Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

Ethyl cellulose nanoparticles as stabilizers for Pickering emulsions

Heleen V.M. Kibbelaar [a],[*],[1], Riande I. Dekker [a],[b],[1], Azeza Morcy [a],[b], Willem K. Kegel [b], Krassimir P. Velikov [a],[c], Daniel Bonn [a],[*]

[a] Van der Waals-Zeeman Institute, Institute of Physics, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
[b] Van 't Hoff Laboratory of Physical and Colloid Chemistry, Debye Institute for Nanomaterials Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands
[c] Unilever Innovation Centre Wageningen, Bronland 14, 6708 WH Wageningen, The Netherlands

GRAPHICAL ABSTRACT
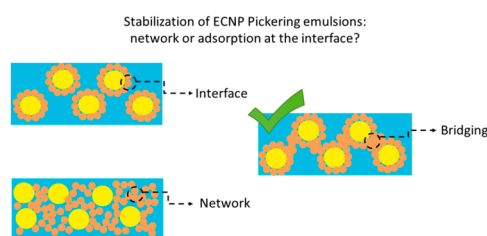
ARTICLE INFO

ABSTRACT

Pickering emulsions stabilized by ethyl cellulose nanoparticles have recently received –great attention for their remarkable stability and numerous industrial applications. De- spite this, the exact stabilization mechanism of such Pickering emulsions is still not fully understood. Both the stabilization of the emulsion by particle adsorption at the inter- face and through network formation in the continuous phase (leading to a yield stress) have been suggested. In this work we study soybean oil-in-water emulsions stabilized by ethyl cellulose nano- particles and find, by the use of confocal microscopy and interfa- cial tension measurements, that the main stabilization mechanism of this nanoparticle- stabilized emulsions is the adsorption of the particles at the interface, instead of forming a network in the continuous phase. At the same time, oscillatory rheology mea- surements reveal that the emulsions exhibit a yield stress well below the random close-packing limit for hard spheres, suggesting short-range interactions between the droplets caused by the presence of the particles at the interface. The presence of the particles at the interface in combination with the observed rheological behavior of an attractive emulsion gives a strong indication for a particle-bridged stabilized emulsions.

1. Introduction

Over the past two decades, there has been widespread scientific interest in the use of colloidal particles to effectively stabilize emulsions, referred to as Pickering emulsions [1–3]. Compared to conventional emulsions, which are stabilized by surfactants [4], Pickering emulsions

---

* Corresponding authors.
  E-mail addresses: h.v.m.kibbelaar@uva.nl (H.V.M. Kibbelaar), r.i.dekker@uva.nl (R.I. Dekker), d.bonn@uva.nl (D. Bonn).
[1] Heleen.V. M. Kibbelaar and Riande. I. Dekker contributed equally.

possess many advantages such as superior stability against coalescence and preventing surfactant contamination of the environment [5–10]. Particle-stabilized emulsions have been used in a large number of applications such as food and cosmetic products [11], templates for the synthesis of functional materials [12], oil recovery from subsurface formations [13,14] and controlled drug delivery [15].

Amongst the various types of particles used for Pickering stabilization, ethyl cellulose nanoparticles (ECNPs) have recently received great attention as stabilizers; notably, their application in the encapsulation of pharmaceuticals [16,17], their low toxicity and environmen- tally responsible character [18], and the remarkable ability to stabilize foams [19]. Recently, their ability to stabilize different oil/water interfaces has also been studied [20–23]. Zhang et al. [20] reported the adsorption of ECNPs at the hexadecane/water interface and Bizmark et al. [22] showed that ECNPs are able to stabilize various higher alkane/water emulsions against co- alescence by adsorption of the particles at the interface, due to the dense coverage of these particles at these interfaces. Wu et al. [18] also reported the potential of ECNPs as Pickering emulsion stabilizers for a dodecane/water system. The nanoparticles were combined with a surfactant to stabilize oil-in-water emulsions. They discovered that a higher ECNP content resulted in improved emulsion stability.

Yet, these studies do not reveal the exact stabilization mechanism of the ECNPs. Es- pecially when the particles are combined with co-surfactants, the exact contribution of the particles to the stability of the emulsions is difficult to investigate. Therefore, we here focus on the exact stability mechanism of emulsions which are solely stabilized by ECNPs, an important question that up to now remains not fully answered. In general, two stabilization mechanisms of Pickering emulsions are proposed. A widespread idea is that the particles adsorb at the oil/water interface and that by doing so, they make Pickering emulsions which are very stable due to the large energy required to remove a particle from the interface [5,24]. However, another explanation of emulsion stabilization is that network formation of the particles in the continuous phase creates a yield stress, and this prevents coalescence and creaming, also leading to stable emulsions [25–30].

In this work we not only study the exact location of the ECNPs and thereby obtain more information about the precise stabilization mechanism, but we also show that ECNPs can stabilize water-oil interfaces with high volume fractions of oils with long carbon chains such as soybean oil, which are widely employed in the food industry [31,32] and in this way expand the potential use of ECNPs as emulsions stabilizers for industrial applications.

