J Am Oil Chem Soc
DOI 10.1007/s11746-016-2933-3

SHORT COMMUNICATION

Fat Crystals Influence Methylcellulose Stabilization of Lipid Emulsions

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Received: 18 August 2016 / Revised: 23 November 2016 / Accepted: 5 December 2016

Abstract Oil-in-water emulsions stabilized with methylcellulose (MC) varied in stability depending on the composition of the fat phase. When droplets were composed entirely of liquid oil, MC was able to form a continuous, protective film around the droplets. Therefore, when two liquid oil droplets were brought into contact, they underwent extreme shape deformation but did not coalesce, even when excess force was used. Subsequently, interfacial crystals extending into the aqueous phase from palm kernel oil droplets were aimed into an entirely liquid oil droplet. The MC-coated droplet would deform wherever the crystal contacted; however, the protruding crystals could not penetrate into the liquid oil droplet. Conversely, when the target droplet was composed of a small amount of solid fat that resulted in localized crystalline regions and the interfacial crystals of the second droplet were aimed at this region, they then easily pierced the droplet. This demonstrates that MC is an excellent stabilizer for liquid oil droplets but internal lipid crystals within fat globules can alter MC surface conformation to allow for crystal penetration and arrested coalescence.

Keywords Coalescence · Arrested coalescence · Partial coalescence · Lipid crystallization · Emulsion stability · Methylcellulose

Introduction

Micromanipulation is a technique that has been used to study coalescence behavior by manually bringing two fat globules into contact. Micromanipulators are fabricated from two capillary tubes in which the hydrostatic pressure can be changed to gently suction fat globules to the tip of each micromanipulator. This technique has been previously used with wax in hexadecane droplets, hexadecane droplets coated with silica particles, and droplets composed of natural fats [1–3].

A well-known theory of arrested coalescence, also known as partial coalescence, was first proposed by van Boeckel and Walstra [4]. This theory necessitates the presence of large lipid crystals protruding out of oil droplets into the continuous phase. Upon close approach, protruding crystal lances from one droplet can penetrate into a neighboring droplet, forming a bridge by which oil can be shared. Subsequently, an oil neck is formed that draws the two droplets together, yet the presence of solid fat will inhibit the droplets from fully coalescing [4–7]. No microscopic evidence of this event has yet been demonstrated.

The current study examines the role of methylcellulose (MC) in stabilizing oil droplets against coalescence. An oil droplet was contacted with either a second droplet or lance-like protrusions extending out of a second droplet. The resulting coalescence behavior, or lack thereof, was observed to understand the conditions that permit this stability to be overcome.

Electronic supplementary material The online version of this article (doi:10.1007/s11746-016-2933-3) contains supplementary material, which is available to authorized users.

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Published online: 18 December 2016

