Phenomenon of Lecithin

Science | Technology | Applications

Waldemar Buxmann
Parris Kidd
Volkmar Wywiol
Rüdiger Ziegelitz

Preface

Lecithins are complex mixtures of polar lipids, mainly phospholipids, obtained by physical procedures from a variety of vegetable and animal sources.

Does that make it sound as if there is anything phenomenal about lecithin? Is the title of this book justified? The answer is definitely YES. Because what makes lecithin so phenomenal are its remarkable properties and its history.

Phospholipids are natural components of all animal and vegetable cell membranes, where they have an essential function. That explains the physiological benefits of lecithin. Because of the amphiphilic structure of the phospholipids, which gives them their surfactant properties, it may be said that lecithin is the most important of all the natural emulsifiers. It also means that from the techno-functional point of view, lecithin is universally usable and practically indispensable for certain applications.

Although considerable literature has become available in recent years referring to the specific properties and benefits of phospholipids, the last books devoted to the scientific and technological principles of the production, processing and use of lecithins in general were – as far as we know – published back in the 1990s. So, the editors, who work with lecithin day in, day out, felt it was important to publish an updated overview of the subject.

The history, technical development and current status of lecithin as a product are very closely bound up with the market situation and changes in our society. Precisely this is the topic of the first chapter of the book. The theoretical principles – the chemical, physiological and physical properties of phospholipids that constitute the basis for understanding the book – are explained in the second part. This is followed by the practical section which deals in considerable detail with the origins, production, processing and modification of lecithin. A very important element of the production process is quality control by chemical, physical and further analyses which are covered in the next chapter. The subsequent descriptions of the numerous applications of lecithin in the food, nutrition, feed, pharmaceutical, cosmetic and technical industries make up the core of the work.

The book “Phenomenon of Lecithin – Science, Technology and Applications” is intended as a source of information not only for both scientists and technologists involved in production, research and development, and quality assurance but also for everyone who works with lecithin or wishes to do so.

I wish to thank the numerous renowned and internationally acknowledged experts in the fields of lecithin research and lecithin applications who agreed to contribute chapters to this book. My thanks also go to my co-editors, Parris Kidd and Rüdiger Ziegelitz, for their valuable cooperation.

In particular, I wish to thank Volkmar Wywiol who initiated the book project and gave it his active support.

Waldemar Buxmann
Hamburg, April 2021

Phenomenon of Lecithin
Science | Technology | Applications

An initiative of Sternchemie on the occasion of the 40th Stern-Wywiol Gruppe anniversary.
www.sternchemie.com

Editors Waldemar Buxmann, Paris Kidd, Volkmar Wywiol, Rüdiger Ziegelitz
English translation Marion Braase, Wieners+Wieners GmbH, Hamburg
Proofreading Sternchemie, Paris Kidd, Wieners+Wieners GmbH, Hamburg
Layout & Design sachdesign, Hamburg
Photos & Illustrations Sternchemie, sachdesign
Project coordination Tina Höhne, Marketing Sternchemie

Publisher
Robert Wenzel
An der Alster 81, 20099 Hamburg, Germany
www.robert-wenzel.de

Production & Print
AlsterWerk MedienService GmbH
www.alsterwerk.com

1st edition 2021

ISBN 978-3-9820751-3-6

Library of Congress Control Number: 2021939002

Distributor
Taylor & Francis Group, LLC
Suite 300, 6000 Broken Sound Parkway, NW
Boca Raton, Florida 33487, United States
www.taylorandfrancis.com

CRC Press
Taylor & Francis Group

Contents

6 Application of Lecithin in Food

6.1 Interactions of phospholipid fractions with the surfaces of solids

Dana Middendorf, Ute Bindrich

The production of foods may involve combining a wide variety of ingredients into greatly differing substance systems. The resulting dispersed, multiphase systems fall into three broad categories: foams, emulsions and suspensions. They each consist of a continuous 'outer' phase and a dispersed 'inner' phase which may be solid, liquid or gaseous (see Table 1).

Table 1.
Selected examples of dispersed multiphase systems.

