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Water migration through fat-based semi solid heterogeneous materials

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A B S T R A C T

Water migration through heterogeneous soft materials is central to many applications including oil recovery and consumer product stability of foods and cosmetics. This slow water transport affects all material properties such as mechanical, optical and electrical, but its understanding and modelling remains challenging due to complex wetting and diffusion processes across the heterogeneous material. Here, we study experimentally the penetration of water through a soft composite with hydrophobic (fat) and hydrophilic (salt) components. Conductivity measurements indicate the emergence of a percolating water network above critical water and salt volume fractions. This is corroborated by mechanical measurements revealing a concomitant stiffening of the material due to proliferating water bridges. Simulations of water absorption at spherical inclusions confirm this scenario and show the underlying cluster growth and percolation process.

1. Introduction

The process of water migration is central to the existence of life on Earth. Understanding and controlling the processes of water permeation through complex, composite networks is also of key importance for many industries like oil recovery, civil engineering, agronomy and foods. It plays a key role in determining the properties of many consumer products such as foods and cosmetics. The slow absorption or expulsion of moisture can significantly affect products from chemical, physical and ultimately microbial point of view, which in turn can impact product shelf lifetime, product performance and ultimately consumer liking (Damodaran and Parkin, 2017; Walstra, 2003). Exposed to ambient air, humidity can enter or leave the material; as moisture is exchanged at the surface, this process must involve a complex water transport process through the porous, heterogeneous material. Such water transport typically involves unsaturated liquid and vapor flows within the material, liquid-vapor phase changes, and vapor transfer from the material surface. Together, these processes lead to material aging on time scales of weeks or even months. The aging process concerns all material properties such as visual and tactile appearance and in particular its mechanical properties such as flow behavior and brittleness. Yet, experimental insight into this aging process, and into the underlying water permeation during the slow aging process is limited. In homogeneous materials, unsaturated liquid transport is described by an extended form of Darcy’s law, as has been studied in building materials (Gummerson et al., 1979; Hall and Hoff, 2009; Hall, 1977; Klute, 1952). Furthermore, in foods, the exchange of moisture has been modelled by effective moisture diffusivities (Guillard et al., 2003) fitted to experimental data, without however providing much microscopic insight of the transport process (Ramos-Cabrera et al., 2006). In particular, in complex consumer products that are typically composite materials consisting of both hydrophobic and hydrophilic components, it is not clear what governs the process of water permeation, and how this is related to the time-dependent properties of the material. This is despite their central importance to product processability (Althaus and Windhab, 2011; Horrobin, 1999) and stability. Understanding water permeation is also important for the swelling and mechanical properties of many hydrophilic/hydrophobic copolymer networks used medical devices, packaging or water storage applications (Xu et al., 2015; Zhao et al., 2019).

Here, we focus on a fat-based composite material, where the driving force for water migration is provided by an additional hydrophilic ingredient, salt. These fat-based pasty products are an essential part in food manufacturing, both as process intermediates or end products. Examples include chocolate spread, margarine, biscuits or bouillon cubes. Such materials are made of a continuous fat phase in which solid...
particles are dispersed, which typically have an affinity for water. The crystallization and deformation of the fat component on its own is a complex multilength-scale topic, which in simplified form ranges from molecular origin of complex triglyceride mixtures to kinetics of crystallization and structure formation on the nano- to meso-scales (nm to \( \mu \text{m} \)) that has attracted significant interest (Acevedo et al., 2011; De Graef et al., 2006; Hubbes et al., 2020; Jacobsberg and Ho, 1976; Kloek, 1998; Kloek et al., 2005; Narine and Maranongi, 1999; Tarabukina et al., 2009).

The presence of particles and moisture, either from the atmosphere, from particulate ingredients or by addition on purpose, is known to additionally affect the mechanical properties in intricate ways; yet, very few studies have characterized the influence of the solid particles on the final product (Thareja et al., 2013; West and Rousseau, 2017, 2018). In the case of a soluble crystalline component like salt, water will have the tendency to dissolve part of the crystals, especially at sharp edges, therefore affecting the size and shape of the crystals.

