



A Review of Pickering Emulsion: Solid Particle Materials, Formulation, Physicochemical Characteristics and Applications

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ABSTRACT:

Since Pickering emulsions are stabilized using solid particles at the oil–water interface, they are a safer and more green alternative to conventional surfactants. They are highly stable, biocompatible, and versatile and have uses in the food, medicine, cosmetics, and material science fields. Various particles, including silica, hydroxyapatite, chitosan, Magnetic Nanoparticles, Cyclodextrin, Carbon Nanotube, Soy Protein, Zein, clay, and starch, have been researched for emulsion stabilization. Advances in formulation technology such as rotor-stator homogenization, sonication, and membrane emulsification improve their physicochemical properties. This work focuses on Pickering emulsion applications, formulation methods, and particle selection.

KEYWORDS: Pickering emulsion, solid particles, hydroxyapatite, silica, chitosan, Magnetic Nanoparticles, Cyclodextrin, Carbon Nanotube, Soy Protein, Zein, clay, starch, stabilization, formulation, physicochemical characteristics, applications

1.INTRODUCTION:

As techniques for the preparation of different types of emulsions are advancing, emulsions are extensively utilized in many industries such as pharmaceuticals, drug delivery, cosmetics, food, and so on.

Some macromolecules and low-molecular-weight emulsifiers that are reported to stabilize the emulsions are capable of inducing cancer and allergic reactions. Pickering emulsion, which utilizes only solid particles as stabilizers, prevents droplets from aggregating by accumulating at the interface between two immiscible liquids (often called the oil and water phase). Though it was discovered a century ago, its benefits have attracted a great deal of study interest lately as models in other disciplines:

- (i) solid particles enhance the stability of emulsions by preventing them from aggregating;
- (ii) various solid particles can confer as-prepared materials with useful properties like porosity, conductivity, and responsiveness;
- (iii) certain food-grade solid particles are less toxic, so safer to use in vivo.

Various inorganic particle types like silica, clay, and hydroxyapatite (Hap), and some organic particles, have been shown in many experiments to act as efficient Pickering emulsifiers ^[1].

Pickering emulsions are made up of stabiliser particles, water, and oil. Size, shape, concentration, and wettability all affect their stability. Stability is also influenced by ionic strength, pH, and oil type. The relationship between particles and emulsion stability can be further investigated from an energy perspective ^[2].

2.SOLID PARTICLES:

The stability, nature, form, and features of Pickering emulsions are influenced by the stabilizing agent solid particles. To achieve the exact type, character, and application of Pickering emulsions, choosing the appropriate NANO/microparticles is essential.

2.1 HYDROXYPATILE:

Pickering mixtures for biomaterials, adsorbents, and catalysts have made use of hap nanoparticles, which are present in teeth and bones. In oil painting, they can assist in the structure of O/W Pickering mixes with ester groups. Hap by itself, however, is not an emulsifier. Researchers looked at how polystyrene moieties affected MSs and droplets stabilised with Hap nanoparticles. The interactions between polymers and Hap nanoparticles were essential for stabilising and controlling drop size and product shape ^[1].

2.2 SILICA:

Silica is an extensively delved solid flyspeck used as Pickering emulsifiers due to its ease of revision and vacuity. Unmodified silica stabilizes O/ W Pickering mixes, while hydrophobically modified silica preferentially stabilizes W/ O Pickering mixes. To ameliorate Pickering mixes, studies have explored different types of modified silica. The goods of pH and swab content on silica- stabilized Pickering mixes have been studied. To increase stabilizing capabilities while maintaining a moderate face charge, suitable moieties should be clicked to bare silica. Pure silica is too hydrophilic to stabilize Pickering mixes due to face charge. One study set up that oleic acid, a unique biocompatibility adipose acid, reduced this issue and produced stable Pickering mixes in colorful sizes^[1].

2.3 CHITOSAN:

Chitosan, a widely used polysaccharide, is biodegradable and biocompatible, making it valuable in pharmaceuticals and biomedicine. Its solubility in diluted acid aqueous solutions makes it green. Studies have explored the creation of MCs using CH₂Cl₂ evaporation and CS nanoparticles as emulsifiers. The pH of the cross-linking process affects the size of MC products and oil leakage. Another study examined the manufacturing state of CS-TPP nanoparticles and curcumin encapsulation^[1].

2.4 CLAY:

Clay is a popular choice for creating Pickering emulsions due to its affordability, availability, and non-polluting nature. Because clay surfaces are hydrophilic, certain molecules must be added to modify them. Surfactants and Laponite XLG were mixed to produce a Pickering emulsion that resembled gel. According to a study, laponite has a major impact on the Pickering emulsion-based styrene polymerisation process, influencing the size, density, and rate of reaction of the final product. PS particles are encased in a thick shell made of clay platelets^[1].

2.5 STARCH:

Food and biomedicine can benefit from starch, a naturally occurring material that is non-toxic and biodegradable. However, its emulsifier function is impacted by its large size range. Modification of natural starch granules using octyl succinic anhydride (OSA) can increase their hydrophobicity without changing important characteristics. By looking at important variables like pH, NaCl concentration, oil percentage, and starch particle concentration, this study enhanced soybean O/W Pickering emulsions^[1].