Food	Dispersed system	Dispersed phase	Continuous phase
Whipped cream, ice cream, beaten egg white	Foam	Gaseous	Liquid
Mayonnaise, milk, dressing	Emulsion	Liquid	Liquid
Hazelnut spread, ice cream	Suspension	Solid	Liquid
Meringue, bread, marshmallows	Solid foam	Gaseous	Solid
Butter, margarine	Solid emulsion	Liquid	Solid
Chocolate	Solid suspension	Solid	Solid
Muesli, sugar, starch	Loose bulk	Solid	Gaseous
Spray (mist)	Aerosol	Liquid	Gaseous

If the relevant quality attributes of foods are to be maintained over a considerable time, their structures must have a certain degree of stability. In this connection, phospholipids play a significant role. Mixtures of phospholipid fractions are often known as lecithin. In the case of emulsions, complexes of proteins and phospholipid fractions adsorb to the surface of the dispersed droplets, reduce the surface tension and increase the repulsive electrostatic and steric forces, thus preventing coalescence and phase separation. In the case of suspensions, the stability is largely determined by processes on the boundary of the dispersed phase. Here, too, adsorption of phospholipids at the surface of the particles has a stabilizing effect, influencing the interactions between particles that result in agglomeration and phase separation (see also Fig. 1).

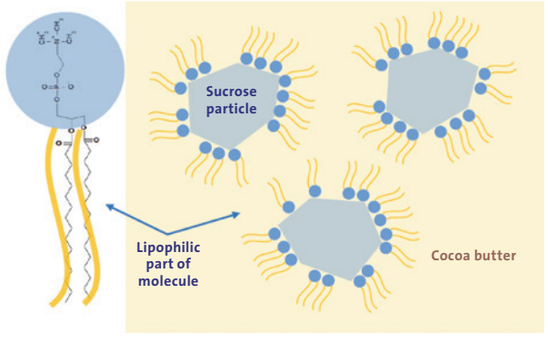

Figure 1.
Diagram showing the functionality of emulsifiers in lipophilic suspensions, taking phosphatidylcholine as an example.

Examples of suspensions in foods include fondant, nougat and also chocolate. In these systems the dispersed phase consists mainly of sugar, cocoa and/or dried milk particles. The nature of these particles and their interactions with each other and with the continuous phase is therefore extremely important for maintaining the quality of the foods.

As already described, the interaction of phospholipids with the surfaces of solids plays an important role in stabilizing suspensions. The atomic force microscope (AFM) offers a diversity of possibilities for characterizing the surfaces of particles (1,2).

In the AFM, the surface of a sample is passed line by line under a probe tip on the end of a cantilever with the aid of a piezoelectric scanner. The cantilever is deflected according to the forces interacting between the probe tip and the surface of the sample – on a vertical plane (attractive or repulsive interaction) or on a horizontal plane (lateral forces, e.g. friction). The deflection of the cantilever is recorded using a laser beam focused on the end of the cantilever and reflected onto a photodiode divided into four segments (3). The deflection of the cantilever on the vertical plane, and thus the difference between the upper and lower segments, results in a topographic signal. The structure and principle of the AFM enable three-dimensional detection of surface characteristics down to the Ångström range (molecular resolution). Besides recording surface topography (imaging modes) it is possible to determine other properties such as viscoelasticity, friction and also the surface charge, surface polarity and layer thicknesses. Spectroscopic measurements of forces are also possible (4,5).

6.1.1 Interactions with sucrose

Dana Middendorf

6.1.1.1 Structure of the boundary layer

Sucrose is used in foods for other reasons besides its sweetness. In bakery products and confectionery, especially, sugar plays an important role in forming the structure of the food matrix and in chocolate, for example, it constitutes the dispersed phase to which the surface-active substances are adsorbed.

Sucrose itself has a crystalline structure in the shape of layers. The AFM can detect these molecular structures in detail. The fractured surface of a sucrose crystal and a height profile of its topography are shown in Fig. 2. In this particular case, the height of a layer of the crystal is 23 Å (see Fig. 2 b). That corresponds approximately to the height of two unit cells of sucrose and illustrates the molecular resolution of these images (6).

