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EXPERIMENTAL STUDY OF DRYING CONDITIONS EFFECT ON STARCH SINGLE DROPLET SHRINKAGE AND MORPHOLOGY DURING DRYING

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ABSTRACT

The product quality is an important issue in pharmaceutical industry. Spray drying process is an appropriate method to obtain dry powders with a controlled quality (size and morphology). In this paper, a single droplet drying suspension device is used for continuous monitoring of the drying process to investigate the shrinkage behavior of hydroxypropyl pea starch (HPS) solution droplet during drying. The understanding of shrinkage behavior of droplets, particle formation and knowledge of the drying conditions effect during drying is of great importance for quality control. HPS powder production by spray drying is widely used as pharmaceutical ingredient; however there are only a few fundamental studies investigating the droplet drying behavior including the shrinkage behavior and morphology. The objective of this study was to establish the prospects to determine the effect of operational conditions on droplet/particle morphology.

Key words: *Hydroxypropylated pea starch, Single droplet drying, shrinkage, morphology,*

NOMENCLATURE

Symboles :
T temperature, °C
U air velocity, m/s
Y air humidity, kg H_2O/kg dry air

Subscript:
g gas

1. INTROUCTION

Better control of product quality and Better understanding of products, ingredients and processes are the two main reasons allowing to improve product performance, optimize the efficiency of manufacturing processes and increase output or improve yield [1]. Dry powders are one of the most common forms of product in food and pharmaceutical industries, they are preferable than liquids form due to its easier transportation and manipulation and less susceptible to microbial deterioration [2]. Many solid dosage forms in the pharmaceutical and biotech industries are based on micro-particles. Dry powders are inhaled as aerosols into the lung, delivered to the nose, filled into capsules, or pressed into tablets for oral applications, or even delivered transdermally [3].

The primary functions of the micronization and drying processes were to achieve a suitable particle size and remove most of the solvent; this perspective has changed as novel drug delivery strategies. More advanced therapeutic approaches have created complex requirements for dosage forms that can only be met by particles that are designed for

a range of functions such as stabilization of the active, transport and targeting of the dose, or release modulation. The particle is no longer seen as a passive carrier, but rather as an essential part of the drug delivery system. [3] Hollow, low density particles with controlled surface morphology, particles with functional layers, or particles comprising smaller subunits such as nanoparticles or defined voids, have been introduced by F. Hamilton et al, (2002), R. Vehring et al,(2007),and D. Lechuga-ballesteros et al,(2008)[4] [5] [6]

In addition to chemical composition, the behavior of particulate materials is often dominated by the physical properties of the constituent particles. These can influence a wide range of material properties including, for example, reaction and dissolution rates, how easily ingredients flow and mix, or compressibility and abrasivity. From a manufacturing and development perspective, some of the most important physical properties to measure are particle size and particle shape. Particle size has a direct influence on material properties such as: • reactivity or dissolution rate e.g. catalysts, tablets •efficacy of delivery e.g. asthma inhalers • texture and feel e.g. food ingredients • appearance e.g. powder coatings and inks • flowability and handling e.g. granules • viscosity e.g. nasal sprays • packing density and porosity e.g. ceramics. As well as particle size, the shape of constituent particles can also have a significant impact upon the performance or processing of particulate materials. Some areas where particle shape can have an impact include: • reactivity and solubility e.g. pharmaceutical actives • powder flow and handling e.g. drug delivery systems • ceramic sinter properties e.g. ceramic filters • abrasive efficiency e.g. Sic wire saws • texture and feel e.g. food ingredients. Particle shape can also be used to determine the state of dispersion of particulate materials. Micro-particles can be manufactured by many different processing methods [3]. The spray drying could be the method of choice for the production of powders with controllable size and morphology [7] [15]. During a powder manufacturing process such as spray drying, process conditions may exhibit appreciable effects on size and shape of dried particles [5], which further impact the quality and functionality of final products [2].The understanding of shrinkage behavior of droplets during drying is of great importance for quality control as well as kinetics study of spray drying, because, In droplet-to-particle transition process, droplets shrink as moisture is removed, while the change in droplet size affects mass and heat transfer coefficients that determine evaporation efficiency [8]. Droplet size change can be studied by video-recording the drying behavior of an isolated droplet in a controlled air flow, known as single droplet drying (SDD) experiments [9];[10].