The mechanical properties of such soft composite depend sensitively on the moisture content and on the nature of how the particles interact with the water. In suspensions with a hydrophobic solvent, it has been shown that water can form capillary bridges between the particles, drastically changing the structure of the suspension (Bosillier and Kooi, 2016; Dittmann et al., 2012; Domenech and Velankar, 2015; Koo et al., 2012) as it starts to form a full network. At the end, as little as 0.5 % of water could greatly affect the properties of the suspension such as its complex modulus. Similar experiments have been conducted on food suspensions (Hoffmann et al., 2014; Scholten, 2019) with similar results. While in these studies, the continuous hydrophobic phase was a Newtonian liquid, however, in many food products such as the material under investigation here, the continuous phase is viscoelastic. The question is then how the composite material behaves mechanically, and how these properties are determined by the water transport through the material.

In this paper, we focus on the permeation of water in a two-phase material consisting of a continuous fat phase and solid inclusions. In order to achieve a relatively well-defined system which is also practicably relevant, a high melting fat (Palm Oil stearin, POs53) is selected, of which its thermal and mechanical prehistory was experimentally controlled, and in which the mobility of water is inhibited (Nelis et al., 2019) by the high amount of solid fat (N\(_2\text{O} \approx 69 \% \)). As solid inclusions, we consider salt, which is hygroscopic, attracts water and behaves inert to the fat.

Conductivity measurements are performed to elucidate the water permeation process, as well as mechanical measurements to probe the existence of a permeating water network based on the mechanical response. Our results suggest that the “wetted” salt crystals form connected clusters, which grow and form larger networks that eventually percolate across the sample as the salt volume fraction is increased. Indeed, a simple percolation model based on absorption of the permeating water phase around randomly placed inclusions provides a good qualitative description of the conductivity measurements. This picture is supported by the observation of a sharp increase of the complex modulus at the critical salt volume fraction, revealing the formation of system-spanning capillary bridges. Long-term measurements at ambient air show that these can lead to drying-induced water transport to inhomogeneous water distribution, where the surface layers become more depleted in water than the bulk, which can have strong effect on the product properties and lifetime.

2. Material and methods

2.1. Samples

The samples consist of heterogeneous mixtures of a continuous fat phase with solid inclusion (salt particles) trapped in it. Palm oil stearin, POs53 (purchased from Sime d’Arby Unimills B.V., Zwijndrecht, the Netherlands), was used for the fat continuous phase. Palm oil stearin is a fraction of palm oil which is enriched in high melting triglycerides by fractionation. It has an iodine value of 36, solids content at 20 °C of 69 wt% as measured by NMR (Duynhoven and Goudappel, 1999), and a slip melting point of 53 °C, as provided by the supplier. Full details of the fat (N-line, fatty acid composition) are given in the supporting information. It was chosen because palm oil and notably its stearin fraction are a ubiquitous source of hard fat in the food industry for which these samples are model systems. The salt used was micro salt sodium chloride NaCl (Akoz Nobel, Deventer, the Netherlands). Its average grain size was measured with a Morphologi G3S setup by spreading a few thousands of salt grains on a plane. The Morphologi measures then the average size by taking pictures of all the grains and deriving a full distribution of their radii. The average grain size was found to be 500 μm, with 10 % of the grains being smaller than 310 μm, and 10 % of them being bigger than 590 μm. The density of the fat phase was measured with a densitometer DMA 45 at various temperatures. At ambient temperature, the density is found to be equal to 0.939 g/ml.