2.6 CYCLODEXTRIN:

A cyclic oligomer of α - D- glucopyranose, natural CD has a large hydrophobic depression and a shallow cone shape. It's appealing for conflation stabilisation in food, medicinals, and skin care products since it's biocompatible and non-toxic. At oil painting- water interfaces, CDs can produce microcrystals and face active composites that stabilise mixes. According to recent exploration, the type of oil painting and CD content affect the size and shape of the droplets^[1].

2.7 CARBON NANOTUBE:

The distinctive characteristics of carbon nanotubes (CNTs) have drawn attention, yet their hydrophobicity makes it challenging to disperse them in aqueous solutions. Researchers have experimented with treating carbon nanotubes (CNTs) with oxygen plasma to boost their hydrophilicity. This process introduces hydrophilic functional groups without causing any harm. According to experimental findings, droplet size and dispersion are strongly influenced by the duration of the plasma treatment, the CNT content, and the sonication time^[1].

2.8 SOY PROTEIN:

The potential of soy protein, a healthy and non-toxic food-grade substance, in Pickering emulsion systems has been investigated. Research indicates that soy protein isolate (SPI) and NaCl can be heat-treated to create gel-like Pickering emulsions, with the gel stiffness rising as the glycinin level rises. The interfacial adsorption of pre-heated SPI is also influenced by surface charge^[1].

2.9 ZEIN:

The hydrophobicity of zein, a protein produced from maize, has been thoroughly investigated. It can be utilised as Pickering emulsifiers without requiring surface modification. Zein-stabilized emulsions, however, are unable to completely cover droplet surfaces and are unstable close to the isoelectric point. Due to the amphiphilic nature of NaCas, modifications have been made to create zein/NaCas nanocomplexes, which improve the emulsive-ability of zein colloidal^[1].

2.10 MAGNETIC NANOPARTICLES:

The biomedical industry has shown a great deal of interest in magnetic Fe₃O₄ nanoparticles because of their beneficial magnetic characteristics and low toxicity. Pickering emulsions and other biomedical products have been created using them. At a contact angle near 90°, hydrophilic Fe₃O₄ nanoparticles were only able to stabilise systems with non-polar or weakly polar oils, according to earlier research. In order to overcome this, scientists altered Fe₃O₄ nanoparticles to make them more hydrophobic. As demonstrated by a recent device for waste extraction from water, magnetic Pickering emulsions have the special benefit of being simple to demulsify and reuse^[1].

3. FORMULATION:

Any of the emulsification methods used to produce surfactant-stabilized emulsions can be employed to make Pickering emulsions. However, the most popular methods for creating Pickering emulsions are sonication, high-pressure homogenisation, and rotor-stator homogenisation. Pickering emulsion preparation has recently additionally used methods like membrane emulsification and microfluidic emulsification^[3].

3.1. ROTOR-STATOR HOMOGENIZATION:

Rotor- stator homogenization is used to prepare further than half of the Pickering mixes that are bandied in this paper. The factors of a rotor- stator homogenizer are a bladed rotor and an apertured stator. A depression is formed when the rotor revolves, pulling the liquid in and out and causing rotation. The high liquid acceleration and the shear force between the rotor and stator beget the drop size of the dispersed phase to drop. When using a rotor- stator homogenizer to acclimate the size of the conflation driblets, the original parameters are the gyration speed and the homogenization time. The rotor- stator homogenizer's speed is generally expressed in revolutions per nanosecond(rpm), which is n't a measure of power, in publications. Rather, the rotor's haste should be handed; still, as the periphery value is infrequently mentioned in utmost sources, it can not be estimated, hence the rpm value will also be handed then. thus, for Pickering mixes, the gyration pets are generally between 5,000 and 30,000 rpm(or, when calculation is possible, a haste of 5 to 20 m/ s), and the emulsification times range from 30 seconds to a many twinkles. The drop size distribution is wide(ranging from a many micrometer to hundreds of microns) for these settings. Rotor- stator homogenization has the following benefits

- i) it is inexpensive to operate and simple to set up, requiring only the rotor-stator probe to be inserted into the container containing the three emulsion components;
- ii) it is quick, usually taking a few minutes to produce an emulsion;
- iii) it uses a small amount of liquid, possibly only a few milliliters (for a preliminary test with expensive components, for example); and
- iv) there is rotor-stator equipment available for every stage of emulsion development, from laboratory to industrial scales.

The rotor-stator homogenisation process has two main drawbacks:

- i) the eventuality for the homogenized sample to be less steady, particularly when operating near to the inquiry's limit volume(which can be avoided by moving the inquiry inside the sample during homogenization);
- ii) the possibility of temperature increase, which is primarily caused by frictional forces during the process and can beget the destabilization of temperature-sensitive patches and/ or the emulsion(to help this effect, the sample can be cooled during homogenization);
- iii) the limited energy input that restricts the conformation of small droplets(droplets formed with a rotor- stator are generally over 1 µm);
- iv) the wide distribution of drop sizes that was achieved; and
- v) the high rate of shear between the stator and rotor, which can beget fragile aggregates or patches to come unstable or deformed during the emulsification process.