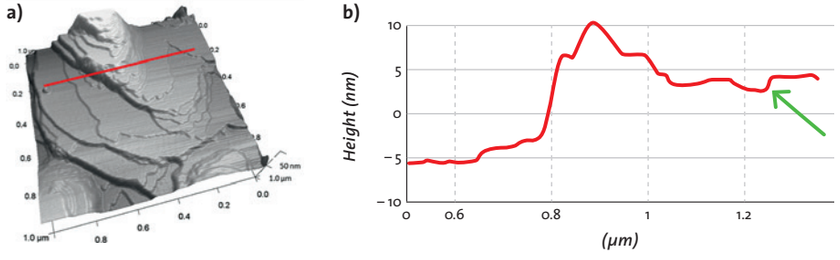

Figure 2.
a) Topography of the fractured surface of a sucrose crystal;
b) Height profile of the topography at the marked position in a).

Changes in the surface of the sugar particles brought about by the adsorption of phospholipids were investigated using model suspensions of cocoa butter and sugar. As in the production of chocolate, 0.5% soy lecithin based on the sucrose content was added to the cocoa butter phase. The sugar was then ground in a ball mill and the model suspension subjected to a conching process during which the emulsifier was adsorbed to the newly formed fractured surfaces (7,8). A suspension without the addition of the emulsifier was made up as a reference.

As a first step, the adsorption of the phospholipids to the interface between the sugar and the cocoa butter was determined with the aid of confocal laser scanning microscopy (CLSM) (9). To permit this, the phospholipids were coloured selectively with a fluorescent dye and activated with a laser beam (helium-neon laser) so that they emitted light with a specific wavelength. This emitted light was recorded pixel by pixel in the observation plane. However, the dye did not react with the sugar particles, which therefore appeared as grey-black spots. A CLSM image of phospholipids adsorbed to sugar particles is shown in Fig. 3.

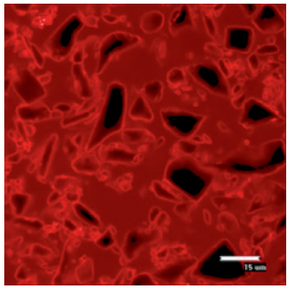

Figure 3.
CLSM image of phospholipids (red) adsorbed to ground sugar particles (grey-black).

This boundary layer was then characterized in greater detail by AFM. Fig. 4 shows that the surface of the sugar particles has undergone radical changes through adsorption of the phospholipids from soy lecithin. The surface no longer contains step-like structures like those previously observed on the fractured surface of a sugar particle (see Fig. 2). The surface topographies now appear less sharply contoured and look much smoother.

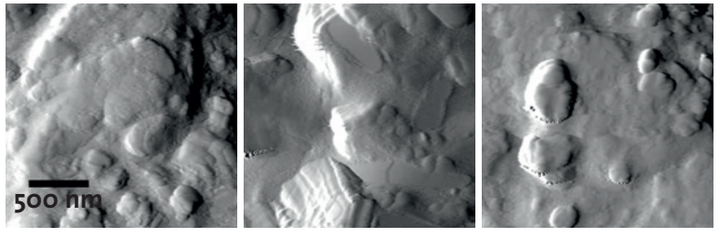

Figure 4.
Typical AFM surface topographies of sucrose ground in a ball mill and in the presence of soy lecithin; after (10).

So-called force – distance curves, which can also be recorded with the aid of AFM, can be used as a further means of characterizing the changes in particle surfaces brought about by the adsorption of emulsifiers (10). To do this, the probe tip is brought closer to the surface of the sample until contact is achieved. The direction of movement is then reversed and the tip drawn away from the sample. The adhesive force occurring between the probe tip and the sample in the course of this process can then be depicted as a function of the distance between the surface of the sample and the tip (see Fig. 5 left). Furthermore, force – distance curves can be strung together in the form of a scan and combined into a chart (see Fig. 5, top right). The values for local adhesion are then converted into colour values, and these are likewise combined to form a chart. In this way it is possible to produce a diagram showing the local degree of adhesion at the surface of the sample. Finally, the force charts can be used to calculate histograms in which the frequency of certain forces in a defined area of the surface is depicted (see Fig. 5 bottom right).