Fat-based composite samples with a range of water and salt volume fractions, \( \phi_{\text{water}} \) and \( \phi_{\text{NaCl}} \), and similar fat pre-conditioning, were prepared according to the following procedure: flakes of fat are initially melted at 90 °C and the resulting liquid phase is then poured on aluminum foils, placed on top of a stainless steel surface, where it crystallizes while cooling down quickly to room temperature and forming sheets of crystallized fat. The salt is poured in a kitchen mixer (Kenwood), equipped with a K-beater type of geometry, and gently mixed with the water during two minutes. The fat is then added into the mixer, and the slurry is mixed until the formation of a compact and solid paste. The mixing is then stopped, to prevent overworking and aeration of the paste. The slurry necessary to prepare cubes of dimension 23 × 28 × 11.5 mm is then individually weighed for each cube. The resulting amount is poured in a mold made of 20 rectangular holes of dimension (23 mm x 28 mm). The slurry is compressed at 3 MPa by a universal testing machine (Instron 5567) until the samples reach the desired height. After compression, the cubes are stored for 4 weeks at ambient temperature so that any post-crystallization and -hardening processes, which are to be expected after the mechanical treatment during mixing and compression, can have proceeded towards comparable quasi-equilibrium. After unmonths and 4 weeks of equilibration, the cuboids very slightly extended, such that their final size is 23.5 mm x 28.6 mm x 11.8 mm. For each salt volume fraction \( \phi_{\text{NaCl}} \), two batches of 20 cubes are prepared.

Upon exposure to water, the salt dissolves into brine, reducing the effective solid particle volume fraction. By assuming the theoretical maximal salt dissolution in water (Haynes, 2014), the theoretical effective volume fraction of salt which remains solid can be estimated. Doing so, we obtain that for the highest volume fraction of water (13 %), the remaining solid volume fraction of salt is 0.478 out of the initial amount of salt of 0.5. Thus, even for the highest water content, almost all of the salt is still in a solid, crystalline form. This however can significantly affect the size, shape and distribution of the initial salt particles. A detailed overview of the sample composition including the mass fraction of each phase and the amount of dissolved water for each \( \phi_{\text{water}} \) is given in the supplementary information.

2.2. Conductivity measurements

The global conductivity of the samples is measured with a TROTEC BM18 hygrometer. This device is designed to measure humidity in woods, based on their conductivity, and it is used here to measure the conductivity of our fat-salt composites. The hygrometer consists of two electrodes separated by 24 mm, and has been calibrated to give the conductivity in S.m \(^{-1} \). For calibration, the conductivity of a set of aqueous solutions with different concentration of dissolved NaCl is measured using a regular electrode and the hygrometer, and a conversion table is deducted.
Electrical conductivity probes the existence of percolated networks of conducting paths, in our case paths of electrolyte made up of water with dissolved salt. The conductivity is measured in a well-defined geometry using thick plate-shaped samples (diameter 80 mm, height 10 mm), in which the two electrodes of the hygrometer are dipped. For this set of measurements, $\phi_{\text{water}}$ is fixed at 0.03 and $\phi_{\text{NaCl}}$ varies from 0.2 to 0.5. To determine the probability of percolation, we repeat the conductivity measurements many times over the same distance, at different points of the sample. The percolation probability is then determined from the number of measurements where a measurable current could be detected, divided by the total number of measurements. Furthermore, to follow the evolution of the sample properties over time, these measurements are repeated after certain aging times: one day, one week, two weeks and 40 days after processing.

2.3. Scanning electron microscopy imaging

To get a more detailed microscopic picture of how the water is structured in the material, scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) analysis are performed on our ternary composites. The samples were frozen in slush liquid nitrogen to allow imaging under vacuum and planed in order to provide a smooth surface for EDX analysis. The SEM images were taken using back-scattered electrons (BSE) and characteristic X-rays. The former signal is strongly related to the atomic number of the compounds present, thus allowing distinction of sodium (Na) representing the salt, oxygen (O), representing the water, and carbon (C) representing the fat. While the latter signal allows identification of the composition and measurement of the abundance of the elements in the sample. Full details of the SEM sample preparation are described in the SI.

