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Progress in Preparation and Application of Gel-Emulsions

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Abstract

Compared to conventional emulsions, gel-emulsions have a higher internal phase volume fraction, unique structures and properties, higher viscosity, and tunable internal structures. These advantages make them widely applicable in the cosmetics industry, food industry, aerospace, and biomedicine, with significant potential in the development of new materials and high-performance products. The factors affecting the stability of gel-emulsions, as well as the types of stabilizers required for their preparation (including solid particles, surfactants, and small molecule gelators), and the corresponding preparation methods (including the one-step method, two-step method, and phase inversion method) are reviewed in this article. The applications of gel-emulsions in porous materials, food, cosmetics, and stimuli-responsive materials are introduced, and future research directions are also discussed.

Keywords

Gel-Emulsions, Stabilizers, Porous Materials

1. Introduction

Emulsions are typically multiphase dispersed systems composed of two or more immiscible liquids. Their main components are the dispersed phase (internal phase) and the continuous phase (external phase), where one liquid is dispersed as tiny droplets within another liquid. Emulsions are usually classified into oil-in-water (O/W) and water-in-oil (W/O) types. They are widely used in the food industry, cosmetics industry, aerospace, and other fields [1].

Gel-emulsions, also known as high internal phase emulsions, are a special type of emulsion. Gel-emulsions typically consist of stabilizers, a dispersed phase, and a continuous phase. Similar to conventional emulsions, the continuous and dispersed phases are generally immiscible. However, unlike conventional emulsions, the dispersed and continuous phases in gel-emulsions form a gel network structure, giving the emulsion a gel-like state. In the 1960s, Lissant [2] proposed that emulsions with a dispersed phase volume fraction greater than 70% are considered gel-emulsions. A few decades later, Princen [3] theoretically calculated that to form a stable gel-emulsion, the volume fraction of the dispersed phase should be at least 74.05%. Gel-emulsions can be classified based on the polarity of the two phases and the type of stabilizer used. The former can be divided into water-in-oil (W/O), oil-in-water (O/W), CO_2-in-water (CO_2/W), and multiple emulsions (W/O/W or O/W/O) [4]. The latter can be categorized into gel-emulsions stabilized by solid micro-nano particles (also known as Pickering emulsions), surfactants, and small molecule gelators [5]. In recent years, due to their unique structure and excellent properties, gel-emulsions have been widely used in the preparation of porous materials, food, pharmaceuticals, stimuli-responsive materials, and other fields [6].

Previous reviews in this field have primarily focused on the applications of traditional emulsions. This review, however, emphasizes the preparation and applications of gel emulsions [7] [8]. This article reviews the factors affecting the stability of gel-emulsions, as well as the types of stabilizers required for their preparation (including solid particles, surfactants, and small molecule gelators) and the corresponding preparation strategies. Additionally, it briefly describes the applications of gel-emulsions as templates in the fields of porous materials and food, etc.

2. Stability of Gel-Emulsions

2.1. The Impact of Stabilizers

The type and concentration of stabilizers play a crucial role in the stability of gel emulsions. The main types include surfactants, solid particles, and small molecule gelators. Surfactant molecules are composed of a hydrophilic head and a hydrophobic tail, making them amphiphilic. Traditional surfactants, due to their amphiphilic nature, adsorb at the oil-water interface to form an interfacial film, reducing direct contact and coalescence between oil droplets, thereby enhancing the stability of the gel-emulsions. Studies have shown that when surfactants are used as stabilizers, the amount required must greatly exceed the critical micelle concentration to form a stable gel-emulsion. However, the use of large amounts of stabilizers undoubtedly increases the toxicity of the system [9]. In contrast, the interfacial film formed by using solid particles as stabilizers in gel-emulsions has strong rigidity, which effectively prevents droplet coalescence, ensuring the formation of a stable gel-emulsion while significantly reducing the system’s foaming rate and toxicity. When small molecule gelators are used as stabilizers to prepare gel-emulsions, the required amount and toxicity are relatively lower, and the dispersed phase volume is not limited to 74%. The principle by which small molecule gelators stabilize gel-emulsions involves the self-assembly of a three-dimensional network structure through weak intermolecular interactions (such as hydrogen bonding, π-π stacking, van der Waals forces, electrostatic interactions, and host-guest interactions), causing the solvent to lose fluidity and form a stable gel-emulsion.

