Complex architectures formed by alginate drops floating on liquid surfaces†‡

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We demonstrate the generation of natural polymeric structures of complex shapes and controlled composition, starting from the collision of aqueous drops of alginate with the surface of a calcium ion-based liquid. We prove that by tuning the impact velocity of the alginate drops on the target surface one can control the floating state of the drops inducing the formation of mushroom-like structures, upon alginate gelation. Besides the geometric peculiarity, the presented approach allows us to provide dual functionality to the polymeric objects, attaching different kinds of functional molecules onto their surface areas, which are immersed or not in the liquid, making such architectures attractive for the development of a novel class of bionanocomposites.

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1 Introduction

The impact of a liquid drop on a surface (solid or liquid) is a well-studied natural phenomenon with applications in spray cooling and coating, inject printing, combustion processes, and meteorology.¹ For a drop impinging on a liquid surface, different collision dynamics can be observed, such as floating, total or partial coalescence, jetting, bouncing, and splashing.^{2,3} Such phenomena depend on various parameters that include the physical and chemical properties of the involved liquids, the depth of the liquid reservoir, and, most importantly, the impact velocity of the drop.⁴ The latter is the key parameter to discriminate the different scenarios associated with drop collision.^{4–6} In fact, the release of a drop above a liquid surface, with moderate or low kinetic energy prior to collision, results in floating, partial coalescence or bouncing;⁷ in contrast, total coalescence, bubble entrapment and formation of jets can be observed after the collision with a drop of high kinetic energy.⁴ Typically, an impinging droplet of low energy approaches gradually the liquid interface and first rests in a floating state for a period that ranges from milliseconds to a few seconds, depending on the nature of the liquid.^{8,9} Then, the interfacial

layer that separates the two liquids dissipates, resulting in complete merging of the drop within the bulk liquid or partial coalescence with the formation of daughter droplets.^{10,11}

For pure water, floating is rarely observed due to the stringent requirements for which it occurs,⁵ and delayed coalescence can be produced only under certain conditions, by using for instance temperature gradients, the continuous motion of the interface by shaking or stirring, and electric fields.¹² The formation of floating drops is, instead, more readily obtained when liquids with different molecular structure consisting of long polar molecules are used for the droplet and the bulk.¹³ A state of permanent non-coalescence can be established by the creation of a lubricant fluid film between the involved interfaces.¹⁴

In this paper, we investigate the floating of drops of sodium alginate, a polysaccharide derived from brown algae, on the surface of a water-based calcium chloride solution, and we follow the subsequent shape modification of the droplets during the alginate gelation due to the calcium ions, giving an insight into the related physics. It is known that polyvalent metal cations, like Ca^{2+} , can bind to the guluronic acid sites, which are arranged along the polymer chain of sodium alginate,^{15,16} forming a stable gel used in the food industry, and in biotechnology.^{17–19} We take advantage of the floating event in combination with the alginate gelation process for the generation of structures of complex shape and anisotropic chemical character. In particular, the formation of “mushroom” shaped objects of calcium alginate is obtained, with geometric characteristics sufficiently controlled by the alginic acid concentration in water and by the impact velocity of the drops onto the aqueous calcium chloride solution. Such “mushroom” architectures are produced when, after the impact of alginate droplets on the liquid surface, the former float, and thus the alginate

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† For our system, we calculated R_v as 0.97, 1.00, 1.03, and 1.06 for Alg1, Alg3, Alg5, and Alg7, respectively.

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gelation due to calcium ion exchange occurs first at the submerged part of the droplets and subsequently to the rest of the structures. Besides the geometric peculiarity, the presented approach allows us also to spatially localize chemical substances only on the portion of the alginate “mushrooms” in contact with the liquid, obtaining structures with spatially controlled functionalities. To this aim, we exploit the exceptional nature of alginate, which is able to encapsulate functional molecules presented in an aqueous environment simultaneously with the gelation process.

