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The potential of magnetic heating for fabricating Pickering-emulsion-based capsules

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ABSTRACT

Pickering emulsions (particle-stabilized emulsions) have been widely explored due to their potential applications, one of which is using them as precursors for the formation of colloidal capsules that could be utilized in, among others, the pharmacy and food industries. Here, we present a novel approach to fabricating such colloidal capsules by using heating in the alternating magnetic field. When exposed to the alternating magnetic field, magnetic particles, owing to the hysteresis and/or relaxation losses, become sources of nano- and micro-heating that can significantly increase the temperature of the colloidal system. This temperature rise was evaluated in oil-in-oil Pickering emulsions stabilized by both magnetite and polystyrene particles. When a sample reached high enough temperature, particle fusion caused by glass transition of polystyrene was observed on surfaces of colloidal droplets. Oil droplets covered with shells of fused polystyrene particles were proved to be less susceptible to external stress, which can be evidence of the successful formation of capsules from Pickering emulsion droplets as templates.

1. Introduction

Colloidal capsules have become the emerging class of structures due to their applications, mainly in the pharmaceutical industry [1], where they may provide great possibilities for controlled release of capsulated species [2,3]. There are several routes for fabricating colloidal capsules from particle-stabilized emulsions (Pickering emulsions), including the use of polyelectrolyte complexation on the particle layers [4], gel trapping [5], polymerization [6] or sintering [7]. The last one leads to the formation of the capsule shell, as particles on the droplet surfaces are fused under high temperature. An important factor here is the glass transition temperature (T_g). Above this value particles can fuse without being completely melted [8]. Other factors, such as time of sintering and particle concentration, should also be taken into account [9]. In this paper, we propose the potential new technique of production of colloidal capsules from oil-in-oil Pickering emulsions by using magnetic particles in the alternating magnetic field.

Magnetic nano- and microparticles have long been known as heating agents. When immersed in a medium, the heat from these sources is then dissipated into their immediate surroundings [10]. The generation of thermal energy by particles placed in the alternating magnetic field is based on energy dissipation owing to three main mechanisms: hysteresis, Néel, and Brownian relaxation, and induction of eddy currents. The last one is, in principle, negligible for small objects such as nano- or microparticles of very low electrical conductivity [11]. Energy dissipation due to hysteresis losses occurs for magnetic particles of sizes above the critical value [12]. Magnetic energy is dissipated into heat by movement of the magnetic domain walls, and heat losses are proportional to the third power of the magnetic field's amplitude [13]. Energy dissipation is also related to two independent relaxation mechanisms: Brown and Néel. In Brownian relaxation rotation of a spontaneous magnetization vector causes rotation of the whole particle. This rotation is being resisted by the surrounding medium due to its viscosity and therefore relaxation occurs. In this mechanism relaxation time τ_B depends on the hydrodynamic volume of a magnetic particle V_h, shear viscosity of the medium η, and temperature T:

$$\tau_B = \frac{3\eta V_h}{k_B T} \tag{1}$$

In Néel mechanism relaxation time τ_N can be expressed as:

$$\tau_N = \tau_0 \exp(\frac{KV}{k_B T}) \tag{2}$$

where $\tau_0 \approx 10^{-9}$ s and KV refers to the energy barrier that the magnetic moment must overcome to reverse its direction within the particle. The most typical situation is when both relaxation mechanisms and

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hysteresis losses arise at the same time. However, the size of the particles determines the dominating mechanism [12,13].

Magnetic heating has been commonly associated with the application in magnetic particles-mediated hyperthermia that is a promising modality to help cancer treatment [14]. However, this temperature rise can also be used in other applications. For instance, magnetic heating can help in fragmentation of cancer cells and destroying them directly [15]. Temperature elevation may also enable reversible emulsion destabilization, as in the work of Kaiser et al., where polystyrene-magnetite particles were used to stabilize emulsions [16]. Using the oscillating magnetic field to affect the organization of so-called endoskeletal droplets was also recently demonstrated [17]. Nano-heating, i.e. a phenomenon allowing for heat to be delivered up to 100 nm away from magnetic nanoparticle surface, were used in chemical procedures like in flow reactors [18,19] or catalysis [20,21]. In the latter case, induction heating by nanoparticles is currently a subject of increasing scientific interest [22].

Various types of particles, e.g. silver [23], gold [24], silica [25], polystyrene [26] or clay [27] can be utilized for fabrication of colloidal capsules. Magnetic particles were also used for that purpose [28,29]. These attempts are of great importance, since the external magnetic field is believed to be one of the methods to trigger a cargo release from capsules [30]. In the literature, one can find some examples of the use of different particles together to stabilize emulsions [16,31] and to form colloidosomes [32]. In our work, we used polystyrene microparticles along with magnetite particles that acted as heat sources. We primarily investigated how the presence of magnetic material affects the temperature rise in particle-stabilized emulsions (Pickering emulsions) placed in the alternating magnetic field. Then, we performed experiments for single droplets with a polystyrene-magnetite coating exposing them to the magnetic field which resulted in a temperature elevation. As we will show, magnetic field-induced heating can provide a new potential method of fabricating colloidal capsules from Pickering droplets. It is a novel contribution to the investigation of heating effect in particle-stabilized emulsions. What is also important, there is a lack of reports on usage of oil-in-oil emulsions for production of colloidal capsules [33].

2. Materials and Methods

2.1. Materials

To form oil-in-oil Pickering emulsions we used silicone oil (Rhodorsil oils 47 V 50, a viscosity of 50 mPa·s) for the dispersed phase and castor oil (MERLIN, MA 220-1, a viscosity of 700 mPa·s) for the continuous phase. As stabilizers we used polystyrene particles (**PSPs**, Dynoseeds, TS10 6317, Microbeads AS) with average size ~10 μm and two types of magnetite particles in the form of powder (**MPs**, Sigma-Aldrich Co.): smaller (**nMPs**, 50-100 nm in size, density of around 4800-5100 $kg{\cdot}m^{-3}$) and bigger (**μMPs**, < 5 μm in size, a density of about 4800-5100 $kg{\cdot}m^{-3}$). Polystyrene particles underwent a surface modification according to the method described in [34]. Briefly, **PSPs** were dispersed in the solution of acrylate polymer (PFC 502AFA, FluoroPEL™, Cytonix as modifier) and methoxy-nonafluorobutane (7100 Engineered Fluid, 3M™ Novec™ as solvent). After the evaporation of the solvent, the **PSPs** were thoroughly washed and dried. After this procedure, their affinity to the continuous phase of the emulsion was increased that facilitated the stability of the particles at the interface.