We prepare stable ECNPs-stabilized emulsions with various oil volume fractions of soy- bean oil up to 0.7. We find that both oil-in-water and water-in-oil emulsions can form depending on the oil volume fraction. We reveal the location of the particles in the emulsion using confocal microscopy and interfacial tension measurements. More information about the flow properties of the emulsion is obtained using rheology. The appearance of a yield stress for the emulsions at relatively low oil volume fractions, i.e. below 0.64 [33], suggests the occurrence of bridging between the emulsion droplets [34,35]. The possibility to form oil- in-water emulsions with relatively high oil content, and the appearance of a yield stress for emulsions with a relatively low oil content allows for new industrial applications.

2. Experimental section

2.1. Materials

Ethyl cellulose is purchased from Sigma Aldrich (code: 247499-100 G). Ethanol (100%, tech- nical grade) is purchased from Interchema. Potassium chloride is obtained from Merck. Soy- bean oil and the dye Direct Yellow 96 – Solophenyl Flavine are kindly provided by Unilever R&D. Nile red and Fluorescein are also purchased from Sigma Aldrich. All products are used as received. All water used is purified by a

Millipore apparatus (18.2 Ω·cm at 25 C).

2.2. Preparation of ECNPs

ECNPs are prepared via a modified 'antisolvent precipitation' technique from literature [36,37]. Here, we briefly describe the method. Ethyl cellulose is dissolved in ethanol before being poured into a large volume of water under fast magnetic stirring, resulting in the spontaneous precipitation of ethyl cellulose as ECNPs due to nanoparticle nucleation. Subsequently, ethanol and some water are removed by rotary evaporation. This dispersion is then passed through a filter paper (Whatman filter paper Grade 1) to remove any large aggregates that formed during the precipitation. The final concentration of the particles is determined by drying a small part of the particle dispersion. The dispersions are diluted with MilliQ water, resulting in a stable aqueous dispersion of 5 wt% of ECNPs.

2.3. Particle size characterization

The size of the ECNPs is characterized by scanning electron microscopy (SEM, FEI XL30FEG) and dynamic light scattering (DLS, Malvern Zetasizer ZS, particle size distributions are ob- tained using a CONTIN fitting).

2.4. Zeta potential measurements

Zeta potential measurements are performed with a Malvern Zetasizer ZS. The ECNPs dis- persions are strongly diluted with MilliQ water before measurements. The measurements are performed with and without the dye Direct Yellow present in the dispersion.

2.5. Preparation of ECNP-stabilized Pickering emulsions

Emulsions with oil volume fractions between 0.4 and 0.7 are prepared with 2 wt% of ECNPs in the aqueous phase. The desired nanoparticle concentration in the aqueous phase is achieved by diluting a 5 wt% ECNP dispersion with a 100 mM potassium chloride (KCl) solution. KCl screens the negative charge of the ECNPs, resulting in a less negative zetapotential (see Fig. S4(c) in the Supporting Information). This enables the particles to go the oil/water interfaces and can induce aggregation of the particles at the interface [38]. The emulsification is performed with an IKA T25 digital Ultra-Turrax homogenizer. The soybean oil is slowly added to the aqueous phase while mixing at 2 krpm. When the oil is added, the mixing speed is slowly increased. Emulsification is eventually performed at 20 krpm for 2 min.

2.6. Confocal scanning microscopy

The emulsions are studied using a Leica TCS SP8 confocal scanning microscope. Nile red is added to the oil phase, which is excited by a solid state 20 mW laser at 552 nm. Fluorescein is added to the aqueous phase and excited by a solid state 40 mW laser at 448 nm. To visualize the ECNPs in the emulsions, a 5 μL at 0.5 wt% solution of Direct Yellow 96 – Solophenyl Flavine is added dropwise to the emulsions. This dye attaches to cellulose molecules and thereby allows us to visualize the particles. The dye is excited by a solid state 40 mW laser at 448 nm. The emulsions that are used for the visualization of ECNPs do not contain Fluorescein in the aqueous phase, as both Direct Yellow and Fluorescein emit at roughly the same wavelengths.

2.7. Interfacial tension measurements

Interfacial tension measurements of the interface between soybean oil and aqueous dispersions of ECNPs are performed using a pendant drop tensiometer from DataPhysics Instruments (OCA 15plus) and analyzed with the DataPhysics Instruments SCA 20 software module for

a duration of roughly 1000 s.

2.8. Contact angle measurements

The wettability of the nanoparticles was determined using a tensiometer from DataPhysics Instruments (OCA 15plus). All the measurements were conducted at room temperature (21 °C). For the wettability experiments, homogeneous films of ECNPs dispersion were prepared by depositing a solution of ethyl cellulose on glass slides, which were left to dry at room temperature. The contact angle of the nanoparticles was determined by injecting deionized water droplets (4 μL each) onto the surface of the dried films. The shape of the droplet was photographed after an equilibration time of 30 s using a digital camera coupled to the equipment. Contact angles were determined automatically, approximating the contour of the imaged droplets with a Laplace–Young fit. Measurements were taken as the average of at least 3 droplets on 2 different ethyl cellulose films.

2.9. Rheology measurements

Dispersions with various concentrations of ECNPs are prepared to measure the shear rheol- ogy. Shear rheology measurements of these dispersions are performed on a stress-controlled rheometer (Anton Paar MCR 302), equipped with a roughened cone plate geometry with a diameter of 50 mm and cone angle of 1°. The experiments are performed at a temperature of 20 °C set by a Peltier system. The steady shear experiments are performed by carrying out a shear rate sweep from 10^{-3} to 10^{2} s^{-1}. Stresses are averaged over 15 s after reaching the steady state.