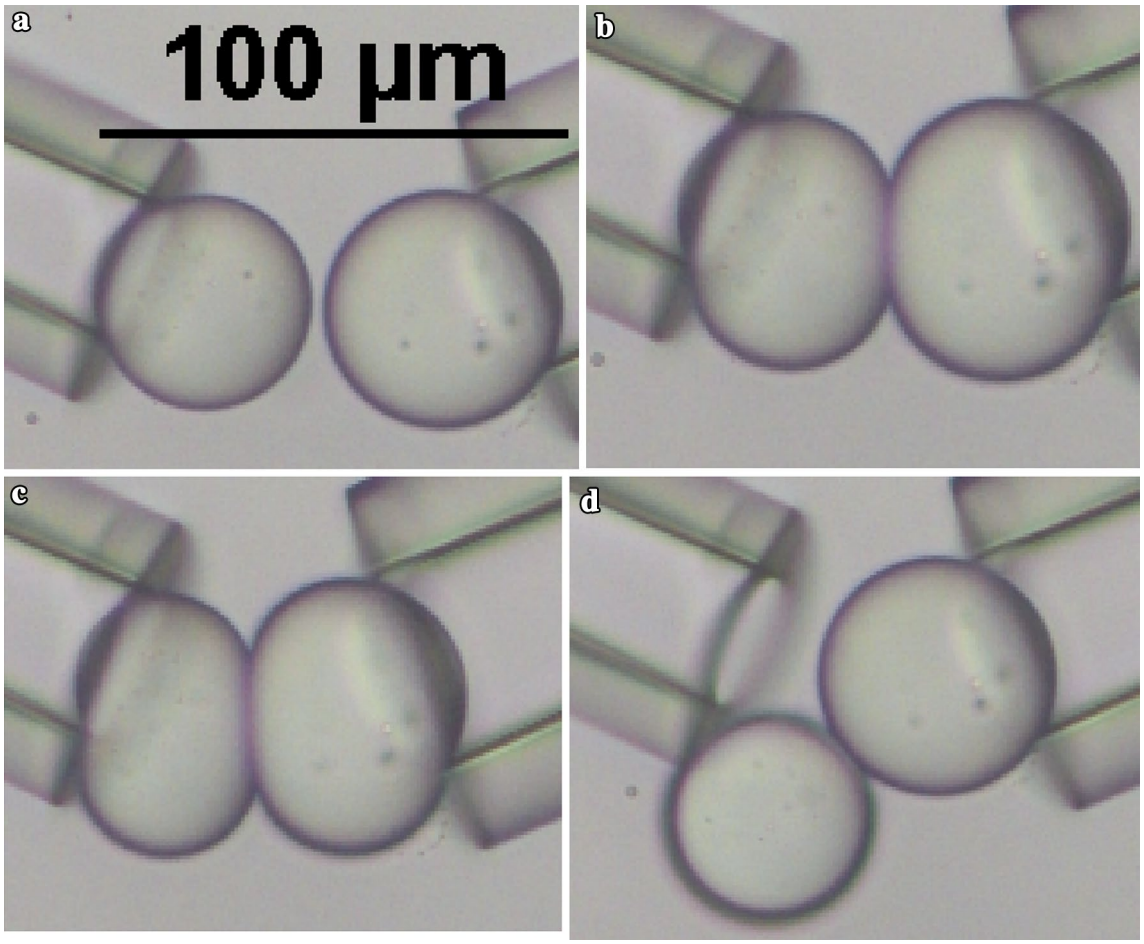

Fig. 1 Micromanipulation of two 100% SO droplets. **a** Before droplets are put in contact; **b** forcing droplets together; **c** droplets undergoing increased shape deformation; **d** left-hand droplet is forced off of micromanipulator

Materials and Methods

The dispersed phase contained palm kernel oil (PKO) (AAK, Malmö, Sweden), soybean oil (SO) (Columbus Vegetable Oils, Des Plaines, IL, USA), or a mixture of the two fats to control solid fat content. The continuous phase was composed of 4 mmol sodium dodecyl sulfate (SDS) (Sigma St. Louis, MO, USA) solution and 1.5% methylcellulose (DOW Chemical Co., Midland, MI, USA). Emulsions were prepared according to the protocol in Thiel *et al.* [3].

Interfacial tension was measured by a ThetaLite optical tensiometer (Biolin Scientific, Vastra Frolunda, Sweden) using the pendant drop method. Solutions containing 1.5% MC and 1.5% MC with 4 mM SDS were measured to have interfacial tensions of 11.40 and 6.76 mN/m, respectively, in SO. Although SDS reduced interfacial tension beyond that of MC, the reduction was relatively minor.

The micromanipulation apparatus and procedure are detailed in Thiel *et al.* [3]. Briefly, two droplets are collected by the micromanipulators and brought together to observe the interactions.

Results and Discussion

Figure 1 and Video 1 show two 100% SO droplets being micromanipulated and put in close proximity. When the two liquid oil droplets were brought into contact, both globules underwent severe shape deformation until one globule was eventually pushed off the micromanipulator. The two liquid droplets never underwent coalescence, even when higher speeds or more force pushed them together. When droplets were composed solely of liquid oil with no lipid crystals present, MC formed a continuous coating around the droplets. Even the presence of SDS did not

