

Dispersion stability of nanoparticle-shielded oil droplets in vegetable oil-in-water emulsions

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ABSTRACT - Dispersion stability of nanoparticle (NP)-shielded oil droplets in soybean oil-in-water emulsions is investigated. TiO₂/SiO₂ NP-shielded oil droplets remain dispersed in emulsions for 28 days (test period). Required amount of NPs appears to be related to droplets surface area which is governed by oil concentration and droplets sizes. Dispersion stability of the droplets is attributed to full/partial coverage of the droplets with anti-coalescing NP-shields whereas excess NPs form NP-agglomerates in the aqueous phase of emulsions.

1. INTRODUCTION

Bio-based vegetable oil-in-water (VO/W) emulsions are promising metal working lubricants. Their excellent lubricity is owed to strong adsorption of fatty acid films on metal surfaces [1,2]. To perform the lubrication role, oil droplets in emulsions must be in stable dispersed state. To achieve stable dispersions, surfactants, surface-active polymers, and nanoparticles (NPs) are used [3]. NPs are particularly more attractive additives as they possess both dispersant and lubrication properties [2,4]. Ability of NPs to stabilise the droplets akin to mechanical NP-shielding of droplets is crucial to overall stability of droplets [3,5]. Formation and stability of NP-shields on droplets depend on shape, size, and mass fraction (% wt.) of NPs, as well as inter-NPs and NP/oil interactions (which are attributed to NPs wettability and oil phase polarity) [6,7].

To enhance the stability of the droplets dispersion, adequate quantity of NPs is required to cover a large area of droplets surface [7,8]. However, full coverage of the droplets may not happen with inhomogeneous NPs or in shortage of NPs supply. In such cases, partial coverage of droplets surface with particular NPs comprising ionisable surface groups (such as silica) can provide stability [3].

Dispersion stability and lubricity of soybean VO/W emulsions improve with TiO₂/SiO₂ composite NPs [2]. However, NPs role and the mechanisms with which the droplets dispersion stability is achieved have not been explored in detail. This work aims to understand the shielding mechanism of TiO₂/SiO₂ NPs on the oil/water interface of soybean oil droplets in VO/W emulsions.

2. METHODOLOGY

Materials and preparation: amorphous TiO₂/SiO₂ NPs (size 35nm) and soybean oil with 15% saturated, 24% monounsaturated, and 61% polyunsaturated fatty acids are used. VO/W emulsions of 0, 0.1, 0.25, 0.5, 0.75 and 1% wt. NPs and 1% vol. soybean oil are prepared using ultrasonic homogeniser with 0.16kJ/ml energy [2].

Characterisations: droplets size distributions and NPs agglomerates are characterised using *zetasizer nano*

S and *Jeol JSM6000*. Dispersion stability is determined with *Shimadzu UV-1800* spectrophotometer. NPs and oil droplets interactions are imaged over time with confocal laser scanning microscopy (CLSM) on *Leica TCS SP8*.

3. RESULTS AND DISCUSSION

Changes of dispersed droplets sizes indicate how stable the dispersions are. Figure 1 shows the distinctions of droplets sizes changes with time in emulsions without and with 0.25% wt. NPs. Without NPs (Figure 1a), sizes evolve from two overlapping distributions with average sizes of 170nm and 550nm on day 0 (after preparation) to two distinct distributions with average sizes of 201nm and 2790nm after 14 days. Further aggregation of the droplets is observed after 28 days with an average size of 2500nm. This is attributed to the strong attraction forces between hydrophobic soybean oil droplets that drives the over-time coalescence of fine droplets. On the contrary, dispersed droplets with average size of 220nm remain stable for 28 days with NPs (Figure 1b). With adsorption of NPs on the droplets surface, the droplets size first decreases by increasing the NPs mass fraction from 0.1 to 0.25% wt. owing to NPs accumulation on the droplets surface (Figure 1c). Droplets average size then increases slightly due to formation of NP-shields on the droplets. When droplets surface saturates with NPs at around 0.5% wt., droplets size remains constant and excess NPs form ~5.5µm agglomerates only, detected by EDS mapping of Ti and Si elements (Figure 1d). ~5.5µm NP-agglomerates are also detected with 0.25% wt. NPs (see Figure 1b). This indicates an equilibrium between adsorbed NPs on the droplets and free NPs in the bulk emulsions [9].