Oscillatory measurements of the emulsions are performed on the same instrument. Am- plitude sweeps are carried out from 0.01% to 100% at a constant angular frequency of 1 rad/s, generating curves of the storage (G′) and loss (G'') moduli as a function of the strain.

3. Results and discussion

The antisolvent precipitation method is used for the preparation of dispersions of ECNPs. From earlier work of Hayden et al. [37] it is known that the particle size of the ECNPs is controlled by the initial EC concentration. Furthermore, it is found that particle sizes around 80 nm provide the highest yield. We therefore prepare ECNPs using the same initial EC concentration and obtain particles with a slightly larger size of 100 nm (PDI 0.16) as measured by dynamic light scattering (DLS) measurements and scanning electron microscopy (SEM) (see Figs. S1 and S2 in the Supporting Information for the particle size distribution
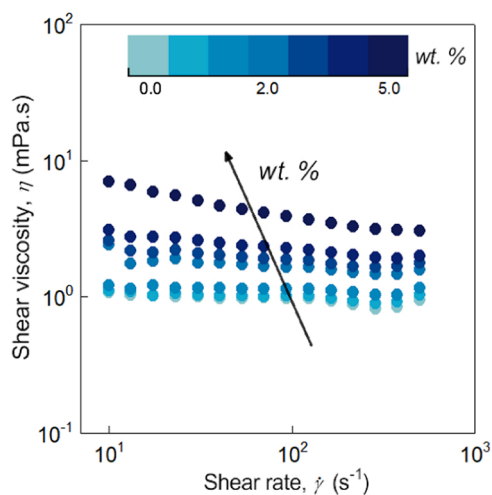
Fig. 1. Shear viscosity as a function of the shear rate for dispersions of different wt% of ECNPs in water.

and the SEM image, respectively). A consistent yield of 70% is achieved. Fig. 1 shows the shear viscosity of these aqueous ECNPs dispersions with different nanoparticle concentrations. The rheological behavior of the aqueous dispersions becomes slightly shear thinning at concentrations of 5 wt%, whilst dispersions with lower concentrations show a roughly Newtonian viscosity. To form a stable Pickering emulsion, it is of importance to have enough particles to cover the oil/water interface. However, in order to prepare ECNPs- stabilized emulsions without any complicated viscoelastic contribution of the aqueous phase, it is important to select a particle concentration with a Newtonian behavior and low viscosity. For these reasons, aqueous dispersions with 2 wt% of ECNPs are selected.

Before preparing the emulsions, we first determine the wettability of the ECNPs. Solid particles that are used as emulsion stabilizers should have a sufficient wettability to allow them to be present at the oil/water interface. The wettability of the particles is determined by the contact angle value which indicates their hydrophilic or lipophilic nature, and hence the type of the Pickering emulsion they can stabilize. Particles that have a contact angle less than 90° are hydrophilic and form o/w Pickering emulsions, while particles with a contact angle higher than 90° are hydrophobic and produce w/o emulsions [5,24]. Particles with a contact angle of 90° are wetted equally by the oil and water phases, and theoretically, result in the formation of emulsions with optimized stability. However, it has been observed that emulsion stability is improved when a lightly greater part of the particle is placed in the continuous phase, i.e., when the particle has a slightly higher affinity to the external phase [39]. The contact angle of the ECNPs is determined to be 62° (see Fig. S3 in the Supporting Information), which reflects their hydrophilic nature and indicates that they are more present in the continuous phase. The contact angle of 62° implies that these particles are capable of stabilizing an o/w emulsion, which we will now explore further.

The upper row of Fig. 2 shows photographs of four emulsions with increasing oil volume fraction. The photographs are taken two months after preparation and clearly show that all four emulsions are stable against coalescence, creaming and Ostwald ripening. The bottom row of Fig. 2 shows confocal images of the same emulsions. The oil phase is rendered in red due to the presence of Nile red, whereas the aqueous phase is rendered in green due to the presence of Fluorescein. The confocal images show that for oil volume fractions of 0.4, 0.5 and 0.6 an oil-in-water emulsion is formed, whereas for the oil volume fraction of 0.7 a water- in-oil emulsion is formed. The oil-in-water emulsions show rather non-uniform oil droplet sizes in the range of roughly 1–10 μm with a high degree of polydispersity. The water droplets in the water-in-oil emulsions are much smaller and more uniform in size. This phase inversion from an oil-in-water to a water-in-oil emulsion with increasing oil volume fraction is often described for Pickering emulsions [8,40–42]. For our emulsions, the phase inversion occurs at an oil volume fraction between 0.6 and 0.7. This is shown by Fig. 3 which depicts a confocal image of an emulsion with an oil volume fraction of 0.6. The image contains regions with oil droplets dispersed in water and regions with water droplets dispersed in oil, indicating that phase inversion occurs around/above the volume fraction of 0.6. The phase inversion, interestingly, does not occur at 50 v% of oil. This is probably due to the more hydrophilic character of the ECNPs, preferring the water phase of the emulsion. Therefore, the phase inversion point is slightly shifted towards higher oil fractions. Phase inversion in emulsions around the jamming transition of 0.64 has been reported before.[40] Above the limit of random close-packing of spherical drops, the droplets are forced into closer proximity and start to deform. This deformation then leads to a catastrophic phase inversion that we observe going from 60 v% of oil to 70 v% of oil. The phase inversion also explains why the 70 v% emulsion is liquid compared to the other emulsions with lower oil content, as now the dispersed phase is only 30 v% of the emulsion.

