



ASSESSMENT OF THE KINETICS OF CONTACT ANGLE DURING THE WETTING OF MALTODEXTRIN AGGLOMERATES

EVALUACIÓN DE LA CINÉTICA DEL ÁNGULO DE CONTACTO DURANTE LA HUMECTACIÓN DE AGLOMERADOS DE MALTODEXTRINA

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Abstract

The wetting phenomenon of thick agglomerates was studied using tablets produced from 8 different fractions obtained from sieving of maltodextrin (DE 15) powder. The fractions ranged in size from 38 to 150 μm . The tablets were produced by applying compression force equivalent to 2 tons by means of a hydraulic press. Wetting kinetics was followed, after deposition of a water droplet on the surface of the tablets, by measuring the changes in contact angle. After an initial descent, the curve showed oscillations due to droplet recoiling phenomenon. Surface texture was rougher for tablet than for the wetting mark as evaluated by Fractal Dimension of Texture and Angular Second Moment. No clear tendency of the effect of particle size on these parameters was observed.

Keywords: wetting, contact angle, agglomerates, maltodextrin, image analysis.

Resumen

Se estudió el fenómeno de humectación de polvos aglomerados en forma de tabletas utilizando como material de trabajo maltodextrina (DE 15). El polvo se hizo pasar a través de una serie de tamices, obteniéndose 8 diferentes fracciones con tamaño promedio de partículas de 38 a 150 μm . Las tabletas se obtuvieron aplicando una fuerza de compresión de 2 toneladas mediante una prensa hidráulica. Se evaluaron cinéticas de humectabilidad de los aglomerados, midiendo los cambios del ángulo de contacto con respecto al tiempo y se observó en las cinéticas, la presencia de oscilaciones después de un breve descenso inicial del ángulo de contacto. La textura de la tableta fue más rugosa que la de la marca de humectación de acuerdo con los valores de la Dimensión Fractal de Textura y del Segundo Momento Angular, obtenidos por medio de análisis digital de imágenes. No se observó una influencia clara del tamaño de partícula sobre estos parámetros.

Palabras clave: humectación, ángulo de contacto, aglomerados, maltodextrina, análisis de imagen.

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1 Introduction

Many natural and synthetic polymers have been used as a support for the controlled release of active compounds. This release depends on many factors such as matrix composition, elaboration technology, properties of the active compound and of the polymeric support. Some of the polymer properties are: molecular weight, solubility in water, degree of crosslinking, resistance of the polymeric chains to shear stress and molecular conformation in an aqueous environment. All these properties are important, in the case of tablets, for the phenomena of swelling and erosion (Garzón *et al.*, 2009). However, before these two processes can take place, wetting of the surface and water penetration must occur.

Wettability is often characterized by measuring the contact angle formed between a liquid drop and a solid surface. This measurement is considered to be relatively simple, useful and it has been shown to be correlated with surface energies of solids and surface roughness (Meiron *et al.*, 2004). The wettability of a solid with respect to a liquid is a straight consequence of molecular interactions between phases coming into contact. Considering a liquid drop put down on a solid surface, for wetting to occur, the molecules of the liquid situated close to the three phase contact line must break off with their surrounding liquid molecules, displace the gas or vapour molecules adsorbed at the solid surface and adhere to the solid by interacting with molecules belonging to the solid (Lazghab *et al.*, 2005). It is evident that in order to evaluate this wettability, the characteristics of the agglomerate must be known. During mechanical compaction, the powder bed is continuously consolidated to bring particles closer together as pressure is applied. This consolidation of powder causes deformation and a significant amount of inter-particle molecular interactions arises. These interactions and structures produce the mechanical strength of a tablet and their modification is necessary for wetting, disintegration and subsequent release of the active principle upon administration of a tablet. The structure of a tablet is very important for its physical properties. Most compressed tablets are porous in nature. It is therefore appropriate to evaluate porosity to try to understand the wettability properties of the tablet (Sun, 2005).

