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Synthesis of Surface-Responsive Composite Particles by Dehydration of Water-in-Oil Emulsions

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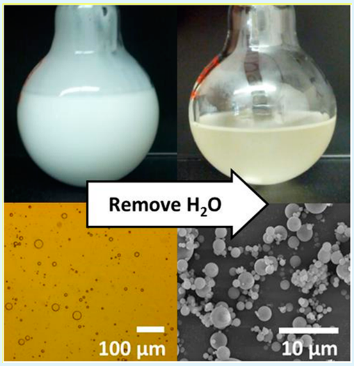
S Supporting Information

ABSTRACT: Organic composite particles were prepared by first emulsifying an aqueous sodium carboxymethyl cellulose (CMC) solution in a nonaqueous ethylcellulose (EC) solution, followed by dehydrating emulsified water droplets. CMC and EC are both biodegradable nontoxic materials, but have contrasting properties. CMC is a charged water-soluble polymer, while EC is an uncharged interfacially active water-insoluble polymer. The simple preparative method does not consume unnecessary chemical reagents and produces no waste material. The composite particles prepared by dehydrating emulsion droplets are readily dispersed in organic media due to its biwettable surface terminated with interfacially active EC molecules, which allows composite particles to preferentially adsorb at the oil−water droplet interface. The surface of composite particles, furthermore, is water-permeable, which allows water to be absorbed from emulsified droplets. The size, composition, and structure of the synthesized composite particles are ideally suited for absorption of stabilized water droplets from oil-continuous emulsions. The use of the composite absorbent particles, described herein, presents another viable strategy for dewatering water-in-oil emulsions.



KEYWORDS: *organic composite, carboxymethyl cellulose, ethylcellulose, emulsion dehydration, water separation*

■ INTRODUCTION

Particles are finite units of matter, defined not only by their composition, but also by their structure. Engineering particles with a high-order organization, from one or more materials, can impart beneficial properties that would otherwise be unattainable. The method for preparing composite particles has a critical effect on the physicochemical properties of the resulting product. Solid particles are prepared through physical processes (e.g., precipitation, condensation, and evaporation) or chemical reactions (e.g., chemical vapor deposition, polymerization, and pyrolysis). The mechanism of particle formation is complex for the majority of preparation methods and involves numerous and interconnected physiochemical processes.[1,2] Preparation of particles having various degrees of complexity and organization is possible by either controlling conditions during particle formation or subsequently transforming previously formed particles (e.g., surface coating, chemical functionalization, annealing, sintering, etc.). Specific methods, such as spray drying[3,4] and emulsion polymerization,[5−7] produce particles with characteristic properties corresponding to the nature of the particle formation processes. Depending on the application, desirable characteristics of particles may include: controlled narrow particle size distribution and low toxicity for pharmaceutical formulations; specific molecular structure and composition for engineering polymers; and extended stability and shelf life for latex coatings. A process for preparing composite materials should ideally provide the desired functions (e.g., dewatering of a water-in-oil emulsion) by combining various materials with desirable attributes in a predefined configuration using a minimal number of preparation steps while simultaneously meeting as many ancillary specifications as possible (e.g., optimal particle size, suitable composition, desired surface properties, and preferred structure).

Particle size is a basic but important physical property that can have a dramatic impact on the physicochemical properties of a given material. The disproportionate change in specific volume and surface area with decreasing particle size is a major issue in both macroscopic terms (i.e., transport phenomena in chemical engineering) and microscopic terms (i.e., nanotechnology). Although the rate of an absorptive process is greater for smaller particles because of greater specific surface area, microscopic particles are more difficult to prepare and more difficult to remove from complex multiphase systems. Particle size reduction to micron or submicron sizes through physical means is challenging due to excessive deformation and difficulties in adequate dissipation of heat generated by friction. Unlike fluids, solids are rigid and resistant to flow. High-intensity cryogenic milling was reported to produce solid particles down to approximately 1−10 µm.[8−10] Liquids, on the other hand, are readily deformable when sufficient shear is applied. Despite the larger amount of energy required to produce very small droplets (i.e., less than approximately 1 µm) due to the increase in interfacial surface area, the energy

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required for emulsification remains less than a fraction of the energy required to reduce solid particles to the similar sizes. However, emulsified droplets are prone to rapid coalescence unless stabilizing chemicals are used. With adequate shear and stabilization, emulsions with droplet sizes of approximately 0.1 μm are routinely prepared.[11]

Particle composition has an obvious influence on the properties and functions of the particles. Unfortunately, not all materials can be readily combined, and their properties are not always additive. For example, phase separation is problematic when extruding incompatible polymer blends.[12,13] In this case, compatible additives with intermediate properties must be added to mediate the interactions between the two incompatible components to achieve a microscopically or macroscopically uniform mixture. In addition to composition, the structure of a particle is another important feature that can be controlled to yield novel and interesting materials. For example, the surface of a Janus particle consists of at least two distinct regions with contrasting wetting properties,[14] which make them excellent stabilizers for Pickering emulsions when one portion is hydrophilic and the other is lipophilic.[15−17] Alternatively, particles made from two different materials can also be arranged in a structured configuration as such that one material is exposed to the surface while the other occupies the interior. Core−shell particles are a typical example of this type of particle and are widely used in providing diagnostic labels or targeted therapy,[18−22] and in medical applications wherein the outer layer acts as an enteric coating (i.e., suppress taste, control release rate, retard degradation, etc.).[23−27] Other possible structural configurations for a composite particle made from two different materials include dumbbell-, acorn-, snowman-, and raspberry-shaped particles.[28,29]