From visual inspection, a clear yield stress can be observed for the 60 v% emulsion. In order to quantitatively confirm the visual observation of a yield stress, we perform rheology experiments on the
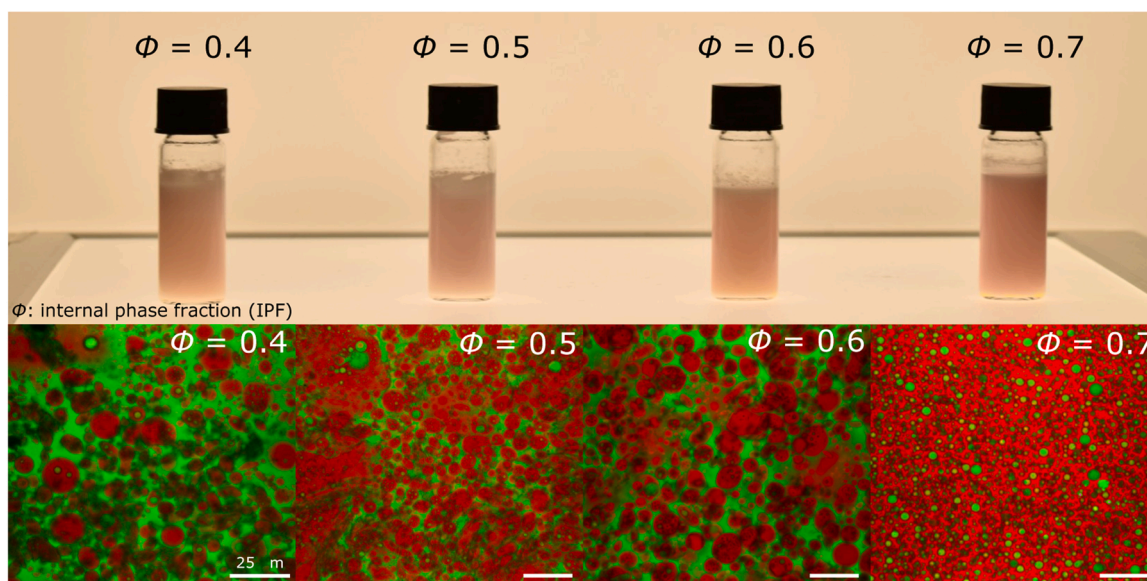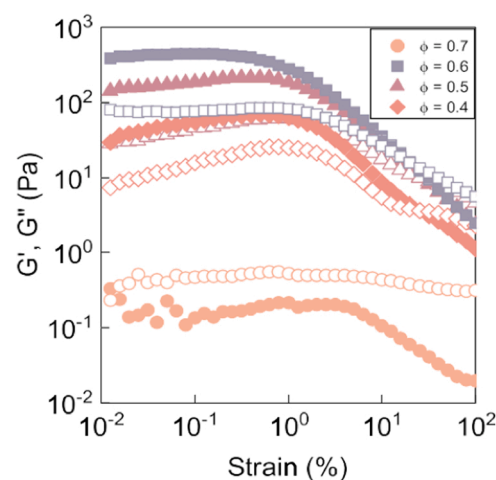
Fig. 2. Photographs and confocal images of emulsions with oil volume fractions ranging from 0.4 to 0.7. All emulsions contain 2 wt% of ECNPs in the water phase to stabilize the emulsions. The oil phase is rendered in red, whereas the water phase is rendered in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
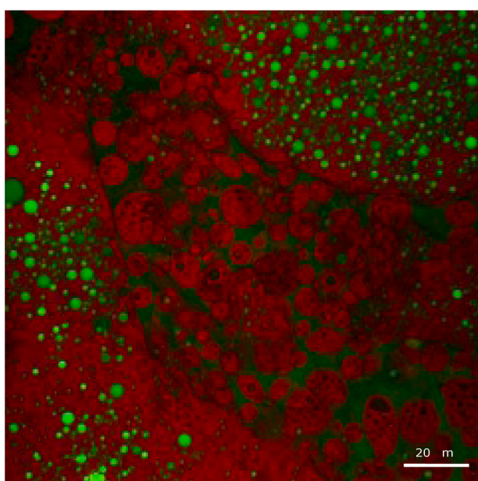
Fig. 3. Confocal image of soybean oil-in-water emulsion with an oil volume fractions of 0.6 showing phase inversion. From the image regions with oil droplets dispersed in water and regions with water droplets dispersed in oil can be observed.


Fig. 4. Oscillatory strain sweep profiles, measured at a constant radial frequency of 1 rad/s, for the emulsions with different volume fractions of oil (φ = 0.4, 0.5, 0.6, 0.7). G' and G" are represented by solid and hollow markers, respectively.

emulsions. Fig. 4 shows the oscillatory strain sweep profiles (at a constant radial frequency of 1 rad/s) of the emulsions with oil volume fractions ranging from 0.4 to 0.7. The figure clearly shows that the water-in-oil emulsion with an oil volume fraction of 0.7 does not exhibit a yield stress behavior, as expected from the liquid behavior observed from visual inspection. The storage modulus (G') is always lower than the loss modulus (G") within the measurement range [43]. However, the oil-in-water emulsions with volume fractions ranging from 0.4 to 0.6 do behave like yield stress fluids as G' > G" at low strains. This rheological behavior, with yield stresses below the jamming point, is typically observed for attractive emulsions, i.e. emulsions with attractive interactions between the droplets [44–46].