SDD experiments could mimic spray dryer environment to some extents, but with more controlled drying conditions for quantitative studies. The technique is capable of generating drying kinetics data [11] as well as monitoring morphological development during droplet-to-particle transition process [2]. Single droplet experiments have been widely used to determine particle morphology since 1952, it allows to observe and control the single droplet easily and continuously[9] [10][11] [12].

Charlesworth and Marshall (1960) investigated the drying behavior and crust formation of single droplets containing dissolved inorganic compounds. They observed that a complete shell was formed initially for all solutes studied. They demonstrated that the final size, shape, and structure of the dried particle depended on the solute used and operating parameters such as heating temperature, rate of evaporation, mass of solute [2]. As image processing technology has developed, and combined with conventional drying equipment, some researchers have used the technology to measure the droplet diameter change during drying in single droplet drying experiments. [9] [11].

In order to establish the kinetics of droplet size change, experiments must be carried out to measure the droplet diameter change during drying [9] [11]. The most common experimental procedures are those collecting the optical (video) images of the droplet being dried, from which the ‘equivalent diameter’ is calculated. Because of the complexity of uneven shrinkage of the droplet, the error between the drying surface area, which is calculated from the ‘equivalent diameter’, and the true drying surface area has not been discussed in the literature. This measurement method has been mostly used in droplet morphology analysis [9]. investigated the droplet/particle transition process of

different carbohydrate solutions and food liquids [13], droplet inflate-deflate cycling and bubble nucleation phenomena were observed. J.-C. Lin & Gentry, (2003) Investigated particle density and morphology as a function of latent heat of crystallization, solubility, and drying rate [8]. The SDD is a powerful method to investigate shrinkage behavior providing a useful tool for linking process conditions with product properties.

The objectives of this study were to:

- recording of droplet/particle equivalent diameter change continuously during drying;
- study of the drying conditions effect upon diameter change;
- study of the initial solid content effect on diameter change;
- determination of surface structure and internal morphology of dried particle using Xray micro tomograph

2. MATERIAL AND METHODS

The thin boiling hydroxypropyl pea starch (HPS) granule (Lycoat NG 780) was a gift from Roquette Company (France). The starch solutions of different concentrations (15% w/w, 20% w/w, 25% w/w and 30% w/w) were prepared by cooking the HPS granules mixed with distilled water under a temperature of 90°C. The starch drying kinetics of was studied in an experimental setup (Fig. 1) for single droplet drying.

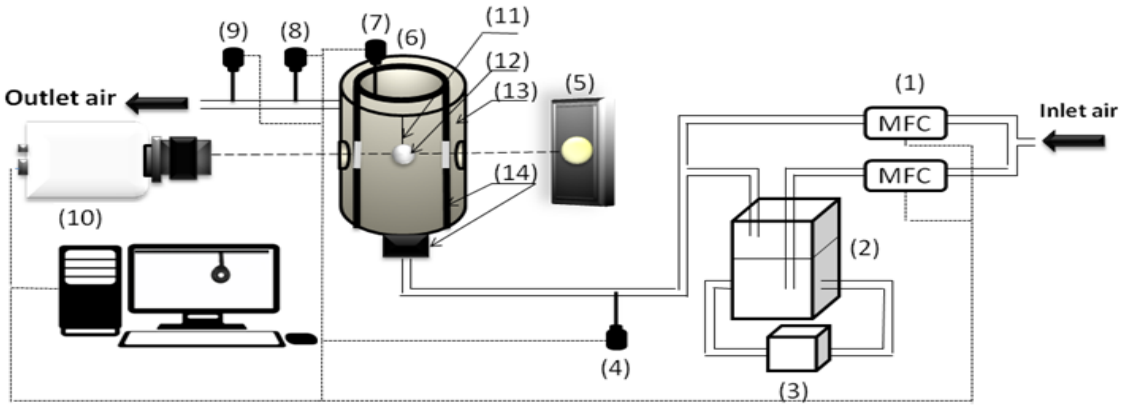


FIGURE 1. Schematic illustration of the single droplet drying system

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

The experiment is realized by attaching a solvent droplet to a dried/ semi-dried single particle in situ and then video-recording the resultant morphological changes. Drying air has been humidified in a saturator, and mixed with dry air by mixer unit to maintain approximately its humidity constant and equal to the desired one; this humidity was measured at the inlet and outlet by dew point mirror (optidew vision, Michell instruments) and infrared spectrometer (NGA 2000, Fisher-Rosemount) respectively. The drying air mass flow rate ranged between [1,500ml/min] was controlled by Bronkhorst Maettig GmbH, F-201CV. An electrical heater was used to heat up the air which was pumped from the bottom to the drying chamber. Drying air temperature could be changed between [20,200°C]; it was measured by tow thermocouples one was placed inside the drying chamber and the second at the outlet. Drying chamber is made of steel with an internal diameter 24mm; it is enclosed from the outside by two layers which are an electrical resistance to heat loss.

