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Experimental study on single droplet drying of hydroxypropylated pea starch: Drying kinetics and particle morphology

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***Abstract*— Spray drying is widely used nowadays in the pharmaceutical and food industries to produce fine dry powders from a liquid solution by rapidly drying with a hot gas. The produced powders can be directly attached to larger particles by cohesive forces in order to improve the surface properties and/or alter the functionality of these larger particles, such as in the dry powder coating technology. For the efficient production of spray-dried fine powders it is crucial to find a suitable operating condition and an appropriate initial composition of the solution. In this paper, a single droplet drying suspension device is employed to investigate the drying process of hydroxypropylated pea starch particles. Using this device the influence of the drying air temperature (80-160°C) and of the initial solid content of the agent (15-30 %w/w) on the drying kinetics, shrinkage and locking point of a single liquid droplet are systematically investigated. Then, a lab-scale X-ray microtomograph is employed to acquire three-dimensional images of dried particles, which are then used to analyze their surface structure and internal morphology. This contribution provides guidelines for the production of powder suitable for the dry powder coatings by using spray dryers, and thus it may serve as a basis for product design.**

***Keywords*— Hydroxypropylated pea starch, Single droplet drying, Particle size, Microstructure**

I. INTRODUCTION

There is an increasing interest in scientific and engineering communities to develop and implement an efficient particle coating technology which can be readily used in food, pharmaceutical, or chemical industries. The conventional method for particle coating process is wet coating. It involves the application of a liquid precursor on particles that is then converted to the desired coating material by subsequent post-treatment steps. The main disadvantage of the wet coating is a high concentration of volatile solvent in the final product. In the case of coating of medicines or other biologically active products, humidity may cause product destruction or its inactivation. It is hence necessary to dry gently the product for a long time, which increases the costs and lengthens the time of the entire process. Dry powder coating is a promising alternative to the traditional coating powder process with organic or aqueous solutions [1]. This technology is simpler, cheaper, safer and more environmentally friendly compared to solvent-based coatings [2]. In this technology, one or more polymers as "guest" dry powders together with a small amount of liquid plasticizer feed directly into a drum coater or a fluidized bed chamber [3]. Then, these powders are attached to "host" large particles by cohesive forces. Thereby, the properties and the functionalities of the host particles can be changed in order to create particles with desirable end-user properties. For instance, the flowability of silicon carbide powder was improved by using fine silica particles as coating and blending material [4]. It was found that the cohesive forces between two primary host particles in the presence of fine coating is directly proportional to the size ratio of the coating particles to the host particle. The kind of selected polymers and physico-chemical, microstructural and dimensional properties such as solubility, morphology, porosity and size

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of powder particles are critical parameters for achievement of a reasonable shell formation around 'host' particles [3]. In this regard, spray drying can be considered as a method for production of powders with controllable properties. In this drying technique, the selection of an appropriate operating condition appears crucial for obtaining optimum dry powders. In order to mimic spray dryer environment to some extent and to control drying conditions, the single droplet drying (SDD) experiments can be used. The SDD technique is capable to generate quantitative data of drying process which has a prominent importance to development of spray drying processes [5]; .

Starch is widely applied for coating process in food and pharmaceutical applications. Amongst starch sources, the legume starches such as pea starch are more competent for coating formation due to high amylose content. High amylose starches possess the improved mechanical strength and gas barrier properties in comparison with low amylose ones [6]. In addition, hydroxypropylated groups introduced into the starch chains are capable of disrupting the inter- and intra-molecular hydrogen bonds. Thereby, weakening the granular structure of starch leads to an increase in motional freedom of starch chains in amorphous regions and an increase in starch solubility [7].

Numerous researches have been conducted to use of hydroxypropylated pea starch as film forming polymer in coating technology. However, to the best of our knowledge, there is not any information on mechanistic investigation of drying behavior and physical, microstructural and dimensional characterization of this polymer for producing of optimum dry powder coating. Therefore, the main purpose of this contribution is to assess the effect of drying air temperature and solid contents on drying behavior, shrinkage, structure formation and microstructural and dimensional properties of a single droplet containing hydroxypropylated pea starch. Such insights can then be utilized to simulate, develop and optimize industrial-scale spray drying for producing polymeric dry powder coatings.