In general, it is accepted that Pickering emulsions are stabilized by one of two following mechanistic theories. One is that particles adsorb at the interface and act as surfactants, modifying the interfacial energy of the oil–water interface [20,22,23]. The other theory is that the particles

form a network in the continuous phase which leads to a yield stress, and thereby stabilize the droplets without changing the interfacial tension [27,28,47,48].

To investigate if the particles in this system form a network in the continuous phase, we perform confocal microscope measurements. To be able to locate the particles in this particular system, we use the dye 'Direct Yellow', a fluorescent dye which solely attaches to.

the ECNPs. We perform zeta potential measurements to verify if the dye has an effect on the surface properties of the particles and thereby their ability to stabilize the emulsions, and find that the dye does not affect the value of the zeta potential of the particles (see Fig. S4 in the Supporting Information for the zeta potential of the particles with and without dye).

Fig. 5 shows confocal images of two of these emulsions. The top row shows emulsions with oil volume fractions of 0.5 and of 0.6. In these confocal images the oil phase is rendered in red by the use of Nile red. The bottom row shows confocal images of the same emulsions at the
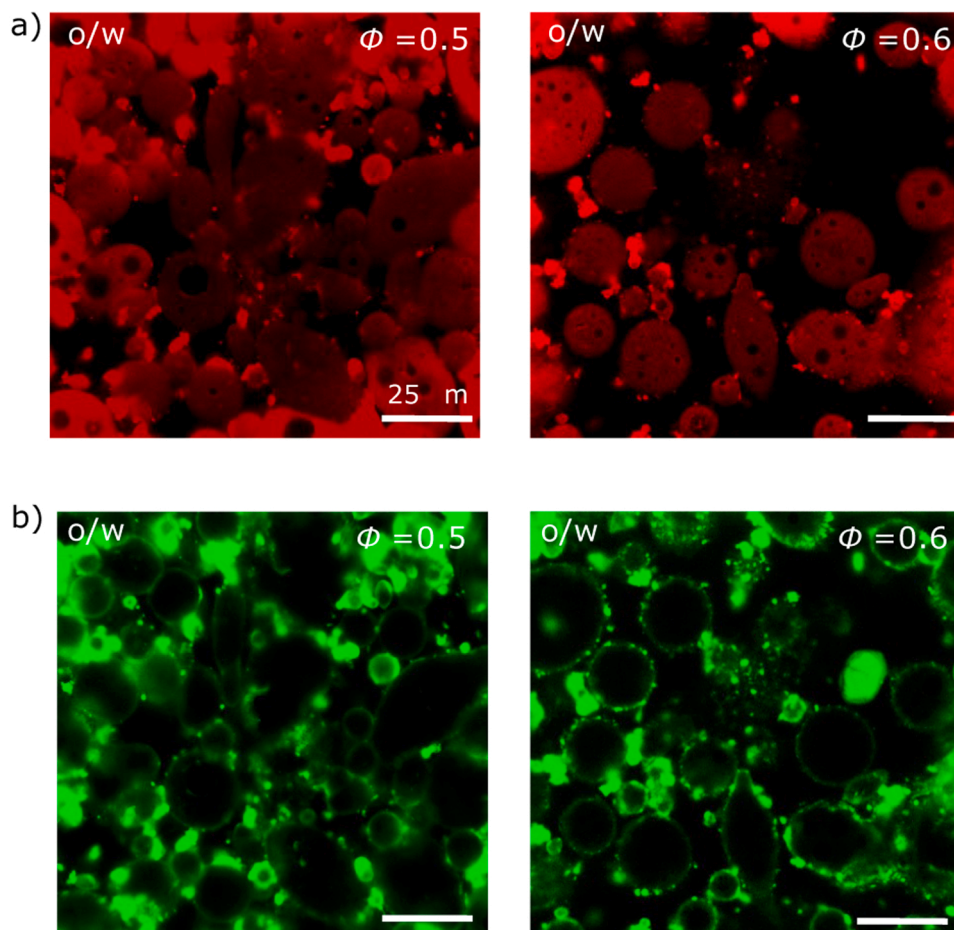
Fig. 5. Confocal images of soybean oil-in-water emulsions with oil volume fractions of 0.5 (a) and 0.6 (b). The emulsions contain 2 wt% of ECNPs in the water phase to stabilize the emulsion. The oil phase is rendered in red, whereas the ECNPs are rendered in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

same location, however this time the Direct Yellow is excited. The green spots in the confocal images therefore show the location of the ECNPs. By comparing the upper and lower pictures, clear rings of ECNPs can be observed around the oil droplets. This clearly indicates that the ECNPs are located at the oil/water interface and thereby stabilize the emulsion [5,24]. From the confocal images a network of particles in the continuous phase, the other possible stabilization mechanism [27,28,47,48], cannot be observed.

