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DOI
10.1016/j.foodhyd.2020.106190

Publication date
2021

Document Version
Final published version

Published in
Food Hydrocolloids

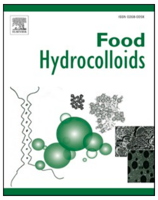
Citation (APA)
Shakeel, A., Farooq, U., Gabriele, D., Marangoni, A. G., & Lupi, F. R. (2021). Bigels and multi-component organogels: An overview from rheological perspective. *Food Hydrocolloids*, *111*, 1-25. Article 106190. https://doi.org/10.1016/j.foodhyd.2020.106190

Food Hydrocolloids 111 (2021) 106190

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: http://www.elsevier.com/locate/foodhyd



Bigels and multi-component organogels: An overview from rheological perspective

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ARTICLE INFO

Keywords:
Organogels
Bigels
Multi-component
Rheology
Synergistic interactions
Food systems

ABSTRACT

Background: Polymeric gels, an important class of soft matter systems, are widely used for commercial applications particularly in food products (i.e., saturated fat replacement). The efficiency of the product for a particular application can be directly linked to its rheological signature. However, the rheological imprint of these structured systems is significantly dependent on the interactions between their individual components. Therefore, the rational understanding of interacting components, their structural arrangements and the resultant characteristics of a hybrid system is vital, in order to speed-up our progress in recognizing the suitable combination of gelling agents and also to tune the technological and functional properties of final product.

Scope and approach: The main aim of this narrative review article is to look at the synergistic interactions (i.e., interpenetrating polymer structures) between different components of the hybrid systems (i.e., multi-component organogels or bigels), in order to unveil the resultant rheological characteristics for different commercial applications including food systems. However, multi-component hydrogel systems have not been discussed in this review.

Key findings and conclusions: The existence of synergistic interactions between different gelators in multi-component organogels (i.e., higher values of hardness and moduli (G' and G'') of multi-component organogel than the corresponding mono-component system) is clearly evident from the literature. This synergy also helps in optimizing the rheological signature of final system by exploiting the concept of formulation engineering. However, this exciting concept of synergistic enhancement in properties has not yet been explored in the field of bigels. The incorporation of colloidal particles in the gelled system resulted in increased stability and higher moduli values, as compared to the gels without particles. This exciting approach can also be quite useful for designing food products by exploiting the useful properties of gelators and (nano)particles, in a single system.

1. Introduction

Polymeric gels, an important class of soft materials, are usually made up of two components, solvent and gelator (i.e., low molecular weight gelling agent). The three dimensional network of gelator molecules physically entraps the oil phase, resulting in a viscoelastic gel (Shakeel, Farooq, et al., 2019). There are various categories of polymeric gels, already investigated in literature, including organogels, hydrogels, emulsion gels, bigels, etc. (Ajazuddin et al., 2013; Co & Marangoni, 2018, pp. 1–29; Li & Mooney, 2016; Shakeel, Lupi, Gabriele, Baldino, & De Cindio, 2018). The interactions between different components of a system can significantly modify its rheological signature, which eventually define its efficacy for the commercial applications. Therefore, rheology is a smart tool to characterize the properties of gels, which might be optimized in terms of composition, to achieve the desired rheological properties for the final application. Hydrogels are usually formed by immobilizing the aqueous phase by using either natural or synthetic polymeric gelators (Peppas, Bures, Leobandung, & Ichikawa,

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https://doi.org/10.1016/j.foodhyd.2020.106190
Received 14 April 2020; Received in revised form 15 July 2020; Accepted 16 July 2020
Available online 10 August 2020

2000). These systems are quite useful for pharmaceutical applications because of their better patient complaint nature (Du, Zhou, Shi, & Xu, 2015). However, the delivery of hydrophobic drugs using hydrogels is not favorable because of their lower skin permeability (Gallardo, Muñoz, & Ruíz, 2005). However, in this review, we will not discuss this type of gels (i.e., hydrogels) as several thorough review articles (Dragan, 2014; Haq, Su, & Wang, 2017; Matricardi, Di Meo, Coviello, Hennink, & Alhaique, 2013) are already available in literature on this particular topic of multi-component hydrogels.

Gelation of oil phase (i.e., organo-gelation) has been adopted as an efficient and interesting approach to transform non-polar liquids into soft solids, due to the formation of three-dimensional network of (organo)gelators. This transformation is usually caused by physical phenomenon (i.e., surface and capillary forces), without affecting the chemical properties of the liquid phase (Ashok R. Patel, 2017; Toro-Vazquez et al., 2013). Usually, the bulk structure of organogels comes from the self-assembly of gelator molecules into crystal lattice, micelles, fibrils or aggregates, which eventually arranged themselves to form a 3D network. This structural conformation provides the rheological signature, physical properties and sensory features to the prepared organogels. The optimization of organogel functionality by varying these macroscopic properties can be directed by formulation engineering (Co & Marangoni, 2018, pp. 1–29). Apart from mono-gelator systems, multi-component organogels can also be prepared by combining the useful characteristics of different gelators, in order to alter the final properties of the gelled system. This review will mainly consider this type of organogels as interpenetrating networks/structures of different components is usually resulted in synergistic enhancement of physical and mechanical properties of organogels.

Bigels (i.e., hybrid systems) are semi-solid formulations, usually prepared by high speed mixing of organogel and hydrogel at certain temperature (Martins et al., 2019; Shakeel, Farooq, et al., 2019; Shakeel et al., 2018). These systems possess better properties than the emulsion gels (with one structured phase (V. K. Singh et al., 2014)) because of two gelled phases, instead of one. Moreover, mixtures of micro-phase separated proteins and polysaccharides can also produce bigels-like systems in a single solvent (i.e., water) (Zhang, Sun, & Li, 2019, pp. 439–445). However, in this review, bigels produced from the structured oil-water phases will be discussed, in order to highlight its potential for food applications.

This review focuses on the structural and rheological characteristics of multi-component organogels and bigels (a hybrid system), in order to unleash the potential of interpenetrating polymeric networks/structures for the fine tuning of resultant properties. A better understanding of synergistic interactions between different components in a polymeric gel (i.e., organogel or bigel) may provide a step forward towards the development of technologically and functionally modified commercial systems. Therefore, the basic science of combining different ingredients and their interactions underpinning rheological fingerprint need to be unveiled for commercial applications.

2. Organogels

Researchers from different fields (i.e., material science, colloid science, food science, etc.) are focusing to explore new gelators and novel processing methods to produce organogels, which provide a rapid development in this research area. However, further research is still needed to understand their structuring mechanisms and manipulation of macroscopic properties by playing with the microstructure of organogels, which makes it quite interesting to produce and analyze this new class of soft materials. Furthermore, this fascinating approach of organogelation has the potential to cover wide range of applications including food, pharmaceuticals, etc. For instance, BECEL™ Pro. Activ spread consist of plant sterol esters (9%), which act as a structuring agent as well in oil-water emulsion (Becel pro. activ,).

One of the key challenges in the field of organogelation is to find the gelators that are cheap, easily available, required in low concentrations to form a structured system and suitable for edible systems (Ashok R Patel, 2015; Ashok R. Patel & Dewettinck, 2016). Apart from these requirements, an optimum balance between the affinity and insolubility of organogelators in oil phase is also needed. This insolubility acts as a trigger for molecular self-assembly and subsequent organization, as a function of gelator concentration and temperature. However, excessive insolubility of gelator (i.e., stronger gelator-gelator interactions) will result in precipitation of aggregates (i.e., phase separation). Therefore, a suitable balance between gelator-gelator and oil-gelator interactions ensures the formation of a continuous 3D network of gelator molecules and subsequent ensnarement of oil phase. Hence, the process of gelation comprises of molecular interactions at primary, secondary and tertiary levels, which eventually makes it quite complex.

Generally, organogels are formed by incorporating gelator within the oil phase at temperatures higher than the melting point of the gelator (i.e., direct approach). Contrarily, organogels can also be produced by using multi-step solvent exchange method (i.e., indirect approach), as reported for the whey protein aggregates (de Vries, Wesseling, van der Linden, & Scholten, 2017). In short, this procedure involves the modification of the polarity of organic phase by replacing the already existing continuous phase with the new phase. For example, replacement of an aqueous phase with an oil phase using particular solvent (i.e., acetone), having affinity for both oil and water. In this review, organogels produced from direct approach will only be discussed. Furthermore, organogels can be produced either with the association of small molecules in the oil phase (i.e., typically edible oil) (Okuro, Martins, Vicente, & Cunha, 2020) or by the crosslinking/self-assembly of polymers in any other solvent (Suzuki & Hanabusa, 2010). However, this review will only cover the first mentioned category of organogels, as this type is widely used for food applications.

On the basis of number of gelators used for the organogelation process, the organogel can be stated either as a single-component or a multi-component (i.e., mixed) organogel. It is usually quite difficult to replace any natural system (i.e., saturated fats) with the single-component organogel. However, use of multiple gelators can provide superior properties of organogels with significant amount of entrapped oil, by modifying the structural organization of gelator molecules (Gravelle, Blach, Weiss, Barbut, & Marangoni, 2017). Furthermore, research has also been directed towards fabricating and investigating hybrid systems, apart from simple organogels, by utilizing different approaches (Okuro et al., 2020) (see Fig. 1). However, this review will be focused on the characteristics of multi-component organogels and bigels (i.e., hybrid system of organogels).

2.1. *Multi-component/mixed organogels*

Multi-component (organo)gels have not yet been thoroughly investigated in the literature to identify their true benefits. Typically, these systems are produced by adding more than one gelator in the solvent phase, in order to modify the microstructure along with the bulk structural organization of gels by having synergistic interactions between the gelators. The intriguing fact about these systems is the possibility of manipulating their characteristics by playing with the concentration of the gelators. These systems can be classified into three different types (see Fig. 2) including: (i) two-component gels (i.e., both components are necessary for gelation and individual components cannot jellify the liquid phase), (ii) multi-gelator gels (i.e., each component is itself gelator and capable of forming self-assembled structures either independently (self-sorting) or together (co-assembly)), and (iii) gelator plus non-gelling additive gels (i.e., additive can hinder the self-assembly behavior of gelator or promote the structural arrangements of gelator molecules or strengthen the structural network by forming linkages with the gelator molecules) (Buerkle & Rowan, 2012). However, these three categories of organogels have already been well described in literature (Buerkle & Rowan, 2012; Ashok R.; Patel,

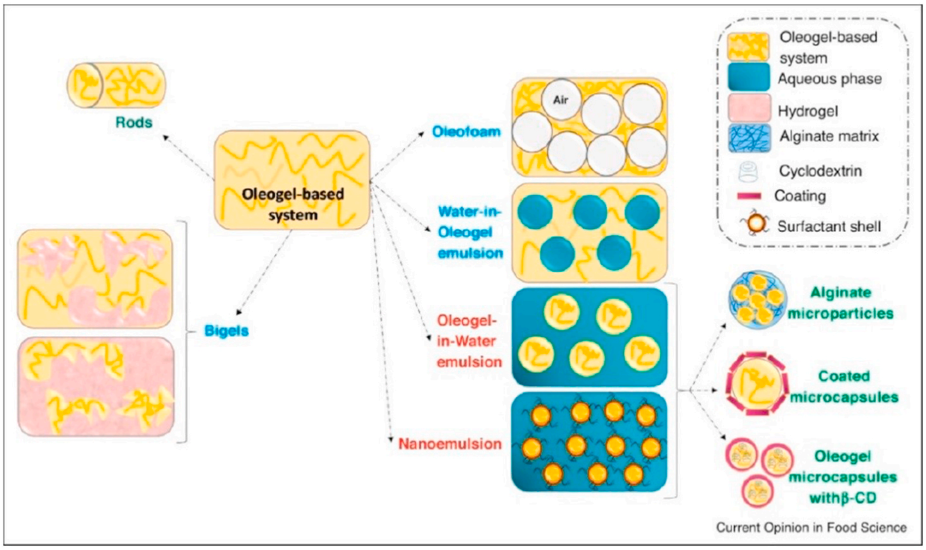

Fig. 1. Schematic representation of different organogel-derived systems. (i) blue color text represents systems with semi-solid texture, (ii) red color text represents systems with liquid-like characteristics and (iii) green color text represents systems having shaped and compartmentalized structures. Reprinted with permission from ref (Okuro et al., 2020), Copyright [2020], Elsevier. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

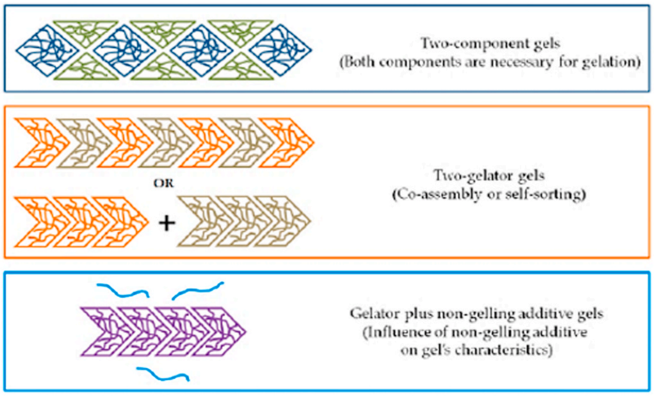

Fig. 2. Schematic representation of three different types of multi-component organogels. The term self-sorting represents the gelators which independently assemble to form distinct (or interpenetrating) networks. Light blue wavy lines represent the non-gelling additives. Adapted with permission from ref. (Buerkle & Rowan, 2012), Copyright [2012], The Royal Society of Chemistry. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2017). Therefore, in the following sections, multi-component organogels will be discussed on the basis of different gelators which are extensively used for food applications, i.e. lecithin, fatty acids, fatty alcohols, natural waxes, etc.