To enhance the stability of gel-emulsions, stabilizers need to reduce interfacial tension while also forming a stable interfacial film through adsorption, aggregation, or crosslinking. Additionally, phase inversion often occurs in gel-emulsions. To prevent this, stabilizers are typically insoluble in the dispersed phase, and their amount should be as high as possible to maintain stability.

2.2. The Impact of the Properties of the Internal and External Phases

Generally speaking, the impact of the internal and external phase properties on gel-emulsions mainly involves two aspects: the polarity of the internal and external phases and the internal phase volume fraction. Firstly, the greater the difference in polarity between the internal and external phases, the more stable the gel-emulsion. For example, gel-emulsions formed with a less polar organic solvent as the internal phase and water as the external phase are relatively stable. However, when a moderately polar organic solvent is used as the internal phase, it is difficult to form a stable gel-emulsion due to partial solubility in water. Secondly, the larger the internal phase volume fraction, the more likely phase inversion is to occur, making it more challenging to prepare stable high internal phase emulsions.

2.3. The Impact of Temperature

Temperature also has a significant impact on the stability of gel-emulsions. Molecular thermal motion is related to temperature, and high temperatures may disrupt the interfacial stability of the gel-emulsion, leading to droplet coalescence. Viscosity, solubility, and vapor pressure are all state functions of temperature, and temperature has a noticeable effect on the viscosity of gel-emulsions. Typically, as the temperature increases, the viscosity of the system decreases, which may result in the breakdown of the gel-emulsions.

2.4. The Impact of Electrolytes

Studies have shown that adding certain electrolytes to gel-emulsion systems can enhance the stability of the gel-emulsion. The possible reasons are: 1) The addition of electrolytes reduces the solubility of the dispersed phase water in the continuous phase, thereby decreasing the tendency for droplet coalescence; 2) The added electrolytes inhibit the Ostwald ripening effect by increasing osmotic pressure [10]; 3) The addition of electrolytes can strengthen the interfacial film, improving the mechanical properties of the gel-emulsion, thus enhancing its stability.

3. Preparation of Gel-Emulsions

3.1. Selection of Stabilizers

Stabilizers play a crucial role in gel-emulsions and are one of the key steps in their preparation. They maintain the dispersed state of the emulsion, prevent phase separation, and extend the stability period of the gel-emulsion. The type and concentration of stabilizers also affect the stability of the gel-emulsion. According to the Bancroft rule, oil-soluble stabilizers tend to form water-in-oil (W/O) emulsions, while water-soluble stabilizers tend to form oil-in-water (O/W) emulsions. Therefore, the solubility of the stabilizers in oil or water affects both the type and stability of the gel-emulsion. Currently, the commonly used stabilizers for preparing gel-emulsions include solid particles, surfactants, and small molecule gelators.

3.1.1. Solid Particles

Gel-emulsions stabilized by solid particles are also known as Pickering emulsions. Early in the 20th century, researchers discovered that in addition to surfactants, colloid-sized solid particles could also stabilize emulsions. Later, Pickering conducted systematic research on this, giving rise to the name Pickering emulsions [11]. The currently recognized stabilization mechanism is that solid particles can adsorb at the oil/water interface to form an interfacial film, and these particles have strong resistance to droplet coalescence, thereby better stabilizing the gel-emulsion. Compared to surfactants, gel-emulsions stabilized by solid particles have advantages such as low toxicity, low foaming rate, and strong stability, making them highly valuable in fields closely related to human life, such as medicine and food. Solid particles can be inorganic or bio-derived organic particles. Inorganic particles mainly include graphene, titanium dioxide, and zinc oxide, while organic particles primarily consist of proteins, polysaccharides, and protein-polysaccharide composite particles.

When the stabilizer is inorganic particles, according to the work of Ikem *et al.* [12] in 2010, gel-emulsions with an internal phase as high as 85% were prepared using TiO_2 as the stabilizer. By using this emulsion as a template to prepare polymers, the pore structure and mechanical properties of the polymer could be adjusted by changing the ratio of the continuous and dispersed phases and the concentration of TiO_2 particles. The study showed that as the volume of the internal phase increased and the concentration of the stabilizer TiO_2 decreased, the pore size and pore size distribution of the polymer gradually increased. Meanwhile, the mechanical properties increased as the porosity decreased. The study concluded that the toughest macroporous polymer had the lowest porosity but the smallest pore size and the narrowest pore size distribution, as shown in **Figure 1**.

