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Rheological and interfacial properties of silicone oil emulsions prepared by polymer pre-adsorbed onto silica particles

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ABSTRACT

Emulsions stabilized by colloidal particles, namely Pickering emulsions were prepared by mixing silicone oil with silica particles pre-adsorbed hydroxypropyl methyl cellulose (HPMC) in the continuous water phase as functions of added amount of HPMC and silicone oil viscosity. Characteristics of the resulting oil dispersed in water (O/W) emulsions were determined by the measurements of adsorbed amounts of the silica particles, oil droplet size, and some rheological responses, such as hysteresis loop, stress–strain sweep curve, and dynamic viscoelastic moduli. These results were compared with those prepared by silica particles without HPMC or HPMC. The adsorbed amounts of the silica particles pre-adsorbed HPMC were increased with an increase in the amount of added HPMC. However, no adsorption of the silica particles without pre-adsorbed HPMC occurred. The size of oil droplets prepared by the silica suspensions pre-adsorbed HPMC decreased with an increase in the adsorbed amount of HPMC and it increased with increasing the viscosity of the silicone oil at the fixed amount of adsorbed HPMC. The emulsions prepared by every emulsifier showed that their stress–strain sweep curves were satisfied with Hooke's law at the smaller deformation, whereas at the larger deformation they showed thixotropic behavior, irrespective of the silicone oil. An increase in the viscosity of the silicone oil gives the larger difference between the up and down curves at lower shear rates for the hysteresis loops. Moreover, dynamic viscoelastic moduli measurements showed that storage moduli of the emulsions were increased by one order of magnitude by adsorption of HPMC, where the elastic responses was controlled by the silica suspensions pre-adsorbed HPMC at the interface.

1. Introduction

Preparation of Pickering emulsions [1] has been performed by using various particles, such as carbon [2,3] silica [4,5], clay [5], latex [5,6], and layered double hydroxides [7]. Sometimes the system contains both particle and amphiphilic molecule [8–12], and pre-adsorbed polymer [13–19] onto various particles. Moreover, some interesting reviews concerning with Pickering emulsions have recently reported [20–24]. The amphiphilic molecule could modify wettability of the particles and thus influence the type and stability of the prepared emulsions. Advances have been made in developing Pickering emulsions prepared by polymer-grafted particles. Some pH-responsive Pickering emulsions were prepared with polystyrene latex particles that were sterically stabilized by block copolymers and statistical copolymer and with lightly cross-linked poly(4-vinylpyridine)-silica microgel particles [19]. Furthermore, highly charged polyelectrolyte-grafted silica particles were used to prepare Pickering emulsions and they were highly efficient emulsifiers and were able to prepare Pickering emulsions as little as approximately 0.04 wt% [18].

On the other hand, Midmore found that highly stable paraffin oil emulsions were able to be formed by silica particles that had been flocculated by adsorption of hydroxypropyl cellulose in water: neither silica nor polymer was an emulsifier for the corresponding paraffin oil by itself [14]. Midmore subsequently found that the formation of oil dispersed in water emulsions prepared by silica and polyoxyethylene surfactants was caused by the synergy between them, namely: (1) flocculation of the silica particles, (2) rendering the silica particle partially wettable and (3) decreasing of the interfacial tension [15]. However, such synergy effects have not been quantitatively estimated.

Our recent preliminary work on preparation of emulsion by mixing silicone oil and fumed hydrophilic silica particles dispersed in water showed that silicone oil droplets are emulsified by the silica particles dispersed in the continuous water phase surrounding the oil droplets. An increase in the silica concentration decreased

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the oil droplet size and increased the amount of oil emulsified. The resulting emulsions showed thixotropic behavior.

Here we report on emulsifying characteristics of the corresponding fumed hydrophilic silica particles modified with pre-adsorption of hydroxypropyl methyl cellulose (HPMC). When HPMC was adsorbed on surfaces of the fumed silica particles, flocculation of the silica particles occurred, they were gradually precipitated at their concentrations lower than 2.5 wt%, and beyond the 2.5 wt% silica concentration a gel-like silica suspension was formed [25,26]. In this study, since the silica concentration is fixed at 1.5 wt%, silica suspensions are flocculated by adsorption of HPMC. HPMC also played a role in an emulsifier of silicone oil and the interfacial and rheological properties of the resulting silicone oil emulsions were investigated as functions of oil viscosity and molecular weight of HPMC [27–29]. The present work is specifically focused on the interfacial and rheological properties of silicone oil emulsions prepared by the fumed silica suspensions containing different adsorbed amounts of HPMC in terms of the quantitative estimation of the synergy effects, such as an amount of the silica particles pre-adsorbed HPMC and a decrease in the interfacial tension, in comparison with those of the corresponding silicone oil emulsions prepared by the silica particles without HPMC or HPMC.

2. Experimental

2.1. Samples

Four silicone oils were kindly supplied by Shin-Etsu Chemical Co. Ltd. and their viscosities of KFL96-1, KF96-10, KF96-100, and KF96-1000 are 1, 10, 100, and 1000 cSt at 25 °C, respectively.