2.1.1. Lecithin based mixed organogels

There are several examples of multi-component organogel systems, already reported in literature, and one of the most common components used in these systems is lecithin. The reasons for its extensive utilization include: biodegradability and sustainability, ease of availability, and capability of interaction with different oils, gelators and non-gelling agents with the help of hydrogen bonding or van der Waals forces (Nikiforidis & Scholten, 2014). Lecithin is usually not able to form a structured system (i.e., gel) on its own. However, in multi-component formulations, it may act as a main or co-gelator, in the presence of gelling or non-gelling additives, depending upon the type and composition of lecithin. For example, lecithin has been reported to act as a main gelator in the presence of small amount of water (0.25–0.9 wt%) (Bodennec, Guo, & Rousseau, 2016) or α-tocopherol (1:1 ratio) (Nikiforidis & Scholten, 2014) as non-gelling additives. In such cases, lecithin (i.e., main gelator) is responsible for giving the basic structuring units (i.e., lamellar or crystalline phases) while the additives are compulsory for adjusting the geometrical packing of gelator molecules, which resulted in cylindrical micelles (i.e., fluid capturing network). The rheological investigation displayed a solid-liquid transition at 50–55 °C, irrespective of lecithin amount (10, 20 or 30 wt%), with the water content of 1.40 (i.e., molar ratio of water and lecithin) (Bodennec et al., 2016).

Furthermore, lecithin has also been investigated as a co-gelator to modify the self-assembly behavior and structural network of main structuring agents including sorbitan tristearate (STS) (Pernetti, van Malssen, Kalnin, & Flöter, 2007), sitosterol (Han et al., 2013), sucrose ester (SE) (Bin Sintang, Danthine, Patel, et al., 2017), fruit wax (Okuro, Tavernier, et al., 2018), and ethylcellulose (Aguilar-Zárate, Macias-Rodriguez, Toro-Vazquez, & Marangoni, 2019). Multi-component organogel produced by using lecithin and STS is an example of two-component gel, where both components are not able to form space filling network on their own (Pernetti et al., 2007). However, a synergistic interaction is observed at LEC:STS ratios of 2:3–3:2, leading to the formation of a gelled structure. In this case, lecithin modifies the morphology of structuring unit (i.e., STS crystals) and the network of STS crystals through weak junctions. The mixed organogels displayed irreversible shear deformation and a reversible solid-liquid transition (i.e., cross-over between $G^{'}$ and $G^{''}$) at 30 °C.

Likewise, lecithin-sucrose ester based organogel shows synergistic association at LEC:SE ratio of 3:7, resulted in the formation of gel structure, which is not observed for the individual components (Bin Sintang, Danthine, Patel, et al., 2017). The microstructural analysis reveals the crystalline structure of sucrose ester and the addition of lecithin results in a finer crystalline network, that is able to physically capture the oil phase. The incorporation of lecithin in mixed organogels resulted in higher storage modulus (i.e., $G^{'}$) values until the LEC:SE ratio of 3:7 and after that a decrease in $G^{'}$ is observed. This result verifies that the sucrose esters provide the building blocks to sustain the solid-like characteristics of the organogels while lecithin only influences the self-assembly behavior of sucrose ester.

The similar modification in the aggregation and crystallization behavior of fruit wax (Okuro, Tavernier, et al., 2018) or ethylcellulose (Aguilar-Zárate et al., 2019) was also observed by adding lecithin, because of the hydrogen bonding between lecithin and polar entities of the gelators. The rheological analysis showed a 10-fold increase in shear moduli and 20-fold increase in hardness, by adding 1 wt% of lecithin in 10 wt% ethylcellulose based organogels. The solid-liquid transition was predominantly controlled by ethylcellulose while the shear thickening response was affected by the addition of lecithin (Aguilar-Zárate et al., 2019).

Apart from improving the structural network of gelators (i.e., either by acting as a co-gelator or a non-gelling additive), lecithin is also reported to hinder the self-assembly behavior of gelator molecules. For example, the addition of lecithin in 12- hydroxystearic acid (12-HSA) based gels resulted in reduced gelation ability, due to the formation of LEC:HSA complexes that eventually disrupted the fibrous network of 12-HSA (Tamura & Ichikawa, 1997). This disruption in structural network of HSA also resulted in a decrease in yield strength from ~450 to ~0 g/cm^2 by increasing the lecithin concentration from 0 to 16 wt%. Table 1 presents some details about the multi-component organogels prepared by using lecithin with other components.

2.1.2. *Fatty acids/alcohols/esters based mixed organogels*

In literature, several examples of two-gelator gels (either co-assembled or self-sorted) have been reported by using mixture of fatty acids and/or alcohols and/or esters, particularly for food applications. Some of these systems include mixture of fatty acids and fatty alcohols (Blach et al., 2016; Gandolfo, Bot, & Flöter, 2004; Schaink, van Malssen, Morgado-Alves, Kalnin, & van der Linden, 2007), fatty acid and sorbitan ester (Uvanesh et al., 2016), sterol and sterol ester (Bot & Agterof, 2006), sterols and monoglyceride (Bin Sintang, Danthine, Brown, et al., 2017; Bin Sintang, Rimaux, Van de Walle, Dewettinck, & Patel, 2017; Kouzounis, Lazaridou, & Katsanidis, 2017), and monoglyceride and ethylcellulose (Lopez-Martínez, Charó-Alonso, Marangoni, & Toro-Vazquez, 2015). Mixture of fatty acids and fatty alcohols (i.e., stearyl alcohol and stearic acid) has been thoroughly investigated in literature, particularly for their potential use in food applications (Blach et al., 2016; Gandolfo et al., 2004; Schaink et al., 2007). The rheological analysis showed a synergistic increase in the properties (i.e., hardness and elastic modulus, G') of mixed organogel having 3:7 ratio (acid: alcohol). The synergistic effect in the properties of these mixed organogels was linked with the formation of fine crystals having modified morphology (i.e., transformation of platelet-like crystals to needle-like crystals) (Schaink et al., 2007). Afterward, this synergistic enhancement in the characteristics of mixed organogels was associated with the increase in crystalline mass and the spatial distribution of mass, instead of crystal shape and size (Blach et al., 2016).

The self-assembly behavior of this particular mixed organogel system can be further modified by adding a hydrophobic polymer (i.e., ethylcellulose) (Gravelle, Davidovich-Pinhas, Barbut, & Marangoni, 2017). The incorporation of ethylcellulose resulted in enhanced gel strength for organogels dominated by pure alcohol or pure acid crystals. Whereas, for gels having mixed crystals, the polymer addition did not provide significant enhancement in gel strength. The addition of ethylcellulose increased the plasticity (i.e., flow of polymer chains under centrifugation) of the prepared gels with intermediate ratios of acid and alcohol (Gravelle, Blach, et al., 2017; Gravelle, Davidovich-Pinhas et al., 2017).

Multi-component systems consist of β-sitosterol and γ-oryzanol are undoubtedly one of the most widely investigated mixed organogels (Bot, den Adel, & Roijers, 2008; Bot, den Adel, Roijers, & Regkos, 2009; Sawalha et al., 2012; Sawalha et al., 2015). Individually, both components form crystalline particles in the oil phase, however, in mixture with particular ratios of each gelator they tend to form tubular structures. These tubular structures self-assemble to form a 3D network, as a function of gelators concentration, that can physically entrap the oil phase resulting in a viscoelastic gel (see Fig. 3a) (AlHasawi & Rogers, 2013; Sawalha et al., 2013; Sawalha et al., 2015). These mixed organogels withstand compressional deformation quite well (up to 10%) but showed yielding at very small shear deformation (Bot et al., 2008; Bot et al., 2009). The self-assembly behavior of these tubular structures was also investigated as a function of the type of oil and lecithin content (Okuro, Malfatti-Gasperini, Vicente, & Cunha, 2018). The results showed that the thermal stability of the prepared mixed gels was improved by using the oils of low polarity. The tubule formation was most affected in medium-chain triglyceride (MCT) by adding lecithin (see Fig. 3b), while sunflower oil resulted in harder organogels as compared to the other investigated oils (Okuro, Malfatti-Gasperini et al., 2018).

Furthermore, mixture of phytosterols and monoglycerides has also been reported in literature to structure the oil phase by having synergistic interactions at particular ratio of gelators (Bin Sintang, Danthine, Brown, et al., 2017; Bin Sintang, Rimaux, et al., 2017; Kouzounis et al., 2017). The results showed that the synergistic enhancement, in this case, is not related to the co-assembly (i.e., co-crystallization) of gelators due to the significant differences in the molecular structure of both gelators. Instead, a self-sorted assembly behavior is observed by microscopic analysis, as both gelators independently self-assemble to form the basic structural units (i.e., fibers and spherulites). This self-sorting behavior of structural units prevented the agglomeration of crystals (i.e., main problem in single component gels), which eventually provided an improved spatial distribution of crystalline mass in the oil phase (Bin Sintang, Rimaux, et al., 2017). This improvement in the distribution of crystalline mass also resulted in better rheological properties (i.e., higher storage modulus within linear viscoelastic regime) at the ratio of 8:2 (MGs:PS) (Bin Sintang, Rimaux, et al., 2017). However, by further increasing the content of phytosterol (i.e., 7:3 and 6:4; MGs:PS), value of storage modulus decreased as compared to the 8:2 and pure monoglyceride organogels, which was again linked with the existence of spherulite crystals (Bin Sintang, Danthine, Brown, et al., 2017).

The characteristics of mixed organogels can also be manipulated by varying the total gelator concentration and the ratio between gelators, apart from using different types of gelators. For example, the excessive interactions between ethylcellulose and lecithin resulted in distorted self-assembled structures, which reduced the overall physical and mechanical properties of the gels (Aguilar-Zárate et al., 2019). Similarly, an increased amount of lecithin in sucrose ester (SE) based system can obstruct the network development of SE, because of the excessive branching of tubules that will distort the normal growth of micellar structures (Bin Sintang, Danthine, Patel, et al., 2017). Furthermore, a decrease in rheological properties (i.e., storage modulus) was observed by increasing the content of phytosterol in monoglyceride based gels, which was attributed to the transformation of crystal habit (Bin Sintang, Danthine, Brown, et al., 2017). These results highlight the importance of optimum gelator ratio and their total concentration, in order to tune the final properties of the mixed organogels. Table 2 presents some details about the mixed organogels prepared by using fatty acids/alcohols/esters.

2.1.3. *Natural waxes based mixed organogels*

Natural waxes have been investigated in literature as potential gelators to structure the oil phase. They are commonly identified as long-chain fatty acids esterified by fatty alcohols. The motivation for using natural waxes as gelators is twofold: (i) bio-based and (ii) suitable for food applications. Natural waxes have the capability to form a 3D network, that can physically entrap the oil phase, at relatively low

Table 1
Different multi-component organogel systems based on lecithin.

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
Sunflower oil	1Lecithin 2STS	6–12	•Organogels with mixture of lecithin and STS showed needle-like crystals •The average length of crystals was about 10 mm	**Hardness (cylindrical probe = 12.7 mm; penetration speed = 2 mm/s; temperature = 5°C)** • Pure lecithin (6–12 wt%) = 0–1 g • Pure STS (6–12 wt%) = 0–10 g • Lecithin/STS: 40/60 (Total 6 wt%) = 40 g • Lecithin/STS: 40/60 (Total 8 wt%) = 97 g • Lecithin/STS: 50/50 (Total 12 wt%) = 109 g **Viscosity** • Lecithin/STS: 50/50 (Total 12 wt%) = 0.86 Pa s (@ 20 °C) **Thermal Analysis** • Lecithin/STS: 50/50 (Total 12 wt%) = 15 °C (gelation temperature) • Lecithin/STS: 50/50 (Total 12 wt%) = 30 °C (melting temperature)	• The individual gelators did not form gel structure within the concentration range of 6–20% while the mixture of gelators at particular ratios (i.e., 40/60 or 60/40) showed the formation of strong gels. • The prepared gels displayed irreversible shear deformation whereas reversible thermal deformation. • The results led to the hypothesis that STS was responsible for structure while lecithin imparted the particular shape to the crystals and also the weak junctions between the crystals.	Pernetti et al. (2007)
High oleic canola oil	1 Ethylcellulose (EC) 2 Lecithin	11–17	–	**Moduli @ 1 Hz** • Pure EC (10–12 wt%): $G' = 3 \times 10^4$-4x10^4 Pa; $G'' = 2 \times 10^3$-2.5×10^3 Pa • Lecithin/EC: 9/91 (Total 11 wt%): $G' = 4 \times 10^5$ Pa; $G'' = 3.1 \times 10^4$ Pa • Lecithin/EC: 8/92 (Total 12 wt%): $G' = 1.8 \times 10^5$ Pa; $G'' = 4.9 \times 10^4$ Pa • Lecithin/EC: 7/93 (Total 13 wt%): $G' = 8 \times 10^5$ Pa; $G'' = 5 \times 10^4$ Pa **Thermal Analysis** • Pure EC (10 wt%) = 99.24 °C (Cross-over temperature) • Lecithin/EC: 9/91 (Total 11 wt%) = 109.01 °C (Cross-over temperature)	• The results showed a 10-fold increase in shear moduli and 20-fold increase in hardness, by adding 1 wt% of lecithin in 10 wt% ethylcellulose based organogels. • A high temperature plateau (@120–130 °C) in moduli along with the thermal reversibility was observed for the mixed organogels. • The solid-to-fluid transition (i.e., elastic softening and failure of network) was predominantly controlled by ethylcellulose while the thickening response was affected by the addition of lecithin.	Aguilar-Zárate et al. (2019)
Sunflower oil	1 Sucrose esters (SE) 2 Sunflower lecithin (SFL)	10	• Fine and denser crystal network was observed for the mixed organogel system • Spherical/globular structure (of about 10 μm) for sucrose ester organogels while for mixed organogels a self-assembled structure was evident	**Moduli @ 1 Hz** • SFL/SE: 20/80 (Total 10 wt%): $G' = 8 \times 10^3$ Pa; $G'' = 6.5 \times 10^2$ Pa • SFL/SE: 30/70 (Total 10 wt%): $G' = 2 \times 10^4$ Pa; $G'' = 1.5 \times 10^3$ Pa • SFL/SE: 40/60 (Total 10 wt%): $G' = 4.7 \times$	• The incorporation of lecithin into sucrose ester resulted in gelation of the system at all investigated ratios. • The organogel having 7:3 ratio (sucrose ester:lecithin) displayed synergistic enhancement in the rheological properties as compared to the other ratios, which was linked to the interruption in the hydrogen	(Bin Sintang, Danthine, Patel, et al., 2017)

(continued on next page)

Table 1 (*continued*)