2 Materials and methods

2.1 Collision experiments

Solutions of sodium alginate at different concentrations, 1 wt% (Alg1), 3 wt% (Alg3), 5 wt% (Alg5), and 7 wt% (Alg7), were prepared by mixing alginic acid sodium salt from brown algae (Sigma-Aldrich) and ultrapure water, and by stirring at 70 °C overnight. Drops of alginate solutions with three volumes, 5.6 μL (diameter, $d \cong 2.2$ mm), 8.2 μL ($d \cong 2.5$ mm), and 14.1 μL ($d \cong 3.0$ mm), were generated at the tip of the stainless steel needle by changing the outer diameter of the needle (0.45, 0.75, and 1.00 mm, respectively), and vertically detached off under their own weight. They were released from different heights (ranging from 5 to 10^3 mm) into a reservoir (volume 200 mL, height of 50 mm) of a 20% w/v aqueous solution of non-purified calcium chloride (CaCl_2 , Sigma-Aldrich). The temperature of the solutions and the laboratory were kept at around 25 °C. Bicolor microstructures were produced by using Rhodamine B isothiocyanate (Sigma-Aldrich), a water-based solution of Crystal violet (Sigma-Aldrich), and a natural green dye for foods.

2.2 Characterization of the liquid solutions and the microstructures

The involved liquids were characterized in terms of density (ρ), surface tension (σ), and viscosity (η). The density was determined by measuring the mass of a known volume (10 mL) of alginate solution for the four different concentrations. For solutions Alg1, Alg3, Alg5, and Alg7, ρ is (996 ± 1) kg m^{-3} , (1006 ± 1) kg m^{-3} , (1013 ± 1) kg m^{-3} , and (1023 ± 1) kg m^{-3} , respectively. Moreover, the surface tension of the produced solutions (alginate and CaCl_2) was measured by the pendant drop method, using the tensiometer KSV-CAM200 instrument (KSV, Finland). σ varies from 70.0 ± 0.4 mN m^{-1} for Alg1, 67.2 ± 0.5 mN m^{-1} for Alg3, 65.8 ± 0.5 mN m^{-1} for Alg5 to 63.9 ± 0.5 mN m^{-1} for Alg7; CaCl_2 solution has a surface tension of 67.8 ± 0.1 mN m^{-1} . Finally, the viscosities of the alginate solutions were analyzed by an Anton-Paar Physica MCR 301 rheometer, equipped with cone plate geometry (CP-25, diameter 25 mm). From the viscosity vs. shear rate plots, we measured an average value of η at the shear rate between 10^{-1} and 10 s^{-1} , a typical range used for the phenomenon of draining under gravity²⁰ that well describes our system. The measured values of η are 0.02, 0.2, 3.8, and 20.1 Pa s for Alg1, Alg3, Alg5, and Alg7, respectively. As expected the viscosity increases as the concentration of alginate increases. The properties of the involved liquid are summarized in Table 1.

Table 1 Physical properties of the alginate solutions used in the experiments

Sodium alginate conc. in water (%)	Density (kg m^{-3})	Surface tension (mN m^{-1})	Viscosity (Pa s)
1	996	70.0	0.02
3	1006	67.2	0.2
5	1013	65.8	3.8
7	1023	63.9	20.1

Photographs of the alginate structures were taken by a Canon EOS 5D (macrolens 100 mm) and used to obtain quantitative information on the dimensions of the particles. Videos of the formation of the anisotropic architectures are recorded by a high speed camera IDT MotionXtra NX4S2, working at a maximum frame rate of 9090 Hz. Finally, the morphology of the produced calcium alginate “mushrooms” was characterized by Scanning Electron Microscopy (SEM), using a JEOL JSM-6490LA microscope working in high vacuum mode, with an acceleration voltage of 15 kV. Before the imaging, the structures were dried in air at room temperature overnight, and coated with a 10 nm film of carbon.