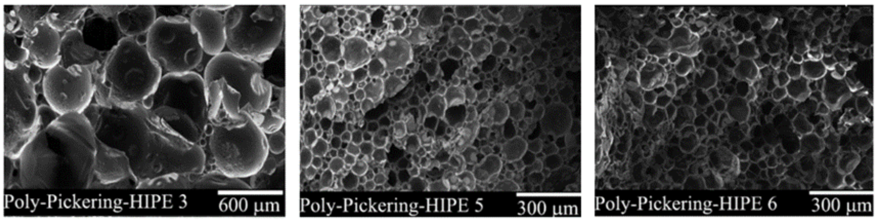

Figure 1. SEM images of poly-Pickering-HIPEs 3, 5, and 6 synthesized from 80 vol % internal phase emulsion templates stabilized by 1, 5, and 10 wt% TiO_2 particles, respectively [12].

When the stabilizer is organic particles, protein-polysaccharide composite particles often perform better than single protein or polysaccharide particles, providing better emulsification and spatial stability. According to the research by Wang *et al.* in 2022 [13], gel-emulsions were prepared using soybean whey protein and soybean hull polysaccharide polymers as stabilizers. The results showed that as the polysaccharide content increased, the polymer's microstructure became denser, and thermal stability improved, providing a theoretical reference for protein-polysaccharide polymer-stabilized gel-emulsions. Zhou *et al.* [14] prepared gel-emulsions using gliadin-chitosan composite particles as stabilizers, with an internal phase exceeding 90%. Using these composite particles as stabilizers also promoted the formation of the pore structure, resulting in porous materials with high porosity in the subsequent preparation.

3.1.2. Surfactants

Traditional gel-emulsions use surfactants as stabilizers, initially employing small molecule surfactants such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), sorbitan monolaurate (Span20), and sorbitan monooleate (Span80), etc. [15]. Studies have shown that although surfactants are among the most commonly used stabilizers, their kinetic instability and tendency to leach out require an addition of about 5-30% of the continuous phase when preparing gel-emulsions. If the gel-emulsion prepared in this way is used as a template to make porous materials, complex procedures and steps are required to remove the surfactant, which limits its application in porous materials.

According to Xu *et al.* [16] in 2014, cetyltrimethylammonium bromide surfactant was used as a stabilizer, with styrene and divinylbenzene as the continuous phase, and an ethanol-water solution as the dispersed phase, to prepare a series of gel-emulsions with internal phase contents ranging from 82.5% to 94.0%. These emulsions were used as templates to fabricate porous polymers. The study indicated that the internal phase content significantly affects the porous materials: increasing internal phase content led to higher absorption values for water and toluene, but decreased compressive strength of the porous materials. Zhu *et al.* [17] used sorbitan monooleate (Span80) as a stabilizer, with butyl methacrylate (BMA), methyl methacrylate (MMA), and styrene (St) as the continuous phase, and sodium chloride aqueous solution as the dispersed phase, to prepare gel-emulsions. By adding the initiator azobisisobutyronitrile, they produced an oil-absorbing material. As shown in **Figure 2**, experimental results showed that this material exhibited excellent oil-water separation performance, selectively adsorbing oil from water rapidly, suggesting promising applications in oil pollution treatment.

3.1.3. Small Molecule Gelators

Small molecule gelators generally refer to compounds with relatively low molecular weight, often possessing unique structural and functional groups. They form three-dimensional networks in solution through weak intermolecular interactions such as hydrogen bonding, Van der Waals forces, π-π stacking, and electrostatic interactions. This enhances the viscosity of the solution, immobilizing the solvent and promoting the stability of gel-emulsions [18]. Compared to solid nanoparticles, gel-emulsions stabilized by small molecule gelators do not require an internal phase volume fraction greater than 74% and are less prone to phase inversion. In contrast to surfactants, they stabilize gel-emulsions without the need for large quantities of small molecule gelators. These advantages significantly broaden the application scope of such gelators.