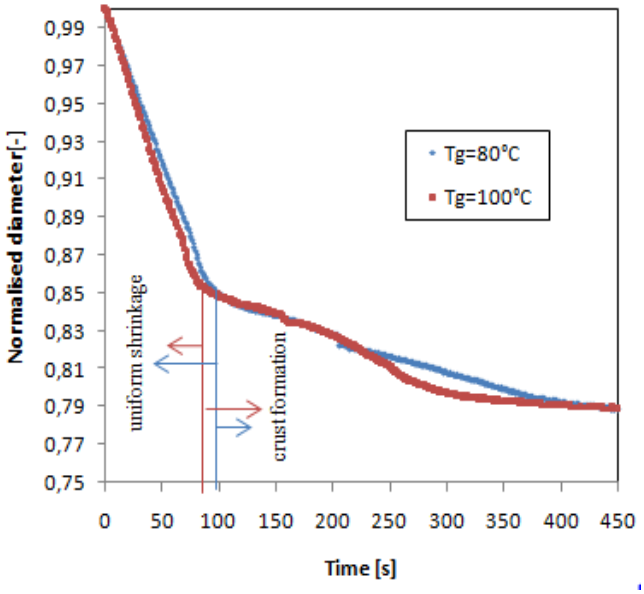
The droplet was inserted by a syringe with a long needle onto the tip of polyamide wire of 0.2mm of diameter which has low thermal conductivity; the generated droplet diameter is around 0.8mm. The single droplet drying was continuously analyzed and optically observed using an image recording system including a high speed video camera

(MC-1009AP/MD, Horn imaging GmbH), a light source for back illumination, and a long-distance microscope lens (Stemi 200-C, Zeiss). The recorded images were analyzed by a matlab program which consists to calculate the equivalent diameter of the single droplet. The dried particles were analyzed by Xray micro tomography instrument to determine the particle internal and external structure.

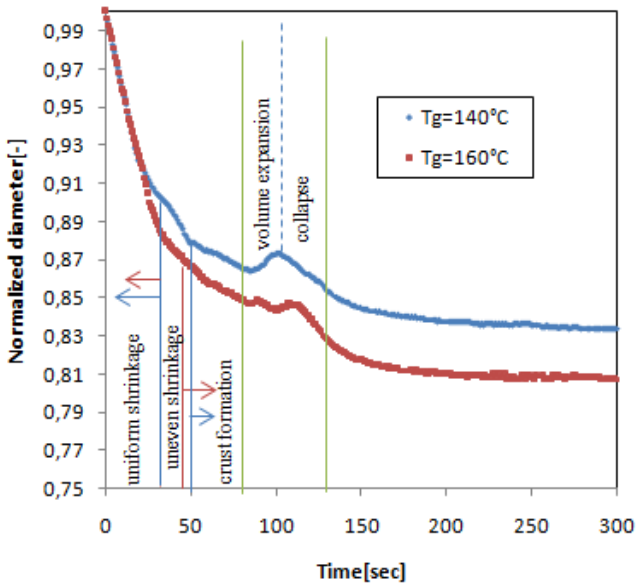
3. RESULTS

Figure 3 shows droplet diameter (Fig 3,a,b,c) and morphological changes (Fig 3,d) during drying. Moisture evaporation from the droplet leads to its shrinkage. The different curves showed a transition point, and tow drying stage has been distinguished, in the first drying period the droplet diameter decreased uniformly because of evaporation of water available at the droplet surface due to the saturation conditions occurring at this drying stage, an increase of solid concentration at droplet surface which form a crust, the droplet shrinkage continues until the formed crust can overcome capillary forces remaining the wetness of the droplet surface [14].