2.2. Preparation of magnetite-polystyrene Pickering emulsions

Pickering emulsions were prepared according to the method described in detail in one of our previous works [35]. Briefly, the mixture of particles and oils was homogenized for 30 seconds using ultrasonic device (Sonoplus HD 300, Bandelin, acoustic intensity estimated as 17 $W{\cdot}cm^{-2}$, working frequency of 18 kHz) resulting in formation of a non-stable emulsion. The main mechanism involved in emulsification using ultrasound is ultrasonic cavitation. The implosion of cavitation bubbles occurs in the presence of high energy ultrasonic waves and causes dispersion of the inner phase. In our case, the acoustic power was high enough to produce what we call “pre-emulsion”, i.e. small silicone droplets but barely covered by particles. In the electric field, due to consecutive events of electrocoalescence, droplets formed during ultrasonication would get gradually covered with particles, up to the point of complete surface coverage. The electric field was supplied to the copper electrodes placed on the sides of a glass cuvette (30 mm x 18 mm x 1.3 mm) by DC-to-DC high voltage amplifier (UltraVolt 1AA12-P4, Advanced Energy Co.). We followed the process of preparation of Pickering emulsions using a CMOS camera (UI-3590CP-C-HQ, IDS) mounted on a high-magnification zoom lens system (MVL12 × 3Z, Thorlabs), a light source and a computer for collecting images and recording videos. In each experiment, for each sample, we used the same amount of the polystyrene particles, silicone oil and castor oil (silicone oil to castor oil mass ratio 1:10, polystyrene particles to silicone oil mass ratio: 1:4). However, samples differed in the amount of magnetic particles used - from 1:8 to 1:1 polystyrene-magnetite mass ratios.

2.3. Calorimetric measurements in magnetic field

Calorimetric measurements were performed using a compact induction heating system (EASYHEAT, Ambrell Co.) as a source of the alternating magnetic field. The frequency of the field was 356 kHz and the intensity was 16.2 kA/m. The temperature in the emulsion sample was measured using a temperature sensor system (FLUOTEMP, Photon Control Inc.) with an optic fiber temperature probe (model FTP-NY2) and a pyrometer (VT02, Fluke Co.). During experiments, the fiber was placed centrally in the sample. The sample cell was the same as the one used for experiments in the electric field. Induction coil was cooled efficiently by an external system, therefore the temperature rise from the coil was found to be negligible (measured as ~0.12 °C). A single measurement lasted 120 seconds. The scheme of the experiment is presented in Fig. 1.

3. Results and Discussion

3.1. Magnetic heating measurements

In the first experimental step, we prepared Pickering emulsions stabilized with magnetite and polystyrene particles used together, as it was described in section 2.2. The optical microscopy measurements were performed to characterize the appearance of emulsions after ultrasonic homogenization and subsequent stabilization in the electric field. The results are presented in Fig. 2.

As one can see, there is no significant aggregation in the emulsion and the droplets were covered sufficiently by both polystyrene and magnetite particles (in size of micrometers) as it is evidenced by dark and bright particles in Fig. 2**b**. Because of a difference in wettability, magnetic particles (**MPs**) were more attached to the droplet interface than polystyrene particles (**PSPs**). However, the distribution of particles suggested that there was a potential for a fusion of polystyrene under exposure to a high enough local temperature. In the experiment, the concentration of silicone oil droplets (10% w/w) was low enough to ensure direct optical observation without any dilution. Speaking of which, we found the possibility of direct observation most significant for our concept of Pickering emulsions formation in the electric field [29]. After formation in the electric field, particles at the droplet interface formed such a dense layer that ensured the stability against further coalescence events.

In order to show the efficiency of heating induced by magnetic particles in an external magnetic field, we investigated such low-concentrated Pickering emulsions (10% silicone oil to castor oil mass ratio) stabilized with both polystyrene and magnetite particles, and compared

