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Research Article

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Effect of pH on the emulsifying performance of protein-polysaccharide complexes

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Abstract

BACKGROUND: Protein-polysaccharide complexes have been successfully used for emulsion stabilization. However, it is unclear how the complex's surface charge influences aggregation stability and coalescence stability of emulsions, and whether a low charged interfacial film can still maintain the coalescence stability of oil droplets. In the present study, the effects of pH (around the pI of protein) on the aggregation and coalescence stability of emulsions were investigated.

RESULTS: Whey protein isolate (WPI) and peach gum polysaccharides (PGP) complexes (WPI-PGP complexes) were synthesized at pH 3, 4 and 5. Their sizes were 598, 274 and 183 nm, respectively, and their ζ-potentials were +2.9, −8.6 and −22.8 mV, respectively. Interface rheological experiments showed that WPI-PGP complex at pH 3 had the lowest interfacial tension, and formed the softest film compared to the complexes at pH 4 and 5. Microfluidic experiments showed that all WPI-PGP complexes were able to stabilize droplets against coalescence within short timescales (milliseconds). At pH 3, no coalescence was observed even under conditions where the continuous phase flow influenced the shape of oil droplets (from spheres to ellipsoids). At pH 4 and 5, the model emulsions were stable over 16 days of storage, extensive aggregation and creaming occurred at pH 3 after 8 days. Importantly, no coalescence took place.

CONCLUSION: The present study confirmed that the aggregation stability of the emulsions was mainly determined by the surface charge of the complex, whereas the coalescence stability of emulsions is expectedly determined by steric repulsion, providing new insights into how to prepare stable food emulsions.

Supporting information may be found in the online version of this article.

Keywords: whey protein isolate; peach gum polysaccharide; pH; emulsion; coalescence stability

INTRODUCTION

Proteins are widely used as emulsifiers as a result of their amphiphilic properties.[1,2] The emulsifying ability of protein is determined by its hydrophobicity, charge, molecular weight and conformation stability.[3] When adsorbing at the oil–water interface, the protein unfolds to expose more hydrophobic groups towards the oil phase. Meanwhile, their hydrophilic groups rearrange into the aqueous phase.[4] When sufficient protein molecules adsorb, they may interact and form a viscoelastic layer at the oil droplet surface.[5] Therefore, proteins can provide steric hindrance to prevent oil droplet coalescence, and, when sufficiently charged, also droplet aggregation. At the isoelectric point (pI) of the protein, however, in the 'absence of net surface charge', oil droplets can easily aggregate or even coalesce if the adsorbed film is not sufficiently thick and elastic.

To improve the emulsion stability, polysaccharides have been introduced in many studies in combination with proteins.[6] On the one hand, polysaccharides increase the viscosity of the continuous phase of the emulsion, which lowers the creaming rate of droplets and slows down drainage, thereby reducing coalescence frequency.[6] On the other hand, polysaccharides can increase the thickness of the interfacial layer, which also reduces droplets coalescence through steric effects.[7] Indigestible polysaccharides have amongst others been applied for targeted delivery of bioactive food ingredients using emulsion systems.[8,9]

To combine the advantages of proteins and polysaccharides, Larichev *et al.*[10] first used bovine serum albumin and dextran sulphate complexes to stabilize decane-water emulsion early in 1983. Subsequently, 1659 manuscripts on protein-polysaccharide complex based emulsions have been published in Web of Science. Evans *et al.*[4] have distinguished three types of protein-

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polysaccharide complexes that are applied for emulsion stabilization: naturally-occurring complexes such as the arabinogalactan-protein and glycoprotein fraction in gum arabic,[11] Maillard conjugates[12] and electrostatic complexes.[13]

Protein-polysaccharide electrostatic complexes can be highly-charged soluble macromolecules or low-charged insoluble coacervates, based on pH and ionic strength.[14] On the one hand, complexes with higher charge increase the electrostatic repulsion between droplets to make them more stable. On the other hand, higher charged complexes also increase the electrostatic repulsion between complexes possibly decreasing the interface load, which in turn influences the emulsion stability. To date, it is still unclear how the surface charge of complexes influences the aggregation and coalescence stability of emulsions.

