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Hole and vacuole formation during drying of sessile whey protein droplets

Jacob Bouman [a,c], Paul Venema [a], Renko J. de Vries [c], Erik van der Linden [a], Maarten A.I. Schutyser [b,*]

[a] *Laboratory of Physics and Physical Chemistry of Foods, Wageningen University, Axis-X, Building 118, Bornse Weilanden 9, 6708WG Wageningen, The Netherlands*
[b] *Laboratory of Food Process Engineering, Wageningen University, Axis-X, Building 118, Bornse Weilanden 9, 6708WG Wageningen, The Netherlands*
[c] *Laboratory of Physical Chemistry and Soft matter, Dreijenplein 6, 6703 HB Wageningen, The Netherlands*

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ABSTRACT

Morphological development from droplet to particle during drying has strong influence on powder structure and functionality. We study the evolving morphological properties of whey protein droplets during single sessile droplet drying experiments as a well-defined model for spray drying. Sessile drying droplets were visualised with a camera and subjected to varying drying conditions such as temperature, initial protein concentration, presence of airflow and droplet rotation. The final particles were imaged by SEM and X-ray tomography. Under all conditions used, the droplets initially shrink steadily while at a specific point a hole nucleates. Subsequently, a vacuole develops until a rigid hollow particle is obtained. The location of the hole was found strongly dependent on the presence and the direction of the applied air flow. We hypothesise that in the early drying stage a skin forms, which becomes more rigid when the hole nucleates. The hole forms at the position where the local modulus of the skin layer is minimal and/or at the point below the skin where the local pressure is minimal, and that after the hole has nucleated, the vacuole develops mainly by evaporation of water through the hole.

1. Introduction

Drying processes do not only remove water, but also have large influence on final product properties. Simple models for industrial drying processes can be used to gain detailed insight into various aspects of drying. For example, the drying behaviour of thin films has been studied to examine the influence of drying conditions on product properties such as film stiffness, flexibility and permeability (Alcantara, Rumsey, & Krochta, 1998; Denavi et al., 2009; Jooyandeh, 2011). Also, the drying of single droplets has been investigated in relation to the properties of powders prepared by spray-drying (Alamilla-Beltrán, Chanona-Pérez, Jiménez-Aparicio, & Gutiérrez-Lopez, 2005; Fang, Rogers, Selomulya, & Chen, 2012). Droplet drying during spray drying involves dehydration and solidification, which may be accompanied by the development of various mechanical stresses. These processes are believed to have a significant impact on the final product properties and in this way co-determine the optimal conditions for a spray drying process that provides both stable operation and the required product quality.

During drying, removal of solvent becomes increasingly difficult because the matrix from which the solvent has to be extracted both concentrates and solidifies. The increase in rigidity of the matrix during drying is crucial, since it has a large influence on particle morphology, which in turn is an important determining factor for attributes of the final powder such as particle size, bulk density, and reconstitution behaviour (Hassan & Mumford, 1996; Vehring, Foss, & Lechuga-Ballesteros, 2007; Walton & Mumford, 1999b).

In industrial spray drying processes, many droplets are dried simultaneously with a large distribution in droplet size, residence time and temperature history. Such processes are not well suited to gain insight in the underlying mechanisms of drying. Instead, many studies employ single droplet drying experimentation to study droplet drying under well-defined drying conditions (Adhikari, Howes, Bhandari, & Truong, 2000; Schutyser, Perdana, & Boom, 2012). Different single droplet drying approaches have been developed, such as acoustic levitation (Fu, Woo, & Chen, 2012), pending or suspended droplet (Walton & Mumford, 1999a; Sadek et al., 2013), and sessile droplet drying (Perdana, Fox, Schutyser, & Boom, 2013). These techniques have been used to characterise drying kinetics (Chen & Lin, 2005), enzyme inactivation (Perdana, Fox, Schutyser, & Boom, 2011; Yamamoto & Sano, 1992), protein denaturation (Haque, Aldred, Chen, Barrow, & Adhikari, 2013) and the final particle morphology (Walton, 2000). Most single droplet studies do not focus on visually monitoring and investigating the development of particle morphology. One recent study focuses on the morphology during drying of whey protein using a pending single droplet approach (Sadek et al., 2013). While this study provides interesting data on the drying of droplets in stagnant air, it is less representative for spray drying. For mimicking spray drying, a convective airflow should be applied, as was done in a previous study that used sessile droplets (Perdana et al., 2013). In this approach a sessile droplet is

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* Corresponding author.
E-mail address: maarten.schutyser@wur.nl (M.A.I. Schutyser).

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positioned on a hydrophobic surface to retain the spherical droplet shape and subsequently the droplet is dried with a convective air flow at a set drying air temperature and relative humidity. The latter parameters are known to affect particle morphology (Fang et al., 2012; Gaiani et al., 2010; Vehring et al., 2007), which we monitored with a camera during drying.

The objective of this study is to exploit the sessile droplet drying platform to characterise particle morphology development during drying of whey protein isolate droplets. Whey protein isolate (WPI) was chosen as a model system for protein drying, as it is a well-characterised protein product and it is applied as an ingredient in a wide range of foods. Morphological changes were studied as function of several drying parameters such as air temperature, airflow, and initial droplet protein concentration. Fully dried protein particles were then subjected to more extensive imaging using scanning electron microscopy (SEM) and x-ray tomography (XRT). We find that a key event in the drying is the formation of a hole, from which subsequently, a vacuole develops. Finally, based on our experimental observations, we hypothesise on the physical mechanisms behind the sequence of events that we observe for WPI droplet drying.