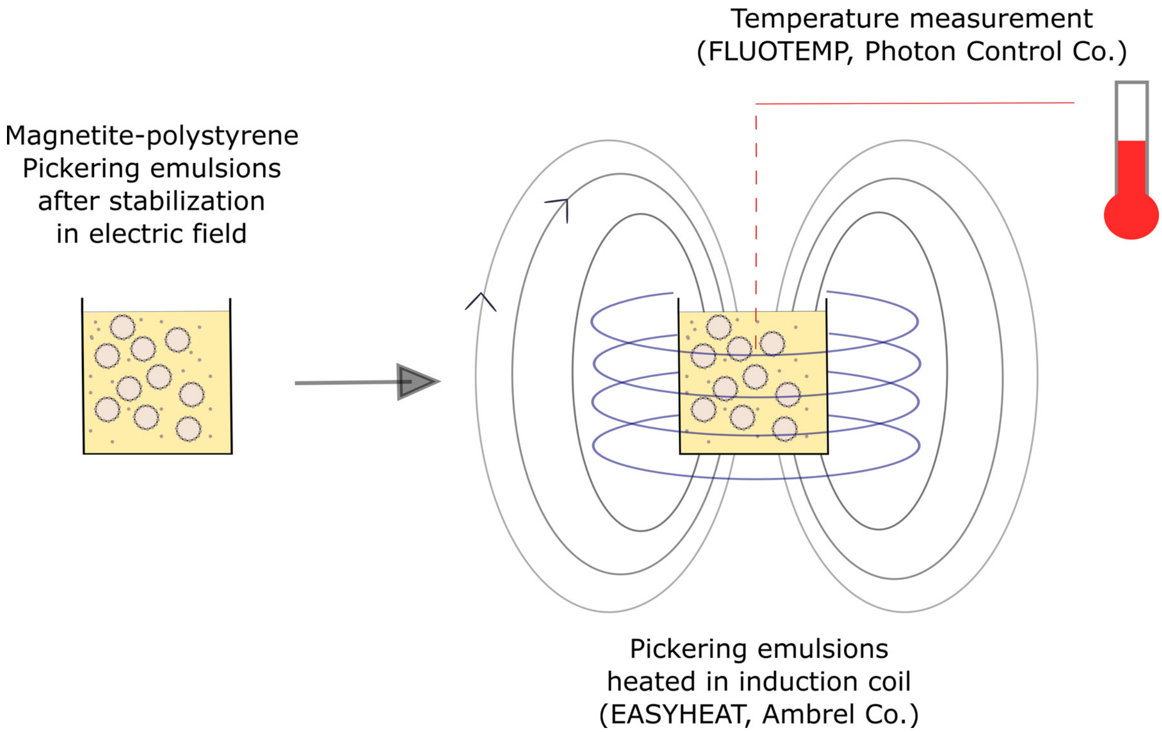


Fig. 1. A schematic illustration of the magnetic heating measurements.

them with corresponding pre-emulsions (i.e. systems where silicone oil droplets were not completely covered by **PSPs** and **MPs**) exposed to the same conditions. The results are presented in Fig. 3.

The increase of temperature was more dynamic and the final temperature increase was higher for the emulsions stabilized by magnetic microparticles (Fig. 3**b,d**). It is in clear accordance with theoretical predictions. The relaxation mechanisms responsible for the generation of heat for small magnetite particles are hindered for sufficiently large particles because the Brown and Néel relaxation times are dependent on particle dimensions. For bigger particles, **μMPs**, relaxation times are very long and the only hysteresis loss can contribute to the generation of heat since particle sizes are above a critical value of the single-domain particles [36]. In Fig. 3, it is also clearly seen that the temperature increase is determined by the amount of the magnetic material in the sample (expressed as a mass ratio to the **PSPs**).

The efficiency of heating is often characterized by the specific absorption rate (SAR), expressed as initial temperature rise $\frac{dT}{dt}$ multiplied the specific heat c_p of a sample:

$$SAR = c_p\left(\frac{dT}{dt}\right)_{t=0} \tag{3}$$

We determined this parameter for emulsions stabilized with **PSPs** and different **MPs** by fitting the experimental curves from Fig. 3 to the Box-Lucas equation [37,38]:

$$\Delta T(t) = T_{max}\cdot\left(1 - \exp\left(-\frac{t}{\tau}\right)\right) \tag{4}$$

The parameters T_{max} and τ were derived from the fitting. Therefore, the initial increase of the temperature during heating can be expressed as a derivative: $\left(\frac{dT}{dt}\right)_{t=0} = \frac{T_{max}}{\tau}$.

We also compared this data with results obtained for pre-emulsions, i.e. emulsions that would only go through the process of ultrasonic homogenization, but not the stabilization in the electric field. The results are presented in Fig. 4.

The tendency observed in Fig. 4 corresponds very well to the temperature elevations. The most effective heating occurred for the emulsions stabilized with the highest concentration of the magnetite

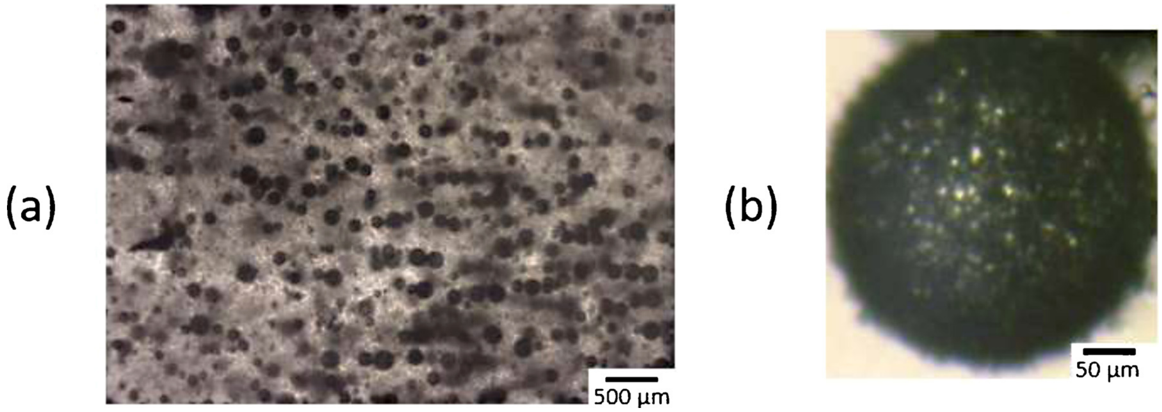


Fig. 2. (a) Optical microscope image of a Pickering emulsion after ultrasonic homogenization and subsequent stabilization in the electric field for 20 minutes. The silicone oil - castor oil mass ratio was 1:10, polystyrene particles - silicone oil mass ratio was 1:4 and magnetite particles (< 5 μm in size) to polystyrene particles mass ratio was 1:8. (b) A single, non-sintered Pickering droplet extracted from the overall picture.

