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TRANSIENT DEM SIMULATION OF STARCH GRANULE SUSPENSION UNDERGOING THERMAL TREATMENT

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KEYWORDS

Discrete Element Modeling, Starch Granule, Starch swelling, Gelatinization, MATLAB

ABSTRACT

During hydrothermal treatment of starch suspension, the starch granules swell with kinetics depending on temperature evolution. Variability of swelling characteristics between starch granules was also observed. A semi-mechanistic and semi-stochastic model for individual starch granule swelling was developed and coupled with a discrete element (DEM) model. The DEM model takes into account the normal elastic forces exerted between the granules when they come in contact and optimally occupy the available volume. The evolution of particle volume fractions, size dispersion, the fraction of overlap volume and elastic energy per unit volume were analysed in the case of chemically modified waxy maize starch. It appears that for this particular starch all the jamming indicators increase rapidly for a volume fraction of about 0.65

INTRODUCTION

Starch is predominant food reserve in plant and provides for 70-80% of calories consumed by humans worldwide from various sources (Bertolini 2009). Hence it has been a perennial subject of research for decades. Starch undergoes the process known as gelatinization when heated in the presence of water. Gelatinization is the process in which starch granules undergo an irreversible chemical transformation when subjected to thermomechanical treatment in the presence of water. Starch granules are semi-crystalline with concentric rings of crystalline and amorphous phases (Ratnayake and Jackson 2008). Gelatinization on the microscopic scale corresponds to melting of crystallites, loss of birefringence, increase in size (swelling), leaching of amylose into the continuous phase and sometimes rupture of the granular structure (Atwell 1988; Biliardieris 1992). Starch majorly consists of amylose and amylopectin. The composition of these two polymers with alpha glucose as a monomer, vary according to the source of starch. This, in turn, has consequences on the physical properties and gelatinization behaviour of starch

(Banks et al. 1974; Hoover 2001; Srichuwong et al. 2005; Visser et al. 1997). The expected range for these transitions is between 60 and 70 °C (Slade and Levine, 1995). The evolution of viscosity during gelatinization is also influenced by the process parameters such as concentration, shear rate, thermal history, pH and presence of other ingredients (Thomas and Atwell 1999). For high amylopectin cereal starches such as waxy maize starch, the granules tend to hydrate with ease, swell rapidly and rupture to a great extent which results in loss of paste viscosity. The rupture of the granules can be avoided by chemically modifying the starch. This involves the introduction of functional groups into the starch molecules, resulting in markedly altered physicochemical properties (Ashogbon and Akintayo 2014). Waxy maize starch is used in a wide variety of applications in the food industry owing to its stability (Tattiyakul and Rao 2000)

During gelatinization, the starch granules swelling and viscosity of the suspension increases multi-fold. Thus it is important to understand this phenomenon both in terms of process equipment design perspective as well as novel product development. Hence, over the years researchers have been modelling starch gelatinization and swelling as kinetic phenomena with various rate equations with respect to metrics such as the median diameter of the granule population. These models ranged from simple first-order rate equation to Nth order, Diffusional, Phase boundary and Avrami-Erofeev type rate equations (Kubota et al. 1979; Okechukwu and Rao 1995; Lagarrigue et al. 2008; Krüger et al. 2003 and Malumba et al. 2013). These were all at the population scale, recently we (preprint submitted to Food structure) suggested first-order reaction kinetics at the granule scale with a random delay time.

One functional property of gelatinized starch is the texture improvement by increasing apparent viscosity. A starch suspension can be postulated as a non-colloidal suspension of soft (elastic) spheres. The apparent viscosity of such a suspension depends on the ratio between the actual volume fraction of particles and its maximum value (ϕ_{rcp}) also called random close packing density. Farr et al. (2009) proposed a novel algorithm to determine ϕ_{rcp} for a suspension of poly-disperse spheres. They presented a simple but accurate ap-

proximation for the random close packing density of hard spheres of any size distribution based upon a mapping onto a one-dimensional problem. To validate the same, they carried out extensive simulations for mixtures of elastic spheres with hydrodynamic friction. In subsequent work, Farr (2013) compared the algorithm with slower direct numeric simulations and showed good agreement between them. Various algorithms exist for such direct numerical simulations and chief among them is Lubachevski-Stillinger (1990) algorithm in which spheres at a low volume fraction are placed in a box with periodic boundary conditions by random sequential addition. The particles are randomised with initial velocities and their radius are increased proportionally to initial radius. This algorithm takes into account three input parameters: the number of spheres, the initial volume fraction ϕ_{init} and the ratio δ of the radial growth. A similar algorithm is used in this work for DEM simulations, however, the rate of increase of radius is governed by the swelling kinetics for a specific type of chemically modified maize starch.

