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Stability and rheology of W/Si/W multiple emulsions with polydimethylsiloxane

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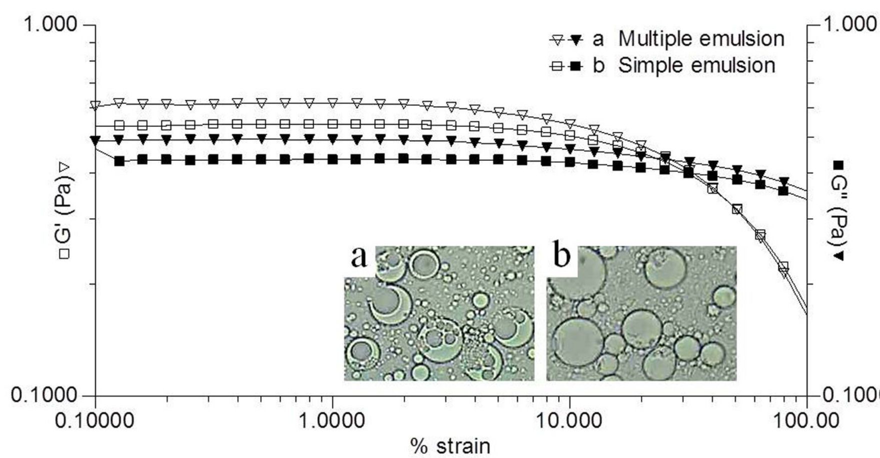
HIGHLIGHTS

- The polydimethylsiloxane was used to prepare W/Si/W multiple emulsion.
- The W/Si/W multiple emulsion was prepared by single-step emulsification.
- The relationship to stability of multiple structures in emulsion with the oil/aqueous rate, $MgSO_4$ and xanthan gum was studied.
- The rheology properties of W/Si/W multiple emulsion and simple emulsion were compared.

GRAPHICAL ABSTRACT



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ABSTRACT

W/Si/W multiple emulsions were prepared with polydimethylsiloxane (PDMS), PEG/PPG-18/18 dimethicone in cyclopentasiloxane and Bis-PEG/PPG-20/5 PEG/PPG-20/5 dimethicone and methoxy PEG/PPG-25/4 dimethicone by single-step emulsification. The formulation factors, including oil/aqueous rate, magnesium sulfate and xanthan gum, were examined. The stability and rheological analysis of multiple emulsions were implemented. An excellent multiple structure occurred with the weight rate between oil and aqueous phase of 1:8, stabilized by 0.005 mol/L magnesium sulfate in external aqueous phase, 0.03 g xanthan gum in internal aqueous phase. W/Si/W multiple emulsions showed shear-thinning behavior, consisting with simple emulsion, except exhibiting a stress yield and steady viscosity area. Both the storage modulus (G') and the loss modulus (G'') of multiple emulsion were slightly higher than that of simple emulsions, implying the existence of multiple structure. Tan (delta) of multiple emulsions had with a same trend but slightly higher than that of simple emulsion when strain increased, showed that multiple emulsions had resistance with the stress in converting viscoelastic character into elastic character.

1. Introduction

Multiple emulsions are complex dispersion systems, which have highly ordered internal structures containing multiple layers and

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probably containing one or multiple smaller engulfed droplets in each layer, which include the oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) emulsion [1–4]. The dispersed phase of a double emulsion itself is an emulsion, an oil-in-water-in-oil (O/W/O) double emulsion consists of small oil (internal oil) droplets dispersed in aqueous phase (W) and this O/W emulsion itself disperse as large droplets in the continuous oil phase (external oil), and the same case to water-in-oil-in-water (W/O/W) double emulsion.

Ostwald proposed "phase volume" theory based on view of three-dimensional geometric point [4,5]. Briefly, assuming dispersed droplets are spherical and try to pack densely, the maximum volume of droplets can reach 74.02% (volume fraction) of the total volume, and the remaining 25.98% (volume fraction) of it is dispersion medium. If aqueous phase volume is less than 26%, the system intends to form W/O emulsion; O/W emulsion was easy to be formed when aqueous phase volume is greater than 74%. Bancroft proposed the "Bancroft rule" about emulsifier solubility that the phase which can dissolve emulsifier easily tends to be the external phase (dispersion medium) [6–9]. And the solubility of the emulsifier in the aqua or oil phase can be expressed by Hydrophilic-lipophilic balance value (HLB). Generally, the hydrophilic emulsifier with HLB value in the range of 8–18, easily form O/W emulsion; the strong lipophilic emulsifier with HLB value ranging from 3 to 6, easily form W/O emulsion [8–12].

Multiple emulsions can be prepared by either a two-step procedure or a single-step procedure [12–17]. Two-step is a common method to prepare double emulsion, in the first step, a primary emulsion (O/W or W/O) is prepared, and in the second step, the primary emulsion (O/W or W/O) is re-emulsified in either an oil solution containing a low HLB surfactant to produce an O/W/O double emulsion or an aqueous solution with a high HLB surfactant to produce a W/O/W double emulsion [12,13]. Single-step has drawn attention recently, which the aqua phase and oil phase including oils, a high HLB surfactant and a low HLB surfactant are emulsified once to prepare a multiple emulsion [14].