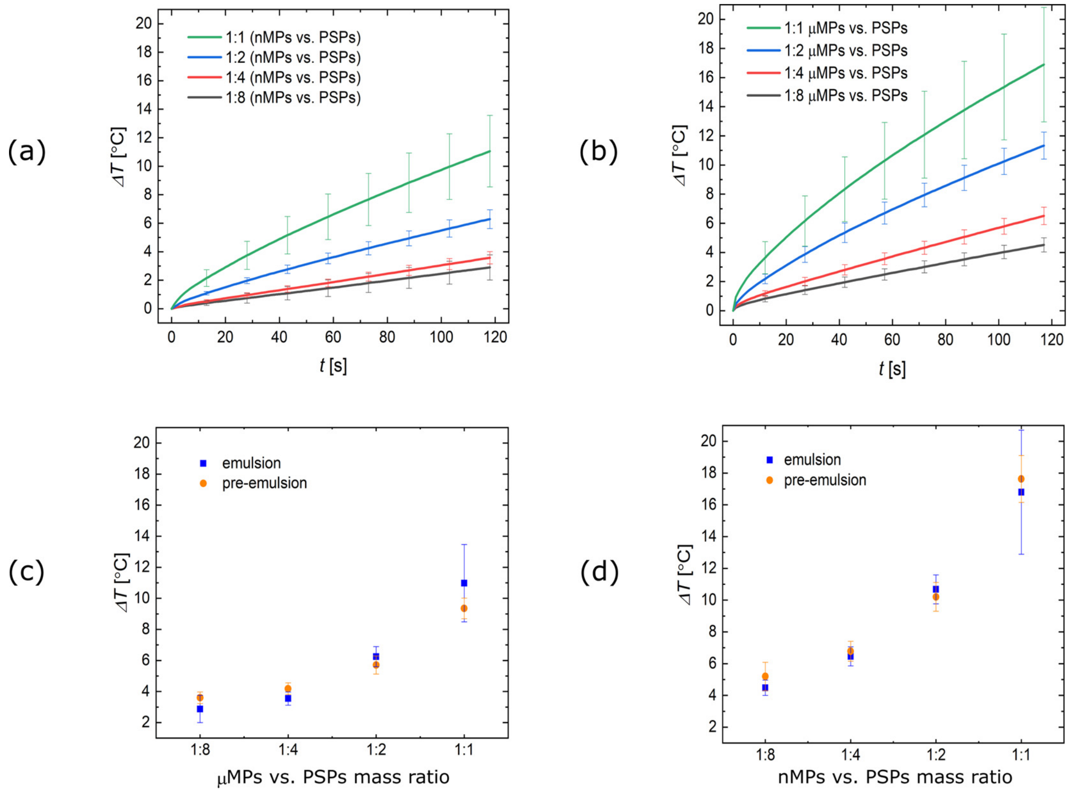


Fig. 3. Temperature increase within 120 seconds under the alternating magnetic field for Pickering emulsions with (a) magnetic nanoparticles, **nMPs**, and (b) magnetic microparticles, **µMPs**. Total temperature rise in 120 s of magnetic heating for (c) magnetic nanoparticles, **nMPs** and (d) magnetic microparticles, **µMPs**.

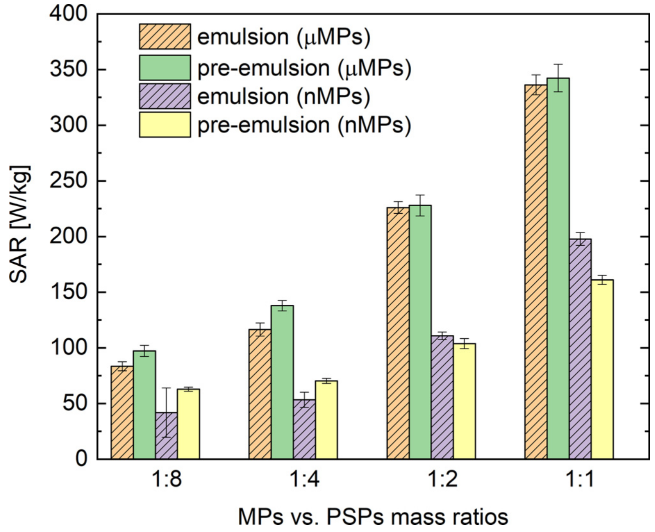


Fig. 4. Specific absorption rate for emulsions and pre-emulsions stabilized with magnetic particles of different sizes (micrometers vs. nanometers) and with different mass ratios.

microparticles, **µMPs**. Again, it is due to an evident hysteresis loss that is exhibited significantly only for bigger magnetic particles. Interestingly, especially when **µMPs** were used, heating efficiency was higher for the pre-emulsions than for the emulsions. It can mean that the influence of attachment of magnetic particles to the droplet interface and their location simultaneously in both of liquids is reflected in our SAR results. There are some explanations for this. In pre-emulsions, there are no dense particle layers around the droplets and not all of the particles are placed on the oil-oil interface. In case of small magnetic particles, **nMPs**, rotation of a whole particle is not suppressed by the attachment to the oil-oil interface, which allows the Brownian mechanism to have a greater impact on the system. For stable Pickering droplets, the particles are packed at the interface so densely, that the particle rotation is difficult due to friction between adjacent particles. For bigger particles, those relaxation mechanisms do not occur.

The differences in heating efficiency between a pre-emulsion and a stabilized emulsion can arise from contrast in thermal properties between the inner and the outer phase of the emulsion and the interactions between stabilizing particles. In literature, the efficiency of magnetic heating is reported to be dependent on the size of particles. However, so far scientists have focused on nanoparticles. It was shown that heating efficiency exhibits an explicit maximum that strongly depends on experimental conditions [39,40]. The bigger particles, micrometer in size, have in turn not been reported in magnetic heating applications. Our results seem to indicate there is a difference in heat generation by a single magnetic particle compared to a particle cluster. Sufficiently large agglomerates cool down slower than the surface of a single particle [41]. The closely packed particles attached to the droplet surface – as in case of particle shell around oil droplets – could be considered as a kind of such hollow sphere particle agglomerate. For particle layer, the magnetic interactions between particles can influence the heat generation as it is for clusters [42].

The temperature rise in samples of magnetic particles dispersed in castor oil was also recorded. The magnetite concentration in these samples was 0.6 % w/w.

The mass concentration of particles in each of the measured samples was the same, hence a difference in temperature rise in Fig. 5 should be linked to the difference in the mechanisms involved in the process of magnetic heating. As for emulsions stabilized by particles, bigger particles (**µMPs**) were more efficient as sources of heat in magnetite suspension. It was due to energy losses from magnetic hysteresis. In parallel, the temperature rise observed for suspensions was higher than for the emulsions, regardless of the size of the particles used.

