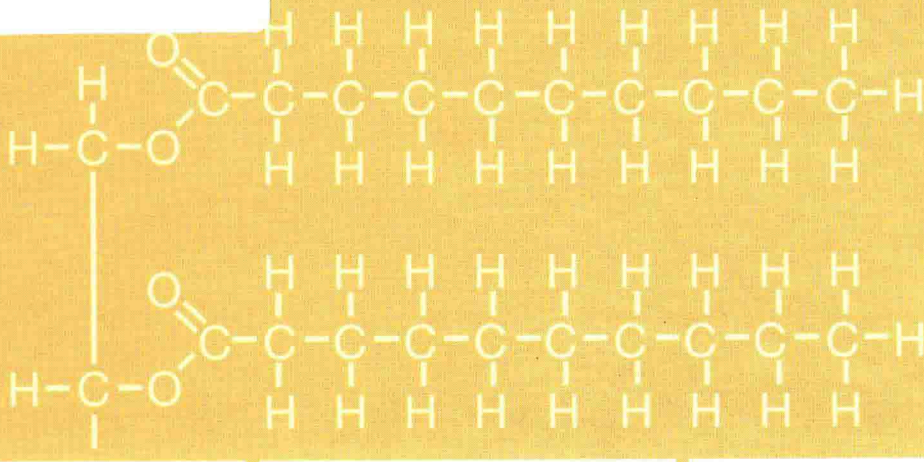
SECOND EDITION

Fats in Food Technology

Edited by
Kanes K. Rajah



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Kanes K. Rajah
Royal Agricultural University, Cirencester, Gloucestershire, UK

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List of contributors

Albert J. Dijkstra	St Eutrope-de-Born, France
Mark Farmer	ADMi, Rolle, Switzerland
Kanes K. Rajah	Dean, School of Business and Entrepreneurship, Professor of Entrepreneurial Behaviour and Innovation, Royal Agricultural University, Cirencester, Gloucestershire, UK
H. M. Premlal Ranjith	Director, Diotte Consulting & Technology Limited, Nantwich, Cheshire, UK
Kiyotaka Sato	Laboratory of Food Biophysics, Graduate School of Biosphere Science, Hiroshima University, Higashi-Hiroshima, Japan
Geoff Talbot	The Fat Consultant, Bedford, UK
Satoru Ueno	Laboratory of Food Biophysics, Graduate School of Biosphere Science, Hiroshima University, Higashi-Hiroshima, Japan
Paul Wassell	Food Nanotechnology Group, Environmental Quality and Food Safety Research Unit, University of Chester, Chester, UK; PVO Innovation Centre, Pasir Gudang, Johor Bahru, Malaysia
Upuli Wijewardene	ProtectFood, Nantwich, Cheshire, UK
Niall W. G. Young	Principal Scientist, DuPont Nutrition and Health, Brabrand, Denmark, and University of Chester, Chester, UK

Preface

This updated second edition is fresh and exciting in a number of ways. First, it is a book about fats in food technology – their role, behaviour and the benefits they impart to the foods we consume. Second, it is about fats that are 'naturally present' in foods (e.g. milk fat in cream) or fats that have been added to help with physical and chemical properties (e.g. cocoa butter in chocolate). Finally, it is a book which has useful information about market issues that have driven change and disciplines that have helped to regulate the trade and use of fats and oils in foods.

My initial challenge in the first edition was to find authors who could write to such exacting and wide-ranging requirement. I was privileged to be able to gather together an internationally respected team of authors from several countries, to contribute, either independently or in joint initiatives, a total of nine chapters. In this edition I have been most fortunate that all who still remain active in their specialisms agreed to join me in updating their respective chapters. To fill the gaps created by those who had retired I have been very fortunate in enlisting new authors who are all with senior-level commercial experience of R&D in oils and fats technology and having also direct exposure to technical developments in world markets.

Consequently, all chapters have been reviewed systematically; established products and processes have been investigated for updates while the latest developments have been introduced and new ideas are presented, not only from the recent literature but often from the personal R&D experiences of the authors. Where efficiencies in processing or economy in the costs of raw materials can be achieved, these have – either implicitly or explicitly, by the choice of appropriate examples or formulations – been discussed within the relevant chapters.

