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Tuning hydrophobicity of zein nanoparticles to control rheological behavior of Pickering emulsions

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ABSTRACT

In the present work, the influence of hydrophobicity of zein/tannic acid complex particles (ZTPs) on the rheological behavior of ZTP-stabilized emulsion gels is described. The hydrophobicity of the particles was controlled by the incorporation of different amounts of hydrophilic tannic acid, while retaining a similar particle size. The resulting ZTPs with varying hydrophobicity were successfully used to form emulsion gels with similar oil droplet size. With a decrease in the hydrophobicity of ZTPs, the storage modulus (G′) of emulsion gels increased, while tan δ and the frequency dependence decreased, indicating the formation of a stronger gel network. The crossover strain, γ_{co}, increased with a decrease in the hydrophobicity of ZTPs, indicating the gel network becomes more resistance against breakdown. In all cases, G′ increased in a power-law manner with an increase in protein concentration ($G' \sim c_p^n$) and oil content ($G' \sim \varphi^m$). The exponent n and m decreased with decreasing particle hydrophobicity, indicating that hydrophobic interactions between particles within the particle network in the continuous phase and the oil droplets provide a relatively larger contribution to the gel strength for emulsion gels stabilized by ZTPs with higher hydrophobicity. Increasing the oil polarity provided a lower gel strength for emulsions stabilized by particles with high hydrophobicity, while it increased the gel strength for particles with low hydrophobicity. The results show that the rheological behavior of ZTP-stabilized emulsion gels can be tuned by changing the particle hydrophobicity and oil polarity, which provide interesting features for various applications in the food industry.

1. Introduction

Pickering emulsions using particles as stabilizers have attracted increasing interest in scientific research and industrial production due to several advantages compared to emulsions traditionally stabilized with small molecular weight surfactants and amphiphilic polymers, such as the long-term stability (Berton-Carabin, 2015; Rayner et al., 2014). For the formation of stable Pickering emulsions, particle wettability is believed to be a key factor, which can be characterized by the contact angle θ at the oil-water interface. In general, particles with $\theta < 90°$ prefer to form oil-in-water emulsions, while particles with $\theta > 90°$ prefer to form water-in-oil emulsions. If the particle is too hydrophobic or too hydrophilic, it will completely immerse in either the oil or water phase instead of adsorbing at the oil-water interface. However, under the right conditions, Pickering particles can be irreversibly adsorbed at the interface, thereby providing long term stability. The free energy, E, for detaching a particle from the oil-water interface depends on the particle size (r), the contact angle (θ), and the interfacial tension (γ) as $\Delta E = \pi r^2 \gamma (1\text{-}|\cos\theta|)^2$ (Rayner et al., 2014). Particles with a contact angle of 90° at the oil-water interface possess the largest desorption energy and thereby provide the highest stability to Pickering emulsions.

To obtain such a situation, the particles should not be too hydrophobic and not too hydrophilic. The hydrophobicity of particles can be controlled by changing the surface properties. For example, single-chain cationic surfactants, such as dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammonium bromide (CTAB), and gemini surfactant II-14-3, were adsorbed onto the surface of hydrophilic silica particles, thereby increasing the particle hydrophobicity (Cui, Yang, Cui, & Binks, 2009). Such

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particle modification was used to improve the stability of oil-in-water Pickering emulsions (Cui et al., 2009). Such an increase in emulsion stability due to increased hydrophobicity was also observed for starch granules that were coated with octenyl succinic anhydride (OSA) (Timgren, Rayner, Dejmek, Marku, & Sjöö, 2013), and for several other particles, such as oleic acid-modified silica particles (Sadeghpour, Pirolt, & Glatter, 2013), methyl orange modified hydroxide particles (Li et al., 2013), and heat-induced soy protein nanoparticles (Liu & Tang, 2013). In our previous work, we have shown that zein particles can also be used as a Pickering stabilizer. Zein is an abundant protein extracted from corn, and therefore food-grade. Due to its special tertiary structure, zein can self-assemble into micro- and nano-particles through liquid-liquid dispersion or solvent evaporation approaches (Patel & Velikov, 2014). Zein particles possess a high hydrophobicity due to a high proportion of nonpolar amino acids (>50%), and such particles do not favor to adsorb onto oil-water interface to form stable Pickering emulsions (Folter, Ruijven, & Velikov, 2012). To produce stable emulsions, the hydrophobicity of zein particles has to be decreased by incorporation of hydrophilic components, such as chitosan (Wang et al., 2015), sodium caseinate (Feng & Lee, 2016), and sodium stearate (Gao et al., 2014). We have recently shown that tannic acid can also be used to increase the hydrophilic properties of such particles, and thereby act as a Pickering stabilizer (Zou, Guo, Yin, Wang, & Yang, 2015).

