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Small scale manufacturing of anti-inflammatory powder-covered liquid marbles. An experimental approach on designing Pickering-like emulsions for topical application

[1]Roxana-Elena Avrămescu, [1]*Mihaela Violeta Ghica, [1]Cristina Dinu-Pîrvu, [1]Lăcrămioara Popa

[1]Department of Physical and Colloidal Chemistry, Faculty of Pharmacy, University of Medicine and Pharmacy "Carol Davila", Bucharest 020956, Romania

Abstract: Superhydrophobicity attracted researchers' attention since the discovery of surfaces with special architectures. An important exponent is represented by particle enwrapped droplets, called liquid marbles. These special formations, known as "soft objects" are made of a liquid core wrapped in a solid shell. Liquid marbles covered in anti-inflammatory powders were previously obtained using salicylic acid as a model hydrophobic powder. The aim of this study is to establish an investigation method regarding the wettability of the model powders in correlation with liquid marbles' formation and with their stability in an external phase. Besides salicylic acid, niflumic acid and ketoprofen are used as shells. The next step of the experiments is represented by immersing previously manufactured liquid marbles into an oily phase (paraffin and coconut oil), resulting in Pickering-like emulsions, which are proposed as models in topical emulsions design, aiming a local anti-inflammatory and cosmetic effect.

Keywords: hydrophobic powders, liquid marbles, Pickering-like emulsions design

INTRODUCTION:

Over the last years, superficial phenomena gained interest through fluids exhibiting a special behavior in contact with surfaces featuring particular architectures. Superhydrophobicity was initially discovered by observing the natural environment. Plants from marshy or flooded environments maintained clean and continued photosynthesis due to special formations on their leaves which repel water and other impurities. Other examples of natural-superhydrophobicity include: the Namib beetle's alternation of superhydrophobic and superhydrophilic edges and protrusions on its back, ensuring water supply, shark skin composed of small scales conferring aerodynamic properties, bird feathers which maintain clean and dry at all time etc. (Bixler, *et al.*, 2012, Darmanin, *et al.*, 2015, Feng, *et al.*, 2002). Thus, the *Lotus Effect* (Bhushan, *et al.*, 2010) and the *Rose Petal Effect* (Feng, *et al.*, 2008) were revealed and remain iconic exponents of special natural-wetting regimes, along with the empirical models of Young, Cassie-Baxter and Wenzel, which characterize superficial phenomena between droplets and supports (Cassie, *et al.*, 1944, Wenzel, 1936). Superhydrophobic surfaces and coatings are adaptation features against unwanted phenomena (rust, icing, bio-contamination) (Aslanidou, *et al.*, 2018, Chatzigrigoriou, *et al.*, 2013, Ishizaki, *et al.*, 2010, Tian, *et al.*, 2014, Tomšič, *et al.*, 2008). A very important exponent of superhydrophobicity is represented by the special formations called liquid marbles. They are in fact liquid drops enwrapped in a solid particle outer shell. Gaining the attribute of "soft objects" and known to display a "double solid-fluid character", liquid marbles also attracted researchers' attention due to their unique properties which include: elasticity, reversible shape changes, induced coalescence, possibility to engulf extraneous objects, self-propulsion (Asare-Asher, *et al.*, 2015, Aussillous, *et al.*, 2001, Aussillous, *et al.*, 2004, Bormashenko, *et al.*, Bormashenko, *et al.*, 2015, Brown, *et al.*, 1980, Janardan, *et al.*, 2015, McHale, *et al.*, 2011, McHale, *et al.*, 2015).

