Dimensionless number analysis for production of spherical ca-alginate beads

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Introduction

In recent years, it has become a common trend to produce mono-dispersed and perfectly spherical ca-alginate particles. The reasons could be: (i) to develop highly reproducible reaction or controlled-release rates which may be critical in some biomedical, pharmaceutical and bioprocess applications. (ii) to develop free-flowing particles during dosing and handling in order to ensure dosage consistency and dust free environment (due to particle abrasion) which could be requirement for pharmaceutical, food and feed applications. (iii) to improve the aesthetic quality which could be a desirable characteristic for pharmaceutical, food and feed products. The most classic and popular way to produce mono-dispersed and round ca-alginate particles is by extruding the alginate solution through a capillary at a low volumetric rate and allowed to drip under gravity. Although the process may seem to be straightforward, there were only limited works that systematically relate the process variables to the shape of the particles. Some studies have shown that the alginate solution properties (e.g. surface tension and viscosity) and the collecting distance have important influence on the particle shape (Seifert and Philips, 1997; Ouwerx *et al*., 1998; Al-Hajry *et al.,* 1999). In practice, spherical particles could be formed through trial and error by adjusting the distance between the dripping tip and the gelation bath. As a guide, a collecting distance of 10 to 20 cm is commonly used. However, the inter-relationships between the process variables in shape deformation as well as their limits in forming spherical ca-alginate particles through the extrusion-dripping process have not been thoroughly investigated before. The main aim of this work was to determine the process condition and limitation of extrusion method for forming spherical ca-alginate particles. The approach is by studying the relationship between the process variables (i.e. experimental set-up and solution properties) on shape of alginate drop before and after gelation, as shown in Figure 1. Dimensionless number groups were subsequently used to establish the operating region for forming spherical ca-alginate particles.

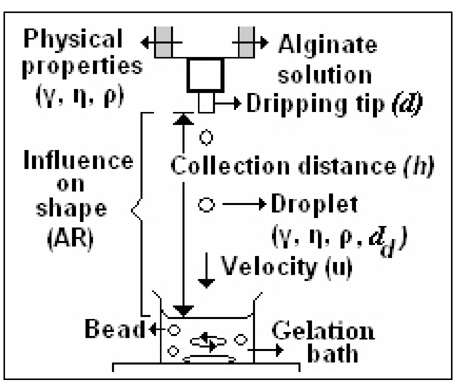

Figure 1: Process variables involved for shape analysis

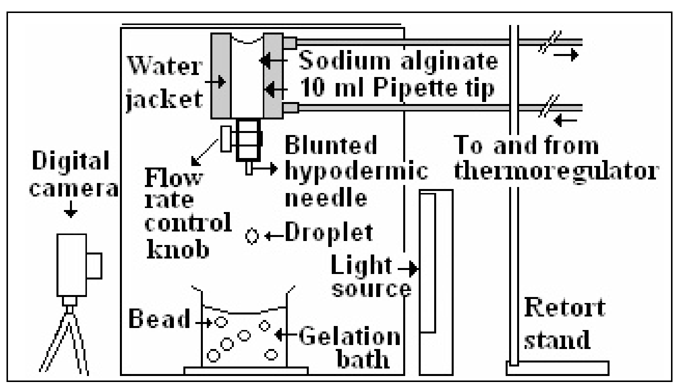

Figure 2: Experimental set-up

Experimental

Physical properties measurement: The density of the sodium alginate solutions (Manugel GHB) (ISP Technologies Inc., UK) at 25^0C was measured by using a digital density meter (Kyoto Electronics Manufacturing Co Ltd, Japan). The viscosity of the solutions was determined by using a viscometer according to the standard procedure (Brookfield Engineering Laboratories, Inc., Model: LV-DV E203, USA). The surface tension of sodium alginate was determined by using the modified drop weight method, or known as the LCP coefficient method.

Experimental set-up: Figure 2 shows the experimental set-up for formation of alginate liquid droplet and ca-alginate particle. All studies were conducted at controlled temperature of 25^0C. Hypodermic needles (Becton Dickinson Medical (S) Pte Ltd, Singapore) of OD ranging from 0.40mm to 1.65mm were used and they were first blunted and shortened to 3mm. The gelation bath was prepared from 1.5%w/v calcium chloride (Mallinckrodt Baker, Mexico) and 0.1%w/v Tween 80 (Fluka, USA). The collecting distance between the dripping tip and gelation bath was varied from 3cm to 270cm. The hardening time of the ca-alginate particles was fixed at 30 minutes. A digital camera (Canon, Japan) was set-up below the dripping tip to capture the images of alginate liquid droplet when falling to the gelation bath.