Because of their special structure, multiple emulsions are widely used in the pharmaceutical, cosmetics and food industries to play the role of barrier layers [16–18]. In food, multiple emulsions slow release and controlled release of the active substance or spice flavors [19]. W/O/W type multiple emulsion prepared by a multi-chamber solid capsules, which the release of the active substance in the aqueous phase is triggered by different mechanisms. In pharmaceuticals, the multiple emulsions mainly have two effects: the drug carrier and liquid separation membrane [20]. As a drug carrier, multiple emulsions can extend drug release time; Liquid separation membrane of multiple emulsions as a semipermeable membrane structure when solute diffusion from one phase to another phase, can be used to separate hydrocarbons from wastewater sets of objects and remove toxins [21]. In cosmetics, multiple emulsions have functions of improving skin feel, stability incompatible materials, and less skin irritation. They have also shown significant promise in waste water treatment and separation of hydrocarbons [21,22].

Multiple emulsions are thermodynamically unstable emulsion system, for W/O/W emulsion, the droplets of the inner aqueous phase will gather occurring in the oil phase and a concave interface, thereby communicating with the external aqueous phase. As the less amount of internal aqueous phase, the multiple emulsion structure was disrupted, and ultimately the W/O/W emulsion converted into an O/W system [23].

Multiple emulsions prepared by single-step emulsification are especially in volatile state, there exit many formation factors such as emulsifiers, oils, the oil/aqueous rate, inorganic salts, and rheological modifiers. Pickering emulsions with graphene oxide (GO) as a stabilizer had been prepared and the effects of the type of oil, the sonication time, the GO concentration, the oil/aqueous rate, and the pH value on the stability, type, and morphology of the systems were investigated [24]. And multiple emulsions with different oils including camelina, fish, camelinae and fish oil blends and lipophilic polyglycerol polyricinoleate (PGPR) and hydrophilic sodium caseinate (SC) as emulsifiers had also been investigated [25].

However, the stable of multiple emulsions still unsettled, whether prepared by two-step or single-step emulsification with different emulsifiers and oils [24–26].

Polydimethylsiloxane (PDMS), also called dimethicone, is a widely used silicon-based organic polymer with its unusual flow properties. The chemical formula for PDMS is $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$, where n is the repeating monomer $[SiO(CH_3)_2]$ units number (Fig. 1). polydimethylsiloxane (PDMS) molecules have quite flexible polymer backbones (or chains) due to their siloxane linkages, which are analogous to the ether linkages used to impart rubberiness to polyurethanes. Such flexible chains become loosely entangled when molecular weight is high, resulting in PDMS (unusually high level of). With properties of water repellent, heat stable, and highly resistant to chemical attack, polydimethylsiloxane (PDMS) are applicated in such diverse industries as cosmetics, drug delivery, fabric care and paints and inks.

However, there is no denying that polydimethylsiloxane are difficult to be emulsified into water because of that insoluble in both hydrophilic and hydrophobic solvents from nano-scale point of view. PEG/PPG-18/18 Dimethicone in cyclopentasiloxane (DC 5225c) was a lipophilic emulsifier with polyethylene glycol and polypropylene glycol, including a branch of dimethicone. Bis-PEG/PPG-20/5PEG/PPG-20/5 dimethicone and methoxy PEG/PPG-25/4 dimethicone (ABIL Care XL80) was a hydrophilic emulsifier with double hydrophilic polyethylene glycol/polypropylene glycol chain, which also have groups of polydimethylsiloxane. Either lipophilic emulsifier or hydrophilic emulsifier, both with polydimethylsiloxane are superior to emulsify silicones.

The aim of this work was to determine the influence on the stability of W/Si/W multiple emulsions formed by single-step emulsification, including oil/aqueous rate, inorganic salts and rheology modifies. Rheological properties of W/Si/W multiple emulsion and simple emulsion were investigated.

2. Experimental

2.1. Materials

Polydimethylsiloxane polymer with density 0.97 g/ml (DOW CORNING 200, viscosity 194 mPa s, Dow Corning, USA) was obtained from Dow Corning Co., Ltd. PEG/PPG-18/18 Dimethicone in cyclopentasiloxane with 10% (w/w) (DOW CORNING 5225c, Dow Corning, USA) was the oil phase emulsifier. Bis-PEG/PPG-20/5PEG/PPG-20/5 dimethicone and methoxy PEG/PPG-25/4 dimethicone (ABIL Care XL80, Evonik, Germany) was the aqua phase emulsifier. Magnesium sulfate anhydrous ($MgSO_4$, Sinopharm Chemical Reagent Co., Ltd.) was purchased from China Pharmaceutical Group Shanghai Chemical Reagent Company. Xanthan gum (KELTROL CG-T, Everhon enterprise Co., Ltd.) was a transparent type of cosmetic grade thickening stabilizer. The water used throughout the experiments was deionized.

2.2. Preparation of W/Si/W emulsions

W/Si/W emulsions were prepared by a single-step emulsification process. The aqua phase, including magnesium sulfate anhydrous, Xanthan gum and water, was added into the oil phase