SEM images of a ternary mix with $\phi_{\text{salt}} = 0.5$, and a water volume fraction of $\phi_{\text{water}} = 0.1$, zooming into a region of two neighboring salt crystals are shown in Fig. 1. The red parts correspond to the water distribution, while blue and green colors represent the salt and fat, respectively. These pictures reveal the actual distribution of water in the crystals are shown in Fig. 1. The red parts correspond to the water dispersed in the fat (~10 μm), in which the two electrodes of the hygrometer are dipped. For this set of measurements, $\phi_{\text{water}}$ is fixed at 0.03 and $\phi_{\text{NaCl}}$ varies from 0.2 to 0.5. To determine the probability of percolation, we repeat the conductivity measurements many times over the same distance, at different points of the sample. The percolation probability is then determined from the number of measurements where a measurable current could be detected, divided by the total number of measurements. Furthermore, to follow the evolution of the sample properties over time, these measurements are repeated after certain aging times: one day, one week, two weeks and 40 days after processing.

2.4. Mechanical tests

We also study the mechanical properties of the water-permeated composite material. Since the conventional oscillatory rheology is ill suited for these types of samples due to their hardness leading to partial melting of the surface layer and to wall slip, micro indentation is used, in which a probe with a defined size and shape indents the material and the resulting force is recorded. Micro indentation is widely used in the study of small-scale behavior of soft materials such as polymers, biomaterials or food products (Ebenstein and Pruitt, 2006; Pharr et al., 2009; Van-Landingham, 2003). Here, we use the stress relaxation method which consists of applying an instantaneous displacement increment, and measuring the force relaxation over time. The well-known elastic response of indentation is given by Hertzian theory (Fischer-Cripps, 2004), which describes the deformation of a semi-infinite elastic plane indented by hemispherical elastic probe. In addition to this elastic response, our samples show highly nonlinear and nonreversible deformations. Several studies using different indenter shapes and protocols (Cheng and Cheng, 2005a, 2005b; Cheng and Yang, 2009; Cheng et al., 2006) have addressed the indentation behavior of visco-elastic samples theoretically, and derived predictive stress-strain relationships that depend on the shape of the probe and the viscoelastic properties of the material. From the derived relaxation results, it is possible to extract the storage and loss moduli with the help of a simple rheological model. For more information regarding such calculation, we refer the reader to (Cheng et al., 2006). To perform stress relaxation measurements, a Texture Analyser (TA instrument) is used, with a spherical-shaped probe made of stainless steel with a diameter of 6.35 mm. The indentation speed was set to 1 mm/s, the indentation depth to 0.5 mm, and the trigger to 5 g. Apart from Fig. 3a which shows typical curves from single experiments, results from Figs. 3b and 4 are obtained by averaging the results from measurements on 5 different samples (per point), with the error bars representing the associated standard deviation.

2.5. Monte Carlo simulations of water percolation

To obtain insight into the formation of percolating water networks,

Fig. 1. Scanning electron microscopy images of the ternary mixture for $\phi_{\text{water}} = 0.1$. The images show the contact zone between two large salt crystals, The colors indicate zones with high concentrations of Na, C and O, and therefore the location of salt crystals (NaCl, blue), water (O, red) and lipid phase (C, green). Black areas represent pockets of air trapped in the system.
we perform Monte Carlo simulations with sample dimensions and particle sizes corresponding closely to those of the experiments. Non-overlapping spherical inclusions are placed randomly throughout the sample, with a size distribution equal to the salt crystal size distribution determined experimentally. To mimic the water adsorption and wetting layer around the salt crystals, shells of thickness $t$ are then added around the inclusions. Because of their random distribution, some neighboring inclusions are closer than others. Neighboring inclusions with radii $R_i$ and $R_j$ are considered being connected if their centers are separated by less than $R_i + R_j + 2t$, meaning that their water layers start to overlap. At a given water layer thickness $t$ therefore, some neighboring inclusions are connected, while others are not. With increasing $t$ and inclusion volume fraction, the number of connected inclusions grows. Connected inclusions are then grouped into clusters using hierarchical clustering algorithms, and the size of each cluster is determined from the number of inclusions that are part of the cluster, i.e. the number of inclusions that satisfy the condition that their water layer overlaps with at least one other particle that forms part of the same cluster. Repeating this procedure for 10 simulations per volume fraction allows us to determine the distribution of cluster sizes, the mean and largest cluster size, and the probability of percolation, i.e. the probability that the largest cluster spans the entire field of view.

