Radius prediction of calcium alginate beads produced through dripping

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Introduction

Tate, a pharmacist was the first to explain the phenomenon of drop formation from a circular nozzle in the middle of 19^{th} century. Based on force balance at a nozzle, Tate's law states that the weight of a detached drop is equal to the product of the surface tension of the liquid and the circumference of the nozzle at which it was formed. In the past, Tate's law has been used to predict sizes of beads which were produced at low flow rate by using simple extrusion technique (Poncelet *et al*., 1999a and b; Muralidhar *et al*., 2001; Heinzen *et al*., 2004). The diameter of the beads can be calculated as below:

$r_b = \sqrt[3]{3r\gamma/2\rho g}$, where r_b is the beads radius, r is the dripping tip radius, ρ is density, γ is surface tension and g is the gravitational force.

On the other hand, a semi-empirical model was reported recently for prediction of liquid droplet size (Yildirim *et al*., 2005). In this paper, we will name this model as Yildirim's model and the equation is shown as below:

$r_d = 0.62r(3.60/BO)^{0.36}$, where r_d is the radius of liquid droplets, r is the dripping tip radius and BO is Bond number ($\rho g r^2/\gamma$). Yildirim's model correlates the size of the liquid droplet which detached from a dripping tip with Bond number.

The objective of this study was to compare the validity of Tate's law and Yildirim's model in predicting the size of alginate droplets before and after cross-linking with calcium cation by using different tip size. The effect of alginate concentration and molecular weight was investigated and recommendation was given to which model could be used for prediction of alginate liquid droplets and ca-alginate bead size

Materials and methods

Materials: Calcium chloride (Mallinckrodt Baker, Mexico). Tween 80 (Fluka, USA). Sodium alginates of different molecular weight were kindly donated by ISP Technologies Inc. (USA). Their details are listed in Table 1. All solutions were prepared by using deionized distilled water.

Type	Molecular weight	G to M ratio
Sodium alginate Manugel GHB	97,000	1.70
Sodium alginate Manugel DMB	120,000	1.70

Table 1: Sodium alginate types

Physical properties measurement: The density of the samples at 25^0C was measured by using a digital density meter (Kyoto Electronics Manufacturing Co Ltd, Japan) and duplicate determination of data was conducted. The surface tension of sodium alginate was determined by using drop weight tensiometer.

Experimental set-up: Figure 1 shows the experimental set-up for formation of alginate liquid droplets and ca-alginate beads. 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 consisted of calcium chloride (1.5%w/v) and Tween 80 (0.1%w/v).

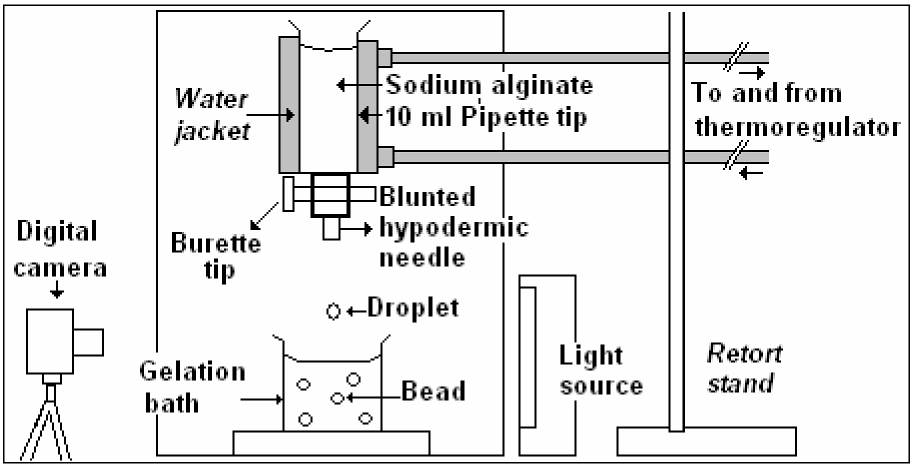

Figure 1: Experimental set-up.

Characterisation of alginate liquid droplets & ca-alginate beads: A digital camera (Canon, Japan) was used to capture images of falling alginate liquid droplets detached from the needle tip and ca-alginate beads after gelation. The radius of the liquid droplets and beads was determined by using an image analyser (SigmaScan Pro 5, SPSS Inc). Since it was found that the shape of a studied object has profound effect on the equivalent diameter computed by the software, only liquid droplets or beads with aspect ratio (AR) between 1.0-1.1 were chosen as samples (AR = 1.0 indicates perfect sphere).

Statistical analysis: The radius of the beads was determined based on the measurement of 25 to30 ca-alginate beads. All standard error bars in the graph were calculated based on 95% confidence level by using t-test. On the other hand, 10 to 20 samples were taken for alginate liquid droplets analysis. All standard error bars in the graph for alginate liquid droplets were calculated based on standard deviation of the samples.

Results and discussion

Validity of prediction models: Figure 2 shows the size of alginate liquid droplet upon detachment determined through experiment and prediction models. It was found that the radius of liquid droplets calculated from Tate's law were consistently higher than the experimental data. It has been reported by many investigators that Tate's law is a poor approximation for droplet size prediction since it was found that a fraction of liquid will not be detached from a tip in practical (Harkins *et al.*, 1919; Wilkinson, 1972, Earnshaw *et al.*, 1996). Therefore, this could explain the over-estimation of the alginate liquid droplet size as shown in Figure 2. In order to allow better prediction by using Tate's law, a set of correction factors as a function of tip radius has to be introduced (Harkins *et al.*, 1919; Wilkinson, 1972). However, this makes the prediction procedure more tedious. On the other hand, Yildirim's model was found to be in good agreement with the experimental data. This is because the model has taken into account the residual liquid by using empirical approach and therefore, it could give better prediction on the size of detached liquid droplets.

