Product Design and Engineering

Formulation of Gels and Pastes
Edited by
Ulrich Bröckel, Willi Meier,
and Gerhard Wagner

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Formulation of Gels and Pastes
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List of Contributors

Muhammad Mohsin Azim
University of Leipzig
Institute of Chemical Technology
Linnestraße 3-4
04103 Leipzig
Germany

Arjen Bot
Unilever R&D Vlaardingen
Olivier van Noortlaan 120
3133 AT Vlaardingen
The Netherlands

Ulrich Bröckel
Institute for Micro-Process-Engineering and Particle Technology (IMiP)
Umwelt-Campus Birkenfeld
Campus Allee 24
55761 Birkenfeld
Germany

Rüdiger Brummer
Beiersdorf AG
R&D cosmid
Unnastrasse 48
20245 Hamburg
Germany

Elisa Conte
Separation Processes Process Technology
AkzoNobel Research, Development and Innovation
Zuthphenseweg 10
7418 AJ Deventer
The Netherlands

Eckhard Flöter
Technical University of Berlin
Institute of Food Process Engineering
Königin-Luise-Straße 22
14195 Berlin
Germany

Rafiqul Gani
Technical University of Denmark
Department of Chemical and Biochemical Engineering
Søltofts Plads
Building 229
2800 Lyngby
Denmark
**List of Contributors**

**Kristina Georgieva**  
Karlsruher Institut für Technologie (KIT)  
Institut für Mechanische Verfahrenstechnik und Mechanik  
Geb. 30.70  
Straße am Forum 8  
76131 Karlsruhe  
Germany

**Navam Hettiarachchy**  
University of Arkansas  
Food Science Department  
2650 N Young Avenue  
Fayetteville, AR 72704  
USA

**Arvind Kannan**  
University of Arkansas  
Food Science Department  
2650 N Young Avenue  
Fayetteville, AR 72704  
USA

**Heike P. Karbstein-Schuchmann**  
Karlsruhe Institute of Technology (KIT)  
Institute of Food Process Engineering  
Kaiserstrasse 12  
76131 Karlsruhe  
Germany

**Michele Mattei**  
Technical University of Denmark  
Department of Chemical and Biochemical Engineering  
Building 229  
2800 Lyngby  
Denmark

**Willi Meier**  
DECHEMA e.V.  
Theodor-Heuss-Allee 25  
60486 Frankfurt  
Germany

**Wilfried Rähse**  
ATS License GmbH  
R&D Cosmeceuticals  
Bahlenstr. 168  
40589 Düsseldorf  
Germany

**Muhammad Ramzan**  
University of Leipzig  
Institute of Chemical Technology  
Linnéstraße 3-4  
04103 Leipzig  
Germany

**Henelyta Santos Ribeiro**  
Unilever R&D Vlaardingen  
Olivier van Noortlaan 120  
3133 AT Vlaardingen  
The Netherlands

**Richard Sass**  
DECHEMA e.V.  
Theodor-Heuss-Allee 25  
60486 Frankfurt  
Germany
Christian Schäfer  
DSM Nutritional Products Ltd.  
R&D Centre Formulation and Application  
4002 Basel  
Switzerland

Anne Schmidt  
University of Leipzig  
Institute of Chemical Technology  
Linnéstraße 3-4  
04103 Leipzig  
Germany

Annegret Stark  
University of Leipzig  
Institute of Chemical Technology  
Linnéstraße 3-4  
04103 Leipzig  
Germany

Tharwat F. Tadros  
89 Nash Grove Lane  
Wokingham  
Berkshire RG40 4HE  
UK

Gerhard Wagner  
Global R&D Director DSM Biotechnology Center  
Alexander Fleminglaan 1  
2613 AX Delft  
The Netherlands

and

Dianastrasse 12  
4310 Rheinfelden  
Switzerland

Martin Wild  
University of Leipzig  
Institute of Chemical Technology  
Linnéstraße 3-4  
04103 Leipzig  
Germany

Norbert Willenbacher  
Karlsruher Institut für Technologie (KIT)  
Institut für Mechanische Verfahrenstechnik und Mechanik  
Geb. 30.70  
Straße am Forum 8  
76131 Karlsruhe  
Germany
Introduction

Gerhard Wagner, Willi Meier, and Ulrich Bröckel

What Is Product Design and Engineering?

