Electrorheology leads to healthier and tastier chocolate

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Chocolate is one of the most popular food types and flavors in the world. Unfortunately, at present, chocolate products contain too much fat, leading to obesity. Although this issue was called into attention decades ago, no actual solution was found. To bypass this critical outstanding problem, two manufacturers introduced some low-calorie fats to substitute for cocoa butter. Somehow, their products are not allowed in most countries. Here we show that this issue is deeply related to the basic science of soft matter, especially to the viscosity of liquid suspension and maximally random jammed (MRJ) density. When the concentration of cocoa solid is high, close to the MRJ density, removing a small amount of fat will jam the chocolate flow. Applying unconventional electrorheology to liquid chocolate with applied field in the flow direction, we aggregate the cocoa particles into prolate spheroids in micrometers. This microstructure change breaks the rotational symmetry, reduces liquid chocolate's viscosity along the flow direction, and increases its MRJ density significantly. Hence the fat level in chocolate can be effectively reduced. We are expecting a new class of healthier and tastier chocolate soon.

electrorheology | viscosity | liquid chocolate | maximum random jammed density | fat in chocolate

Chocolate is one of the most popular food types and flavors in the world. Cocoa solids are one of the richest sources of antioxidant flavonoids. They also contain alkaloids such as theobromine, phenethylamine, and caffeine, having physiological effects on the body and linked to serotonin levels in the brain. Some research has found that chocolate, eaten in moderation, can lower blood pressure. Cocoa or dark chocolate may positively affect the circulatory system (1–3). Unfortunately, at present, chocolate products contain too much fat, mainly cocoa butter, which leads to obesity. For example, a typical molding chocolate has various fats up to 40% in total. Among them, 25–30% are cocoa butter and the rest are other oils and fats. Chocolate for covering ice cream has 50–60% fat. Especially because children are the leading chocolate consumers, reducing the fat level in chocolate products to make them healthier is important and urgent. Although this issue was called into attention and elaborated in articles and books decades ago and led to some patent application (3, 4), unfortunately no actual solution was found. To bypass this critical outstanding problem, two manufacturers, Proctor & Gamble and Nabisco, introduced some low-calorie fat to substitute for cocoa butter in their chocolate products. Somehow, their fats are not allowed in most countries, such as Canada and western Europe. The products from Proctor & Gamble and Nabisco are denied as chocolate in these countries.

Why is reducing fat in chocolate so difficult? What is the underlying science? This issue, in fact, is found to be deeply related to the basic science of liquid suspensions. Most people think of chocolate as a solid because this is how they buy and eat it. To the chocolate maker, however, chocolate is a liquid for the whole process of production and only solidified just before it is ready to be packed and sent to the warehouse or store.

Liquid chocolate is a suspension of solid particles consisting of cocoa, sugar, milk solids, etc., in a base liquid of melted fat and oil, mainly cocoa butter. For all liquid suspensions, there are two important quantities: random close-packing density, or a more recent concept, maximally random jammed (MRJ) density, ϕ_x (5); and particle's intrinsic viscosity, ν, which depends on the particle shape. If the suspension has monodisperse spherical particles, for example, ϕ_x is about 64% and $\nu = 2.5$.

Einstein first studied the viscosity of dilute liquid suspension of uniform spheres and found $\nu = 2.5$ for spherical particles (6–8). The following formula is generalized from Einstein's work to liquid suspensions with different particle shape and all volume fractions (9):

$$\eta = \eta_0 (1 - \phi/\phi_x)^{-\nu\phi_x}, \quad [1]$$

where η_0 is the viscosity of base liquid; ϕ and ν are the particle's volume fraction and intrinsic viscosity, respectively. The suspension is completely jammed for infinite viscosity if $\phi \geq \phi_x$. Even if $\phi < \phi_x$, the viscosity increases dramatically as ϕ approaches ϕ_x.

Under microscope, the cocoa solids are confirmed to be spherical (Fig. 1*A*). The size is around 2 μm. Therefore, if a liquid chocolate consists of cocoa solids and cocoa butter only, then the fat level cannot be lower than $1 - \phi_x = 36\%$. Otherwise, the liquid chocolate is jammed in the pipeline and the production becomes impossible. If ϕ is smaller than, but close to, ϕ_x, as shown in Fig. 2, removal of a small amount of fat from liquid chocolate would sharply increase the viscosity of liquid chocolate as ϕ gets closer to ϕ_x. Without an unconventional method to reduce the viscosity under such a condition, the liquid chocolate becomes too thick to be handled for production. Therefore, the key to reduce the fat level in chocolate is that we need some new method, which should enable us to accomplish the following two tasks simultaneously: (*i*) Reducing the viscosity of liquid chocolate effectively at high volume fraction of solid particles for chocolate production and proper texture; (*ii*) Increasing ϕ_x, the MRJ density.