The presence of particles at the interface observed by confocal microscopy, in combination with the typical rheology data of attractive emulsions indicates that droplet bridging leads to stabilization of this emulsion system. Strong short-range adhesive forces between droplets, leading to attractive emulsions, can occur when they share a particle monolayer [49–51]. Similar observations (with rheology data) have been reported before in literature and were indeed designated to particle bridging [35,52,53].

To further confirm that the particles are present at the interface, we perform interfacial tension measurements between soybean oil and aqueous dispersions of 0.03 wt% ECNPs. Fig. 6 depicts the results of these interfacial tension measurements of soybean and water and soybean oil an water with 0.03 wt% ECNPs. These results immediately show that the ECNPs decrease the interfacial tension. Although ethyl cellulose is highly insoluble in water, it can be argued that free ethyl cellulose causes the decrease in the interfacial tension because ethyl cellulose from the nanoparticles might possibly dissolve in the oil phase during or after emulsification. In order to verify if free ethyl cellulose (if any) in the emulsion contributes to a decrease in the interfacial tension
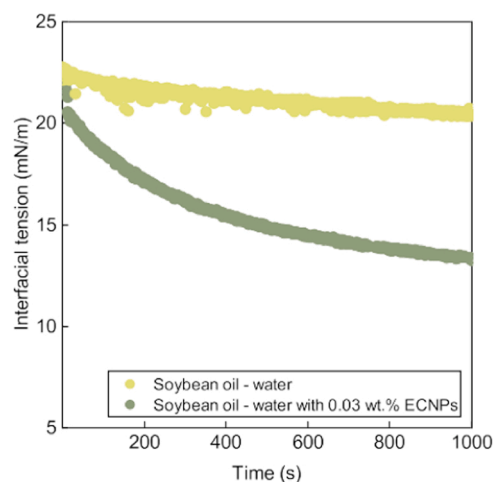
Fig. 6. Interfacial tension measurement of soybean oil - water and soybean oil - water with 0.03 wt% ECNPs. The ECNP clearly cause a reduction in the interfacial tension of the soybean oil - water interface.

we performed interfacial tension measurements on soybean oil/water mixtures with non nanoparticle ethyl cellulose either added to the water phase or the oil phase (see Fig. S5 in the Supporting Information). From this figure, it can be seen that the presence of free ethyl cellulose in either the oil or water phase does not contribute to a decrease in

interfacial tension. A decrease in interfacial tension caused by (nano) particles has also been observed before [22,54–56] and are another proof that the stabilization in our Pickering emulsions is by particle adsorption at the oil/water interface.

4. Conclusion

In this study we have demonstrated that 2 wt% of ECNPs can stabilize emulsions of various soybean oil/water ratios. Phase inversion (from oil in water to water in oil) occurred at oil volume fractions between 0.6 and 0.7. Soybean oil-in-water emulsions show a yield stress well below the jamming transition. This yield stress is likely a result of short-range interactions between particles surrounding different oil droplets, making the emulsions slightly attractive. To further study the stabilization mechanism of this system, the ECNPs are stained using Direct Yellow, a dye that attaches to ethyl cellulose molecules. Confocal microscopy images show that the ECNPs are located at the oil/water interface, rather than forming a network in the continuous phase. The presence of the particles at the interface together with the observed rheological behavior of an attractive emulsion give a strong indication for a particle-bridged stabilized emulsion. Furthermore, the particles strongly decrease the oil/water interfacial tension, conforming the adsorption of the particles onto the interface. With the outcomes of this study we do not only show the potential of ECNP Pickering emulsions for industrial applications, but also further reveal the main stabilization mechanism of this system.

CRediT authorship contribution statement

Heleen. V. M. Kibbelaar and **Riande. I. Dekker:** Conceptualization, Methodology, Investigation, Writing – original draft. **Azeza Morcy:** Methodology and Investigation. **Willem. K. Kegel:** Supervision, Writing – review & editing. **Krassimir. P. Velikov:** Supervision, Writing – review & editing. **Daniel Bonn:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2022.128512.

References

[1] S.U. Pickering, Pickering: emulsions, J. Chem. Soc. 91 (1907) 2001–2021.

[2] W. Ramsden, Separation of solids in the surface-layers of solutions and 'suspensions'(observations on surface-membranes, bubbles, emulsions, and mechanical coag- ulation).—preliminary account, Proc. R. Soc. Lond. 72 (1904) 156–164.

[3] H. Jiang, Y. Sheng, T. Ngai, Pickering emulsions: Versatility of colloidal particles and recent applications, Curr. Opin. Colloid Interface Sci. 49 (2020) 1–15.

[4] J. Bibette, F. Leal-Calderon, Surfactant-stabilized emulsions, Curr. Opin. Colloid Interface Sci. 1 (1996) 746–751.

[5] B.P. Binks, Particles as surfactants—similarities and differences, Curr. Opin. Colloid Interface Sci. 7 (2002) 21–41.

[6] S. Tcholakova, N. Denkov, A. Lips, Comparison of solid particles, globular proteins and surfactants as emulsifiers, Phys. Chem. Chem. Phys. 10 (2008) 1608–1627.

[7] E. Dickinson, Food emulsions and foams: Stabilization by particles, Curr. Opin. Colloid Interface Sci. 15 (2010) 40–49.

[8] T.S. Dunstan, P.D. Fletcher, S. Mashinchi, High internal phase emulsions: catastrophic phase inversion, stability, and triggered destabilization, Langmuir 28 (2012) 339–349.