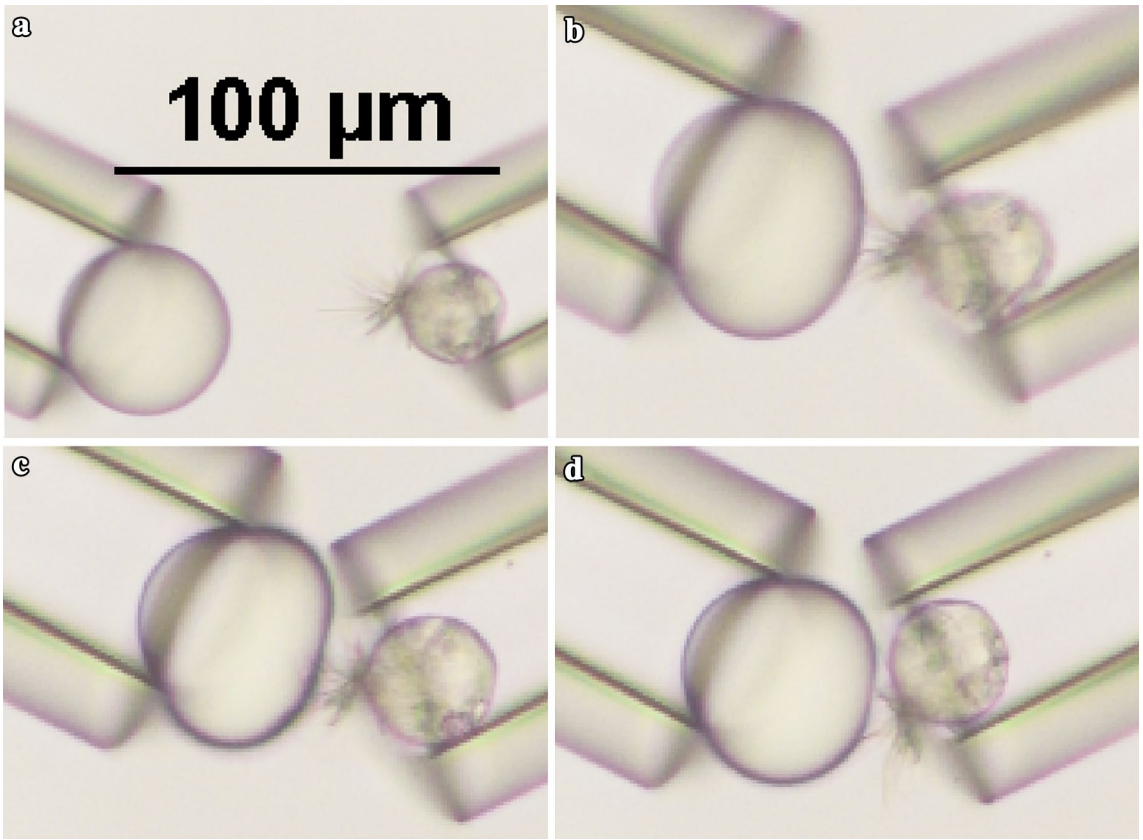

Fig. 2 Using the interfacial crystals of a 100% PKO droplet (*right*) to try and pierce into a 100% SO droplet (*left*). **a** Before droplets are put in contact; **b** using interfacial lances to contact the 100% SO droplet; **c** 100% SO droplet further deforming as lances are driven closer; **d** retracting the interfacial lances and 100% SO droplet begins to return to its original shape

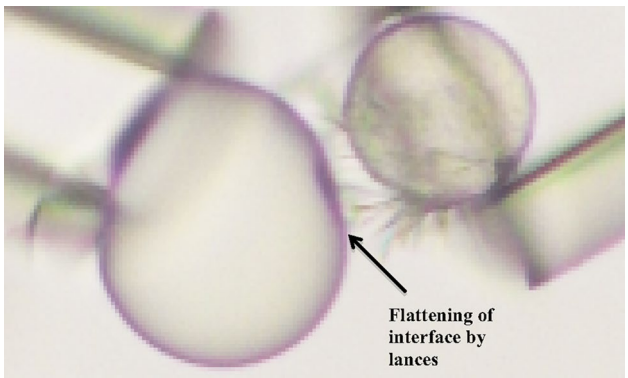

Fig. 3 The interface of a 100% SO droplet (*left*) undergoing deformation due to contact from interfacial lances of a 100% PKO droplet (*right*)

