Is Plastic Fat Rheology Governed by the Fractal Nature of the Fat Crystal Network?

Alejandro G. Marangoni* and Dérick Rousseau
Department of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada

ABSTRACT: The rheological properties of interesterified and noninteresterified butterfat–canola oil blends do not seem to be strongly related to either solid fat content (SFC) or crystal polymorphic behavior, but rather to the microstructure of the fat crystal network. The microstructure of the fats was quantified by using fractal geometric relationships between the elastic moduli (G') of the fats and their SFC values using the approach of Shih, W.H., W.Y. Shih, S.I. Kim, J. Liu, and I.A. Aksay [*Phys. Rev. A 42*:4772–4779 (1990)] for weak-link regimes. Chemical interesterification decreased the fractal dimension of the fat crystal network from 2.46 to 2.15. We propose that fat microstructure, as quantified by a fractal dimensionality, could be modified to attain specific rheological properties.
JAOCS 73, 991–994 (1996).

KEY WORDS: Butterfat, fractal dimension, interesterification, plastic fats, rheology, spreadability, texture.

The formation of a fat crystal network is of key importance in the manufacture of plastic fats because it provides firmness or solid-like properties (viscoelasticity) (1). This network can be visualized as being built from aggregates of fat particles (1) rather than straight chains of fat particles (2), and can be thought of as a colloidal aggregate, analogous to a protein gel. Each of the fat particles is, in turn, comprised of several aggregated fat crystals. The quantitative description of such a complex, aggregated "random" system is difficult. Recently, fractal geometry has proven extremely helpful in the characterization of these fractal objects (see Theoretical considerations section).

Work by our group has recently concentrated on improving the rheological properties of butterfat by blending with canola oil and chemical interesterification of these blends (3–5). Our aim was to improve the cold-temperature spreadability of butter. To understand which parameters control the rheology of this plastic fat, a comprehensive study on the melting properties, microstructure, and mechanical characteristics of these blends was undertaken (3–5).

During these studies, we noticed some interesting trends. First, chemical interesterification of butterfat or butterfat–canola oil blends did not substantially decrease the solid fat content (SFC) of butterfat or the blends—the maximum decrease being ~5% (3). Second, melting characteristics, as determined by differential scanning calorimetry, were similar for interesterified and noninteresterified blends in the range of 60–100% (w/w) butterfat (3).

However, when studying the rheological properties of the blends, we noticed that the hardness index, as determined by cone penetrometry, of the blends containing 90 and 80% (w/w) butterfat dropped by 63 and 59%, respectively, after interesterification, relative to their noninteresterified counterparts (5). Hardness of the 100 and 70% butterfat blends dropped 21 and 30%, respectively (5). These drastic changes could not be correlated with their SFC values. Further rheological studies showed that the storage modulus (G'), or elasticity, of the interesterified blends was lower relative to their noninteresterified counterparts (5).

Light and scanning electron microscopy of the blends showed that the fat crystal morphology (size and shape) and crystal arrangement had changed drastically after interesterification (4). In general, both incorporation of canola oil and interesterification led to the creation of larger spherulitic particles. X-ray diffraction studies of the blends confirmed that the predominant crystal form of butterfat and butterfat–canola oil blends was the β' form. Even though small changes were observed in butterfat crystal polymorphism due to canola oil incorporation and/or interesterification, no drastic changes in the polymorphic behavior of the fat crystals were observed (4).

All of these results pointed toward the possibility that it is not the actual SFC and/or crystal polymorphic form that determines the mechanical properties of butterfat–canola oil blends, but rather the macroscopic structure of the network of fat crystals in liquid oil (see figures in Ref. 4). The problem remained how to describe the structure of a fat crystal network quantitatively.

In this paper, we report on the use of fractal geometry to characterize the structure of the fat crystal network in butterfat–canola oil blends to determine the effects of interesterification on the fractal nature (structure) of the plastic fat. We propose that the mechanical properties (elasticity) of plastic fats are linked to the geometry of the fat crystal network.