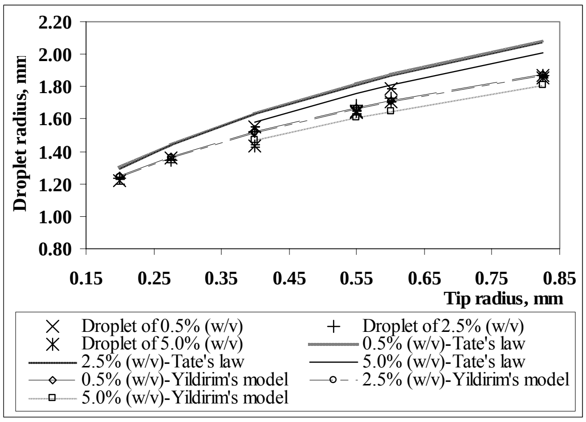

Figure 2: Comparison of alginate liquid droplets size determined through experiments and prediction models

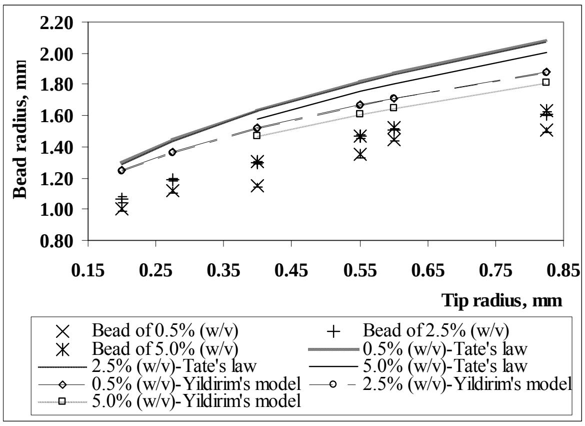

Figure 3: Comparison of ca-alginate beads size determined through experiments and prediction models

Figure 3 shows the size of ca-alginate beads determined through experiment and prediction models upon cross-linking. It was found that neither model could give satisfactory prediction of the bead size because both models consistently over-estimated the bead size. It has been speculated that the hydrogel network formation during cross-linking could reduce the space occupied by alginate that cause water loss and thus reduces the volume of ca-alginate beads (Velings *et al*., 1995). Therefore, the over-estimation of bead size was attributed to the shrinkage of alginate liquid droplets upon gelation and this behaviour was not taken into account in the prediction models. Therefore, a simple experiment was conducted to determine the size difference before and after cross-linking. As shown in Figure 4, it was found that the average diameter reduction of alginate liquid droplets and their corresponding ca-alginate beads was about 14% regardless of needle size and it only varied slightly with alginate concentration.

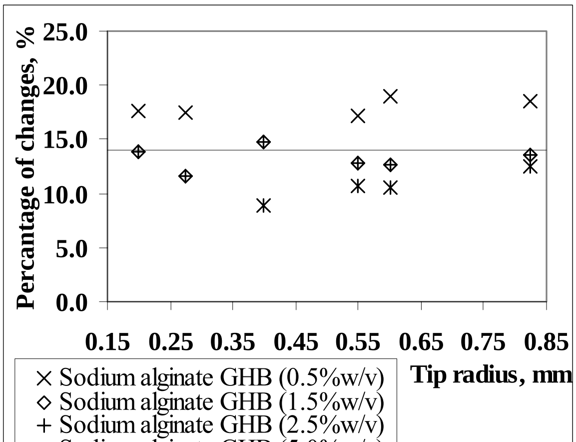

Figure 4: Changes in alginate liquid droplets size before and after cross-linking

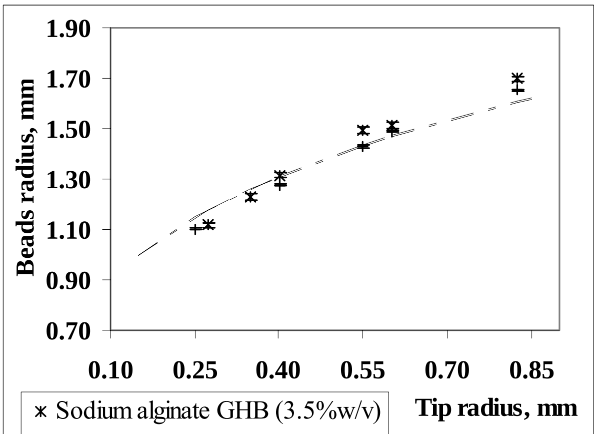

Figure 5: Validation of the modified Yildirim's model with experimental data. The dotted lines indicated the predicted beads radius.

Validation of the modified model: As a result, Yildirim's model was modified by taking into consideration the effect of bead shrinkage and it is shown as follows:

$r_b = 0.53r(3.60/BO)^{0.36}$ where r_b is the beads radius, r is the dripping tip radius, and BO is Bond number ($\rho g r^2/\gamma$).

Figure 5 shows that the comparison between experimental data and model prediction of ca-alginate bead size produced at various tip sizes. It could be seen that the modified model is in good agreement with the experimental data and the model gave a better prediction on the ca-alginate bead size if compared to the unmodified model.

Conclusion

In conclusion, it was found that Tate's law (in its raw form) could not give satisfactory size prediction of alginate liquid droplet and ca-alginate bead unless a set of correction factors was introduced. On the other hand, Yildirim's model gave good prediction of liquid droplets size but the model has to be modified by taking into account bead shrinkage upon cross-linking in order to predict bead size.

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