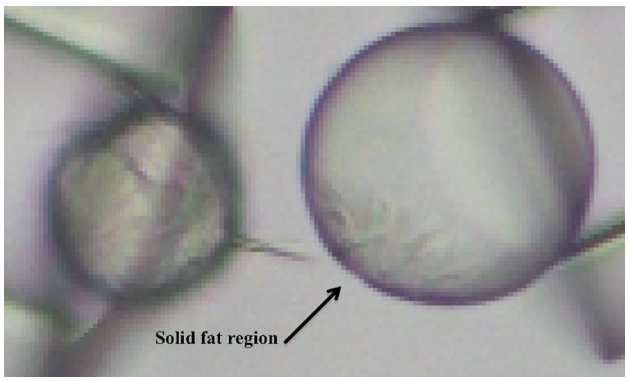

Fig. 4 *Arrow* pointing toward the localized region of crystalline fat within a 40% PKO and 60% SO droplet

reduce the ability of MC to stabilize two liquid oil droplets. This may be attributed to SDS forming complexes with the highly substituted areas of MC and tightly packing at the interface, not necessarily displacing MC [8]. Therefore, the strong MC film was able to protect the globules and ultimately stabilize them against coalescence.

Emulsions containing either 100% SO or 100% PKO droplets were mixed together and then micromanipulated. The 100% PKO droplets had interfacial crystals pointing