The outermost layer of a particle is critical in determining its stability in colloidal systems, as the compatibility with dispersing media is largely controlled by surface wettability. A hydrophobic particle with water contact angle greater than 90° prefers nonaqueous media, while a hydrophilic particle with water contact angle smaller than 90° exhibits a stronger affinity for aqueous media.[30] When particles are dispersed in a liquid, they either remain individually suspended or aggregate to form larger masses, depending on the properties of the particle surface and type of media. Aggregation may be suppressed by providing an electrostatic or steric energy barrier between the particles. Conversely, aggregation is promoted by neutralizing surface charge or by introducing specific chemicals (e.g., high molecular weight polymers) to induce flocculation. Latex paint, for example, must possess sufficient stability to last from time of manufacture to application by the end-user. In medical and environmental applications, it is essential that the surface coating is both nontoxic and biocompatible. Although an impermeable coating is useful in reducing the toxicity of a core substance, permeability is desirable in applications where a substance must be expelled from the particle (i.e., controlled drug delivery) or a foreign substance must enter into the particle (i.e., absorption).

In this study, we present an innovative yet simple method, as schematically illustrated in Figure 1, to produce organic composite particles by dehydration of emulsion droplets. The process takes advantage of the liquid phase, wherein droplets are readily emulsified in the presence of an interfacially active polymer. The interfacially active polymer functions both as an emulsifier for liquid droplets, before removal of the dispersed phase, and a stabilizer for the residual solid particles to be highly dispersed in organic media after removal of the dispersed aqueous phase. Material, initially dissolved or dispersed inside the droplets, solidifies after the dehydration of emulsion droplets and forms the interior of composite particles. To realize this simple method, the selection of continuous phase is of paramount importance. For the desired synthesis, we selected ethylcellulose (EC)-containing toluene as the organic phase to form carboxymethyl cellulose (CMC)-containing water-in-oil emulsions. Toluene forms an azeotrope with water to feature a boiling point of 84 °C, and thus allows dehydration of the emulsified water droplets by distillation using a simple Dean−Stark trap.[31] During the distillation process, emulsified water must diffuse into the continuous phase, as only water in the continuous phase is vaporized along with the solvent as an azeotropic mixture. Upon condensation of the vapor phase, the water-rich phase is removed in the Dean−Stark trap, while the solvent-rich phase is returned. This process leaves oil-insoluble CMC as the central feature of the resultant particles and interfacially active EC on the surface of resultant particles. The lipophilic EC on the surface of synthesized particles imparts colloidal stability to composite particles in an organic continuous phase. This well-thought preparation method is capable of incorporating a number of hydrophilic materials into the interior of the composite particles, while at the same time, coating the particles with an interfacially active material of desired functionality, all without the need for chemical derivitization reactions.

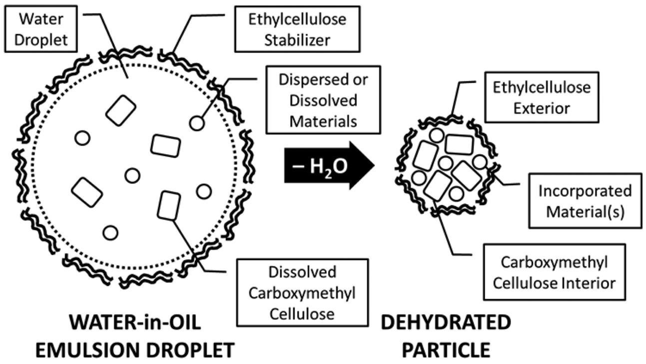

Figure 1. A composite particle is produced after removal of water from a water-in-oil emulsion droplet containing CMC and other desirable substances (such as magnetic nanoparticles), if needed, in the interior and interfacially active EC on the surface.

The composite particles prepared according to Figure 1 could have many important applications, including the separation of emulsified water from petroleum emulsions by absorption. In downstream petroleum processing, for example, the presence of water can lead to accelerated corrosion, increased scale build-up, and catalyst poisoning; all of which adversely affect process performance. Although emulsions are known to lack thermodynamic stability, coalescence and phase separation in well-stabilized emulsions are often extremely slow. The enhanced kinetic stability of emulsion droplets is provided by interfacial materials such as surfactants and biwettable fine particles, which present an electrostatic or steric barrier. Both electrostatic and steric barriers prevent intimate contact between droplets and reduce the rate of droplet coalescence. Separation of water from emulsions is further delayed when the difference in density between the continuous phase and the dispersed phase is minute or when the continuous phase is extremely viscous. Emulsified water may be separated using absorbent materials, which are typically very hydrophilic. However, hydrophilic materials are generally poorly compatible with a nonaqueous continuous phases, leading to rapid aggregation of dispersed particles and poor contact with emulsified water droplets. This shortcoming can be addressed by producing a composite absorbent particle from two distinct materials of contrasting properties in a particular structural arrangement (i.e., a particle with CMC in its interior coated with a permeable outer layer of EC). The method described in this study is well suited for preparing such composite absorbent particles for removal of emulsified water, as illustrated in Figure 2. CMC and EC are both cellulosic polymers produced from renewable resources and share structural similarity. The solubility behavior of both EC and CMC is closely related to the degree of substitution in the polymer chains. EC with sufficient ethoxy content is soluble in a variety of organic solvents (e.g., ethanol, ethyl acetate, chloroform, and toluene) and is used as enteric coating for many pharmaceutical products.[32−36] CMC with sufficient carboxymethyl content, on the other hand, is water-soluble and commonly used as a viscosity modifier and water absorbent.[37] The absorbent portion of the composite particle made of CMC is capable of absorbing water, while the permeable interfacial coating made of EC allows effective dispersion of the composite particles into organic solvents and further promotes effective attachment of the particles onto emulsified water droplets.