Significance

Chocolate is one of the most popular food types and flavors in the world. Unfortunately, at present, chocolate products contain too much fat, leading to obesity. Although this issue was called into attention decades ago, no actual solution was found. To bypass this critical outstanding problem, two manufacturers introduced some low-calorie fats to substitute for cocoa butter. Somehow, their fats are forbidden in most countries. Here we show that, by applying an electric field to liquid chocolate in the flow direction, we aggregate the suspended particles into prolate spheroids. This microstructure change reduces the viscosity in the flow direction and enables us to reduce the fat level by 10–20%. A new class of healthier and tastier chocolate should come soon.

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Conflict of interest statement: Temple University holds patents on a methodology to alter the viscosity of liquid chocolate through the application of an electric field. R.T. and H.T. are the inventor of the patents. The authors received funding from Mars Chocolate, Inc.

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APPLIED PHYSICAL SCIENCES

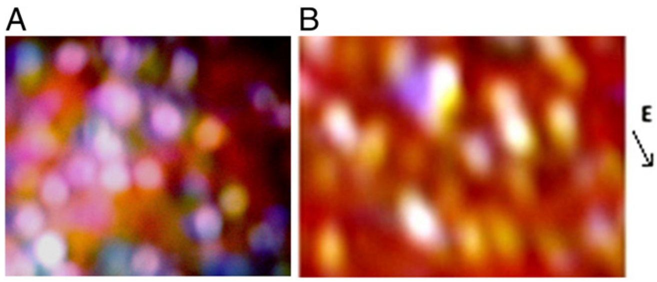

Fig. 1. Under microscope, (*A*) the original cocoa solids in liquid chocolate are spherical around 2 μm; (*B*) the electric field aggregates these particles into short chains, which are similar to prolate spheroids.

The failure of previous efforts in reducing the fat level in chocolate products clearly indicates that conventional methods cannot accomplish these two tasks; new technology based on new soft matter science is critically needed. In this paper, we report that unconventional electrorheology (ER) provides a solution for this critical outstanding issue (10, 11). Application of an electric field in the flow direction of liquid chocolate can aggregate the solid particles into prolate spheroids along the flow direction (Fig. 1*B*). This microstructure change breaks the rotational symmetry, leading to increased ϕ_x and the viscosity significantly reduced along the flow direction. Therefore, we are looking forward to a new class of healthier and tastier chocolate products soon.

We should also mention that our ER application is significantly different from traditional ER fluids, where the applied electric field is perpendicular to the flow direction, leading to increase the effective viscosity or even solidify the ER fluids (10–12). Here we apply the electric field in the flow direction and control the size of aggregated particles. Then the viscosity along the flow direction is significantly reduced. The basic science developed here is general and useful for many other liquid suspensions when they need to reduce viscosities, etc.

This approach is illustrated in Fig. 3. Liquid chocolate flows from left to right along a production pipe. Initially at left, the viscosity is high. Because the electric permittivity for the cocoa solid $\varepsilon_p \approx 2.5\varepsilon_0$ is higher than the electric permittivity of melted cocoa butter $\varepsilon_f \approx 1.8\varepsilon_0$, the particles are polarized when they are in the electric field (12, 13),

$$\vec{p} = 4\pi\varepsilon_f \vec{E}_{loc} a^3 (\varepsilon_p - \varepsilon_f)/(\varepsilon_p + 2\varepsilon_f), \quad [2]$$

where ε_0 is the vacuum permittivity and $\vec{E}_{loc}$ is the local electric field acting on the particles, which is stronger than the applied electric field. The interaction between two induced electric dipoles is given by

$$U = p^2(1 - 3\cos^2\theta)/(4\pi\varepsilon_f r^3). \quad [3]$$

Here r is the distance between the two particle centers and θ is the angle between the field and the line joining the two dipoles. When the two particles align in the field direction and touch each other, $\theta = 0$ and $r = 2a$, U has the minimum, $U_{\min} = -p^2/(16\pi\varepsilon_f a^3)$. Therefore, the induced dipolar interaction forces the particles to aggregate into short chains. The observations under microscope (Fig. 1*B*) have confirmed the fact that under the electric field, the cocoa solid particles in liquid chocolate aggregate into short chains along the field direction. The aggregates are similar to prolate spheroids with their long axis in the flow direction. This microstructure change immediately brings two significant outcomes to the macroscopic properties of liquid chocolate.

