Skin formation in drying droplets of dairy proteins

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The evaporation of a colloidal dispersion is characterized by solute accumulation at the air-liquid interface, leading to the gradual formation of a gelled skin. From the preliminary colloid deposit to complete solidification, the development of this layer affects the overall drying process and final sample morphology. Despite progress in the last decades, the mechanisms governing skin formation in drying colloidal suspensions have not yet been fully clarified, especially in complex polydisperse systems. This work investigates droplet skin formation in a binary dairy proteins system, i.e. whey proteins isolates (WPI), and native phosphocaseinates (NPC). A single droplet approach was used to explore both droplet morphology evolution and drying kinetics as a function of WPI relative fraction in the overall protein content (WPI\%\textsubscript{R}). The observation of the evaporation stages highlighted the separate role of WPI and NPC on drying dynamics, leading to two shape categories characterized by skin buckling (WPI\%\textsubscript{R} ≤ 20\%) and rigid convex shell (WPI\%\textsubscript{R} ≥ 50\%), respectively. Mainly, estimating droplet drying kinetics and sol-gel transition characteristic times highlighted WPI significant impact above a critical value (WPI\%\textsubscript{RC}), resulting in a rigid skin with high resistance to buckling. Such enhanced mechanical properties suggests WPI external segregation during skin formation, whose evidence was provided by the direct observation of dry skin section structure. The hypothesis of protein stratification by size was corroborated by the agreement with recent predictive models on the evaporation of bidisperse model colloidal suspensions. Finally, the organization of protein molecules throughout the interface gelification process was also investigated by interfacial rheology tests, stressing significant similarities between ageing-induced and drying-induced gelled interface behavior above WPI\%\textsubscript{RC}. This study contributes to a better understanding of the competitive drying mechanisms occurring in binary colloidal systems. Moreover, these outcomes are potentially valuable for the optimization of milk powder production in the dairy industry.

Keywords: drying mechanisms, dairy colloids, skin formation, stratification