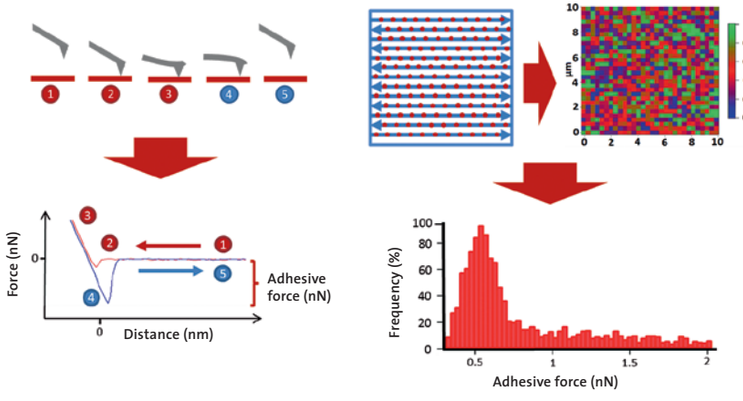

Figure 5.
Force – distance curve, measured by AFM; for explanations see text.

Fig. 6 now shows some frequency distributions typical of the condition of the surface of sugar particles ground in a ball mill without adsorbed phospholipids. The adhesive forces between the probe tip and the surface are in the range of 5 to 50 nN; at 10 to 40 nN (e.g. blue bar), the distribution of the forces in the surface area shown on the left is slightly narrower than in the area on the right, where it is 15 to > 50 nN (e.g. red bar).

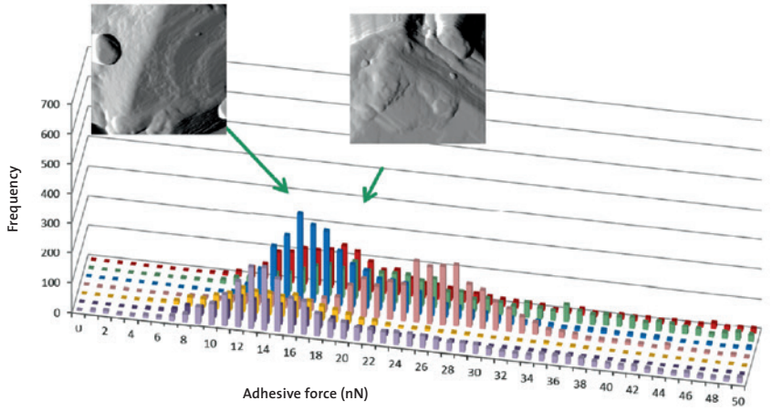

Figure 6.

Histograms from the force charts of AFM measurements of sucrose particles ground in a ball mill; size of scan: 1 × 1 µm.

Fig. 7 shows the histograms derived from the force charts of the surfaces of the sugar particles coated with soy lecithin. When compared directly with the surface of the uncoated particles, the relevant area of the forces is now considerably wider (up to > 100 nN). Moreover, it can be divided into several sections: the bottom section represents forces of 10 to 30 nN, the middle section those between 20 and 60 nN, and the forces in the top section are from 40 to about 100 nN, in some cases even greater. The narrower distribution in the bottom section corresponds to that found on uncoated particle surfaces. The position of the distributions in the middle and top sections shows that the adhesive properties of the surfaces of the sugar particles have changed substantially through adsorption of the emulsifier. The fact that it is possible to differentiate between these areas may be interpreted as indicating the different phospholipid fractions and fatty acid groups with differing degrees of adhesion between the probe tip and the surface of the sample.

The coating of the surfaces of the particles with emulsifiers can be calculated from the difference between the quantity of emulsifier added and the concentration of the emulsifier still detectable in the lipophilic phase after conching of the suspension. This difference is set in relation to the surface of the particles, which can be determined by laser diffraction. For coating of the surface of the sugar particles with soy lecithin, this calculation results in a value of 2.8 mg lecithin per m² of surface area, corresponding to 98% of the quantity of lecithin used.