Applications of liquid marbles derive from their unique characteristics and cover many domains such as medical, pharmaceutical, chemical, biochemical etc. In the pharmaceutical field, liquid marbles are known as precursors of hollow granules, microcapsules and Pickering -like emulsions. Emptied and dried liquid marbles are reported as hollow granule precursors, including para-ethoxybenzamide, salicylic acid, Ballotini spheres, PTFE (poly-tetrafluoroethylene), aerosil as external shells, water and glycerol as liquid cores and PVP (polyvinylpyrrolidone), HPMC (hydroxypropyl methylcellulose), HPC (hydroxypropyl cellulose) and PEG's (polyethylene glycol) as binders. Various drying methods (temperature variations and humid/dry air) and many other conditions (particle dimension and structure) must be fulfilled depending on the desired final product, so that it attains the specific properties (Eshtiaghi, *et al.*, 2009, Khanmohammadi, *et al.*, 2007). Liquid marbles obtained by rolling water droplets into a PDEA-PS (sub micrometer size polystyrene particles carrying poly 2-(diethylamino)ethyl methacrylate) powder bed and dried at high temperatures, lose their internal phase through evaporation and maintain their shape, transforming into microspheres, due to PDEA-PS's plasticization (polymerization). These spheres are used to obtain drugs with a modified/delayed/targeted release of the active substance, making liquid marbles important candidates as microsphere precursors (Ueno, *et al.*, 2014).

Although they were ignored since their discovery in 1907 (Pickering, 1907), Pickering emulsions newly draw attention, exhibiting numerous advantages. They resemble common emulsions (W/O or O/W; water in oil or oil in water), but are different from them through lack of surfactants. The role of stabilizers is played by

Correspondence: mihaela.ghica@umfcd.ro

surface adsorbed particles, partially wetted by both phases, conferring integrity to the system (Binks, 2002, Chevalier, *et al.*, 2013). In the pharmaceutical and also cosmetical field, Pickering emulsions gain the appropriate importance due to a surfactant free formulation, removing possible side effects such as irritations, hemolytic or cytotoxic reactions, which may occur in a common topical applied surfactant (ionic/non-ionic) stabilized emulsion. Also, the increased stability of Pickering-like emulsions is an important property, which arises from the micro-/nano-metrical particles adsorbed at the liquid phases interface. Particle wettability plays an important role in establishing emulsions' type, as does the HLB (hydrophil-lypofil) balance for common emulsions. Thus, if the particles are more hydrophobic exhibiting contact angles (CA) smaller than 90°, they stabilize an O/W emulsion, whilst if they are more hydrophilic (CA>90°) they stabilize a W/O emulsion.

Pickering-like emulsions are obtained using liquid marbles as constituent parties. Versatility in liquid marbles formulation allows using raw materials such as water, glycerol as liquid cores and PTFE, PVDF (poly-vinylidene floride), PE (poly-ethylene), carbon black, *Lycopodium* spores, as powders forming external shells. Silicone fluids, aromatic and chlorinated solvents were proposed as external phases of the emulsions. Stability is investigated upon different air-solvent interfaces and after immersion in solvents. Correlations are made with different solvent polarities as follows: liquid marbles are less stable in polar solvents DMF (dimethylformamide), DMSO (dimethylsulfoxide), ethanol and no emulsion is formed; Pickering-like emulsions are stable when liquid marbles are immersed in silicone and aromatic solvents (Bormashenko, *et al.*, 2012). It is a fact that both the external phase and particles' wettability influence stability of these emulsions.

Coconut oil is proposed as a candidate for the role of emulsion's external phase, due to its proposed antiseptic and skin moisturizing effect. Some studies also suggest it as a proactive treatment of atopic dermatitis, demonstrated through in vitro activity against *Staphylococcus aureus*. In control studies, coconut oil also proved mosquitos-repellency. Moreover, it is considered to form a barrier against UV radiation once applied to skin. Histopathological tests show increased neovascularization, fibroblast proliferation, pepsin-soluble collagens synthesis and turnover of collagen in wounds as a result of coconut oil topical application (Agero, *et al.*, 2004, Nevin, *et al.*, 2010, Petry, *et al.*, 2017, Sylla, *et al.*, 2003, Verallo-Rowell, *et al.*, 2008).

Paraffin oil is known as a common component of topical products, with the amendment of possible paraffinoma (tumors) if injecting for therapeutical or cosmetic aims. Early tests on open wounds showed no antibacterial activity, but a slight anti-inflammatory effect. Literature suggests co-administration along with antibacterial agents, in order to stop eventual bacterial proliferation in wounds (Beiter, 1917). More recent studies demonstrate that it only penetrates the outermost layers of the *stratum corneum* and goes no deeper than that (Petry, *et al.*, 2017).