II. MATERIAL AND METHODS

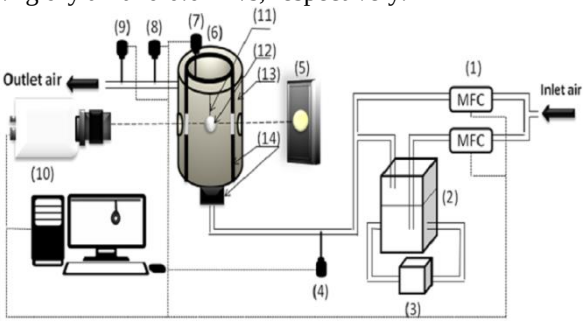
A. *Material and solution preparation*

The thin boiling hydroxypropylated pea starch (HPS) granule (Lycoat NG 780) was generously supplied from Roquette Company, France.The starch solutions with a total solid content of 15 to 30 (%w/w) were prepared by reconstituting of hydroxypropylated pea starch in deionized water. Then, these solutions were heated at the temperature of approximately 90°C for 15 minutes to gelatinize starch. The solution samples prepared in this way were then used for single droplet drying experiments.

B. *Single droplet drying*

Fig. 1 shows a schematic of single droplet drying system used in this study. The main unit of this device is a cylindrical chamber made of steel with an inner diameter of 24 mm. The chamber was enclosed by an electrical resistance to heat the drying medium. In addition, an insulator covered the chamber to prevent heat losses to the ambient. An electrical heater was used to heat inlet drying air. Heated air was pumped from the bottom to the chamber. Inlet drying air has been humidified in a saturator and mixed with dry air by a mixing unit so as to adjust its humidity to a constant value. A dew point mirror (Optidew Vision, Michell Instruments GmbH, Germany) and an infrared spectrometer (NGA 2000, Fisher-Rosemount) were employed to measure inlet and outlet air humidity inside the chamber, respectively. The volumetric flow rate of air was adjusted in the range of 1-500 ml/min to obtain an optimum drying condition. The air flow rate controllers (F-201CV) were supplied from Bronkorst Meattig GmbH, Germany. The droplet was inserted by a syringe with a long needle onto the tip of polyamide wire of a 0.2 mm diameter; the wire has a low thermal conductivity. The average droplet diameter was around 0.8 mm. The single droplet drying process was continuously monitored by using an optical image recording system including a high speedvideo camera (MC-1009AP/MD, Horn Imaging GmbH, Germany), a light source for back illumination, and a long distance microscope lens (Stemi 200-C, Carl Zeiss GmbH, Germany). The recorded images were then analyzed by MATLAB program to assess particle/droplet diameter, surface area and volume changes.

The experiments were performed at four different inlet air temperatures of 80, 100, 140 and 160 °C. The inlet moisture content and the velocity of drying air were around 8 g H_2O/kg dry air and 0.02 m/s, respectively.



(1) Mass flow rate controller	(9)Thermocouple
(2)Saturator	(10) CCD camera
(3)Thermostat	(11) Polyamide wire
(4) Dew point Mirror	(12) Droplet
(5) Back light illumination	(13) Insulator
(6) Dryingchamber	(14) Heater
(7)Thermocouple	
(8)Infraredmoisturemeter(IRM)	

Fig. 1 A schematic of drying system used for single droplet drying experiments.

C. *Data evaluation*

Integral drying curves of single liquid droplets were determined by measuring the outlet moisture content of drying air Y_{out} over time. The mass change of a droplet Δm_i at drying time i is calculated by

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$$\Delta m_i = \dot{m}_g (Y^i_{out} - Y_{in}) \Delta t \quad (1)$$

Where $\dot{m}_g$ is the mass flow rate of drying air and Y_{in} denotes the inlet air moisture content being kept constant in drying experiments. Then, the evaporation rate and the evaporation flux of water at drying time i were, respectively, computed by

$$E^i_r = \frac{\Delta m_i}{\Delta t} \quad (2)$$

$$E^i_f = \frac{E^i_r}{A^i_d} \quad (3)$$

Where A^i_d is the surface area of droplet/particle obtained after post-processing of optical images.

The total water mass evaporated from the droplet/particle until the end of the drying process (i=n) was calculated by

$$m_t = \sum_{i=1}^{i=n} \Delta m_i \quad (4)$$

The water mass remaining in the droplet/particle at the beginning of time step $i+1$ was determined from the previous time step i as follows

$$m_{i+1} = m_i - \Delta m_i \quad (5)$$

The locking point was estimated by plotting water evaporation flux versus moisture content. The locking point was considered when the evaporation flux reaches maximum value, i.e. the onset of second drying stage. The method utilized here to determine the drying kinetics of single droplet/particle can be applied even if there is no correlation between droplet size and mass loss in the second drying stage as well as in the inflation/deflation periods.