Dispersion stability of droplets with/without NPs is also inferred from UV-vis spectrophotometry (Figure 2a). Higher peak wavelength is obtained with 0.25% wt. NPs compared to the NP-free emulsion. This is attributed to a local density increase within the emulsion, by the virtue of adsorption of NPs on the droplets surface [10]. Peak wavelength increases slightly with 0.5% wt. NPs due to accumulation of more NPs on droplets. Large presence of NP-agglomerates is expected with 1% wt. NPs. This is also inferred by significant increase in peak wavelength by increasing the NPs mass fraction to 1% wt. [11,12].

Relative concentration (RC) is used to assess the droplets dispersion stability. RC is defined as the ratio of absorbance intensity to the corresponding initial value on day 0. Figure 2b shows high stability (RC > 95 %) for the emulsions with 0.25 and 0.5% wt. NPs for up to 96 hours. On the contrary, 10% RC reduction in NP-free emulsion after 48 hours shows low stability in absence of the NPs. Interestingly with excess NPs (1% wt.), RC decreases to

87% and 84% after 72 and 96 hours. This is thought to be related to formation of NP-agglomerates in emulsion that consequently lowers the dispersion stability.

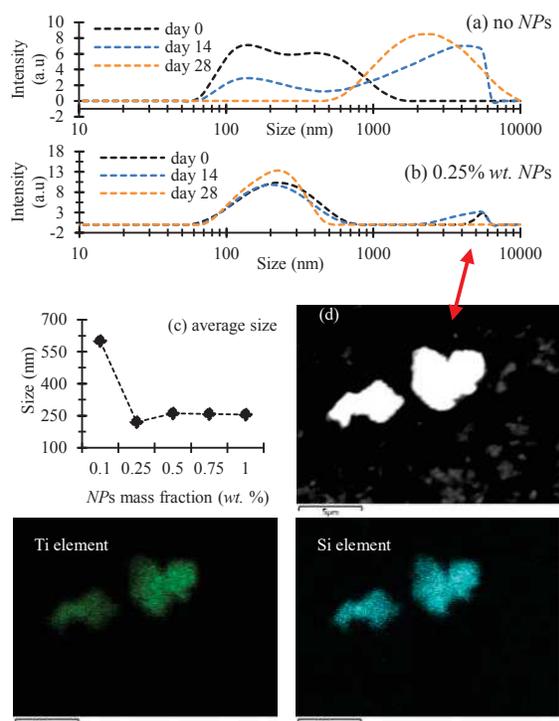


Figure 1 (a-c) droplets sizes with/without NPs, and (d) SEM/EDS images of NP-agglomerates (scale 5 μ m).

To explain the above observations, we hypothesize NPs forming anti-coalescing NP-shields on the droplets surface [3,5]. CLSM is used to examine this in emulsions with 0 and 0.25% wt. NPs (Figure 3, Rhodamine B dye is used to mark NPs). Without NPs, over-time coalescence of droplets increases the average droplets size over time (see Figures 3a-b). On the contrary with 0.25% wt. NPs droplets with varying sizes are covered with NP-shields which prevent the droplets from interacting with other droplets (Figure 3c). However, 0.25% wt. NPs is below the required amount for full coverage of droplets surface. This results in partial NP-shielding of some droplets. Hence, two stabilisation pathways with 0.25% wt. NPs are proposed. With initially fully-covered droplets, high dispersion stability is obtained owed to the effectiveness of NP-shields on the droplets surface. On the contrary, initially partially-covered droplets are hypothesised to undergo limited coalescence where the droplets coalesce initially until an equilibrium is reached [13]. At this state, as the large droplets approach other droplets short-ranged anti-coalescing repulsion forces between the NP-shields outruns attractive forces between the droplets, increasing the stability at close proximity. Hence mechanism with which the stability of droplets is provided is related to the surface area of droplets (which depends on droplets size and preparation energy [1]) and availability of adequate quantity of NPs in the aqueous phase.

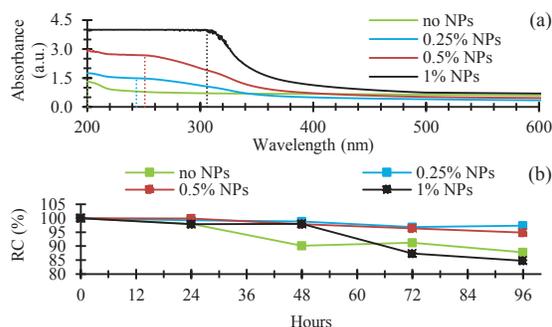


Figure 2 (a) absorbance (peaks are shown by dash line), and (b) relative concentration (RC) with/without NPs.