This paper investigates wettability of pharmaceutical anti-inflammatory agents, as liquid marbles components (shells). The analysis is carried out on salicylic acid and NSAID (non-steroidal anti-inflammatory drugs) powders: niflumic acid and ketoprofen, using a goniometer and applying a special protocol developed for contact angle determinations. The powders are included as coatings in liquid marbles formulation. Apparent contact angles of the marbles are also evaluated following an adaptation of the protocol developed for the goniometer. Afterwards, the liquid marbles are immersed into an oily phases (paraffin and coconut oil), obtaining Pickering-like emulsions. Pickering-like emulsions stability is macroscopically investigated in correlation with powders' wettability and liquid marble formulation, aiming to propose a design for topical emulsions.

MATERIALS AND METHODS:

Materials include: salicylic acid provided by Chemical Company (Romania), NSAID powders: niflumic acid from ICN Biomedicals (USA), ketoprofen from Sigma-Aldrich; deionized water, glycerol, coconut oil and paraffin oil provided by Sigma-Aldrich.

Contact angle evaluations of anti-inflammatory powders and apparent contact angles of liquid marbles were carried out using a CAM 101 goniometer from KSV Instruments, equipped with a video camera, connected to a computer through a special plug and running a specific soft-ware. The experiments also include Hamilton syringe with needle from Biolin Scientific, microscope blades, double adhesive tape and a sieve. The goniometer is placed onto a perfectly horizontal surface, away from drafts and any vibrations.

Contact angle evaluations of powders

Experiments take place at room temperature (23°C), using the previously described set-up.

The contact angle determination protocol starts with preliminary steps: the microscope blade is covered in double adhesive tape and the analyzed powders are sieved onto it, in order to ensure homogenous distribution; the syringe is filled with distilled water.

Actual contact angle determinations take place by dispensing a droplet (a few milliliters in volume) onto the investigated powder sample, as presented in Fig. 1a. At the same time as the droplet falls, images (frames) are recorded in real time, at a certain preset speed (Normal regime: 1 frame at every 5 ms). The captured images are afterwards processed by the soft-ware in terms of the drops' curve fitting, resulting in actual contact angle values, as presented in Fig. 1b. All registered values are accessed through the data base and further analyzed.

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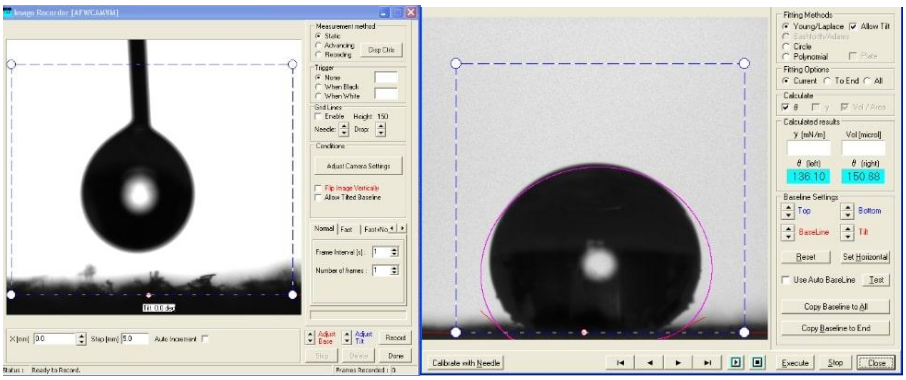
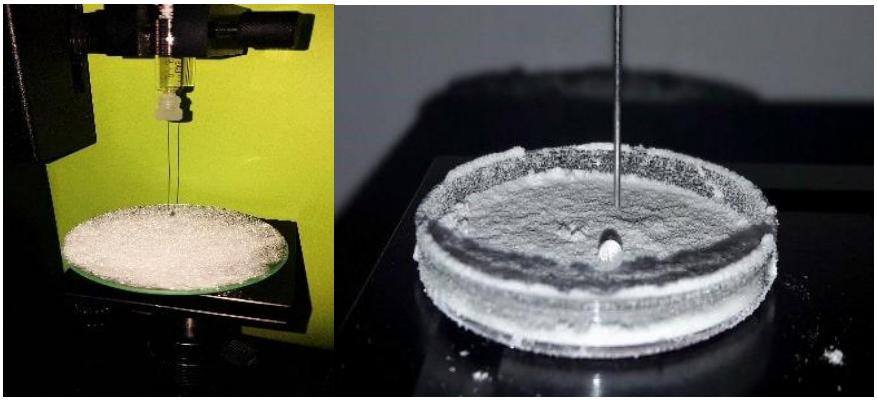


