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Effect of liquid pool concentration on chemically reactive drop impact gelation process

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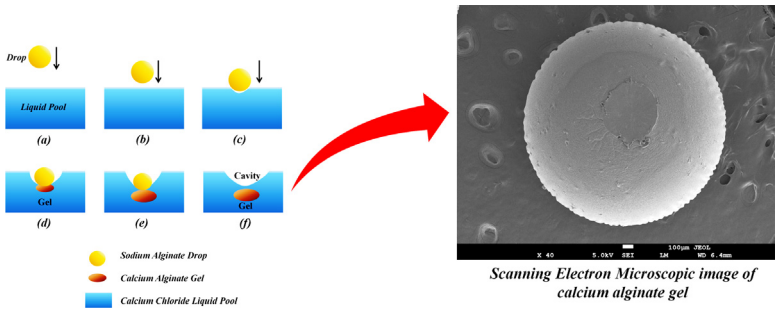
GRAPHICAL ABSTRACT



Scanning Electron Microscopic image of calcium alginate gel

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ABSTRACT

Coupled effects of hydrodynamics and chemical reaction during gelation process have been studied in the current work. Here, a viscous sodium alginate liquid drop impacts on calcium chloride liquid pool, chemically reacts with the pool, forms a crater, and instantaneously changes its phase from liquid to soft solid called as gel. The drop impingement height and liquid pool concentration are varied to study the effect on this process. This phenomenon is captured in a time resolved high-speed camera and the dynamics of the crater is traced using image processing technique. We also use a mathematical model for crater growth which we assume to be influenced by the rate of gelation. By validating the theoretical trend with the experimental counterpart, the gelation energy has been obtained. Scaling analysis has been executed to determine significant contributory energy in the crater growth. It is also observed that the gel swelling occurs beyond a critical concentration of calcium chloride. Also, the effect of gelation on the homogeneity and strength of alginate gel are interpreted from the surface morphology examination in scanning electron microscope. Thus a new insight of gelation process has been elucidated from the context of fluid dynamics.

1. Introduction

The study of encapsulation is an emerging area of research which accounts a phase change process called gelation. The encapsulations of vitamin, cell, oil, flavour, protein, food ingredients [1–8] etc. are vital contents to be encapsulated. A liquid drop impinging on a chemically reactive liquid bath can form a gel. The gelation dynamics is associated with three major phenomena such as drop hydrodynamics, chemical reaction and phase change. Scientists have worked out on drop hydrodynamics related to coalescence [9–12], vortex ring evolution [13–17], jetting [18–20], crater formation [21–24] etc. But drop hydrodynamics in context of gelation is not studied extensively [25–27]. The major

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drop impact outcomes which are relevant to the gelation are air film rupture, bubble entrapment and crater propagation.

The studies on crater propagation have been pioneered by Engel [21]. A model equation of crater growth has been developed based on energy balance after liquid drop impact on liquid pool and an expression for maximum crater depth has been evolved. In the continuing work, Engel [22] proposed the expression of velocity potential, crater depth and crater wall velocity of crater dynamics. Van de Sande et al. [23] also studied theoretically the temporal behaviour of crater during single water drop impact on water pool. Similar dynamic model of crater evolution during jet formation from the water pool after drop impact has been developed by Fedorchenko and Wang [24]. They found that maximum crater width is dependent on dimensionless Froude Number and capillary length. An extensive study of different features during crater propagation after viscoelastic drop impact on liquid interface has been studied by Pregent et al. [28]. The variation of crater depth, interfacial area, and drop energy with the liquid pool viscosity, molecular weight of polymers are reported in their work. The drop kinetic energy and viscosity are the primary contributing factors compared to the viscoelasticity in the role of deformation of the drop. Similar study on crater morphology for Newtonian and non-Newtonian liquid had been carried out by Ogawa et al. [29]. In an experimental and theoretical work of Berberovic et al. [30], the penetration depth of crater was suggested by taking the liquid surface tension, viscosity, inertia and gravity in to account. They concluded that depth of crater evolution and time of maximum crater depth is irrespective of impact velocity for the same film thickness. They also numerically predicted the role of capillary wave in the crater wall. Bisighini et al. [31] also developed a model on crater growth from stress balance at the interface accounting the effects of inertia, surface tension, viscosity and gravity. Chen and Lai [32] studied crater dynamics, drop disintegration beneath the liquid pool using high-speed camera for water drop impact on deep diesel fuel pool. They determined a critical Weber number for which number of droplets disintegration become constant. Recent study of Murphy et al. [33] reveals the phenomena of seawater aerosol formation by studying the high speed imaging of underwater crater dynamics and splashing and crown formation. Most recently, cylindrical shaped crater is assumed to derive a formula for maximum crater depth and its effect on jet breakup [18]. However, none of the research works have considered the influence of phase change in the crater growth equation.