[9] A. Sarkar, E. Dickinson, Sustainable food-grade Pickering emulsions stabilized by plant-based particles, Curr. Opin. Colloid Interface Sci. 49 (2020) 69–81.

[10] V. Calabrese, J.C. Courtenay, K.J. Edler, J.L. Scott, Pickering emulsions stabi- lized by naturally derived or biodegradable particles, Curr. Opin. Green. Sustain. Chem. 12 (2018) 83–90.

[11] C.C. Berton-Carabin, K. Schroën, Pickering emulsions for food applications: background, trends, and challenges, Annu. Rev. Food Sci. Technol. 6 (2015) 263–297.

[12] H. Yang, L. Fu, L. Wei, J. Liang, B.P. Binks, Compartmentalization of incompatible reagents within Pickering emulsion droplets for one-pot cascade reactions, J. Am. Chem. Soc. 137 (2015) 1362–1371.

[13] N. Kumar, T. Gaur, A. Mandal, Characterization of SPN Pickering emulsions for application in enhanced oil recovery, J. Ind. Eng. Chem. 54 (2017) 304–315.

[14] J. Lee, T. Babadagli, Optimal design of pickering emulsions for heavy-oil recovery improvement, J. Dispers. Sci. Technol. 41 (2020) 2048–2062.

[15] F. Porta, A. Kros, Colloidosomes as single implantable beads for the in vivo delivery of hydrophobic drugs, Part. Part. Syst. Charact. 30 (2013) 606–613.

[16] S. Prasertmanakit, N. Praphairaksit, W. Chiangthong, N. Muangsin, Ethyl cellulose microcapsules for protecting and controlled release of folic acid, AAPS PharmSciTech 10 (2009) 1104–1112.

[17] M.M. Abdel-Mottaleb, B. Moulari, A. Beduneau, Y. Pellequer, A. Lamprecht, Nanoparticles enhance therapeutic outcome in inflamed skin therapy, Eur. J. Pharm. Biopharm. 82 (2012) 151–157.

[18] X. Wu, L. Zhang, X. Zhang, Y. Zhu, Y. Wu, Y. Li, B. Li, S. Liu, J. Zhao, Z. Ma, Ethyl cellulose nanodispersions as stabilizers for oil in water Pickering emulsions, Sci. Rep. 7 (2017) 1–10.

[19] H. Jin, W. Zhou, J. Cao, S.D. Stoyanov, T.B. Blijdenstein, P.W. de Groot, L. N. Arnaudov, E.G. Pelan, Super stable foams stabilized by colloidal ethyl cellulose particles, Soft Matter 8 (2012) 2194–2205.

[20] Y. Zhang, A. Shitta, J.C. Meredith, S.H. Behrens, Bubble meets droplet: particle-assisted reconfiguration of wetting morphologies in colloidal multiphase systems, Small 12 (2016) 3309–3319.

[21] N. Bizmark, M.A. Ioannidis, D.E. Henneke, Irreversible adsorption-driven assembly of nanoparticles at fluid interfaces revealed by a dynamic surface tension probe, Langmuir 30 (2014) 710–717.

[22] N. Bizmark, M.A. Ioannidis, Ethyl cellulose nanoparticles at the alkane–water interface and the making of Pickering emulsions, Langmuir 33 (2017) 10568–10576.

[23] E. Melzer, J. Kreuter, R. Daniels, Ethylcellulose: a new type of emulsion stabilizer, Eur. J. Pharm. Biopharm. 56 (2003) 23–27.

[24] R. Aveyard, B.P. Binks, J.H. Clint, Emulsions stabilised solely by colloidal particles, Adv. Colloid Interface Sci. 100 (2003) 503–546.

[25] J. Thieme, S. Abend, G. Lagaly, Aggregation in Pickering emulsions, Colloid Polym. Sci. 277 (1999) 257–260.

[26] M. Dinkgreve, K. Velikov, D. Bonn, Stability of LAPONITE®-stabilized high internal phase Pickering emulsions under shear, Phys. Chem. Chem. Phys. 18 (2016) 22973–22977.

[27] A. Drelich, F. Gomez, D. Clausse, I. Pezron, Evolution of water-in-oil emulsions stabilized with solid particles: Influence of added emulsifier, Colloids Surf. A Physicochem. Eng. Asp. 365 (2010) 171–177.

[28] R. Pichot, F. Spyropoulos, I. Norton, Competitive adsorption of surfactants and hydrophilic silica particles at the oil–water interface: Interfacial tension and contact angle studies, J. Colloid Interface Sci. 377 (2012) 396–405.

[29] C. Chuanuwatanakul, C. Tallon, D.E. Dunstan, G.V. Franks, Controlling the microstructure of ceramic particle stabilized foams: influence of contact angle and particle aggregation, Soft Matter 7 (2011) 11464–11474.

[30] W.J. Ganley, J.S. Van Duijneveldt, Controlling the rheology of montmorillonite stabilized oil-in-water emulsions, Langmuir 33 (2017) 1679–1686.

[31] J.L.M. Mundo, H. Zhou, Y. Tan, J. Liu, D.J. McClements, Stabilization of soybean oil-in-water emulsions using polypeptide multilayers: cationic polylysine and anionic polyglutamic acid, Food Res. Int. 137 (2020) 109304.