Whey protein isolate (WPI) is a widely used emulsifier known for its emulsification efficiency, good biocompatibility and high nutritional value.[15] Peach gum polysaccharide (PGP) is a natural highly branched heteropolysaccharide, which can act as a steric stabilizer.[16] In the present study, we aimed to make best out of both worlds by creating complexes from these components. The study objective was to mechanistically study how pH values around the pI (pH 3–5) affects the emulsifying performance of complexes of WPI and PGP. First, the size and ζ-potential of WPI-PGP complexes were compared at different pH values. Then, the interfacial tension and rheology of the complexes were measured. Microfluidics were applied to directly investigate coalescence of oil droplets stabilized by different complexes. Finally, in model emulsions, aggregation and coalescence were investigated in relation to emulsion stability. These findings provide new insights into how to prepare stable food emulsions around the pI of the protein.

MATERIALS AND METHODS

Materials

PGP was extracted according to our previous method.[17] WPI was purchased from Davisco Foods (Biopro, Port Huron, MI, USA). Sunflower oil was purchased from the local market (Jumbo Supermarket, B.V., Veghel, The Netherlands). Both sodium dodecyl sulphate (SDS) and hydrochloric acid (HCl) were of analytical grade and purchased from Sigma-Aldrich (St Louis, MO, USA). Hexadecane was from Alfa Aesar (Karlsruhe, Germany). Ultrapure water for the whole experiment was acquired from a Millipore Milli-Q system (Millipore Corp., Billerica, MA, USA).

Synthesis of WPI-PGP complex

Both WPI and PGP were first completely dissolved in ultrapure water at a concentration of 2 mg mL^{-1}. Then, the WPI solution and PGP solution were mixed at a volume ratio of 1:1. Finally, WPI-PGP mixture was divided into three portions, and their pH was adapted to 3.4, 4.4 and 5.0 by dropwise addition of 0.5 mol L^{-1} HCl solution. The samples were marked as complex pH 3, 4 and 5, respectively, and stored overnight at 4 °C before use.

To characterize the WPI-PGP complexes present after emulsification, an aliquot was treated with 35% ultrasonic intensity (of the maximum available amplitude of mechanical vibrations) (SFX550; Branson, Dietzenbach, Germany) for 3 min (5 s on, 5 s off) to simulate the preparation process of emulsions.

The size and ζ-potential of WPI-PGP complex

The measurements of size and ζ-potential of WPI-PGP complex was performed on a Zetasizer Ultra (Malvern Instruments, Malvern, UK). The initial concentration of WPI-PGP complex was 2 mg mL^{-1} and this was diluted two times in ultrapure water to avoid multiple scattering effects. Before measurement, the temperature was set at 25 °C and the equilibration time was 120 s. Each sample was tested in triplicate.

Interfacial tension and rheology measurement

The interfacial tension and rheology between the WPI-PGP complex solution and sunflower oil were measured with a drop tensiometer (Tracker, Teclis, Longessaigne, France) in accordance with a previous study with some modifications.[18,19] The WPI-PGP complex solutions at different pH were first diluted five times with water at the corresponding pH and then transferred to an optical glass cuvette as continuous phase. The oil droplet was formed at the J-shape needle tip immersed in the WPI-PGP complex solution. Before interfacial tension measurement, the drop status was set as rising, temperature was set at 25 °C, droplet volume was set at 20 μL and the adsorption time was set as 3 h. Windrop software was applied to calculate the value of interfacial tension based on the boundaries of oil droplet according to the Young–Laplace equation.[19] After 3 h, dilatational rheology measurement was performed. The amplitude sweeps ($\Delta A/A_0$) ranged from 0.05 to 0.30 with five active and five passive cycles each, and the frequency was 0.1 Hz. After fast Fourier transformation of interfacial tension (γ), the dilatational elastic modulus (E'_d) and viscous modulus (E''_d) were calculated according to intensity and phase of the first harmonic as:

$$E'_d = \Delta\gamma \left(\frac{A_0}{\Delta A}\right) \cos\delta \quad (1)$$

$$E''_d = \Delta\gamma \left(\frac{A_0}{\Delta A}\right) \sin\delta \quad (2)$$

where $\Delta\gamma$ is the change of tension signal during oscillation, A_0 is the droplet area before deformation, ΔA is the change in droplet area during oscillation and δ is the phase shift of $\Delta\gamma$ compared to the ΔA.

