

Long-Term Stabilization of Foams and Emulsions with In-Situ Formed Microparticles from Hydrophobic Cellulose

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We report a simple method to produce foams and emulsions of extraordinary stability by using hydrophobic cellulose microparticles, which are formed in situ by a liquid–liquid dispersion technique. The hydrophobic cellulose derivative, hypromellose phthalate (HP), was initially dissolved in water-miscible solvents such as acetone and ethanol/water mixtures. As these HP stock solutions were sheared in aqueous media, micron sized cellulose particles formed by the solvent attrition. We also designed and investigated an effective and simple process for making HP particles without any organic solvents, where both the solvent and antisolvent were aqueous buffer solutions at different pH. Consequently, the HP particles adsorbed onto the water/air or water/oil interfaces created during shear blending, resulting in highly stable foams or foam/emulsions. The formation of HP particles and their ability for short-term and long-term stabilization of interfaces strongly depended on the HP concentration in stock solutions, as well as the solvent chemistry of both stock solutions and continuous phase media. Some foams and emulsion samples formed in the presence of ca. 1 wt% HP were stable for months. This new class of nontoxic inexpensive cellulose-based particle stabilizers has the potential to substitute conventional synthetic surfactants, especially in edible, pharmaceutical and biodegradable products.

Introduction

Foams and emulsions have been a subject of much research in colloid science due to their wide practical applications, including many products in chemical, food and cosmetic industries. Foams and emulsions are thermodynamically unstable or metastable systems consisting of two immiscible phases that, if given sufficiently long time, will separate into two distinct phases. As a practical way to obtain stable foams and emulsions, dispersion stabilizer are added to kinetically stabilize these systems by impeding instability factors such as creaming, Ostwald ripening, flocculation and coalescence.¹ Dispersion stabilizers are generally classified in three types depending on their structure—small molecular surfactants, amphiphilic polymers, and particulates.² Although synthetic surfactants of small molecular weight are well studied and widely applied in various industries, the interest in solid particulate stabilizers made of environmentally benign materials has been surging in academia as well as industry due to their novel applications and functionalities.

A particle-stabilized emulsion—so-called “Pickering emulsion”—was first reported in early 1900s by Pickering.³ Numerous studies aimed at understanding the properties and stabilization mechanisms of particle-stabilized emulsions have been reported.^{4–15} Particulate stabilizers of a kind, such as casein micelles

and fat crystals have been used for decades, particularly in the food industry.^{5,16} Solid particles with intermediate hydrophobicity can adsorb strongly at the interface between immiscible fluids (e.g., air/water or oil/water). Removing such particles from the interface requires the expense of a significant transfer energy ($-\Delta E$) whose magnitude can be estimated by^{17–22}

$$-\Delta E = \pi r^2 \gamma_{OW} (1 - \cos \theta_{OW})^2 \quad (1)$$

where θ_{OW} is the contact angle, r is the particle radius, and γ_{OW} is the interfacial tension.

Equation 1 assumes a negligible gravity force and is valid for particles of diameter much smaller than the curvature of the

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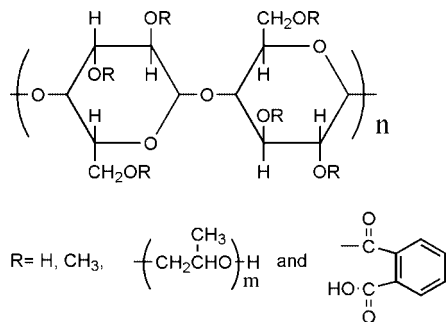


Figure 1. Chemical structure of hypromellose phthalate (HP). The nominal content of methoxyl, hydroxypropyl and phthalyl groups in the substituent (R) is 18–22%, 5–9% and 27–35%, respectively.

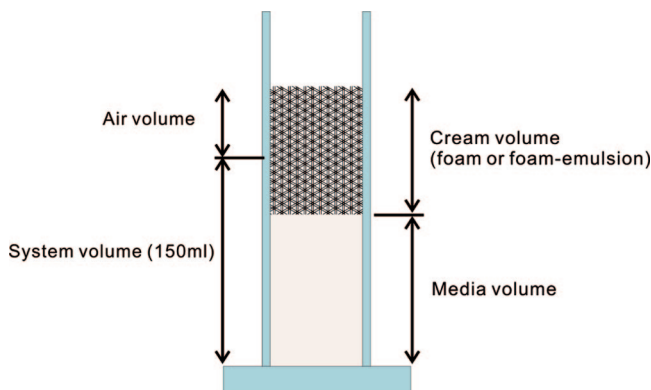


Figure 2. Schematics of the methodology of cream and air volume measurements in a test cylinder.

interface (exact for a flat interface).^{23–25} For a typical water/oil system, the transfer energy is much higher than the kinetic energy (kT) of Brownian motion,⁶ implying such a particle adsorption would be virtually an irreversible process. This strong, irreversible adsorption provides the physical basis for formation of foams and emulsions with long-term stability. Model systems of silica particles with varying hydrophobicity have demonstrated that particles of intermediate hydrophobicity are good stabilizers,^{26–30} while highly hydrophobic particles tend to self-aggregate and form gels in water, and those of low hydrophobicity have an insufficient affinity to an air or oil phase.

Recently, we reported the formation of superstable foams using polymer microrod particles, which were synthesized by a liquid–liquid dispersion method.^{31–33} The volume of rod-stabilized foams remained effectively constant for more than several weeks, even after water evaporation through the foam layer. Microscopic observations indicated that the air bubbles were covered with rigid shells of intertwining rods, which provided mechanical rigidity of the bubble interface and steric hindrance to film breakdown, resulting in an exceptional foam stability.^{32,33}

The application of particles as long-term stabilizers is important for the development of novel food, pharmaceutical, or biodegradable products, especially for foams where long-term stability is difficult to achieve. For example, foams containing partially hydrophobic silica nanoparticles are stable for several days and possibly infinitely,²⁹ while foams formed with protein stabilizers under similar conditions typically collapse in several hours.^{29,34} Most particulates presently used to form foams or emulsions with long-term stability are not of biological origin⁶ and are not suitable for consumption in food formulations. Although some natural bioparticles such as spores,³⁵ pollens,³⁵ cells³⁶ or viruses³⁷ were recently explored in processes for formation of foams of high stability, the larger scale application of such bioparticles in industrial products does not appear to be practical. Furthermore, particles used in food and pharmaceutical emulsions and foams must be FDA-approved or generally recognized as safe (GRAS). To advance in this area, therefore, one needs to identify low-cost, natural origin polymers of intermediate hydrophobicity and develop techniques to synthesize particles from them.