Authors have attempted to provide relevant market information in respect of regulation, legislation or directives currently enforced in the major markets, especially within the United States and Europe. Market trends and changes which facilitate a better understanding of the scope and potential for fat technology are also presented. In an integrated approach, the issues concerning greater consumer awareness of health, diet and lifestyle are interwoven into some of the relevant chapters, such as, typically, lower fat products and high moisture emulsions. The technology of non-aqueous fat systems has been brought up-to-date water-in-oil and oil-in-water emulsions are discussed far more extensively in this book than previously.

The book begins with a presentation of the physical properties of fats and emulsions in Chapter 1. Chapter 2, on bakery fats, deals with solid, fluid and powdered fats. New developments in water continuous emulsions and dairy cream technology are explained in Chapter 3. Cream liqueur and ice cream production processes are also included. Hydrogenation and fractionation, which are the most widely used techniques of fat modification, are covered as separate subjects in Chapter 4. Products from these processes often replace, complement or supplement each other. This is evident from the discussion and also in the examples seen in those chapters dealing with end-use, e.g. bakery, spreads and confectionery. Chapter 5 on confectionery products has been widened to cover both chocolate and sugar confectionery fats. Chapter 6 on spreadable products includes the results of specific secondary market research on important developments in butter, margarine and low fat spreads technology and packaging. The significant growth in fat-based sweet and savoury spreads is also acknowledged in this important chapter. The treatment of emulsifiers is comprehensive and Chapter 7 guides the reader through the technology of current products used in, for example, recipes and formulations to ensure that shelf-life, emulsion stability and anti-spattering properties are optimised. We have introduced a unique new chapter, Chapter 8 on 'Food Safety and Quality Issues of Dairy Fats' consists of the most up-to-date information on the subject. Finally, culinary fats appear as a separate chapter (Chapter 9) because they focus on some of the unique features and benefits of fats, frying oil, ghee and vanaspati and speciality fats in the kitchen and discuss these in terms of flavour, eating quality, texture, aroma and benefits to health.

This book should be helpful to anyone who is interested in the technology of fat-containing products. Food technologists in either the dairy industry or the edible oils industry and indeed the food industry generally should find that this volume provides important ideas for product and process development. For scientists in academic research establishments, the book offers important insights into some of the more significant scientific developments that have been commercialised. The book will also serve as a useful source of reference to traders and marketing personnel in the oils, fats and butter industries.

This has been yet again a major challenge and a creative experience for all of us. It has been possible only because those who participated in crafting both editions gave of their best, unflinchingly. My warmest thanks, therefore, to the following much valued colleagues who have retired but whose original chapters remain with new authors taking up the task to update: Tetsuo Koyano, John Podmore, Ralph E. Timms, David Robinson and Clyde E. Stauffer. I am saddened that Ian M. Stewart, a much admired and highly respected colleague passed away. He will be missed greatly. Finally, Timothy P. Guinee and Barry A. Law were unable to update their chapter on 'Role of milk fat in hard and semihard cheeses' and so their original chapter in the first edition remains as the reference point on the subject and is not included in this second edition. I record my gratitude to all our colleagues who had contributed to the first edition.

A special thanks to my fellow authors in this book for their hard work and for generously sharing their knowledge, insight and experience in producing such excellent chapters. Any perceived shortcomings in this book are entirely my own responsibility. I am equally grateful to Dr Graeme MacKintosh as the Publisher who invited me to

undertake the first edition, and to the Commissioning Editor of this edition Mr Andrew Harrison and to Fiona Seymour – Senior Project Editor, who took over from him. Thank you to all on the Wiley team for your invaluable assistance and unstinting support at all times.

Finally, to the three special people in my life who make me still want to undertake such projects, to Heera, Tamara and Tara, thank you.

Contents

1

Physical properties of fats in food[1]

Kiyotaka Sato and Satoru Ueno

Laboratory of Food Biophysics, Graduate School of Biosphere Science, Hiroshima University, Higashi-Hiroshima, Japan

1.1 Introduction

Oils and fats are important ingredients in a wide variety of manufactured foods, and constitute a significant part of food recipes. The major foods in which they are used are all discussed in detail in this volume. However, it is important to note that the forms in which oils and fats are made available to food manufacturers have changed significantly over the years, particularly since the 1960s, largely because of the major shifts that have taken place in consumer lifestyles and the increasing concerns with health, food safety and a balanced diet. Many of the food products that are now available to consumers reflect this new direction. Important examples arising out of the lipid research that has followed are *trans-free* fatty acids, reduced high-melting, in particular saturated, fats, very-low-yellow fat emulsions, spreadable butter, aerated fats, structured oils, molecularly designed structured fats with new nutritional advantages, and so on. All these initiatives have required an in-depth understanding of the behaviour of the fats concerned so that they can be used effectively as ingredients in food. Consequently, the study of their physical properties is of major interest and is covered in this chapter.