The presence of pores (micropores) is therefore very important for water absorption. It has been shown that the blockage or reduction in size of these pores will reduce the penetration of water into the interior

of a dry solid (Azuara and Beristain, 2007). This is even more important if the tablet support has low hydrophilicity. It is feasible that the rate of water penetration into a tablet is dependent on the particle size of the powder used and number of pores in tablets. Different experiments have shown that tablet disintegration time decreases with increasing tablet porosity (Sun, 2005).

It has been observed that the use of different particle size fractions in the elaboration of tablets leads to the formation of different matrices, as well as different pore networks and therefore different structures (van Veen *et al.*, 2005). These structures are hard to describe due to their complexity. However, image fractal analysis has been successfully used to characterize and study structural and mechanical properties of many substances including foods and pharmaceutical products (Santacruz-Vázquez *et al.*, 2008). This tool is useful to characterize changes in some physical properties in terms of changes in volume, area and shape (Pérez-Alonso *et al.*, 2009). Imaging techniques are useful as methods for analyzing tablets. They are often non-destructive and allow for the acquisition of texture information over a relatively large area of a tablet. They also require minimal sample preparation and manipulation, leaving the sample intact and in its original state during analysis. Image analysis has then an important potential for monitoring the evolution of processes such as wetting.

Li *et al.*, (2008) reported that when a droplet of a low viscosity liquid (such as water) is deposited on a solid surface it might recoil producing different morphologies and textures on the surface which can be analyzed through image analysis. Image texture analysis is a well-developed technology that has been used for the analysis of all kind of images and that can be defined as the distribution of color in an image with respect to the spatial coordinates and is then a function of spatial variation in pixel values (Fernández *et al.*, 2005). Texture can have different features which can provide useful information such as: the Angular Second Moment (ASM), which is a measure of the homogeneity of the image; the Entropy, which is a measure of the randomness of the distribution of the gray scale or disorder in the image; the Contrast, which is a measure of the amount of local variation in an image.

The overall objective of this work was to study the kinetics of wetting of thick maltodextrin agglomerates through the measurement of changes in contact angle as well as the evaluation of image texture of original

tablets and wetting mark after liquid evaporation.

2 Materials and methods

2.1 Materials

Maltodextrin (DE 15) was purchased from CPI Ingredientes (México) and hexyl alcohol (H13303) was purchased from Sigma-Aldrich Co. (USA).

2.2 Separation of maltodextrin into fractions of different particle size

Eight stainless steel sieves (US standard sieve series, W.S. Tyler Co., USA) with mesh numbers 100, 120, 170, 200, 230, 270, 325 and 400 corresponding to 150, 125, 90, 75, 63, 53, 45 and 38 μm -pore size were stacked in two groups of four sieves with the largest pore size on top. Maltodextrin (200 g) was spread on top of the sieve stack and shaken in a Tyler RX-86 sieve shaker (W.S. Tyler Co., USA) for 5 min (Barbosa-Cánovas *et al.*, 2010).

2.3 Morphometric parameters

Powder samples were observed in an Axiophot 1 light microscope (Carl Zeiss, Germany) and 70 images were acquired for each size fraction in bit map (bmp) format to be preprocessed and segmented. Thresholding process was applied to each image by manually adjusting level to 179. Image processing was carried out according to Pedreschi *et al.*, (2004) using the software ImageJ 1.34 (National Institutes of Health, USA). The evaluated morphometric descriptors were: Feret diameter, perimeter, maximal perimeter and shape factor. With these results, particle size distribution could be evaluated.

2.4 Preparation of agglomerates

Thick agglomerates in the form of tablets (13 mm diameter, 4.5 mm height) were prepared by using a Carver hydraulic laboratory press (Model C S/N 32000-224, USA) and a 13 ton die (WQ09D Perkin Elmer, UK) by pouring 0.7 g of the powder samples (corresponding to the eight sieved fractions) into the die and compressing the sample (Palzer, 2005; Chantraine *et al.*, 2007). A compaction force of 2 Ton (equivalent to 220 MPa) was applied to each of the eight fractions obtained from the sieving process.