METHODS

Swelling model

We have described the granules swelling kinetics at the individual granule scale using a semi-mechanistic model in a separate work under review for publishing in food structure journal. According to microscopy observation of modified waxy maize starch granules during heating in the presence of water, variability in swelling kinetics from granule to granule was observed. Each granule has a specific delay time associated with the onset of swelling. Also, the granules which begin to swell at later instant tend to swell slower compared to the granules which begin to swell earlier for a given time-temperature profile. No swelling was observed below $T_{min} = 60^\circ C$. The higher the temperature, the lower the delay time and the faster the diameter increases. These phenomena were cast mathematically as below. The reader is advised to refer the pre-print submitted by us to food structure for further details regarding the same. The earlier work describes in detail the Kinetic model for swelling of individual starch granules in a suspension. In this work, we make use of the already developed kinetic model and couple it with the DEM model for prediction of suspension material properties such as volume fraction. In the subsequent future works, one would like to simulate and predict the transient rheology such complex fluids for better design and operation of industrial-scale food processing equipment. However, in the interest of the readers and completeness, we touch briefly on the concepts and terms of the kinetic model we make use of in the present work.

A parameter called ‘‘difficulty of swelling’’ $\alpha \in [0, 1]$ was introduced. For a granule, α is selected at random from a uniform distribution.

For a constant temperature, for example, $T_{ref} = 62^\circ C$, the

onset delay time follows an exponential distribution

$$\ln(1 - \alpha) = -\frac{t_{onset}}{\tau_{ref}} \quad (1)$$

where τ_{ref} is the characteristic latency time at T_{ref} . For variable temperature, the time delay in onset of swelling t_{onset} is given by solving equation 2.

$$\ln(1 - \alpha) = -\int_0^{t_{onset}} \frac{1}{\tau} dt \quad (2)$$

$$\tau = \max\left(0, \left(\frac{T_{ref} - T_{min}}{T - T_{min}}\right)\right) \tau_{ref} \quad (3)$$

Non dimensional diameter S is given by the equation 4.

$$S(t) = \frac{D(t) - D_i}{D_f - D_i} \quad (4)$$

The reaction kinetics is given by equation 5 after the time delay t_{onset} is overcome.

$$\frac{dS}{dt} = K(1 - S) \quad (5)$$

$$K = K_{ref}(1 - \alpha)^{0.5} \left(\frac{T - T_{min}}{T_{ref} - T_{min}}\right)^2 \quad (6)$$

where K_{ref} is the rate constant at T_{ref} for a granule which has no difficulty to swell ($\alpha = 0$).

For the chemically modified maize starch that was studied the following parameter values were estimated; $\tau_{ref} = 190s$, and $K_{ref} = 0.0023s^{-1}$. From the above set of equations, one can describe the swelling kinetics of this starch. The same has been used for the DEM simulations in this work. The following assumptions regarding the starch granules population were made. Initial diameters and swelling ratio are from a random normal distribution.

$$D_i \subset \mathcal{N}(14.77\mu m, 4.44\mu m),$$

$$D_f/D_i \subset \mathcal{N}(2.34, 0.33),$$

DEM model

For Discrete Element Modelling of the starch granules during swelling, the following assumptions are made.

- All the granules are spherical and have the same Young’s modulus.
- No tangential forces are considered.
- No gravity force on the particles are considered.