First, the MRJ density, ϕ_x, strongly depends on the particle shape. For spheroids, $\phi_x \geq 0.72$, higher than that (0.64) for spheres (14, 15). Therefore, the minimum amount of base liquid, i.e., melted fat, is down from 36% to 1 − 0.72 = 28%, reduced by 22.2%. In fact, because the ER aggregation also makes the particle size more polydispersed, the polydisparity further increases the MRJ density ϕ_x. The amount of cocoa butter can thus be significantly reduced.

Second, the aggregation of short chains along the field direction breaks the rotational symmetry, making the viscosity of liquid chocolate anisotropic. Along the field direction, the viscosity is significantly reduced. Especially, as the applied electric field is in the flow direction, the reduced viscosity will improve the liquid chocolate flow (16, 17).

Let us denote a prolate spheroid with its rotational z axis along the flow direction as

$$(x^2 + y^2)/b^2 + z^2/a^2 = 1. \quad [4]$$

For such spheroid with $a > b$, the intrinsic viscosity along the z axis $\nu_{\parallel}$ is smaller than the intrinsic viscosity of spheres 2.5, whereas the intrinsic viscosity along the directions perpendicular to the z axis, $\nu_{\perp}$, is higher than 2.5 (18). If $b/a = 1/3$, for example, we have $\nu_{\parallel} = 2.089$, while $\nu_{\perp} = 3.099$.

To estimate the viscosity, let us consider a liquid chocolate consisting of 60% cocoa solid and 40% melted fat as an example. For comparison, in Fig. 2 we plot the original viscosity versus the viscosity of the ER-treated liquid chocolate along the flow direction. Before the ER treatment, the relative viscosity of liquid chocolate is given by

$$\eta/\eta_0 = (1 - 0.6/0.64)^{-2.5*0.64} = 84.45. \quad [5]$$

After the ER treatment, if all particles are aggregated into the prolate spheroids of the same size, the relative viscosity along the flow direction is reduced to

$$\eta_{\parallel}/\eta_0 = (1 - 0.6/0.72)^{-2.089*0.72} = 14.80, \quad [6]$$

which is down 82.47% from the original viscosity. The relative viscosity along the direction perpendicular to the flow is given by

$$\eta_{\perp}/\eta_0 = (1 - 0.6/0.72)^{-3.099*0.72} = 54.48. \quad [7]$$

The higher viscosity in the directions perpendicular to the flow does not provide any resistance to the flow, but helps to suppress vortex formation and turbulence (17).

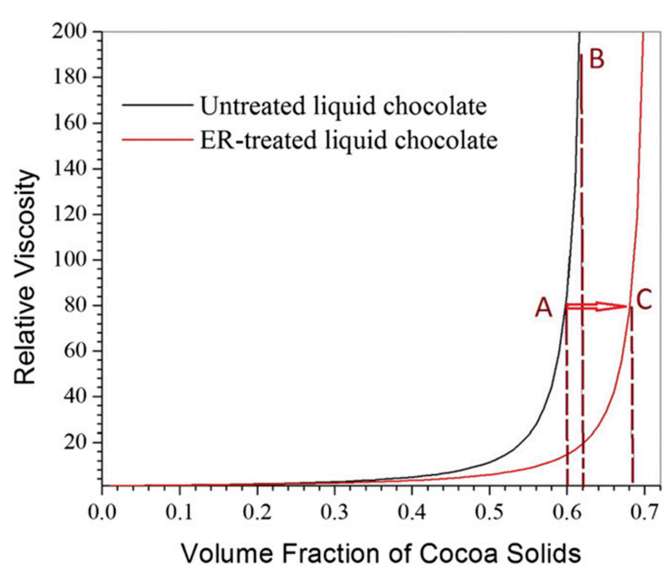

Fig. 2. Viscosity of original liquid chocolate and the viscosity of ER-treated liquid chocolate along the flow direction. Point *A* represents the original state at $\phi = 0.6$. Without the ER treatment, removing a small amount of fat leads to dramatically increased viscosity (point *B*). With the ER treatment, the fat can be reduced by 20% and the viscosity remains the same (point *C*).