2.5 Tablet wettability evaluation

Contact angle (θ) is the primary parameter for determining wettability. Contact angles formed between a droplet of water and one of the faces of the agglomerates were measured with a contact angle micrometer (CAM Plus Series, Tanteq Inc., USA). Water droplets (10 μL) were allowed to fall from 5 mm and the contact angle was measured at the beginning (initial contact angle) and then every 30 s until the equilibrium was reached or the droplet was absorbed by the agglomerate as shown in Fig. 1. (Shubert, 1980; Chibowski and Perea, 2001; Elkhyat *et al.*, 2004; Meiron *et al.*, 2004; Lazghab *et al.*, 2005; Meiron *et al.*, 2007). Contact angle was reported as: ratio of contact angle at current time to maximum contact angle with dimensionless time (τ , ratio of current time to total time).



Fig. 1. Contact angle between water drop and maltodextrin tablet

2.6 Microstructure analysis of dry and wetted tablets

For the structure analysis of the tablets, a Scanning Electron Microscope (SEM) Vega IILMU (Tescan, Brno Czech Republic) at 15kV and 0 Pa, equipped with an integrated program for digital image capturing at a magnification of 500X was used. Samples were placed on the SEM after wetting treatment. Images were stored as bit-maps in a gray scale with brightness values between 0 and 255 for each pixel constituting the image. A generalization of the Box Counting method was used to evaluate the fractal dimension of the images. In this work, the shifting differential box-counting method (SDBC) (Chen *et al.*, 2003) was used to measure the fractal dimension and angular second moment for the 2-D gray-level of SEM images using the ImageJ 1.34 software. Image segmentation and extraction were also performed using the ImageJ 1.34 software to evaluate macroscopic structural changes. Images obtained from top views of the agglomerates were captured in RGB color and stored in BMP

format. Image segmentation included cropping, conversion of color image to grey-scale values, and background subtraction to obtain the binary image from the original color image.

3 Results and discussion

3.1 Morphometric parameters of maltodextrin powders

Feret diameter, perimeter and maximum perimeter were directly proportional to particle size. As expected, the shape factor (SF) did not show the same tendency than the other parameters but rather similar values for all particle sizes, except for the smallest and the largest particle sizes in which very large and very small and even deformed samples not as spherical as in the other sieves were included given the nature of sieving. In general, morphological parameters were significantly different ($p \leq 0.05$) for the eight fractions obtained throughout sieve analysis (Figs. 2-5). Feret diameter steadily decreased 80.7% with particle diameter.

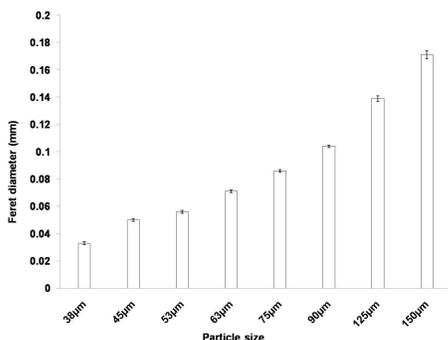


Fig. 2. Feret diameter for the different particle size fractions.

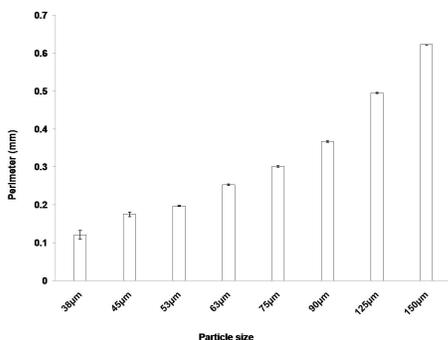


Fig. 3. Perimeter for the different particle size fractions.

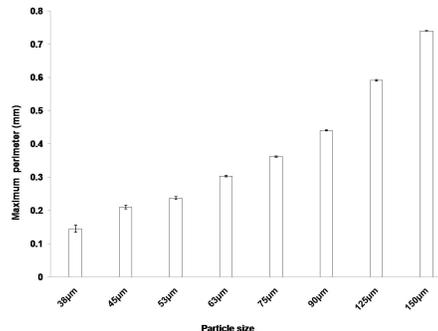


Fig. 4. Maximum perimeter for the different particle size fractions.