D. *X-ray Microtomography(XMT)*

A laboratory-scale X-ray Microtomograph (CT-ALPHA-160 by ProCon X-Ray GmbH, Germany) was used to investigate three-dimensional morphology of final particles. This device is equipped with a microfocus X-ray source and has a detector size of 2300×2300 pixels. Table 1 presents the XMT settings applied for the scanning measurements.

TABLE I
THE XMT SETTINGS USED IN EXPERIMENTS

Measurement parameters	**Value (Unit)**
Voltage	50 [KV]
Current	120 [µA]
Detector-sample Distance	293 [mm]
Angle increment	0.3
Exposure time	1500
Voxel size	2.4 [µm]
One scanning time	1 [h]

III. RESULTS AND DISCUSSIONS

A. *The Effect of Drying Air Temperature*

Fig. 2 shows the effect of different drying air temperatures on moisture content histories of particles/droplets containing hydroxypropylated pea starch at a constant total solid content20% w/w. It was clear that there are two drying stage in drying kinetics curves. At the first drying stage the moisture content decreased linearly with time. It is because of the evaporation of free water from the droplet surface. After that, the rate of moisture removal declined very much due to formation of a solid crust on the surface of droplet. Overall, drying of a liquid droplet occurs in two successive stages: In the first drying stage, the droplet contains an excessive amount of liquid and drying occurs at a constant rate along with droplet diameter shrinkage. The second drying stage commences when the droplet moisture content decreases to some critical value. At this moment, the so-called “locking point” [8]; [5], a porous-structured dry solid crust encloses a wet core [9]. Accordingly, the rate of internal water evaporation dramatically decreases towards the end of the drying process due to an increase of the crust thickness. During the second drying stage the outer diameter of particle remains constant, whereas the interface of the crust/wet core shrinks due to the water evaporation [9].An increase of drying air temperature enhanced the moisture removal rate [10] due to increase heat and mass transfer coefficients.

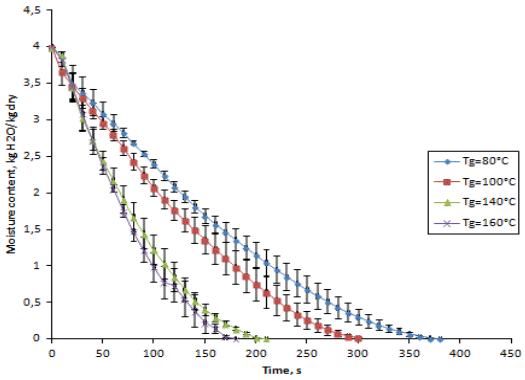

Fig. 1 Effect of different drying air temperatures on moisture content histories of particles/droplets containing hydroxypropylated pea starch at a constant total solid content 20 % w/w

Fig. 3 manifests the effect of different drying air temperatures on evaporation flux of particles/droplets at a constant solid content 20% w/w. It can be seen, evaporation flux of particles/droplets increased and reached to a maximal value at the first drying stage. Then, it decreased with decreasing moisture content in second drying stage [11]. As previously explained, the beginning of second drying stage that is locking point has a maximum evaporation flux. It should be noted that the time of crust formation and locking point affect on structure formation of particle, significantly [12]; [13]. With increasing drying air temperatures, migration of solute components to the droplet surface and water evaporation flux from the surface increased. It could lead to a sooner locking point.

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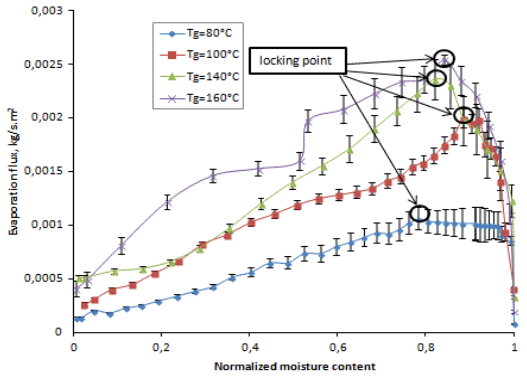

Fig. 3 Effect of different drying air temperatures on evaporation flux of particles/droplets at a constant total solid content 20% w/w