Theoretical considerations. The purpose of this section is to briefly introduce the reader to the topic of fractal geometry and its application in the study of plastic fat structure. It is our experience that studies available in the literature fail to jus-

---

*To whom correspondence should be addressed.

tify theoretically the use of expressions for the calculation of a fractal dimension. Of particular importance in this respect is the realization that there are weak-link regimes (low SFC fats) and strong-link regimes (high SFC fats) in colloidal systems (see below).

Fractal objects. This section contains highlights from the review on fractal aggregates by Meakin (6). The aggregation of small particles to form larger structures is a process of considerable importance in many areas of science and technology. The resulting aggregates have a seemingly random structure with low average density (6). The inherent difficulties in characterizing these random aggregates in a quantitative fashion have hampered efforts in the development of an understanding of their properties. Recently, fractal geometry (7) has proven useful in the characterization of these aggregated structures, both in terms of overall structure and their mechanism of formation (6).

The structure of a wide variety of objects (mountains, coastlines, rivers, vascular systems, gels, turbulence, crystal networks) cannot be readily described in terms of the concepts of Euclidean geometry. The recently developed "fractal" geometry allows us to describe and understand many of these structures and processes. Fractal geometry is concerned with the geometric scaling relationships and symmetries associated with fractal objects. A characteristic of fractal objects is their "self-similarity," or in other words, fractal objects look the same under different magnifications, at least over a limited range of scales (6).

However, it is difficult to apply these concepts directly to most structures found in nature for which we do not observe exact self-similarity, but rather an average or statistical self-similarity. For these statistically self-similar objects, geometric scaling relationships are valid for a limited range of scales (6).

For colloidal aggregates, fat crystal networks, and other random fractals in real space, it is convenient to think of fractal dimensionality in terms of scaling relationships between mass (M) and radius of a particle or aggregate (r):

$$M \sim r^{D} \qquad [1]$$

where D is the fractal dimension of the structure (1,6).

Many properties of fractal objects are different than those of typical Euclidean objects. In cases in which the fractal dimension (D) is smaller than the Euclidean dimension (d), the density (ρ) of the fractal object increases as the aggregates decrease in size:

$$\rho \sim r^{(D-d)} \qquad [2]$$

Therefore, because of their low density, fractal aggregates are usually mechanically weak structures. This limits the range of length scales over which scaling can be maintained. In the case of a colloidal aggregate, composed of particles of radius r_0 and aggregates of overall radius R_0, scaling is usually encountered in the range $r_0 < r < R_0$ (5).

Scaling behavior of the elastic properties of colloidal gels. What follows are highlights of the theories used to characterize the fractal nature of colloidal aggregates in terms of their mechanical properties taken from the paper by Shih *et al.* (8). The elastic constant of a colloidal aggregate (in our case the fat crystal network in liquid oil) as a function of particle concentration (in our case, the SFC or volume fraction of crystals) is dictated by the fractal nature of the colloidal flocs. The colloidal aggregate is considered a collection of fractal flocs that are closely packed throughout the sample. Depending on the strength of the links between flocs relative to that of the flocs themselves, we can have strong-link behavior or weak-link behavior.

Strong-link regime. This behavior is observed at low particle concentrations (low SFC or low crystal volume fraction). This regime can be achieved by allowing the individual flocs to grow very large, so that each floc is considered a weak spring. In this case, the links between flocs have a higher elastic constant than the flocs themselves. Therefore, the elastic constant of the system as a whole (K) as a function of particle concentration (φ) is dominated by the elastic constant of the flocs. For this case:

$$K \sim \varphi^{[(d+x)/(d-D)]} \qquad [3]$$

where d is the Euclidean dimension (usually 3), D is the fractal dimension, and x is the backbone fractal dimension, usually a constant between 1 and 1.3. In the case of low-SFC plastic fats, the elastic modulus of the fat crystal network increases as a function of the SFC in a power-law fashion with a slope $[(d+x)/(d-D)]$.