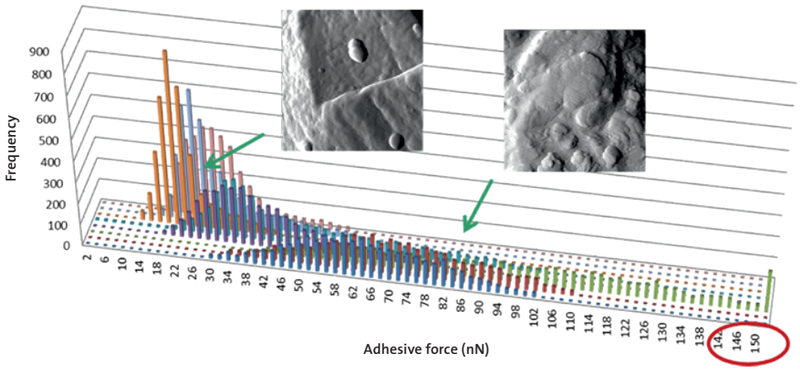

Figure 7.

Histograms from the force charts of AFM measurements of sucrose particles ground in a ball mill (ball diameter 1.5 cm) and coated with soy lecithin; size of scan 2 × 2 µm.

Besides the coating of the surface, the thickness of the layer of emulsifier can be determined. To achieve this, the force – distance curves recorded by AFM are used again. On the basis of these curves it is possible to determine the depth to which the probe tip has penetrated a surface coated with the emulsifier and then estimate the thickness of the coating.

The depth of penetration results from the difference between the force – distance curves for approach and withdrawal of the tip of the probe while this is in contact with the surface (see red double-arrow in Fig. 8, left). In the case of a particle surface coated with emulsifier, the cantilever is therefore immersed deeper on its way out (blue line) than on the way in (red line). This results in a difference of, for example, 34 ± 2 nm as a measurement of the thickness of the coating of soy lecithin (10,11). The standard deviation can be calculated from the difference measured on an uncoated surface (see Fig. 8, right).

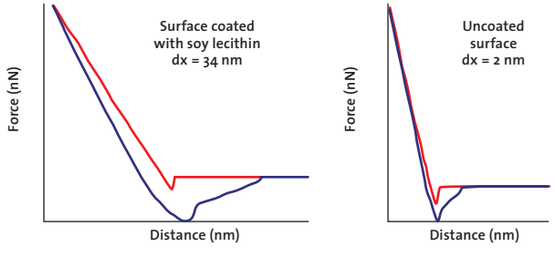

Figure 8.

Force – distance curves from an AFM force chart of a particle surface coated with soy lecithin (left) and an uncoated particle surface (right).

6.1.1.2 Mechanisms of phospholipid adsorption

The process of adsorption of soy lecithin in a lipophilic suspension was investigated more closely on the molecular level with the aid of phosphatidylcholine (PC), the main component of lecithin. To do so, a fractured surface of sugar particles was prepared for AFM measurement in a phase consisting of liquid cocoa butter. The local changes in the condition of the surface were then determined on an area of 10 × 10 µm before and after adsorption of the PC. The AFM topography of the surfaces and the corresponding force charts are shown in Fig. 9 a) to c).

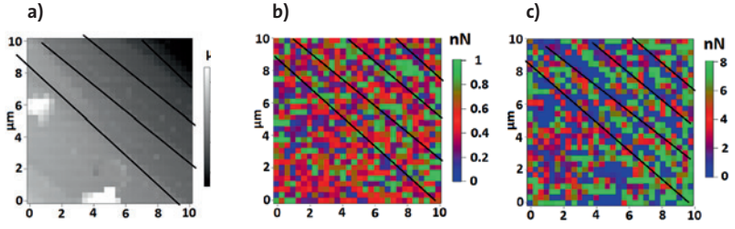

Figure 9.

Changes in surface adhesion brought about by application of the emulsifier PC to a sucrose surface (see also Fig. 2 a); the steps in the surface are indicated by diagonal lines. a) Topography, b) chart of adhesion before and b) after the addition of PC (AFM).