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
				10^3 Pa; $G'' = 4.6 \times 10^2$ Pa **Thermal Analysis** • Pure SE (10 wt%) = 27.83 °C (gelation temperature) • SFL/SE: 10/90 (Total 10 wt%) = 35.53 °C (gelation temperature) • SFL/SE: 20/80 (Total 10 wt%) = 30.90 °C (gelation temperature) • SFL/SE: 30/70 (Total 10 wt%) = 26.13 °C (gelation temperature) • SFL/SE: 40/60 (Total 10 wt%) = 24.83 °C (gelation temperature)	bonding between the monomers of sucrose ester.	
Canola Oil	1 Lecithin 2 Stearic acid (SA)	20–30	• Organogels: primary structure of lecithin fibers (i.e., clusters of worm-like micelles) interacted with stearic acid crystals • Organogel emulsions: primary structure of stearic acid interlinked with the micelles of lecithin.	**Hardness (cylindrical probe = 4 mm; penetration speed = 3 mm/s; temperature = 4°C)** • Pure lecithin (20–30 wt%) = 2–10 g • Pure SA (20–30 wt%) = 230–670 g • Lecithin/SA: 70/30 (Total 20 wt%) = 4 g • Lecithin/SA: 50/50 (Total 20 wt%) = 50 g • Lecithin/SA: 30/70 (Total 20 wt%) = 55 g • Lecithin/SA: 70/30 (Total 30 wt%) = 20 g • Lecithin/SA: 50/50 (Total 30 wt%) = 30 g • Lecithin/SA: 30/70 (Total 30 wt%) = 60 g	• The firmness of the organogels and organogel emulsions displayed an increase whereas the accelerated oil loss from the systems showed a decrease with the increase of stearic acid content in lecithin based formulations. • Organogel emulsions displayed improved hardness as compared to the organogels, which showed the synergistic interaction between the organogelators.	Gaudino, Ghazani, Clark, Marangoni, and Acevedo (2019)
Sunflower oil	1 Soybean lecithin (SL) 2 Fruit wax (FW)	5.25–14	• Fruit wax organogel (7:0) = branched dendritic crystals • Fruit wax organogel (5.25:0) = smaller spherulite crystals • Mixed organogel (5.25:1.75) = rosette-like crystals (densely packed and uniformly distributed) • The crystals became more spherical, smaller and higher in number as a function of increasing lecithin concentration.	**Moduli @ 1 Hz** • Pure FW (5.25–7 wt%): $G' = 70–450$ Pa; $G'' = 25–100$ Pa • SL/FW: 25/75 (Total 5.25 wt%): $G' = 1.5 \times 10^4$ Pa; $G'' = 1.4 \times 10^3$ Pa • SL/FW: 50/50 (Total 5.25 wt%): $G' = 2.6 \times 10^3$ Pa; $G'' = 3.5 \times 10^2$ Pa • SL/FW: 25/75 (Total 7 wt%): $G' = 2.5 \times 10^4$ Pa; $G'' = 2.5 \times 10^3$ Pa • SL/FW: 50/50 (Total 7 wt%): $G' = 8.0 \times 10^3$ Pa; $G'' = 1.0 \times 10^3$ Pa	• The addition of lecithin resulted in gel formation, even below the critical gelling concentration of fruit wax. • A synergistic interaction between fruit wax and lecithin was observed at 75:25 and 50:50 ratios of wax: lecithin, as evident by the higher gel strength than the individual organogels. • The incorporation of lecithin also influenced the thermal behavior of fruit wax organogels (i.e., delayed the crystallization and gel formation of fruit wax).	Okuro, Tavernier, et al. (2018)

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Table 1 (*continued*)

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
				Viscosity (@ 5^{o}C) • Pure FW (5.25–7 wt%) = 39.36–53.48 Pa s • SL/FW: 25/75 (Total 5.25 wt%) = 376.20 Pa s • SL/FW: 50/50 (Total 5.25 wt%) = 267.47 Pa s • SL/FW: 25/75 (Total 7 wt%) = 346.70 Pa s • SL/FW: 50/50 (Total 7 wt%) = 288.17 Pa s		
Sunflower oil	1 α-tocopherol 2 PC	25	• PC organogels = spherical reverse micelles • Mixed organogels = cylindrical wormlike micelles	**Hardness (cylindrical probe = 20 mm; penetration speed = 1 mm/s)** • PC/tocopherol: 35/65 (Total 25 wt%) = 15 g • PC/tocopherol: 50/50 (Total 25 wt%) = 92 g • PC/tocopherol: 65/35 (Total 25 wt%) = 31 g **Thermal Analysis** • PC/tocopherol: 50/50 (Total 25 wt%) = 35 °C (melting temperature)	• Gel formation was not observed for the individual gelators whereas their mixture at 1:1 resulted in structural organization in the oil phase (i.e., solid-like system), which was attributed to the formation of entanglements of these polymers. • Total concentration of gelators required for the gelation of oil phase was observed to be higher than 25 wt%, which resulted in shear thinning and thermo-reversible organogel.	Nikiforidis and Scholten (2014)
Sunflower oil	1 Sitosterol (SS) 2 Lecithin	16	• The shape of the crystal was dependent on the ratio of organogelators and the storage temperature • The plate-like crystals were evident for mono-component system while needle-shaped crystals were formed from two-component organogel.	**Moduli @ 1 Hz and 5^{o}C storage temperature** • Pure SS (Total 16 wt%): $G' = 6.8 \times 10^5$ Pa; $G'' = 6.0 \times 10^4$ Pa • Lecithin/SS: 20/80 (Total 16 wt%): $G' = 1.9 \times 10^5$ Pa; $G'' = 3.0 \times 10^4$ Pa • Lecithin/SS: 30/70 (Total 16 wt%): $G' = 1.5 \times 10^5$ Pa; $G'' = 2.0 \times 10^4$ Pa **Moduli @ 1 Hz for different storage temperatures** • Lecithin/SS: 20/80: $G' = 1.9 \times 10^5$ Pa; $G'' = 3.0 \times 10^4$ Pa (@ 5 °C) • Lecithin/SS: 20/80: $G' = 6.9 \times 10^5$ Pa; $G'' = 6.0 \times 10^4$ Pa (@ 15 °C) • Lecithin/SS: 20/80: $G' = 1.4 \times 10^6$ Pa; $G'' = 1.3 \times 10^5$ Pa (@ 25 °C) **Thermal Analysis** • Pure SS (Total 16 wt%) = 51.52 °C (melting temperature)	• The rheological analysis showed that the organogel prepared at higher storage temperature (i.e., 25 °C) was stronger and thermally stable, which was attributed to the increased micro-platelet length and enhanced interactions between crystal network.	Han et al. (2013)

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Table 1 (*continued*)

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
				• Lecithin/SS: 20/80 (Total 16 wt%) = 59.05 °C (melting temperature) • Lecithin/SS: 30/70 (Total 16 wt%) = 52.01 °C (melting temperature)		

STS = Sorbitan tri-stearate; PC = Phosphatidylcholine.

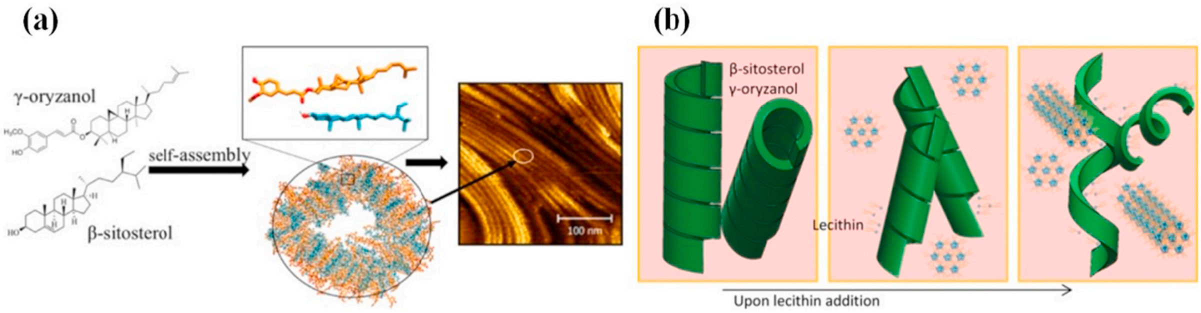

Fig. 3. (a) Self-assembly behavior of β-sitosterol and γ-oryzanol analyzed by using atomistic molecular dynamics (MD) simulations and atomic force microscopic (AFM) images, reprinted with permission from ref. (Dalkas et al., 2018), Copyright [2018], American Chemical Society. (b) schematic representation of the effect of lecithin on the tubules of β-sitosterol and γ-oryzanol, reprinted with permission from ref. (Okuro, Malfatti-Gasperini et al., 2018), Copyright [2018], Elsevier.

concentrations (Tavernier et al., 2017).

Multi-component organogels based on natural waxes have been studied, in order to tailor the mechanical and rheological properties of mixed gels. For example, the mixed organogels composed of rice bran wax and sunflower wax showed higher storage modulus (i.e., more solid-like behavior) than the other prepared organogels (Jana & Martini, 2016). The organogels based on the mixture of sunflower wax and beeswax displayed lower firmness as compared to the individual organogels, which indicated the incompatibility between these two waxes. Similarly, mixed organogels based on sunflower and candelilla waxes exhibited lower firmness as compared to the individual gels, by adding smaller amounts of candelilla wax (90:10 to 60:40, SFW: CLW). The highest firmness was obtained with the mixed organogels of sunflower and candelilla waxes with the ratio of 10:90 (SFW: CLW), which was attributed to the changes in crystal morphology and size (Winkler-Moser, Anderson, Felker, & Hwang, 2019).

The gelation and crystallization behavior of multi-component organogels having mixture of high and/or low-melting waxes (i.e., rice bran wax (RBW), sunflower wax (SW)) and berry wax (BEW)) were also investigated (Tavernier et al., 2017). The results showed a sequential gelation and crystallization for the mixture of SW or RBW (i.e., high-melting) with BEW (i.e., low-melting) while the mixture of SW and RBW (i.e., both high-melting) resulted in simultaneous gelation and crystallization. The rheological analysis revealed the weakening of network structure (i.e., reduced storage modulus) by adding RBW in SW based systems (Fig. 4a). However, a synergistic enhancement in the rheological properties (i.e., higher storage modulus within linear viscoelastic limit, higher critical stress and higher cross-over stress) of mixed organogels based on SW and BEW was observed, having weight percent of 4:1 or 2.5:2.5 (SW%:BEW%) (Fig. 4c). A similar synergetic effect in the rheological characteristics was also evident for the combination of BEW and RBW (Fig. 4b). This synergy in properties was linked with the process of sintering (i.e., bond formation of low-melting wax crystals with the high-melting wax crystals), which resulted in cohesive network and modified rheological fingerprint of mixed organogels. Furthermore, it should be noted that the linear viscoelastic regime of such systems (i.e., gels having low molecular weight gelators) is quite narrow as compared to the gelled systems obtained from cross-linked or self-assembled polymers (Buerkle, Li, Jamieson, & Rowan, 2009), which may be attributed to the weaker interactions between the gelator molecules in the former case.

Recently, the mechanical and rheological properties of mixed organogels based on binary and tertiary mixtures of different gelators (i.e., candelilla wax (CW), sorbitan monostearate (SMS) and fully hydrogenated palm oil (HPO)) have been characterized. The mixed organogel based on CW and HPO showed better thermal stability, low phase angle viscosity and shear thinning behavior, which was attributed to the formation of a structured system. The incorporation of a third component (i.e., SMS) resulted in reduction of the structuring phenomenon, which was linked with the proportion and gelation mechanism of each gelator. The results showed an increase in the hardness of organogels with the increasing concentration of CW above 4 wt% (Godoi et al., 2019). Another interesting approach for preparing multi-component organogels is to use the components that may possess both technological (i.e., gelator) and health features. For example, an increase in the mechanical properties of organogels was observed by adding β-carotene in beeswax-based organogels, presenting both structural and functional characters of the carotenoid component (Martins, Cerqueira, Cunha, & Vicente, 2017). Table 3 presents some details about the mixed organogels prepared by using natural waxes.

Overall, organogel production with tuned rheological and mechanical properties can be accomplished by combining a wide range of non-gelling agents and/or gelators in different proportions with varying total concentration of gelators. This will provide the utilization of ingredient engineering to optimize the characteristics of organogels for different applications particularly for food systems.

Table 2
Different multi-component organogel systems based on fatty acids/alcohols/esters.

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
Hexadecane, Sunflower oil, Medium-chain triglyceride (MCT)	1 Mixture of β-sitosterol and γ-oryzanol (BG) 2 Lecithin	20	• The fibril (i.e., tubule) formation of sitosterol and oryzanol was suppressed by adding lecithin • Tubules completely disappeared above 50 wt% replacement of lecithin	**Moduli @ 1 Hz (Hexadecane)** • Pure BG (Total 20 wt%): $G' = 3.0 \times 10^6$ Pa; $G'' = 3.0 \times 10^5$ Pa • Lecithin/BG: 20/80 (Total 20 wt%): $G' = 3.0 \times 10^6$ Pa; $G'' = 3.0 \times 10^5$ Pa • Lecithin/BG: 40/60 (Total 20 wt%): $G' = 2.0 \times 10^5$ Pa; $G'' = 5.0 \times 10^4$ Pa **Moduli @ 1 Hz (Sunflower oil)** • Pure BG (Total 20 wt%): $G' = 2.5 \times 10^6$ Pa; $G'' = 9.0 \times 10^5$ Pa • Lecithin/BG: 20/80 (Total 20 wt%): $G' = 2.0 \times 10^6$ Pa; $G'' = 4.0 \times 10^5$ Pa • Lecithin/BG: 40/60 (Total 20 wt%): $G' = 1.5 \times 10^3$ Pa; $G'' = 2.5 \times 10^2$ Pa **Moduli @ 1 Hz (Medium-chain triglyceride)** • Pure BG (Total 20 wt%): $G' = 2.7 \times 10^6$ Pa; $G'' = 3.0 \times 10^5$ Pa • Lecithin/BG: 20/80 (Total 20 wt%): $G' = 3.0 \times 10^4$ Pa; $G'' = 4.0 \times 10^3$ Pa • Lecithin/BG: 40/60 (Total 20 wt%): $G' = 2.5$ Pa; $G'' = 0.8$Pa	• The tubule formation was observed to depend on type of oil and lecithin content. • The thermal stability of the prepared gels was improved by using the oils of low polarity. • The tubule formation was most affected in MCT by adding lecithin while sunflower oil resulted in harder organogels.	Okuro, Malfatti-Gasperini, Vicente, and Cunha (2018)
Sunflower oil, Soybean oil, Rapeseed oil	1 Fatty acids 2 Fatty alcohols	5	• The stearic acid showed lozenge-shaped crystals of about 200 μm • The stearyl alcohol showed an aggregate of platelet-like crystals of about 1800 μm • The mixture of organogelators displayed the existence of a large number of small crystals of about 80 μm • The microstructure of the mixed organogelator system was linked with one of the following three phenomenon: (1) heterogeneous nucleation, (2) higher nucleation rate, or (3) alteration of crystal habit	**Hardness (Sunflower oil; cylindrical probe = 12.7 mm; penetration speed = 2 mm/s; temperature = 5°C)** • Pure fatty acid (Total 5 wt%) = 50 g • Pure fatty alcohol (Total 5 wt%) = 150 g • Fatty acid/Fatty alcohol: 30/70 (Total 5 wt%) = 250 g • Fatty acid/Fatty alcohol: 70/30 (Total 5 wt%) = 580 g **Hardness (Soybean oil; cylindrical probe = 12.7 mm; penetration speed = 2 mm/s; temperature = 5°C)** • Pure fatty acid (Total 5 wt%) = 105 g • Pure fatty alcohol (Total 5 wt%) = 325 g • Fatty acid/Fatty alcohol: 30/70 (Total 5 wt%) = 150 g	• The organogels with mixture of fatty alcohol and fatty acid, having same chain length, displayed a synergistic enhancement in rheological properties at a particular concentration (5 wt%) and specific ratios 7:3 or 3:7 (w/w). • This synergetic effect particularly in case of stearyl alcohol/stearic acid in oil phase was linked to the enhanced nucleation rate because of lowering of the interfacial energy.	Gandolfo et al. (2004)