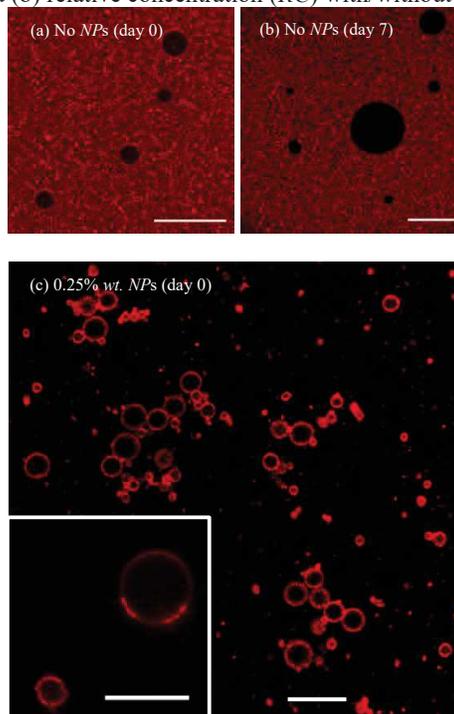


Figure 3 CLSM images of emulsions (a-b) without NPs (scale 5 μ m), and (c) with 0.25% wt. NPs (scale 3 μ m).

4. CONCLUSION

The dispersion stability of NP-shielded droplets in VO/W emulsions is investigated. Small amount of NPs proportional to the droplets sizes and oil concentration is required for stability by full/partial coverage of droplets surface with NP-shields. Fully-covered droplets promote better stability than partially-covered droplets. Partially-covered droplets undergo a limited coalescence initially, but retain their stability. Excess NPs at above saturation mass fraction (0.5% wt.) degrade the stability.

REFERENCES

- [1] Taheri, R., Kosasih, B., Zhu, H., & Tieu, A. K. (2016). Surface film adsorption and lubricity of soybean oil in-water emulsion and triblock copolymer aqueous solution: a comparative study. *Lubricants*, 5(1), 1.
- [2] Taheri, R., Kosasih, B., Zhu, H., & Tieu, A.K. (2017). Suspension stability and lubricity of eco-friendly vegetable oil-in-water emulsions stabilised

- by TiO_2 nanoparticles. In *6th World Tribology Congress, Beijing*.
- [3] [3] Ridel, L., Bolzinger, M. A., Gilon-Delepine, N., Dugas, P. Y., & Chevalier, Y. (2016). Pickering emulsions stabilized by charged nanoparticles. *Soft matter*, *12*(36), 7564-7576.
- [4] Alves, S. M., Barros, B. S., Trajano, M. F., Ribeiro, K. S. B., & Moura, E. (2013). Tribological behavior of vegetable oil-based lubricants with nanoparticles of oxides in boundary lubrication conditions. *Tribology International*, *65*, 28-36.
- [5] Dickinson, E. (2010). Food emulsions and foams: stabilization by particles. *Current Opinion in Colloid & Interface Science*, *15*(1-2), 40-49.
- [6] Binks, B. P., & Whitby, C. P. (2005). Nanoparticle silica-stabilised oil-in-water emulsions: improving emulsion stability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *253*(1-3), 105-115.
- [7] Binks, B. P., & Lumsdon, S. O. (2000). Catastrophic phase inversion of water-in-oil emulsions stabilized by hydrophobic silica. *Langmuir*, *16*(6), 2539-2547.
- [8] Simovic, S., & Prestidge, C. A. (2003). Hydrophilic silica nanoparticles at the PDMS droplet– water interface. *Langmuir*, *19*(9), 3785-3792.
- [9] Simovic, S., & Prestidge, C. A. (2003). Adsorption of Hydrophobic silica nanoparticles at the pdms droplet – Water interface. *Langmuir*, *19*(20), 8364-8370.
- [10] Lacava, J., Ouali, A. A., Raillard, B., & Kraus, T. (2014). On the behaviour of nanoparticles in oil-in-water emulsions with different surfactants. *Soft Matter*, *10*(11), 1696-1704.
- [11] Sharma, P., Baek, I. H., Cho, T., Park, S., & Lee, K. B. (2011). Enhancement of thermal conductivity of ethylene glycol based silver nanofluids. *Powder Technology*, *208*(1), 7-19.
- [12] Lee, M. H., Oh, S. G., Suh, K. D., Kim, D. G., & Sohn, D. (2002). Preparation of silver nanoparticles in hexagonal phase formed by nonionic Triton X-100 surfactant. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *210*(1), 49-60.
- [13] Chevalier, Y., & Bolzinger, M. A. (2013). Emulsions stabilized with solid nanoparticles: Pickering emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *439*, 23-34.