We report here how a simple liquid–liquid dispersion technique can be used to form superstable foams and foam-emulsions containing in situ formed particles of hydrophobically modified cellulose–hydroxypropyl methylcellulose phthalate, also called hypromellose phthalate (HP). Although currently not a food ingredient (more extensive toxicity studies are needed for food applications), the HP has a long history of coating applications in pharmaceutical products. Since the cellulose is nontoxic, inexpensive and abundant in nature, numerous cellulose derivatives have been commercially developed for various applications. However, only a few of them, including HP, have a sufficient hydrophobicity, which is essential for particle stabilizer action—as demonstrated by eq 1, where the maximal stabilizing effect occurs at $\theta = 90^\circ$. Furthermore, the HP has easy to control solubility depending on the selection of either solvent or pH. The HP was initially dissolved in water-miscible solvents such as acetone, ethanol/water mixture and acetate buffers. As these solutions were sheared in the aqueous media, micron-size cellulose particles were created from the hydrophobic cellulose solution by a solvent attrition mechanism. Consequently, these in situ formed particles were adsorbed onto water–air or water–oil interfaces created during shear blending, resulting in “superstable” foams or emulsions, which could survive over time periods much longer than the ones stabilized by regular molecular surfactants.

Experimental Section

Materials. Hypromellose phthalate (grade HP-55, M_w 84 000 g/mol, M_n 21 000 g/mol) was provided by Shin Etsu Chemical Co., Ltd. (Tokyo, Japan). The structural formula of this material is represented in Figure 1. Ethanol (anhydrous reagent grade), acetone (reagent grade) and hexadecane (reagent grade 99+%) were procured from Acros Organics (Morris Plains, NJ). The acetic acid and sodium acetate were from Fisher Scientific (Pittsburgh, PA). Soybean oil (Wesson vegetable oil, saturated fat 15%, polyunsaturated fat 58%, monounsaturated fat 22%) was purchased from Conagrafoods Inc. All chemicals were used as received without further purification. Deionized water was prepared from a Millipore water purification system (Millipore Milli-Q+, Billerica, MA).

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Table 1. Summary of Particle and Foam Characteristics Affected by Acetone-Based Stock Solution Composition and the Ratios (p) of Stock Solution Viscosity (η_1) to Viscosity of the Continuous Phase (η_o)

[HP], w/v %	$p = \eta_1/\eta_o^a$	particle size (μm)	particle morphology	foam characteristics
2	1.06	7.6 ± 3.7	mostly rod-like, fiber-shape	good foamability, poor stability
5	4.19	77.6 ± 29.6	irregular, fiber-shape	good foamability, poor stability
15	121	114.3 ± 59.7	irregular shape, spherical, fiber and sheets	moderate foamability, excellent stability
30	3360	226.8 ± 120.6	mostly sheets, some irregular shape, spherical and fiber-like	poor foamability, excellent stability

^a The continuous phase viscosity was assumed to be 0.001 Pa·s for water at 20 °C.

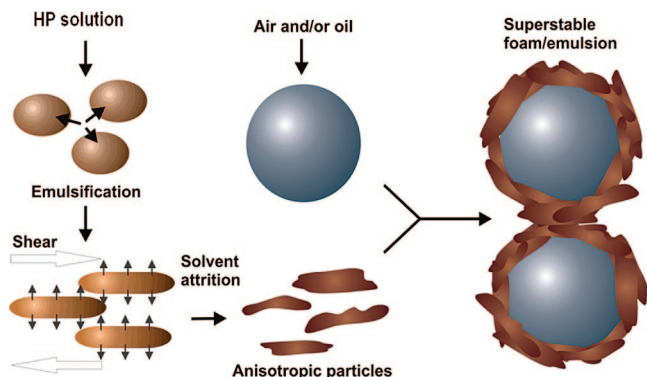


Figure 3. Schematics of the mechanism of forming foams and emulsions stabilized by in situ formed HP particles. Structures are not drawn to scale.

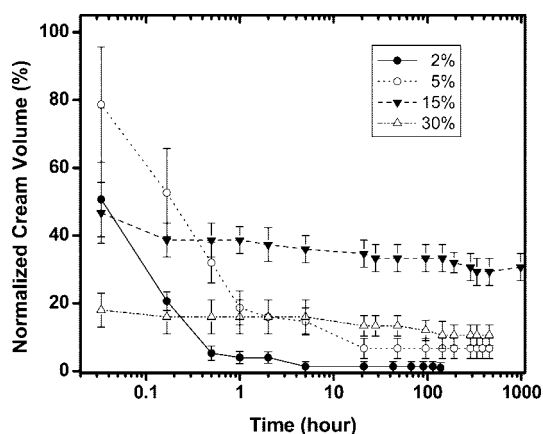


Figure 4. Time dependence of the cream volumes of foam systems prepared with stock solutions of different HP concentrations in acetone (2, 5, 15, and 30% w/v). The cream volumes reported are percentages normalized to the total system liquid volume before blending (see the Experimental Section).

Protocol for Preparing Foams. HP stock solutions for foam experiments were prepared at room temperature by dissolving varying amounts of HP powder in acetone, ethanol–water (8:2 v/v) mixture or acetate buffer solutions. For the acetone and ethanol–water systems, 10 mL of the stock solution was slowly poured into a food blender running at 15,000 rpm (Oster Model 4242, Sunbeam Products, Inc., Boca Raton, FL) containing 140 mL of deionized water. The foams immediately formed during the blending process for 60 s and were then transferred into a 250 mL graduated cylinder. The volumes of the creamed foam, the liquid portion underneath, and sediment (if applicable) were measured over time by reading the marks on the graduated cylinders. These volumes were used to evaluate the foamability (short-term foam volume) and foam stability (long-term foam volume) at room temperature.

