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ARTICLE

Tuning Particle-Particle Interactions to Control Pickering Emulsions Constituents Separation

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We demonstrate that the separation and recovery of solid-stabilized (Pickering) emulsions constituents is significantly improved via a simple filtration approach – without any additional chemical agent – by initially grafting sodium alginate (SA), a natural polysaccharide, onto silane-modified sub-micrometer silica particles. The combination of surface-grafted trimethoxy(propyl)silane (TMPS) and (3-aminopropyl)trimethoxysilane (APTMS) controls particle wettability, verified via zeta potential and contact angle measurements. Rheometry and filtration experiments reveal that further grafting of SA via APTMS enhances particle-particle and droplet-droplet interactions. This work provides an approach towards the design of environmental-friendly Pickering emulsions based chemical engineering processes with easy-to-separate and reusable particles, allowing waste reduction and reduced toxicity advantages.

Introduction

Solid-stabilized (or Pickering) emulsions are multiphase systems composed of liquid droplets dispersed in a second immiscible liquid. They are stabilized by sub-micrometer or nanometer-sized particles adsorbed at the liquid/liquid interface.[1] This surfactant-free composition, combined with an exceptional stability, has generated interests in fields such as food formulations,[2] cosmetics,[3] drug delivery,[4] oil recovery,[5] nanocatalysis,[6, 7] and waste water treatment,[8] to name a few. However, their stability is also a concern when it comes to designing processes in which these emulsions must be broken, and the components separated, for material recovery.

As a result, the separation of Pickering emulsions constituents has become an important research topic over the years. For example, one of the major issues in the petroleum industry is the breakdown of undesirable Pickering emulsions formed during the different stages of oil recovery processing.[9] At the moment, synthetic and/or toxic chemicals and polymers are often used.[10, 11] In pharmaceutical and food applications,[4,12] the possibility of triggering the release of encapsulated compounds is likewise of significant interest. As a result, emulsions that can be destabilized on demand by modifying the surface activity of the particles in response to an external trigger such as changes in pH,[13-17] CO_2 concentration,[18] light sensitivity,[19] temperature,[20] magnetic field,[21, 22] or combinations thereof, have recently been developed.

The main approaches currently explored to separate Pickering emulsion constituents can be classified as chemical,[23] mechanical,[24] magnetic[25] and electrically-based.[26] Chemical techniques are the most common and popular; however, they often involve large quantities of additives such as surfactants or polymers,[27,28] leading to water contamination and environmental pollution.[23] Mechanical destabilization methods such as centrifugal separation require high initial capital investment and maintenance.[29] In the case of magnetic and electrical approaches, the former is effective only under certain circumstances such as breaking droplets stabilized by magnetic particles, while the latter is feasible only for charged particles.[22] As a result, there is still a demand for simple, ecofriendly and low-cost techniques for the separation of solid-stabilized emulsions constituents.

In our previous work, we demonstrated that surface-modified particles grafted with sodium alginate (SA), a natural pH sensitive gelling polysaccharide composed of two randomly distributed guluronic and mannuronic acid units on its chain, displayed enhanced aggregation/disaggregation properties. This behavior in aqueous solution is due to the reversible hydrogen bond formed between neighboring particles – these "sticky" particles form significantly larger flocs as compared to unmodified particles, resulting in easier and faster sedimentation.[30] Chen et al. have also synthesized pH-responsive SA grafted silica nanoparticles in applications related to drug delivery, exploiting the formation of a three-dimensional network of grafted SA chains to create high-stability systems.[31]

In the present work, we hypothesize that these "sticky" particles could not only enhance interparticle interactions in solution, but also droplet-droplet interactions when adsorbed

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x at the oil/water interface in Pickering emulsions. Therefore, the main objective of this work is to design and prepare solid-stabilized emulsions using SA-modified silica particles, and to assess if these particles can facilitate the separation and recovery of the emulsion's constituents by a simple filtration approach.

Experimental section

Materials

Sub-micrometer silica particles (SP) were provided by Nippon Shokubai Trading Co. (average diameter $d \approx 290 \pm 13$ nm validated by SEM, specific surface area $S = 42 \pm 2$ $m^2 \cdot g^{-1}$, measured by BET with a Micromeritics ASAP 2020 instrument). (3-Aminopropyl)trimethoxysilane (APTMS, 97%), alginic acid sodium salt from brown algae (CAS 9005-38-3, low viscosity, molecular weight ≈ 60 kDa, pKa = 3.5),[32] *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC, > 98%), trimethoxy(propyl)silane (TMPS, 97%), *N*-hydroxysuccinimide (NHS, 98%), sodium azide (> 99%), Na_2CO_3-$NaHCO_3$ buffer solution (pH 10.01) and 5-(4,6-dichlorotriazinyl) aminofluorescein (DTAF) (D0531) were all purchased from Sigma-Aldrich and used without further purification. Ethanol (99.8%) was obtained from Thermo Fisher Scientific. HCl 1 N and NaOH 12 N solutions were of analytical grade and prepared without further purification with Milli-Q water (DI water, 18.2 MΩ·m, Synergy 185 system by Fischer Scientific). Low viscosity white mineral oil (Puretol^{TM} 7, density of 0.846 kg/l and viscosity of 12.2 cSt at 40 ˚C) was provided by Petro-Canada.

Particles Surface Modification

Silane Grafting

In order to graft SA onto silica particles and to control particle wettability, two types of silane agents were surface-grafted simultaneously. In a typical batch, 10 g of SP particles were dispersed in a hydrophobized Erlenmeyer flask containing 100 ml of a 95% v/v ethanol solution and DI water, while stirring at 600-700 rpm with a magnetic stirrer.[33] The pH was then adjusted to 4.5 - 5.5 using HCl 1 N. APTMS and TMPS were added dropwise while stirring at room temperature, targeting a surface coverage of 10 molecules·nm^{-2} (1:1 APTMS:TMPS relative composition) (**Scheme S1**).[34] Typically, to modify 10 g of particles, 6.10×10^{-1} ml of APTMS and 6.15×10^{-1} ml of TMPS were added to the medium and the reaction was carried for 12 h at room temperature. The particles were collected by centrifugation (Sorvall RC 6+, Thermo Fisher Scientific) at 8000 rpm for 15 min and cleaned by washing twice with ethanol in order to rinse off any remaining unreacted silane. The particles were finally dried in a vacuum oven at 70 ºC for 2 h.