Weak-link regime. This behavior is observed at high particle concentrations (high SFC or high crystal volume fraction). Small flocs are stronger springs than large flocs, and therefore the elastic constant of the system as a whole is dominated by the elastic constants of the interfloc links, rather than by the elastic constants of the flocs, as for the strong-link regime. For this case:

$$K \sim \varphi^{[(d-2)/(d-D)]} \qquad [4]$$

where d is the Euclidean dimension (usually 3), and D is the fractal dimension.

In the case of high-SFC plastic fats, the elastic modulus of the fat crystal network increases as a function of the SFC in a power-law fashion with a slope $[(d-2)/(d-D)]$. The elastic constant K for the weak-link regime increases more slowly as a function of particle concentration than for the strong-link regime.

MATERIALS AND METHODS

Butterfat–canola oil blends were prepared and interesterified as outlined in Rousseau *et al.* (3). The determination of SFC was performed by pulsed nuclear magnetic resonance (NMR) as outlined in Rousseau *et al.* (3). The melted fats were placed in NMR tubes and crystallized in a refrigerator (5°C) for 24 h. The storage (or elastic) modulus (G') of the plastic fat was determined as outlined in Rousseau *et al.* (5). Values of G' used in this study were obtained from the midpoint of the G' vs.

frequency sweep spectra of the plastic fats, at 1 Hz. The strain was kept constant at 0.1 mrad deformation.

The natural logarithm of the obtained values of G' and SFC were plotted against each other:

$$\log G' = m \cdot \log \text{SFC} \qquad [5]$$

and the slope of the line (m) was derived by linear regression.

The slope of this line is related to the fractal dimension of the crystal network, assuming a weak-link regime, by:

$$m = (d - 2)/(d - D) \qquad [6]$$

where d is the Euclidean dimension (i.e., 3) and D is the fractal dimension.

RESULTS AND DISCUSSION

Figure 1 shows that the slope of the log G' vs. log SFC line for noninteresterified and interesterified butterfat–canola oil blends decreases due to chemical interesterification. The fractal dimension for the noninteresterified butterfat–canola oil blends was calculated as 2.46, while the fractal dimension for the interesterified butterfat–canola oil blends was 2.15. This is a substantial decrease in the fractal dimension of a colloidal aggregate, in our case, the fat crystal network. We propose that this large change in the "structure" of the fat crystal aggregate network is responsible for the drastic decrease in hardness observed by cone penetrometry (5).

Pioneering work in the application of the principles of fractal geometry to the study of fat crystal networks (1) showed how the fractal dimension of tristearin crystal aggregates in olive oil could be determined from light-scattering measurements. These authors also determined the fractal dimension of tristearin crystals in paraffin oil using small amplitude oscillatory shear measurements and yield stress measurements from literature values. These authors reported good agreement among all techniques used and determined the fractal dimension (D) of tristearin in olive oil to be about 1.7–1.8. This value increased upon aging of the fat to $D = 2$. Low fractal dimensions are indicative of low density, open structures. Upon aging, the crystallization, aggregation, and network formation processes continue, creating a more dense, compact, more tightly packed structure with a higher fractal dimension. Aggregates with low fractal dimensions are prone to restructuring.