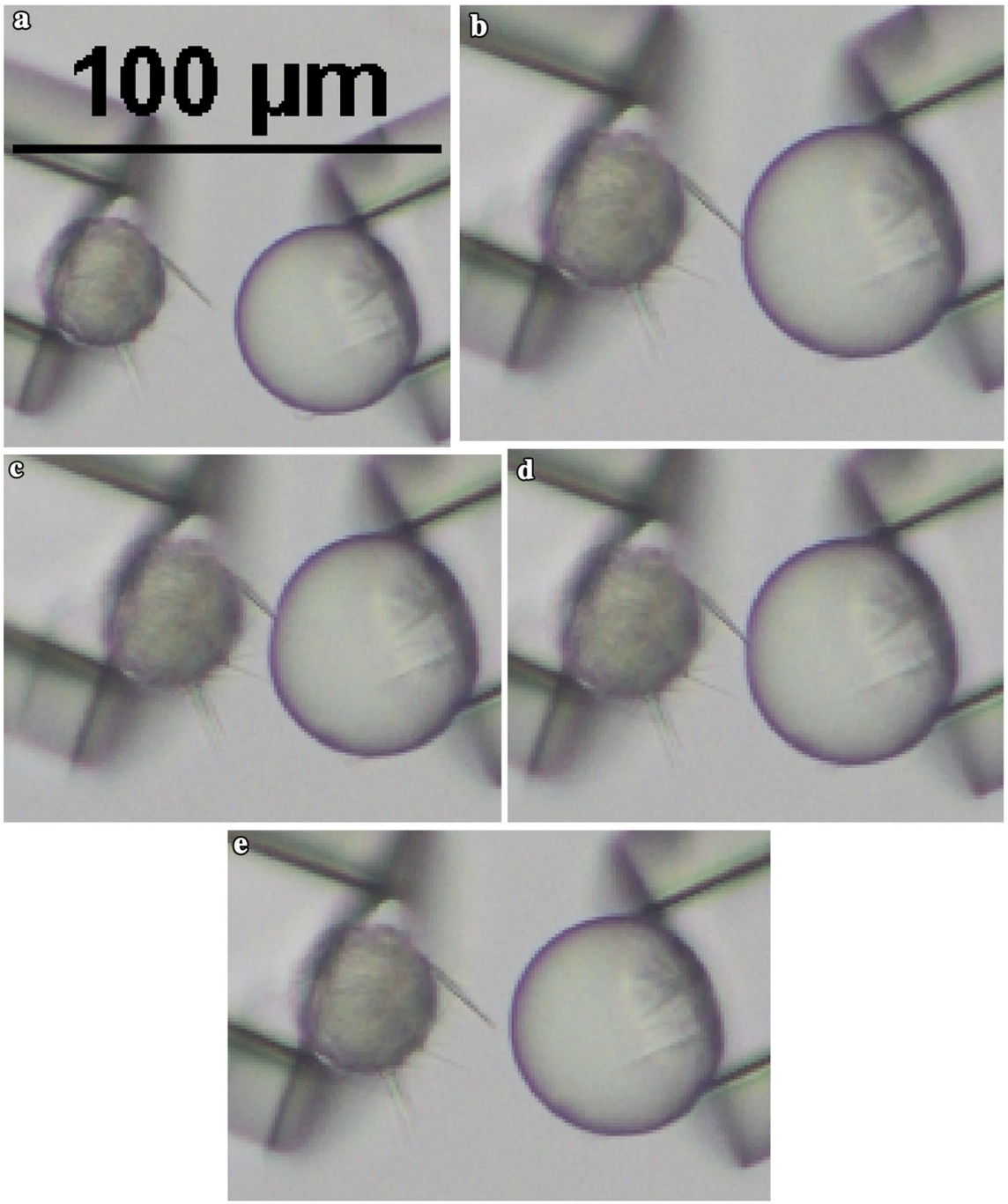

Fig. 5 Aiming the interfacial protrusion of a 100% PKO droplet (*left*) into the liquid region of a 40% PKO and 60% SO droplet (*right*). **a** Initial state of the droplets; **b** contacting interfacial lance with liquid portion of 40% PKO and 60% SO droplet. **c** Attempting to pierce lance into 40% PKO and 60% SO droplet; **d** withdrawing lance as it is unable to penetrate neighboring droplet; **e** lance is fully retracted and droplets return to original state

out into the continuous phase (crystalline lances), similar to those seen in Boode and Walstra [7]. These were then brought into contact with the 100% SO droplet. In Fig. 2 and Video 2, these lance-like protrusions were not able to penetrate into the liquid oil droplet, and coalescence did not occur. Instead, the 100% SO droplet again deformed wherever the lance contacted (Fig. 3), taking different shapes as the lance was moved over its surface. As the pressure from the lance-like protrusions was removed, the liquid droplet regained its original spherical shape. Again, MC was able to stabilize the liquid droplets from coalescence even as a lance was used to try and pierce into the droplet.