An acetate buffer system was used to study the effect of the continuous phase pH on foam properties. The stock solution, 10 mL of a 10% (w/v) solution of HP in an acetate buffer (1 M, pH 5.3) was blended into solutions adjusted with acetic acid to a final pH

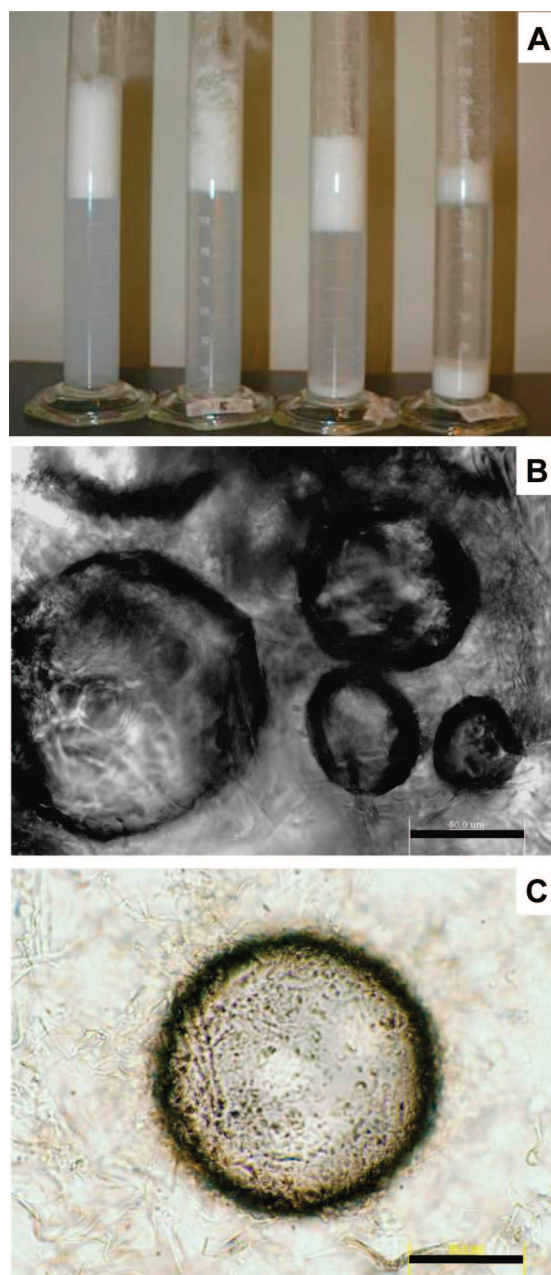


Figure 5. Appearance of the foams immediately after formation with 5%, 2%, 15% and 30% HP in stock solutions (from left to right) (A). Optical micrographs of foam system prepared from the stock solution of 15% HP in the first hour after formation (B) and after 20 days of incubation (C). The scale bars in images (B) and (C) are 50 μm .

of 3.2 or 4.2 after mixing or with 1 N NaOH to pH 5.1, 6.1, or 11.4. The remaining procedures were the same as the other two systems.

Protocol for Preparing Foam-Emulsions. The HP stock solution was prepared by dissolving 10% (w/v) HP in an acetate buffer (1 M, pH 5.3). A predetermined amount of soybean oil was blended for 10 s at room temperature into aqueous acetic acid solutions,

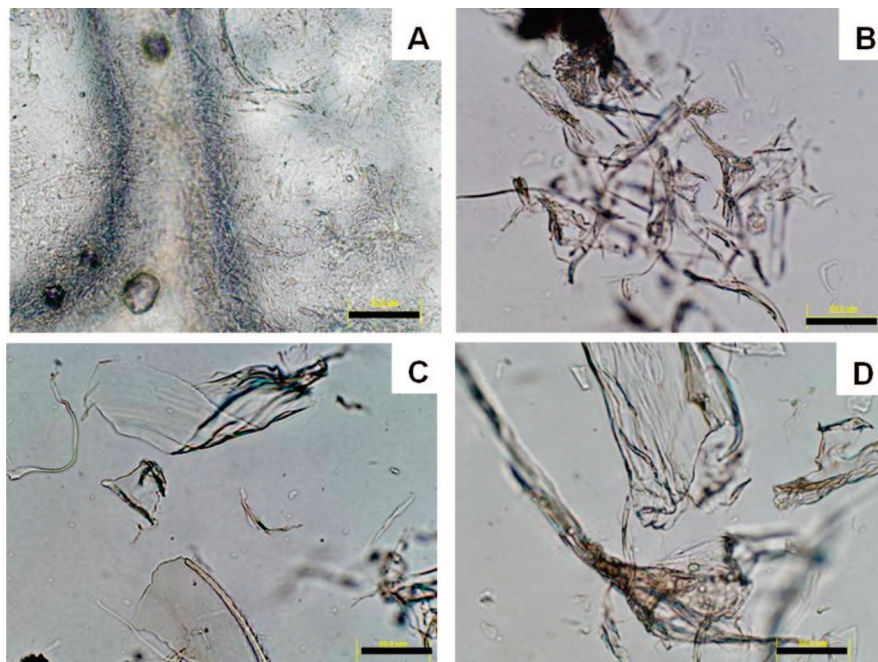


Figure 6. Optical micrographs of the morphology of typical particles formed from 2% (A), 5% (B), 15% (C), and 30% (D) of HP stock solutions in acetone, respectively. Scale bars are 50 μm .

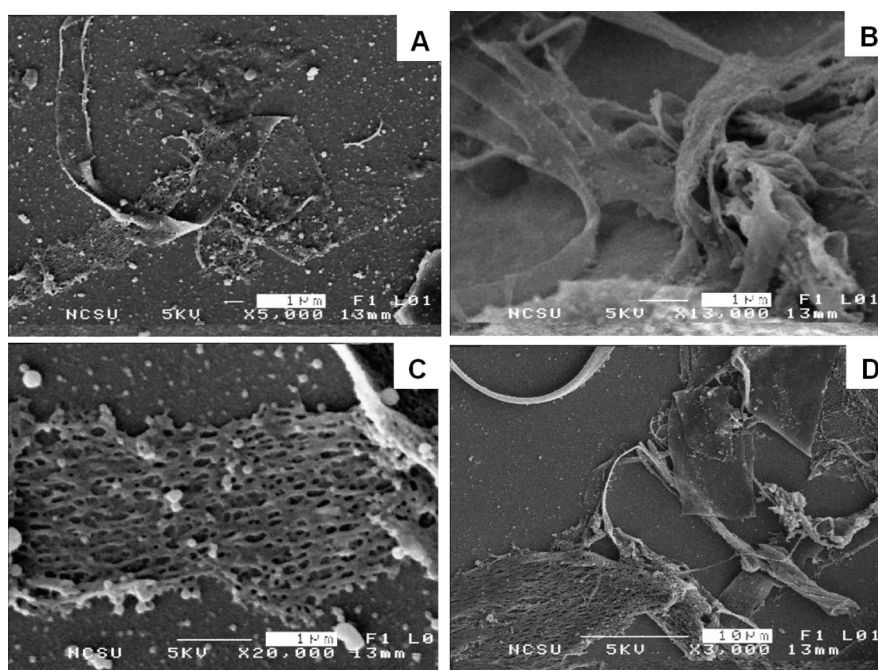


Figure 7. Scanning electron micrographs of the morphology of particles formed from 2% (A), 5% (B), 15% (C), and 30% (D) of HP stock solutions in acetone, respectively. Scale bars are 1 μm in images A, B, and C and 10 μm in image D.