Sodium Alginate Grafting

A fraction of the silane-modified particles (SP-Sil) were further modified by grafting SA on their surface. In a typical experiment, 0.4 g of SA was first dissolved in 40 ml of DI water (1% w/v). 1.4×10^{-2} g of EDC and 0.9×10^{-2} g of NHS (1:1 EDC:NHS molar ratio) were then added to the solution (EDC/-COOH molar ratio = 0.1, relative to the -COOH groups of alginate).[35] Then, 4 g of SP-Sil particles were added to the reaction medium and the pH was adjusted to 4.5 with HCl 1 N (**Scheme S1**). The reaction proceeded for 15 h at room temperature and the mixture was subsequently centrifuged at 8000 rpm to collect the modified particles, which were washed with DI water 3 times. Finally, the particles modified with alginate (SP-SA) were dried in a vacuum oven at 70 °C for 10 h.

Particle Surface Characterization

Zeta Potential Measurements

The zeta potential (ζ) of particles was measured with a Zetasizer Nano ZSP instrument (Malvern Instruments Ltd., Worcestershire, UK). Particles were first dispersed in DI water at pH 3.0, pH 7.0 or pH 10 (adjusted by adding HCl 1 N and NaOH 12 N) at a 0.001 g·ml^{-1} concentration. The measurements were performed at 25 °C, using at least three different samples for each particle type, by microelectrophoresis. Disposable zeta potential folded capillary cells (DTS1070) were used. The instrument determined the electrophoretic mobility, and the Smoluchowski model was then applied by the software for the calculation of ζ.[36]

Contact Angle Measurements

Since the silica particles locate at the oil/water interface (the contact angles are formed between the silica, water and oil phases), contact angles were measured by depositing a droplet of water on a disk of compressed particles, immersed in oil. Contact angles were measured using an OCA20 optical tensiometer (DataPhysics Instruments GmbH) at 25°C. First, disks composed of compressed particles (SP, SP-Sil or SP-SA) were prepared with a laboratory press (Model C 3100-212, Carver laboratory Press, USA). For each disk (12 mm diameter, 0.5 mm thick), 0.1 g of dried particles were compressed at 70.2 MPa for 2 min. For a typical contact angle measurement experiment, a disk was immersed in a quartz cuvette containing 5 ml of mineral oil. Then, a 4 µL droplet of deionized water was carefully deposited on the disk's surface with a syringe (0.52 mm internal needle diameter, Hamilton model 1750TLL 500 µL). Images of the sessile water droplet were automatically acquired at 10 frames per second, until the water droplet completely penetrated into the pellet. The image illustrating the first contact between the water droplet and the pellet was considered as corresponding to the contact angle, $\Theta_{o/w}$. Four compressed disks were prepared for each type of particles, and one measurement was realized on each.

Emulsions Preparation and Characterization

Emulsions were prepared in screw cap glass vials (internal diameter = 1.2 cm, height = 4.6 cm) using a Cole-Parmer LabGEN 125 Homogenizer with a homogenization element of inner diameter 0.5 cm, at 18,000 rpm for 4 min. All emulsions contained 4% (w/v) particles (0.6 g) dispersed in 15 ml of liquid, at pH 3.0 or 7.0 (adjusted with HCl 1N or NaOH 12N), with the oil volume fraction ϕ_o ranging from 0.1 to 0.9. Particles were added in the vial and dispersed in water by homogenization, followed by the dropwise addition of the required volume of oil, while homogenizing. Pictures of emulsions in glass vials and other photographs were taken with a Nikon DX AF-S Nikkor 18-55mm f:3.5-5.6 G VRII objective camera. Homogenizer processing did not alter or break silica particles, as the SEM of **Figure S1** illustrate.

Droplet Observation and Diameter Measurement

Dispersed phase droplets were observed by dark field optical microscopy (Olympus BX51 by Cytoviva, objectives = 10x UPL Fluorite Oil, and 100x UPL Fluorite Oil Camera Q imaging, Retigna 2000R fast 1394, cooled color 12 bit). A drop of emulsion was first diluted in water at pH 3.0 or 7.0 before observation using glass slides (Fisher Scientific). Images were analyzed using the ImageJ software to determine drop size and to calculate the number-average diameter *d* of the observed droplets. Droplet size was also measured by laser diffraction using a MasterSizer 3000 instrument (Malvern Instruments, Canada).

Rheological Behavior

The rheological properties of freshly prepared emulsions with SP or SP-SA particles were measured with an Anton Paar MCR502 stress-controlled rheometer instrument. Disposable measuring plates D-PP25/AL/S07 (diameter: 25 mm) and dish EMS/CTD 600 (diameter: 56 mm) geometries from Anton Paar, covered with extra fine (320) sand paper, were used to avoid emulsion slipping. To prevent water evaporation during experiments, the geometry was covered with a solvent trap. All experiments were performed at 21˚C.

After emulsion preparation, prior to the rheological tests, the samples were first stored under vacuum for 15 min to remove any trapped air bubbles. Then, the samples were carefully loaded into the rheometer and the top plate geometry was lowered to a 1 mm gap. Samples were pre-sheared at 0.1 s^{-1} for 2 min. After determining the linear viscoelastic (LVE) regime, the storage and loss moduli (*G′* and *G″*, respectively) were measured during dynamic time sweeps (ω = 1 rad·s^{-1}, γ_0 = 1%) for 2 h.

Self-holding Properties and Yield Stress

Oil-in-water emulsions (4% particles (SP or SP-SA), ϕ_o = 0.8, pH 3.0 and pH 7.0) were transferred into plastic molds (14 mm internal diameter, 22 mm height, as shown in **Figure S2**) for 48 h at room temperature covered with aluminum foil to prevent water evaporation. The molds were then removed, and the emulsions' mechanical strength was evaluated by applying three incremental stresses (193, 290, 387 Pa) on the samples. The normalized height ($h(t)/h_0$) over 275 min was analyzed by using ImageJ.