Product design is, in principle, a term that describes a very broad variety of designs, ranging from industry design of goods, for example cars, measurement instruments and furniture, to scientific and technological product design. Scientific and technological product design can be subdivided into four main clusters:

- **Biological product design**: This includes, for example, product design for proteins, probiotics [1], or enzymes for various specific purposes such as biomass utilization [2] or food processing [3], animal feed utilization, agricultural, brewery, fuel and textile finishing applications.
- **Chemical product design**: [4] according to Cussler and Moggridge this aims for new speciality chemicals or pharmaceuticals. Other examples of chemical product design are modified starches, polyols [5] or polymers with tailor-made properties.
- **Food design** or **food engineering** [7]: this covers a wide range of technologies and raw materials. Numerous books [8] and journals are focusing on this subject.
- **Physical product design**: this avoids a modification of the chemical structure of the active components (e.g., vitamins, pharmaceuticals, pigments, etc.) but modifies instead the physical properties of the components, for example particle size, shape, surface morphology or crystal habit. Physical product design also includes the wide field of formulation and Galenic formulation in which additives and excipients change, for example, the appearance, stability, bioavailability or even the purpose of the products over a very wide range.

All four clusters of product design have in common a need for a multidisciplinary approach based on biology, chemistry and physics combined with engineering skills and sciences; furthermore, disciplines like nutrition, pharmacy and ergonomics and form design are crucial to ensure a suitable product. Product design is more of an iterative than a linear process; the understanding of the different disciplines is therefore important at the different steps of product design depending of the scale of the product design. Figure 1 shows how the disciplines impact on the physical properties relevant to product qualities within the different size ranges.
In the first two volumes of this book series we focused mainly on basic technologies and solids. The very important aspect of liquid-like or gel-type applications have been excluded so far. In this third volume of our book series we will, therefore, elaborate these applications in more detail.

Product design has become a growing field of interest during recent years. The reasons for this are manifold. Looking at the markets of the chemical engineering field today, we observe well-established and quite saturated markets. Breakthrough innovation with brand new products is difficult to accomplish. Product design is, therefore, crucial to improve the following properties of a product:

- handling
- applicability
- appearance
- stability
- performance, activity, or bioavailability.

With product design, existing products can be optimized, improved and positioned in the market, prolonging their life cycle or differentiating and making them applicable for new markets.

Product design has been seen as a paradigm shift in process design away from the unit operation concept to a new interdisciplinary thinking [9], speeding up the development process. But, obviously, there is still a long way to go before enough knowledge and basic understanding of the complex interactions of multicomponent systems is gathered in order to calculate the composition and the processing conditions in order to predict the performance of a new formulation using a computer.
As mentioned in the introduction of the first two volumes of this series, product design is much more than a buzz word and is of the highest importance for related industries. For example, Aspirin® as a highly developed pharmaceutical bulk chemical is available in new formulations every few years [10]. The same is true for formulated and encapsulated carotenoid products, which also show a continuous development in their product form and composition. In addition, beverages, like soft drinks, energy drinks and coffee-based beverages or washing powder, laundry products or detergents are subject to on-going development, owing to customers expecting an improved taste or a better performance of the new product. These kinds of improvements ensure the lifecycle management of products.

Several company strategies clearly state the importance of product design and engineering for the future of process industries. Customer demands have to be recognized and turned into products with the help of well-established processes and technologies. Fulfilling customer needs will automatically lead the business to new applications and new markets were real growth is created.

For such examples we elaborated in Volumes I and II different technologies, raw materials and additives. One area we were not able to investigate in more detail, even though we touched on emulsion technologies, is liquid and gel-type applications, which are very important for the broad field of, among other industries, the life science industry.

Volume I describes the basics and fundamentals of chemical engineering that are essential for product design and engineering. This enabled us to give an overview of the basic knowledge and related activities. The second volume describes recent applications that turn the technologies described in Volume I into customer oriented products. Volume II shows some examples of these new products with an introductory chapter on product design fundamentals. The superior behavior of, for example, coffee, aspirin and carotenoid products is crucial. The taste of coffee, the bioavailability of aspirin and carotenoid products and the UV absorption of polymers can be adjusted. Product design offers opportunities to change, to adopt, and to improve products.

The intention of this, the third volume of this series is to discuss in more detail the basics of rheology and how product design is carried out in liquid and gel-type applications. Differentiation and product design is essential for raw materials and additives. The behavior of, for example, starches and gelatins is designed and changed by product design to give a specific texture and/or performance of the final product.

The structure of the third volume of this series is illustrated in Figure 2. The fundamentals are the basics in rheology, which are important for describing and quantifying the properties of gels or pastes.

