes both in the quantity of fluid immobilized and in how the fluid phase is bound to or otherwise immobilized by the suspended particles.

Fluid immobilization occurs via three main mechanisms. In volume FIM (V-FIM), fluid is trapped in the pores and voids of the suspended particles or particle agglomerates. Surface FIM (S-FIM) arises when fluid is bound to particle or agglomerate surfaces. The third mechanism, hydrodynamic FIM (H-FIM), is associated with fluid binding that arises from the position and motion of the particles in the chocolate flow. H-FIM is less important for concentrated suspensions like chocolate than for dilute suspensions.

A large fraction of the solid particles in chocolate—sugar, cocoa, and milk solids—form agglomerates during the manufacturing process, in particular during the refining and mixing operations. During conching, which is a mechanical deagglomeration treatment, and other flow processes that occur after refining, those agglomerates usually become somewhat deagglomerated. As a result, the immobilized fluid fraction changes. How much it changes is a function of mechanical stress and time.

When a particle agglomerate breaks down, the fluid that had been immobilized in the agglomerate's pores or voids is released, which leads to a lower viscosity. Such deagglom-



Particle microstructure has a significant impact on the rheology of chocolate. Increasing the order among the particles suspended in chocolate leads to decreased viscosity; details of how viscosity varies with shear stress (red curve) and definitions of the characteristic stresses are given in the text. The dashed blue lines correspond to a representative shear rate in the mouth of 20/s. Particle-fluid interactions also affect the rheology of chocolate. For the particle structures with yellow backgrounds, fluid is immobilized principally by being trapped in pores or voids; for the other structures, surface binding is the main cause of fluid immobilization.

eration, however, also generates new interfaces at which fluid can be immobilized, which contributes to higher viscosity. If the agglomerates have a large inner-pore or void volume, V-FIM will dominate and deagglomeration will make the viscosity decrease. Conversely, when dense agglomerates or unagglomerated primary particles are refined, S-FIM at the newly generated particle interfaces dominates and viscosity increases. Which effect will be most important in practice depends on the details of the manufacturing process.

The shapes of individual particles and the morphology of particle agglomerates also play a role in fluid immobilization and so affect viscosity. Particles can have a number of shapes, ranging from spherical to fiberlike. Because particles in dilute suspensions can move more freely, orientation and rotation effects allow the H-FIM mechanism to be more strongly developed. In concentrated chocolate suspensions, shear flow can lead to an orientation of non-spherical particles parallel to the shear direction. In the oriented suspension, a particle's rotation is hindered by its neighbors. As a consequence, H-FIM is minimized and, thus, so is viscosity. Systematic investigations with spin milk powder (fiberlike milk-powder particles) confirmed the reduction of viscosity with concentration and observed a viscosity minimum when the fiberlike particles were 10–15% of the total solid content by volume.

The most important particle morphology parameters are porosity and the distribution of inner-pore sizes. Consider different kinds of milk powders. Those with fully incorporated milk fat and high inner porosity would be expected to show the greatest V-FIM effects. And studies have indeed shown that those samples had the highest milk-chocolate viscosities. Other samples with the same milk-fat content were formed by a process in which the fat was sprayed on top of the milk-powder particles. In that case, the viscosity was reduced by more than a factor of five when compared with the maximum-viscosity systems. Moreover, the greater the fraction of particles covered with fat, the greater the reduction.

Happy customers

With the fluid immobilization concept, one can derive general rules that relate particle size, shape, and agglomerate morphology to viscosity. To obtain chocolate with low shear

viscosity, one should have large particles, a high solid packing density, a low tendency to agglomerate, and a low continuous fluid phase affinity to the solid-particle surfaces so that S-FIM is minimized.

Suspensions with many different particle sizes generally form agglomerates with a high packing density. However, the small particles may also form their own agglomerates, which are not necessarily very densely packed; those tend to increase viscosity due to V-FIM. Large particles or agglomerates may also be associated with an undesirable rough texture in the chocolate. Indeed, the finest chocolate manufacturers use intensive refining techniques, including conching, to ensure that particle structures are no more than about 25 microns in diameter.

The formation of agglomerates and their packing density strongly depend on the intensity of attractive particle interactions. The particles' own properties are important, of course, but surfactants in the continuous fluid phase also have an important influence. Long-chain surfactants can strongly inhibit agglomeration. If, nonetheless, agglomeration still takes place, the surfactants' chains may encourage the formation of looser agglomerates with an increased volume-immobilized fluid fraction. That effect would lead to increased viscosity.

Consumers like smooth, fast-melting, low-viscosity chocolate. To keep them happy, chocolate makers must take into account not only a complex array of particle properties but also how particles interact, both with like entities and with specific other materials—including, of course, the palate and tongue.

Further Reading

- E. J. Windhab, in *Proc. Third International Symposium on Food Rheology and Structure*, I. Marti, P. Fischer, E. J. Windhab, eds., Kerschensteiner Verlag, Lappersdorf, Germany (2003), p. 489.
- A. Attaie, B. Breitschuh, P. Braun, E. J. Windhab, *Int. J. Food Sci. Technol.* **38**, 325 (2003).
- E. J. Windhab, *Appl. Rheol.* **3**, 134 (2000).
- E. J. Windhab, D. Hugelshofer, P. Braun, in *Proc. Thirteenth International Congress on Rheology*, D. M. Binding et al., eds., British Society of Rheology, Glasgow, UK (2000), p. 416. ■

The online version of this Quick Study provides access to additional tutorial material on desirable aspects of chocolate.