2.3 Parameters of impacting drops

There are two main dimensionless parameters that describe the impinging process of liquid drops onto a liquid surface: the Weber number (We), which is the ratio of the kinetic energy to surface tension forces, and the Froude number (Fr), which is the ratio of the characteristic velocity to gravitational forces.² They are defined as $We = \rho v^2 d / \sigma$ and $Fr = v^2 / g d$, where ρ is the density of the liquid drop, v is the impact velocity, d is the drop diameter, σ is the surface tension of the liquid that forms the drop, and g is the gravitational acceleration.⁵ The classification of the different impact regimes is typically obtained by the plot of We as a function of Fr .⁶ In particular, it has been demonstrated that when $Fr \leq 7$ and $We \sim Fr$ the drop floats onto the liquid surface; when $We < 10$ and $Fr > 7$ coalescence or bouncing events can be observed.⁵ Maintaining constant the drop diameter and changing only the impact velocity, the ratio We/Fr , known as the Bond number (Bo), depends exclusively on the surface energy of the drop.⁸ Actually, low values of the Bo (less than 1) indicate that the collision process is dominated by the drop surface tension that balances the gravity. Moreover, the relative importance of the viscous forces is evaluated by the Ohnesorge number, $Oh = \eta / (\rho \sigma r)^{1/2}$, which is independent of the impact velocity (where r is the radius of the droplet). In particular, high values of Oh ($\gg 1$) indicate a great influence of the viscosity on the drop deformation.⁸

3 Results and discussion

We first analyze the final shape of the alginate structures formed into the CaCl_2 solution by changing the impact velocity of the drops, expressed by $v = (2gh)^{1/2}$ (where h is the falling height from the tip of the needle to the target surface), considering a free falling motion and neglecting the drag force

Fig. 1 Ratio d_A/d_B as a function of the falling height and of the corresponding impact velocity for calcium alginate microstructures obtained from 5.6 μL droplets of Alg3 solution. Photographs of the produced beads are reported for specific falling heights: for $h = 0.01$ m, the tail on the top of the beads is clearly visible. Inset: schematic representation of the alginate bead, indicating d_A and d_B .

of air. In Fig. 1, the shape of calcium alginate beads, obtained starting from 5.6 μL Alg3 drops, is investigated for different falling heights and the corresponding impact velocities, evaluating the ratio d_A/d_B , where d_A and d_B are the diameters parallel and perpendicular to the falling direction, respectively (inset Fig. 1). We observed that for high impact velocity (higher than 2.4 m s^{-1} , corresponding to h bigger than 0.3 m) the particles are deformed and compressed at the bases, resulting in an elliptical geometry with $d_A < d_B$ ($0.81 \leq d_A/d_B \leq 0.86$); when h decreases with a consequent reduction of v (down to 0.6 m s^{-1}), the particles tend to assume a more spherical shape ($0.86 < d_A/d_B \leq 0.98$). For even lower velocity values, in the range of 0.4–0.6 m s^{-1} , the beads become spherical ($d_A/d_B \approx 1$), whereas a tail starts to appear on their upper part for v around 0.4 m s^{-1} . The formation of the tail is due to the slow transit of the droplet across the air– CaCl_2 interface, as it has also been observed in alginate microbeads produced by means of microfluidic devices.²¹ We noted a similar behavior also for Alg1, Alg5, and Alg7 solutions and for bigger droplets.

When h is further reduced (< 8 mm) and the corresponding impact velocity becomes smaller than 0.4 m s^{-1} , drop floating on the liquid surface occurs for all types of alginate solutions used.

The evolution in the time of the floating event was investigated by a high-speed camera with a frame rate of 9090 Hz, and displayed in Fig. 2 for a drop of Alg3 with a volume of 8.2 μL . We observed that, after detaching from the needle, the sodium alginate droplet collides with the target liquid interface that bends to accommodate the impact (Fig. 2a); then, it starts to deform and penetrate inside the calcium chloride solution (Fig. 2b). During the first 100 ms after the impact (Fig. 2c–f), the droplet continues to undergo shape modifications, eventually

Fig. 2 (a–f) Time sequence of the floating event observed for a 8.2 μL drop of Alg3 solution and a falling height of 4 mm. $t = 0$ ms represents the contact of the droplet with the surface of the CaCl_2 solution. Scale bar: 1 mm.

becoming hemispherical (Fig. 2f) with a flat upper surface exposed in air and not in contact with the CaCl_2 bath. The remaining part of the drop is instead immersed in the liquid, where the diffusion of the Ca^{2+} ions starts the cross-linking reaction of the alginate. After 100 ms, the system reaches the