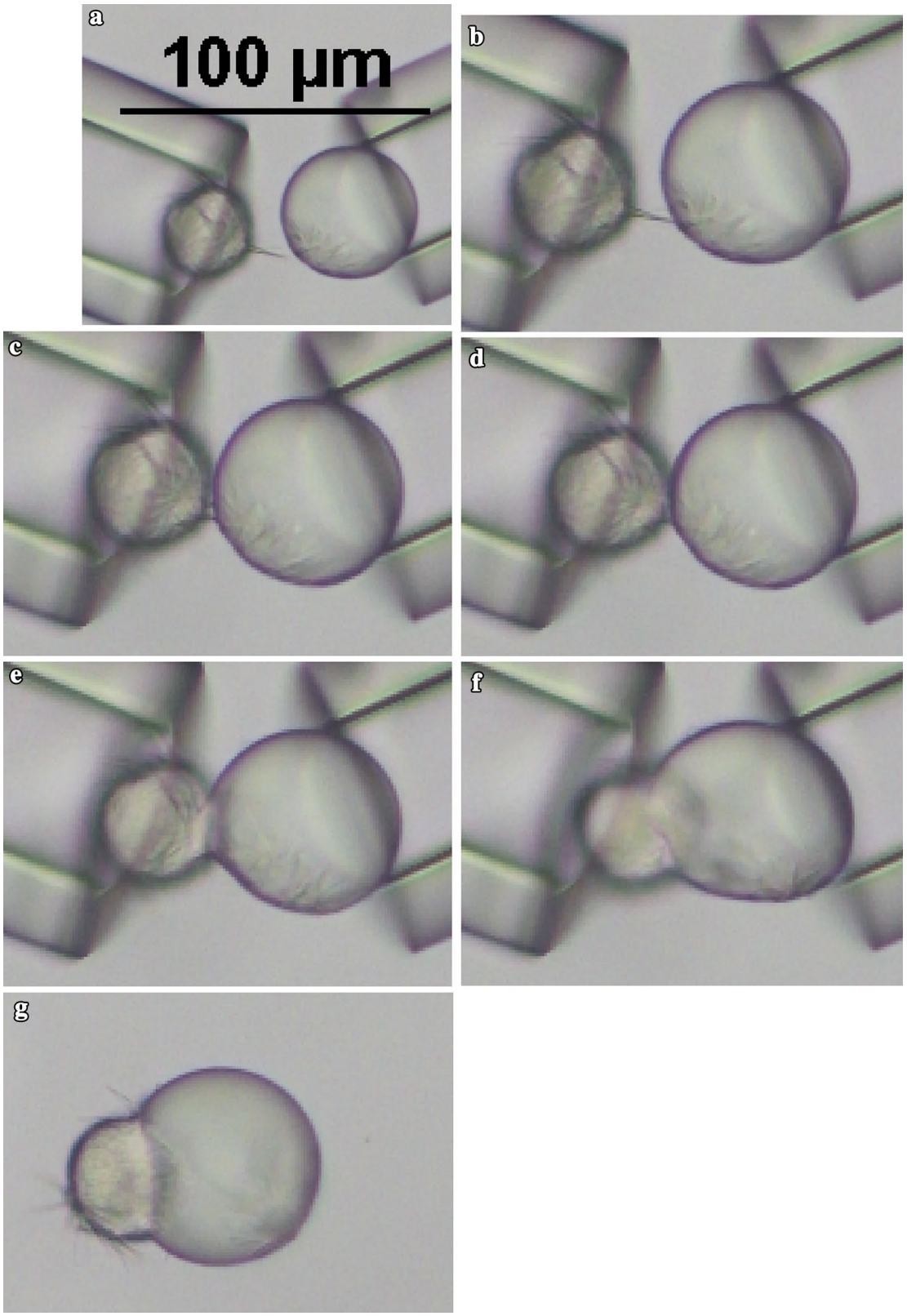

Fig. 6 Aiming the interfacial protrusion of a 100% PKO droplet into the crystalline region of a 40% PKO and 60% SO droplet resulting in arrested coalescence. **a** Droplets before contact; **b** directing interfacial protrusion toward crystalline region of neighboring droplet; **c** lance pierces into 40% PKO and 60% SO droplet; **d** oil is starting to be shared between the two droplets; **e** droplets are drawn together; **f** merging of the two droplets; **g** final arrested structure achieved by the droplets