Confocal Microscopy (CLSM)

Emulsions were observed using an Olympus IX 71 inverted confocal microscope (Olympus Canada Inc., Richmond Hill, ON, Canada). SA was covalently labeled with 5-(4,6-dichlorotriazinyl) aminofluorescein (DTAF) (D0531, Sigma). This fluorescent dye directly reacts with hydroxyl groups to form stable, covalent links between the dye and substrate at room temperature in an aqueous solution at pH 9.[37] Briefly, 10 mg of DTAF was first dissolved into a 50 mL Na_2CO_3-$NaHCO_3$ buffer solution (0.1 M, pH = 10). 2.0 g of SA was then solubilized into the prepared DTAF solution. The mixture was allowed to react overnight at room temperature at a stirring speed of 600-700 rpm. The pH was adjusted to 7.0 to stop the reaction, as well as to ensure a quick diffusion rate for counterions during the following dialysis step. The mixture was dialyzed against Milli-Q water for 48 h to remove unreacted DTAF and the counterions. Sodium azide (0.02% (w/v)) was added to inhibit bacteria growth, and the Milli-Q water was changed every 2 h during dialysis. Suspensions were next cooled at -20 ˚C. After freeze-drying, a yellow powder was obtained. Observation of fluorescent SP-SA particles was made by excitation of DTAF at 488 nm (emission recorded between 510 and 550 nm). Micrographs were taken after approximately 24 h using 40x and 60x objective lenses at a 2048×2048 pixels resolution (1 pixel = 0.9 x 0.9 μm^2).

Separation Tests and Particles Recovery

Emulsions composed of 4% (w/v) particles (SP or SP-SA) and various oil contents ϕ_o were prepared and stored for about 4 weeks at room temperature. The emulsions were then filtered using stainless steel strainers (2 mm mesh size). The filtered oil droplets were weighted to calculate the mass fraction of retained oil droplets and solid particles.

The filtered oil droplets were then collected and transferred into vials containing 10 ml of mineral oil, which were next stirred with a magnetic stirrer at 600 rpm for 5 min. The mixtures were then centrifuged at 10 000 rpm for 10 min. The separated top oil phase was removed, and 30 ml of ethanol were added to the particles remaining in the container. They were hand-shook and re-centrifuged at 1,000 rpm for 10 min. This step was repeated twice to ensure there was no oil remaining. Finally, particles were dried in a vacuum oven at 60 °C for 2 h. The particles were weighted to calculate the recovery yield.

Results

Zeta Potential and Contact Angle Measurements Confirm Sodium Alginate Grafting

The zeta potentials (ζ) and contact angles ($\Theta_{o/w}$) were measured as a function of pH for bare silica particles (SP), silanized particles (SP-Sil) and particles modified with SA (SP-SA) (**Table 1**). SP particles display a slightly positive ζ at pH 3.0 that decreases to negative values as the pH increased to 7.0 and 10.0. This behavior is expected due to the deprotonation of hydroxyl groups on the surface (pka ~ 4.5).[38, 39]

Table 1. Zeta potential ζ and contact angle $\Theta_{o/w}$ of silica particles: pristine (SP), silanized (SP-Sil), and grafted with sodium alginate (SP-SA), as a function of pH (3.0, 7.0 and 10.0).

	pH = 3.0		**pH = 7.0**		**pH = 10.0**	
Particle type	**ζ (mV)**	**$\Theta_{o/w}$ (°)**	**ζ (mV)**	**$\Theta_{o/w}$ (°)**	**ζ (mV)**	**$\Theta_{o/w}$ (°)**
SP	7.4 ± 1.8	103 ± 2	-52.2 ± 1.5	98 ± 4	-52.1 ± 1.7	93 ± 2
SP-Sil	77.4 ± 3.2	157 ± 9	45.1 ± 2.1	151 ± 2	36.9 ± 0.16	159 ± 6
SP-SA	7.6 ± 2.1	98 ± 8	-47.7 ± 2.9	100 ± 3	-47.2 ± 2.6	97 ± 10

SP-Sil show a positive ζ value of +77.4 mV at pH 3.0 due to the substantial protonation of $–NH_2$ groups of APTMS. Increasing the pH to 7.0 and 10.0 resulted in a decreasing but still positive ζ of +45.1 and +36.9 mV, respectively. This is explained by the deprotonation of surface bound hydroxyl groups and the gradual deprotonation of APTMS $-NH_3+$ groups to neutral $–NH_2$ groups. At pH 3.0, SP-SA particles present a similar behavior as compared to unmodified SP particles (ζ = +7.6 mV) because of the protonation of the SA carboxylate groups (pKa = 3.5),[32] confirming the subsequent grafting of SA with surface-bound APTMS. At pH 7.0 and 10.0, ζ drops to -47.7 mV and -47.2 mV, respectively, since we are above the pKa of SA and the -COOH groups on the surface are deprotonated, like a number of other polysaccharides (e.g. xanthan gum). The wetting properties of bare SP, and modified SP-Sil and SP-SA were evaluated via the contact angles ($\Theta_{o/w}$) of water droplets deposited on compressed disks of particles, immersed in a white mineral oil bath, at pH 3.0, 7.0 and 10.0 (**Table 1**). On bare SP, $\Theta_{o/w}$ slightly decreases from 103° to 93° as the pH increases from 3.0 to 10.0. After modification with APTMS and TMPS (SP-Sil), $\Theta_{o/w}$ increased above 150°, the particles becoming more hydrophobic due to the aliphatic carbon chains grafted on their surfaces. Further modification with SA resulted in a decrease of $\Theta_{o/w}$ to values nearly identical to unmodified SP particles, due to the hydrophilic nature of SA that compensates the hydrophobic character of the grafted silanes. Both ζ and $\Theta_{o/w}$ confirmed surface grafting of APTMS and TMPS silanes onto bare silica particles, followed by the covalent reaction of SA with APTMS, yielding pH-sensitive sodium alginate grafted sub-μm particles.[30]

XPS and FTIR characterization of the particles before and after surface modification was completed previously.[30] These experiments confirmed the sequential grafting of the silane coupling agent (APTMS) and sodium alginate onto SP particles. The presence of grafted APTMS was confirmed by two different components related to N-H bonds observable in the spectra (extracted from the N1s peak in high resolution XPS) and one component linked to C-N bonds. Grafting of APTMS was also confirmed independently by FTIR analysis with a band associated to N-H bond asymmetrical deformation vibration at 1450 cm^{-1}.