To visualize the rheological behavior of the interface, Lissajous plots were made by plotting the surface pressure ($\gamma_0 - \gamma$) against deformation ($(A_0 - A)/A_0$).

Microfluidic experiments

The layout of the microfluidic coalescence chip is shown in Fig. 1; it was custom-designed and produced by Micronit Microtechnologies B.V. (Enschede, The Netherlands) in collaboration with the food process engineering group. Detailed information is available in a previous study[20]; the meandering channel length used in the present study is 173 ms. The continuous phase was WPI-PGP complex solution (filtered with a 1-μm filter membrane before use) and the dispersed phase was hexadecane. The flow rate for continuous phase and dispersed phase were ~40 and 2 μL min^{-1}, respectively; both were controlled by a pressure system (OB1; Elveflow, Paris, France) and a mini flow sensor (CORI; Bronkhorst B.V., Veenendaal, Netherlands). The images at the inlet and outlet of the coalescence channel were captured by a high-speed camera (1000 frames at 30 fps, 1.321 μm pixel^{-1}) (MotionPro Y4-A2; Integrated Design Tools, Tallahassee, FL, USA) connected to a light microscope (Axiovert 200 MAT; Carl Zeiss, Jena, Germany).

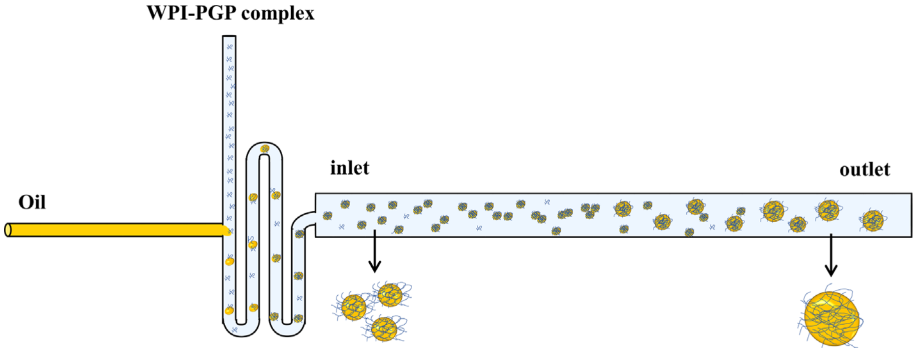

Figure 1. Layout of the applied microfluidic chip.

Emulsion preparation

The emulsions were prepared at 10% (v/v) sunflower oil. Briefly, the sunflower oil was mixed with the three different WPI-PGP complex solutions (2 mg mL^{-1} at pH 3, 4 and 5) and pre-emulsified at 7104 × g for 120 s using a high-speed homogenizer (T18l; IKA, Staufen, Germany). Then, the coarse emulsion was subjected to ultrasonic treatment with a probe sonicator (SFX550; Branson) at 35% ultrasound intensity (of the maximum available amplitude of mechanical vibrations) for 3 min (5 s on, 5 s off). The final emulsions were stored at 4 °C (16 days at maximum) for further measurement.

Droplet size of emulsions

The droplet size distribution of the emulsions was measured with static light scattering (Mastersizer 3000; Malvern Instruments). Before measurement, the emulsion samples were diluted four times with water or SDS solution (1 wt.%).[21] SDS shows strong surface activity and can replace the complexes at the interface, thereby separating the aggregated oil droplets. Hence, SDS could differentiate aggregation and coalescence. The refractive index for dispersed phase and dispersant was set at 1.47 and 1.33, respectively. The absorption index was 0.01. Each sample was tested in triplicate.