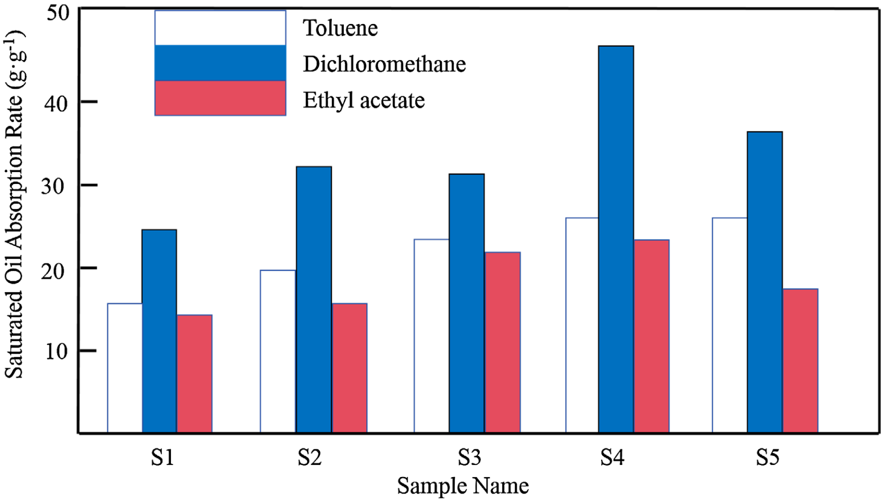

Figure 2. The effect of monomer mass ratio on the saturated oil absorption rate of macroporous superhydrophobic oil-absorbing materials [17].

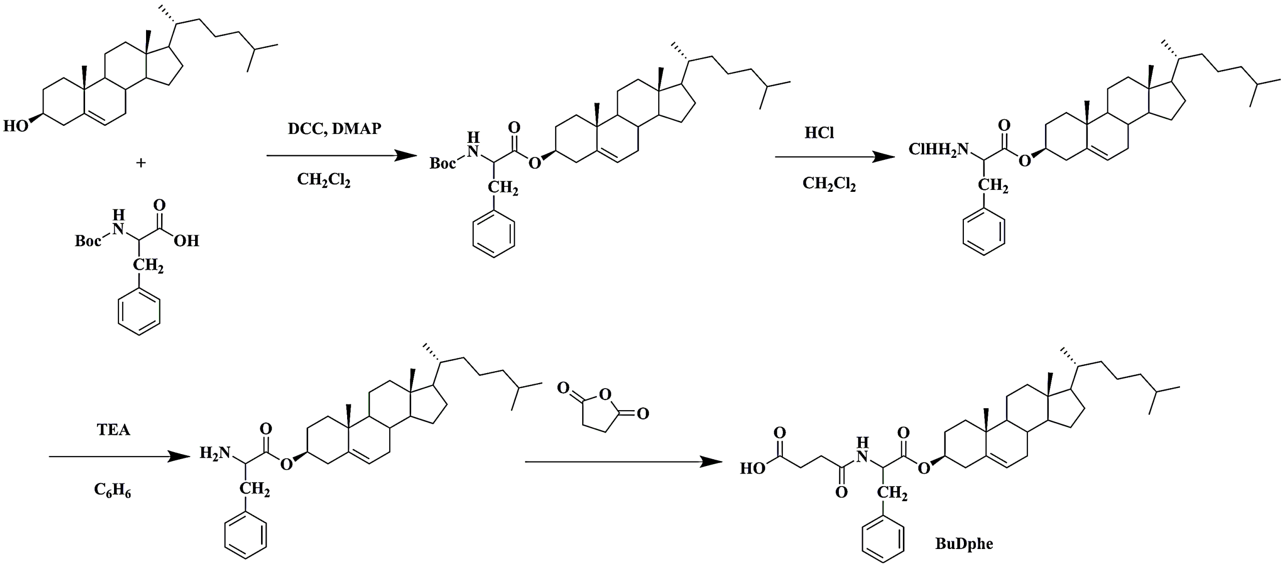

Figure 3. Synthesis route of BuDphe [19].

In 2015, Fang's research group [19] synthesized the gelator BuDphe (**Figure 3**), a low molecular weight cholesterol derivative, and utilized it as a stabilizer to prepare various W/O type gel-emulsions and polymers. Comparative experiments demonstrated that the optimized materials not only exhibited hydrophobicity, porosity, and low density, but also unprecedented flexibility in dry conditions. After undergoing compression deformation exceeding 70%, they could fully recover to their original thickness. Additionally, the prepared materials showed excellent adsorption properties.