Sodium-Alginate Modified Particles Stabilize Oil-in-Water Emulsions

We next assessed the amphiphilic properties of SP and SP-SA particles via their propensity to stabilize emulsions comprised of white mineral oil (O) and water (W). Two complementary compositions were prepared (ϕ_o = 0.3 or 0.7), with the addition of 4% (w/v) particles. Two pHs were tested (3.0 and 7.0), and the particles were always dispersed first in the major liquid phase, followed by the gradual addition of the minor liquid phase. **Figure 1** shows that, for all tested conditions, SP and SP-SA particles stabilize oil-in-water emulsions and hence display a more hydrophilic character.[40] Note that the more hydrophobic SP-Sil were not able to stabilize any emulsion. Also, grafting the two silanes along with alginate was necessary to stabilize emulsions with SP-SA particles (using only APTMS with alginate did not allow emulsion stabilization).

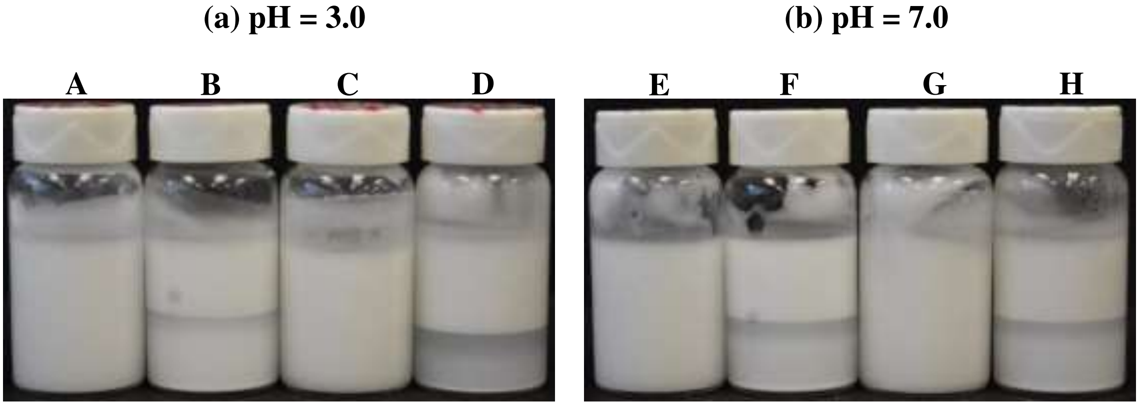

Figure 1. Oil-in-water emulsions all comprising 4% (w/v) particles at pH 3.0 (a) and 7.0 (b). pH 3.0: (A) SP particles, ϕ_o = 0.7; (B) SP, ϕ_o = 0.3; (C) SP-SA, ϕ_o = 0.7; (D) SP-SA, ϕ_o = 0.3. (E) to (H) same as (A) to (D), but at pH 7.0

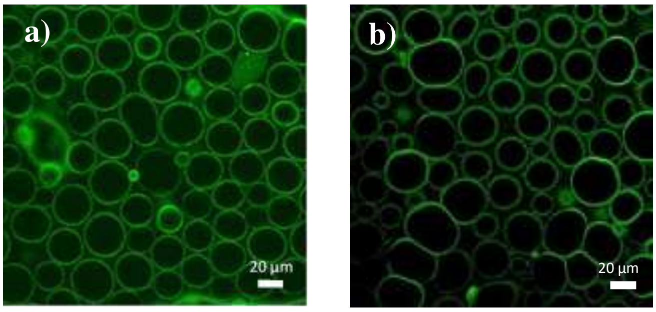

Figure 2. CLSM pictures of Pickering emulsions (ϕ_o = 0.8) with 4% SP-SA (w/v) particles at pH 3.0 (a) and 7.0 (b).

Interestingly, emulsions stabilized with SP-SA particles display a much thicker/viscous aspect compared to SP particles, at similar particle concentration and oil composition. It does support our initial hypothesis since stronger attractive interactions between neighboring "sticky" particles should lead intuitively to a higher concentrated emulsion viscosity, or higher viscoelastic properties (G' and G''). Average droplet sizes as a function of composition, and the emulsions' rheological properties results, are presented next to quantify these initial observations.

CLSM pictures confirm the interfacial activity of SP-SA particles at pH 3.0 and 7.0 (**Figure 2**). The particles were rendered visible by labeling SA with DTAF. We can observe that particles are adsorbed at the oil/water interface and form barriers preventing coalescence, as a number of deformed neighboring droplets illustrate. The oil volume fraction ϕ_o is another important parameter that can have an effect on emulsion type and stability. Keeping the concentration of particles constant at 4% (w/v), ϕ_o was gradually increased from 0.1 to 0.9 (**Figure S3**). Both unmodified (SP) and sodium alginate-modified (SP-SA) particles can stabilize oil-in-water emulsions up to ϕ_o = 0.8 (after 4 weeks, the emulsions were still stable, **Figure S4**). As mentioned previously, all emulsions prepared with SP-SA particles display a thicker or more viscous texture as compared to emulsions prepared with SP particles (**Figure S3e-f**). In agreement with previous findings[30], particles modified with SA could experience stronger attractive interparticle interactions due to hydrogen bond formation – especially at pH 3.0, below the pKa of SA –, which might explain the more viscous appearance. Optical microscopy was employed to calculate the average droplet size as a function of ϕ_o and pH. **Figure 3** displays the micrographs of emulsions prepared with SP and SP-SA particles, at pH 3.0 and 7.0. As expected, increasing the mineral oil volume fraction up to ϕ_o = 0.7 at a constant particle content leads overall to an increasing average droplet size, from 10 µm to 30 µm (**Figures 3 and 4**). For a given ϕ_o, and for both pHs, droplets are slightly bigger with SP particles (especially at ϕ_o = 0.3 and 0.5), compared to SP-SA. A sudden increase in droplet size for SP particles is observed when the oil content increases to ϕ_o = 0.8 (**Figure 4**). The results from optical microscopy observations are consistent with the results of laser diffraction experiments, as the same trends were obtained (see **Figure S5** in **Supporting Information).**