Morphology of oil droplets

To check the morphology of oil droplets (i.e. free, flocculated, coalesced), a light microscope (Carl Zeiss) was used, equipped with an AxioCam Mrc5 camera. Before observation, the emulsion samples were diluted four times with water. The images were taken with 100× objective lens. To obtain a general overview of the sample, multiple images were analyzed in various locations of the slides.

Statistical analysis

All measurements were performed three times, and the results are presented as the mean ± SD. Statistical analysis was conducted via SPSS, version 24.0 (IBM Corp., Armonk, NY, USA), One-way analysis of variance following Duncan's multiple range test was performed. $P < 0.05$ was considered statistically significant.

RESULTS AND DISCUSSION

The size and ζ-potential of WPI-PGP complexes

Complexes of WPI and PGP were synthesized, and characterized at a range of pH values. As shown in the Supporting information (Fig. S1), the PGP molecules were negatively charged (−24.5 mV) even at pH 3 because of the large number of carboxyl groups in its structure.[22] The ζ-potential of WPI changed from positive to negative within the investigated pH range, and showed an isoelectric point at pH 4.7 (see Supporting information, Fig. S2). Therefore, at pH 3 and pH 4, the WPI was positively charged, whereas, at pH 5, the WPI was negatively charged. Around pH 3, strong electrostatic attraction existed between PGP and WPI, leading to WPI-PGP complexes with size of ∼600 nm and ζ-potential of +2.9 mV (Fig. 2A), showing that the charge of PGP was practically completely compensated for by the interaction with WPI. At higher pH, the interaction between WPI and PGP weakened, leading to smaller complexes at pH 4 and 5 (274 and 183 nm, respectively). Their ζ-potential changed from positive to negative: −8.6 and −22.8 mV, respectively (Fig. 2B). Figure 2 also shows that after ultrasonic treatment (carried out to get a good impression of the effect that the emulsification method of choice may have on the complex), the size of the WPI-PGP complexes decreased and their ζ-potential became more negative. Apparently, the energy delivered by the ultrasonic treatment is sufficiently high to break some of the bonds formed in the complexes.

Interface rheological measurements

It is generally known that a low interfacial tension results in reduced surface free energy of oil droplets, thereby improving the emulsion stability.[23] Figure 3(A) shows the development of interfacial tension of a single oil droplet in different continuous phases over time. When the oil droplet was in pure water, its interfacial tension was highest, reaching 19.8 mN m^{-1} after adsorption for 3 h, showing that some surface active components such as phosphatides, gums and mucilaginous substances are present in the oil.[24,25] The surface tension for WPI-PGP complexes at pH 3, 4 and 5 were 8.9, 9.8 and 11.4 mN m^{-1}, respectively, implying their high surface activities. WPI-PGP complexes at pH 3 exhibited the lowest surface tension, indicating that the largest number of WPI-PGP complexes could be adsorbed.

After equilibration, dilatational rheology was performed to study the structural properties of the interfacial films. It has been reported that interfacial rheology is determined by the type, density, conformation and interaction of the adsorbed molecules.[5,26] Figure 3(B) shows that pH has significant influence on the E'_d of the WPI-PGP complex films. The WPI-PGP complex at pH3 had the lowest E'_d, whereas, at pH 5, the highest E'_d was measured. At pH 3, the WPI-PGP complex has low charge and is expected to have higher surface load (characterized by the lower interfacial tension) as a result of the weaker electrostatic repulsion and larger size of the complex.[5] At pH 3, the WPI-PGP complex has the most compact configuration, which makes it less likely to interact with