The obtained results indicate there is a high potential of efficient

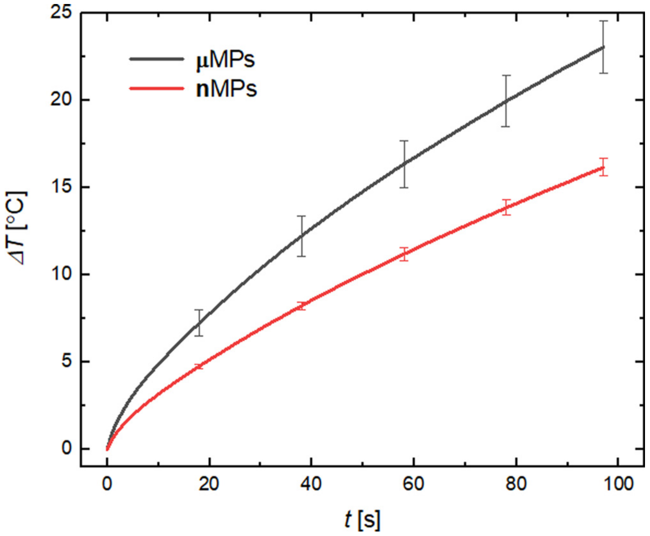


Fig. 5. Temperature rise in time of magnetic heating for different-size magnetic particles suspended in castor oil.

heating when **MPs** are used as mediators. The longer the exposure to the alternating magnetic field and/or the concentration of **MPs**, the higher the observed temperature increase. This rise is significant and occurs not only for the emulsions but also for the suspensions. This fact is of importance for colloidal capsule formation that will be described in the next section.

3.2. Formation of Pickering-emulsion-based capsules

In the previous paragraph, we showed that under alternating magnetic field magnetite particles acted as a good heat source in both Pickering emulsions and suspensions. This insight could be applied to the formation of Pickering-emulsion-based colloidal capsules if a sufficiently high sample temperature can be achieved.

A conceptual scheme of colloidal capsules formation using the magnetic field is presented in Fig. 6. In the first case (Fig. 6a), emulsion droplets prepared as described in section 2.2. were placed in the alternating magnetic field in a glass cuvette. The observed temperature increase was high enough to facilitate sintering of polystyrene particles attached to the droplets of the emulsion and enable formation of colloidal capsules. In the second case (Fig. 6b), a single silicone oil droplet with a polystyrene particle shell was formed in castor oil under the electric field using a mechanical pipette. At first, the particles were located inside the silicone oil droplet. Due to the presence of electrohydrodynamic flows, the particles were moved to the droplet's surface and got attached to the interface [43]. After a few minutes in the electric field, all particles were brought to the droplet's surface and formed a dense layer. This way we obtained Pickering droplet as those presented in our emulsions.

The findings from paragraph 3.1. show clearly the efficiency of heating when oil-in-oil Pickering emulsions were exposed to the external magnetic field. It was also proved that this efficiency depended strongly on the amount of the magnetic material used. In case of particles used in this work, the obtained local temperature can exceed the required temperature of glass transition of polystyrene as it is shown in Supplementary Materials, Fig. S**1**. It presents mixtures of polystyrene and magnetite particles in the form of a powder sprinkled onto the slide (Fig. S**1a**). After 2 minutes in the alternating magnetic field (parameters exactly the same as for other experiments) the transition into the glass was clearly visible (see inset pictures in Fig. S**1c**). In addition, rough pyrometer measurements (Fig. S**1b)** indicate that the temperature in the mixture of powders was high enough for **PSPs** to be sintered. It is worth pointing out that pyrometer measurements are sensitive only to the temperature of particle surface. Inside the mixture of powders, the temperature observed would be even higher.

In section 3.1. we showed that the temperature rise is a function of **MPs** concentration in a given emulsion system. Thus, high concentration of **MPs** in the emulsion is able to induce a sufficiently high-temperature rise for sintering **PSPs** to occur. Fig. 7**.** presents the appearance of a dense emulsion (1:2 silicone oil to castor oil mass ratio) after stabilization in the electric field and following magnetic heating. In Fig. 7**c** the corresponding temperature measured in this sample is depicted.

As one can see, the temperature increase in such a dense emulsion (50% mass concentration of silicone oil, 7.5% mass concentration of magnetite particles) was very dynamic and a high final rise was achieved. For long heat treatment it was possible to reach the temperature of **PSPs** allowing for their fusion. In this case, it is possible to form numerous capsules at the same time. Because of small dimensions of such droplets and capsules, there are no facile routes to prove evidently that a robust shell around the droplet was formed and, as a result, a capsule was formed. However, in the future, non-direct methods can be proposed to cope with this, e.g. an ultrasound technique [44].

Various types of colloidal particles, including magnetic, may be used for formation of Pickering emulsions [45,46]. Here, we studied those stabilized with magnetite particles due to their potential as templates for fabrication of colloidal capsules in a magnetic field. Induced heat generation is their defining feature. Other groups have also used magnetic particles in this context, for instance to laden bubbles [47]. In addition, preparation of capsules containing magnetic materials is of great importance for magnetic hyperthermia applications [48] and magnetic resonance imaging [49]. An important feature of such droplets and capsules is that they can be administered to a specified region in the patient's body using static magnets. Then an alternating magnetic field may be applied to induce heat generation and cargo release, if thermally responsive soft particles were used in addition to the magnetic particles [50,51].

Now we show a potential of formation of a single colloidal capsule in a magnetite suspension in castor oil. In this case, the capsule does not contain any magnetic particles on its surface. The experiment was performed based on the scheme presented in Fig. 6**b**. A colloidal capsule obtained this way differs from a non-sintered particle-covered droplet in susceptibility to external stress. Because a particle-covered droplet is less rigid than a capsule, a surface deformation should be observed. In Fig. 8, we present results from the experiment where droplets and subsequently formed capsules were subjected to the electric field of increasing intensity (from 0 V·mm^{-1} to 195 V·mm^{-1}). The pictures were recorded using the system described in section 2.1. As **µMPs** provided a higher temperature rise in the emulsion system, we used them in this experiment as well.