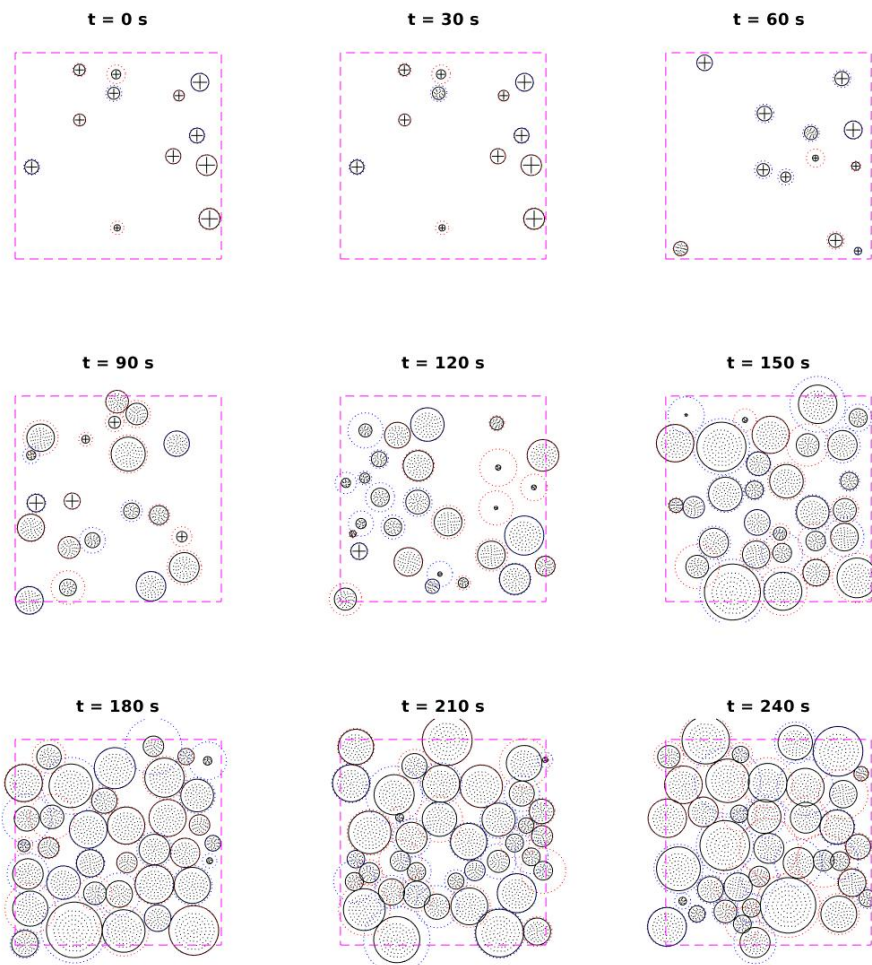
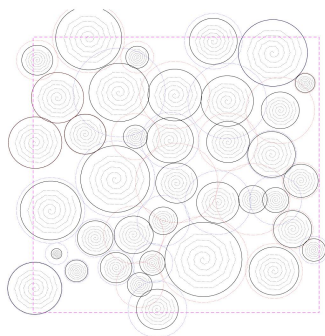
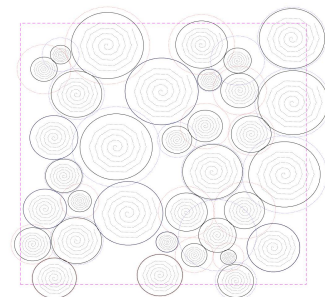


Figure 1: Granules contours at every 30 seconds



(a) Run 1 completely swollen state



(b) Run 2 completely swollen state

Figure 2: Contour comparison of different runs

- The particles are considered Non-Brownian.
- No Lubrication forces are considered.
- Periodic boundary conditions are applied.

To determine a realistic initial state(position and radius) of a total number I of unswollen granules in a cubic box, a step-wise Monte-Carlo procedure was applied:

- For the granule of index i (among I), α is chosen as $\alpha_i = (i - 1/2)/I$ (uniform distribution).
- Similarly D_0 and D_f/D_0 are randomly chosen from $\mathcal{N}(14.77\mu m, 4.44\mu m)$ and $\mathcal{N}(2.34, 0.33)$.
- Then the location of the granule in the simulations box is determined by choosing randomly x, y and z coordinates. If there is an overlap with the previously placed granule, a new location is proposed for granule i . This approach is guaranteed to work as initially the volume occupied by the granules is low compared to the total volume of the box and hence granule insertion in the cubic domain is fairly straightforward by this trial and error method.