Aerosil 130 silica powder supplied from Nippon Aerosil Co. was treated as described previously before use [30]. From the manufacturer of the Aerosil 130, the primary silica has an average diameter of 16 nm, a surface area of 130 m^2/g, and a silanol density of 2.0 nm^{-2}, but in air the silica particles tend to form aggregates due to the hydrogen bonding between the silanol groups.

An HPMC sample obtained from Shin-Etsu Chemical Co. Ltd. was purified by the same method as previously reported [26–29]. The molecular weight of HPMC was determined to be 38.8×10^4 and its molecular weight distribution was 2.47. The degrees of the substitution of methoxy and hydroxypropoxyl groups were measured to be 1.8 and 0.25, respectively [27].

Water was purified by a Milli-Q Academic A10 ultra-pure water system.

2.2. Preparation of emulsions

The respective silicone oils of 15 g were mixed with 0.45 g silica dispersed in 30 g water to prepare silicone oil emulsions in a 100 mL glass bottle and agitated for 30 min under 8000 rpm at 25 °C, using a Yamato Ultra Disperser with an S-25N-25F agitation shaft.

Silica suspensions pre-adsorbed HPMC were prepared as follows: 30 g water dissolved 0.015, 0.030, and 0.05 g HPMC, which is less than the overlapping concentration of HPMC, 0.172 g/100 mL, where HPMC chains in water start to contact each other, in a 50 mL glass bottle were mixed with 0.45 g Aerosil silica powder at 25 °C for 24 h, where the added amounts of HPMC should almost adsorb on the silica surfaces according to the previous our study [26]; the resulting silica suspensions were sedimented using a Kubota 6500 centrifuge, the separated silica suspensions were three times rinsed with water, and then the resulting separated silica suspensions were re-dispersed in water to maintain at the same silica concentration as 0.45 g silica dispersed in 30 g water; and the re-dispersed silica suspensions are named the silica suspensions pre-adsorbed HPMC as follows. Since the silica suspensions pre-adsorbed HPMC were flocculated as mentioned above, they were agitated to well disperse in water at ca. 500 rpm by a Tokyo-Rikaki CM1000 mixer until they are used for emulsifiers, and their pH was 5.5 [26].

To prepare an emulsion stabilized by the silica suspensions pre-adsorbed HPMC, they were mixed with 15 g the KFL96-1 silicone oil by the same method as described above. To understand the effects of oil viscosity on the formation of emulsion, 15 g other silicone oils of KF96-10, KF96-100, and KF96-1000 were also mixed with the silica suspensions pre-adsorbed HPMC, i.e., an adsorbed amount of 0.03 g HPMC. Moreover, the respective silicone oils of 15 g were mixed with 0.015, 0.030, and 0.050 g HPMC dissolved in 30 g water to emulsify silicone oil by HPMC. The resulting emulsions were kept at 25 °C in an incubator after preparation to separate into two or three phases. The code of 1-45-1.5 was designed for an emulsion prepared by mixing of 1 cSt silicon oil, 0.45 g silica, and 0.015 g HPMC. The applied shear rate in the preparation of emulsions was calculated to be approximately 2200 s^{-1} from the diameters of the shaft and bottle and the speed of 8000 rpm.

2.3. Interfacial tension measurements

The values of interfacial tension γ of the KFL96-1 silicone oil against water, aqueous solutions prepared by dissolution of 0.015, 0.030, and 0.050 g HPMC into 30 g water, the silica suspensions pre-adsorbed HPMC dispersed in 30 g water, and the silica suspension dispersed in 30 g water were measured using a Du Noüy tensiometer at 25 °C.

2.4. Measurements of adsorbed amounts of emulsifiers

To determine quantitatively the adsorbed amounts of the emulsifiers, such as HPMC, the silica particles, and the silica particles pre-adsorbed HPMC at the interfaces between water and the silicone oil of the emulsified phase for the elapsed time of 1 week after preparation of the corresponding emulsions, 5 mL of the bottom phase parts were extracted, evaporation of water was carried out by heating and the residue was weighed after drying in vacuum.

This gravimetric analysis gives the concentrations of the respective emulsifiers that are suspended in the continuous part of the emulsion phase. In order to determine their actual adsorbed amounts, the calculated amounts are subtracted from the initially added amounts of the emulsifiers. The gravimetric analysis for the adsorbed amounts of the respective emulsifiers was performed at least twice and the experimental errors were less than 5%. From the sensitivity of a Mettler AT250 electronic balance used, this method allows us to determine the lowest concentration of 2×10^{-6} g/mL.

2.5. Optical microscopy measurements

Optical microscopic observation of the emulsified phase as a function of the elapsed time after preparation was carried out using an Olympus STM5-UM light microscope to estimate their droplets and changes in the appearances of the emulsions after the addition of water or silicone oil. An aliquot of the emulsified phase was placed in the hollow of a depth of 0.5 mm in the center of a slide glass and covered with a cover glass.

Furthermore, optical microscopic observation was performed using a Thermo Haake Rheo Scope 1 with the cone-plate geometry (diameter, 70 mm; cone angle, 1°), which is designed by the concept of rheo-optics consisting of microscopic and rheological techniques, with and without shear flow [29].