Fig. 9 a) first shows the topography of the surface of the sample. The black lines drawn on it indicate the steps in the structure already described (see Fig. 2 a). The corresponding adhesion of this surface is to be seen in Fig. 9 b). The position of the steps is again indicated by black lines but does not correlate with the distribution of the forces on this surface. The spectrum of the adhesive forces in the chart ranges from 0 to 1 nN. Fig. 9 c) shows the condition of the surface after adsorption of the PC to the surface of the sucrose particles. Here, too, the step-like pattern is indicated by the black lines. However, a connection can now be seen with the colour pattern of this chart, and the force range of the spectrum is wider. It now extends from 0 to 8 nN. A comparison of the charts shows that the changes in the adhesive force tend to be in the flat areas of the surface, whereas the forces in the area of the steps in the crystal have changed only slightly or not at all. A consideration on the molecular level shows why it is quite plausible that the emulsifier adsorbs to the flat areas rather than the steps. Fig. 10 shows the three-dimensional structure of the sucrose in the unit cell of the crystal, which is made up of two sucrose molecules. The atoms of the molecule are indicated by different colours (light grey: hydrogen, red: oxygen, dark grey: carbon). The illustration makes it clear that the surface of the particle is made up largely of the oxygen atoms of the molecule.

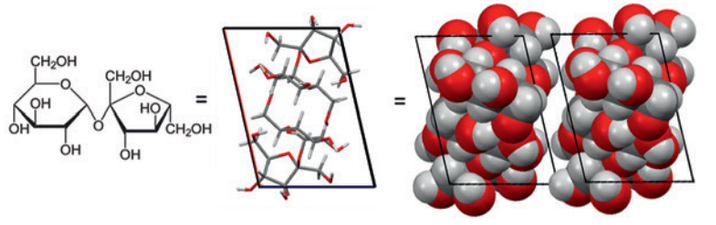

Figure 10.

Molecular structure of sucrose. Left: structural formula; centre: two sucrose molecules arranged in the unit cell; right: three-dimensional representation of the atoms as a ball model (Mercury 3.0, CCDC, Cambridge, UK; data base after Brown and Levy (12), accessible online at http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/platon-spek/pub/special/.cif; last accessed on 17 May 2018).

Because of the free electron pairs of the oxygen atoms, interaction with the positively charged head group of the PC is advantageous (see Fig. 11 a). A different view of the three-dimensional model of the sucrose molecule shows that the positively polarized carbon and hydrogen atoms tend to be on the 'edges' of the crystal (see Fig 11 b). Interaction with the positively charged head group of the PC is not very likely; it might rather be classified as repulsive. Moreover, adsorption of PC in the vicinity of the edges is much more difficult for steric reasons.

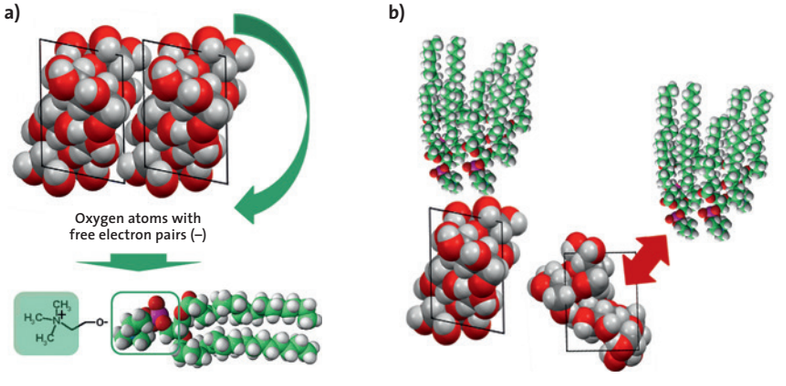

Figure 11.

a) Interaction of the PC head group with the surface of the sucrose molecule; b) comparison of interactions on the surface with interaction at a broken edge. Illustration of the lecithin molecule by kind permission of Avanti Polar Lipids, Inc.; for explanations, see text.

In further tests using AFM, the time frame was now investigated in which PC is adsorbed to the surface of the sucrose particles. For this purpose, a fractured surface of a sugar particle was prepared in a liquid phase of cocoa butter, and several force charts of one and the same area were recorded (13). PC was then injected into the liquid cocoa butter in the measuring cell. Distribution was controlled entirely by diffusion; active mixing was not possible because of the experimental set-up and the measuring principle of the AFM. Force charts were then measured in the same area.