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Table 2 (*continued*)

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
				- Fatty acid/Fatty alcohol: 70/30 (Total 5 wt%) = 460 g **Hardness (Rapeseed oil; cylindrical probe = 12.7 mm; penetration speed = 2 mm/s; temperature = 5°C)** - Pure fatty acid (Total 5 wt%) = 55 g - Pure fatty alcohol (Total 5 wt%) = 60 g - Fatty acid/Fatty alcohol: 30/70 (Total 5 wt%) = 175 g - Fatty acid/Fatty alcohol: 70/30 (Total 5 wt%) = 505 g		
Sunflower oil, Commercial diet oil	1 Stearyl alcohol 2 Stearic acid	3.2–10	- Stearic acid/stearyl alcohol (1:0) = plate-like crystals - Stearic acid/stearyl alcohol (7:3) = elongated feather-like crystals - Stearic acid/stearyl alcohol (5:5 and 3:7) = small needle-like crystals - Stearic acid/stearyl alcohol (0:1) = foliated mica-like crystals	**Elastic Modulus (@ 5°C)** - Pure stearic acid (Total 5 wt%) = 5.5 × 10^5 Pa - Stearic acid/Stearyl alcohol: 70/30 (Total 8.5 wt%) = 3.1 × 10^6 Pa **Elastic Modulus (@ 10°C)** - Pure stearic acid (Total 5 wt%) = 5.4 × 10^5 Pa - Stearic acid/Stearyl alcohol: 70/30 (Total 8.5 wt%) = 3.1 × 10^6 Pa **Elastic Modulus (@ 15°C)** - Pure stearic acid (Total 5 wt%) = 5.0 × 10^5 Pa - Stearic acid/Stearyl alcohol: 70/30 (Total 8.5 wt%) = 2.9 × 10^6 Pa **Elastic Modulus (@ 20°C)** - Pure stearic acid (Total 5 wt%) = 4.8 × 10^5 Pa - Stearic acid/Stearyl alcohol: 70/30 (Total 8.5 wt%) = 2.4 × 10^6 Pa **Elastic Modulus (@ 25°C)** - Pure stearic acid (Total 5 wt%) = 3.5 × 10^5 Pa - Stearic acid/Stearyl alcohol: 70/30 (Total 8.5 wt%) = 1.8 × 10^6 Pa **Elastic Modulus (@ 30°C)** - Pure stearic acid (Total 5 wt%) = 2.0 × 10^5 Pa - Stearic acid/Stearyl alcohol: 70/30 (Total 8.5 wt%) = 4.0 × 10^5 Pa	- A synergistic increase was evident in the rheological impression (hardness and elastic modulus) of mixed organogel having 3:7 ratio (acid:alcohol), which was attributed to the interlinked crystals.	Schaink et al. (2007)

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Table 2 (*continued*)

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
Canola oil	1 Stearyl alcohol 2 Stearic acid	5	• The crystal network was similar for the strongest (2:8 and 3:7, acid: alcohol) and weakest (5:5 and 6:4, acid:alcohol) gels • Platelet-like crystals were evident for all the organogels instead of needle-like crystal structure	**Hardness (cylindrical probe = 10.2 mm; penetration speed = 1.5 mm/s; temperature = 10°C)** • Pure stearic acid (Total 5 wt%) = 0.15 g • Pure stearyl alcohol (Total 5 wt%) = 0.08 g • Stearic acid/Stearyl alcohol: 20/80 (Total 5 wt%) = 0.24 g	• The organogels having 3:7 and 2:8 ratios (acid: alcohol) displayed enhanced strength and no loss of oil during stability tests, as compared to the other systems. • This synergistic enhancement in technological features was associated with the spatial distribution of crystalline mass and also to the increase in the amount of crystalline mass, instead of crystal shape, size or density.	Blach et al. (2016)
Canola oil	1 Stearyl alcohol 2 Stearic acid 3 Ethylcellulose (EC)	3–11	• Needle-like oriented platelets were noticed in alcohol/acid mixed gels • Feather-like crystal structure was observed in ethylcellulose/acid/alcohol mixed system. • The microstructure of crystal network was controlled by ethylcellulose while alcohol:acid ratio governed the crystal size and organization of crystal network.	**Hardness (cylindrical probe = 10.2 mm; penetration speed = 1.5 mm/s; temperature = 10°C)** • Pure stearic acid (Total 5 wt%) = 0.15 g • Pure stearyl alcohol (Total 5 wt%) = 0.08 g • Stearic acid/EC: 55/45 (Total 9 wt%) = 0.47 g • Stearyl alcohol/EC: 55/45 (Total 9 wt%) = 0.30 g • Stearic acid/Stearyl alcohol/EC: 33/22/45 (Total 9 wt%) = 0.09 g	• The incorporation of ethylcellulose resulted in enhanced gel strength for organogels dominated by pure alcohol or pure acid crystals. Whereas, for gels having mixed crystals, the polymer addition did not provide significant enhancement in gel strength. • The addition of ethylcellulose increased the plasticity (i.e., flow of polymer chains under centrifugation) of the prepared gels with intermediate ratios of acid and alcohol. • A decrease in the gelation temperature (from ~110 °C to 90 °C) was observed in temperature ramp-up test, by adding ethylcellulose in acid/alcohol mixed gels, which was attributed to the plasticization of polymer chains by alcohol/acid molecules.	(Gravelle, Blach, et al., 2017; Gravelle, Davidovich-Pinhas et al., 2017)
Extra virgin olive oil	1 Policosanol 2 Glyceryl stearate	3.4–25	–	**Elastic Modulus** • Policosanol/Glyceryl stearate: 50/50 (4–16 wt%) = 7.0×10^2 – 8.0×10^4 Pa **Thermal Analysis (Onset of Crystallization Temperature)** • Policosanol/Glyceryl stearate: 50/50 (4 wt %) = 47.54 °C • Policosanol/Glyceryl stearate: 50/50 (6.8 wt %) = 54.10 °C • Policosanol/Glyceryl stearate: 50/50 (16 wt %) = 61.50 °C	• Rheological analysis showed that the organogels having policosanol had higher consistency, crystallization and gelation temperatures as compared to the gleceryl stearate based gels. • The gelation and crystallization temperatures of mixed gels were dependent on the content of policosanol while the dynamic moduli was controlled by both organogelators. • Mixed gels displayed lower gel strength than the organogels prepared with the same content of policosanol, which was attributed to the interruption in the van	Lupi, Shakeel, et al. (2017)

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Table 2 (*continued*)

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
					der Waals interactions between policosanol molecules.	
Sunflower oil	1 Oleic acid 2 Sodium oleate	4–16	• The spatial distribution of crystals was dependent on the composition of gels	**Elastic Modulus** • Pure oleic acid (Total 16 wt%) = 10 Pa • Pure sodium oleate (Total 16 wt%) = 1.2×10^4 Pa • Oleic acid/Sodium oleate: 50/50 (Total 16 wt%) = 2.3×10^4 Pa	• Oleic acid alone was not able to jellify the oil phase whereas the mixture of oleic acid and sodium oleate formed a gel structure in oil. • The addition of small amount of water enhanced the gel strength whereas the amount of water higher than 2% inhibited the gel formation.	Nikiforidis, Gilbert, and Scholten (2015)
Sunflower oil	1 Monoacylglycerol 2 Diacylglycerol	21–24	–	**•Complex Modulus** • Pure diacylglycerol (Total 21–24 wt%) = 1.1×10^5-2.0×10^5 Pa • Monoacylglycerol/ Diacylglycerol: 5/95 (Total 21 wt%) = 3.0×10^4 Pa • Monoacylglycerol/ Diacylglycerol: 9/91 (Total 22 wt%) = 5.0×10^3 Pa • Monoacylglycerol/ Diacylglycerol: 17/83 (Total 24 wt%) = 7.0×10^3 Pa	• The incorporation of monoacylglycerol into the diacylglycerol based system hindered the development of crystal network, which resulted in lower network strength as evident from rheological analysis.	Tavernier, Moens, Heyman, Danthine, and Dewettinck (2019)
Canola oil	1 Monoacylglycerol 2 Phytosterols	10	• Monoacylglycerol/Native phytosterol (1:0) = large irregularly shaped crystal aggregates • Monoacylglycerol/Native phytosterol (7:3) = thin fibrils • Monoacylglycerol/Native phytosterol (5:5) = needle-like structures • The crystal structure became thinner and less dense with increasing content of native phytosterol	**Complex Modulus** • Pure monoacylglycerol (Total 10 wt%) = 1.0×10^5 Pa • Monoacylglycerol/ Phytosterol: 70/30 (Total 10 wt%) = 5.4×10^4 Pa • Monoacylglycerol/ Phytosterol: 50/50 (Total 10 wt%) = 4.5×10^4 Pa **Thermal Analysis (Onset of Crystallization Temperature)** • Pure monoacylglycerol (Total 10 wt%) = 49.2 °C • Monoacylglycerol/ Phytosterol: 70/30 (Total 10 wt%) = 44.1 °C • Monoacylglycerol/ Phytosterol: 50/50 (Total 10 wt%) = 39.6 °C	• A decrease in complex modulus values (i.e., reduction in consistency or strength) was evident by increasing the content of phytosterols in mixed organogels. • Lower values of complex modulus of mixed organogels was also observed by using faster cooling rates, which resulted in smaller crystals and more stable pickering emulsion (i.e., whipping time reduced to 80%).	Truong, Prakash, and Bhandari (2019)
Sunflower oil	1 Monoglycerides 2 Phytosterols	20	• Monoglycerides/ Phytosterols (10:10) = large phytosterols crystals and some smaller monoglycerides crystals • Monoglycerides/ Phytosterols (15:5) = rosette-like crystal aggregates and some smaller structures	**Moduli @ 1 Hz** • Pure monoglyceride (Total 15 wt%): $G' = 1.0 \times 10^6$ Pa; $G'' = 7.0 \times 10^4$ Pa • Monoglyceride/ Phytosterol: 75/25 (Total 20 wt%): $G' = 2.0 \times 10^6$ Pa; $G'' = 3.0$	• Mixed organogels were observed to have stronger gel network, increased hardness and storage modulus values and decreased melting temperatures as compared to the monoglycerides based organogels, which was attributed to the	Kouzounis et al. (2017)

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Table 2 (*continued*)

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
				$\times 10^5$ Pa	synergistic interaction between the organogelators. • The stronger gels were also produced by increasing cooling or heating times, as evident by oscillatory tests and large deformation mechanical analysis.	
Sunflower oil	1 Monoglycerides 2 Phytosterols	10	• Monoglycerides/ Phytosterols (1:0) = clustered-like crystals • Monoglycerides/ Phytosterols (8:2) = needle-like crystals with clusters of monoglyceride crystals • Monoglycerides/ Phytosterols (7:3 and 6:4) = spherulite crystals along with monoglyceride crystals • Monoglycerides/ Phytosterols (0:1) = three different morphologies: needle-like, plate-like, and spherulite crystals	**Moduli @ 1 Hz** • Pure monoglyceride (Total 10 wt%): $G' = 3.0 \times 10^5$ Pa; $G'' = 1.9 \times 10^4$ Pa • Monoglyceride/ Phytosterol: 80/20 (Total 10 wt%): $G' = 5.0 \times 10^5$ Pa; $G'' = 2.8 \times 10^4$ Pa • Monoglyceride/ Phytosterol: 70/30 (Total 10 wt%): $G' = 1.1 \times 10^5$ Pa; $G'' = 1.6 \times 10^4$ Pa • Monoglyceride/ Phytosterol: 60/40 (Total 10 wt%): $G' = 1.5 \times 10^5$ Pa; $G'' = 1.6 \times 10^4$ Pa	• The monoglyceride/ phytosterol (8:2) mixed organogel displayed higher storage modulus (i.e., strength) than the pure monoglyceride based organogel, which was attributed to the change in crystal morphology and crystal habit. • However, by further increasing the content of phytosterol (i.e., 7:3 and 6:4), value of storage modulus decreased as compared to the 8:2 and pure monoglyceride organogels, which was again linked with the existence of spherulite crystals.	(Bin Sintang, Danthine, Brown, et al., 2017)

CHEMS = cholesteryl hemisuccinate.

3. Bigels

Bigels are semi-solid formulations, usually obtained by high speed mixing of organogel and hydrogel at particular temperature (Martins et al., 2019; Shakeel, Farooq, et al., 2019; Shakeel et al., 2018). These systems are known to have better properties than the emulgels/emulsion gels (only one structured phase (V. K. Singh et al., 2014)) because of two gelled phases, instead of one. Bigels possess interesting properties of each of its phases (oil and water) including: cooling and moisturizing effect, delivery of hydrophilic and hydrophobic active agents, improved spreadability, better absorptivity of drugs through skin and water washable after its application (Almeida et al., 2008; Beauty; Behera, Dey, Sharma, & Pal, 2015; Beauty; Behera, Sagiri, Singh, Pal, & Anis, 2014). These characteristics of bigels make them an ideal candidate for several applications including food, cosmetics and pharmaceutical systems (Lee & Mohraz, 2010).