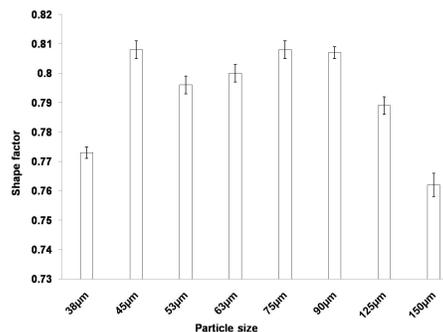


Fig. 5. Shape factor for the different particle size fractions.

3.2 Evaluation of the wettability of the agglomerates

Manservigi *et al.*, (2009) studied the simulation of the impact of a droplet on solid surfaces and divided the evolution of impact in three stages: the first one is controlled by the inertial forces on top of the drop. The second one was controlled by the dynamics of the contact angle and the third one by capillary forces that induce equilibrium of the contact angle. In our work, these stages showed overlapping since the morphology of the solid surface is affected by wetting and dissolution.

The variations of the water-agglomerates dimensionless contact angle for the different particle sizes with dimensionless time are presented in Fig. 6. Wetting kinetics, showed initial values of the contact angle within an interval of 30-35°, equivalent to 1 in the dimensionless format. After initial contact, the liquid started to dissolve the solid and to penetrate within inter-particle spaces and pores, and the contact angle decreased according to kinetics shown in Fig. 6. It is noteworthy that all the kinetics depicted

in this Figure, presented an oscillatory behavior of the contact angle, which was due to recoiling phenomena of the droplet and which presented the onset when penetration-dissolution started. Recoiling phenomena has been reported in the literature on the basis of theoretical considerations for different liquids contacting a wide variety of solids (Prabhu *et al.*, 2009; Ravi *et al.*, 2010). Liquids and solids may upon contact, give place to a variety of shapes of the liquid phase on top of the solid depending on the interaction among the phases and this will also control the recoiling and magnitude of the contact angle during time. However this phenomenon has not been reported for food-related materials.

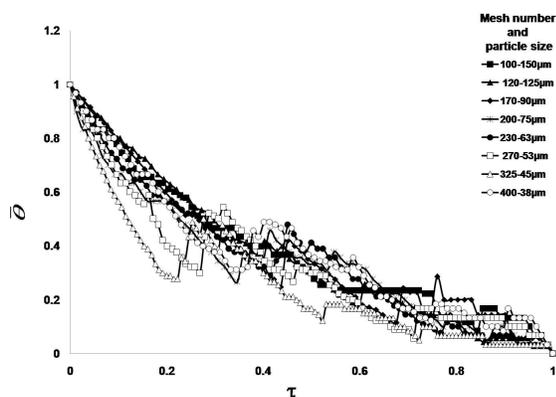


Fig. 6. Kinetics of the water-agglomerates dimensionless contact angle for tablets prepared at two ton of compaction force with dimensionless time for eight different particle sizes.

With the exception of the agglomerate produced with the largest particles, all the others showed a final contact angle of zero. This indicated that large particles tend to form a stable hump that prevailed with time even after the liquid evaporated. The existence of such a hump was also evident given the prevalence of a constant value of the dimensionless contact angle ($\bar{\theta} > 0$) at the final stage of the contact angle kinetics shown in Figure 6. Similar effects have been reported for the drying of ink drops on Li *et al.*, (2008) and are due to drying out of the maltodextrin solution on top of the agglomerate before the liquid was uptaken by the solid surface. In Fig. 7, an illustration of recoiling is presented.

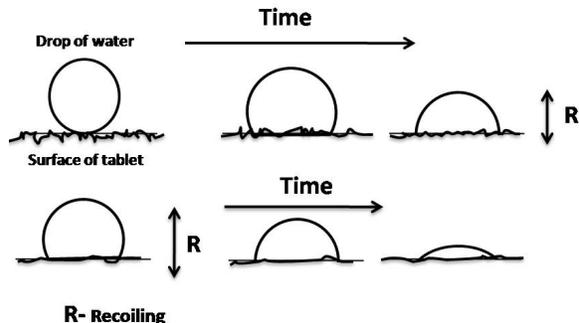


Fig. 7. Illustration of the recoiling phenomenon for water-tablet contact.