The quantitative evaluation based on the pictures was also performed. The deformation was calculated using the equation:

$$D = \frac{x_l - x_p}{x_l + x_p} \tag{5}$$

where x_l and x_p are the dimensions of droplets in the longitudinal and parallel direction to the electric field. The magnitude of D is determined by the dielectric constants of the droplet, particles and the continuous phase as well as surface tension [52,53]. We can observe how the deformation evolved as electric field intensity was changed. The values are presented as the inset table in Fig. 8**c**.

The results indicate clearly that after heating treatment in the alternating magnetic field droplet shell became rigid. Electric field stress did not cause an increase of deformation D as it was in the case of a droplet before heating. This is evidence that our approach to sintering works properly. We performed these experiments using polyethylene microparticles (27-32 µm in size) as well. Also, in this case, we managed to induce a change in the appearance of the particle shell during the heating in an alternating magnetic field. The results are presented in Fig. 9. Because of the difference in glass transition temperature, **PSPs**

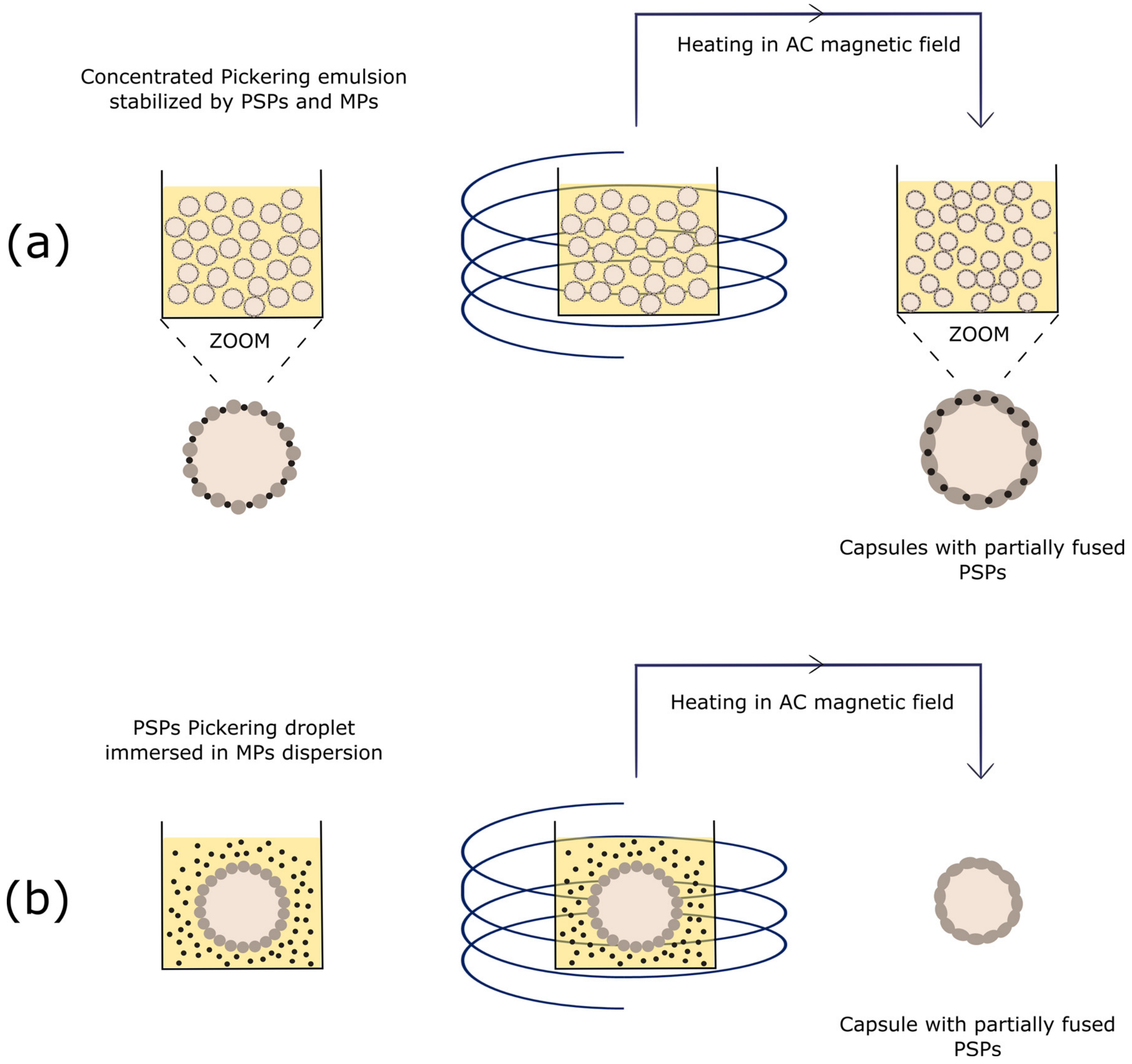


Fig. 6. The concept of fabricating colloidal capsules in the alternating magnetic field.

were detached from the surface, whilst PE particles formed characteristic patches.

Other example of using polyethylene particles is presented in Supplementary Materials, Fig. **S2**. In this picture, one can see patches of some sort on the droplet's surface formed during the heating process. Based on that observation we think that fabrication of not only colloidosomes but also patchy colloidosomes may be possible, especially when a combination of particles differing in thermal properties (namely, glass transition temperature T_g) is used. Using the presented method of capsule formation, it is possible to achieve results comparable to heating by using other methods, e.g. in a microwave device (Fig. S**3**). However, by changing parameters such as concentration of magnetite particles in the process of capsule formation, one can achieve greater control compared to heating in a microwave device while making the procedure easier.

In our experiments, the temperature rise induced by the magnetic particles exposed to an alternating magnetic field and immersed in a carrier liquid was accompanied by convection flows observed in the sample cell. These flows could be utilized e.g. to break agglomerates of droplets in emulsions, analogically to breaking droplet chains by strong electrohydrodynamic flows (as it was described in [35]). In the presence of a higher temperature-controlled destabilization of the emulsion systems is possible [16]. In addition, particles [54] and molecules [55] were reported to be more efficient emulsifiers under those conditions. Magnetic particles could be used as agents for providing temperature elevation in these systems.