3. Results and discussion

The electrical conductivity at fixed amount of added water has been measured as function of salt concentration. For each sample, we perform measurements at different physical locations on the sample, and define the percolation probability as the ratio of the number of measurements that yield a measurable current, to the total number of measurements performed. The resulting percolation probability as a function of salt volume fraction at fixed amount of added water is shown in Fig. 2. A sharp conductivity onset is observed at a salt volume fraction $\phi_{NaCl}=0.275$. The transition from non-conducting to partially conducting samples is very distinct, occurring over a small $\phi_{NaCl}$ interval. This sharp transition reminds of the diverging network size in a percolation transition. We repeated the measurement after a week, two weeks, and 40 days, and found that the transition becomes slowly more gradual. The older the sample, the more gradual the onset of conductivity becomes, though even for the sample aged for more than a month, the probability rises closely to unity within a small interval from $\phi_{NaCl}$ = 0.3 to 0.4. This aging trend is confirmed in the actual conductivity of conducting samples as a function of age as shown in the inset. At intermediate salt concentrations, the samples show a clear drop of the conductivity over time, while at higher salt concentrations, they show a more stable conductivity, which however also drops after long aging time.

Another independent evidence of the water percolation comes from mechanical measurements. Previous studies have shown that the formation of water bridges can stiffen the material, as is well known from building sand castles with wet sand (Pakpour et al., 2012). In our viscoelastic samples, such properties can be measured through the stress relaxation of the sample upon the indentation of a spherical probe. To measure the stiffening effect due to the build-up of water bridges we keep the solid particle volume fraction fixed, and vary only the amount of added water in the material. We choose a salt volume fraction of $\phi_{NaCl}$ = 0.5, deep in the percolation regime, and $\phi_{water}$ ranging from 0 to 0.13. If the water had no effect at all on the structure of the system, it would simply replace the semi-solid fat, and the samples would become increasingly soft. However, we observe an intriguing nonmonotonic trend as shown in Fig. 3a. For $0 < \phi_{water} < 0.03$, the samples become more viscous and weaker with increasing water content, as evidenced by the faster decay of the force relaxation curves. Then, when $\phi_{water}$ is between 0.03 and 0.07, the samples become harder and also more elastic. Finally, upon further increase of the water content, the samples become extremely soft and the rate of non-reversible deformation rises strongly. This nonmonotonic behavior is most clearly shown in Fig. 3b, where we plot the ratio of the late-stage to initial force, $F(t=\infty)/F(t=0)$, also known as force conservation rate, as a function of the water volume fraction. The nonmonotonic behavior is clearly observed. We also show the results of the conductivity measurements on the same samples (blue stars, right axis). A clear correlation is observed: Initially, when the amount of water is low, no macroscopic conductivity is observed, and the material becomes weaker upon adding water as expected. This is understandable, since when there is not enough water, it is impossible to build a macroscopic path from one point to another, and, therefore, to conduct electricity. When $\phi_{water}$ reaches 0.03, a macroscopic conductivity starts to appear; simultaneously, the material starts to harden and increase in elasticity. The onset of both the conductivity and hardening indicate the appearance of percolating water bridges. Hence, at this point, the water capillary bridges form a connected structure that stiffens the material, in agreement with previous observations of capillary bridges reinforcing a soft composite structure (Acevedo et al., 2011; Jacobsberg and Ho, 1976). The coincidence in the onset of conductivity and stiffening shows that indeed both are related to the same phenomenon of network formation of water bridges. Upon further increase of the water content, the conductivity keeps rising as there are more and thicker percolative path, while mechanically, the material becomes softer and relaxes more due to the excess water content, which gradually lowers the effective volume fraction of the solid salt particles and of the semi-solid fat phase. (see supplementary information, table 1)