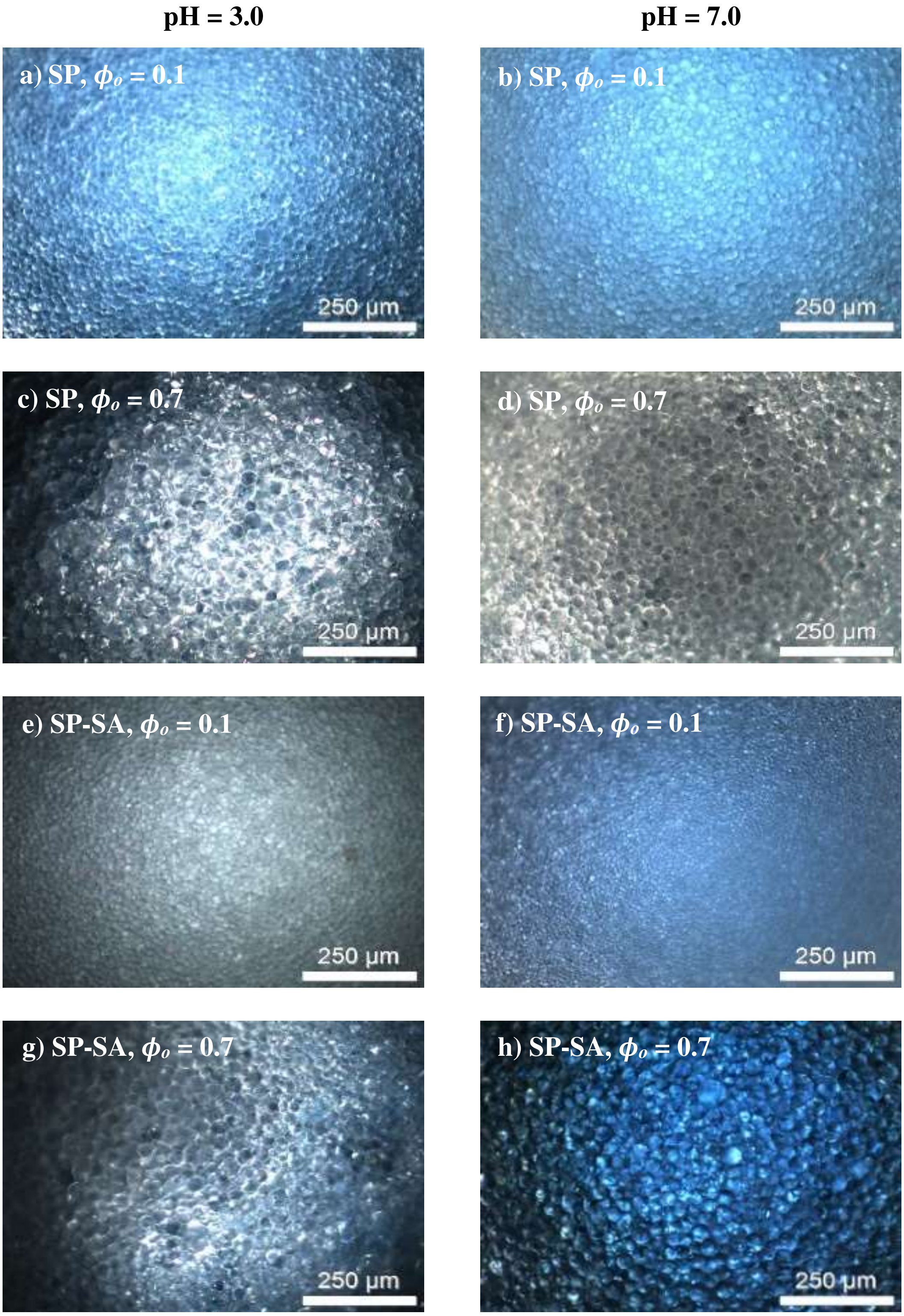

Figure 3. Dark field optical microscopy micrographs showing oil droplets, as a function of oil content ϕ_o, at pH 3.0 (left column) and 7.0 (right column), for SP (a to d), and SP-SA (e to h) particles.

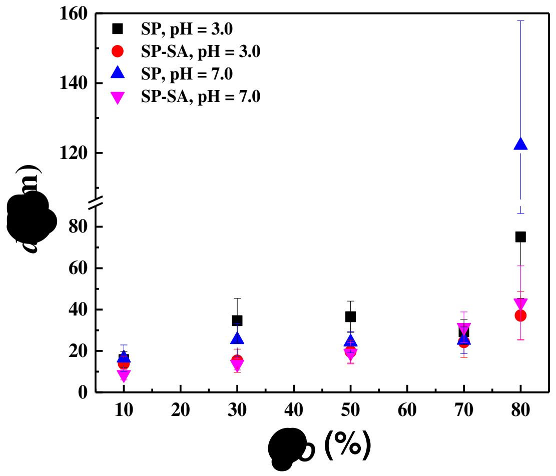

Figure 4. Number average diameter *d* of oil droplets as a function of oil volume fraction ϕ_o, for both SP and SP-SA particles, at pH 3.0 and pH 7.0.

Sodium Alginate-modified Particles Enhance the Rheological Viscoelastic Properties of Emulsions

Figure 5 shows the evolution of the storage modulus (*G′*) and loss modulus (*G″*) as a function of time, at pH 3.0 and 7.0, for concentrated emulsions at ϕ_o = 0.8 with 4% (w/v) particles. *G′* and *G″* of emulsions prepared with SP-SA particles are about 10 times superior to emulsions prepared with pristine SP particles, in accordance with the qualitative observation in **Figure S3e-f,** at both pH 3.0 and 7.0. For a given particle type, *G′* is about 5 to 5.5 times higher than *G″*, evidence that these concentrated emulsions behave as weak gels. *G′* and *G″* are also time-dependent and gradually increase, indicating a slow structuration or reorganization process.

The enhanced viscoelastic properties and self-holding property of concentrated emulsions prepared with SP-SA particles (**Figures S3e-f and 5**) also suggest the possible existence of a yield stress in these systems – i.e. the need to apply a finite mechanical stress to induce flow. To verify this hypothesis, the emulsions were then molded and subjected to three increasing compressive stresses (193, 290, and 387 Pa) over 275 min (**Figure 6**) in order to measure sample compression as a function of time.