After deposition of the required number of granules inside the simulation box, The transient swelling of granules is undertaken. At this instant where transient swelling is undertaken is the initial time $t = 0$ seconds. For every granule, if the criteria of time delay in onset are met, then new radii are calculated using the kinetics of swelling as per equation 5 and 6.

The normal Hertzian force due to overlap of the spherical granules is calculated based on the following equations (Di Renzo and Di Maio 2005)

$$F_n = -\frac{4}{3}E\sqrt{R_{12}}(\delta_n)^{1.5} \quad (7)$$

$$E = \frac{E}{1 - \nu^2} \quad (8)$$

$$R_{12} = \frac{R_1 R_2}{R_1 + R_2} \quad (9)$$

Here, E and ν are the young's modulus and Poisson's ratio of granules respectively. R_1 and R_2 correspond to radii of granules 1 and 2 respectively. Also, δ_n is the overlap distance between the two spheres.

Thus, new particle positions are calculated based on timestep using newton's equations of motion. Each particle radius is increased at every time step according to equations 5 and 6. As particles grow and overlap the normal force due to overlap is calculated and repulsive force begins to originate between particles. The coordinates of the particles are updated after

calculation of this repulsive force due to overlap. The particles move away from each other and the force exists until the overlap exists. The time step for DEM simulations was $10ms$. The timescales of the swelling are much lower compared to the timescales of force resolution, this ensures that particles do not overlap excessively causing the particles to experience large forces. For each particle, a list of neighbour lists is maintained, whose centres are within cut off distance. The contacts are searched for within these neighbour particles to reduce the computational time. The neighbour lists are updated periodically. The contacts are deemed to be active when the distance between two-particle centres is less than the sum of their radii.

RESULTS

The simulation was performed for a single ramp rate of $5^\circ C/min$ from $60^\circ C$ to $80^\circ C$ in 4 minutes. The overall computation time required for the entire simulation was about 2 hours on a single core work station. The entire program was scripted in MATLAB. Figure 1 shows the granules contours at a cross-section of the simulation box. The dotted lines represent the actual granule diameter and continuous lines are the intersection of the granule with the cross-section plane. The cross at the centre of the granule indicates that the granule is yet to swell and dotted lines take over when the granule starts to swell. The notation for the same is to mimic the Maltese cross observed on the un-swollen starch granules when observed through polarised light under a microscope and the disappearance of the same when swollen. This phenomenon is called the loss of birefringence during gelatinization. For the simulation 200 granules(I) were inserted in a cubic box of length 0.2 mm. The initial volume fraction $\phi_0 = 5.1\%$ (when $S = 0$ for all the granules) and $\phi_{max} = 71.5\%$ at the end of 4 minutes of simulation (when mean value of $S = 0.983$, signifying almost complete swelling). The Young's modulus was taken as 10000 Pa for unswollen as well as for swollen granules. Parallel experimental work is underway to estimate this parameter more precisely.

Figure 1 shows the cross-section of the box every 30 seconds. We observe that at the initial instances when the granules are yet to swell there is the low volume fraction of granules and subsequently there is no movement of the grains as there are no forces acting (no gravity, no Brownian agitation, zero initial velocity). However, at the later instances when the granules come in contact with each other and Hertzian interaction forces act, the granules push each other and move freely in the system such that Hertzian interaction energy remains close to zero. This is quite notable for times between 90 seconds and 150 seconds. At later instances when granule volume fraction reaches close to ϕ_{rcp} the granules cannot move freely but they reorient optimally to minimize the energy in the system. Since the insertion of particles and the swelling characteristics are random we compare the contours of two different runs at the fully swollen state in Figure 2.