[32] Y. Liu, Z.-C. Wei, Y.-Y. Deng, H. Dong, Y. Zhang, X.-J. Tang, P. Li, G. Liu, M.-W. Zhang, Comparison of the effects of different food-grade emulsifiers on the properties and stability of a casein-maltodextrin-soybean oil compound emulsion, Molecules 25 (2020) 458.

[33] J. Paredes, M.A. Michels, D. Bonn, Rheology across the zero-temperature jamming transition, Phys. Rev. Lett. 111 (2013), 015701.

[34] D.J. French, P. Taylor, J. Fowler, P.S. Clegg, Making and breaking bridges in a Pickering emulsion, J. Colloid Interface Sci. 441 (2015) 30–38.

[35] M.N. Lee, H.K. Chan, A. Mohraz, Characteristics of Pickering emulsion gels formed by droplet bridging, Langmuir 28 (2012) 3085–3091.

[36] N. Bizmark, M.A. Ioannidis, Effects of ionic strength on the colloidal stability and interfacial assembly of hydrophobic ethyl cellulose nanoparticles, Langmuir 31 (2015) 9282–9289.

[37] D.R. Hayden, H.V. Kibbelaar, A. Imhof, K.P. Velikov, Size and optically tunable ethyl cellulose nanoparticles as carriers for organic UV filters, ChemNanoMat 4 (2018) 301–308.

[38] S. Simovic, C.A. Prestidge, Adsorption of hydrophobic silica nanoparticles at the PDMS droplet- water interface, Langmuir 19 (2003) 8364–8370.

[39] J. Wu, G.-H. Ma, Recent studies of Pickering emulsions: particles make the difference, Small 12 (2016) 4633–4648.

[40] B. Binks, S. Lumsdon, Catastrophic phase inversion of water-in-oil emulsions stabilized by hydrophobic silica, Langmuir 16 (2000) 2539–2547.

[41] B. Binks, S. Lumsdon, Transitional phase inversion of solid-stabilized emulsions using particle mixtures, Langmuir 16 (2000) 3748–3756.

[42] B.P. Binks, J.A. Rodrigues, Inversion of emulsions stabilized solely by ionizable nanoparticles, Angew. Chem. Int. Ed. 44 (2005) 441–444.

[43] M. Dinkgreve, M.M. Denn, D. Bonn, "Everything flows?": elastic effects on startup flows of yield-stress fluids, Rheol. Acta 56 (2017) 189–194.

[44] S.S. Datta, D.D. Gerrard, T.S. Rhodes, T.G. Mason, D.A. Weitz, Rheology of attractive emulsions, Phys. Rev. E 84 (2011), 041404.

[45] M. Dinkgreve, M. Fazilati, M. Denn, D. Bonn, Carbopol: From a simple to a thixotropic yield stress fluid, J. Rheol. 62 (2018) 773–780.

[46] P.L. Fuhrmann, G. Sala, M. Stieger, E. Scholten, Clustering of oil droplets in o/w emulsions: controlling cluster size and interaction strength, Food Res. Int. 122 (2019) 537–547.

[47] S. Lam, K.P. Velikov, O.D. Velev, Pickering stabilization of foams and emulsions with particles of biological origin, Curr. Opin. Colloid Interface Sci. 19 (2014) 490–500.

[48] Z. Yu, R.M. Schmaltz, T.C. Bozeman, R. Paul, M.J. Rishel, K.S. Tsosie, S.M. Hecht, Selective tumor cell targeting by the disaccharide moiety of bleomycin, J. Am. Chem. Soc. 135 (2013) 2883–2886.

[49] E.J. Stancik, M. Kouhkan, G.G. Fuller, Coalescence of particle-laden fluid interfaces, Langmuir 20 (2004) 90–94.

[50] E.J. Stancik, G.G. Fuller, Connect the drops: Using solids as adhesives for liquids, Langmuir 20 (2004) 4805–4808.

[51] H. Xu, M. Lask, J. Kirkwood, G. Fuller, Particle bridging between oil and water interfaces, Langmuir 23 (2007) 4837–4841.

[52] H. Katepalli, V.T. John, A. Tripathi, A. Bose, Microstructure and rheology of particle stabilized emulsions: Effects of particle shape and inter-particle interactions, J. Colloid Interface Sci. 485 (2017) 11–17.

[53] C. Griffith, H. Daigle, Manipulation of Pickering emulsion rheology using hydrophili- cally modified silica nanoparticles in brine, J. Colloid Interface Sci. 509 (2018) 132–139.

[54] H. Cuthill, C. Elleman, T. Curwen, B. Wolf, Colloidal particles for Pickering emulsion stabilization prepared via antisolvent precipitation of lignin-rich cocoa shell extract, Foods 10 (2021) 371.

[55] L. Bai, S. Huan, W. Xiang, L. Liu, Y. Yang, R.W.N. Nugroho, Y. Fan, O.J. Rojas, Self-assembled networks of short and long chitin nanoparticles for oil/water interfacial superstabilization, ACS Sustain. Chem. Eng. 7 (2019) 6497–6511.

[56] F. Qi, J. Wu, G. Sun, F. Nan, T. Ngai, G. Ma, Systematic studies of Pickering emulsions stabilized by uniform-sized PLGA particles: preparation and stabilization mechanism, J. Mater. Chem. B 2 (2014) 7605–7611.