Figure 4 illustrated the effect of different drying air temperatures on the droplet/particle diameter changes at a constant solid content 20 %w/w. There was a significant difference in droplet/particle diameter changes amongst drying air temperatures below and above 100°C. It can be seen, the trend of the droplet/particle size curves were approximately similar for drying air temperatures of 80 and 100 °C.(normalized diameter was This is consistent with the observations of Tran et al. (2016) for single droplet drying of lactose solutions. However, there was a considerably difference between higher inlet air temperatures (140 and 160 °C) and lower air temperature (100°C) .Interestingly, particle diameter was bigger for air temperature of 140 and 160°C (normalized diameter was approximately 0.85). It might be related to inflation/deflation phenomenon that happens in air temperatures above 100 °C [14]. In during inflation/deflation the formed crust on the droplet/particle surface was pushed outwards due to an increase of internal pressure inside wet particle until water vapour escapes to the ambient [15]. It seems a stronger volume expansion [15] in inflation/deflation cycles might lead to a wider collapse at lower initial solid content. Furthermore, the shrinkage behaviour of dried droplets/particles at the inlet air temperatures above 100 °C might be divided in to three stages in this study (see Fig. 4). In the first stage, droplets/particles diameter linearly decreased with time due to the evaporation of free water on the droplet/particle surface [16]. In the second stage, a layer with higher concentration was formed on the droplet/particle surface. As the evaporation continued, the thickness of layer increased and a skin formation initiated. In this stage the reduction of droplet diameter continued but much more slowly. In the third stage, the droplet diameter is fixed and the evaporation of water controlled by hard skin layer. As the thickness increases a new resistance for the water evaporation is added [11] and water has to diffuse thorough the solidifying structure to reach the surface.

It should be noted that particle size plays an important role during the adhesion process of dry powder coating on “host” particles [17], because the adhesion forces are the sum of Van der Waals, electrostatic, and capillary forces, where capillary force is the most important. If “guest” particles have a low mean diameter (below 100 μm) and a homogeneous size distribution, the surface forces (interparticle attractions) become stronger than gravity force. In this condition, the adhesion forces between “host” core and “guest” particles are strong and coating efficiency is higher (see Fig. 5)[3]

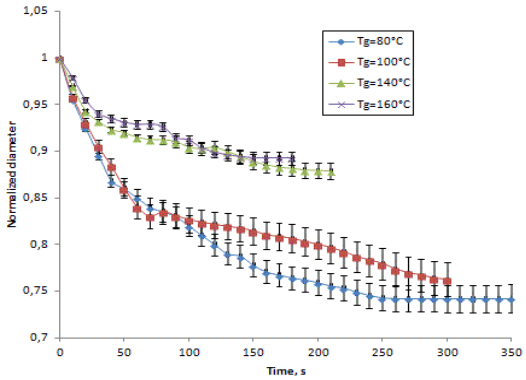

Fig. 4 Effect of different drying air temperatures on the droplet/particle diameter changes at a constant total solid content 20%w/w

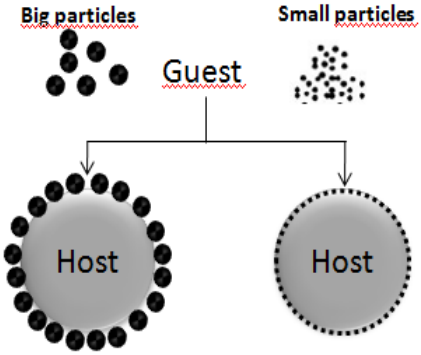

Fig. 5 Schematic illustration of the effect of particle size on the adhesion process of dry powder coating on “host” particles

Fig. 6 displays the effect of drying air temperature on the droplet/particle morphological changes during drying of total solid content of 20 % wt. Furthermore, the inter and surface microstructure as well as the crust thickness at different drying air temperatures and different solid contents is shown in Fig. 7. Interestingly, the particle shrinkage was lower at lower drying air temperature compared with the higher drying temperatures owing to the rapid formation of dry crust around the droplet. Obviously, final particles were hollow in all of experimental conditions due to the quick formation of rigid shell [14]. The crust thickness decreased with increasing of drying air temperature. It is probably because the ratio of water evaporation rate from the droplet surface to the component diffusion rate increased. This led to an early locking point (thinner crust), which limited the migration of the component towards the particle surface. However, in lower drying air temperature, diffusion of components could follow evaporation rate; this means the ratio of evaporation rate to the diffusion rate is low. Therefore, the components participated more homogenously in the crust formation. Under this circumstance a compact particle with thick crust