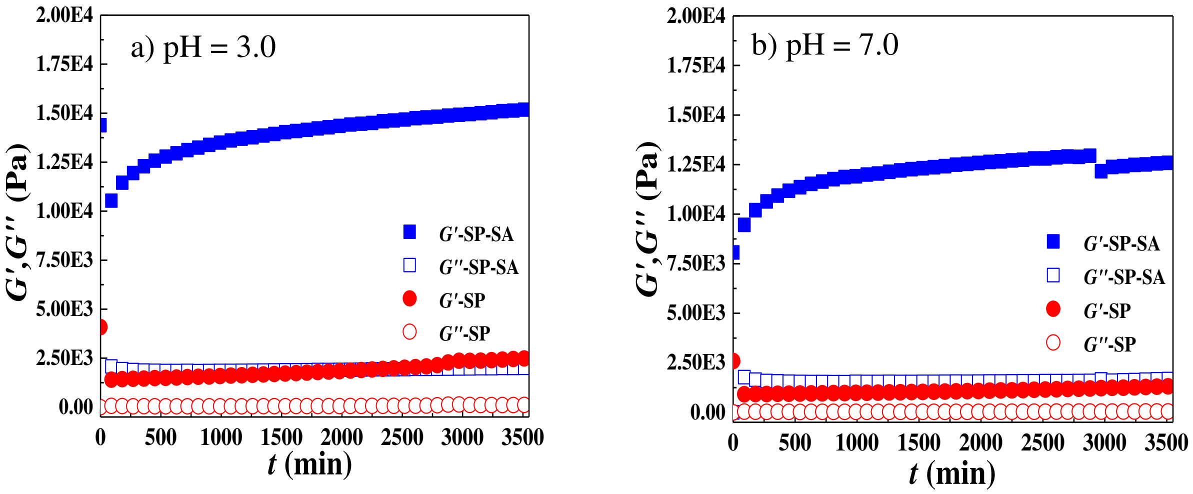

Figure 5. Storage (G′) and loss modulus (G″) as a function of time (*t*) at 20 ˚C, for concentrated emulsions (ϕ_o = 0.8 and 4% (w/v) particles) at pH 3.0 (a) and 7.0 (b). All tests were performed at ω = 1 rad/s, γ_0 = 1%.

At pH 3.0, emulsions prepared with SP-SA particles could withstand all three stresses over the experiment duration, the molded emulsion losing no more than 6% of its initial height (**Figure 6a**, for version with error bars see **Figure S6**). A similar result was obtained at pH 7.0. As **Figure 6b-c** illustrate, they are quite solid and can be easily manipulated. In comparison, emulsions prepared with SP particles failed to withstand the lowest applied stress and instantly collapsed, as **Figure 6d** illustrates. Finally, as demonstrated in a previous article, SP-SA particles in aqueous suspension strongly interact at pH 3.0 via hydrogen bonding, and a less compact bed is formed after sedimentation (**Figure S7**). [30]

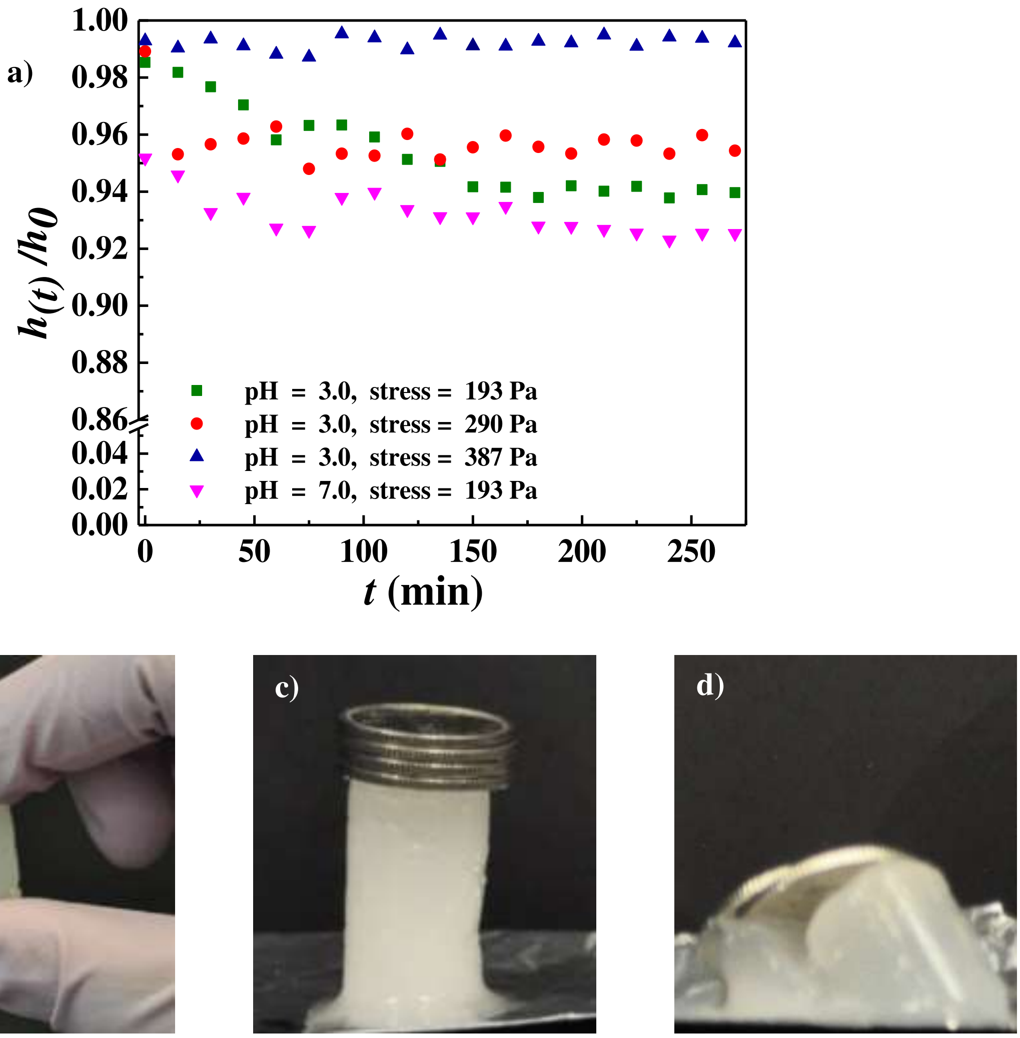

Figure 6. a) Normalized height ($h(t)/h_0$) as a function of time *t* and applied stress on molded concentrated emulsions (ϕ_o = 0.8) comprising 4% SP or SP-SA particles, at pH 3.0 and 7.0; b-c) visual aspect of the solid-like behavior of molded Pickering emulsions comprising 4% SP-SA particles, compared to a concentrated emulsion (d) prepared with pristine SP displaying no yield stress, at pH 3.0;

Sodium Alginate-Modified Particles Improves the Separation of Pickering Emulsions Constituents