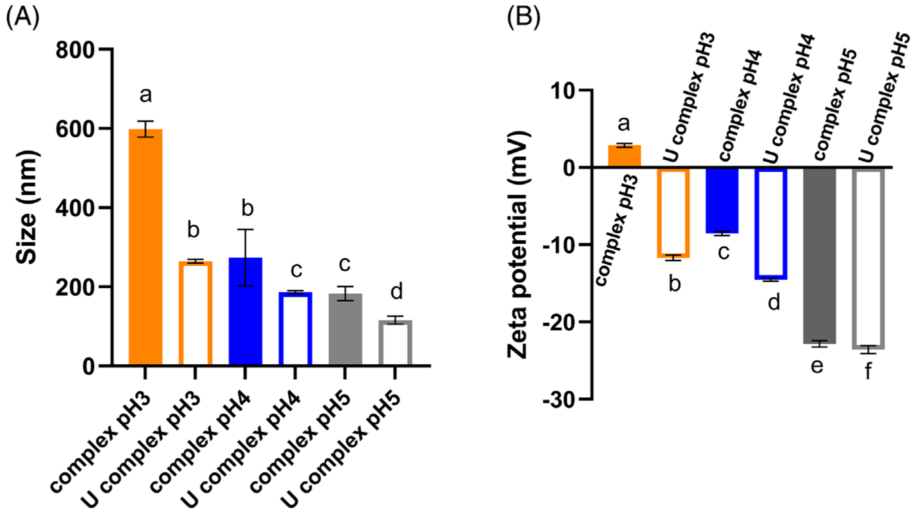

Figure 2. The size (A) and ζ-potential (B) of Whey protein isolate-peach gum polysaccharides (WPI-PGP) complexes at different pH before and after ultrasonic treatment. Complex pH 3, complex pH 4 and complex pH 5: WPI-PGP complexes prepared at the pH values around 3, 4 and 5, respectively; U complex pH 3, U complex pH 4 and U complex pH 5: ultrasound treatment of WPI-PGP complexes (described in the section on emulsion preparation) prepared at the pH values around 3, 4 and 5, respectively. Different letters indicate a significant difference ($P < 0.05$).

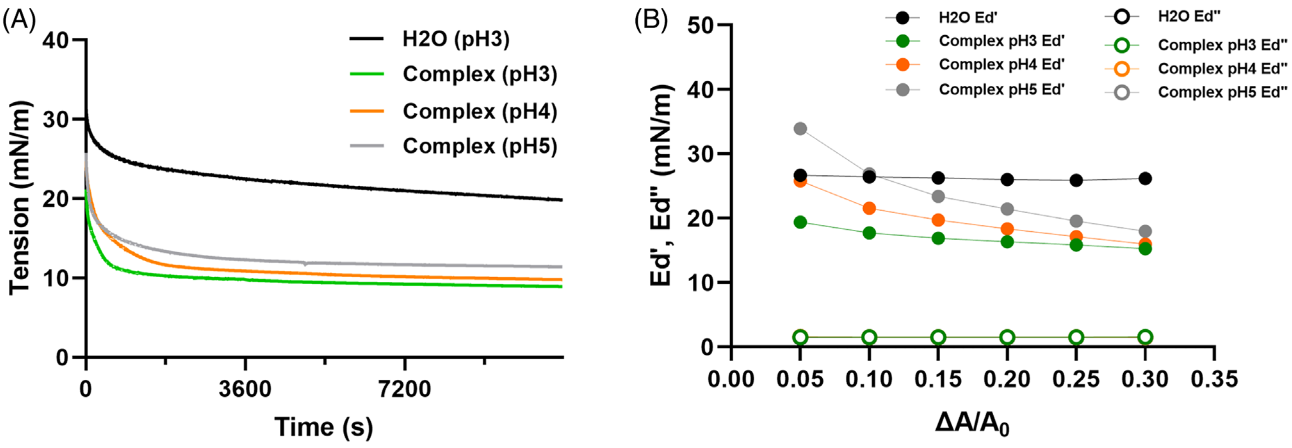

Figure 3. Interfacial tension during equilibration (A), the E_d' and E_d'' of the interface at different deformation (B). Complex pH 3, complex pH 4 and complex pH 5: whey protein isolate-peach gum polysaccharides (WPI-PGP) complexes solutions prepared at the pH values around 3, 4 and 5, respectively, and receiving the same ultrasound treatment as the emulsions described in the section on emulsion preparation.

other complexes present at the interface, leading to the lowest E'_d, as found for proteins at their isoelectric point.[5,27] The highest E'_d values were measured at pH 5, indicating that the WPI-PGP complex had the strongest interaction at pH 5. The Lissajous plots of samples at 30% deformation are shown in the Supporting information (Fig. S3), which provides more detailed information of the interfacial layer structure during expansion and compression.