In 2016, Fu *et al.* [20] designed and synthesized a polymeric cholesterol derivative (CEA) possessing dual functions as a small molecule gelator and polymerizable monomer. Using CEA as a stabilizer, stable W/O type gel-emulsions were prepared with a continuous phase of toluene, *n*-heptane, and D-PDMS mixture, and water as the dispersed phase. **Figure 4** shows photographs of gel-emulsions formed with different ratios of *n*-heptane to toluene. The introduced D-PDMS acted as a crosslinking agent, and a small amount of hydrophobic silica served as a thickener. Polymerization under heating produced well-shaped, compressible porous polymer materials. By adjusting the ratio of the continuous phase, control over the internal structure of the porous materials was achieved. Experimental results demonstrated that porous materials prepared using this gel-emulsion exhibited excellent adsorption performance towards formaldehyde and toluene at room temperature, and could be reused multiple times.

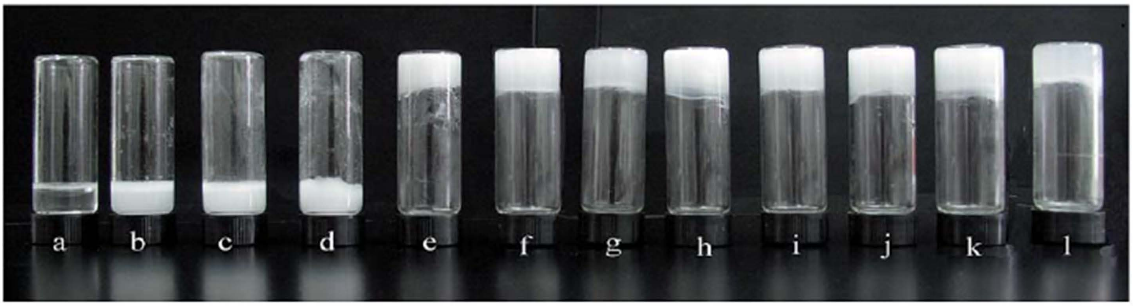

Figure 4. Photographs of gel-emulsions with different volume ratios of *n*-heptane to toluene: (a) 0:10, (b) 0:10, (c) 1:9, (d) 2:8, (e) 3:7, (f) 4:6, (j) 5:5, (h) 6:4, (i) 7:3, (g) 8:2, (k) 9:1, and (l) 10:0. CEA concentration of the gel-emulsion was 2 wt% of the organic phase, of which (a) was without CEA, water content was 90% [20].

3.2. Preparation Strategy

After the stabilizer selection, design and preparation are successful, the next step is to prepare the gel-emulsion. The traditional preparation methods include one-step method, two-step method and phase inversion method [5]. The general preparation process of gel-emulsions is shown in **Figure 5**, and a brief description of various preparation methods is as follows.

The single-step method typically involves mixing the dispersed phase, continuous phase, and stabilizer together to form gel-emulsions, with the stabilizer dissolving or dispersing in the continuous phase before homogenization. Single-step methods include high-speed shearing, ultrasonication, or manual shaking/stirring [21], with high-speed shearing being the most commonly used due to its simplicity, speed, and cost-effectiveness. This method uses high-speed shearing to mix the continuous and dispersed phases, generating strong shear forces that disperse droplets and form gel-emulsions [22]. Peng *et al.* [23], for example, used linseed oil as the dispersed phase, water as the continuous phase, and composite protein nanoparticles as stabilizers to prepare Pickering emulsions using high-speed shearing (5000 rpm, 60 s).

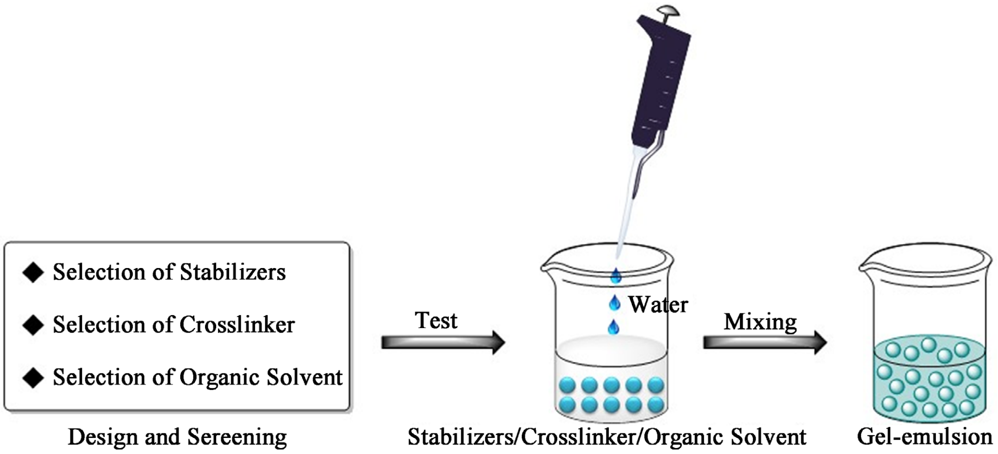

Figure 5. Schematic diagram illustrating the general preparation process of gel-emulsion.