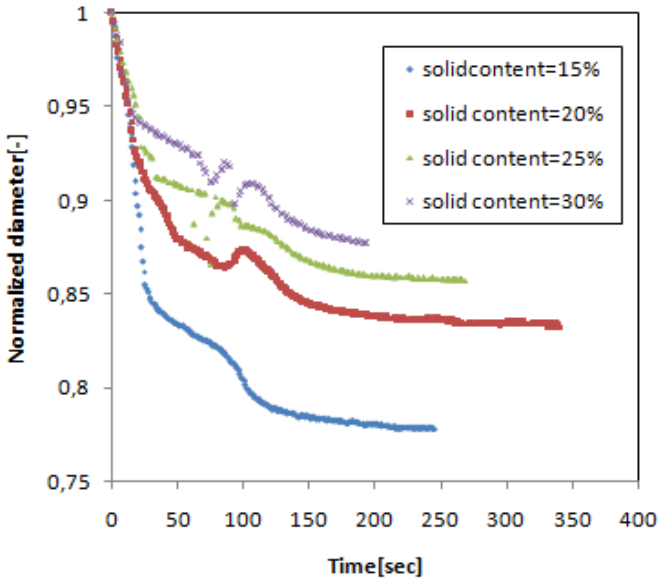
(a)



(b)



(c)



(d)

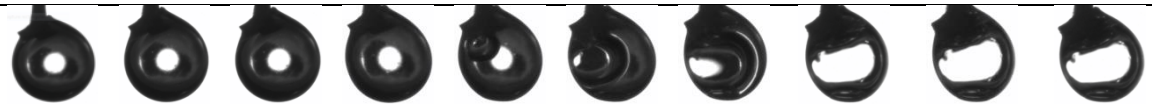
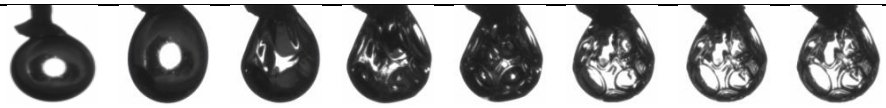
Time (s)	t=0	t=20	t=25	t=55	t=75	t=100	t=160	t=270	t=360	t=400
Tg=80°C										
Tg=100°C										
Tg=140°C										
Tg=160°C										

FIGURE 2.Normalized diameter vs. Time for droplets of constant initial concentration (20 wt %) at different air temperatures (a) at low temperatures (b) at high temperatures (c) constant air temperature(140°C) and different initial concentrations (d) camera capture of droplet at different air temperatures (U=0.02 m/s, Y=8g/kg)

In Figure (2-a,b,c) it was distinguished a similar behavior in the first drying stage, it was noticed that the faster shrinkage is at higher temperature (see Fig2-a,b) and higher concentration (see Fig2-c), the droplet shrinks evenly, sustaining a spherical shape approximately and a skin begins to appear, afterwards, the surface exhibits slight contractions and folds.[9] This period will end with a critical value called "locking point" at which the crust starts to form. Exceeding the locking point, second drying stage starts, in this period two different behaviors was distinguished, unlike the ideal shrinkage at which at higher temperature a particles with lower final diameter was obtained because of the residual moisture content decrease. A slight decrease with negligible deformation of wet particle was observed at low temperature (≤100°C) (Fig2-a) in which the diameter is remain constant and approximately equal to the value at the locking point due to the delicate crust formed which could not sustain the constant particle size. However, at high temperature above the solvent boiling point(>100°C), the crust formation start earlier [12] and an inflation/deflation phenomenon occurred (Fig2-b) after the locking point at which a bubbles was nucleated inside the droplet growing finally and in some cases exploding outward over the droplet/particle surface [9] due to the influence of internal water pressure because of the residual solvent (water) evaporation, this solvent was trapped inside the droplet and further drying cause its evaporation resulting the droplet/particle bubbling which leads to its expansion [12]resulting on final larger particle.

At the drying beginning, the initial solid content has an irrelevant effect shown in the slight variation of the slope in (Fig2-c). further drying act on the droplet/wet particle resulting in a significant expansion with increased concentration due to the important vapor amount occurred inside the wet particle preventing it from escaping due to rapid crust formation[12], the particle final diameter is larger at higher initial concentration. This volume expansion leads to hollow particle formation because of starch shell elasticity.