The enhanced soft gel properties (soft solid in the previous section), along with the droplet-droplet and particle-particle attractive interactions in emulsions prepared with SP-SA particles,[30] led us to hypothesize that the separation of constituents could be realized by filtration – *i.e.* separating the continuous water phase from the oil droplets. **Figure 7** illustrates the process for three emulsion compositions (ϕ_o ranging from 0.1 to 0.5) at a constant particle content of 4% (w/v). The initial emulsions are displayed (typically comprising an emulsified oil phase on top (white), an aqueous phase below it (transparent), and un-adsorbed particles at the bottom (white), see bottle on the left in Fig. 8a), along with the collected oil droplets and uncollected material. For all three oil compositions, the filtration of emulsions prepared with SP-SA particles at pH 3.0 yielded a significantly higher collected mass fraction of material, as compared to emulsions prepared with SP particles (**Table 2**). For example, at ϕ_o = 0.1, there is no oil droplets remaining on top of the aqueous phase after filtration when using SP-SA particles (**Figure 7d**), as compared to SP particles (**Figure 7a**). Furthermore, the collected fraction for the SP-SA system even reaches 176% (calculated by dividing the initial emulsion content, by the mass of collected material), meaning that water is also retained with the oil droplets. As the oil fraction increases, the collected mass fraction gradually decreases for both SP-SA and SP emulsions due to the collected fraction's own weight. However, in all cases, the collected mass for SP-SA emulsions is nearly twice as much compared to SP systems. As a result, the amount of recovered dried particles (calculated based on the amount of emulsified particles) is always significantly superior for SP-SA particles, as compared to SP particles, at a given oil content ϕ_o, as the last column of **Table 2** illustrates. Finally, the recovered oil and SP-SA particles (for the emulsion composed of 10% oil) were next re-used, with additional fresh SP-SA particles to reach 4% w/v), to form an emulsion again (at ϕ_o = 0.7), as **Figure 8** illustrates, demonstrating the potential of reusing particles. This opens up interesting perspectives for cleaner separation processes.

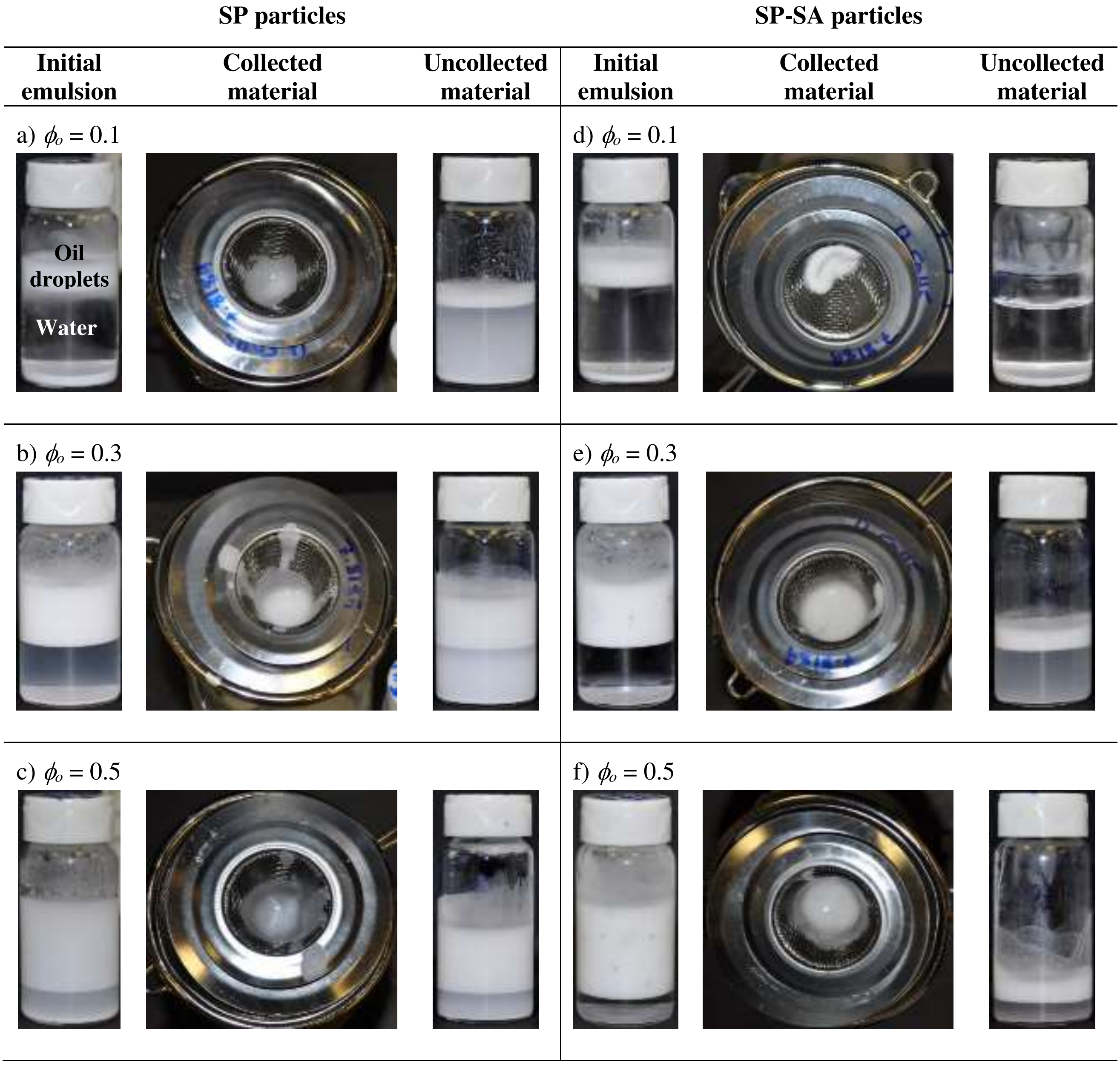

Figure 7. Filtration of Pickering emulsions prepared at pH 3.0 with 4% particles: a-c) emulsions prepared with pristine SP particles with oil content ϕ_o = 0.1, 0.3 and 0.5, respectively; d-f) same as (a-c), but with sodium alginate modified particles (SP-SA).