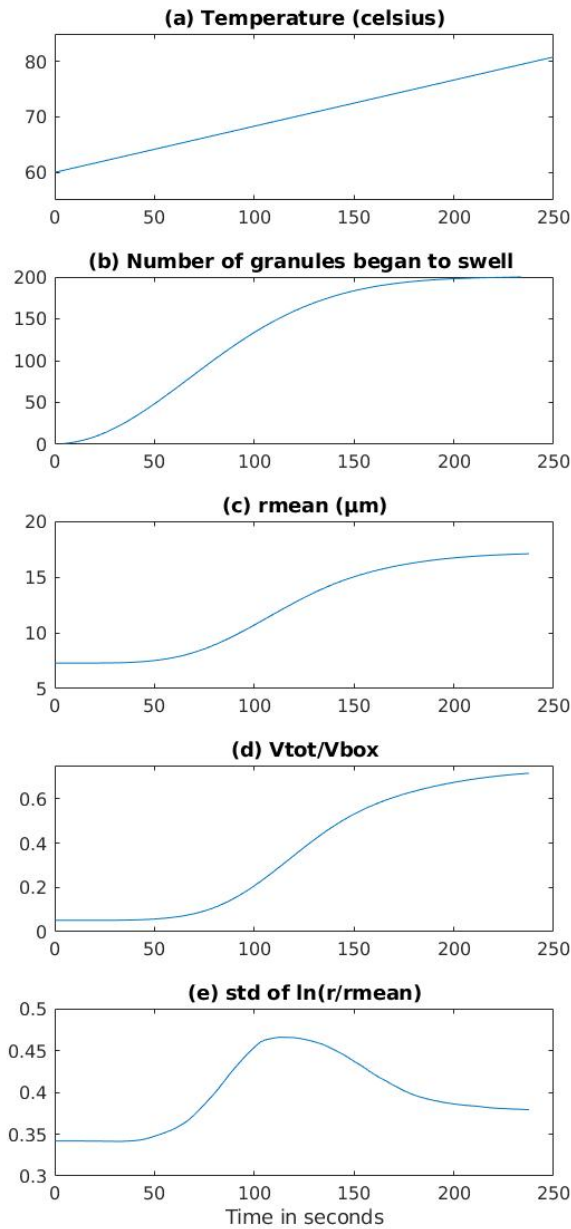


Figure 3: Time evolutions of parameters

In Figure 3 we can see the time evolution of different parameters. Temperature is linearly increased from 60 °C to 80 °C as depicted in figure 3a. In figure 3b we see the total number of granules which began to swell plotted as a function of time. Note that the total number of granules used for the simulation is 200 and all begin to swell after 200 seconds. In figure 3c, we see the mean radius of the starch granule population evolving with time. In figure 3d, we see the volume fraction of granules increase with time as the granules are

swelling. The mean radius is increased by a factor of 2.34 the volume of the granules rises by a factor of 12.8. Figure 3e depicts the size dispersion among the granule population. Since there is variability in the onset of swelling initially the dispersion increases as some granules begin to swell and the ratio of largest granule to smallest granule increases, but as time progresses other granules also catch up as they begin to swell and hence the dispersion decreases. However, the final dispersion is higher than the initial level as the ratio of swelling is also random and as expected the variability is higher after swelling compared to initial unswollen granules.

In figure 4 we have the ratio of volume overlap and Hertzian interaction energy in the function of time(left) and volume fraction of the granules(right). We calculated ϕ_{rcp} based on the chart provided by Farrand Groot (Farr and Groot 2009) for the starch granule population at the end of the simulation($t=4\text{min}$, mean value of $S = 0.983$). The same has been overlaid in the plots to compare with the DEM simulations.

Interestingly since the starch granules are soft spheres the increase in interaction energy is slower compared to hard spheres and hence the algorithm proposed by Farrand Groot which predicts the ϕ_{rcp} for hard poly-disperse spheres gives a lower value compared to the DEM simulations reported in this work. Through these simulations, we can study the dynamic evolution of particle and bulk properties of the system during the swelling of the chemically modified starch granules.

CONCLUSION

In this study, we have demonstrated the modelling of starch granule suspension evolution during gelatinization using DEM. The earlier developed kinetic model for individual starch granule swelling was coupled to the DEM model resulting in the transient DEM simulation of the suspension. This is particularly interesting as the macro scale properties such as volume fraction are obtained by modelling the granule level details. Using this approach one can get the size evolution as a function of time and also the interaction parameters such as elastic Hertzian energy as a function of time. From this study, we see that since the granules are soft spheres the increase in jamming indicators occur at a volume fractions greater than the prediction based on an analytical solution for hard spheres. This is of physical significance since a multi-fold increase in suspension viscosity occurs near this jamming transition. Thus, having an accurate prediction of such phenomena is critical for the process of equipment design and optimal operation. Going forward in the future works, one should be in principle able to predict the rheology of such complex material. Transient DEM with evolving particulate sizes and properties could also be coupled with computational fluid dynamics using multiscale modelling approaches to study flow, heat transfer and starch-based product transportation inside heat-treatment equipment.