3.3. Discussion

In the presented study, the sources of heating were magnetite nano- and microparticles. As indicated in section 3.1., the temperature elevation measured in a system depended on a concentration and a size of magnetic particles. Higher temperatures obtained in emulsions with **μMPs** compared to those with **nMPs** can be explained by microparticles being multi-domain and thus hysteretic loss being an additional mechanism of heat generation. In our calorimetric measurements, we only changed the concentration and the size of particles with magnetic properties, i.e. the amount of dispersed phase (silicone oil) and polystyrene particles (**PSPs**) remained the same for all tested samples. However, the change in the concentration of silicone oil and **PSPs** could affect the magnetic heating indirectly by changing heat capacity of the sample and, in general, the mechanism of heat transfer through it. For investigating the influence of different concentrations and sizes of magnetite particles on the heating efficiency of emulsions, calorimetric measurements were carried out for constant parameters of magnetic field. The increase of the intensity of the alternating magnetic field would facilitate the heating efficiency of emulsions and shorten the time when the temperature of the sample exceeds the temperature of

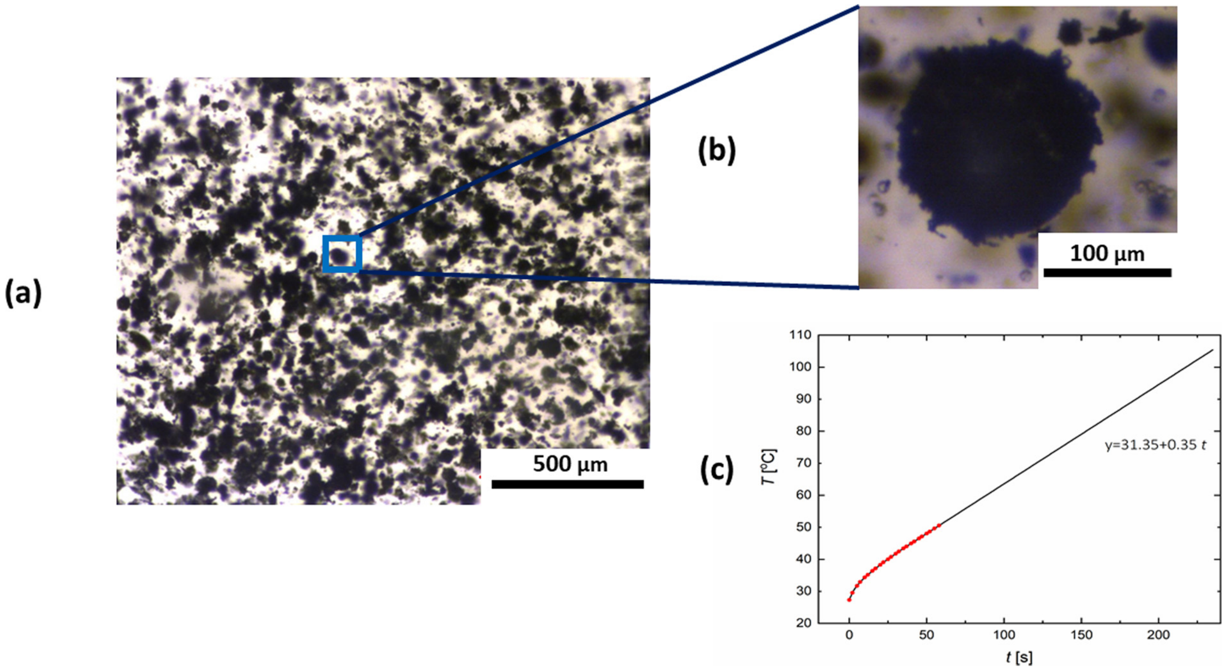
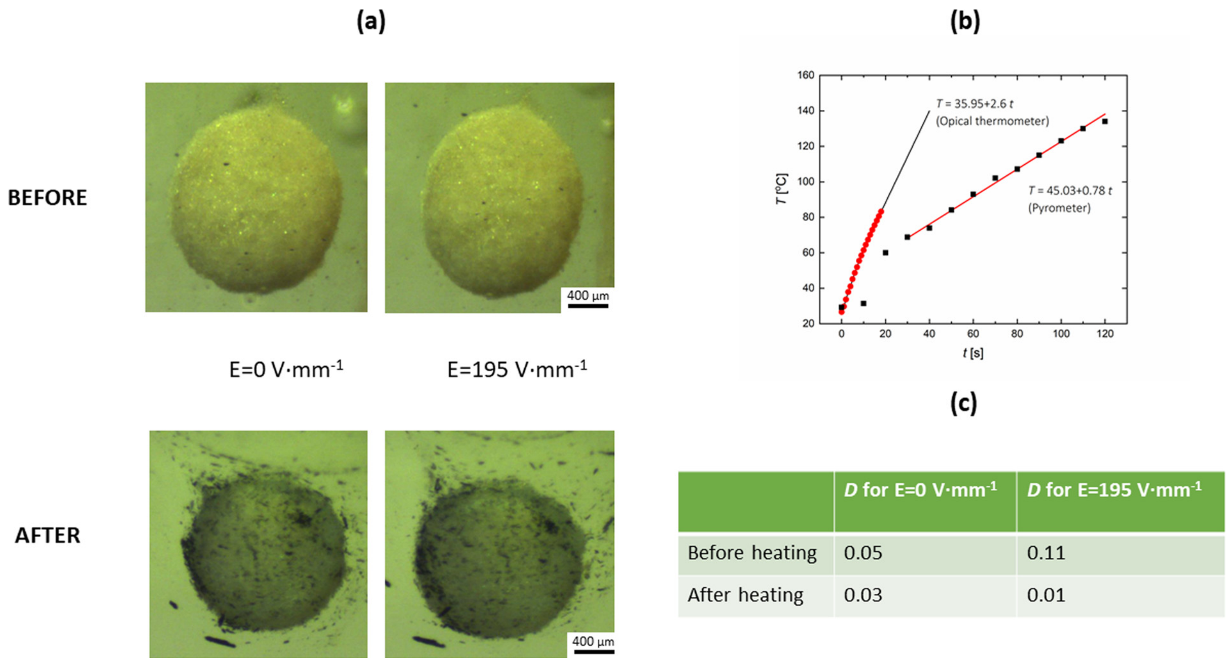


Fig. 7. (a) Appearance of a concentrated emulsion (1:2 silicone oil to castor oil mass ratio) after exposure to heating in the alternating magnetic field (suspension of colloidal capsules). (b) An extracted single Pickering droplet after magnetic heating. (c) Temperature rise recorded in the emulsion sample for mass concentration of magnetic particles equal to 7.5% w/w.

glass transitions.