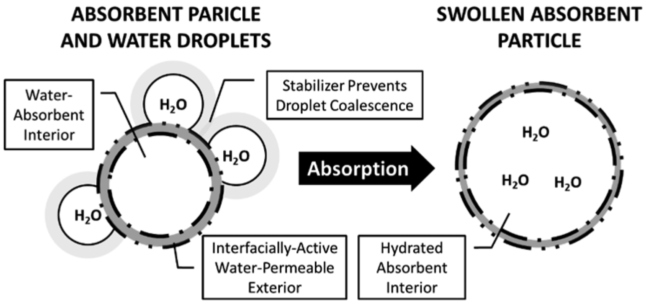

Figure 2. Composite absorbent particles, comprising an absorbent interior and an interfacially active exterior, are ideally suited for removing emulsified water by water absorption mechanism. The surface of the composite absorbent particles is biwettable and thus promotes attachment to the oil−water interface (i.e., water droplet surfaces), while the interior of the composite absorbent particles is capable of absorbing emulsified water through water permeable EC coatings on the composite particles.

EC is an effective demulsifier for water-in-diluted bitumen emulsions and functions by displacing indigenous emulsion-stabilizing materials (e.g., asphaltenes) from the oil−water interface of stabilized water droplets.[38] Coating an absorbent substance, which is generally prepared from hydrophilic material (i.e., CMC), with a substance of intermediate wettability (i.e., EC) should increase its performance in biphasic systems, such as diluted-bitumen emulsions wherein stabilized water droplets are dispersed in a nonaqueous continuous phase. Because of this unique combination of properties, CMC−EC composite particles were expected to perform effectively as absorbents for removing emulsified water. The purpose of this study is to synthesize and characterize interfacially active composite water-absorbent particles using the approach illustrated in Figure 1. As potential application, the synthesized particles were evaluated as dewatering agents for water-in-oil-type emulsions.

EXPERIMENTAL SECTION

Materials. Sodium carboxymethyl cellulose (Acros Organics; average MW 250 000 g/mol; degree of substitution = 0.7), ethyl cellulose (Sigma-Aldrich; 48% ethoxyl content), iron oxide nanoparticles (Sigma-Aldrich, < 50 nm diameter), toluene (Fisher Chemical; HPLC grade), ethanol (Commercial Alcohols; 99%), ethyl acetate (Fisher Chemical; ACS grade), butyl acetate (Fisher Chemical; ACS grade), Pluronic P123 (BASF), and Span 80 (Sigma-Aldrich) were used as received without further purification. Deionized water (>18.0 MΩ·cm) was produced from Thermo Fischer Barnstead Nanopure ultrapure water purification system.

Instrumentation. Optical diameters were obtained using Malvern Mastersizer 2000 with a small volume dispersion accessory or using Malvern Mastersizer 3000 with an extended volume dispersion accessory. Thermal properties were investigated using a TA Instruments Q200 thermogravimetric analyzer. BioRad 2000 Fourier transform infrared spectrometry with diffuse reflectance accessory was used to acquire IR spectra. Micrographs were acquired using a Hitachi S-2700 scanning electron microscope.

General Particle Preparation. An aqueous solution of CMC was prepared by slowly dissolving CMC powders in deionized water (e.g., 2.0 g of CMC was dissolved in 98.0 g of water). Optionally, superparamagnetic Fe_3O_4 nanoparticles were dispersed into the prepared CMC aqueous solution. The pH of the 2.0 wt % CMC aqueous solution was determined to be approximately 8.5. An organic solution of EC was prepared by dissolving EC powders in toluene (e.g., 1.0 g of EC was dissolved in 99.0 g of toluene). The prepared CMC aqueous solution was emulsified into the EC solution using Fisher Scientific PowerGen hand-held homogenizer for 60 s. The resulting water-in-toluene emulsion was transferred to a round-bottom flask equipped with a magnetic stirrer on a Dean−Stark apparatus. Alternatively, the round-bottom flask was equipped with a Fisher Scientific Model 500 ultrasonic dismembrator. The dehydration was performed at approximately 84 °C, which is the boiling point of the azeotrope formed by toluene and water. Under typical distillation conditions, water was removed from emulsion at a rate of 20 mL/h. For example, dehydrating a 60 g emulsion containing 20 g of emulsified water required approximately 1 h. After cooling to ambient temperature, the mixture was transferred into a centrifuge tube and the solids were separated by centrifugation at 1500 g-force. Particles were washed several times with toluene and ethanol. Recovered particles were placed in a vacuum oven at 120 °C for 72 h. After drying, a white solid was recovered, crushed into a free-flowing white powder, and stored in a desiccator. The water absorbency of the synthesized particles was determined by placing 0.1−1.0 g of solid particles into 20−50 mL of deionized water and agitating the mixture using a vortex mixer for 30 s. After an additional 90 s, free water was separated by decantation and gravity filtration.

Critical Surface Tension. To confirm the biwettable nature of the synthesized organic composite absorbent particles, the critical surface tension of the particle was determined by conducting film flotation experiments using binary solutions of water and methanol.[39] The surface tension of binary water−methanol solutions ranges from 22.5 mN/m for pure methanol to 72.8 mN/m for pure water. To probe particle wettability, a known amount of solid particles was carefully placed on the top of the solution containing different proportions of methanol and water. After 30 s, any particles remaining on the surface of the solution were physically separated and dried overnight in the vacuum oven at 110 °C. The mass fraction of the particles remaining on the surface was plotted as a function of the liquid surface tension, and the critical surface tension of the particle was estimated as the surface tension of the solution for which one-half of the particles remained on the surface of the solution.

