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Olive oil and hyperthermal water bigels for cosmetic uses

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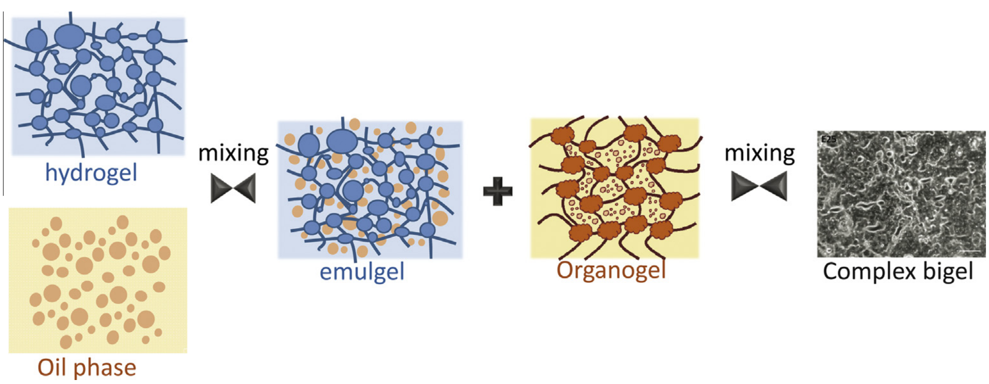
GRAPHICAL ABSTRACT



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ABSTRACT

Bigels are biphasic systems produced with an organogel (or oleogel) and a hydrogel mixed together at high shear rates. These systems are promising for different uses, among them the formulation of new cosmetic matrices for cosmetic agents delivery is under investigation. In the present paper, a common cosmetic formulation for skin care was enriched with increasing fractions of monoglycerides of fatty acids/olive oil organogels, in order to understand the rheology and the microstructure of these systems. Small amplitude oscillation tests, NMR-self diffusion analysis, contrast phase microscopy and electric conductivity confirmed that the addition of the organogel caused a microstructural change of the starting material, which turned from O/W to a more complex system where, probably, a matrix-in-matrix structure is present at the highest fractions of added organogel.

1. Introduction

Structured two-phase systems are used in a great variety of industrial fields (food, cosmetic, pharmaceutical) owing to their peculiar properties coming from the presence of two different phases (usually a lipophilic and a hydrophilic ones) and to the possibility of finely tuning the consistency of the final product by modifying both the consistency of the single phases and their

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relative amount. Different systems can be obtained, according to the structure level of the single phases. When only the continuous phase is structured these systems are, usually, named "emulgels" or "filled gels" to take into account both the emulsion-like behaviour of these materials and the relevant role played by the solid-like dispersing phase [1–5]. When only the internal phase is gelled they behave mainly like suspensions made of soft (and deformable) particles with a maximum packing fraction according to the particle rheological properties [6]. When both phases are structured a more complex behaviour, according to the properties of both phases, is observed and the systems can be classified as "bigels" or "biphasic gels" [5,7,8]. Emulgels and bigels are particularly interesting owing to their potential use in the cosmetic and pharmaceutical area because they can merge the advantages of emulsions and gels (both hydrogels and organogels) to control drug delivery for topical and transdermal use [5].

In the case of cosmetic formulations, in particular face and body/skin care creams, all the mechanical and textural properties requested by consumers should be guaranteed by manufacturers. In the light of this, these materials have to be humectant, emollient, skin softeners and, often, a carrier for active ingredients (antioxidants, vitamins, colouring agents or pigments) which should permeate through the skin [9]. In addition, in order to meet consumers' preference they should ensure specific rheological properties i.e. smoothness, thickness but also spreadability, often influenced by the texture of the product [10]. Another very important characteristic of cosmetic preparations is high storage stability, which has to be maintained over several months or, in some cases, years [11]. In fact, cosmetic products such as lotions or creams are formed by two immiscible phases, one polar (the aqueous phase) and the other one nonpolar (the oil phase). According to their different physical and chemical properties, biphasic systems can incur phases instability such as creaming, coalescence, flocculation, sedimentation, Ostwald ripening, and phase inversion [12]. The modification of the mechanical properties of both the aqueous and the oil phase (by thickening and/or gelation) is, therefore, necessary for improving the spreadability and the smoothness of the cream and, on the other hand, for enhancing its storage stability. In fact, owing to the difficulty of droplets to move easily through the three-dimensional network of the gel, they cannot aggregate or flocculate, stabilizing the system.