Microfluidic investigation of emulsions stability

Microfluidics have been used in recent years to directly study coalescence stability of emulsions at sub-second range.[28] As shown in Fig. 1, the oil droplets were first formed at the T-junction. Then, emulsifier adsorption took place in the meandering channel of which the length determines the adsorption time.[20] Finally, the images of oil droplets in the inlet and outlet of the coalescence channel were captured and analyzed to investigate the coalescence stability. As shown in Fig. 4 (see also Supporting information, Movie S1), in the absence of the complex, the oil droplets were unstable and easily coalesced. The ζ-potential of the complex determines the surface charge of oil droplets; the higher the ζ-potential, the higher the surface charge. Oil droplets stabilized by WPI-PGP complex at pH 3 easily aggregated (because of low ζ-potential of the droplets being as low as +2.9 mV). Despite this, no coalescence took place, even under conditions that the oil droplet shape changed, which is indicative of effective surface stabilization (see Supporting information, Movie S2). WPI-PGP complexes at pH 4 and pH 5 showed an excellent emulsifying ability because no aggregation and coalescence were observed at the outlet of the coalescence channel (see Supporting information, Movies S3 and S4). This result indicates that the aggregation stability of oil droplets was mainly determined by the high electrostatic repulsion. However, the coalescence stability was not affected by surface charge, and so is most likely determined by steric repulsion.

Droplet size and morphology of emulsions

The emulsifying performance and stability of emulsions stabilized by WPI-PGP complexes measured at different pH values. Figure 5