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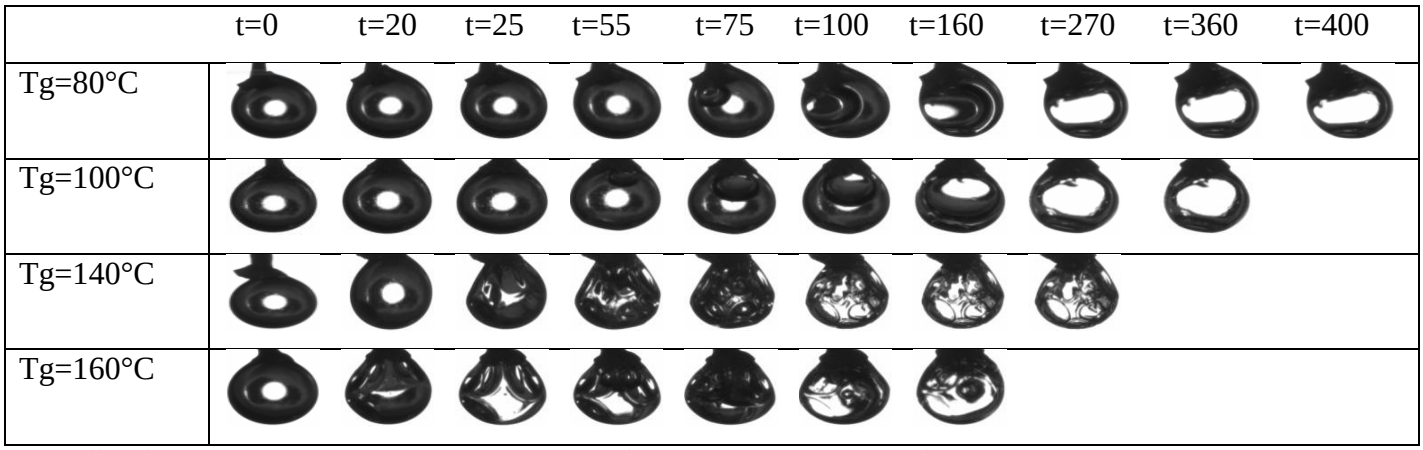

Fig. 6 Effect of drying air temperature on the morphological changes of droplets/particles during drying of 20wt%

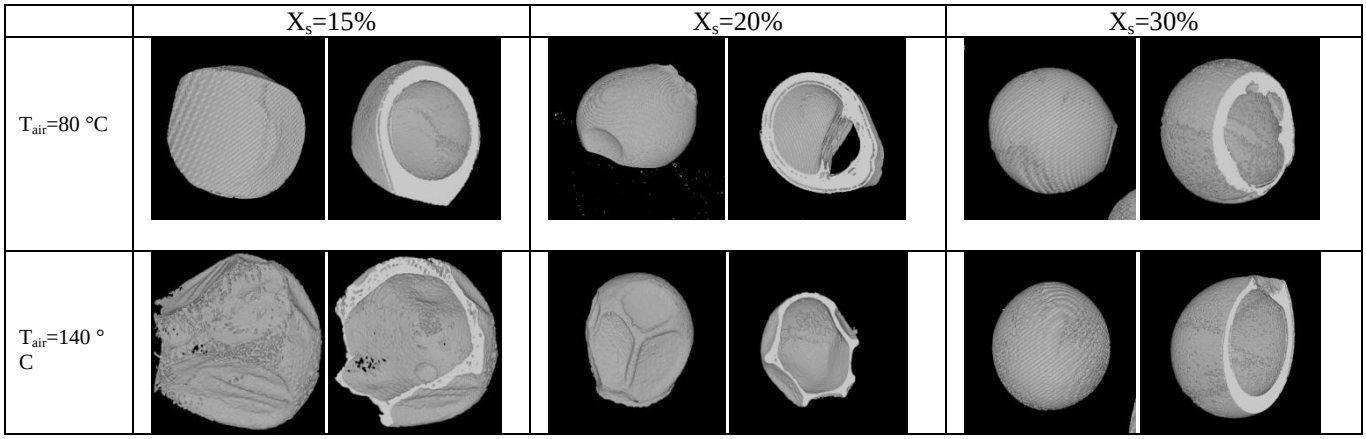

Fig. 7 Effect of different drying air temperatures and different total solid contents on inter and surface structures of produced particles (T_{air} and X_s are drying air temperatures and total solid contents, respectively

may form [18]. Furthermore, an increase of air temperature incremented shrinkage of prepared particles with a total solid content below 30% because of inflation/deflation cycles.