Bigels are interesting innovative two-phase systems that have been recently proposed [5,13] as structured systems able to properly control the delivery of active ingredients; they possess the advantages typical of both gels, such as: ease of preparation, absence of huge quantities of surfactants sometimes toxic, and possible controlled delivery of both lipophilic and hydrophilic active agents [5,8]. Looking at these interesting properties, a growing number of authors is studying bigels as active agent carriers. Rhee et al, proposed bigels for ketoprofen transdermal administration [13]; Behera et al. investigated the physical properties of bigels made of synthetic polymers hydrogels (PVA and PVP), and sunflower oil and span 40 oleogels, for the delivery of metronidazole [14]; metronidazole was also added to carbopol hydrogel/Sorbitan monostearate-sesame oil organogel studied by Singh et al. [15], and the controlled delivery of ciprofloxacin was studied, again by Singh et al. [8], with a guar gum hydrogel and sorbitan monostearate-sesame oil based organogel.

All the cited papers discuss the mechanical and microscopic characteristics of bigels. Singh et al. [8] studied the microscopic morphology of samples and the rheological properties in terms of viscosities and 'creep and recovery' tests; the same group carried out also small amplitude oscillation tests for similar systems [7] and fluorescent microphotographs were moreover taken in their work based on carbopol-based bigels [15]. Texture analysis (creep recovery tests) were also taken by Satapathy et al. [4] in their study comparing gelatin-based hydrogels, emulsion hydrogels, and bigels, while Rehman et al. [16] characterised the polarized optical microscopy, viscosity and texture properties of polymer-fish oil bigels. Finally, flourence microscopy and rheological tests (texture analysis, viscosity, stickiness and stress relaxation) was investigated by Behera et al. [14]. Apart from these techniques of investigation, no other works were published dealing with the microstructure of the systems and further investigations can be very useful to better understanding structure and behaviour of these materials.

In the present paper, structured two-phase systems (bigels) were prepared and investigated by using rheological methods and Nuclear Magnetic Resonance (NMR) techniques aiming at better understanding the relationship between rheological properties and microstructure and to describe the effects of the structured dispersed phase on final product behaviour. In fact, different fractions of olive oil organogels were added to a typical basis for oil-in-water cosmetic creams, and different techniques were used to study the effect of this addition on the rheological and microstructural properties of the systems.

Colloidal suspensions characterisation by using Nuclear Magnetic Resonance (NMR) techniques is a vast and even expanding scientific endeavour [17,18]. Owing to its non-invasive nature, and ability to probe structures over a broad range of length scales, NMR has established itself as a tool for the structural characterisation of anisotropic domain sizes in liquid crystals [19], fluctuations in ordered lamellar phases under weak shear [20] and the sizing of shear-induced multi-lamellar vesicles [21,22]. It was also used for cosmetic emulsions [23] and food emulsions [24–27] characterisation. With respect to two-phase systems, NMR offers a variety of unique insights into both molecular orientation and transport kinetics within the various phases. One of the major contributions arguably is the possibility of easily deciding whether a given emulsion is of the discrete oil-in-water (O/W), discrete water-in-oil (W/O), or bicontinuous type from the oil and water self-diffusion coefficients [28]. Moreover, it is used to provide the droplet size distribution (DSD) of the emulsions [17,27] and even long-range order of droplets in structured emulsions [24,29,30]. Even though a vast literature is available on emulsion studies, to the best of our knowledge, there is no available work on NMR characterisation of bigels. Starting from these considerations it has been considered interesting to use this non-invasive powerful technique to investigate bigel evolution with increasing oleogel content. Moreover, the characterisation was completed by using phase contrast microscopy and electrical conductivity determination to evaluate potential changes in relative distribution of the phases.

Bigels investigated in this paper are based on sulphurous hyperthermal water, and olive oil. Hyperthermal water is well-known because it exerts anti-inflammatory, anti-pruriginous, keratoplastic and keratolytic effects [31]; olive oil, used alone or as an ingredient in dermo-cosmetology and topical applications, shows therapeutic effects (e.g., anti-inflammatory, anti-neoplastic, and anti-aging), and prevents skin alterations physiologically caused by time and different external irritating factors [32].

The aqueous phase was structured by using a common hydrocolloid, acting as gelling agent and thickener, such as potato starch. Olive oil was organogelled with a mixture of monoglycerides of fatty acids. Previous studies were carried out to investigate the main characteristics of different kinds of organogels [33,34], and in particular, monoglycerides/olive oil organogels alone [34,35], and mixed with other semisolid matrices [36] were investigated. The organogel was added to the base cream at room temperature, and the bigel preparation resulted easy, giving very smooth and homogeneous materials.