Shape of alginate drop: The shape of the alginate drops were quantified by using the dimensionless parameter, aspect ratio (AR), which can be described by equation: AR = D_{Max}/D_{Min}, where D_{Max} is the largest diameter and D_{Min} is the smallest diameter perpendicular to it. The length of both diameters was determined by using SigmaScan Pro 5 (SPSS Inc, USA) and the AR was computed by using Microsoft Excel (Microsoft Corporation, USA). The aspect ratio of less than 1.1 was considered as spherical in this study.

Dimensionless number analysis: The impact Reynolds number (Re_I) was used to measure the importance of the inertia force to viscous force of falling liquid droplets and it can be described by the following equation: $Re_I = u\ d_d / v$, where u is the velocity of the alginate liquid drop (mm/s) at the point of impact, d_d is the diameter of the of the alginate liquid drop (mm) and v is the kinematic viscosity of the alginate solution (mm^2/s). Since the initial drop velocity could be assumed to be negligible, the drop velocity at the point of impact could be derived from 1-dimensional kinematics equation: $u = (2\ g\ h)^{1/2}$, where h is the collecting distance, cm. On the other hand, the impact Ohnesorge number (Oh_I) was used to measure the importance of the viscous force to surface tension force and it can be described by the following equation: $Oh_I = v\ \rho_L/(\rho_L\ d_d\ \gamma)^{1/2}$, where ρ_L is the density of the alginate solution (kg/m^3) and γ is the surface tension of the alginate solution (mN/m).

Results and discussion

The results (Figure 3 & 4) show that the shape deformation of ca-alginate particles is basically due to the impact between the falling alginate liquid droplets and liquid surface of gelation bath. The shape deformation during impact could be dependent on two main factors, which are the liquid properties and the momentum of the liquid droplets. Previous works showed that the critical viscosity could range from 60 cP to 125 cP (Seifert and Philips, 1997; Ouwerx *et al*., 1998; Al-Hajry *et al.*, 1999; Lee and Heo, 2000). This is in good agreement with this work since the critical viscosity was about 100 cP. Although it has been reported that the surface tension force could be an important parameter in retaining the sphericity of a droplet during falling (Frankel and Weihs, 1983; Al-Hajry *et al.*, 1999; Sostarecz and Belmonte, 2003), its influence during impaction cannot be clearly seen in this study since it could be subdued by the viscous effect.

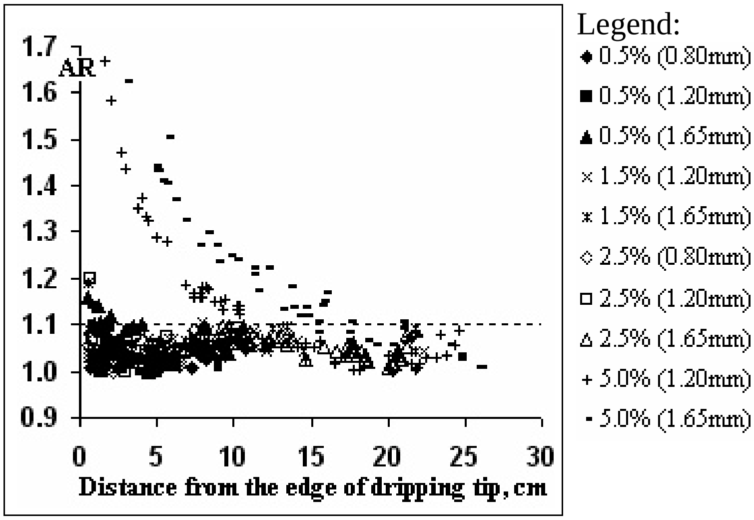

Figure 3: The aspect ratio (AR) of the alginate liquid drop at different traveling distance

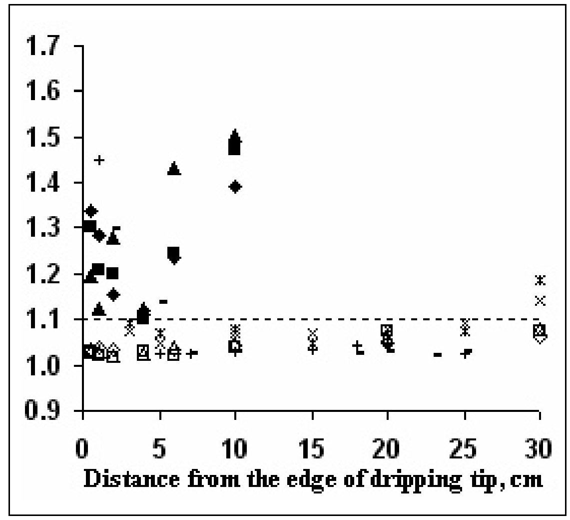

Figure 4: The aspect ratio (AR) of the ca-alginate particles formed at different colleting distance.