Preparation of Absorbent Substrate. CMC substrates were prepared by evaporation of an aqueous solution containing 2.0 g of CMC in a 100 mm glass dish. Similarly, additional EC substrate was prepared by evaporation of a toluene solution containing 2.0 g of EC. To prepare CMC−EC substrate, the CMC substrate prepared above was placed in a vacuum oven at 70 °C to remove remaining water. Ten milliliters of 2 wt % EC in toluene solution was then placed on the top of dried CMC substrates and left to evaporate the solvent. Excess EC was washed away with an ample amount of toluene. Variable amounts (0.20, 0.10, and 0.05 g) of EC were deposited in such a manner onto the CMC substrates. The mass of the initial EC coating layer was determined gravimetrically.

Contact Angle. The static contact angle of water droplets, placed directly onto CMC substrates covered with variable amount of EC, was measured using Krüss DSA instrument. Small water droplets (3−4 mm) suspended from the tip of the needle point were brought carefully in contact with the substrate, upon which the water droplet detached from the needle and spread on the substrate. The contact angle of the water droplet on the substrate was measured immediately after the three phase contact line stopped moving, roughly within 10−15 s of contact. The contact angle measured as such represents the advancing equilibrium contact angle or static contact angle.[40] Considering the penetration and absorption of water by underlying CMC film, the reproducible measurement of advancing and receding contact angle was difficult if not impossible for the CMC−EC composite films on glass substrates. For this reason, the measurement of advancing and receding contact angle was not attempted in this study.

Oil−Water Separation. A water-in-mineral oil emulsion was prepared by emulsifying approximately 3.6 g of deionized water using a high-speed homogenizer into 57.0 g of mineral oil (Acros Organics) with 0.4 g of SPAN 80 as emulsifier. Initial water content of mineral oil emulsion was determined accurately to be 5.9 wt %. Small aliquots of emulsion were taken using a syringe at the midway point depth. The amount of remaining water was determined by Karl Fischer titration.

■ RESULTS AND DISCUSSION

The CMC−EC composite particles were prepared by dehydration of a water-in-toluene emulsion. Because of its surface active nature, EC adsorbs at the toluene−water droplet interface to stabilize the emulsion. As shown in Figure 3, the opacity of the emulsion, consisting of emulsified CMC-containing water droplets, diminished during dehydration as a result of decreasing the size of dispersed droplets, which eventually become smaller dehydrated CMC particles. The surface active nature and contrasting solubility of EC from CMC ensure that EC remains on the surface of the CMC solid particles after dehydration, forming the desired composite particle structure with biwettable surface characteristics.

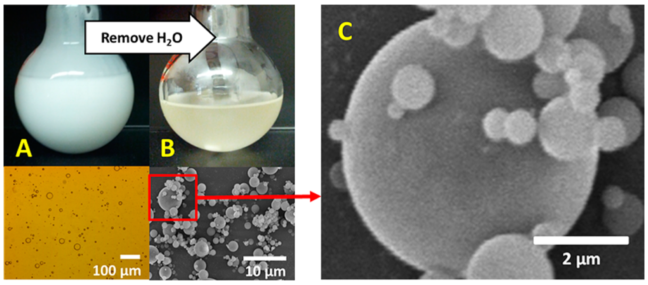

Figure 3. Preparation of CMC−EC composite particles by emulsion dehydration showing transition from (A) an emulsion containing emulsified water droplets to (B) a dispersion containing dispersed CMC−EC composite particles. (C) The enlarged micrograph shows the spherical shape and polydispersed nature of the synthesized particles in the red box from panel B.

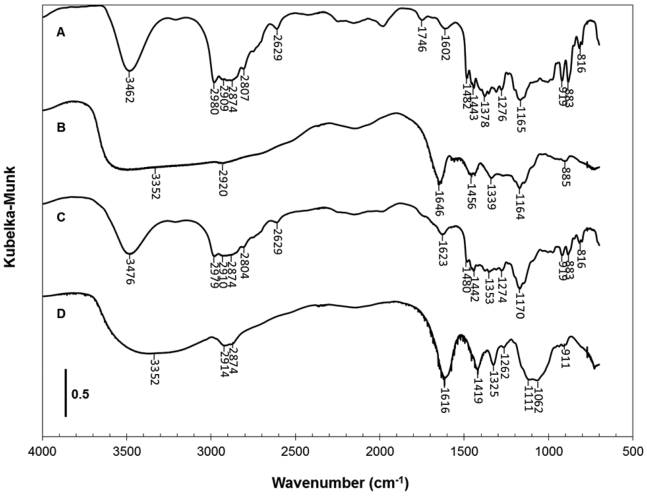

Figure 4. Diffuse reflectance infrared Fourier transform spectra of (A) ethylcellulose, (B) carboxymethyl cellulose, (C) a mixture of CMC and EC, and (D) CMC−EC composite particles. The shift of $-COO^-$ stretching vibrational band from 1646 and 1456 cm^{-1} for CMC solid to 1616 and 1419 cm^{-1} for CMC−EC composite absorbent particles indicates the binding of $-COO^-$ groups with EC molecules.