From these force-relaxation curves, the storage and loss moduli of the samples can be quantitatively derived assuming a simple rheological model for the relaxation. A previous study (de Cagny et al., 2019) showed that for such kind of materials, performing stress relaxation experiments at a depth of up to 1 mm allows us to remain in the linear regime of the mechanical deformation, and that the force relaxation curves can be fitted by a sum of three exponential decays, each with a different time constant and amplitude. In this case, a simple rheological model consisting of three standard linear solid elements in parallel is enough to describe the stress relaxation curves measured experimentally, see supplementary material. From this model, it is ultimately possible to derive the complex modulus as shown in Fig. 4. The values plotted here are for a frequency of $f = 1$ Hz. This time, it is possible to quantify the elastic deformation, and to show that a composite mix with $\phi_{water}$ = 0.07 water is more elastic and has a higher modulus than its water-poor counterpart. This clearly shows the effect of water bridges on
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actual non-spherical shape of the salt crystals, as well as possible partial spatial distribution of the particles, some neighboring particles are their spherical shells touch, corresponding to the formation of water to model the water wetting layer, see Fig. 5 a. The model neglects the fractions. A layer of fixed thickness connects, while other neighboring particles with larger distances do not closer than others, and at a given layer thickness fraction is chosen within the range of the experimental salt volume fraction determined experimentally, and the volume of connected structures diverges. These results correspond qualitatively well to the experimental data, lending credence to the hypothesis of a percolated structure. The simulations allow us to further elucidate the growth of the connected cluster. We plot the cluster size $S$ as a function of inclusion volume fraction in Fig. 5c. It grows sharply until it reaches the system size at a volume fraction of $\sim 0.4$ (for thick enough layers). Plotting the cluster size as a function of distance to the critical volume fraction $\phi_{\text{crit}}$, we find a divergence of the cluster size according to the scaling relation $S \sim (\phi_{\text{crit}} - \phi)^{1/\nu}$, where we determine $1/\nu = 2.2 \pm 0.2$, in agreement with predictions from 3D percolation theory (Fig. 5d). Some deviation from this critical divergence is observed for small $\phi_{\text{crit}}$ due to finite size effects. The specific value for the critical volume fraction $\phi_{\text{crit}}$ depends on the thickness of the water layers and the range over which they can form a capillary bridge, while the scaling exponent does not, as shown in Fig. 5 (d). Assuming water layers of 1 mm that form capillary bridges when the salt crystals are close enough for the water layers to touch, we find $\phi_{\text{crit}} = 0.45$. Boundary effects in finite-scale geometries like real consumer products will mean that a percolated network may already form at inclusion volume fractions below $\phi_{\text{crit}}$ for an infinite system, as can be observed in Fig. 5(a–c). We further stress that the layer thickness here is an effective thickness for complete wetting; future modelling should include the partial wetting of the salt crystals and their non-spherical shape.