This volume starts with the essential chapter entitled “Rheology of Disperse Systems” (Chapter 1) while Chapter 3 gives an insight view into “Rheology Modifiers, Thickeners, and Gels.” The stability of dispersions is crucial for the shelf life of customer related products. This problem is discussed in the chapter
on the “Use of Rheological Techniques for Assessment and Prediction of Stability of Dispersions (Suspensions and Emulsions)” (Chapter 4). The specific chapter “Rheology of Cosmetic Emulsions” (Chapter 2) focuses on products closer to cosmetic daily life application. A theoretical approach can be found in the chapters on the “Prediction of Thermophysical Properties of Liquid Products” (Chapter 5) and “Sources of Thermophysical Properties for the Efficient Use in Product Design” (Chapter 6). A more forward-looking contribution is “Trends in Ionic Liquid Research” (Chapter 7). The possibilities in terms of modifying the viscosity of liquid formulations are given in “Gelling of Plant Based Proteins” (Chapter 8) and “Enzymatic Texturized Plant Proteins for the Food Industry” (Chapter 9). Examples of some important applications are given in the “Design of Skin Care Products” (Chapter 10) and “Emulsion Gels in Foods” (Chapter 11).

A complete prediction of product formulation based on scientific knowledge is not possible given the current state of the art. Very specific and often still empirical knowledge and specific trials in the laboratories are still needed to ensure the design of a product. Product design and engineering it is a very multifaceted area. Nevertheless, this book aims to give a good overview of the different fields of technologies and successful instances for liquid and gel-type applications.

As product design will become increasingly important in the near future the teaching of students in this field should be intensified given that:

• profound physical and chemical knowledge is needed;
• product design is the interaction of multiple disciplines.

It is our intention to contribute with this book series to the on-going improvements in technologies, fundamentals and discussions in the community about teaching product design. Finally, without the highly qualified contributions of the persons most important for this book, our authors, this volume would still only be a nice idea.
References

1 Rheology of Disperse Systems

Norbert Willenbacher and Kristina Georgieva

1.1 Introduction

The rheology of disperse systems is an important processing parameter. Being able to characterize and manipulate the flow behavior of dispersions one can ensure their optimal performance. Waterborne automotive coatings, for example, should exhibit a distinct low-shear viscosity necessary to provide good leveling but to avoid sagging at the same time. Then, a strong degree of shear thinning is needed to guarantee good pump- and sprayability. The rheological properties of dispersions, especially at high solids content, are complex and strongly dependent on the applied forces and flow kinematics. Adding particles does not simply increase the viscosity of the liquid as a result of the hydrodynamic disturbance of the flow; it also can be a reason for deviation from Newtonian behavior, including shear rate dependent viscosity, elasticity, and time-dependent rheological behavior or even the occurrence of an apparent yield stress. In colloidal systems particle interactions play a crucial role. Depending on whether attractive or repulsive interactions dominate, the particles can form different structures that determine the rheological behavior of the material. In the case of attractive particle interactions loose flocs with fractal structure can be formed, immobilizing part of the continuous phase. This leads to a larger effective particle volume fraction and, correspondingly, to an increase in viscosity. Above a critical volume fraction a sample-spanning network forms, which results in a highly elastic, gel-like behavior, and an apparent yield stress. Shear-induced breakup and recovery of floc structure leads to thixotropic behavior. Electrostatic or steric repulsion between particles defines an excluded volume that is not accessible by other particles. This corresponds to an increase in effective volume fraction and accordingly to an increase in viscosity. Crystalline or gel-like states occur at particle concentrations lower than the maximum packing fraction.

Characterization of the microstructure and flow properties of dispersions is essential for understanding and controlling their rheological behavior. In this chapter we first introduce methods and techniques for standard rheological tests and then characterize the rheology of hard sphere, repulsive, and attractive particles. The effect of particle size distribution on the rheology of highly concentrated
dispersions and the shear thickening phenomenon will be discussed with respect to the influence of colloidal interactions on these phenomena. Finally, typical features of emulsion rheology will be discussed with special emphasis on the distinct differences between dispersion and emulsion rheology.

### 1.2 Basics of Rheology

According to its definition, rheology is the science of the deformation and flow of matter. The rheological behavior of materials can be regarded as being between two extremes: Newtonian viscous fluids, typically liquids consisting of small molecules, and Hookean elastic solids, like, for example, rubber. However, most real materials exhibit mechanical behavior with both viscous and elastic characteristics. Such materials are termed *viscoelastic*. Before considering the more complex viscoelastic behavior, let us first elucidate the flow properties of ideally viscous and ideally elastic materials.

Isaac Newton first introduced the notion of viscosity as a constant of proportionality between the force per unit area (shear stress) required to produce a steady simple shear flow and the resulting velocity gradient in the direction perpendicular to the flow direction (shear rate):

\[ \sigma = \eta \dot{\gamma} \]  

(1.1)

where \( \sigma = F/A \) is the shear stress, \( \eta \) the viscosity, and the \( \dot{\gamma} = \nu/h \) is the shear rate. Here \( A \) is the surface area of the sheared fluid volume on which the shear force \( F \) is acting and \( h \) is the height of the volume element over which the fluid layer velocity \( \nu \) varies from its minimum to its maximum value. A fluid that obeys this linear relation is called *Newtonian*, which means that its viscosity is independent of shear rate for the shear rates applied. Glycerin, water, and mineral oils are typical examples of Newtonian liquids. Newtonian behavior is also characterized by constant viscosity with respect to the time of shearing and an immediate relaxation of the shear stress after cessation of flow. Furthermore, the viscosities measured in different flow kinematics are always proportional to one another.