CMC−EC composite particles produced using the emulsion dehydration method were characterized using infrared spectroscopy. As shown in Figure 4, the DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) spectra of CMC−EC composite particles taken in KBr matrix encompass all characteristic peaks of CMC and EC, including a broad peak at 3352 cm^{-1} due to stretching vibration of hydrogen-bonded −OH groups, multiple peaks between 2914 and 2874 cm^{-1} assigned to C−H stretching, strong peaks at 1616 cm^{-1}, 1419 cm^{-1}, and 1325 cm^{-1} as a result of $-COO^-$ vibration, strong peaks between 1062 and 1111 cm^{-1} from ring stretching, and a peak at 911 cm^{-1} due to CH_3 vibrations. It is interesting to note the shift of $-COO^-$ stretching vibration band from 1646 and 1456 cm^{-1} for CMC (Figure 4B) to 1616 and 1419 cm^{-1} for CMC−EC composite absorbent particles (Figure 4D), indicating the binding of carboxylate groups of CMC with EC molecules. To further confirm the binding of CMC with EC, the spectra were further analyzed by calculating the arithmetic spectra of CMC and EC mixture and comparing the resultant arithmetic spectra with measured spectra of CMC−EC mixture and CMC−EC composite absorbent particles. The results in Figure S3 show an excellent matching for the measured spectra of CMC−EC mixture but a clear shift for the CMC−EC composite absorbent particles.

The EC content of the synthesized CMC−EC composite particles was estimated by thermogravimetric analysis performed using a constant heating rate of 5 °C/min. The results in Figure 5 show the onset temperature of EC decomposition at 317 °C and complete decomposition at 450 °C. The onset temperature for CMC decomposition was 264 °C, and approximately 45 wt % of CMC remained after being heated to 450 °C. The decomposition of the CMC−EC composite particles started at 246 °C with only a single decomposition event below 300 °C. The decrease in the onset temperature for thermal decomposition of the CMC−EC composite particles along with the lack of the decomposition event for EC at 317 °C suggests the complexation of EC with CMC, most likely on the surface of the composite particles. The thermal decomposition characteristics of the CMC−EC composite particles was distinctively different from that of a simple physical admixture of CMC and EC, which shows characteristic decomposition peaks of CMC and EC, as anticipated. The finding further confirms the binding of EC with CMC in the synthesized composite particles.

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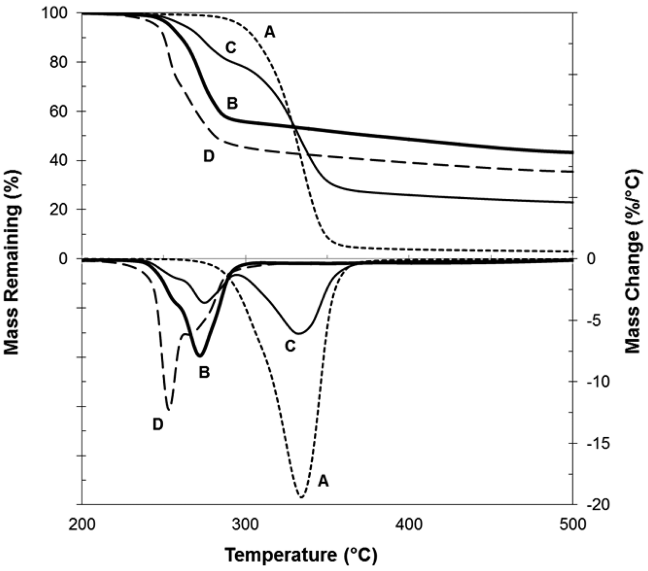

Figure 5. Thermogravimetric analysis (top) and derivative thermogravimetric analysis (bottom) curves for (A) ethylcellulose, (B) carboxymethyl cellulose, (C) a mixture of CMC and EC, and (D) CMC−EC composite particles.

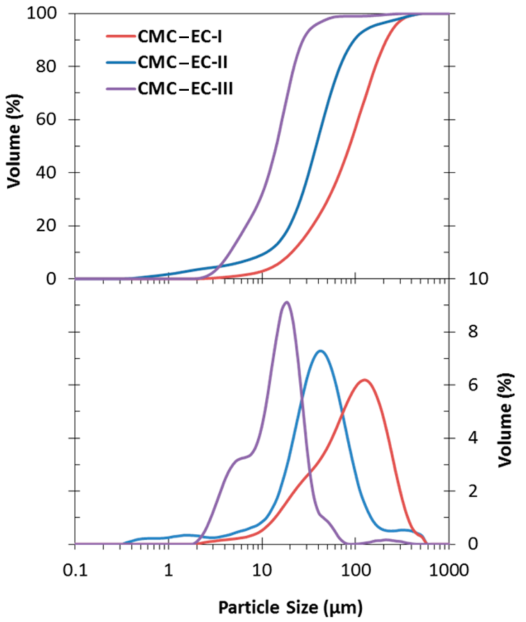

Figure 6. (A) Cumulative and (B) differential particle size distribution of CMC−EC composite particles prepared using different concentrations of EC in the continuous phase.

Water-in-toluene emulsions (1:1 ratio by mass) stabilized by more than 0.5 wt % EC (based on the mass of the organic phase) prepared using a high-speed homogenizer did not show any noticeable phase separation at ambient condition. However, sedimentation was observed with lower EC concentration and when the emulsion was heated. Primary CMC−EC composite particles prepared by the dehydration of the emulsion droplets are spherical in shape and micron in size as revealed in scanning electron microscopy (SEM) micrographs. The lower size limit of CMC−EC composite particles prepared by emulsion-dehydration using a magnetic stirrer during dehydration was approximately 2 μm. However, particles are polydispersed in size, most likely due to the polydispersity of the precursor emulsion water droplets prepared by intermittent simple high-speed mechanical agitation. Continuous coalescence of water droplets during the dehydration process may also contribute to nonuniform size distribution of the resulting particles.