Table 2. Gravimetric analysis of collected material after filtration experiments

Emulsion Composition (Particle type / ϕ_o)	Emulsion (oil + particles) initial content[1] (g)	Collected Material[2] (g) / (%)	Recovered Particles in Collected Material[3] (%)
SP / 0.1	1.39	0.96 ± 0.08 (69%)	2
SP / 0.3	4.22	1.51 ± 0.71 (36%)	9
SP / 0.5	6.79	1.77 ± 0.24 (26%)	29
SP-SA / 0.1	1.41	2.48 ± 0.57 (176%)	47
SP-SA / 0.3	4.37	2.81 ± 0.59 (64%)	23
SP-SA / 0.5	6.95	3.27± 1.03 (47%)	34

[1]: obtained by subtracting the mass of un-adsorbed particles, $m_{un\text{-}adsorbed}$, obtained by image analysis; [2]: % is calculated by dividing the mass of collected material, by the initial emulsion content in column 2; [3]: compared to weight of emulsified particles (0.6 g – $m_{un\text{-}adsorbed}$).

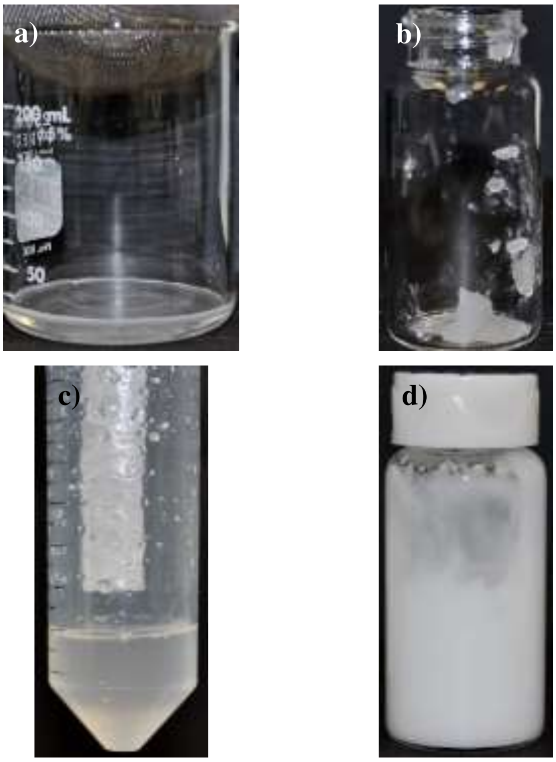

Figure 8. a) Remaining aqueous phase after the filtration of oil droplets, b) collected oil droplets and particles, c) re-dispersion of collected material (oil + particles) in oil phase and d) stabilization of emulsion using recovered particles.

Discussion

By modifying the surface properties of silica particles with a natural polysaccharide, in this case sodium alginate, we have improved the separation process of Pickering emulsions constituents via a simple filtration process, avoiding the use of potentially toxic chemicals. The collected mass fraction after filtration does not reach 100% (**Figure 7** and **Table 2**), even for emulsions prepared with SP-SA particles, mainly because fractions of oil droplets and emulsified particles pass through the mesh, as the uncollected fraction illustrates for ϕ_o = 0.3 and 0.5. This could be improved by increasing interparticle and droplet-droplet interactions via careful tuning of particle surface chemistry. Increasing the SA molecular weight, changing the SA guluronic/mannuronic block ratio, and testing other gelling polysaccharides such as xanthan gum, would be pertinent to look at. From a more fundamental perspective, controlling how grafting occurs – i.e. controlling the conformation of grafted molecules on the surface - also needs to be investigated. The combined result would be a significant improvement of particle recovery and overall components separation.

Particle surface modification in this work serves two purposes. One is to adjust the wettability properties of particles in order to form Pickering emulsions (**Table 1**), a strategy that has been employed by various groups in past publications.[11, 27, 35] In our case, we first use two complementary silanes. The first one, TMPS, increases the hydrophobic character of silica particles. The second, APTMS, is a linker allowing sodium alginate grafting, which is more hydrophilic.

The second purpose of surface modification is to tune interparticle interactions, in order to increase particle-particle attraction – in the case of SA, via hydrogen bond formation, as we demonstrated in a previous article.[30] Interparticle interactions can occur between particles adsorbed on the same droplet – which should increase the mechanical resistance of the particle layer, a hypothesis that remains to be verified –, or between particles in contact adsorbed on neighboring droplets – increasing at the same time droplet-droplet interactions. In that case, we should expect, for concentrated emulsions, increases for G′ and/or G″ values, which we did observe (**Figure 5**). Similar results were obtained by Chen et al. in Pickering emulsions comprised of paraffin oil, water and sodium alginate modified particles.[31] Enhanced attractive interactions are also supported by the existence of a yield stress for concentrated emulsions prepared with SP-SA particles (**Figure 6**), which is not observed for emulsions prepared with pristine SP particles. Finally, stronger attractions help to retain oil droplets in the collected materials after emulsion filtration.

In a previous article,[30] we demonstrated that interparticle attractive interactions between sodium alginate modified particles are maximized at low pH. SA in solution forms a gel at low pH due to the protonation of its carboxylic acid groups (the molecule is nearly neutral), which promotes the formation of intermolecular hydrogen bonds. While we observed significant increases for both G′ and G″ at pH 3.0 for concentrated emulsions prepared with SP-SA particles, as compared to SP particles, unexpected increases were also observed at pH 7.0, which might be due to the confinement of the particles both at the oil/water interface, and close contact between neighboring droplets. This remains to be elucidated.

Conclusion

This article demonstrates that grafting a natural polysaccharide, sodium alginate, on the surface of silica particles stabilizing oil-in-water Pickering emulsions, can significantly improve the subsequent separation and recovery of the initial constituents via a simple filtration approach – leading to significant waste and toxicity reductions by avoiding the use of toxic chemicals to alter the chemical state of the emulsion (pH, ionic strength). Particle surface modification, herein realized with two silane agents and sodium alginate, plays two distinct and complementary roles. The first is to tune particle wettability in order to stabilize the emulsions – this is achieved with the choice of silane reagents. The second is to enhance particle-particle and droplet-droplet attractive interactions, in order to facilitate their filtration and the separation of constituents – achieved with sodium alginate via intermolecular hydrogen bonding. As a result, two opposite features – stabilization vs separation – are independently controlled with a single type of particles. The wide choices of silane agents and natural polysaccharides/proteins should next allow a finer tuning and optimization of this approach, which is of interest for the development of chemical engineering processes involving particulates dispersed in fluids with reduced environmental impact.

Conflicts of interest

There are no conflicts to declare.

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