On the other hand, the momentum of the falling droplets determines the degree of impact between the falling droplet and gelation bath. The momentum of a falling droplet is a function of the droplet mass (or size) and its velocity. Therefore, larger droplet or longer collecting distance (i.e. higher velocity) increases the momentum of the falling droplet. As a result, the degree of impact between the droplet and surface of the gelation bath would be greater. In this work, the droplet mass could be easily calculated from the volume of droplet, determined through image analysis, and the solution density. The droplet velocity at the point of impact was calculated from 1-dimensional kinematics equation. The shape analysis suggests the existence of a critical momentum that should not be exceeded when the droplet hits the gelation bath. However, the critical momentum value was not determined because the value was dependent on the liquid properties. Instead, dimensionless number analysis was performed to simplify the inter-relationships between the process variables as well as to establish the operation limits within which spherical ca-alginate particles could be formed.

Figure 5 shows the correlation between Re_I and Oh_I. The plot reveals a clear operating region within which spherical ca-alginate particles could be formed. The lower boundary of the area is given by $Oh_I = 0.25$. It is independent of Reynolds number and the limit is mainly influenced by the critical viscosity of the alginate solution. The upper boundary of the area is also independent of Reynolds number and it is given by $Oh_I = 10$. It is mainly limited by the solution viscosity. On the other hand, the boundary at the right of the area varies with the physical properties of liquid drop. Within the conditions of $0.25 < Oh < 10$, the boundary is given by the equation: $Oh_I = 130\ Re_I^{-1.46}$. The position of the boundary is expected since it is located before the limit suggested by Fujitmasu *et al.* (2003) for a liquid drop to disintegrate in a liquid-liquid impact. However, there is no fixed boundary on the left side of the area and the boundary is mainly limited by the position of dripping tip. In general, non-spherical ca-alginate particle would be formed if the collecting distance were too short, where the teardrop shape of the liquid droplet would be retained after gelation. As a guide, a collecting distance of about 10 cm could be adequate to avoid this phenomenon.

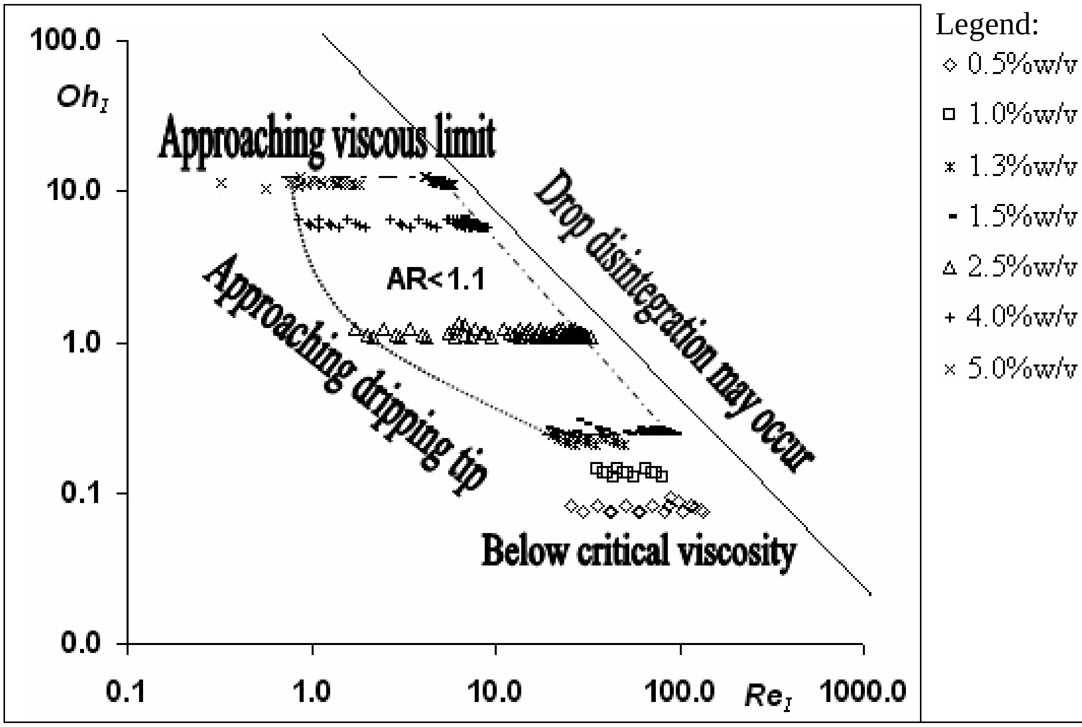

Figure 5: Process limits for forming spherical ca-alginate particles through extrusion method

Conclusion

In general, the plot of Oh_I and Re_I for determining the process conditions in forming spherical beads could be an useful tool in the product or process development stage when formulating the liquid solution and setting-up of the extrusion-dripping apparatus. In fact, it could also be applied in other extrusion system such as vibration break-up of liquid jet, electrostatic generator, jet-cutting technique, rotating disc and etc. The dimensionless numbers could be easily calculated as long as the liquid properties, droplet size and impact velocity could be determined through experiment or estimation. A free and simple software is currently under development to aid users in the calculation.

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