3.1. *Synthesis of bigels*

In the past decade, several researchers have comprehensively investigated the bigel systems, prepared by mixing organogel and hydrogel, specifically for controlled delivery of drugs (V. K. Singh, Anis, Al-Zahrani, Pradhan, & Pal, 2014b). The synthesis procedure (i.e., parameters) can significantly affect the final properties of the bigel systems particularly the mixing speed, mixing temperature and storage conditions. The effect of mixing speed on the rheological properties of bigels has been reported by (Fasolin & Vicente, 2017). The results showed that the higher mixing speed led to the development of fine droplets with the higher viscous modulus (G''). Whereas, the stronger system with higher complex modulus values (G^*) and improved consistency was obtained with lower mixing speed. The weaker structure obtained at higher speed may be linked with the formation of oil/water droplets due to the structural breakup.

In literature, both lower (A. Patel, Mankoč, Sintang, Lesaffer, & Dewettinck, 2015) and higher (Satapathy et al., 2015) mixing temperatures have been used to prepare bigels. Similarly, two different approaches have been used in literature for storage conditions: (i) storage of bigels after mixing individual phases (F. R. Lupi et al., 2016), or (ii) the storage of individual gels before mixing for certain time (Rehman, Amin, & Zulfakar, 2014). However, the systematic analysis of effect of these parameters on the rheological properties of bigels needs to be done. The pictorial representation of synthesis of bigels by mixing organogel and hydrogel is shown in Fig. 5.

3.2. *Conventional Bigel systems*

The rheological/mechanical properties of a system can be directly linked with their applicability for particular commercial application (Craig & Reading, 2006; Shakeel, Kirichek, & Chassagne, 2019; Shakeel, Mahmood, et al., 2019; Yu, Yan, Han, & Huang, 2013). Different factors (i.e., parameters) have been reported in literature to finely tune the rheological impression of bigels including type of solvent (i.e., oil), hydrogel/organogel ratio, type and structure of hydrogelator, gelators concentration and nature of organogelator (Shakeel, Farooq, et al., 2019). The effect of most important parameters on the properties of bigels are explained as follows.

3.2.1. *Effect of organogel/hydrogel ratio*

The organogel/hydrogel ratio seems to be the most important factor for controlling the rheological behavior of the bigel systems and, therefore, its effect has been extensively studied in literature. Different structural morphologies can be obtained by playing with the organogel/hydrogel ratio (see Fig. 6), which can, in turn, significantly affect the rheological behavior of bigels. The organogel is usually observed to

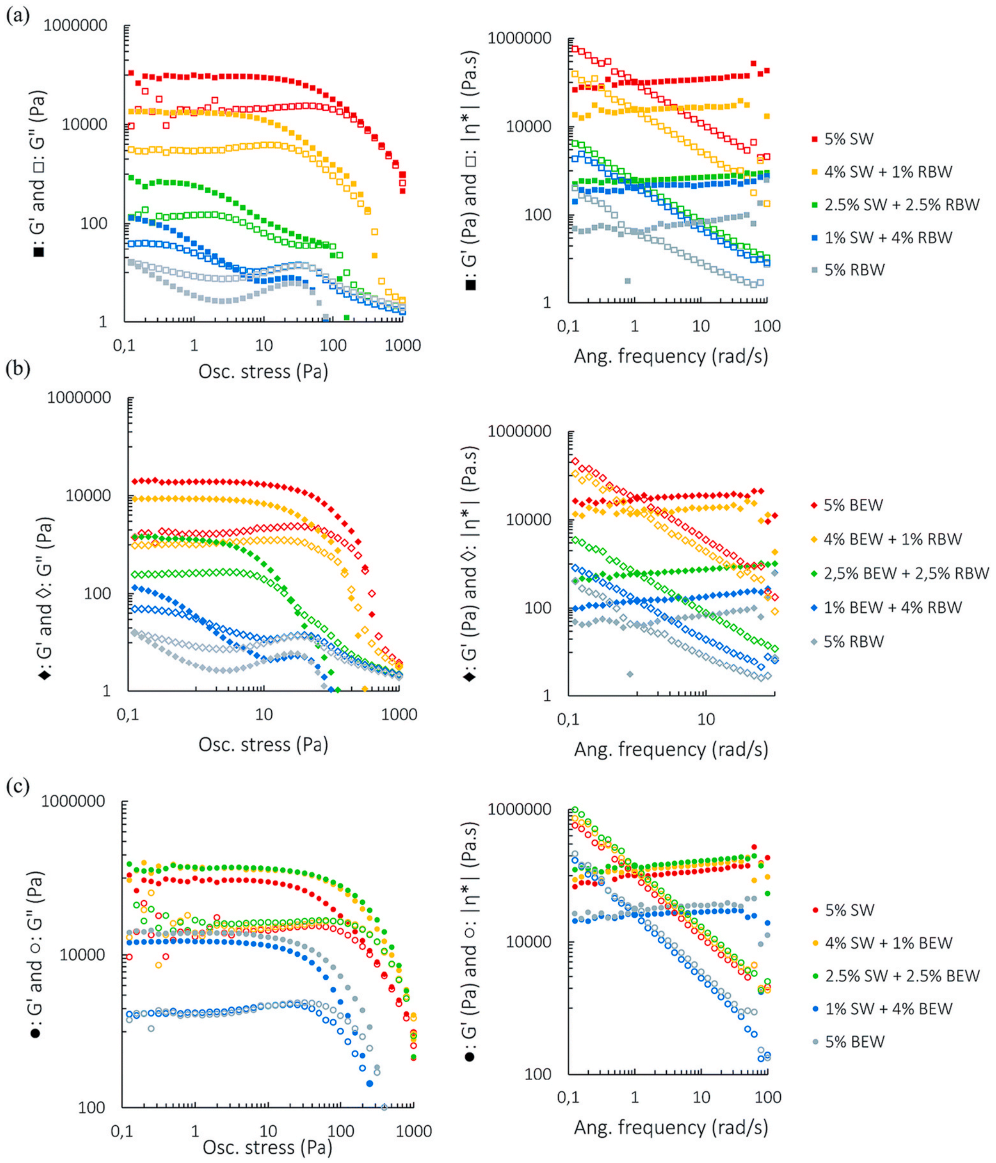

Fig. 4. Oscillatory amplitude sweep (left) and frequency sweep (right) tests performed at 5 °C for 5 wt% binary-wax-based organogels of (a) SW: RBW, (b) RBW: BEW, and (c) SW: BEW. Reprinted with permission from ref. (Tavernier et al., 2017), Copyright [2017], The Royal Society of Chemistry.

impart better properties to the bigel formulations as compared to the hydrogel. The increasing organogel fraction resulted in enhanced thermal stability, smooth texture, higher viscosity and larger yield stress values of bigels (Andonova, Peneva, Georgiev, et al., 2017; Andonova, Peneva, Apostolova, et al., 2017; V. K. Singh, Anis, Al-Zahrani, Pradhan, & Pal, 2014a; V. K. Singh et al., 2014; V. K. Singh, Banerjee, et al., 2014).

The results of frequency sweep tests for pectin/policosanol/olive oil based bigels (F. R. Lupi et al., 2016) showed an increase in complex modulus (G^*) and a decline in phase angle (δ) at 1 Hz as a function of organogel fraction (Fig. 7a). Furthermore, an increase in crossover temperature (where G' crosses G'' in temperature ramp test) as a function of organogel content was also observed for the same system (Fig. 7b). These results verified the enhancement in consistency (i.e., G^*), degree of structuration (i.e., δ) and thermal stability (i.e., T_{cross}) of bigels as a function of increasing organogel fraction.

The other characteristics of bigels which can be manipulated by increasing the organogel content include firmness, cohesiveness, stickiness, adhesiveness and creep recovery (V. K. Singh et al., 2014; V. K. Singh, Banerjee, et al., 2014). The positive effect of organogel fraction on bigels properties is limited to a certain organogel/hydrogel ratio because, after that critical level, system can become hydrogel dominated instead of organogel. For example, a decrease in firmness, adhesivity, spreadability and hardness of bigels was observed after a certain critical concentration of organogel (Kodela et al., 2017; Martins et al., 2019).

There are also few studies which reported the hydrogel dominated behavior of bigels. The results showed an increase in viscosity, consistency, hardness and firmness of bigels with the increase in hydrogel content (Mazurkeviciute, Ramanauskiene, Ivaskiene, Grigonis, & Briedis, 2018; Rehman et al., 2014; Rehman & Zulfakar, 2017; Zulfakar, Chan, Rehman, Wai, & Heard, 2018). However, further research is needed to produce more bigel systems with hydrogel dominated characteristics because of its wide applicability in pharmaceuticals, food and cosmetics. Table 4 summarizes the bigel systems investigated in literature to analyze the effect of organogel/hydrogel ratio on the resultant bigels properties.

Table 3
Different multi-component organogel systems based on natural waxes.

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
Soybean oil	1 Candelilla wax (CW) 2 SMS 3 HPO	6	- HPO crystals facilitated the crystal network of CW and SMS, resulting in denser and stable crystal network	**Moduli** - Pure CW (Total 6 wt%): $G' = 6.9 \times 10^4$ Pa; $G'' = 3.8 \times 10^4$ Pa - Pure SMS (Total 6 wt%): $G' = 1.3 \times 10^1$ Pa; $G'' = 6.5$ Pa - Pure HPO (Total 6 wt%): $G' = 2.1 \times 10^4$ Pa; $G'' = 6.7 \times 10^3$ Pa - CW/SMS: 50/50 (Total 6 wt%): $G' = 1.4 \times 10^3$ Pa; $G'' = 8.4 \times 10^2$ Pa - CW/HPO: 50/50 (Total 6 wt%): $G' = 5.2 \times 10^4$ Pa; $G'' = 2.3 \times 10^4$ Pa - SMS/HPO: 50/50 (Total 6 wt%): $G' = 6.0 \times 10^3$ Pa; $G'' = 1.2 \times 10^3$ Pa - CW/SMS/HPO: 33.3/33.3/33.3 (Total 6 wt%): $G' = 2.4 \times 10^3$ Pa; $G'' = 9.7 \times 10^2$ Pa - CW/SMS/HPO: 66.7/16.6/16.6 (Total 6 wt%): $G' = 4.7 \times 10^3$ Pa; $G'' = 2.3 \times 10^3$ Pa - CW/SMS/HPO: 16.6/66.7/16.6 (Total 6 wt%): $G' = 2.9 \times 10^2$ Pa; $G'' = 1.3 \times 10^2$ Pa - CW/SMS/HPO: 16.6/16.6/66.7 (Total 6 wt%): $G' = 3.7 \times 10^3$ Pa; $G'' = 2.1 \times 10^3$ Pa **Viscosity (@ 25°C and 10 s^{-1})** - Pure CW (Total 6 wt%): 0.66 Pa s - Pure SMS (Total 6 wt%): 0.07 Pa s - Pure HPO (Total 6 wt%): 0.45 Pa s - CW/SMS: 50/50 (Total 6 wt%): 0.44 Pa s - CW/HPO: 50/50 (Total 6 wt%): 1.80 Pa s - SMS/HPO: 50/50 (Total 6 wt%): 0.83 Pa s - CW/SMS/HPO: 33.3/33.3/33.3 (Total 6 wt%): 0.80 Pa s - CW/SMS/HPO: 66.7/16.6/16.6 (Total 6 wt%): 0.75 Pa s - CW/SMS/HPO: 16.6/66.7/16.6 (Total 6 wt%): 0.30 Pa s - CW/SMS/HPO: 16.6/16.6/66.7 (Total 6 wt%): 1.34 Pa s	- The organogel based on CW and HPO showed better thermal stability, low phase angle viscosity and shear thinning behavior, which was attributed to the formation of a structured system. - The incorporation of a third component (i.e., SMS) resulted in reduction of the structuring phenomenon, which was linked with the proportion and gelation mechanism of each gelator. - The results showed an increase in the harness of organogels with the increasing concentration of CW above 4 wt%.	Godoi et al. (2019)
Pomegranate seed oil	1 Beeswax (BW)	5–15	- Propolis wax organogel = needle-like crystals	**Moduli**	- The moduli (G' and G'') and firmness of the propolis wax	Fayaz et al. (2017)

(continued on next page)

Table 3 (*continued*)