PSPs undergo glass transition in the temperature above 100 °C [56]. The temperature of glass transition (T_g) varies for different soft particles. For instance, polyethylene particles (the results presented in Fig. S2) are believed to undergo glass transition in lower temperatures, i.e. 70-80 °C [57]. The process of capsule formation can therefore be optimized by using different particles with lower T_g and better efficiency of heat transferring, i.e. with lower heat capacity. Also, different concentrations and sizes of soft particles can have an impact on the effective process of rigid shell formation around droplets.

The influence of changing the frequency of the magnetic field on the heating efficiency in magnetic hyperthermia has been documented in the literature. For instance, for magnetic fluid with magnetite nanoparticles coated by a dextran layer Skumiel et al. indicated a significant dependency of heating efficiency on frequency [58]. At the same time, the Brown relaxation is strongly dependent on the viscosity of the medium in which magnetic particles are immersed (see Eq. 1). The high viscosity limits the ability of particles to rotate in samples under the



	D for E=0 V·mm^{-1}	*D* for E=195 V·mm^{-1}
Before heating	0.05	0.11
After heating	0.03	0.01

Fig. 8. (a) Pickering droplets before and after alternating magnetic-field induced heating for ~40 seconds. Pictures are taken using an optical microscope (section 2.1.). (b) Temperature rise recorded by an optical thermometer and a pyrometer in a suspension of **µMPs** in castor oil during the fabrication of the capsule (c) Deformations *D* calculated before and after magnetic heating treatment (Eq. 5).

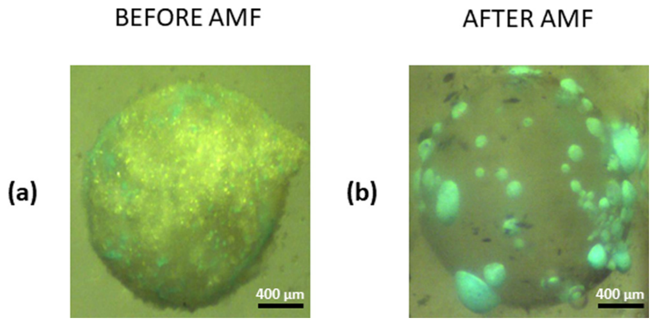


Fig. 9. Pickering droplets covered by both polystyrene (**PSPs**) and polyethylene particles (**PEPs**) (a) before and (b) after the application of the alternating magnetic field (AMF). Pictures are taken using an optical microscope (section 2.1.).

alternating magnetic field [46,59]. Thus, using emulsions with different outer phase i.e. oil-in-water emulsions, would increase the heating effect of a sample and speed up the process of capsule formation from emulsions as templates. A subtle point was that particles resided at the same time in the outer and inner phase of emulsion with different dynamic viscosity (700 mPa·s vs. 50 mPa·s respectively). In the case of fabricating capsules from polystyrene-covered droplets immersed in **MPs** dispersion, the situation is much simpler, i.e. the change of viscosity of carrier liquids to those of lower viscosity should facilitate the process of heating because of the increased influence of Brown relaxation mechanism.

We conducted the appropriate and indispensable experiments to evaluate calorimetric properties of Pickering emulsions with droplets covered by soft particles (**PSPs**) and magnetic particles as well as to investigate the potential of capsule formation from Pickering droplets precursors. As indicated above, the process can also be optimized by changing parameters connected to the alternating magnetic field and emulsions. Our concept to use the heat generated under an alternating magnetic field to increase the temperature of Pickering emulsions and to fabricate sintered shells around droplets can be widely utilized in the future as it is not limited to oil-in-oil emulsion systems. The other types of particles, including those of biological origin, can be explored as well. Our approach to the formation of Pickering emulsions takes advantage of limited coalescence that results in a facile control of the size of droplets. With the use of smaller particles for the stabilization of emulsion precursors, fabrication of much smaller capsules (micrometer in size) will be also possible, further extending the applicability of our method.

4. Conclusions

In this study, the formation of capsules by using magnetic heating was proposed as a novel potential application of alternating magnetic fields. Oil-in-oil Pickering emulsions stabilized by both magnetite and polystyrene colloidal particles were exposed to the alternating magnetic field. As a result, we observed a temperature rise in the emulsion system that can be utilized to form colloidal capsules either from corresponding single Pickering droplet precursors or from bulk Pickering emulsions.

The results of the calorimetric measurements indicated that the efficiency of the heating depended on the size and the concentration of magnetite particles used to co-stabilize emulsions. This efficiency was also shown by the specific absorption rate (SAR) calculations that delivered almost 1.5 times higher values for bigger magnetite particles.

We showed two different but complementary approaches to capsule fabrication. We managed to form droplets with partially fused **PSPs** from stable emulsion droplets. Sufficient temperature increase was observed for highly concentrated Pickering emulsion. Formation of a single droplet covered by non-magnetic particles and further placing it into magnetite suspension was also proved to work as intended.

5. Author Contribution

AJ designed the original idea of using an alternating magnetic field to form colloidal capsules. RB designed the experiments. RB and DS performed them. RB analyzed and presented the data. KK participated in data presentation and description. RB wrote the first version of the manuscript. All authors contributed to the finalization of the manuscript.

Conflict of Interests

here is no conflict of interest to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.colsurfb.2020.111070.

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