followed by blending for additional 60 s after adding 10 mL of the stock solution and adjusting pH to 4.2. The total liquid volume in the formulations was kept constant at 150 mL. The cream volume and the air uptake volume were measured as illustrated in Figure 2. The values reported in the figures are normalized to the system volume (150 mL) by the following relations: [normalized cream volume %] = [cream volume/system volume] \times 100; [normalized air uptake %] = [air uptake volume]/[system volume] \times 100.

Characterization of the Particles, Foams and Emulsion Structure. The structure and morphology of HP particles, foams and foam-emulsions prepared from different formulations were characterized with an optical microscope (Olympus BX-61, Tokyo, Japan) during incubation at room temperature. The HP particle size

and distribution were obtained by measuring the lengths and widths of over one hundred particles from digital microscopy images. Scanning Electron Microscopy (model S3200, Hitachi Ltd., Tokyo, Japan) was performed at 5kV with vacuum-dried HP particle samples. To improve the imaging quality, a 200 Å thick gold layer was predeposited on the sample surface.

Contact Angle Measurements. Contact angle experiments were performed using Rame-Hart goniometer (Model 100-00). HP films were prepared by spin-coating HP stock solutions with different solvents, followed by drying in a vacuum oven at 90 °C for 6 h. The advancing contact angles onto these HP films were measured with droplets of 10 μL deionized water at room temperature. The contact

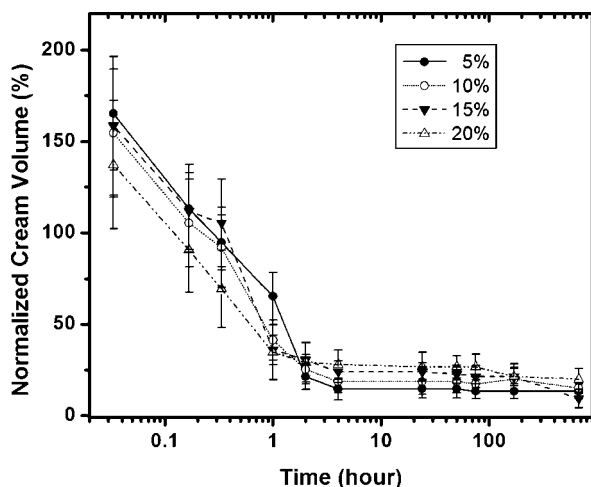


Figure 8. Time-dependence of the normalized volumes of foam systems prepared with stock solutions of different HP concentrations (5, 10, 15, and 20% w/v) in 8:2 (v/v) ethanol/water mixtures.

angle values were averaged over 3 measurements, collected at different sample positions.

Viscosity Measurements. The viscosities of the stock solutions with varying HP concentrations were determined by an AR2000 rheometer (TA Instruments, New Castle, DE) at room temperature. Shear rate ramps were performed from 0.01 to 100 s^{-1} at 20 °C using a Searle set up (bob OD = 28 mm and cup ID = 30 mm). The polymer solutions showed a weak shear-thinning behavior at low shear rate, while the viscosity is almost constant at a shear rate greater than 1 s^{-1} . Because of the difficulty in quantifying the exact shear rate during blending, the average viscosities (stock solution viscosity (η_1) in Table 1) were determined from the measurements at the shear rate higher than 1 s^{-1} .

Zeta Potential. The surface charges of HP particles were estimated using zeta potential meter (Lazer Zee Meter Model 501, PenKem, Inc., NY). Zeta potentials of the HP particles prepared from different stock solutions were determined from average values of three measurements.

Results and Discussion

In a typical experiment, shearing the HP stock solution in the continuous phase produces HP particles by solvent attrition, leading immediately to formation of stable foams or foam-emulsions (containing both air bubbles and oil droplets if the system had oil during blending, as will be discussed in later sections). In this section, the mechanism of particle and foam or foam-emulsion formation is first discussed. Subsequently, the results for the foam systems are presented, followed by discussing more complicated foam-emulsion systems. We focus particularly on acetate buffer systems, where both stock and bulk solutions are water-based, due to the environmental advantages of this organic solvent-free process.

Mechanism of Particle and Foam/Foam-Emulsion Formation. The liquid–liquid dispersion processes leading to particle formation are based on the solvent attrition, triggered by an abrupt solubility change of HP in the continuous media. Basic requirements for designing an experimental system using this technique include i) finding a good solvent for HP to prepare stock solutions, ii) using an antisolvent for HP as the continuous medium, and iii) having a good miscibility between the above two solvents (i.e., the good-solvent and antisolvent). When the solvent is transferred into the much larger volume of antisolvent, the HP is separated in the form of particles. The continuous antisolvent phase in all experiments was either deionized water or aqueous buffer at pH < 5. Two principally different types of