2. Materials and methods

2.1. Sessile droplet drying experiments

Protein solutions were prepared by adding whey protein isolate (WPI) powder (Davisco Foods International Inc. Le Sueur, MN, USA) to de-mineralised water. The solutions were prepared at concentrations of 5, 10, 20 and 30% (w/w). Sessile droplets were deposited on a hydrophobic surface using a micro-dispenser as described by Perdana et al. (Fig. 1) (Perdana et al., 2011, 2013). The hydrophobic surface consists of a polypropylene membrane (Akzo Nobel Faser Ag., The Netherlands) positioned on a metal sample holder. The droplet was dried by temperature-controlled air streaming from the tunnel. The temperature at the droplet position was monitored with a thermocouple Type K (NiCr–NiAl; RS Component, United Kingdom). A µEye 1480ME CCD camera (Imaging Development Systems GMBH, Germany) is used to image the droplet shape during drying. Experiments were performed using dry air (relative humidity RH = 0%) heated to temperatures, near the droplet, between 20 °C and 80 °C with a streaming velocity of the air of about 0.20 m/s. Image analysis on the data was performed using imageJ.

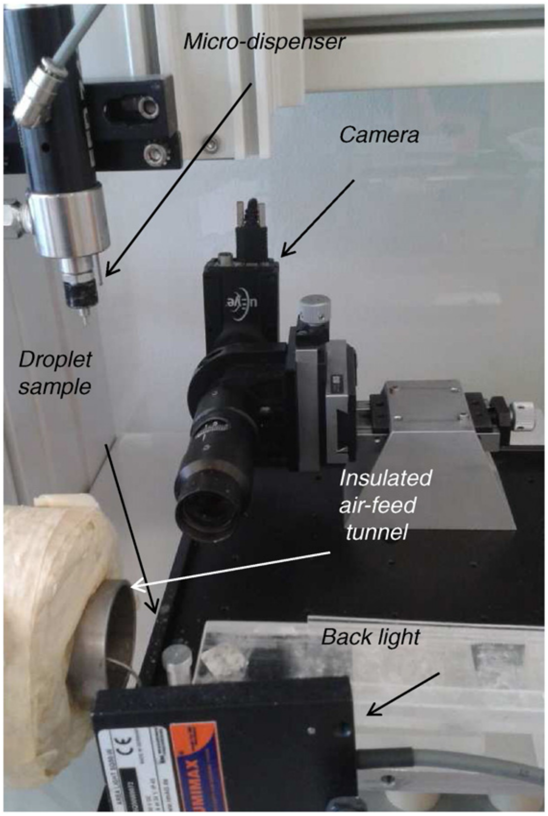

Fig. 1. The experimental set-up used for drying of sessile single droplets.

2.2. Laboratory-scale spray drying experiments

Similar to the sessile droplet drying experiments solutions were prepared at concentrations of 20% (w/w). The liquid samples were spray dried in a Buchi B-290 spray dryer (Buchi Labortechnik AG, Switzerland). Dry air (RH = 0%) was used while the inlet and outlet spray drying temperature was set to 160 °C and 80 °C, respectively.

2.3. Droplet analysis, microscopy and x-ray tomography

Images obtained during the droplet drying experiments were analysed with Image-J analysis software. Initial droplet shrinkage and subsequent vacuole formation were quantified to calculate initial evaporation rates. After the drying was finished, whey protein particles were collected and studied using a Phenom G2 pure desktop electron microscope. Additionally, XRT images were taken using a Phoenix v[tome]x m (General Electric, Wunstorf, Germany). This technique allows for non-invasive measurement of the 3D structure of objects at a spatial resolution of 1 µm. A 3D image of a fixed particle can be reconstructed from a large series of two-dimensional radiographic images taken around the axis of rotation (Herman, 2009).

3. Results and discussion

Time series of images of drying WPI droplets is shown in Fig. 2 for different drying temperatures. The droplets had an initial concentration of 20% (w/w) WPI and a radius of 0.5 mm. The temperature of the airflow was fixed. During the first stage of the drying process, the droplets just shrink, but after a while a hole nucleates or buckles inward at the downstream side of the air flow. Subsequently, it can be clearly observed that a front moves inwards into the droplet and a vacuole develops. Although the radius of the particle slowly continues to decrease, it is expected that the evaporation of water from the droplet is mainly taking place from the vacuole through the hole. After hole formation, the radius of the particle decreases much more slowly. This strongly suggests that hole formation is correlated with the formation of a more rigid skin at the surface of the droplet, and that hole formation occurs at spot where the rigidity of the skin is minimal and/or where the mechanical stresses are maximal. Eventually, a hollow particle is obtained with a rigid outer shell and a single hole. In the next sections we study the initial drying phase, the skin- and hole-formation phase, and the final phase of vacuole development and shell formation in more detail.

3.1. Initial drying

We observed that all air temperatures lead to a qualitatively similar morphological development including hole formation in the downstream direction of the airflow, the development of a vacuole and the final formation of a solid shell. First, images were analysed to determine the decrease in droplet radius until the moment of hole formation. In Fig. 3A the radius squared value of the droplets are shown for different temperatures and found to decrease linearly with drying time, thus