Materials such as dispersions, emulsions, and polymer solutions often exhibit flow properties distinctly different from Newtonian behavior and the viscosity decreases or increases with increasing shear rate, which is referred to a shear thinning and shear thickening, respectively. Figure 1.1a,b shows the general shape of the curves representing the variation of viscosity as a function of shear rate and the corresponding graphs of shear stress as a function of shear rate.

Materials with a yield stress behave as solids at rest and start to flow only when the applied external forces overcome the internal structural forces. Soft matter, such as, for example, dispersions or emulsions, does not exhibit a yield stress in this strict sense. Instead, these materials often show a drastic change of viscosity by orders of magnitude within a narrow shear stress range and this is usually termed an *“apparent” yield stress* (Figure 1.2a,b). Dispersions with attractive interactions,
1.2 Basics of Rheology

Shear stress

Dilatant
Newtonian
Shear-thinning

(a) Shear rate

Viscosity

Dilatant
Newtonian
Shear-thinning

(b) Shear rate

Figure 1.1 Typical flow curves for Newtonian, shear thinning and shear thickening (dilatant) fluids: (a) shear stress as a function of shear rate; (b) viscosity as a function of shear rate.

Figure 1.2 Flow curve of a material with an apparent yield stress $\sigma_y$: (a) shear stress as a function of shear rate; (b) viscosity as a function of shear stress.

such as emulsions and foams, clay suspensions, and ketchup, are typical examples of materials with an apparent yield stress. Note that there are various methods for yield stress determination and the measured value may differ depending on the method and instrument used.

The flow history of a material should also be taken into account when making predictions of the flow behavior. Two important phenomena related to the time-dependent flow behavior are thixotropy and rheopexy. For materials showing thixotropic behavior the viscosity gradually decreases with time under constant shear rate or shear stress followed by a gradual structural recovery when the stress is removed. The thixotropic behavior can be identified by measuring the shear stress as a function of increasing and decreasing shear rate. Figure 1.3 shows a hysteresis typical for a thixotropic fluid. Examples of thixotropic materials include coating formulations, ketchup, and concentrated dispersions in the two-phase region (Section 1.4.1.1). The term rheopexy is defined as shear-thickening followed by a gradual structural recovery when the shearing is stopped. Tadros pointed out that rheopexy should not be confused with anti-thixotropy, which is the time dependent shear thickening [1]. However, rheopexic materials are not very common and will not be discussed here.
So far we have considered the flow behavior of viscous fluids in terms of Newton’s law and a nonlinear change of viscosity with applied stress that can occur either instantaneously or over a long period of time. At the other extreme is the ideal elastic behavior of solids, which can be described by Hooke’s law of elasticity:

\[ \sigma = G\gamma \]  

(1.2)

where \( \gamma \) is the shear deformation (also termed strain) and \( G \) is the shear modulus characterizing the rigidity of a material. The shear modulus of an ideal elastic solid is independent of the shear stress and duration of the shear load. As soon as a deformation is applied a constant corresponding stress occurs instantaneously. In viscoelastic materials stress relaxes gradually over time at constant deformation and eventually vanishes for viscoelastic liquids. When the stress relaxation is proportional to the strain we are talking about the so-called linear viscoelastic regime. Above a critical strain the apparent shear modulus becomes strain dependent. This is the so-called nonlinear viscoelastic regime. The linear viscoelastic material properties are in general very sensitive to microstructural changes and interactions in complex fluids.

A dynamic test or small amplitude oscillatory shear (SAOS) test is the most widely used rheological measurement to investigate the linear viscoelastic behavior of a fluid, since it has a superior accuracy compared to step strain or step stress experiments. When a sinusoidal oscillatory shear strain is applied with amplitude \( \gamma_0 \) and angular frequency \( \omega \) the deformation \( \gamma(t) \) can be written as:

\[ \gamma(t) = \gamma_0 \sin(\omega t) \]  

(1.3)

where \( t \) denotes the time. The shear rate is the time derivative of the shear strain and then reads as follows:

\[ \dot{\gamma}(t) = \frac{d\gamma(t)}{dt} = \gamma_0 \omega \cos(\omega t) \]  

(1.4)

A linear viscoelastic fluid responds with a sinusoidal course of shear stress \( \sigma(t) \) with amplitude \( \sigma_0 \) and angular frequency \( \omega \), but is phase shifted by an angle \( \delta \) compared to the imposed strain:

\[ \sigma(t) = \sigma_0 \sin(\omega t + \delta) \]  

(1.5)