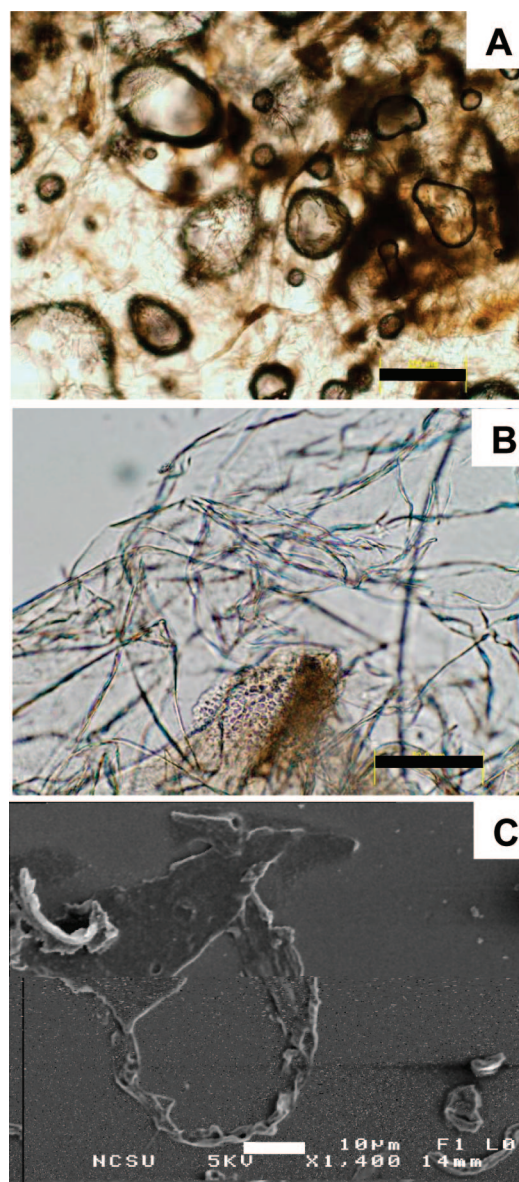


Figure 9. Optical micrographs of structures formed with 10% HP in the ethanol–water mixture, taken (A) 20 min and (B) 20 days after formation. (C) SEM image of the dried particles from the same foam. Scale bars are 200 μm in (A) and (B) and 10 μm in (C).

Table 2. Surface Properties of HP Made from Different Solvents

	HP from acetone solution	HP from ethanol–water solution
water contact angle of HP film	72°	55°
zeta potential of HP particles at pH 3.5	−22 mV	−29 mV

solvent were tested for the dispersed phase. The first solvent/antisolvent process makes use of common organic solvents — acetone or ethanol. The second approach to particle formation is based on the HP solubility in acetate buffer at pH > 5. The HP dissolved in the buffered water media at high pH is separated into particles when the droplets are diluted into the larger water volume buffered to pH < 5. In effect, water is used as *both* solvent and antisolvent, depending on the pH.

The processes of particle and foam formation during the one-step blending process are illustrated in Figure 3. When a stock solution (concentrated HP solution in good solvent) is mixed with the medium (antisolvent for HP) by shear flow in

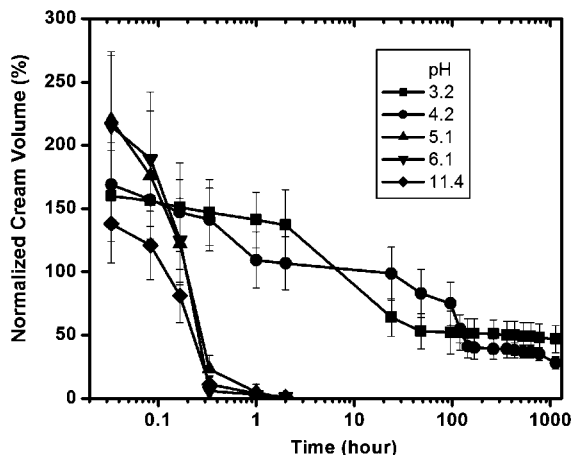


Figure 10. Effect of pH in the continuous phase on the foamability and foam stability of HP-stabilized foams. The volumes are normalized to the total system volume before blending. The pH values in the legend are the final values after blending, and the stock HP concentration is 10% w/v in an acetate buffer at pH 5.3. The drastic change in stability at pH 4.2 and lower can be correlated to the formation of particles under these conditions and prove the major stabilization effect of the particles.

the running blender, it becomes dispersed into small droplets. The HP that is molecularly predissolved in the droplets loses its solubility due to the attrition of the solvent into the bulk water phase, and consequently solidifies to form microparticles. During this process, the droplets are deformed into far-from-equilibrium shapes because of the low interfacial tension and the turbulent flow in the blender, leaving behind irregularly shaped HP particles after the solvent attrition. These particles, with intermediate hydrophobicity, adsorb onto the air–water or oil–water interfaces created in the blending process and subsequently stabilize them.

The breakup of droplets in the liquid–liquid dispersion stage can be characterized by a dimensionless capillary number, N_{Ca} ³²

$$N_{Ca} = \mu_o \dot{\gamma} a / \sigma \quad (2)$$

where μ_o is the viscosity of the dispersion medium, $\dot{\gamma}$ is the shear rate, a is the drop radius before deformation, and σ is the interfacial tension. The dispersion medium viscosity, μ_o , shear rate, $\dot{\gamma}$, and droplet radius, a , were similar in all experiments because we used a fixed blender speed, a constant volume of 10 mL stock solutions, and either deionized water or aqueous buffers as the bulk medium. Because all solvents used are completely miscible with water, the droplet interfacial tension is expected to be small except for the systems that contain oil. Relative viscosity of the stock solution to that of continuous medium is another critical parameter determining particle size and morphology.³² Variables we controlled included the viscosity of stock solutions (by changing HP concentration) and solvent chemistry (by dissolving HP in stock solutions with different solvents and shearing the stock solutions into a continuous phase at different pH conditions). The complexity was then increased to incorporate oil into the system (forming mixture of foams and emulsions, i.e., foam-emulsions).

Foams Prepared with Acetone-Based Stock Solutions. The effects of HP concentration in acetone-based stock solutions on the foamability and foam stability were evaluated by measuring the foam volumes shortly after blending and during the subsequent incubation at room temperature (Figure 4). The foamability (volume shortly after formation) was generally higher at a lower HP concentration, whereas the foam stability (residual volume at long incubation time) was better at a higher stock HP concentration. For the 2% stock solution, it was difficult to accurately measure the foam volume immediately after blending because the foam was very unstable in the first hour and completely collapsed within the first day. The foamability was the highest with 5% HP in the stock solution, while its long-term stability was poor since foam collapsed to a constant cream volume of ~ 9 mL within one day. The stock solution with 15% HP demonstrated the best overall foam properties, where we obtained not only a large initial foam volume but the foam was also very stable even after incubation for 40 days. In contrast, after further