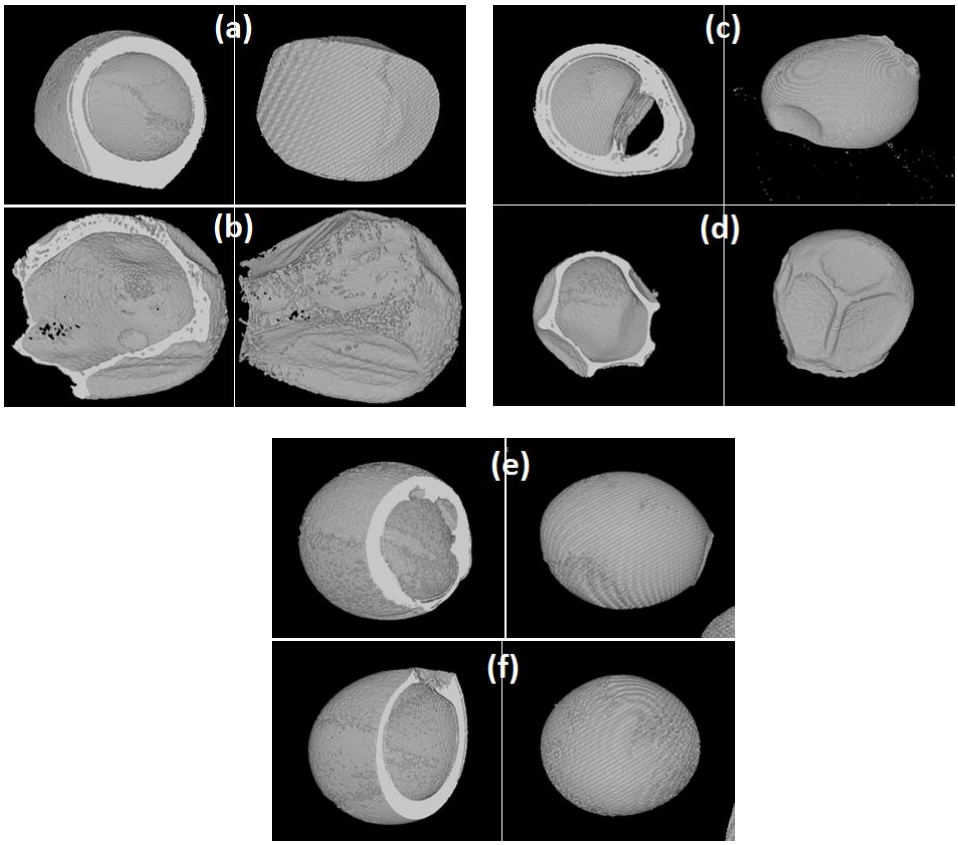


FIGURE 3: Morphology of final dried particles of different initial solid content (15%w/w, 20% w/w, 30% w/w) dried at different drying air temperatures (80°C, 140°C) (Y=8g/kg, U=0.02m/s), (a) 15% w/w,80°C; (b) 15% w/w,140°C; (c) 20% w/w,80°C; (d) 20% w/w,140°C; (e) 30% w/w,80°C; (f) 30% w/w,140°C

Figure 3 shows the internal morphology of dried particles at different conditions, the images were obtained from customized X-ray µ-CT scanner (CT6Alpha-2000, Pro-Con X-Ray Co.).Several different structures have been observed at low and high temperature, i.e at 80°C it was observed that the external surface of dried particle is relatively smooth for all initial solid contents, a slight deformation was observed for 20%w/w, however, at high temperature (140°C) the surface is smoother when increasing initial solid content; there are signs of expansion and collapse, i.e for 15%w/w we have observed a wrinkled fragile surface with folds which may be due to the small amount of solid content in the droplet and the inflation/deflation phenomenon occurred inside the droplet which is also the reason of having internal voidage resulted in hollow particles [9] in addition the elastic property of starch. For 20%w/w it was observed the presence of the folds but the surface is more or less rigid because of the increase of the solid amount in the drop. It was distinguished that the initial solid content increase leads to an increase in the shell thickness. There is some artifact of the technique

4. CONCLUSION

In general, the droplet diameter reduced during the drying process; it have be seen also a non linearities on the diameter vs. drying time plots. The single droplet drying was carried out under different air temperature below and above the solvent (water) boiling point, this air temperature has a major effect on droplet diameter changes, indicated in the fast shrinkage due to water removal at higher temperature and in the final dried particles morphology residing in hollowness, wrinkled surface with folds, and high final droplet size due to the inflation/deflation phenomenon. The initial solid contents has also an effect on the single droplet drying process, it have been observed a production of particles with higher shell thickness at higher initial solid content with smooth surface this shell thickness decrease by decreasing initial solute concentration and increasing drying air temperature. Moreover , the final dried particle morphology was investigated using the X-ray micro-computed tomography providing not only the external

morphology but the internal one too, it have be seen that the final particles contain one big hole which become smaller at high initial solid content and low temperature.
Finally, the SDD method used for determining pea starch single droplet shrinkage and morphology appears to be a powerful method providing a useful tool for linking process conditions with product properties.

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