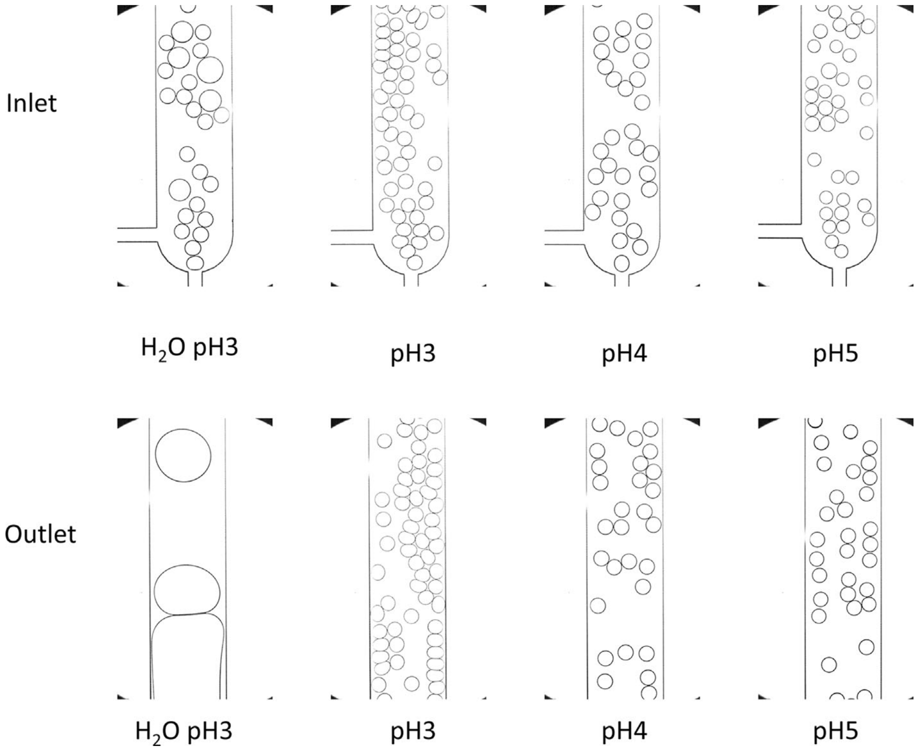

Figure 4. The morphology of oil droplets in the inlet and outlet of chip stabilized by H_2O and Whey protein isolate-peach gum polysaccharides (WPI-PGP) complexes at different pH. pH 3, pH 4 and pH 5: WPI-PGP complexes solutions prepared at the pH values around 3, 4 and 5, respectively, and receiving the same ultrasound treatment as the emulsions described in the section on emulsion preparation.

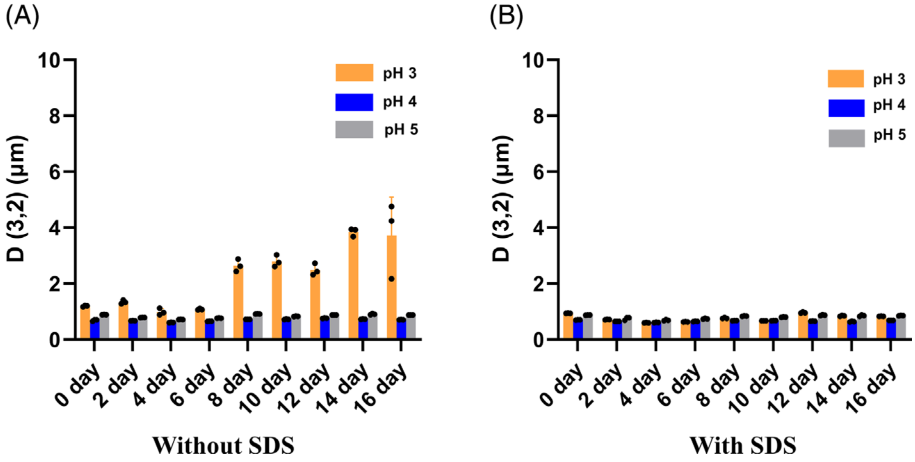

Figure 5. The mean droplet size of emulsions stabilized by whey protein isolate-peach gum polysaccharides (WPI-PGP) complex at different pH during storage. Emulsion samples were diluted with water (A) or SDS solution (B) before measurement. Each black dot indicated the each measurement result of $D_{2,3}$.

shows the oil droplet size of the emulsions during storage. The initial droplet sizes ($D_{2,3}$) were 1.19, 0.69 and 0.89 μm at pH 3, 4 and 5, respectively. The increase in 'droplet size' at pH 3 (to 3.72 μm after storage for 16 days) is a result of aggregation because, after SDS addition, the same droplet size is measured as at the start of the experiment. These results are in line with previous results, indicating that aggregation occurred at pH 3 because of the low electrostatic repulsion between oil droplets,[6] although, importantly, no coalescence took place. The visual appearance of emulsions is shown in Fig. 6. After storage for 10 days at pH 3, oil droplets creamed and a subnatant water phase was formed, which confirms aggregation at pH 3 in WPI-PGP complex stabilized emulsions, unlike emulsions at higher pH.

CONCLUSIONS

The results of the present study have confirmed that pH has a significant impact on the size and surface charge of WPI-PGP complexes, which influenced their interfacial and emulsifying properties. Within a pH range of 3 to 5, the size decreased and the ζ-potential increased with pH. The WPI-PGP complex at pH 3, 4 and 5 exhibited high surface activity, whereas, at pH 3,