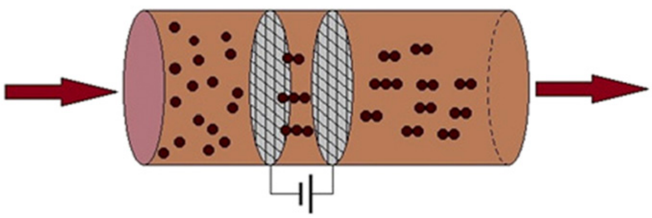

Fig. 3. As the liquid chocolate flow passes a strong local electric field, the solid particles aggregate along the field direction to form streamline aggregates and the viscosity along the flow direction is significantly reduced.

Our approach uses the basic physics of ER, but significantly differs from the traditional ER applications. In conventional ER fluids, the applied electric field is always perpendicular to the flow direction and the aggregated structures should be large to connect the two electrodes; therefore, in conventional ER fluids, application of electric field would dramatically increase the viscosity. Here we apply the electric field in the flow direction and control the size of aggregated particles. Then the viscosity along the flow direction is significantly reduced.

Because $\eta_{\parallel}$ is significantly reduced, we can reduce the fat level inside the liquid chocolate. For example, because $(1-0.682294/0.72)^{-2.089*0.72} = 84.45$, we can increase the particle volume fraction to 68.2% and reduce the total fat from 40% to 31.8% while keeping the viscosity of the treated liquid chocolate the same as the original one. The new chocolate has the fat reduced by 20.5%, which is better than the expectation.

If we just want to reduce the total fat by 10%, from 40% down to 36%, we make the particle volume fraction 64%. The relative viscosity of ER-treated chocolate along the flow direction is then $(1-0.64/0.72)^{-2.089*0.72} = 27.24$, still reduced by 67.7% from the original viscosity, favorable for the chocolate production.

The above theoretical prediction has been verified by our experiments. The key issue is to confirm that application of electric field can effectively reduce the viscosity of liquid chocolate along the flow direction. Then we can decide the amount of fat to be reduced.

Traditionally, measuring chocolate's viscosity uses rotational viscometers. However, rotational viscometers cannot measure anisotropic viscosity properly. Therefore, we invented our own device, which is shown in Fig. 4. The liquid chocolate is inside the top container and maintained at a prespecified temperature. In addition to gravity, we also use pressured nitrogen gas to control the flow velocity of liquid chocolate. As the chocolate flows down, it passes the electrodes, metal meshes, then along a capillary tube to a cup on a microbalance. We can apply a voltage upon the two electrodes to produce an electric field in the flow direction. The microbalance is used to measure the collected chocolate mass as a function of time. Hence we determine the chocolate flow rate, Q. The capillary tube serves as a viscometer, providing the chocolate's viscosity along the flow direction with the following formula:

$$\eta = \frac{\pi\rho^2 g R^4}{8Q}\left(1 + \frac{h}{L} + \frac{\mathrm{P}}{L\rho g} - \frac{v^2}{2gL}\right), \qquad [8]$$

where R is the capillary tube's radius, L is the capillary tube's length, h is the height of chocolate level above the capillary tube, ρ is the liquid chocolate's density, g is the acceleration of earth gravity, and P is the pressure of nitrogen gas. The average flow velocity is given by $v = Q/(\rho\pi R^2)$. For our present tests, L = 15 cm, R = 0.284 cm; the height h = 18 cm at the beginning and slowly decreases as the chocolate flows out. We monitor h during our tests.