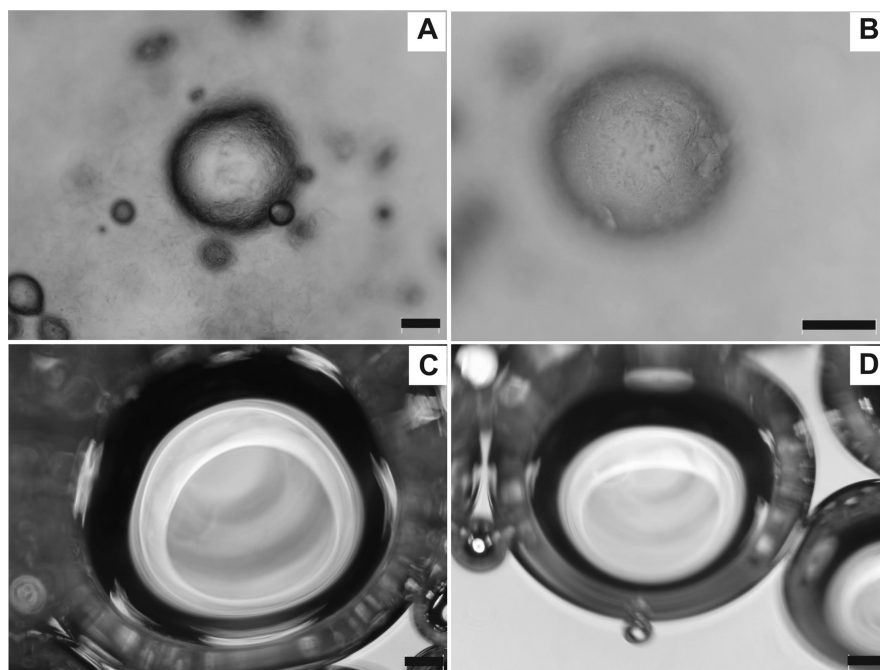


Figure 11. Micrographs of bubble/foam systems formed from a stock solution of 10% HP in 1 M acetate buffer, sheared into a continuous phase medium of pH 3.2 (A), 4.2 (B), 5.1 (C) and 6.1 (D), respectively, taken 10 min after formation. Scale bars are 100 μm .

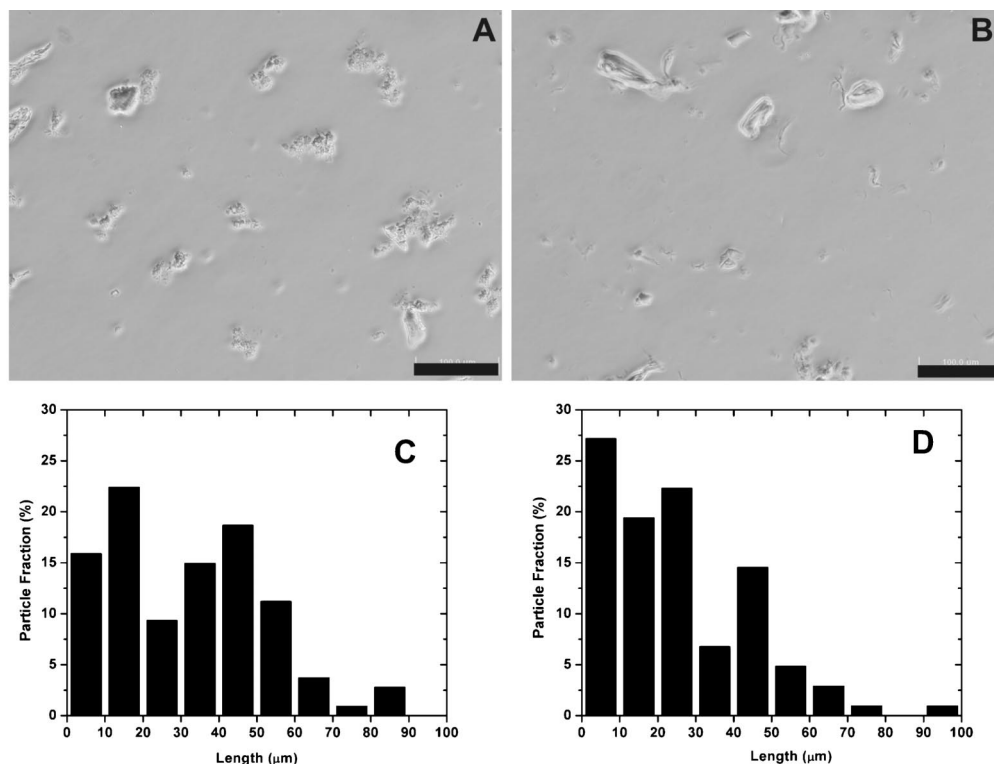


Figure 12. Optical micrographs and size distributions of HP particles formed by mixing 10% HP in 1 M acetate buffers with aqueous media at pH 3.2 (A, C) and 4.2 (B, D). Average particle lengths and standard deviations at pH 3.2 and 4.2 are $33.6 \pm 20.8 \mu\text{m}$ and $26.3 \pm 19.0 \mu\text{m}$, respectively. Scale bars in (A) and (B) are $100 \mu\text{m}$.

increasing the HP concentration to 30%, we observed poor foamability (small initial volume) with good foam stability (maintaining a constant volume). Based on these results, we conclude that an intermediate HP concentration in the stock solution (e.g., 15%) would lead to the formation of a large volume of foam with good stability.

The appearance of the actual foams is presented in Figure 5A. Optical micrographs of foam structures made from the 15% HP stock solution immediately after formation and after 20 days incubation are presented in Figure 5B and C, respectively. Evidently, the HP particles formed had a strong affinity to the air–water interface, building up voluminous shells around the bubbles (Figure 5B). The intertwined HP particles adsorbed onto the interface provided steric hindrance. The dense shells of HP particles in the foam are holding the individual bubbles far apart thus preventing their interaction and possible coalescence. After 20 days of storage, the air bubbles were still stabilized by the particles although there were indications that some wetting of the particles had occurred (Figure 5C).