Fig. 12 shows the changes in the distribution of surface adhesion in a surface area of 10 × 10 µm as a function of time. Initial changes in the distribution of the forces took place approximately two hours after injection of the PC into the AFM measuring cell. The frequencies in the range of forces below 2–3 nN decreased; the spectrum was initially widened to a range of about 8 nN. Over the course of time the distributions widened further, until an equilibrium was reached after about 10–11 h. This equilibrium was characterized by a continuous process of adsorption and desorption of the PC molecules; the distribution of the adhesive forces shown in Fig. 12 remained unchanged, but local changes in adhesion to the surface of the sucrose particles were observed (see force charts in Fig. 13).

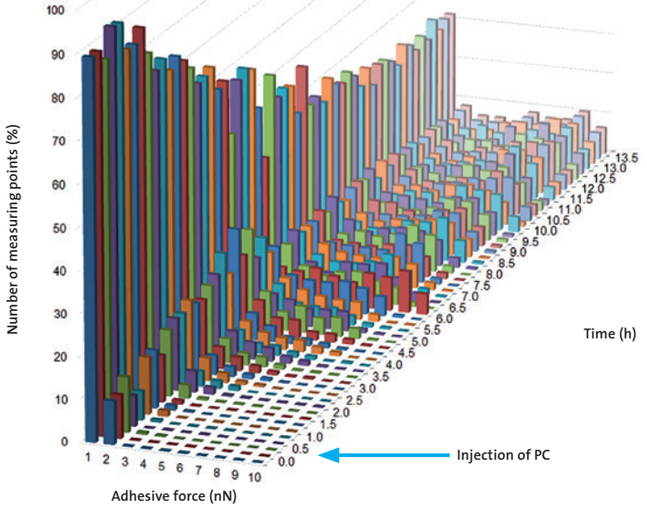

Figure 12.

Changes in the distribution of adhesion to the surface of a sucrose crystal (AFM) after injection of a solution of phosphatidylcholine and cocoa butter as a function of time; times of injection are marked with an arrow.

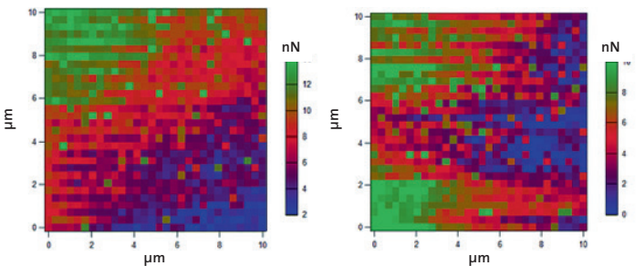

Figure 13.

Two AFM force charts recorded in a state of equilibrium after a period of 12 h; the time between two measurements is approx. 15 min. For explanations see text.

It is very probable that these simultaneous processes of adsorption and desorption of the PC also take place during conching of liquid chocolate masses, for example. But in this case a much shorter time up to the establishment of a state of equilibrium is to be expected because of active mixing of the suspension. This assumption was confirmed by CLSM images of sugar particles with marked phospholipids after different conching times (see Fig. 14). Immediately after grinding, sugar particles in an unconched suspension a) showed very irregular coating of the surface with the phospholipids. As the conching process continued, the phospholipid film became increasingly regular, as shown especially in Fig. 14 d).

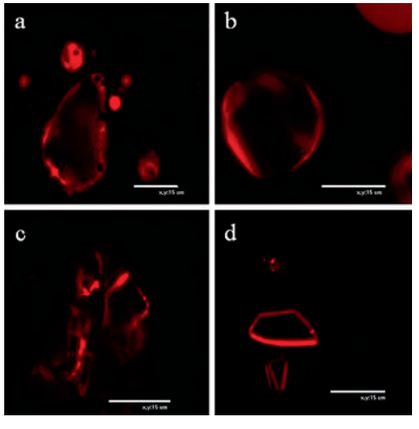

Figure 14.

CLSM image of finely ground sugar particles with coloured phospholipids after different conching times of a suspension of sugar and cocoa butter; a) without conching, b) after 1 h, c) after 2 h and d) after 2:45 h.