Fig. 3 (a) Pictures at different time intervals of the formation process of an anisotropic structure, starting from a 8.2 μL drop of Alg3 solution and a falling height of 4 mm. Scale bars: 1 mm. In the picture $t = 400$ s, the characteristic dimensions of the structures are reported. (b) d_{em} (full circles) and h_{em} (empty circles) as a function of the generation time. By changing the alginate concentration it is also possible to control the gelation time and, consequently, the time needed for the formation of the structures.

equilibrium static state, where the gravity is balanced by the surface tension, and the floating state is maintained. Interestingly, for all the different alginate concentrations and drop diameters, the Fr and We numbers (see Section 2.3) calculated for h lower than 8 mm are smaller than 7, as expected for floating events (Table S1 in the ESI†),⁵ while Bo is around 1 (Table S2 in the ESI†) indicating a balance between the involved surface tensions and gravitational forces.

Therefore, in the first 0.1 s, the geometry of the submerged portion of the drop is defined by the collision and gel formation at the interface of the sodium alginate and the $CaCl_2$ solution. In this phase, the upper flat surface of the floating drop is still in the liquid non-polymerized state. Subsequently, it starts to change its shape, from flat to concave (Fig. S2†): at 4 s this modification is more obvious, and it continues until 400 s as shown in Fig. 3a. During this period, the gelation front of the alginate (known as contraction layer) propagates from the immersed to the emerged portion of the particle, as a consequence of the diffusion of the calcium ions. We can assume that the cross-linking reaction strongly affects the generation of the final cylindrical shape of the emerged part. The formation progress of the contraction zone in fact is accompanied by the movement of the alginate chains (chain contraction) with a consequent mass transport.²² This exerts a frictional force per

volume on the surrounding solution, directed towards the gel-liquid phase, determining the elongation of the particle along the vertical direction.

We investigate the variations in shape of the floating alginate as a function of time, considering the height and the diameter of the immersed and emerged part, as presented in Fig. 3b. For the analyzed case (8.2 μ L in volume, Alg3 solution), the height (h_{im} , Fig. S1†) and the diameter of the immersed part (d_{im} , Fig. S1†) become stable almost from the beginning of the process, at values around 1.1 mm and 2.1 mm, respectively. In contrast, the height (h_{em} , empty circles in Fig. 3b) and the diameter (d_{em} , full circles in Fig. 3b) of the emerged part change much more dramatically over time. In particular, h_{em} rises from 0.54 mm ($t = 4$ s) to the final value of 1.4 mm ($t = 340$ s), and d_{em} decreases from 2.5 mm ($t = 4$ s) to 1.2 mm ($t = 340$ s). Moreover, we observed that the volume of the floating drop decreases with time, and remains constant after 400 s. This shrinkage can be related to the difference in osmotic pressure between the $CaCl_2$ solution and the alginate drop.²³ At the end of the process, in order to ensure the completion of the polymerization of the emerged part of the alginate, which occurs partially during the floating state, we force the submersion of the entire microstructures into the $CaCl_2$ solution.

Fig. 4 Photographs of alginate “mushrooms” obtained from 5.6 μ L drops of (a) Alg1, (b) Alg3, (c) Alg5, and (d) Alg7 solution (scale bar of 1 mm). Characteristic dimensions of the produced structures as a function of the alginate concentration and Oh number; (e) h_{im} , (f) d_{im} , (g) h_{em} , and (h) d_{em} , for different droplet volumes: 5.6 μ L (magenta triangles), 8.2 μ L (green circles), and 14.1 μ L (black diamonds). Inset: SEM image of one single dried structure.

Taking advantage of the ion-exchange between sodium alginate and CaCl_2 , and of the consequent gel formation, we succeed in generating calcium alginate structures with remarkable geometries. In fact, we exploit this floating state to produce anisotropic alginate architectures with a “mushroom”-like shape, where the submerged portion represents the cap of the mushroom and the emerged one the stalk. As presented in Fig. 4a–d, the “mushroom”-like shape of the produced structures can vary with the alginate concentration and the diameter of the starting droplet.