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
	2 Propolis wax (PW)		• Beeswax organogel = smaller crystals than PW organogel • Mixed organogel = intermediate behavior • The amount of crystals observed to depend on the concentration of wax	• Pure BW (5–15 wt%): $G' = 5.5 \times 10^4$-1.1×10^6 Pa; $G'' = 1.6 \times 10^4$-2.4×10^5 Pa • Pure PW (5–15 wt%): $G' = 1.9 \times 10^4$-3.6×10^5 Pa; $G'' = 5.0 \times 10^3$-9.2×10^4 Pa • BW/PW: 50/50 (Total 5 wt%): $G' = 3.3 \times 10^4$ Pa; $G'' = 1.1 \times 10^4$ Pa • BW/PW: 50/50 (Total 10 wt%): $G' = 2.4 \times 10^5$ Pa; $G'' = 6.5 \times 10^4$ Pa • BW/PW: 50/50 (Total 15 wt%): $G' = 9.2 \times 10^5$ Pa; $G'' = 2.7 \times 10^5$ Pa **Thermal Analysis (Onset of Crystallization Temperature)** • Pure BW (5–15 wt%): 46.64–53.02 °C • Pure PW (5–15 wt%): 43.64–50.30 °C • BW/PW: 50/50 (Total 5 wt%): 45.25 °C • BW/PW: 50/50 (Total 10 wt%): 50.04 °C • BW/PW: 50/50 (Total 15 wt%): 52.38 °C	based organogels were lower than the beeswax organogels, which was attributed to the existence of larger crystals along with the disordered network. • The mixed organogels, however, displayed an intermediate behavior of the individual gels, which was linked with the formation of mixed crystal network.	
Soybean oil	1 Beeswax (BW) 2 Rice bran wax (RBW) 3 Sunflower wax (SFW)	2.5	• All the organogels showed needle-shaped crystals	**Moduli** • Pure SFW (Total 2.5 wt%): $G' = 2.0 \times 10^4$ Pa; $G'' = 4.0 \times 10^3$ Pa • Pure BW (Total 2.5 wt%): $G' = 1.0 \times 10^2$ Pa; $G'' = 1.2 \times 10^1$ Pa • Pure RBW (Total 2.5 wt%): $G' = 2.5 \times 10^4$ Pa; $G'' = 3.5 \times 10^3$ Pa • SFW/BW: 50/50 (Total 2.5 wt%): $G' = 1.5 \times 10^4$ Pa; $G'' = 1.2 \times 10^3$ Pa • RBW/BW: 50/50 (Total 2.5 wt%): $G' = 3.0 \times 10^4$ Pa; $G'' = 3.0 \times 10^3$ Pa • RBW/SFW: 50/50 (Total 2.5 wt%): $G' = 7.0 \times 10^4$ Pa; $G'' = 2.0 \times 10^4$ Pa	• The organogels based on rice bran wax displayed the highest storage modulus values followed by sunflower wax based organogels and beeswax organogels. • The mixed organogels composed of rice bran wax and sunflower wax showed higher storage modulus (i.e., more solid-like behavior) than the other prepared organogels.	Jana and Martini (2016)
Soybean oil	1 Candelilla wax (CLW) 2 Triacylglycerols	5	• All the organogels displayed microplatelet-shaped crystals • The amount of crystals observed to depend on the concentration of hardfat	**Moduli** • Pure CLW (Total 5 wt%): $G' = 1.5 \times 10^5$ Pa; $G'' = 2.5 \times 10^4$ Pa • CLW/HCr: 50/50 (Total 5 wt%): $G' = 6.5 \times 10^4$ Pa; $G'' = 9.0 \times 10^3$ Pa	• The mixed organogels (i.e., based on wax and palm hardfat) showed similar storage modulus values and oil loss as observed for the candelilla wax based organogels, only by adding small amount of palm hardfat (i.e., wax/hardfat = 0.75/0.25 or 0.5/0.5) • In case of soybean hardfat, this similarity in properties of mixed	da Silva, Arellano, and Martini (2019)

(*continued on next page*)

Table 3 (*continued*)

Oil Phase	Gelling Agents	Total Concentration of Gelling Agents (wt%)	Morphology	Key Rheological Parameters	Key Findings	Ref.
				• CLW/HPl: 50/50 (Total 5 wt%): $G' = 6.0 \times 10^4$ Pa; $G'' = 9.9 \times 10^3$ Pa • CLW/HPk: 50/50 (Total 5 wt%): $G' = 2.5 \times 10^4$ Pa; $G'' = 5.0 \times 10^3$ Pa • CLW/HSb: 50/50 (Total 5 wt%): $G' = 1.2 \times 10^4$ Pa; $G'' = 3.5 \times 10^3$ Pa	gels was observed only for the ratio of 0.75/0.25 (i.e., wax/hardfat). • On the other hand, palm kernel hardfat did not present any interaction with the wax, which was attributed to the different composition of this particular hardfat.	
Soybean oil	1 Beeswax (BW) 2 Sunflower Wax (SFW) 3 Candelilla Wax (CLW)	5	• Candelilla wax organogel = randomly oriented platelets of about 5 μm • Beeswax organogel = loosely arranged larger platelets of about 30–50 μm • Sunflower wax organogel = larger platelets of about 30–50 μm	**Firmness/Hardness** • Pure SFW (Total 5 wt%): 0.13 g • Pure BW (Total 5 wt%): 0.18 g • Pure CLW (Total 5 wt%): 0.27 g • CLW/BW: 40/60 (Total 5 wt%): 0.45 g • SFW/BW: 50/50 (Total 5 wt%): 0.08 g • SFW/CLW: 70/30 (Total 5 wt%): 0.02 g • SFW/CLW: 10/90 (Total 5 wt%): 0.44 g **Thermal Analysis (Onset of Crystallization Temperature)** • Pure SFW (Total 5 wt%): 63.24 °C • Pure BW (Total 5 wt%): 47.27 °C • Pure CLW (Total 5 wt%): 44.10 °C • CLW/BW: 40/60 (Total 5 wt%): 41.08 °C • SFW/BW: 50/50 (Total 5 wt%): 58.04 °C • SFW/CLW: 70/30 (Total 5 wt%): 59.50 °C • SFW/CLW: 10/90 (Total 5 wt%): 42.50 °C	• The organogels based on the mixture of sunflower wax and beeswax displayed lower firmness as compared to the individual organogels, which indicated the incompatibility between these two waxes. • Similarly, mixed organogels based on sunflower and candelilla waxes exhibited lower firmness as compared to the individual gels, by adding smaller amounts of candelilla wax (90:10 to 60:40, SFW: CLW). • The highest firmness was obtained with the mixed organogels of sunflower and candelilla waxes with the ratio of 10:90 (SFW: CLW), which was attributed to the changes in crystal morphology and size.	Winkler-Moser et al. (2019)

SMS = Sorbitan monostearate; HPO = Hydrogenated palm oil; HCr = Crambe fat; HPl = Palm fat; HPk = Palm kernel fat; HSb = Soybean fat.

3.2.2. *Effect of organogelator/hydrogelator type*

Apart from organogel/hydrogel ratio, the rheological and mechanical properties of bigels can also be significantly influenced by the nature of hydrogelator (gelling agent for water phase). Several authors reported the effect of different hydrogelators on the resultant properties of bigels. The branched polysaccharides imparted better gel strength, higher firmness, improved resistance to deformation and higher critical stress values required to break the structure of bigels, as compared to the linear polysaccharides. The results of frequency sweep tests also showed the improved elastic character (higher storage modulus values) of bigels based on branched polysaccharides (Beauty Behera et al., 2014). The improved properties in branched polysaccharides based bigels were linked with the increased entanglements of polymeric chains.

The comparative analysis of the effect of different natural gums (i.e., hydrogelator) on the rheological/mechanical characteristics of bigels was also investigated. Guar gum based bigels showed higher values of critical strain, improved strength and firmness as compared to the acacia gum and xanthan gum based bigels (B Behera, Dey, et al., 2015; Sahoo et al., 2015). The strong interaction between organogelator and hydrogelator molecules was responsible for the better rheological and mechanical properties of guar gum based bigels.

There are few more studies as well which compared the properties of bigels prepared from different hydrogelators. For example, sodium alginate based bigels showed higher viscosity, improved hardness and larger peak stress values as compared to the hydroxy propyl methyl cellulose (HPMC) based bigels (Rehman et al., 2014). The better mechanical properties were also reported for the polyvinyl alcohol (PVA) based bigels as compared to the polyvinyl pyrrolidone (PVP) based bigels, which were attributed to the higher molecular weight of the polymer (PVA) which resulted in more compact structure (B Behera, VK Singh et al., 2015). Likewise, whey protein based bigels displayed better thermal stability as compared to the gelatin based bigels whereas the

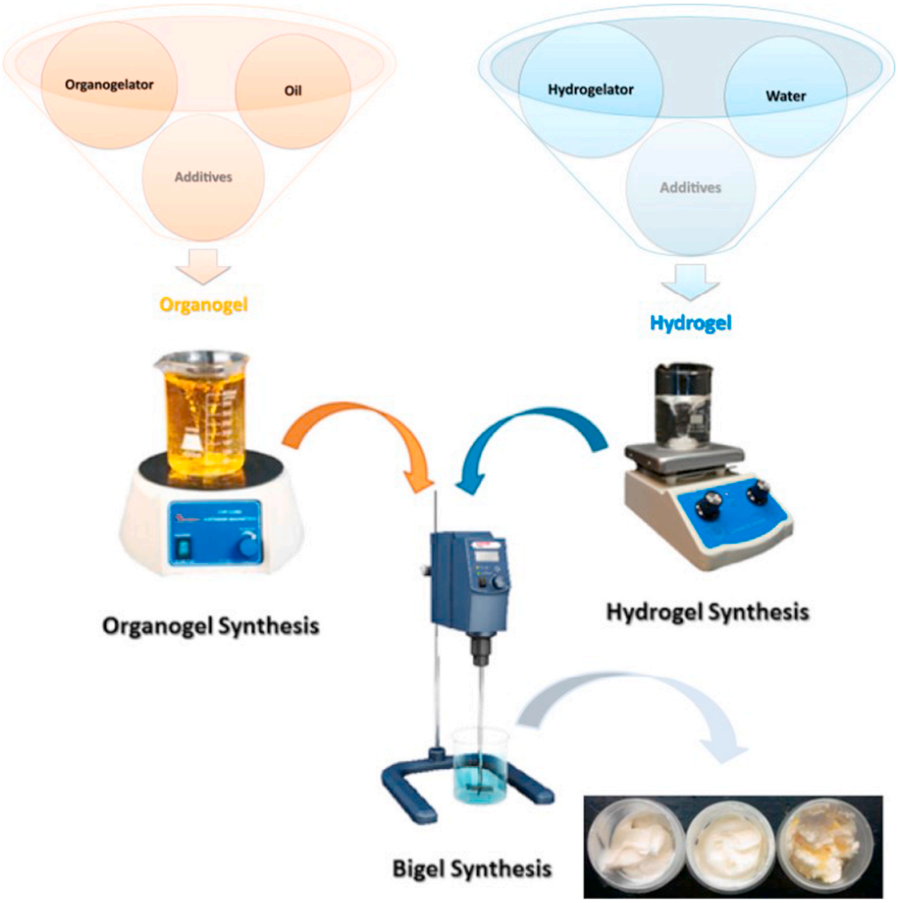

Fig. 5. Pictorial representation of synthesis of bigels by mixing organogel and hydrogel. Reprinted with permission from ref. (Shakeel, Farooq, et al., 2019), Copyright [2019], Elsevier.

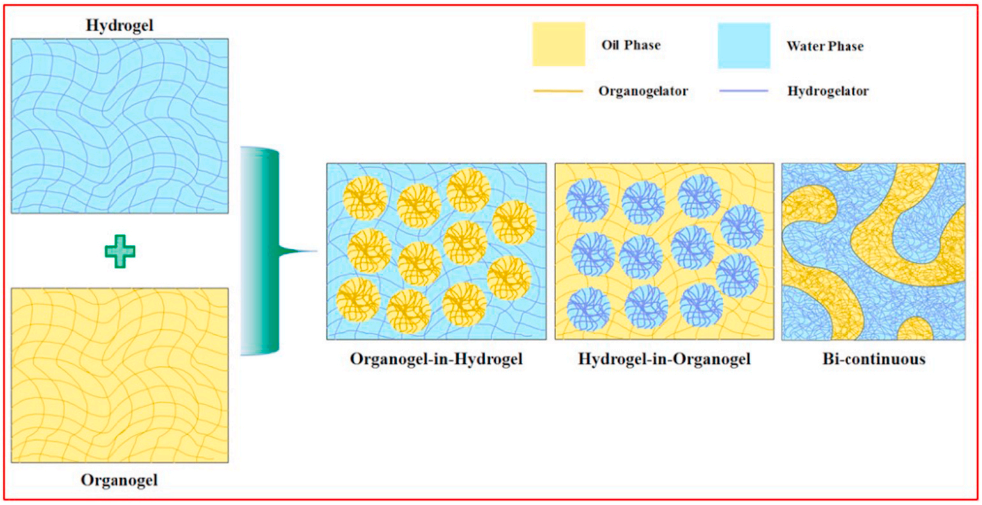

Fig. 6. Schematic representation of different conventional bigels obtained by varying organogel/hydrogel ratio.

gelatin based bigels revealed improved spreadability and stickiness (Behera, Sagiri, et al., 2015).

Though several organogelators have been reported in literature to prepare bigels (Shakeel, Farooq, et al., 2019), yet, the influence of different organogelators on the resultant properties of bigels has not much investigated in literature. One study compared the properties of the bigels prepared from cetyl alcohol or span 60 (i.e., organogelator) with or without the addition of different surfactants (span 80, tween 20 and tween 80) (Ibrahim, Hafez, & Mahdy, 2013). The results revealed an increase in the viscosity of the bigels with the addition of surfactants.

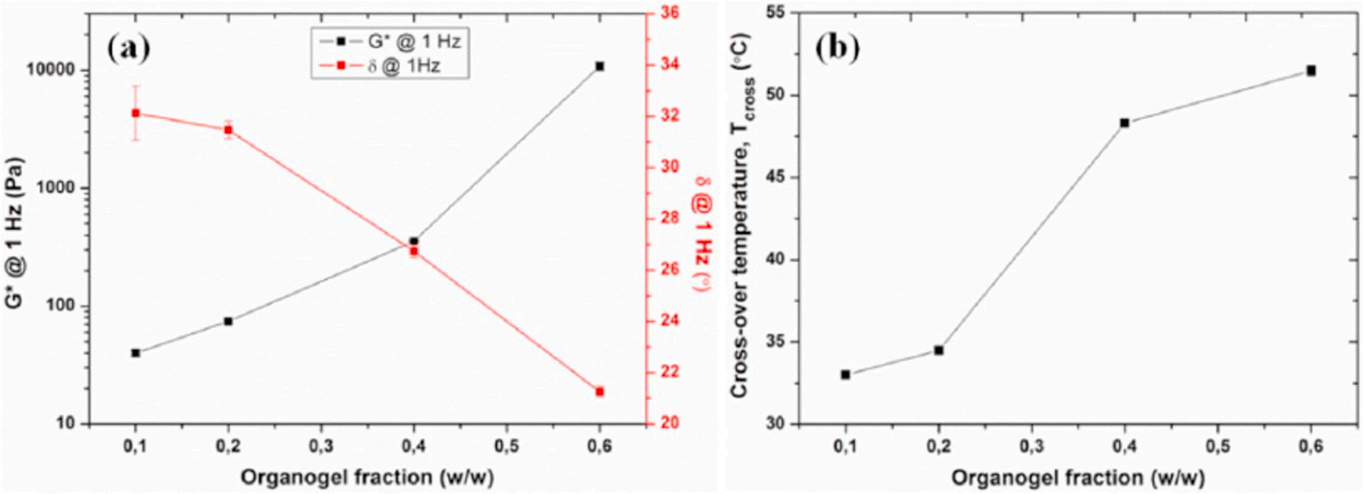

Fig. 7. (a) Complex modulus (G^*) and phase angle (δ) at 1 Hz, and (b) cross-over temperature (T_{cross}) (where G' crosses G'' in temperature ramp test) as a function of organogel fraction for pectin/policosanol/olive oil based bigels, (bars represent standard deviation and the solid line is just a guide for the eye). Frequency sweep tests were performed at 25 °C and temperature ramp tests were performed at a heating rate of 1 °C/min from 10 to 70 °C. Adapted with permission from ref. (F. R. Lupi et al., 2016), Copyright [2016], Elsevier.