The morphologies of particles formed at different HP concentrations in the stock solutions are demonstrated in Figures 6 and 7 and summarized in Table 1. The particles were small and fiber-like at low HP concentrations (2% and 5%), while they became big sheet-like structure at higher HP concentrations (15% and 30%). At lower HP concentrations, the stock solution was sheared more easily due to its low viscosity and the resulting droplets subsequently solidified into smaller particulates. These smaller particles adsorbed rapidly onto an air–water interface and provided good short-term foamability (Figure 4). However, smaller particles hardly interlocked to create rigid shells preventing the foam destabilization, resulting in the film rupture and poor foam stability. On the other hand, big, irregular or sheet-shaped particles (Figure 6C and D) were formed at higher HP concentrations, probably due to the interplay of higher

viscosity and higher degree of supersaturation. Since big particles require a longer time to reach and adsorb onto the air–water interfaces, they originally resulted in poorer foamability (Figure 4). Once bigger particles adsorbed onto the interfaces, however, they formed rigid shells that provided steric hindrance against the film rupture, resulting in good stability. These larger particles were also unstable against the gravity force and tended to sediment, as shown in Figure 5A where a substantial amount of particles has settled for the stock solution with 30% HP. An optimum condition, therefore, for both foamability and foam stability was found at an intermediate HP concentration of 15%, where enough particles with appropriate particle size and morphology could be obtained.

The SEM micrographs in Figure 7 represent the morphologies of HP particles in higher detail, supporting the trends of particle size and shape observed from optical micrographs (Figure 6). Additionally, the SEM images showed that sheets formed at higher HP concentrations had a porous structure (Figure 7C and D). This porous morphology may have resulted from solvent phase separation in the viscous droplets of the sheared stock solution at a high HP concentration. The formation of porous particles is of general interest for processes leading to foam and emulsion stabilization as it allows more efficient use of the stabilizer, however, the porous particles formed here were too large to stabilize voluminous foams.

Foams Prepared with Ethanol-Based Stock Solutions. To further investigate the mechanism of particle formation and subsequent foamability and stability, we applied the same protocol with stock solutions of HP dissolved in a binary mixture of ethanol and water (8:2, v/v). In this ethanol-based system, varying the HP concentration produced no qualitative and only weak quantitative differences in foam properties (Figure 8). Comparing Figure 4 with Figure 8, the ethanol-based systems enabled much better foamability (larger short-term foam

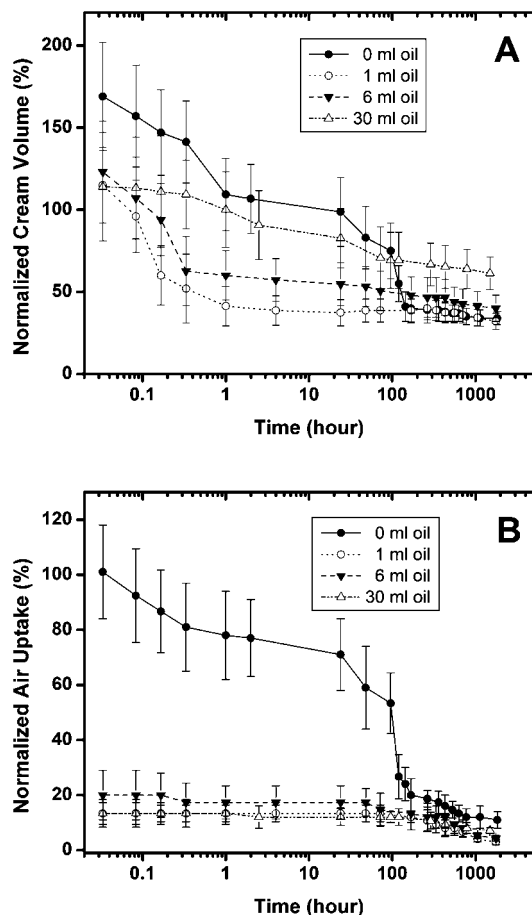


Figure 13. Cream volume (A) and net air uptake (B) of foam-emulsions stabilized by in situ formed HP particles from acetate-buffer-based stock solutions with 10% (w/v) HP. The normalized cream volume and normalized air uptake are defined in the Experimental Section. The numbers in the legend are volumes of oil added to the system.



Figure 14. Optical micrographs of an air bubble in the foam-emulsion stabilized by HP in acetate buffer solution. The bubble is surrounded by both HP particles and oil droplets. The system contains 6 mL of vegetable oil. Scale bar is 20 μm .

volumes), whereas the foams collapsed rapidly indicating poorer foam stability.

The micrographs in Figure 9 demonstrate that big HP sheet-like structures were formed when ethanol/water mixtures were used as a solvent. Initially, these sheet-like particles adsorbed onto the air bubble surfaces (Figure 9A). After 20 days of aging, however, they extensively detached from the interfaces (Figure

9B) leading to defoaming, implying a decrease in their affinity to the air/water interface. This result is quite different from the acetone-based system (Figure 5C), where particle-stabilized air bubbles were still intact after 20 days.

The destabilization of the ethanol-containing systems could be correlated to slow hydrophilization of the particles, resulting in desorption. We confirmed this hypothesis by evaluating the hydrophilicity of the aged particles from acetone and ethanol based system by two different methods, contact angle and zeta potential. The results are shown in Table 2. Water contact angles on HP films formed from acetone and ethanol stock solutions were 72 and 55 $^{\circ}\text{C}$, respectively, i.e., the former are much more hydrophobic and closer to the optimal contact angle of 90 $^{\circ}$. This conclusion is also supported by zeta potential measurements indicating that the surface charges on the HP particles formed from ethanol-based stock solution (−29 mV) were higher than that from acetone-based solution (−22 mV). Thus the particles in the ethanol media are more charged and hydrophilic, have a suboptimal contact angle and act as poor foam stabilizers.

The difference between acetone and ethanol–water solvent systems may also be related to the different volatilities of the solvents and hydrophobicity of HP in different solutions. Acetone is much more volatile than ethanol (the vapor pressures of acetone, ethanol and water at 20 $^{\circ}\text{C}$ are 24604, 5851 and 2338 Pa, respectively^{38,39}). Because of the high acetone volatility, it is likely that a higher fraction of the original HP solvent (i.e., acetone) escaped from the system during blending, transferring, and aging. The presence of the volatile organic compound may have led to lower foamability for acetone-based systems, but it also leaves behind HP particles that are insoluble in the continuous water phase and that would change little over time. In contrast, a much higher portion of the less volatile ethanol remained in the continuous phase during the particle formation process. The different attrition rate of ethanol is probably the reason for the formation of dominantly sheet-like structures and a higher total short-time foam volume. The ethanol remaining in the water phase (~5%), however, likely makes the HP particles more wettable and soluble as demonstrated by the data in Table 2. Since the surface tension of ethanol (22.1 mN/m) is much smaller than that of water (72.8 mN/m), the presence of ethanol decreases both surface tension and contact angle, resulting in significant reduction of transfer energy in eq 1. Thus, it is likely that the HP particle's affinity to air–water interface decreases in the presence of ~5% ethanol. As a result, HP particles might detach from the interfaces, leading to poorer long-term foam stability.