The two-step method is typically used to prepare gel-emulsions with smaller droplets. Initially, the oil and water phases are mixed together using a high-shear emulsifier to form a coarse emulsion, which is then further homogenized using methods such as ultrasonication, microfluidization, or high-pressure valve homogenization. Tan *et al.* [24], for instance, prepared polysaccharide microspheres using ultrasonication and centrifugation, concentrating under a high centrifugal field to exclude excess continuous phase and achieve high internal phase volume fraction gel-emulsions. In this method, the formation of cross-linked interfaces is crucial to suppress phase separation under high centrifugal forces and maintain the stability of gel-emulsions.

Gel-emulsions can also be prepared using phase inversion methods, where W/O emulsions can be converted to O/W emulsions. This method can induce phase inversion by changing the oil-to-water ratio, pH, temperature, or type of surfactant.

4. Gel-Emulsion Applications

4.1. Preparation of Porous Materials

Porous materials generally refer to materials with a certain amount of micro- and nano-scale pore structures, characterized by high surface area, high porosity, adjustable pore size, and relatively low density, making them highly sought after in recent years [25]. Gel-emulsion templating is a significant method for preparing porous materials, enabling precise control over their microstructure and types (**Figure 6**). By adjusting the dispersion phase of the emulsion, the porosity of porous materials can be regulated. The use of gel-emulsions as templates for preparing porous materials offers numerous advantages, facilitating wide applications of porous materials in fields such as separation, adsorption, and tissue engineering.

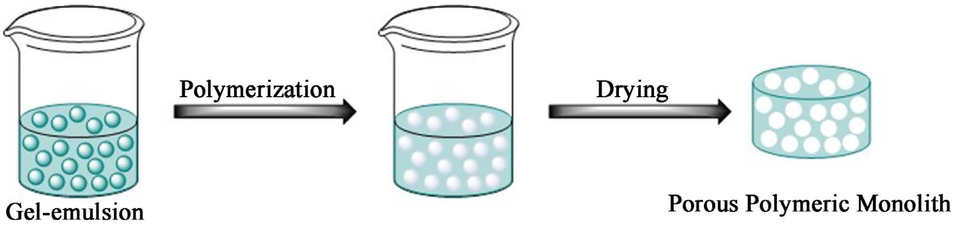

Figure 6. Schematic diagram illustrating the preparation of porous polymeric monolith by gel-emulsion template method.

Yu *et al.* [26] used surfactant Span80 and oyster shell powder (OSP) as stabilizers, styrene and divinylbenzene as the continuous phase, and water as the dispersed phase to prepare stabilized gel-emulsions. By adding azobisisobutyronitrile and conducting heat polymerization and drying, they obtained porous materials. Experimental results showed that the material exhibited superhydrophobicity and excellent absorption capacity for certain organic solvents. The oil-water separation performance was outstanding, and the material could be reused after compression or centrifugation. **Figure 7** illustrates the oil absorption rates of this gel-emulsion for different organic substances.