a b

Fig. 1. a – Droplet dispersed onto a powder bed; b – Curve fitting of the droplet and actual contact angle determination

Liquid marbles preparation

Liquid marbles are obtained by rolling water/glycerol droplets (a few microliters in volume) onto the previously prepared powder bed. The powder bed is obtained as previously presented, by sieving onto a convex watch glass, so that the drops can roll by tilting. The droplets are formed using the Hamilton syringe with needle and are released from it by pushing a dispenser button included in the set-up, as presented in Fig. 2.



a b

Fig. 2. a - Water drop released from the syringe onto the watch glass; b - Close-up on the droplet

Contact angle evaluation of liquid marbles

Apart from powder wettability investigations, apparent contact angles corresponding to anti-inflammatory powders covered-liquid marbles were also determined. Evaluations were carried out in the same conditions, using the CAM 101 goniometer set-up. Previously obtained liquid marbles are placed onto a glass blade. Images are captured by the camera and the curve fitting provides contact angle measurements (Fig. 3).

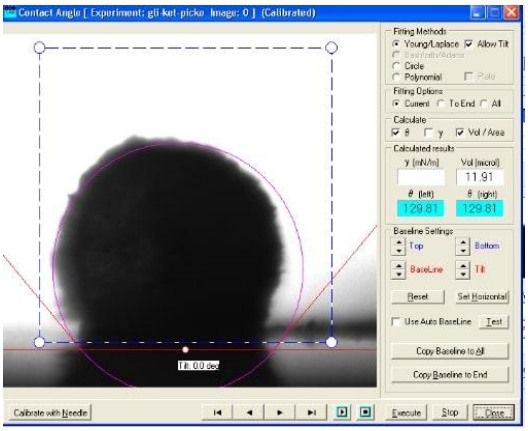


Fig. 3. Curve fitting of the liquid marble

Pickering-like emulsions preparation

Liquid marbles obtained as previously presented are immersed into paraffin and coconut oil,

obtaining Pickering-like emulsions, which are further macroscopically analyzed from stability point of view, after 24 hours from preparation.

RESULTS AND DISCUSSIONS:

Contact angle evaluation results for powders

Contact angle determinations are presented as average values, calculated from 9 determinations corresponding to each sample.

Table 1 refers to contact angle evaluations for the model powders, using water (WCA°) and glycerol (GCA°) as model fluids.

Tab. 1.

Contact angle values of the tested powders, using water (WCA°) and glycerol (GCA°) as model fluids

	Salicylic acid	Niflumic acid	Ketoprofen
WCA (°)	106.93±2.06	125.98±1.78	127.14±1.56
GCA (°)	106.0±3.1	111.85±1.66	129.83±0.88

Corresponding images of water drops on the powder beds are presented in Fig. 4.