The dependence of the dimensions on the alginate concentration can be associated to the different viscosities of the used solutions and, consequently, to the corresponding Oh number, which is lower than 1 for Alg1 and Alg3 for all droplet diameters, and in the range of 12–14 and 67–77 for Alg5 and Alg7, respectively (Table S2†). In particular, starting from the same droplet volume and increasing the Oh number by increasing the viscosity of the alginate solution, we observed that the height of the immersed (h_{im}) and the emerged part (h_{em}) increases (Fig. 4e and g). Consequently, the cap becomes more elongated and the total height of the mushroom-like microstructures is enhanced. On the other hand, the diameter of the immersed region (d_{im}) decreases (Fig. 4f) with increasing alginate viscosity, whereas the diameter of the stalk (d_{em}) initially increases and reaches a plateau for alginate concentrations above 3% ($\text{Oh} \geq 0.7$, Fig. 4h). Hence, the final geometry of the alginate structures can be tuned by acting on the alginate concentration.

A closer look at the morphology of the formed objects demonstrates a perfect hemispherical structure of the “mushroom’s” cap (Fig. S3†), corresponding to the globe formed at the CaCl_2 interface upon droplet’s impact. The base of this hemisphere (that is connected with the stalk) is not flat but presents a concavity (Inset Fig. 4g), where the external regions (towards the edge of the cap) are protruding with respect to the central one. This geometry can be associated with the motion of liquid in the vertical (upward and downward) and horizontal (away from and towards the centre of the droplet) direction during the formation of the structures, or to the subsequent emergence of the central part of the hemisphere to eventually form the stalk.

Adding to the initial aqueous solutions of either the sodium alginate or the calcium salt functional molecules or nanoparticles, we manage to incorporate the additives respectively either into the entire alginate structures or exclusively into the cup of the “mushroom”, adding new functionalities to the produced asymmetric structures. As a proof of concept, dye molecules were dissolved either into the sodium alginate solution or in the Ca^{2+} ion solution. The mushroom-like particles were subsequently formed as described above, and removed from the liquid surface by withdrawing them using a pipette. As displayed in Fig. 5a, structures with different colors are obtained when the aqueous sodium alginate solution was mixed with Rhodamine B (pink structure), Crystal violet (violet structure), and a natural dye for foods (green structure), respectively. The dye molecules are uniformly distributed throughout the entire structures. More interestingly, when the alginate droplets without added dyes float after their impact

Fig. 5 Pictures of anisotropic structures, formed by 5.6 μL droplets of Alg3 solution, (a) fully treated with different dyes, (b) and (c) partially functionalized with Rhodamine B and a green dye for foods, respectively. Scale bar of 1 mm.

with the surface of CaCl_2 solution mixed with dyes, asymmetric structures characterized by a controlled spatial deposition of the dye molecules are produced. As displayed in Fig. 5b and c, the deposition of the functional compounds is obtained exclusively on the cap portion of the alginate structures in contact with the dye/ CaCl_2 solution. After the cross-linking of the alginate, the cap becomes colored, whereas the stalk remains transparent, characteristic of pure alginate. In this way, the proposed fabrication process results in alginate architectures with both geometric and chemical anisotropy, easily imposing a double character to the alginate “mushrooms”. The developed method can be extended to other water-soluble compounds, particularly of interest in pharmaceutical applications for the encapsulation of drugs, or other compounds and nanoparticles soluble in water-compatible solvents.

4 Conclusions

In conclusion, we demonstrated that starting from sodium alginate drops floating on a liquid surface it is possible to generate polymeric anisotropic structures with a mushroom-like shape. The impact velocity of the droplet, and the viscosity of the involved liquids are the key parameters to control the floating state and the final shape of the structures. Moreover, the fabrication method presented here allows us to easily localize chemical substances only on one specific portion of the structures, resulting in different functionalities of the cap and stalk. This double character of the produced natural polymeric structures, hard to achieve with other fabrication techniques, is

of interest in the controlled deposition of functional molecules and in the synthesis of bionanocomposites.²⁴

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