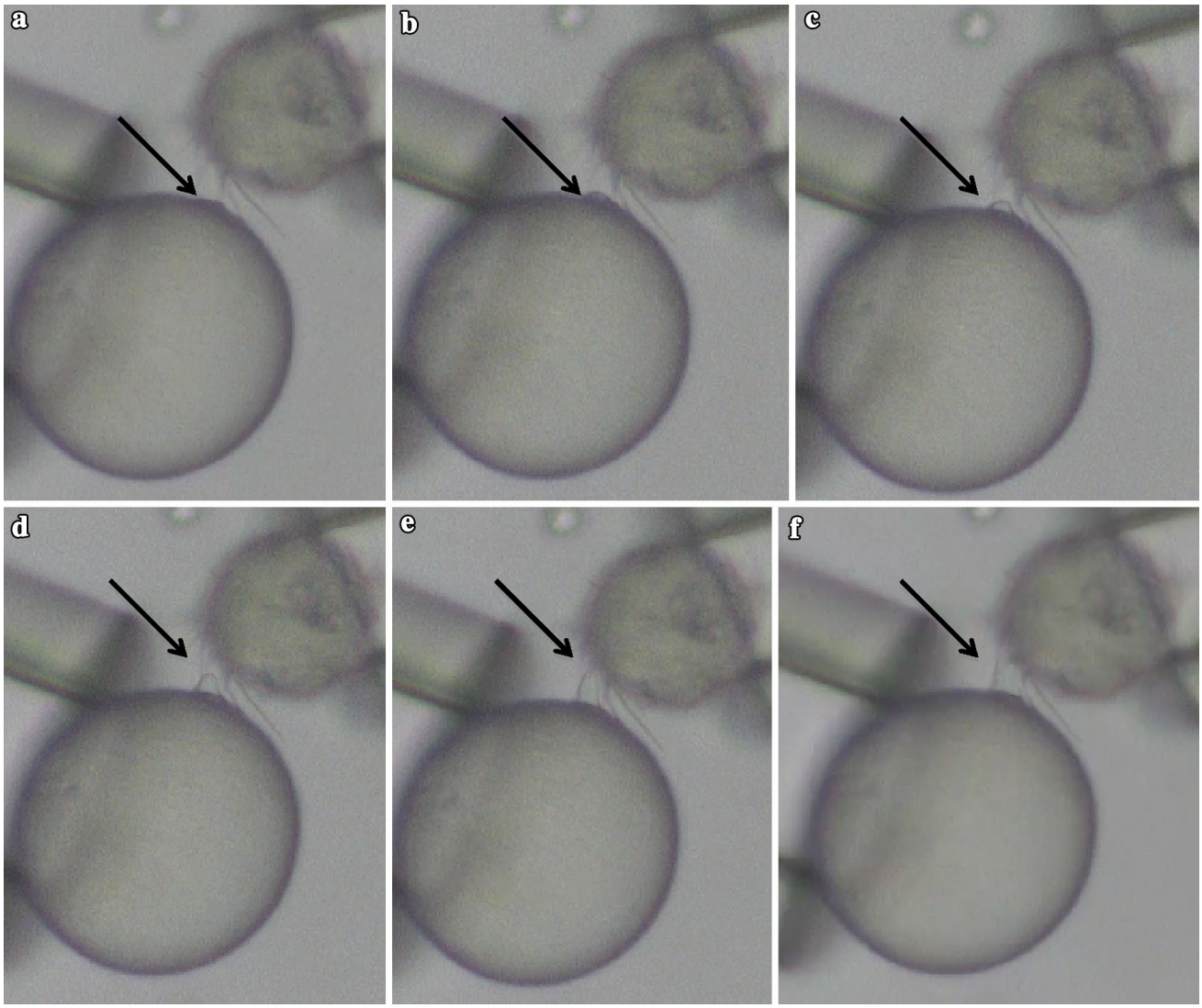

Fig. 7 **a** Lance penetrating into 40% PKO and 60% SO droplet; **b** a small amount of oil is released from 40% PKO and 60% SO droplet; **c** free oil begins to wet the interfacial lance; **d** oil continues moving along the lance toward the second droplet; **e** oil crosses the full length of the lance reaching the second droplet; **f** oil neck is formed between the two droplets. *Arrow* points to liquid oil flowing from one droplet to the other along the crystal lance

Droplets composed of 40% PKO and 60% SO had discrete regions of crystallized fat (~4% solid fat content), seen as dendritic crystalline wisps over a portion of the droplet surface, but otherwise appeared liquid-like (Fig. 4). The interfacial crystals of 100% PKO droplets were used to probe into both the liquid and crystalline regions of the same droplet. When the lance was pushed toward the liquid-like area, as seen in Fig. 5 or Video 3, again the globule distorted or pushed the crystalline protrusions out of the plane of view. The lance could not penetrate into the neighboring droplet. However, if the two droplets were rearranged on the micromanipulators so that the lance was aimed toward the localized crystalline region of the same neighboring droplet, the lance easily penetrated the other droplet as seen in Fig. 6 or Video 4. Once the lance pierced the target droplet, oil began to wick across the crystal, and an oil neck was formed pulling the droplets together as seen in Fig. 7. The presence of internal lipid crystals seems to have changed MC conformation at the interface allowing for lance penetration and arrested coalescence to occur.

A key observation from these micromanipulation experiments is the requirement of some solid fat at the interface in order to initiate coalescence. Regardless of the type of globule put in contact with a 100% SO droplet, no coalescence was ever observed as a strong MC film rendered the droplets stable, even against lance penetration. The liquid droplets deformed when contacted and returned to

their initial shape once the force was removed. However, when there was a small region of solid fat at the interface and lance-shaped crystals from a second droplet were contacted near this area, the lance penetrated and arrested coalescence occurred. It appears that the fat crystals at or near the surface of the droplet disrupted the MC film surrounding the globule, enabling the lance to pierce into the droplet and coalescence to be initiated.

Acknowledgements This project was supported by [National Research Initiative or Agriculture and Food Research Initiative] grant no. 2014-67017-21652 from the USDA National Institute of Food And Agriculture, Nutrients and health, improving food quality—A1361.

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