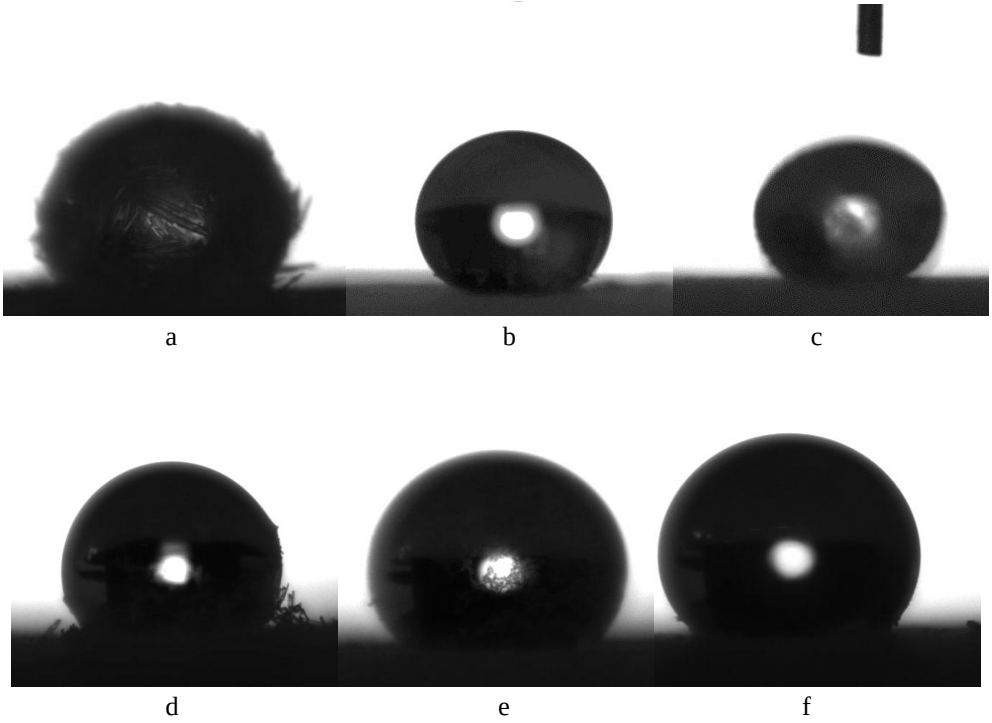


Fig. 4. Water drop dispensed on: a - salicylic acid, b - niflumic acid, c - ketoprofen and glycerol drops dispensed on: d - salicylic acid, e - niflumic acid, f - ketoprofen.

Contact angle values are higher than 90°, demonstrating a hydrophobic character of all the powders. The most hydrophobic powder is ketoprofen (WCA=127.14° and GCA=129.83°).

The hydrophobic character of the powders evaluated using both water and glycerol as model fluids, allows using the proposed anti-inflammatory powders as shells, part of liquid marbles further formulation.

Moreover, after liquid marbles were obtained, the contact angle described with the glass blade was also evaluated. Since liquid marbles don't exactly contact the support surface like plain drops do, the contact angle is referred to as an apparent contact angle. The contact angle cos θ of plain drops corresponds to Young's equation (Eq.1):

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (0)$$

Where γ_{SV} is the surface tension at the solid-vapor interface, γ_{SL} is the surface tension at the solid-liquid interface and γ_{LV} is the surface tension at the liquid-vapor interface.

The apparent contact angle cos θ' is described by an adaptation of Young's equation, which considers the particle's radius (r) (Eq. 2):

$$\cos\theta' = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = r\cos\theta \quad (0)$$

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Liquid marbles preparation results

After rolling water and glycerol droplets into the powder beds, stable liquid marbles were obtained.

After 24 hours, water marbles lose their liquid core through evaporation, leaving behind an empty shell. Glycerol marbles did not lose the entire core but look like deflated spheres due to possible particle agglomeration at the air-particle-glycerol interface. The appearance of both water and glycerol marbles immediately after formation and after 24 hours are presented in Fig. 5.

a b c

Fig. 5. a - Liquid marbles after preparation (camera and macroscopical vision); b - Water marbles after 24 hours from preparation; c - Glycerol marbles after 24 hours from preparation.