In general, fats form networks of crystal particles, maintaining specific polymorphic forms, crystal morphology and particle–particle interactions (Marangoni, 2005). The control of the physical properties of food fats has therefore been of importance in research efforts and can be considered under five headings:

- clarification of molecular and crystal structures of triacylglycerols (TAGs) with different fatty-acid moieties (Kaneko *et al.*, 1998; Kaneko, 2001);
- crystallisation and transformation mechanisms of TAG crystals (Sato, 1996, 1999; Sato and Koyano, 2001; Sato and Ueno, 2005);

[1]The original chapter was written by Tetsuo Koyano and Kiyotaka Sato.

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- clarification of formation mechanisms of mesoscale and macroscale fat crystal network starting from nanoscale primary fat crystals (Acevedo *et al.*, 2011);
- rheological and texture properties that are dominated mainly by fat crystal networks (Boode *et al.*, 1991; Marangoni and Hartel, 1998; Marangoni *et al.*, 2012; Walstra *et al.*, 2001);
- influences of external factors such as shear, ultrasound irradiation, minor lipids on fat crystallisation kinetics (Martini *et al.*, 2008; Mazzanti *et al.*, 2011; Smith *et al.*, 2011; Wright *et al.*, 2000).

The first topic is of an introductory nature and so will not be elaborated in this chapter (for more details, see the cited references). The remaining four topics are related to observed systems of food fats, with which this chapter is mainly concerned.

The chapter begins with a brief review of the three basic physical properties of fats by collecting together recent work on the crystallisation and transformation of the fats in bulk and in emulsion states. We will then focus on fundamental aspects of the crystallisation and transformation of fats employed in real food systems, through describing the use of important examples, such as cocoa butter, palm oil and palm mid-fractions. Since these natural fats are multi-TAG systems, knowledge of the fundamental properties of pure TAGs composing the natural fats may be necessary, as will be argued. Those who wish to compare real fats with pure fats are directed to the literature (Himawan *et al.*, 2006; Sato, 1996; Sato and Koyano, 2001; Sato and Ueno, 2001; Sato *et al.*, 1999).

1.2 Basic physical properties of fat crystals

The physical properties of the food fats are influenced primarily by three factors: (1) polymorphism (structural, crystallisation and transformation behaviour); (2) the phase behaviour of fat mixtures; and (3) the rheological and textural properties exhibited by fat crystal networks. In this section we cover the fundamentals and look at recent research work on these three properties.

1.2.1 Polymorphic structures of fats

Polymorphism is defined as the ability of a chemical compound to form different crystalline or liquid crystalline structures. The melting and crystallisation behaviour will differ from one polymorph to another.

Table 1.1 summarises the basic physical properties of the three typical polymorphic modifications of α, β' and β. Polymorph α is least stable, easily transforming to either the β' form or the β form, depending on the thermal treatment. Polymorph β', the meta-stable form, is used in margarine and shortening because of its optimal crystal morphology and fat crystal networks, which give rise to optimal rheological and texture properties. The most stable β form tends to form large and plate-like crystal shapes, resulting in poor macroscopic properties in shortening and margarine.

Table 1.1 Three typical polymorphic forms of fats and their main physical properties.

Form	Stability	Density	Melting point	Morphology
α	Least stable	Lowest	Lowest	Amorphous-like
β′	Metastable	Intermediate	Intermediate	Rectangular
β	Most stable	Highest	Highest	Needle-shaped