Table 4

Different bigel systems investigated in literature to analyze the effect of organogel/hydrogel ratio.

Solvent	Gelling agent		Total Gelling agent concentration (wt%)	Organogel/hydrogel ratio (wt/wt)	Ref.
	Oil phase	Water phase			
Sesame oil	Span 60	Guar gum	2.5–5.7; 4.8–5.6	11.1/88.9–33.3/66.7	V. K. Singh et al, (2014); V. K. Singh, Banerjee, et al, (2014)
Sesame oil	Span 60	Carbopol	2.5–5.7	11.1/88.9–33.3/66.7	V. K. Singh et al, (2014)
Almond oil	Span 60	Carbopol	5.2; 3.8–6.6	20/80–40/60	Andonova, Peneva, Georgiev, et al. (2017); Andonova, Peneva, Apostolova, et al. (2017)
Liquid paraffin	PE[b]	Poloxamer 407[b]	32.2–54.7[a]	10/90–50/50	Mazurkeviciute et al. (2018)
Olive oil	SMP	SpAAm	–	5/95–25/75	B. Singh & Kumar (2019)
Extra virgin olive oil	MGFAs	Potato starch	4.8–7.3	28.6/71.4–44.9/55.1	F. Lupi et al, (2015)
Vegetable oil	Beeswax	Sodium alginate	2–4	50/50–99/1	Martins et al. (2019)
Fish oil	Beeswax	Carbopol	3.7–6.5	50/50–90/10	Rehman & Zulfakar (2017); Zulfakar et al, (2018)
Rice bran oil	Stearyl alcohol	Agar	2.4–6.5	12.5/87.5–50/50	Kodela et al. (2017)
Rice bran oil	Stearic acid	Tamarind gum	4.2–5.4	40/60–80/20	Paul et al. (2018)
Corn oil	GMS	κ-carrageenan	6.1–15.4	25/75-75/25	Zheng, Mao, Cui, Liu, and Gao (2020)

PE = Polyethylene; SMP = Sorbitan monopalmitate; SpAAm = Sterculia-cl-poly(AAm); MGFAs = Monoglycerides of fatty acids; GMS = Glyceryl monostearate.

[a] Including the weight fraction of oil as well.

[b] Not suitable for food applications.

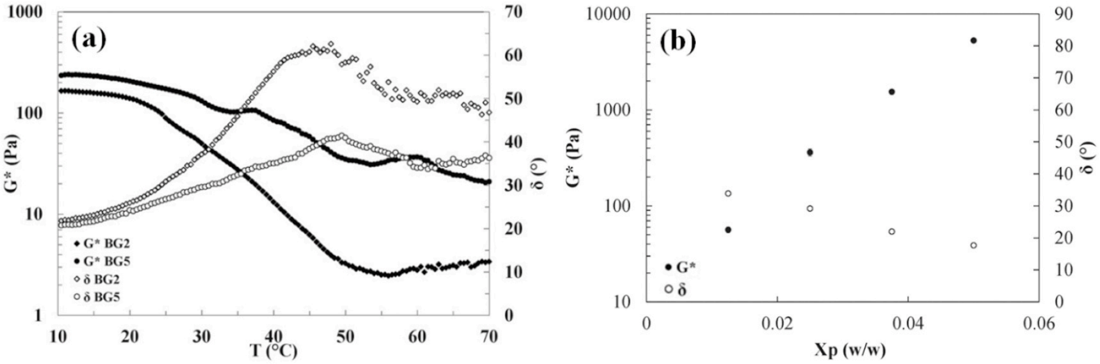

Fig. 8. (a) Complex modulus (G^*) and phase angle (δ) at 1 Hz as a function of temperature obtained at a heating rate of 1 °C/min for pectin/policosanol/olive oil based bigels with 5 wt% organogelators (BG2) and 10 wt% organogelators (BG5), reprinted with permission from ref. (F. R. Lupi et al., 2016), Copyright [2016], Elsevier, (b) complex modulus (G^*) and phase angle (δ) at 1 Hz and 25 °C as a function of hydrogelator (pectin) concentration for pectin/policosanol/olive oil based bigels, reprinted with permission from ref. (Francesca R Lupi, De Santo, et al., 2017), Copyright [2017], Springer Nature.

Another study reported the production of smooth and homogenous bigel systems using cholesterol or span 60 as organogelator while the other two organogelators (zinc stearate or silicic acid) resulted in non-smooth and heterogeneous bigel systems (Almeida et al., 2008). Further research is needed to perform a systematic comparative analysis of the effect of different organogelators on the rheological properties of bigels, in order to formulate bigel systems with enhanced properties for different commercial applications.

3.2.3. *Effect of organogelator/hydrogelator concentration*

There are very few studies which investigated the rheological properties of bigels as a function of organogelator or hydrogelator content. It is usually observed that the rheological properties of bigels can be enhanced by increasing organogelator/hydrogelator content (F. R. Lupi, De Santo, et al., 2017). For example, an increase in consistency (i.e., higher G^* values) and degree of structuration (i.e., lower δ values) was observed by increasing the organogelator amount in pectin/policosanol/olive oil based bigels (F. R. Lupi et al., 2016). The temperature ramp tests revealed the improved thermal stability of bigels (i.e., dominated elastic character even at higher temperatures by having phase angle (i.e., δ) lower than 45°) with higher organogelator fraction (Fig. 8a). Francesca R Lupi, De Santo, et al, (2017) also investigated the influence of hydrogelator content on the rheological properties of same bigel system. The improved consistency and degree of structuration was obtained by increasing the hydrogelator (pectin) content (Fig. 8b). The authors reported that the effect of varying hydrogelator content was more pronounced on the rheological characteristics of bigels as compared to the organogelator amount, for the considered system. The hydrogelator content was also observed to influence the viscosity, stickiness, firmness, hardness, spreadability and resistance to deformation of bigels (B Behera, VK Singh et al., 2015; Martín-Illana, Notario-Pérez, Cazorla-Luna, Ruiz-Caro, & Veiga, 2019). However, extensive studies are still required to investigate the rheological properties of bigels by varying the organogelator and hydrogelator content, in order to develop an appropriate model for the rheological fingerprint of bigels. Table 5 presents the bigel systems investigated in literature to analyze the effect of nature and concentration of organogelator or hydrogelator.

3.3. *Unconventional Bigel systems*

Apart from conventional bigel systems, usually obtained by mixing mono-component organogel and hydrogel phases, there are some studies which reported the synthesis of unconventional bigel systems (F. Lupi et al., 2015; A. Patel et al., 2015; Shakeel, Farooq, & Chassagne, 2020; Wakhet et al., 2015). These unconventional systems resulted in enhanced technological and functional outputs. Few examples of these interesting approaches are explained as follows.

3.3.1. *Multi-component organogel/hydrogel based bigels*

Instead of mono-component (i.e., mono-gelator) organogel and hydrogel, multi-component individual phases have also been used to produce bigel systems with technological enhancement. Fig. 9 shows the schematics of the bigels prepared by using multi-component organogel or hydrogel. For example, mixture of glyceryl monostearate and policosanol (fatty alcohol mixture) was used as organogelator to prepare bigels (Francesca R Lupi, De Santo, et al., 2017; F. R. Lupi et al., 2016). Glyceryl monostearate was incorporated as an emulsifier but it also acted as an organogelator, which is described in another study (Francesca R. Lupi, De Santo, et al., 2017). The results showed that the rheological properties of multi-component organogel/bigel was primarily controlled by policosanol instead of glyceryl monostearate.

Recently Bollom, Clark, & Acevedo (2020) reported the synthesis of bigels using mixture of soy lecithin and stearic acid as organogelator for food applications. The authors also investigated the influence of hydrogel/organogel ratio, hydrogelator content and water content in oil phase (oleogel emulsion) on the rheological impression of bigels. The results showed the existence of shear sensitive structure (i.e., lower value of critical strain) in organogel phase which was attributed to the presence of soy lecithin (70% of organogelator content). The preparation of bigels using multi-component hydrogel has also been reported in literature. Wakhet et al, (2015) studied the properties of bigels prepared by using organogel and a co-hydrogel (phase separated mixture of agar and gelatin). The authors compared the characteristics of organogels, emulgels and bigels. Table 6 presents the bigel formulations prepared by using multi-component organogel or hydrogel, in literature.

In short, bigel systems with enhanced rheological properties, covering wide range of applications, can be produced by employing multi-component hydrogel or organogel. Therefore, further research should be directed towards the development of bigel systems using multi-component individual phases.

3.3.2. *Emulsion gel based bigels*

In addition to the conventional hydrogel and organogel systems, complex individual phases such as organogel emulsion or hydrogel

Table 5

Different bigel systems investigated in literature to analyze the effect of nature and concentration of organogelator or hydrogelator.

Solvent	Gelling agent		Total Gelling agent concentration (wt%)	Ref.
	Oil phase	Water phase		
Effect of type of organogelator/hydrogelator				
Sunflower oil	Span 40	Gelatin, Whey protein	10	Behera, Sagiri, et al. (2015)
Sunflower oil	Span 40	Guar gum, Acacia gum, Xanthan gum	9.6	Behera, Dey, Sharma, & Pal, (2015)
Sunflower oil	Tween 80, Span 80	Guar gum, Acacia gum	40.3	Sahoo et al. (2015)
Sunflower oil	Span 40	NaCMC, Sodium alginate, Starch, Maltodextrin	9.5	Beauty Behera et al, (2014)
Sunflower oil	Span 40	PVP[a], PVA[a]	10–14	B Behera, VK Singh et al, (2015)
Fish oil	Beeswax	Sodium alginate, HPMC	3.7–6.5	Rehman et al. (2014)
Sweet almond oil, Liquid paraffin	Cholesterol, Span 60, Zinc stearate, Silicic acid	Carbopol	0.8–2.5	Almeida et al. (2008)
Soya-bean oil	Span 60, Cetyl alcohol	HPMC	10	Ibrahim et al. (2013)
Effect of concentration of organogelator/hydrogelator				
Sesame oil	Span 60	Pectin, chitosan, HPMC	6.8–8.8	Martín-Illana et al. (2019)
Sunflower oil	Span 40	PVP[a], PVA[a]	10–14	B Behera, VK Singh et al, (2015)
Extra virgin olive oil	Mixture of policosanol and GMS	LM pectin	3.63–15.5	F. R. Lupi et al, (2016)
Virgin olive oil	Mixture of policosanol and GMS	LM pectin	4–16	Francesca R Lupi, De Santo, et al, (2017)

NaCMC = Sodium carboxy methyl cellulose; PVP = Polyvinyl pyrrolidone; PVA = Polyvinyl alcohol; HPMC = Hydroxy propyl methyl cellulose; GMS = Glyceryl monostearate; LM = Low methoxyl.

[a] Not suitable for food applications.

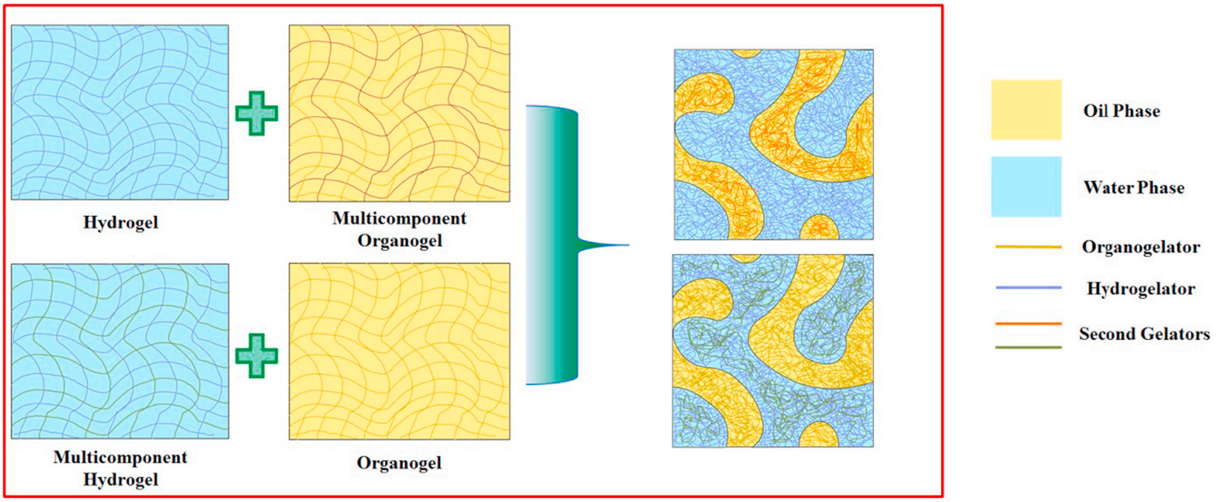

Fig. 9. Schematic representation of unconventional bigel systems obtained by using multi-component organogel or multi-component hydrogel.

Table 6
Different bigel systems investigated in literature prepared by using multi-component organogel or multi-component hydrogel.