As shown in Table 1, the size of CMC−EC composite particles prepared by dehydrating 2 wt % CMC water droplets emulsified in an equal mass of continuous organic toluene phase decreases from 76 μm with 0.5 wt % EC in toluene to 35 μm and further to 13 μm with 1.0 and 2.0 wt % EC in toluene, respectively. Increasing the concentration of EC appears to increase the stability of CMC-containing water-in-oil emulsions and hence leads to smaller sizes of CMC−EC composite particles, as shown in Figure 6. At 2 wt % of EC in toluene as the continuous phase, increasing CMC concentration in the aqueous phase from 1 wt % to 3 wt % did not lead to any significant change in the size of resulting CMC−EC composite particles. The difficulty encountered in controlling monodispersity of particle size by varying EC and CMC concentration highlights the kinetic nature of emulsions. Despite being stabilized by EC, emulsion droplets at high temperature are continuously coalescing during the dehydration of precursor emulsions.[11,41] Without sufficient emulsification during the dehydration process, dispersed droplets are prone to coalescence, which inevitably leads to the formation of larger particles with a wider particle size distribution.

Table 1. Properties of Various Micron Size CMC−EC Composite Particles

sample	aqueous phase	organic phase	particle size (μm)	EC content (wt %)
CMC−EC-I	2.0 wt % CMC	0.5 wt % EC	76	22
CMC−EC-II	2.0 wt % CMC	1.0 wt % EC	35	30
CMC−EC-III	2.0 wt % CMC	2.0 wt % EC	13	38

We further studied the possibility to control the size and size distribution of CMC−EC composite particles by adjusting the intensity of agitation and sonication during the dehydration of emulsions. In this case, emulsions were first prepared by emulsifying an aqueous CMC solution into an equal volume of EC in toluene solutions using a high-speed homogenizer followed by an ultrasonic dismembrator with a microtip probe (500 W; 20 kHz). The emulsion was then transferred into a round-bottom flask with Dean−Stark apparatus and heated to reflux. Over the course of the dehydration process, intermittent pulses of low-intensity sonication (20−30% amplitude) were applied to the emulsion in the reaction vessel. The energy supplied by the sonic dismembrator was sufficient to break up emulsion droplets; however, no broken CMC−EC composite particles were seen from SEM micrographs of the resultant particles. As shown in Figure 7, the resulting CMC−EC composite particles are 580 ± 80 nm in size with a polydispersity index (PDI) of 0.2, which demonstrates the critical importance of continuous agitation during dehydration of emulsions for the synthesis of CMC−EC organic composite particles.

The critical surface tension at which small particles no longer remain attached to the air−liquid interface is indicative of particle wettability. For a high surface tension liquid, hydrophobic particles will remain at the interface, while hydrophilic particles will quickly sink into the liquid. Uncoated CMC

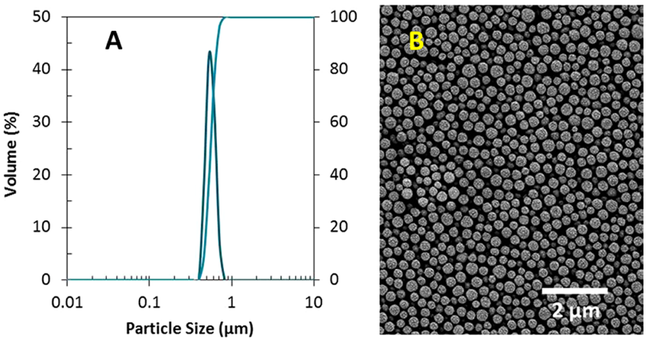

Figure 7. (A) Cumulative and differential particle size distribution of CMC−EC organic composite particles prepared under intermittent sonication during dehydration of CMC aqueous emulsion droplets in EC−toluene solutions. (B) SEM micrograph of the resultant particles.

powders were completely wetted by pure water (72.8 mN/m), while EC powders were completely wetted only by pure methanol (23 mN/m). The wettability of CMC−EC composite particles was evaluated using critical surface tension measured using binary mixtures of methanol and water, with the surface tension of the liquids being tuned by adjusting mixture composition. CMC−EC particles synthesized with different amount of EC in toluene all exhibited similar critical surface tension of approximately 26−28 mN/m. The lower critical surface tension of the synthesized CMC−EC organic composite particles indicates that the surface of these composite particles is more hydrophobic than that of unmodified CMC particles. As a result, the EC-coated CMC composite particles are more compatible with organic solvents and are therefore more suitably dispersed in a continuous oil phase, ensuring effective accessibility to emulsified water droplets. It should be noted however that the hydrated CMC−EC organic composite particles upon contact with emulsified water droplets in silicon oil were completely water-wet, indicating not only absorption of water by CMC−EC organic composite particles, but also the change of CMC−EC composite particles from biwettable to water wet. Once hydrated, the surface properties of the CMC−EC composite particles are more CMC dominant and become more hydrophilic.

Samples of CMC−EC composite particles were placed inside sealed vials with deionized water and agitated using a vortex mixer for 30 s. After an additional 90 s, excess free water was carefully removed by decanting and filtration. As shown in Table 2, the water absorption capacity of various EC-coated CMC composite particles was dependent on its composition. Samples with greater CMC content were able to absorb more water, as anticipated. Since EC is unable to absorb a significant amount of water, the ability of the synthesized CMC−EC organic composite particles to absorb water confirms that the EC shell is permeable to water, despite its biwettable nature.