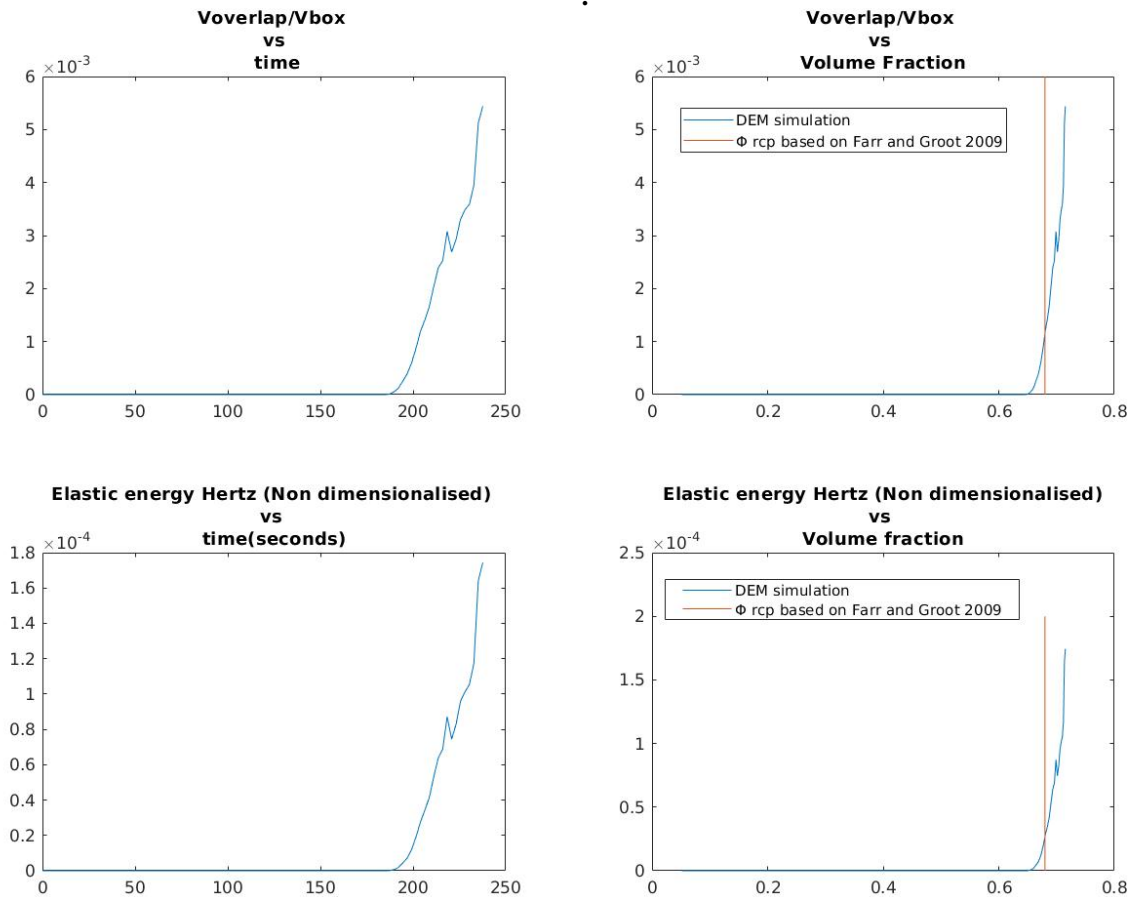


Figure 4: Interactions energy vs volume fraction

FUTURE WORK

- Estimate experimentally Young's modulus vs Gelatinization degree which is characterized by S . Incorporate the same in the model.
- Include tangential forces, lubrication forces and other effects as deemed necessary.
- Study the influence of the box size on the results.
- Perform shear flow simulations for the same system and capture the viscosity evolution of the suspension.

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