Solvent	Gelling agent		Total Gelling agent concentration (wt%)	Ref.
	Oil phase	Water phase		
Multi-component organogel based bigels				
Isopropyl palmitate	Mixture of soy lecithin and pluronic	HPMC	9.8–13.5	Charyulu, Muaralidharan, and Sandeep (2018)
Extra virgin olive oil	Mixture of policosanol and GMS	LM pectin	3.63–15.5	(F. R. Lupi et al., 2016)
Virgin olive oil	Mixture of policosanol and GMS	LM pectin	4–16	(Francesca R Lupi, De Santo, et al., 2017)
Soy bean oil	Mixture of soy lecithin and stearic acid	Whey protein	15.3–20.1	Bollom et al. (2020)
Multi-component hydrogel based bigels				
Sunflower oil	Hydrophilic fumed silica[a]	Mixture of LBG and Carrageenan	9.4–13.6	(A. Patel et al., 2015)
Soya-bean oil	Stearic acid	Mixture of Agar and Gelatin	12	Wakhet et al. (2015)

HPMC = Hydroxy propyl methyl cellulose; GMS = Glyceryl monostearate; LBG = Locust bean gum; LM = Low methoxyl.
[a] Not suitable for food applications.

emulsion have also been reported to synthesize distinctive bigel formulations. Fig. 10 shows the schematics of the bigels prepared by using organogel emulsion or hydrogel emulsion. F. Lupi et al, (2015) studied the characteristics of bigels prepared by mixing cosmetic emulsion (hydrogel emulsion) with the organogel phase. The authors reported the transition from oil-in-water type morphology to a complex bi-continuous morphology along with the variation in the consistency of the system, as a function organogel/hydrogel ratio. The prepared formulations were also thermally stable (no cross-over between $G^{'}$ and $G^{''}$) for the whole investigated range of temperature (25-70°C), as evident by the values of loss tangent (i.e., <1). This characteristic behavior was associated with the non-thermoreversible nature of hydrogelator (i.e., potato starch).

Recently, an interesting study has been reported on bigels, produced by combining organogel emulsion and hydrogel phases (Bollom et al., 2020). The characteristics of the prepared formulations were tuned by varying the organogel/hydrogel ratio, hydrogelator content and water content in the organogel emulsion phase. Bigels showed better rheological properties (i.e., higher critical strain required to break the structure) by having larger content of hydrogel. Likewise, an increase in storage modulus and yield stress (6 and 10 times, respectively) of the bigel samples was observed by increasing the hydrogelator content from 15 wt% to 25 wt%. Regarding the effect of water content, a positive influence was observed on the rheology of organogel emulsion while no obvious trends were evident in case of bigel systems. The structural distribution of individual phases was also manipulated (i.e., transition between O/W, W/O and bi-continuous type morphologies) by playing with the organogel/hydrogel ratio.

These systems present an interesting approach (i.e., combination of structured and unstructured phases in a stable system) to modulate the technological features particularly the rheological impression of bigel formulations. Therefore, further research is required to elucidate the clear influence of each component (particularly unstructured oil/water phase) on the rheological properties of bigels.

3.3.3. Colloidal particles based bigels

Another intriguing approach to produce bigel systems was reported by A. Patel et al, (2015). Instead of using low-molecular-weight or polymeric gelators, the authors reported the structuration of oil phase using hydrophilic colloidal silica particles. The authors analyzed the effect of organogel/hydrogel ratio on the resultant properties of the bigels. The results revealed a synergistic enhancement in viscosity (Fig. 11a) and complex modulus (Fig. 11b) of bigel formulations as compared to the individual phases. However, the structural recovery in

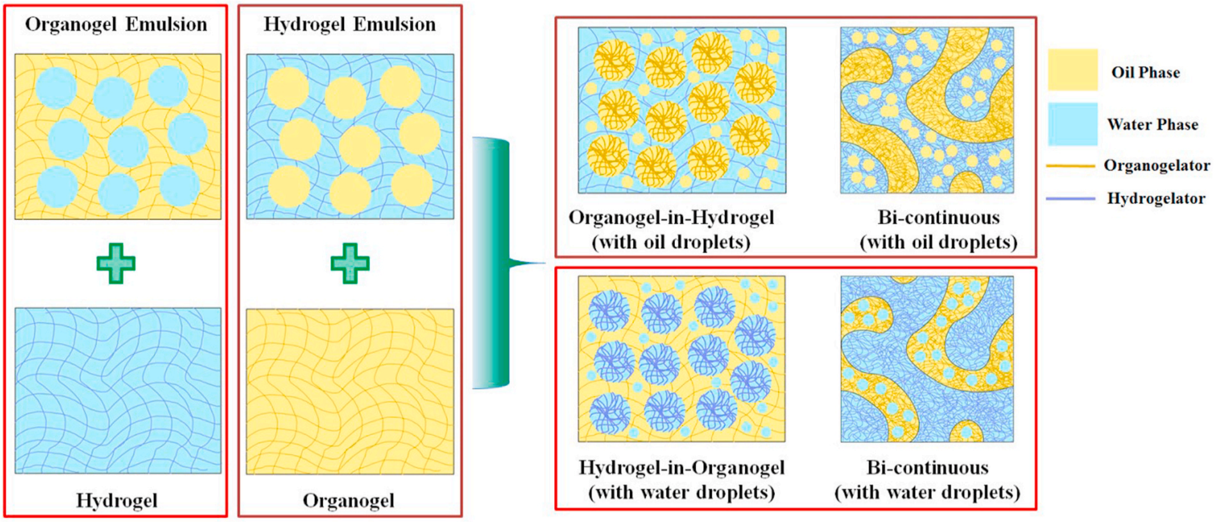

Fig. 10. Schematic representation of unconventional bigels obtained by using organogel emulsion or hydrogel emulsion.

bigels was much lower than the organogel. During the temperature ramp-up test, an increase in storage modulus was also observed, which was attributed to the interactions between the colloidal particles and polymeric chains of hydrogelators (mixture of locust bean gum and carrageenan). This was the first study where the bigel formulations displayed even better properties than the individual phases (i.e., organogel and hydrogel). Fig. 12a shows the schematics of the bigels prepared by using colloidal particles to structure the oil phase.

Recently, a further enhancement in the rheological characteristics of bigel formulations was reported in literature by using silica nanoparticles to stabilize the interface of structured oil and water phases (Shakeel et al., 2020). The authors compared the rheological fingerprint of different formulations including hydrogel, organogel, pickering emulsion (unstructured oil and water phases with nanoparticles), conventional bigel (structured oil and water phases without nanoparticles), hydrogel pickering emulsion (unstructured oil and structured water phases with nanoparticles), organogel pickering emulsion (structured oil and unstructured water phases with nanoparticles) and nanoparticles based bigels (structured oil and water phases with nanoparticles). The results showed the synergistic enhancement in the complex modulus (i.e., consistency) of nanoparticle based bigels as compared to the conventional systems, which was attributed to the bulk stabilization of the system with polymeric gelators and the interfacial stabilization with the help of nanoparticles. The authors proposed that the investigated approach can also be used to prepare dual stabilized bijel formulations (bi-continuous structured O/W system with interfacial stabilization by nanoparticles) (Fig. 12b). Although, the colloidal particles used in both studies were not food grade but the knowledge acquired can further be applied to produce bigel systems with bio-based colloidal materials, as these are extensively used for food applications.

In summary, conventional bigel systems have been thoroughly investigated in literature as a function of several parameters including organogel/hydrogel ratio and type of hydrogelator, in order to tune the rheological parameters of the resultant bigel systems. However, a systematic analysis is still missing to analyze the effect of type and content of gelators, apart from organogel/hydrogel ratio. This systematic analysis will also provide a base for developing a rheological model to predict the rheological fingerprint of these complex systems. Unconventional bigel systems, on the other hand, opens up new possibilities of improving the technological features of the conventional bigels. Therefore, extensive research is required to unleash their potential for different commercial applications particularly drug delivery and food systems. Fig. 13 presents the summary of different conventional and unconventional approaches to produce bigel systems with distinguished rheological characteristics.

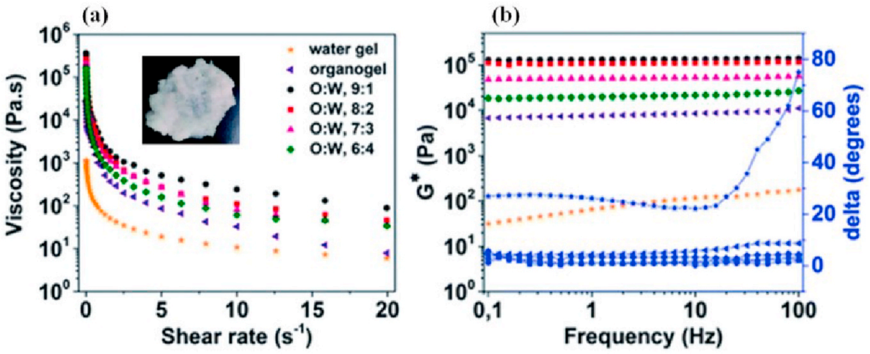

Fig. 11. (a) Viscosity as a function of shear rate and (b) complex modulus (G^*) and phase angle (delta) as a function of frequency for organogel, hydrogel and bigels with different organogel/hydrogel ratio, reprinted with permission from ref. (A. Patel et al., 2015), Copyright [2015], The Royal Society of Chemistry.

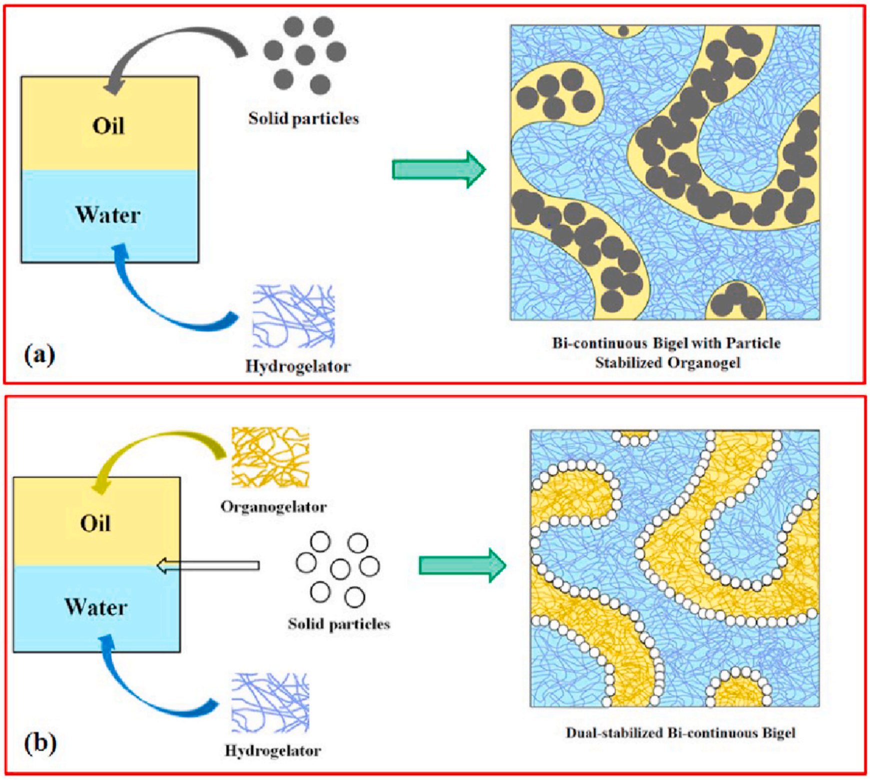

Fig. 12. Schematic representation of unconventional bigels obtained by: (a) mixing hydrogel and solid particles stabilized organogel, (b) interfacially stabilizing conventional bigels with solid particles (dual stabilization), adapted from ref. (Shakeel et al., 2020).

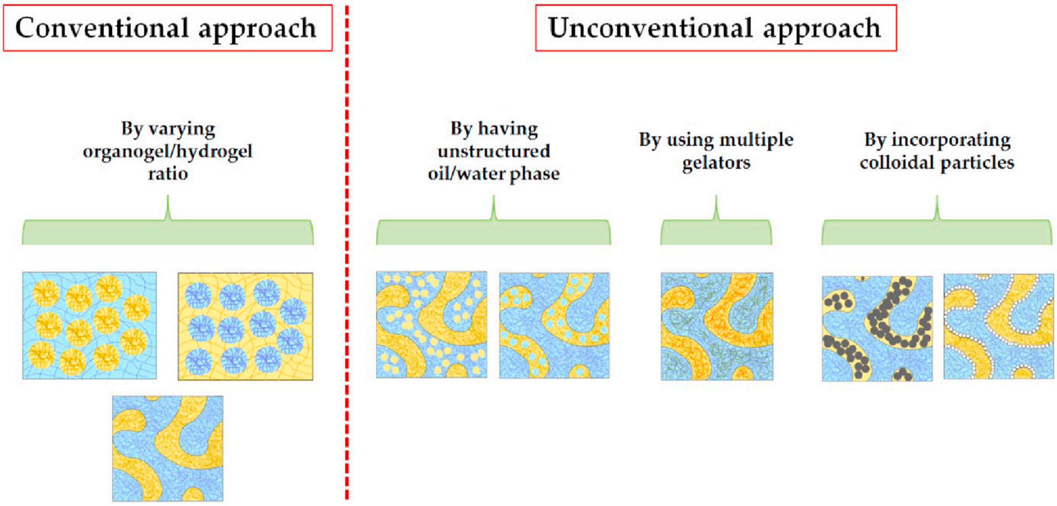

Fig. 13. Schematic representation of conventional and unconventional approaches to formulate different bigel systems.

4. Conclusion and future perspective

In recent times, different multi-component organogel systems have been prepared and fine-tuned according to the requirements of particular applications. The literature presented in this review article clearly shows that there are numerous studies which displayed the existence of synergistic interactions between different gelators in multi-component organogels. This synergy also helps in optimizing the rheological signature of final system by exploiting the concept of formulation engineering. However, a thorough investigation of self-sorting and co-assembly behaviors of gelling agents in multi-component systems may reveal new synergistic combinations of structuring agents and also bridge the gaps between the fundamental and commercial design of multi-component organogels.

Bigel (i.e., a hybrid system of organogels) belongs to an emerging class of soft materials and, therefore, extensively investigated in the past few years. The synthesis parameters of bigels, i.e., storage and mixing temperatures, can significantly alter the rheological properties of the system, which needs further attention from the researchers. Furthermore, the potential of synergistic interactions between different components has not yet been explored in the field of bigels, which presents an interesting area of research for future work. There are only few studies in literature which presented the superior rheological characteristics of bigels, as compared to the individual gels, by using colloidal (nano)particles. This exciting approach can further be investigated in future to exploit the benefits of (nano)particles, in addition to the polymeric gelators, for producing efficient commercial systems particularly for food applications.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

CRediT authorship contribution statement

Ahmad Shakeel: Conceptualization, Investigation, Writing - original draft. **Ujala Farooq:** Writing - review & editing, Visualization. **Domenico Gabriele:** Conceptualization, Supervision, Writing - review & editing. **Alejandro G. Marangoni:** Writing - review & editing. **Francesca R. Lupi:** Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2020.106190.

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