Table 2. Absorbent Properties of Micron Size CMC−EC Composite Particles

sample	EC content (wt %)	water absorbency (g/g)[a]	critical surface tension (mN/m)[b]
CMC	0	7.8 ± 1.0	> 73
EC	100	< 0.01	< 23
CMC−EC-A	15	4.6 ± 1.0	26 ± 2
CMC−EC-B	24	3.8 ± 0.6	30 ± 3
CMC−EC-C	36	2.3 ± 0.4	28 ± 2

[a] Amount of deionized water retained by a specific sample of dry solid particles within 2 min. [b] Surface tension of binary mixtures of methanol and water for which particles drop through the interface into the solution.

CMC substrates were prepared by evaporation of aqueous CMC solutions. EC substrate was prepared by evaporation of an organic EC solution prepared using toluene as solvent. A thin coating with variable amounts of EC was deposited onto the CMC substrate by placing toluene solutions with variable EC concentration on the CMC substrate and removing solvent by evaporation. Substrates were then placed in a vacuum oven at 70 °C to remove remaining toluene. The initial contact angle of water on the CMC substrates with a variable amount of EC was measured in air.

Table 3. Properties of Substrates Prepared with CMC and EC

substrate	EC coverage (mg/m^2)	contact angle (deg)[a]	water flux (g/s/m^2)[b]
CMC	n/a[e]	54 ± 9	3.0
EC	n/a	82 ± 4	<0.01
CMC−EC[c]	1.6	52 ± 7	n/a
CMC−**EC**[d]	1.6	89 ± 5	n/a
CMC−EC-1	8.0	88 ± 5	0.4
CMC−EC-2	14.5	91 ± 6	0.2

[a] Initial contact angle of a water droplet placed directly onto substrate surface. [b] Time require for substrate to completely absorb a 500 µL water droplet in air. [c] Contact angle was measured on the CMC layer of the composite CMC−EC film. [d] Contact angle was measured on the EC layer of the composite CMC−EC film. [e] n/a, not available.

The results summarized in Table 3 show that CMC substrate is weakly hydrophilic, as indicated by a contact angle value of 54 ± 9°, while EC is weakly hydrophobic as indicated by a contact angle of 82 ± 4°.[30] Oh and Luner reported similar contact angle values between 83.5−86.6° for EC films prepared from solutions of different solvents and EC concentrations with or without annealing of the film.[42] As expected, all the composite EC films on CMC coatings were initially weakly hydrophobic with the measured contact angle value of 90 ± 16°, a value similar to the contact angle values measured on EC films.[42] The surface of CMC−EC composite was responsive to water-absorption; initially more hydrophobic-like EC (before absorbing water) but becoming more hydrophilic-like CMC after absorbing water. Measurement of contact angle on composite surfaces after being hydrated became more variable, usually between 10−40°. The rate of water absorption for CMC cast in glass molds and coated with EC was influenced by the amount of EC and excessive coating of CMC with EC hindered water absorption.

To test the interfacial activity of the synthesized CMC−EC composite particles, EC, CMC, and CMC−EC samples were carefully placed on an immiscible mixture of toluene and water (1:1 by volume). As shown in Figure 8, EC powders are hydrophobic and do not cross through the interface. They remain essentially in the organic phase where they slowly begin to dissolve. CMC powder absorbs water once they reach the oil−water interface and quickly penetrated into the aqueous phase where they also begin to dissolve. In contrast, the synthesized CMC−EC composite particles remained attached

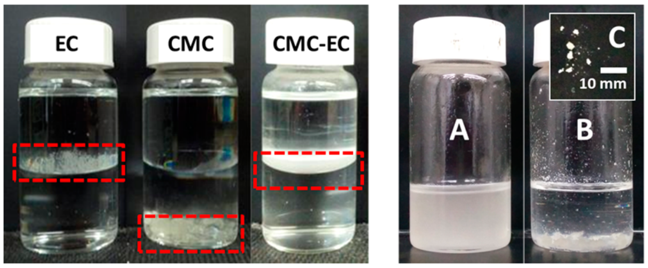

Figure 8. EC particles are hydrophobic and remain in the nonaqueous phase; CMC particles are hydrophilic and reside in the aqueous phase; CMC−EC composite particles are biwettable or interfacially active and attach to the toluene−water interface. The original CMC−EC composite particles are highly dispersed in toluene before absorbing water (A), but aggregate together (B) to form larger aggregates after absorbing water (C).

to the toluene−water interface, indicating the biwettable nature of the particles. As a result, the CMC−EC composite particles are readily dispersed in toluene. However, colloidal stability of the synthesized CMC−EC composite particles in toluene was lost after water addition to toluene.

The responsive nature of the CMC−EC composite particles is most evident when attempting to stabilize emulsions. The CMC−EC composite particles, as synthesized, are interfacially active and could provide sufficient stability to prevent immediate phase separation of a water-in-mineral oil emulsion, as shown in Figure 9. The synthesized CMC−EC composite particles experienced a drastic change in wettability after absorbing water. Before water absorption, the surface of CMC−EC composite particles with a contact angle of approximately 89° is similar to that of EC. The particle with this hydrophobicity is capable of stabilizing water-in-oil emulsions, as shown in Figure 9, panel A. Upon absorbing water, the surface of CMC−EC composite particles becomes more like CMC, which has a contact angle of approximately 52°. As a result, they aggregate in the nonaqueous phase and hence lose their ability to stabilize any type of emulsions. For this reason, the stability of the water-in-mineral oil emulsion stabilized by CMC−EC composite particles is lost, as shown in panel B of Figure 9. The responsive surface of the CMC−EC composite particles ensures that absorbent particles have only finite colloidal stability, which is lost upon absorbing water and eventually leads to the formation of large aggregates of hydrated absorbent particles. The increased size of absorbent aggregates facilitates separation of hydrated CMC−EC composite particles from emulsions for the purpose of water removal and sorbent particle regeneration.