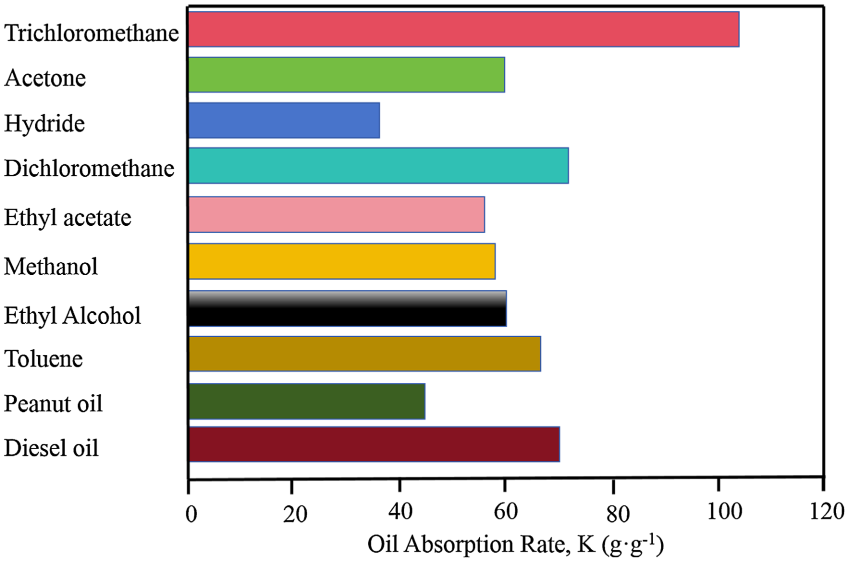

Figure 7. The oil absorption rate of the material for different organic compounds [26].

Fu *et al.* [27] utilized small molecule polymerizable star-shaped compounds as stabilizers, toluene as the continuous phase, and water as the dispersed phase to prepare stable gel-emulsions, with D-PDMS as a crosslinker. They added azobisisobutyronitrile as an initiator and silanization reagents, followed by heat polymerization and drying to obtain porous materials. Experimental results demonstrated that the material exhibited excellent adsorption performance for volatile aromatic derivatives and possessed good flexibility, compressibility, and reusability. **Figure 8** shows photographs of block materials obtained from gel-emulsion preparations with different stabilizer contents.

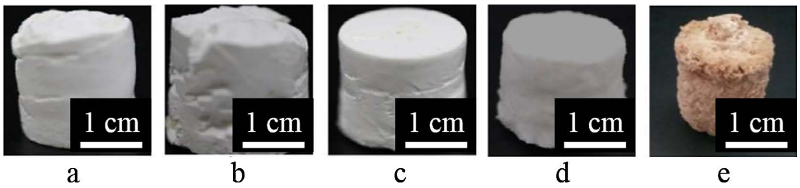

Figure 8. Images of the monoliths prepared from gel-emulsions with different contents of BTN [27].

Tan *et al.* [28] used gelatin nanoparticles as stabilizers and acrylamide as monomers to prepare stable O/W type gel-emulsions. They successfully used these emulsions as templates to fabricate large-pore 3D scaffolds, with pore diameters around 104 μm. Cell culture experiments with HepG2 (human liver cancer cells) demonstrated that cells could adhere to and grow on these scaffolds, showing excellent biocompatibility. This work highlights the broad application prospects of gel-emulsion templating in biomedical fields for preparing porous materials.

4.2. Food

The application of gel-emulsions in food primarily focuses on Pickering emulsions stabilized by solid particles, particularly biologically sourced organic solid particles. While inorganic solid particles can be used to prepare traditional gel-emulsions, they often suffer from poor biocompatibility and low absorbability in the human body, limiting their application in the food industry. Organic solid particles used to stabilize gel-emulsions include 1) polysaccharide particles such as chitosan and starch, 2) proteins like gelatin and soy protein, and 3) composite particles such as corn soluble protein-chitosan and OSA starch-chitosan composite particles [29].

Yang *et al.* [30] prepared a series of O/W Pickering emulsions using different concentrations of cassava nano starch as stabilizers. Experimental results showed that the emulsion had optimal emulsification, longest stability, and strongest viscoelasticity when the stabilizer concentration was 7.5%. The emulsion performed best under storage conditions of 25˚C - 70˚C and pH range of 2.00-6.00. Thus, gel-emulsions stabilized with cassava nano starch are feasible for applications in the food and pharmaceutical industries due to considerations of human absorption and storage.

Yan *et al.* [31] constructed gel-emulsions using octenyl succinic anhydride modified starch (OSA starch) and chitosan complexes through electrostatic interactions. The addition of chitosan enhanced the wettability of OSA starch, facilitating the formation of composite particles. The study investigated the effects of different concentrations and pH of chitosan on the internal structure and stability of gel-emulsions, confirming that the addition of OSA starch/chitosan composites promoted the formation of stable gel-emulsions with excellent antioxidant properties, thereby contributing to their potential applications in the food industry.