Our device is placed inside a Queue Cell Culture Incubator, which is maintained at a prespecified temperature. Mars Chocolate specifies 40 °C for their samples, whereas Blommer Chocolate specifies 43 °C for their samples. After the chocolate sample inside the top container is stabilized at the prespecified temperature, we begin to let the liquid chocolate flow down along the capillary tube to the cup on the microbalance. There is no electric field applied at first. Chocolate manufacturers usually specify a preferred shear rate $\dot{\gamma}$ for the tests. Then, the flow velocity should be $v = R\dot{\gamma}$ and the flow rate is given by $Q = \rho\pi R^2 v = \rho\pi R^3\dot{\gamma}$, where R is the radius of the capillary tube. Therefore, in addition to gravity, we use pressurized nitrogen gas to apply additional pressure to liquid chocolate to reach the prespecified flow rate. The LabVIEW software enables us to record the mass of chocolate collected in the cup as a function of time. As shown in Fig. 5*A*, the flow rate is the slope of the curve. The initial curve is a straight line, indicating that the flow rate is very stable in the absence of electric field. Therefore, after 20–30 g of liquid chocolate flow out, we turn on the electric field at a preselected strength. The applied pressure and other conditions remain the same. After the untreated chocolate inside the capillary tube flows out, we notice that the curve's slope is up significantly, indicating that the chocolate flow rate is up as the result of reduction of viscosity along the flow direction. To search for better viscosity reduction conditions, we also vary the applied electric field strength and repeat the above process.

The typical test results are shown in Fig. 5*A*. This chocolate sample was from Mars Chocolate Inc. and had the density $\rho = 1.35$ g/cm^3. The temperature for tests was 40 °C. In addition to gravity, we applied 3-psi pressure. Without electric field

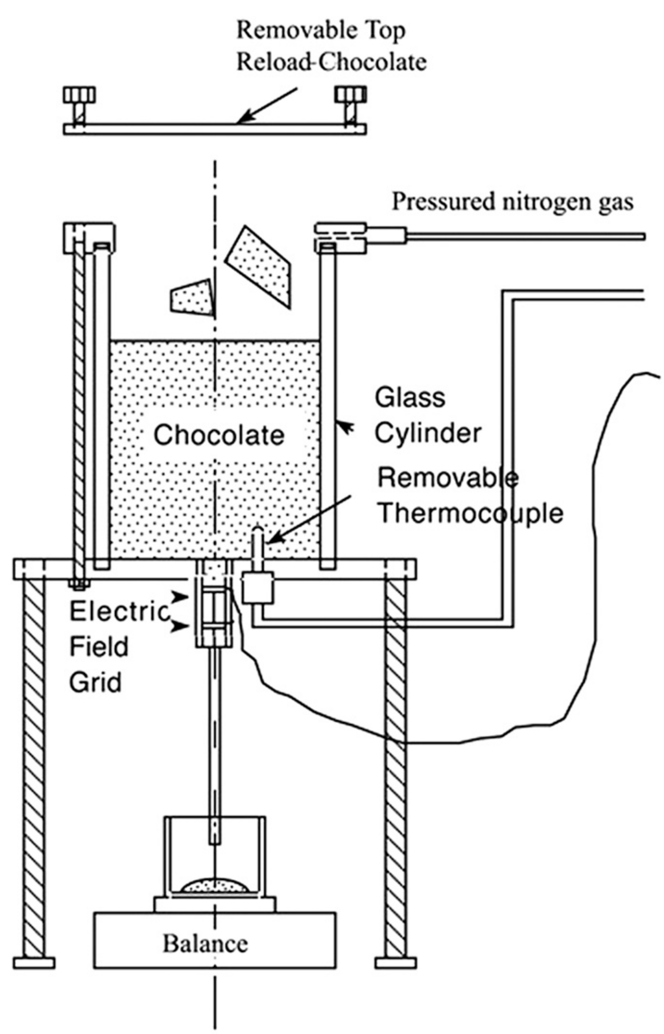

Fig. 4. Sketch of the device.