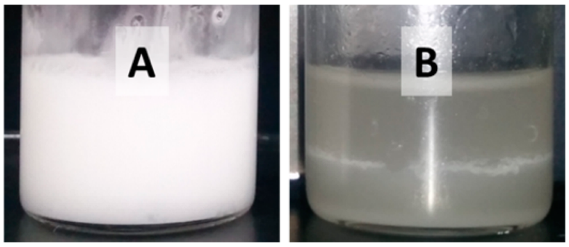

Figure 9. (A) Water-in-mineral oil emulsion stabilized by 2.5 wt % CMC−EC composite particles with initial contact angle of approximately 89° (before absorbing water); (B) phase separation of the emulsion after 24 h as the particles absorb water and become increasingly hydrophilic with contact angle of approximately 52°.

Given their initial biwettability, interfacial activity, and water absorptivity, the synthesized CMC−EC composite particles are ideally suited for removing water from emulsions through absorption. Removal of water from water-in-mineral oil emulsions stabilized by a nonionic surfactant (0.75 wt % SPAN 80) was enhanced using both nonmagnetic (CMC−EC) and magnetic (CMC−EC/MAG) composite absorbent particles. Magnetic CMC−EC composite absorbent particles were prepared by dispersing superparamagnetic Fe_3O_4 nanoparticles into the aqueous CMC solution prior to emulsification. After dehydration, magnetic Fe_3O_4 particles were incorporated into the interior of the CMC−EC composite absorbent particles, leading to magnetically responsive particles. The amount of emulsified water that remained at the midway point of samples treated by various types of particles is shown in Figure 10.

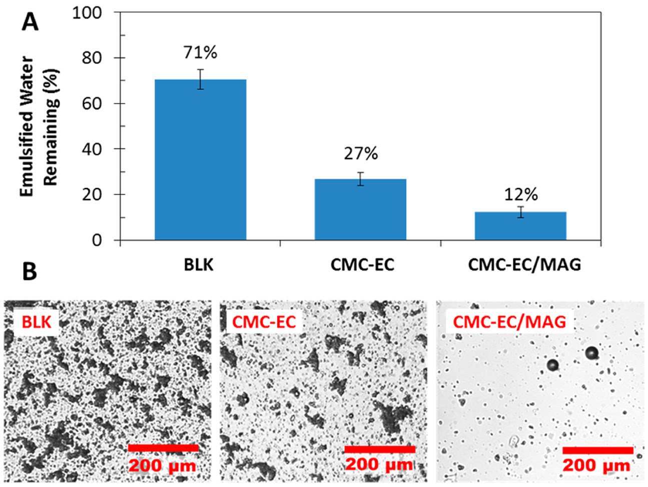

Figure 10. (A) Amount of water emulsified in a mineral oil emulsion was lowered after samples were treated with either CMC−EC composite absorbent particles or magnetic CMC−EC composite absorbent particles. (B) Micrographs of emulsion samples taken at the midway point show the reduction in amount of emulsified water droplets in treated samples.

Untreated emulsion samples exhibited poor phase separation with over 70% of emulsified water remaining after 12 h of mechanical agitation followed by 1 h of gravity settling. By adding 2.5 wt % CMC−EC composite absorbent particles, water content at midway point of treated emulsion (following 12 h of mechanical agitation and 1 h of gravity settling) was reduced to less than 30% of the original emulsified sample. Following 12 h of mechanical agitation and separation of spent magnetic CMC−EC composite absorbent particles using a hand magnet, emulsions treated with 2.5 wt % magnetic CMC−EC composite absorbent particles exhibited reduced water content at the midway point corresponding to less than 12% of the originally emulsified water. The additional magnetic force further accelerated dewatering of water-in-mineral oil emulsion.

■ CONCLUSION

Interfacially active organic CMC−EC composite water-sorbent particles were successfully synthesized by dehydration of CMC-containing water-in-EC-containing toluene emulsions. The size of CMC−EC composite particles could be tuned by increasing

EC concentration in the continuous phase or continuous emulsification during dehydration of the emulsions. The proposed synthesis of CMC−EC composite particles did not require chemical derivatization and generated no chemical waste. EC-coated water absorbent particles possessed a greater compatibility with hydrophobic media and were readily dispersed in organic solvents. The surface of CMC−EC composite particles remained permeable, as they were capable of absorbing water. Because of the absorptive properties of CMC and the interfacial activity of EC, the CMC−EC composite absorbent particles were effective in removing water from water-in-oil emulsions by absorption. By using a similar procedure with Fe_3O_4 nanoparticles dispersed within CMC-containing emulsion water droplets, magnetic CMC−EC composite absorbent particles were also prepared and showed superior performance in removing water from similar stable water-in-mineral oil emulsions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05093.

> Morphology of aggregated CMC-EC composite absorbent particles; water removal from motor oil emulsions using CMC−EC; overlay plot of FTIR spectra of CMC−EC and component materials (PDF)

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Notes

The authors declare no competing financial interest.

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