The interactions between such Pickering particles at the interface and those present in the continuous phase influence the interfacial properties and the properties of the particle network. The oil droplet and particle network formation influences the rheological property of such Pickering emulsions, which can affect the visual appearance and the final sensory perception of such emulsions. This is relevant for various applications in the food, pharmaceutical, and cosmetic industry (Tadros, 1994). In our recent work, we have analyzed the structure formation and rheological properties of ZTP (107 nm)-stabilized Pickering emulsion gels (Zou, Yang, & Scholten, 2018). It was found that by changing the particle concentration and the oil content, the obtained emulsion gel networks presented three distinct regimes in their rheological behavior as a function of particle content. The regimes were a result of a different network formation between the particles and the oil droplets (Zou et al., 2018).

The hydrophobicity of the Pickering particles is often discussed as an important parameter for the stability of emulsions (Wang & Wang, 2016). Emulsions are observed to be stable between contact angles, θ, of 60–80° for quartz particles in carbon tetrachloride-in-water emulsions (Koretzki & Kruglyakov, 1971), between 80 and 90° for silica particles for water-in-toluene emulsions (Binks, Dyab, & Fletcher, 2007), and between 60 and 110° for halloysite nanotubes for dodecane-in-water emulsions (Owoseni et al., 2015). However, studies on the effect of particle hydrophobicity on the rheological properties of Pickering emulsions and emulsion gels are still scarce, especially for bio-derived Pickering particle. Chen and coworkers showed that for a decrease in the hydrophobicity of silica particles (~330 nm), the rheological properties including the viscosity, the storage modulus, as well as the critical strain of Pickering emulsions (particle concentration, 0.1–0.3 w/w %; paraffin liquid, 50 v/v %) significantly increased (Chen et al., 2017), indicating that particle hydrophobicity plays an important role. However, an understanding on the network formation based on changes in the hydrophobicity is still limited. In this work, we focus on the effect of particle hydrophobicity on the network formation of emulsion gels. ZTPs as used in our previous work (Zou et al., 2018) are convenient for such a study, as the hydrophobicity of the particles can be adjusted by the tannic acid content. In this work, we used four ZTPs with different hydrophobicity to investigate the effect of particle hydrophobicity on network formation of Pickering stabilized emulsions. Considering the fact that the particle size may have an effect on the particle network formation, they were prepared with a similar diameter of 85 nm. The changes in hydrophobicity leads to changes in the interactions between the particles at the interface and the particle network, thereby affect both interfacial and bulk properties by particle adsorption and particle network formation. Additionally, we also changed the oil hydrophobicity to alter the interactions between the structural elements in the emulsion system. The prepared Pickering emulsions were investigated for their stability and their rheological behavior.

2. Materials and methods

2.1. Materials

Zein powder with a purity around 88–96% was purchased from Acros Organics (Geel, Belgium). Tannic acid (TA), 6-propionyl-2-(*N*, *N*-dimethyl-amino) naphthalene (PRODAN), and castor oil were obtained from Sigma-Aldrich, Co (Steinheim, Germany). Ethanol and acetone were supplied by VWP International B.V (Amsterdam, the Netherlands) and Actu-All Chemicals (Oss, the Netherlands), respectively. Sunflower oil of the brand Reddy (Vandermoortele NV, Breda, the Netherlands) was bought at the local supermarket and used without further purification. Throughout the experiments demineralized water was used and all chemicals were of analytical grade.

2.2. Colloidal particle synthesis

Zein/tannic acid complex particles (ZTPs) were prepared using an anti-solvent precipitation technique according to the method used in our previous study (Zou et al., 2015). In short, a 2.5% (w/v) zein solution was prepared by dispersing zein powder in a 70% (v/v) ethanol-water solution and stirring for 2 h, and was stored overnight to reach an equilibrium. TA was added in a dry powdered form to the zein stock solution at four different zein:TA ratios (1:0.1–1:0.4, w/w). To form the complex particles, the mixture was quickly poured into demineralized water in a 1:2.5 vol ratio (mixture solution:water) under continuous stirring (1000 rpm) for 15 min. Due to a decrease in solubility, zein proteins self-assemble into particles while different levels of TA are incorporated. Finally, all ethanol and part of the water was removed using a rotative evaporator (Büchi Rotavapor R-215, Flawil, Schweiz) to increase the protein concentration to 3% (w/v), according to the volume of solution. The four particle solutions were stored at 4 °C for further use.

2.3. Particle size and zeta-potential measurements

Both the size and zeta-potential of ZTPs with various zein:TA ratios were measured using dynamic light scattering (Nano ZS Zetasizer, Malvern Instruments, Malvern, UK). The particle solutions were diluted to a protein concentration of 0.1% (w/v) using demineralized water. The size of the particles was measured at a pH of 3.5. The zeta-potential of the particles was measured at 8 different pH values (3.5–7.0) to determine the charge density at different conditions. The pH of the particle suspension was adjusted by addition of 2 M HCl and NaOH. All measurements were conducted in triplicate at a constant temperature of 20 °C.

2.4. Particle surface hydrophobicity measurement

The surface hydrophobicity of ZTPs with various zein:TA ratios