To elucidate the water percolation process in more detail, we perform Monte-Carlo simulations of percolating water bridges. Samples with randomly distributed, non-overlapping spherical inclusions are generated. The size distribution of the inclusions is chosen to match the salt crystal size distribution determined experimentally, and the volume fraction is chosen within the range of the experimental salt volume fractions. A layer of fixed thickness $t$ is then added around each inclusion to model the water wetting layer, see Fig. 5a. The model neglects the actual non-spherical shape of the salt crystals, as well as possible partial wetting and coalescence effects that would lead to non-spherical shapes of the water shells. Neighboring inclusions are considered connected if their spherical shells touch, corresponding to the formation of water capillary bridges in the experimental system. Because of the random spatial distribution of the particles, some neighboring particles are closer than others, and at a given layer thickness $t$, these particles may connect, while other neighboring particles with larger distances do not connect yet. With increasing layer thickness or inclusion volume fraction, more and more particles connect, and clusters of connected particles grow, as shown in Fig. 5b. The evolution of networks formed from connected particles is then studied as a function of layer thickness and inclusion volume fraction. These simulations allow us to determine the size of connected structures, and the eventual percolation of the largest cluster across the system. We use clustering algorithms to identify interconnected points. In each cluster, a particle satisfies two conditions: firstly, it is connected to another particle in the cluster, secondly, there is no connection to a particle that does not form part of the cluster. The probability that two arbitrary points in the system are connected in the same cluster can thus be determined. The probability of a system-spanning network is plotted as a function of inclusion volume fraction for three different wetting layer thicknesses of 1, 1.2 and 1.4 mm in Fig. 5b. A sharp rise is found at inclusion volume fractions between 30 and 40%, similar to the experiments, indicating the rise of a percolating network. The similar onset and shape of the curves lend credence to the idea that the conductivity is indeed mediated by the occurrence of a connected water network localized at the inclusions. Increasingly larger structures form with increasing inclusion volume fraction, until, at a critical volume fraction, the size of connected structures diverges. These results correspond qualitatively well to the experimental data, lending credence to the hypothesis of a percolated structure. The simulations allow us to further elucidate the growth of the connected cluster. We plot the cluster size $S$ as a function of inclusion volume fraction in Fig. 5c. It grows sharply until it reaches the system size at a volume fraction of $\sim 0.4$ (for thick enough layers). Plotting the cluster size as a function of distance to the critical volume fraction $\phi_{\text{crit}} = \phi$, we find a divergence of the cluster size according to the scaling relation $S \sim (\phi_{\text{crit}} - \phi)^{1/\nu}$, where we determine $1/\nu = 2.2 \pm 0.2$, in agreement with predictions from 3D percolation theory (Fig. 5d). Some deviation from this critical divergence is observed for small $\phi_{\text{crit}}$ due to finite size effects. The specific value for the critical volume fraction $\phi_{\text{crit}}$ depends on the thickness of the water layers and the range over which they can form a capillary bridge, while the scaling exponent does not, as shown in Fig. 5 (d). Assuming water layers of 1 mm that form capillary bridges when the salt crystals are close enough for the water layers to touch, we find $\phi_{\text{crit}} = 0.45$. Boundary effects in finite-scale geometries like real consumer products will mean that a percolated network may already form at inclusion volume fractions below $\phi_{\text{crit}}$ for an infinite system, as can be observed in Fig. 5(a–c). We further stress that the layer thickness here is an effective thickness for complete wetting; future modelling should include the partial wetting of the salt crystals and their non-spherical shape.

3.1. Aging effects

When repeating the conductivity experiments after several days and weeks of aging, while storing the samples in water-tight boxes, we saw that the percolation threshold shifted to higher salt volume fraction (see Fig. 2), and the average conductivity decreased over time, especially at the percolation transition zone (inset of Fig. 2). A similar reduction of conductivity is observed when we monitor samples with varying initial water content, see Fig. 6a. For high water concentration, where the conductivity reaches a plateau, the conductivity drops by about a factor of 2. The most obvious explanation for this conductivity drop is water evaporation. We therefore monitored the weight of fresh samples of

![Fig. 3. Rheology of fat-salt-water composites.](image)

![Fig. 4. Complex modulus and phase angle extracted from the indentation curves of the ternary mixes with $\varphi_{\text{NaCl}} = 0.5$ shown in Fig. 3.](image)
may sensitively break connected paths so that already small water loss
loss of conductivity, which could happen on similarly long time scales,
distribution towards more hydrophilic regions may contribute to the
leads to a large loss of conductivity. In addition, internal water re-
be easily explained by the small water loss. This suggests that the drying
(by around a factor of two in the saturation regime), which still cannot
a clear conclusion. Also, both conductivities have dropped significantly
One way to verify this hypothesis is to compare the measured conduc-
ronments is needed to fully elucidate this drying process.