Apparent contact angle results for liquid marbles

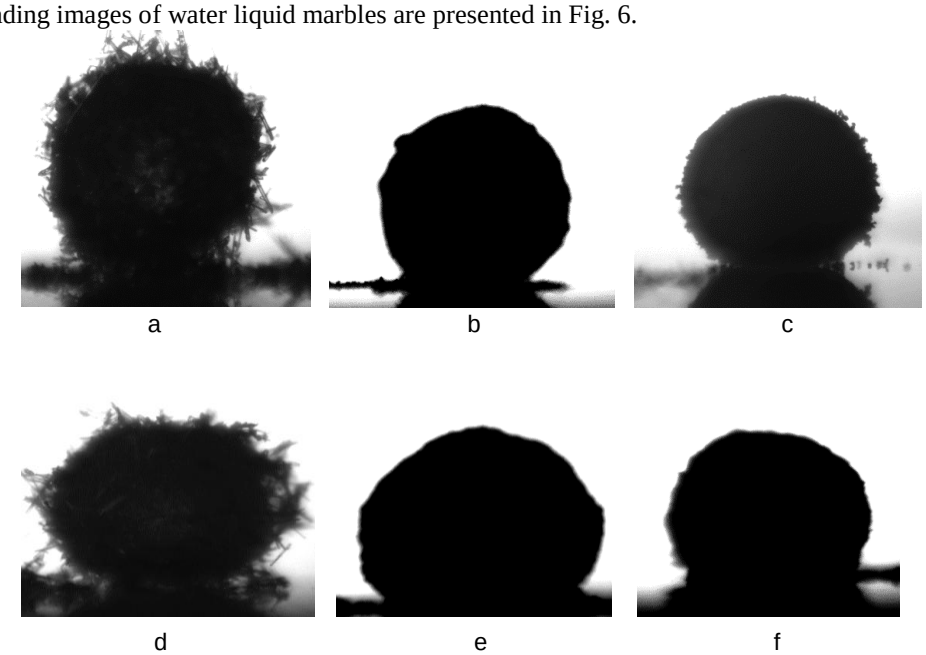
Table 2 refers to apparent contact angle evaluations for anti-inflammatory powder-covered water (WCA_{app}°) and glycerol (GCA_{app}°) liquid marble.

Tab. 2.

Apparent contact angle values of anti-inflammatory powder-covered water (WCA_{app}°) and glycerol (GCA_{app}°) liquid marbles

	Salicylic acid	Niflumic acid	Ketoprofen
WCA_{app} (°)	120.49±1.53	127.46±1.95	136.86±0.71
GCA_{app}(°)	121.46±1.72	120.77±2.02	129.62±0.89

Corresponding images of water liquid marbles are presented in Fig. 6.



a b c

d e f

Fig. 6. Water liquid marbles covered in: a - salicylic acid, b - niflumic acid, c - ketoprofen and glycerol liquid marbles covered in d - salicylic acid, e - niflumic acid, f – ketoprofen

As expected, liquid marbles exhibit a hydrophobic character. Apparent contact angles have bigger values than contact angles of plain drops. Moreover, liquid marbles formulated with ketoprofen exhibit bigger values compared to the other anti-inflammatory powders (WCAapp =136.86°, GCAapp =129.62°).

Images captured by the goniometer's camera are illustrative for the acicular form of salicylic acid powder, in comparison with the other powders which display as smooth shells.

Pickering-like emulsion preparation results

After manufacturing, liquid marbles are immersed into the oily phase, two phenomena take place: ketoprofen covered marbles maintain stability and sink at the bottom of the bottle (Fig. 7b); the same happens in case of salicylic acid marbles (Fig. 7a); niflumic acid liquid marbles lose their outer shell during sinking, leaving behind powder traces in the oily phase (Fig. 7c).

After 24 hours, the best stability was observed in Pickering-like emulsions with ketoprofen covered liquid marbles, for both coconut and paraffin oil external phases. The marbles maintained their spherical shape and no changes were noted regarding the external shell (Fig.7e).

Pickering-like emulsions containing salicylic acid-coated liquid marbles were not as stable, because the outer shell began to destabilize. The reason is the acicular crystallization state of the salicylic acid powder, which lead to an uneven external shell with gaps. It allowed water capillarization and lead to destabilization of the marble's coating (Fig. 7d).

Pickering-like emulsions with niflumic acid liquid marbles showed no stability. Some of the marbles bursted, others lost parts of the shell, resulting in destabilized emulsions (Fig. 7f). High oil density draws away the very fine powder from the marbles' coating.