4.3. Cosmetics

Cosmetics can be broadly categorized into cleansing, skincare, and makeup products. With the increasing emphasis on the safety and sustainability of cosmetic production, there is growing interest among researchers in developing surfactant-free gel-emulsions for cosmetics. Pickering emulsions offer advantages such as high stability, good biocompatibility, low foaming, and minimal environmental pollution. In particular, Pickering emulsions stabilized by plant-derived organic particles have significant potential in the cosmetics industry. Additionally, compared to other industries, the application of gel-emulsions in cosmetics has specific characteristics. Beyond conventional functions, a good sensory experience is crucial because the end users are consumers. Therefore, when applied to cosmetics, factors such as viscosity, texture, scent, and skin feel are particularly important.

In sunscreen applications, according to research by Marto *et al.* [32], a Pickering emulsion with titanium dioxide particles as the emulsifier and coffee oil as the continuous phase was successfully developed, demonstrating excellent sun protection efficacy with an SPF value greater than 50. It also exhibits good water resistance, with an SPF value remaining above 40 even after two washes. In terms of antioxidant properties, research by Tan *et al.* [33] used gelatin particles to create an O/W type Pickering emulsion loaded with β-carotene. After 27 days of storage, the β-carotene retention in the Pickering emulsion was significantly higher than that in bulk oil, with a retention rate close to 90%, compared to only 8% for unloaded β-carotene. When preparing Pickering emulsions, the user experience is a key consideration, as it can greatly influence the market value of the cosmetic product. Braisch *et al.* [34] prepared stable Pickering emulsions using 230 nm hydrophilic silica particles as the emulsifier and explored their rheological properties. By adjusting particle concentration and oil phase volume, they were able to endow the emulsion with rheological responsiveness to meet various skin feel requirements.

4.4. Stimuli-Responsive Materials

Stimuli-responsive materials, also known as smart materials, are functional materials that undergo reversible chemical or physical changes in response to external environmental changes, such as temperature, light, humidity, or pH [35]. Some unique gel-emulsions can also exhibit stimuli-responsiveness. For instance, gel-emulsions prepared by introducing responsive groups can be applied in drug delivery and release, tissue engineering, and catalysis [36].

Cui *et al.* [37] developed a pH-responsive Pickering emulsion using negatively charged silica nanoparticles and a small amount of amphoteric carboxybetaine surfactant as stabilizers. The emulsion remains stable at pH ≤ 5, but when pH > 8.5, phase separation occurs between the oil and water. This is because, in acidic solutions, carboxybetaine molecules become cations and adsorb onto the silica nanoparticles through electrostatic interactions, enhancing surface activity and causing hydrophobic flocculation. When sodium hydroxide is added, increasing the pH above the isoelectric point, the betaine deprotonates and transitions to a zwitterionic form, desorbing from the particle surface. This recovery and enhancement of particle hydrophilicity lead to emulsion breakdown. This pH-responsive Pickering emulsion can cycle between stability and instability multiple times. However, as the process is repeated, the accumulation of sodium chloride in the system causes droplet size to gradually increase, which shields the electrostatic interactions between positively charged carboxybetaine molecules and negatively charged particles.

Zhang *et al.* [38] developed a novel CO_2-switchable O/W type Pickering emulsion stabilized by functionalized silica nanoparticles containing trace amounts of myristylamidopropyl amine oxide ($C_{14}PAO$). Under the same conditions, the Pickering emulsion can switch between stable and unstable states upon the introduction of CO_2 or N_2. Additionally, other amine surfactants, such as $C_{12}PAO$, $C_{16}PAO$, and alkyl dimethylamine oxides, can also be used as modifiers for silica nanoparticles to form similar CO_2-switchable Pickering emulsions.

5. Conclusion

This article primarily discusses the factors affecting the stability of gel-emulsions, the types of stabilizers used in their preparation, and the corresponding preparation strategies. It also briefly summarizes the applications of gel-emulsions in porous materials, food, cosmetics, and stimuli-responsive materials. Currently, significant progress has been made in the preparation and performance development of gel-emulsions. However, challenges remain, such as issues with biocompatibility. Existing food-grade gel-emulsions mainly consist of polysaccharides, proteins, etc., while many other gel-emulsions contain organic solvents, initiators, etc., which do not meet food-grade requirements. Future efforts could focus on designing small molecules and polymerizable monomers with better biocompatibility, developing cost-effective and sustainable preparation methods, and expanding their applications in industries such as food, pharmaceuticals, and cosmetics.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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