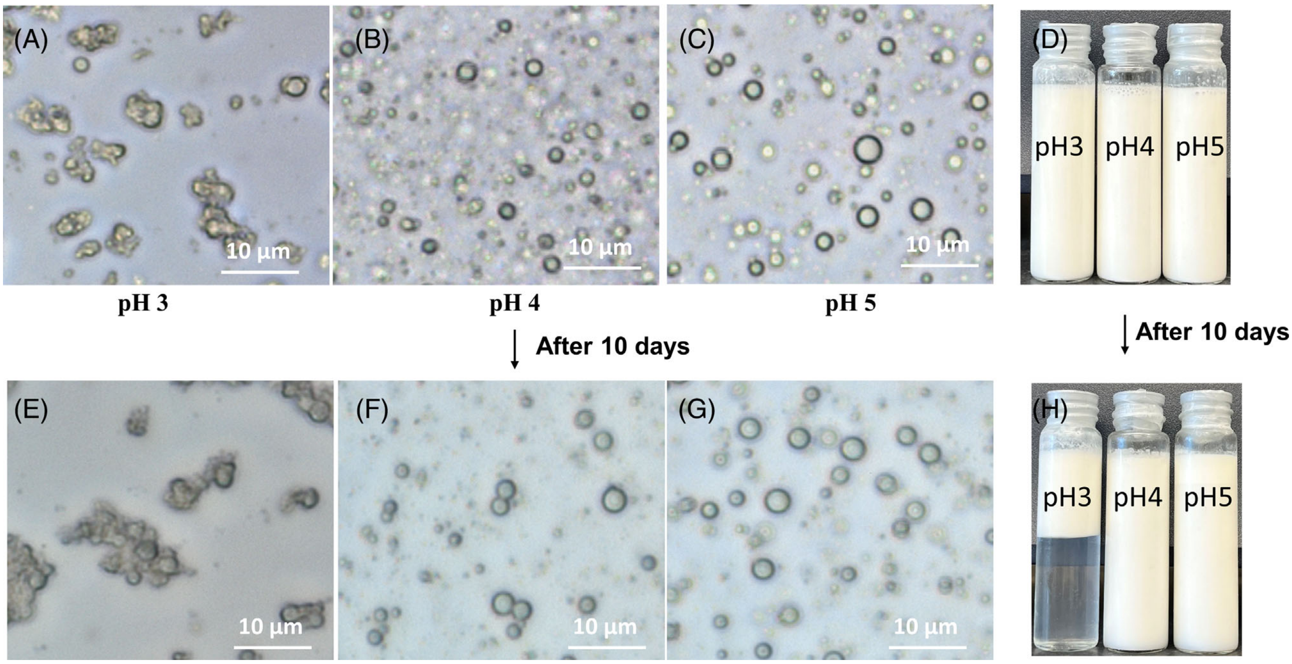

Figure 6. Morphology of oil droplets and emulsions prepared with whey protein isolate-peach gum polysaccharides (WPI-PGP) complexes at different pH before and after storege for 10 days. Storage for 0 day at pH3 (A), 0 day at pH4 (B) and 0 day at pH5 (C), visual appearance of fresh prepared emulsions (D), storage for 10 days at pH3 (E), 10 days at pH4 (F) and 10 days at pH5 (G), visual appearance of emulsions storege for 10 days (H).

the softest interfacial film was formed. Microfluidic experiments showed that all WPI-PGP complexes are able to stabilize droplets already within short timescales (ms), even though they aggregated at pH 3. Model emulsions confirmed these findings for larger time (weeks) and length scales, showing stable emulsions at pH 4 and 5, but aggregation and creaming at pH 3 as a result of the low electrostatic repulsion. No coalescence took place in all emulsion samples. The aggregation stability of emulsions was mainly determined by the surface charge, whereas coalescence stability is expectedly determined by steric repulsion. In summary, the present study systematically shows how a pH around the pI of the protein affected the emulsifying performance of WPI-PGP complexes at the oil/water interface, providing new insights into how to prepare stable food emulsions.

AUTHOR CONTRIBUTIONS

RZ, MC, JC and KS were responsible for study conceptualization. RZ was responsible for data curation. RZ was responsible for investigations. RZ was responsible for writing the original draft. MC, ZL and KS were responsible for supervision. MC and KS were responsible for reviewing and editing. ZL and KS were responsible for funding acquisition.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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