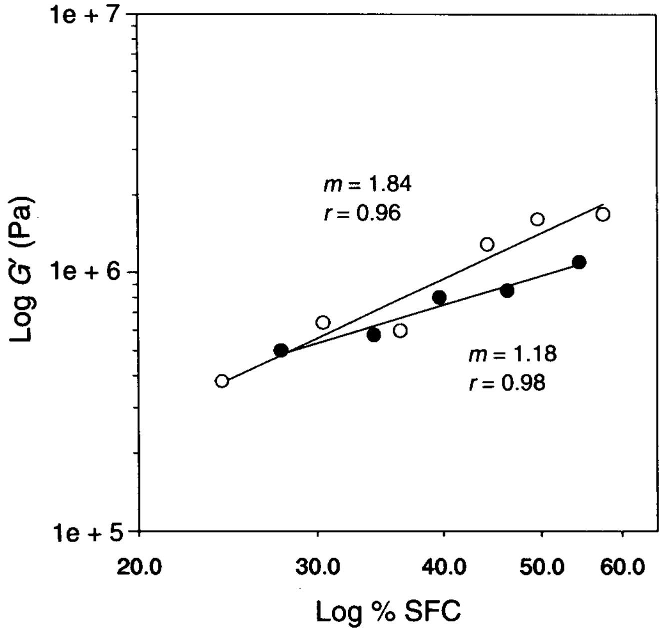

FIG. 1. Relationship between the elastic moduli (G') of noninteresterified (○) and interesterified (●) butterfat–canola oil blends and their solid fat content (SFC). The slope of the lines (m) and the correlation coefficient (r) are indicated.

Theoretical work (computer simulations) on fractal structures (6) has indicated that fractal objects with low fractal dimensions ($D \approx 1.8$) are created *via* a diffusion-limited mechanism (6). Structures with higher fractal dimensions ($D \approx 2.08$) are characteristic of structures formed *via* reaction-limited mechanisms (6). There are several other possible mechanisms responsible for the formation of fractal aggregates as well. These have been reviewed by Meakin (6). One point to be made is that it is dangerous to extrapolate this relationship of the fractal dimension of a particular object to the mechanism by which it was created. In real systems, rearrangements occur readily, and it is possible for the fractal dimension of a structure to change from 1.8 to 2.18 after only three rearrangements (6). Care must be exercised when attempting to relate the fractal dimensionality to an aggregation mechanism.

In summary, fractal geometry can be used to characterize the structure of plastic fats. Interesterification changed the structure of triglycerides. This, in turn, led to a change in the kinetics of crystal formation and therefore of the resulting fat crystal network responsible for the macroscopic structure of the plastic fat. The fractal dimension is a better parameter for predicting rheological behavior of plastic fats than the SFC and appears to have great potential for targeting specific rheological properties of plastic fats, e.g., spreadability.

ACKNOWLEDGMENTS

We are indebted to Dr. John deMan for the use of his equipment and helpful comments throughout the study. This research was funded by the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) through the Ontario Food Processing Research Fund (OFPRF), and in part by the Natural Sciences and Engineering Research Council of Canada (NSERC). The authors thank Dr. Robert Lencki for the many stimulating conversations on fractals, chaos, and kinetic modeling.

REFERENCES

1. Vreeker, R., L.L. Hoekstra, D.C. den Boer, and W.G.M. Agterof, The Fractal Nature of Fat Crystal Networks, *Colloids and Surfaces 65*:185–189 (1992).
2. van den Tempel, M., Mechanical Properties of Plastic-Disperse Systems at Very Small Deformations, *J. Colloid Sci. 16*:284–296 (1961).
3. Rousseau, D., K. Forestiere, A. Hill, and A.G. Marangoni, Re-

structuring Butterfat Through Blending and Chemical Interesterification. 1. Melting Behavior and Solid Fat Content, *J. Am. Oil Chem. Soc. 73*:963–972 (1996).

4. Rousseau, D., A. Hill, and A.G. Marangoni, Restructuring Butterfat Through Blending and Chemical Interesterification. 2. Microstructure and Crystal Polymorphism, *Ibid. 73*:973–981 (1996).
5. Rousseau, D., A. Hill, and A.G. Marangoni, Restructuring Butterfat Through Blending and Chemical Interesterification. 3. Rheology, *Ibid. 73*:983–989 (1996).
6. Meakin, R., Fractal Aggregates, ***Advances in Colloid and Interface Science*** *28*:249–331 (1988).
7. Mandelbrot, B.B., ***The Fractal Geometry of Nature***, W.H. Freeman and Company, New York, 1982.
8. Shih, W.H., W.Y. Shih, S.I. Kim, J. Liu, and I.A. Aksay, Scaling Behavior of the Elastic Properties of Colloidal Gels, *Phys. Rev. A 42*:4772–4779 (1990).

[Received December 19, 1995; accepted April 22, 1996]