Foams Prepared with Acetate Buffer HP Stock Solutions.

HP is widely used in enteric coatings for pharmaceuticals since it possesses pH-dependent solubility. The product HP-55 is soluble in buffer solutions at pH > 5, where carboxyl moieties in the phthalate group (Figure 1) become negatively charged because of deprotonation, providing good solubility. This pH-dependent ionization^{9,40} allowed us to design simple and effective process for particle formation and foam stabilization in aqueous buffers by manipulating the pH of stock and bulk solutions. Stock solutions with HP dissolved in an acetate buffer (pH 5.3) were blended into acidic or basic solutions preadjusted to give a final pH value of 3.3, 4.2, 5.1, 6.1, or 11.4 after mixing. The results, plotted in Figure 10, show that the foamability was very high at all pH conditions. However, a remarkable dependence of foam stability on pH was found. The foams at pH > 5 completely

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broke down within 30 min, whereas the cream volumes of the foams at $\text{pH} < 5$ initially slowly decreased over a couple of days, and then stabilized and remained almost constant with a normalized cream volume of $\sim 30\%$ for over 6 weeks. As shown in Figure 11A and B, the bubbles prepared at $\text{pH} < 5$ are covered with particles residing at the air/liquid interface, whereas at a $\text{pH} > 5$, HP remained dissolved, as demonstrated by the smooth bubble surface without any particle detectable with optical microscopy (Figure 11C and D). At high pH , HP is soluble (no particle formation after blending) and acts as a molecular surfactant, whose good foamability followed by poor long-term stability are characteristic properties of the small surface active molecules.³⁴ These results provide clear evidence that insoluble solid particles are the key reason for the long-term foam stabilization.

The morphologies of HP particles formed at final pH 3.2 and 4.2 are illustrated in Figure 12. The particles are of slightly elongated shape with an aspect ratio of ca. 2, and their average lengths were determined as $33.6 \pm 20.8 \mu\text{m}$ and $26.3 \pm 19.0 \mu\text{m}$ for pH 3.2 and 4.2, respectively. Bigger particles were formed at lower pH , which might be attributed to the decreased HP solubility in aqueous medium as pH decreases. The slightly elongated particle shape is quite different from the long fiber or sheet shapes observed in acetone or ethanol system discussed in earlier sections. Though the details of the particle formation mechanism are still not elucidated, we believe this particle shape and size difference is related to the difference in the modes of HP dispersion and solidification, since the chemistry as well as kinetics of the solidification process during pH -induced jump are quite different from the ones in regular solvent attrition mechanism (i.e., acetone or ethanol systems). The detailed mechanism of pH induced particle formation and their foaming properties are under investigation.

Unlike the acetone or ethanol-based system, the foams produced from organic solvent-free, aqueous buffer systems are particularly promising for environmentally friendly, biodegradable, pharmaceutical or edible dispersions where both good foamability and good stability are required.

Foam-Emulsions Prepared with Acetate-Buffer-Based Stock Solutions. Many food dispersions (e.g., ice creams and whips) and cosmetic products are complex colloid systems containing both oil and air in dispersed phases, i.e., foam-emulsion systems. We extended the investigation to foam-emulsion systems stabilized by HP particles via the simple blending process. The affinity of HP particle to oil–water interface as well as emulsion-foam stability were examined with the acetate-buffer-based foam protocol followed by adding soybean oil, as a model foam-emulsion system. The foam-emulsion system prepared with ethanol-based stock solution was also investigated and its results are included in the Supporting Information.

The cream volumes and net air contents of foam-emulsions are presented in Figure 13 and compared to the oil-free system. To take into account the amount of air included during the blending, the net air uptake by the system was estimated as the relative volume increase of the system. The volumes of the cream formed from acetate-buffer-based foam-emulsions were smaller

than that of oil-free foam at an identical HP concentration (Figure 13A), whereas they had better long-term stability than oil-free foam. The much smaller initial air content of the foam-emulsion systems in comparison to the oil-free foam (Figure 13B), implies that the HP particles preferentially adsorbed onto oil droplet surfaces and stabilized them instead of the bubbles.

The optical micrograph in Figure 14 shows that oil droplets and HP particles together formed aggregates that further adsorbed onto air bubbles. Before adding the HP stock solution, the oil is sheared into small droplets, which coexist with air bubble during blending. Upon addition of the HP stock solution the HP droplets solidify to form particles by solvent attrition as in the oil-free case. The HP particles, however, preferentially adsorb onto the oil surface, forming particulate-stabilized oil droplets. Subsequently, these HP particle-stabilized oil droplets, along with free HP particles, adsorb onto a few air bubbles, forming bubbles stabilized by composites of particle-stabilized oil droplets and particles, i.e., foam-emulsions. Thus, the microscopic droplets of insoluble oil may provide an additional particulate component for stabilization of foams containing HP particles. We performed similar experiments with pure hexadecane oil instead of vegetable oil that might contain impurities such as surface active compounds. The morphologies and the stability of foam-emulsions of hexadecane oil system (data not shown) were similar to those of vegetable oil system.

Concluding Remarks

The results demonstrate that cellulose derivatives can be dispersed into surface active particles, which in turn produce superstable Pickering foams and emulsions. Both the short-term and long-term ability of HP to stabilize interfaces strongly depended on the concentration of HP in the stock solution and the composition of both stock and continuous phases. The hydrophobicity and the wetting properties of the in situ formed HP particles strongly affected the dispersion stability. Although the use of organic solvent—ethanol or acetone—may be acceptable in some applications, we also report an efficient “organic-solvent-free” process where both the stock solution and continuous phase were aqueous buffers at different pH . Celluloses are abundant, renewable, and economically attractive. The processes described in this paper are simple and scalable. The finding of such excellent foam/emulsion stability, based on inexpensive and biologically safe cellulose derivatives, could be promising in developing novel applications, including food, pharmaceutical, cosmetic and personal care products where edibility and biodegradability as well as long-term stability are desired.

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Supporting Information Available: Additional results of the foam-emulsions prepared with ethanol-based stock solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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