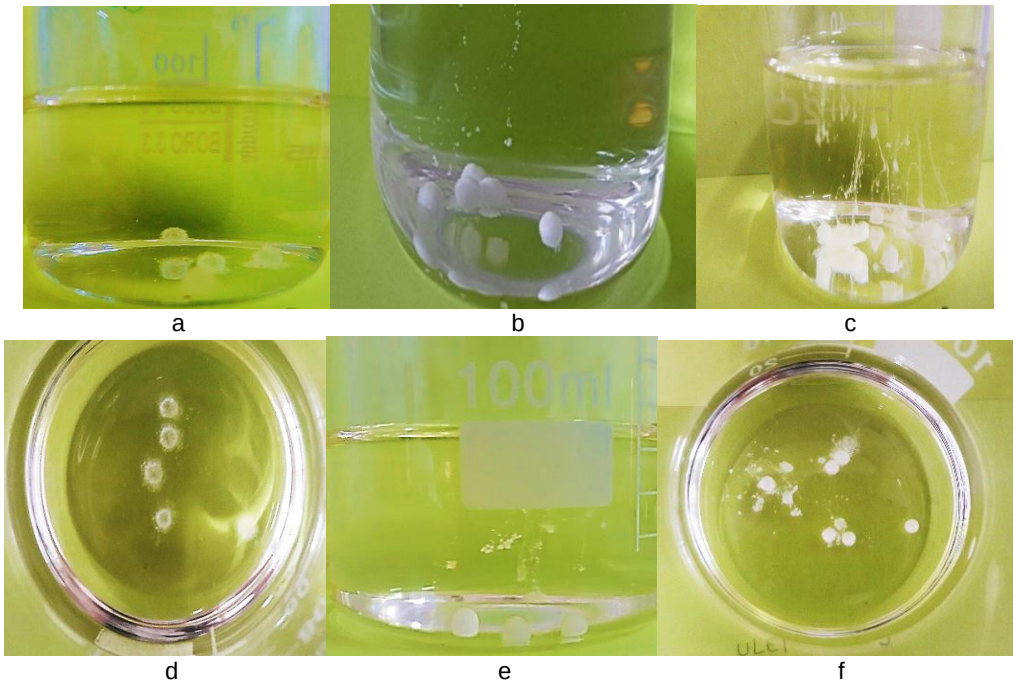


Fig. 7. Pickering-like emulsions immediately after preparation (a, b, c) and after 24 hours from preparation (d, e, f).

CONCLUSIONS:

This study demonstrates how anti-inflammatory-covered liquid marbles can be manufactured in small scale experiments. The wettability evaluation of the powders is carried out according to a special protocol for contact angle determinations. Powders' hydrophobicity indicates the possibility to form liquid marbles by simply rolling droplets onto the powder bed. The apparent contact angle of the marbles is also evaluated, using an adaptation of the above-mentioned protocol. Results indicate that among the analyzed anti-inflammatory agents, ketoprofen exhibits the greatest hydrophobicity. Moreover, ketoprofen covered liquid marbles successfully stabilize the Pickering-like emulsions. This paper is considered a preliminary step in manufacturing liquid marbles in small scale experiments and including them in Pickering-like emulsion formulations. The established contact angle determination protocol is also suitable for other wettability investigations regarding any pharmaceutical powders, either hydrophilic or hydrophobic.

The proposed Pickering-like emulsions formulations are suggested as candidates in designing topical drug products. Advantages include lack of possible irritating stabilizers, innocuity, skin tolerability, creating an un-washable (by water) layer on the skin which offers UV protection, penetrability into superficial skin layers, emollient, protective and anti-inflammatory effects, versatility in terms of including many other active ingredients in the formulation, depending on its aim. Time stability and the possibility to overcome possible incompatibilities between ingredients due to internal phase (liquid marbles) formulation before including it into the

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external phase are also to be considered in the preformulation stage of the Pickering-like emulsions.

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Author contributions

All authors have equal contributions.

Conflict of interests

The authors declare no conflicts of interest.

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