However, we note that the significant error bars do not allow us to reach
the same side (Fig. 6 d), suggesting water depletion in the surface layer.
(Fig. 6 c), after 40 days of drying, the trend of the data suggests the latter
conductivity to be higher than that measured with electrodes on
surface layer to dry more quickly than the bulk. Since the electrodes
measure primarily the conductivity close to the surface, the measured
conductivity drops faster as the surface layer becomes depleted in water.
One way to verify this hypothesis is to compare the measured conduc-
tivity with that using two electrodes placed on the two opposite sides of
the sample, which should give a better representation of the bulk con-
ductivity. Indeed, while initially, the two conductivities are very similar
(Fig. 6 e), after 40 days of drying, the trend of the data suggests the latter
(bulk) conductivity to be higher than that measured with electrodes on
the same side (Fig. 6 d), suggesting water depletion in the surface layer.
However, we note that the significant error bars do not allow us to reach a clear conclusion. Also, both conductivities have dropped significantly (by around a factor of two in the saturation regime), which still cannot be easily explained by the small water loss. This suggests that the drying may sensitively break connected paths so that already small water loss leads to a large loss of conductivity. In addition, internal water re-
distribution towards more hydrophilic regions may contribute to the
loss of conductivity, which could happen on similarly long time scales, without affecting the total water content in the samples. Further research under different storing conditions in different humidity envi-
ronments is needed to fully elucidate this drying process.

We note that the water loss observed here is nevertheless much larger than that measured in pure fat recently (Thareja et al., 2013). Comparing the water loss rates in our system with this study, it turns out that our system releases water more than two orders of magnitude faster than the pure fat networks, i.e. 400 mg over 40 days compared to less than 2 mg in 45 days. As the samples are of similar dimensions (centimeters), while the gradient in water activity is even lower in our system, we speculate that this difference in water evaporation rate reflects the different water permeation rates of the two materials. This again sug-
gests that moisture transfer in our system is facilitated by the permeating water bridges. Also, we note that the solids level in our fat phase is high, which would make the water migration through the fat phase even lower compared to systems presented in literature (Peng et al., 2020). Hence, the presence of a secondary continuous network due to the presence of salt is required to allow for the observed moisture migration and conductivity.

4. Conclusion

We have studied the effect of water permeation in binary mixes of viscoelastic fat and solid sodium chloride inclusions. The onset of macroscopic conductivity at salt and water volume fractions above $\phi_{\text{water}} \approx 0.03$ and $\phi_{\text{NaCl}} \approx 0.275$ indicates the emergence of a percolating water network mediated by the salt inclusions attracting the water. This conductivity onset is linked with an increase of the sample’s elasticity due to formation of water bridges. At low water content, the material first softens with increasing water volume fraction, while beyond a critical amount of water, it tends to harden and become more elastic, revealing the emergence of connected water bridges. This hardening of the material is qualitatively in line with the rheology measured for lubricated suspensions where the liquid phase is hydrophobic. Yet, compared to suspensions, the solid fat matrix has a significant elasticity.
itself (the elastic modulus of the order of $10^6$ Pa is comparable to what can be estimated as the maximum elasticity of a capillary suspension), contributing to a relative increase in the storage modulus in addition to the capillary bridging, making the mechanical response rather complex. The concomitant onset of conductivity and elasticity is a strong hint that a percolated water structure is formed in the material. Indeed, this is confirmed by Monte Carlo simulations of water absorption at spherical inclusions, showing percolation with an exponent consistent with 3D percolation theory. As the mechanism of capillary bridges and their effect on the rheological properties is a general phenomenon in food and non-food systems (de Vries et al., 2018; Koos and Willenbacher, 2011; Scholten, 2019; Strauch and Herminghaus, 2012), we speculate that the observed mechanism of water permeation may be more generally occurring in systems with three immiscible phases. Additional experiments on different three-phase systems, i.e. with other hydrophilic inclusions and other oil/fat phases are needed to elucidate this point.

Finally, the continuous decrease of the conductivity and percolation rate over long times is associated with a surprisingly small water loss; from weight measurements and surface versus bulk conductivity measurements, we conclude that the evaporation primarily dries the surface layer, while already a small water loss sensitively affects the conductivity, possibly by interrupting conductive paths.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