When it came to microgels, it was shown that the emulsification energy changed the shape of the microgel. At the low energy emulsification contact, the microgels remained spherical. whereas they were flattened at the interface of emulsions made with a high energy input. Additionally, they observed that in the event of high energy emulsification, bridging between the droplets occurred^[3].

4. PHYSIOCHEMICAL CHARACTERISTICS:

4.1. DETERMINATION THE DIRECTION OF THE EMULSION:

Several methods can be used to determine the type of emulsion and, consequently, the nature of the exterior phase:

- i) Through tests on the dispersibility of a tiny amount of emulsion in an aqueous or oily phase: An example of this would be an emulsion of type H/E (or E/H) if the sample was soluble in water or oil.

ii) By measuring conductivity: Unlike oil, water typically includes electrolytes. As a result, the aqueous phase's conductivity is 100–1000 times greater than the oil's. Since an emulsion's conductivity depends on its external phase, identifying whether it is of the W/O or O/W kind is quite easy. The conductivity of an emulsion and the conductivity of the exterior phase and its volume fraction are directly related. Therefore, the following linear connection can be utilized as a preliminary approximation:

$$X_{em} = f_w \cdot X_{ext}$$

When interpreting emulsion-related occurrences, the exterior phase might also be crucial, especially when identifying phase inversion during the emulsification process. Through dye tests: Determining the water solubility or liposolubility of dyes like methylene blue or Nile red (Sudan III) in the resulting emulsion is the foundation of these methods^[5].

4.2. DETERMINATION OF DROPLETS SIZE:

The size of the droplets, which can be measured using a technique known as "particle size," is one of the crucial characteristics of emulsions. Particularly indicative of the stirring and formulation conditions used to prepare the emulsion is the size of the droplets. Due to the partially or completely random nature of the agitation processes, an emulsion typically comprises droplets of varying sizes. Consequently, the distribution of droplet sizes functions as a statistical inventory of the population contained within the emulsion. One diameter measurement that represents the average of the entire drop population can be used to describe the emulsion^[5].

4.3. DETERMINATION OF VISCOSITY:

Because of the influence of numerous parameters inherent in the structure (size and organization of the droplets) or the chemical compounds utilized, the rheological behavior of an emulsion is frequently complex. There are numerous theories in the literature that link an emulsion's viscosity to its properties, however they are primarily empirical in nature and only apply to particular situations. The exterior phase's viscosity, which is typically represented by the following relationship, determines the viscosity of an emulsion:

$$\eta_r = \eta_{ext}$$

where "em" and "ext" stand for the emulsion and the external phase, respectively. When the droplet volume tends to zero, f , which stands for the contribution of the impacts of the other variables (droplet sizes, etc.), tends to unity. This equation is frequently expressed as follows:

$$\eta_r = \eta_{em} / \eta_{ext}$$

The relative viscosity is denoted by η_r . The viscosity of an emulsion's exterior phase frequently determines its rheological behavior^[5].

4.4. DETERMINATION OF PH:

When it comes to emulsion stability, pH is crucial. The Zeta potential, the contact angle, and the particle adsorption at the interface are among the variables that are impacted by pH. An rise in pH improves the resilience of the particle dispersion structure and regulates the adsorption of the particles at the oil/water interface. The higher the pH, the lower the zeta potential. Although there is little change, the contact angle also rises as pH rises. All things considered, emulsion stability rises as pH rises^[5].

5. APPLICATION:

Even though the idea that particles stabilize emulsions has been around for a while, their uses are constantly being developed. When the formulation of these emulsions is anticipated or presents a technological challenge, knowledge of Pickering's emulsion stabilization processes is essential in many industrial sectors. Pickering emulsions' exceptional stability and unique interfacial characteristics seem to be two of its most intriguing features. One way to create a shell around droplets is to assemble nanoparticles with fluid interfaces, as in the stabilization of Pickering emulsions. This kind of structure is compatible with encapsulation methods, which offer the benefits of encapsulating and shielding labile active ingredients from being broken down by digestive fluid enzymes or an unfavorable pH media. Because of their unique stability against coalescence and resistance to desorption by intestinal biosurfactants, they modulate the crucial biological process of fat digestion. Drug delivery methods can also make use of Pickering emulsions^[5]. Starch serves as an adsorption agent, enzyme inhibitor, and delivery mechanism for medicinal and bioactive food additives. Numerous disorders could be diagnosed and treated with the use of biomedical apps (silica)^[6].

6. CONCLUSION:

Because of their stability, safety, and broad range of applications, pickering emulsions offer a promising platform. Their functional performance and physicochemical characteristics are directly influenced by the formulation methods and stabilizing particle selection. They have a great deal of promise for improving food science, medicines, and advanced material design with continued research.

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