The application based study of crater dynamics and phase change had been done by Beesabathuni et al. [34]. Their studies were focused on wax drop impact on liquid pool and simultaneous solidification and drop deformation. They varied the temperature of molten wax which indirectly modulates viscoelasticity of drop. Also their studies include morphology of wax after solidification, which includes the role of inertial, viscous and thermal forces.

Drop based chemical reaction has been studied long ago but only the effects of ultrasound have been studied [35]. Later, Balachandran et al. further explored the cavitation based chemical reaction [36]. Recently, several contributions by combining the hydrodynamics and chemical reaction have been found. Mishra et al. [37] proposed that during cavity collapse, solute advection creates concentration difference which in turn leads to species transport and increase in reaction rates. Even, Lattice Boltzmann Method simulation method has been introduced to investigate the dual effects of hydrodynamics and chemical reaction [38]. However, during droplet based reaction, the advection of chemical species around the droplet depends on the hydrodynamics and a concentration gradient has been created locally to enhance the kinetic rates [39]. The drop based chemical reaction study on acid-base neutralization reaction was also studied using high-speed camera by Tsuji & Muller [40].

Drop dynamics study in the context of gelation has been executed recently by Davarcı et al. [27] where they vary the viscosity and surface tension of the gelling solution. Their studies include penetration depth of solidified bead which has been captured by a high-speed camera at a very low frame rate. They found that sphericity of encapsulated bead decreases with increasing viscosity and surface tension of $CaCl_2$ solution. Bremond et al. [41] studied the hydrodynamics of vortex ring formation during the sodium alginate drop impact on calcium chloride solution. Their observations include variation of critical shell thickness along with the change in viscosity and impingement height. Experimental studies of process variables during oil encapsulation characteristics were done by Abang et al. [42]. The role of bubble entrapment during gel formation after alginate and calcium chloride reaction was experimentally observed by Deng et al. [43]. They inferred that chemical reaction just after drop impact solidifies the drop and pins the crater bottom. The bubble entrapment is caused when the bulk focusing flow collapses the pinned crater bottom. Also, capillary wave pinching and the viscous weakening of the crater results in bubble entrapment [44]. High-speed imaging study of clinical grade microencapsulation was performed by Meiser et al. [26]. Their study finds out the temporal variation of horizontal width, bead velocity and bead acceleration. An excellent investigation of drop solidification during encapsulation revealed that final shape of the frozen microcapsules was dependent on the droplet penetration and alginate concentration but not on calcium chloride concentration [45].

Sodium alginate, the sodium salt of alginic acid is the most easily available biopolymer. By nature, it is an anionic polysaccharide found in the cell walls of seaweed, brown algae. The basic structure of sodium alginate linear unbranched polymers consists of β-(1–4)-linked D-mannuronic acid (M) and α-(1–4) - linked L-guluronic acid (G) residues (See Fig. 1). The viscosity of sodium alginate is dependent on the ratio of these two acids. It can form a hydrogel (See Fig. 1) in the presence of calcium cation, which is thermally, chemically stable, biocompatible and has large fluid absorption capacity. Thus it is used in encapsulation industry tremendously. The reaction which takes place is crosslinking polymerisation reaction.

The key focus of this present work is the simultaneous study of hydrodynamics and solidification during alginate drop impact on the gelling solution of calcium chloride. The outcomes of this work are to determine gelation energy and critical concentration of a gelling solution by correlating the phase change mechanism with drop hydrodynamics parameters. The novelty of our experiments is comprehending the physical mechanism of phase change from liquid to solid of a biopolymer from the concept of fluid dynamics. The outcomes of our work are a new insight of gelation mechanism from the perspective of fluid dynamics and chemical reaction, undertaken by us which are unavailable in existing literature.

2. Experimental setup

2.1. Materials

The low viscosity sodium alginate powder has been purchased from LOBA Chemie (CAS NO: 9005-38-3). The molecular weight of this material has been determined as 191417 g/mol by using Gel Permeation Chromatography (Agilent Technologies). The calcium chloride dihydrate ($CaCl_2$,$2H_2O$) of molecular weight 147.01 g/mol has been procured from Merck Specialities Private Limited (CAS NO: 10035-04-8).

Sodium alginate solution of 5% concentration has been prepared by adding 5 gm of alginate powder slowly in 100 ml of distilled water under continuous stirring. After 5–10 min of stirring, the