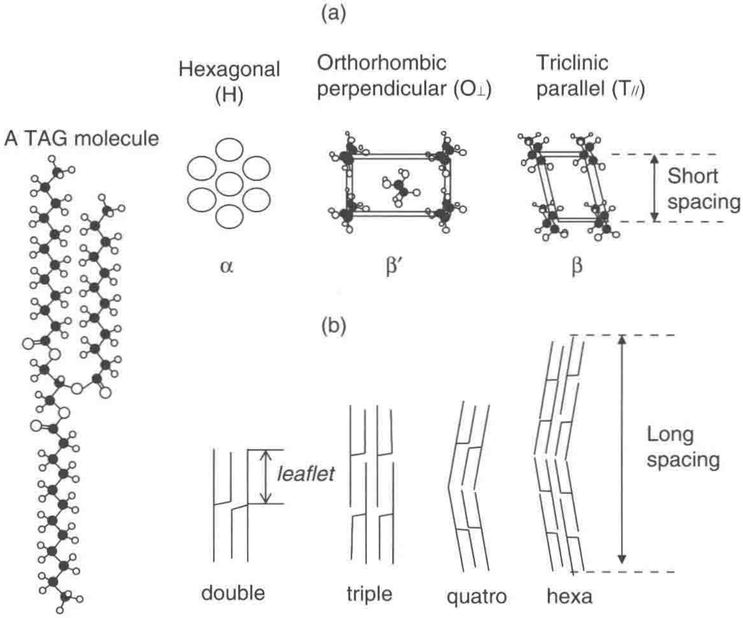

Figure 1.1 Polymorphic structures of three typical forms of triacylglycerol (TAG). (a) Subcell structures and (b) chain length structures.

The three main polymorphs, α, β′ and β of fats, are defined in accordance with subcell structure: α polymorphs have a hexagonal subcell (H); β′ polymorphs have an orthorhombic–perpendicular subcell ($O_\perp$); and β polymorphs have a triclinic–parallel subcell ($T_{//}$) (Larsson, 1966; see Figure 1.1 (a)). The subcell structures can be determined most clearly by measuring X-ray diffraction (XRD) short spacing patterns of poly-crystalline samples.

Figure 1.1 (b) shows the chain-length structure, illustrating the repetitive sequence of the acyl chains involved in a unit cell lamella along the long-chain axis (Larsson, 1972). A double chain-length structure (DCL) is formed when the chemical properties of the three acid moieties are the same or very similar. In contrast, when the chemical properties of one or two of the three chain moieties are largely different from those of the moieties, a triple chain-length (TCL) structure is formed because of chain sorting. The relevance of the chain-length structure is revealed in the mixing phase behaviour of the different types of the TAGs in the solid phase: when the DCL fats are mixed with the TCL fats, phase separation readily occurs. The chain length structures can be determined solely by measuring the XRD long spacing patterns of the poly-crystalline samples.

In food fats, transformation from polymorph β′ to polymorph β often causes deterioration of the end product, mostly because of changes in the crystal morphology and network, as indicated in Table 1.1. The β-type polymorph is found in confectionery fats made of cocoa butter (Timms, 2003). There are two β-type crystals: a meta-stable β_2 form is more useful than the more stable β_1 form (Sato and Koyano, 2001; Van Mechelen *et al.*, 2006a, 2006b). Atomic-level structure analyses of the TAGs have been attempted to resolve the microscopic mechanism of the polymorphic β′–β transformation. Results were reported first for the β forms (as reviewed for the β forms in Kaneko, 2001), and have been reported for the β′ form (Sato *et al.*, 2001; van Langevelde *et al.*, 2000). Mechanistic processes of solid-state transformation from β′ to β forms in trilauroyl-glycerol crystals were observed by a cutting-edge method with synchrotron radiation microbeam XRD (SR-μ-XRD) (Ueno *et al.*, 2008), as will be presented below.

As the physical properties of food fats are greatly influenced by fat polymorphism, it is a prerequisite for those who are engaged in the material production of oils and fats to know how the fatty-acid composition influences the fat polymorphism. Two categories of fatty-acid composition may be considered: (1) mono-acid TAGs in which the three fatty-acid moieties of the TAG are of the same type; and (2) mixed-acid TAGs in which different fatty-acid components are connected to three different glycerol carbons on the TAG. The following diversity in fatty-acid composition of TAGs can be found:

- Mono-acid TAGs:
  - the acids may be saturated;
    - the number of carbon atoms in the fatty-acid chain, N_c, may be odd or even;
  - the acids may be unsaturated.
    - the number of carbon atoms in the fatty-acid chain, N_c, may be odd or even;
    - there may be a *cis* or a *trans* conformation around the double bond;
    - the number of double bonds may vary;
    - the position of the double bonds may vary.
- Mixed-acid TAGs:
  - there may be three saturated acids with different chemical species;
  - there may be three unsaturated acids with different chemical species;
  - there may be three acids containing saturated and unsaturated species;
  - the different fatty acids may be connected to carbon atoms of different stereospecific number (*sn*).

In 1988, Hagemann summarised the melting behaviour of TAGs with different combinations of fatty-acid moieties with different chemical species (Hagemann, 1988).