B. The effect of total solid content

The polymer concentration in producing process of dry powder for coating process is a crucial factor. It should be sufficiently high to result in the formation of particles with a relatively high density and thus with good mechanical characteristics [3]. The effect of total solid concentration on moisture content and water evaporation flux of single droplets/particles dried at a constant inlet air temperature 140°C was shown in Fig. 8 and 9, respectively. The moisture removal rate and water evaporation flux were higher in the lower polymer concentration due to a higher saturated vapor pressure on the surface of these droplet/particles.

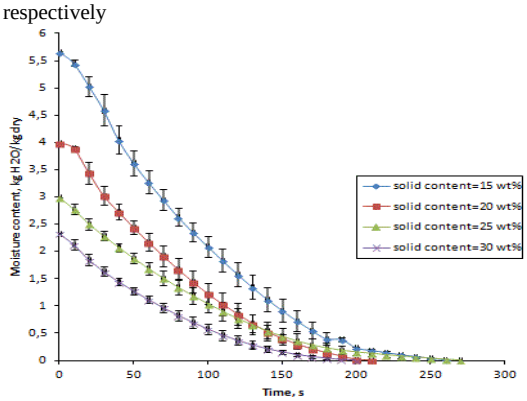

Fig. 8 Effect of total solid concentration on the moisture content histories of single droplets/particles dried at a constant inlet air temperature 140°C

Figure 10 shows the effect of different total solid contents on droplet/particle diameter changes during drying at a constant inlet air temperature of 140°C. An increase of solid content increased particle diameter because of a sooner locking point and a faster crust formation on the droplet surface. It led to a lower shrinkage of droplets/particles during drying (see Fig. 7).

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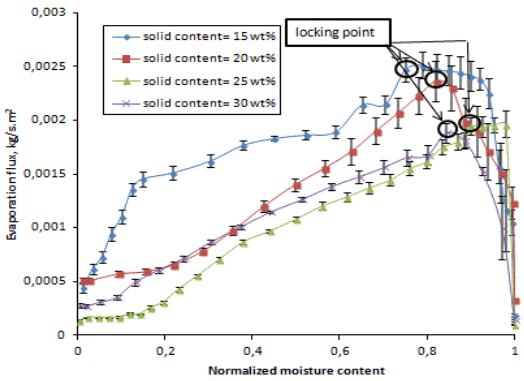

Fig. 9 Effect of total solid concentration on the water evaporation flux of single droplets/particles dried at a constant inlet air temperature of 140°C

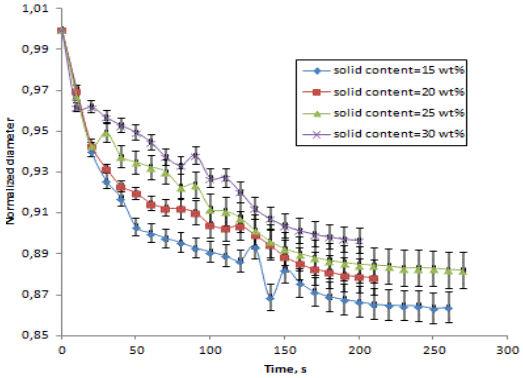

Fig. 10 Effect of different total solid contents on droplet/particle diameter changes during drying at a constant inlet air temperature of 140°C

IV. Conclusions

Progress in understanding the drying behaviour of single droplets containing modified starches can encourage coating industries for development of dry powder coatings based on starch by using spray drying technology. The single droplet drying was carried out under different inlet air temperatures and solid concentrations. The dried droplets/particles in the higher air temperature indicated wrinkled surface with a higher shrinkage due to intensifying of evaporation rate. Although, particle size enhanced with increasing of air temperatures from 80 °C to 160°C. The initial solid contents had also an effect on the single droplet drying process, an increase of solid concentration decreased evaporation rate and increased particle size. Moreover, the surface and inter morphology of final dried particles was investigated using the X-ray micro tomography. It have be seen that the final particles were hollow and had different morphologies in different operational conditions. The investigation of the changes observed in the microstructural and dimensional characterization of droplets/particles provides a comprehensive knowledge for optimization of dry powder coating efficiency using the modified starch in industries.

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