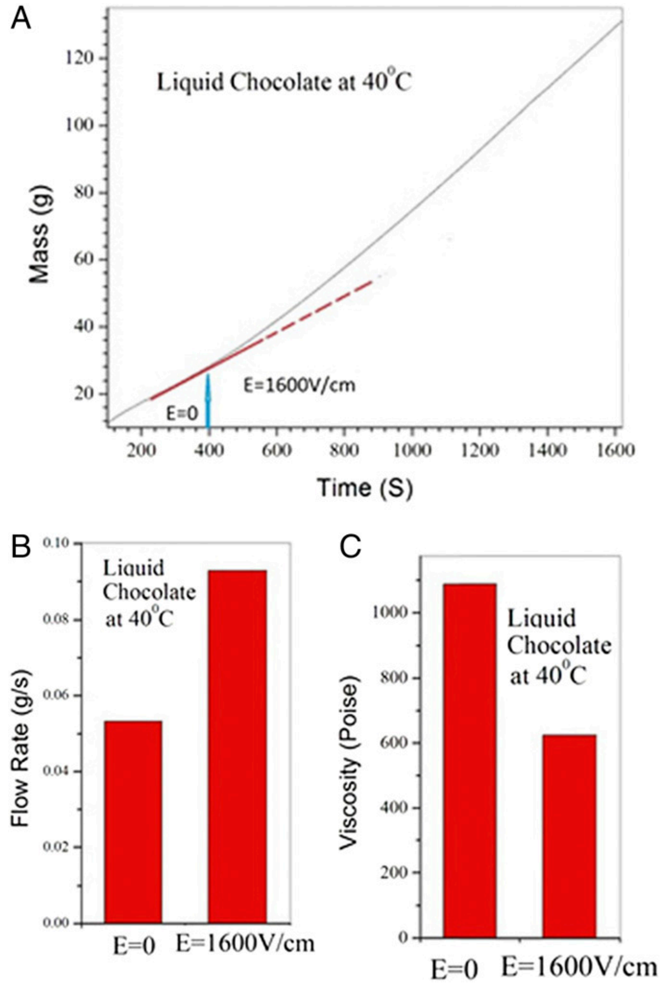

Fig. 5. (*A*) Application of 1,600-V/cm electric field significantly increases the flow rate. (*B*) The flow rate was increased by 74.3%. (*C*) The viscosity was reduced by 43.5%.

applied, the flow rate was 0.05327 g/s and the viscosity was 1,088.59 poise. After an electric field of 1,600 V/cm was applied, the flow rate was increased to 0.09284 g/s, up 74.3%, indicating that the viscosity along the flow direction was reduced to 614.65 poise, down 43.5% (Fig. 5 *B* and *C*). With such viscosity reduction, we can easily reduce the fat level by 10% or more. Note that the electric current during the process was too small to be measured with our electric meter. It was well below 0.1 μA, the sensitivity of our electric meter. This implies that the method is extremely energy-efficient.

Recently, we conducted tests with various chocolate samples from major chocolate manufacturers, such as Mars, Hershey, and Blommer. The results are quite similar to Fig. 5. With application of ER, we can effectively reduce the viscosity of all kinds of chocolate by 40–50%. Therefore, we can easily reduce the fat level by 10% or more for all these samples. It is clear that this method is universal, applicable to all kinds of chocolate.

The above results fully confirm our theoretical analysis. On the other hand, in comparison with the theoretical prediction, it indicates that there is still some room for improvement. This implies that in our ER treatment we have not reached the optimal situation for viscosity reduction; some particles may not be aggregated into short chains. There are two important parameters: the electric field strength and the time for chocolate inside the electric field. The optimal situation can be reached at a good combination of these two parameters.

We note that for liquid chocolate, the relationship between the shear stress and shear rate can be approximated by the Casson model (3). Hence there is a shear-thinning effect, which was used to reduce its viscosity for a short period (4). In our tests, when the electric field is applied, there is no additional shear force or pressure applied. The viscosity reduction by the ER effect also well exceeds the reduction from the shear-thinning effect.

Naturally, there is a question: How long can such reduced viscosity last after the ER treatment? Because the viscosity reduction is the result of aggregated short chains along the flow direction, the viscosity will return to the original value after the aggregated chains are completely dissembled. To answer the above question, we conducted a number of tests. If the liquid chocolate is immediately solidified after the ER treatment, the aggregated short chains remain as long as the chocolate is in the solid state. When the solid chocolate melts, it will show a low viscosity after the short chains are tilted along the flow direction. If the treated chocolate remains in the fluid state after the treatment, we have found that the reduced viscosity keeps for more than 48 h.

The above results are understandable. The aggregated short chains make the suspension a viscoelastic fluid. It is well known that the dissembling of such viscoelastic chains by thermal motion is very slow (17). On the other hand, if we deliberately shake the chocolate violently, the chains will be broken and the viscosity will return to the original value quickly.

The ER-treated chocolate also has wonderful taste. Some people even claim that the ER-treated chocolate has a slightly stronger cocoa solid flavor, better than the original chocolate. We are thus expecting a new class of healthier and tastier chocolate products soon. Moreover, the basic physics presented in this article is general, applicable to many other suspensions when they need to reduce the viscosity, improve the flow, or increase the particle volume fractions. For some fluids, we may also use magnetic field, instead of electric field, to reach the goal.

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