3.3 Microstructure analysis of dry and wetted tablets

Morphological characteristics of the wetting mark of the agglomerates are a consequence of the solid-liquid interaction mechanisms and provide useful information regarding the affinity of both phases in terms of the extent and manner of water spreading on top of the tablet. Angular second moment (ASM) and fractal dimension of texture for wetting mark and tablet (FDT) were evaluated by means of image analyses as described in the section of materials and methods. ASM for tablet and wetting mark showed that wetting mark presented higher ($p \leq 0.05$) values than the surface of the tablet given the more homogeneous texture of the wetting mark produced by the dissolution process upon solid-liquid contact as shown in Figs. 8 and 9 (Haralick *et al.*, 1973; Fernández *et al.*, 2005). FDT for tablet and wetting mark also showed that upon contact, roughness of tablet surface decreased significantly ($p \leq 0.05$). Both parameters indicate that the liquid wets and dissolves a part of the solid thus filling up cracks and pores giving place to a smoother appearance. No differences on ASM and FDT values between particle sizes (for wetting mark and tablet) were observed ($p > 0.05$). In Fig. 10, a micrograph of one agglomerate (tablet) prepared with $45 \mu\text{m}$ maltodextrin particles and corresponding zooming of wetting mark and tablet as well as their respective values of FDT and ASM are shown. It is evident the smoother texture of the wetting mark as compared with that of the original tablet. This work contributed to the knowledge of the wetting process of maltodextrin compact agglomerates in the form of tablets produced by means of higher compaction forces than those commonly used for producing tablets (USP, 2000). Also, the reported findings on variation of contact angle with wetting

time provided an insight on the recoiling phenomena on surfaces formed by compaction and showed that Image Analysis is a powerful tool for characterizing and differentiating original and wetted surfaces of such agglomerates by means of FDT and ASM.

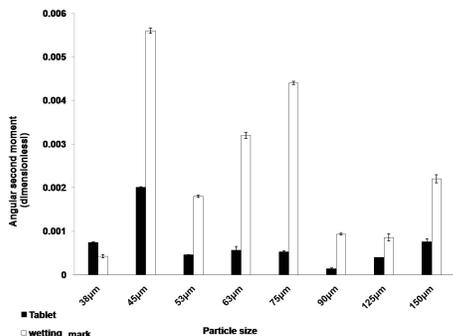


Fig. 8. Angular second moment for the different particle size fractions.

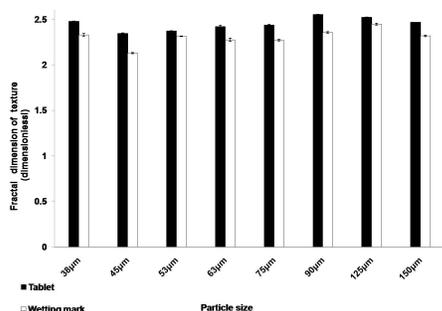


Fig. 9. Fractal dimension of texture for the different particle size fractions.

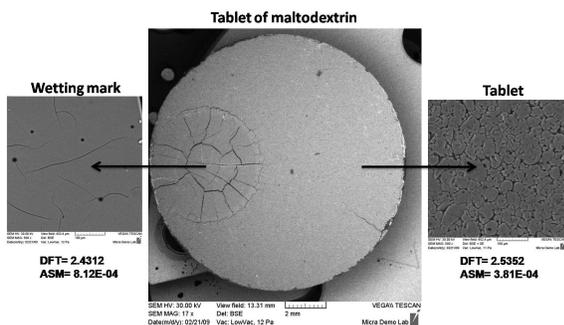


Fig. 10. Micrograph of agglomerate (tablet) prepared with 45 µm maltodextrin particles and corresponding zooming of wetting mark and tablet as well as their respective values of FDT and ASM.

Conclusions

Perimeter, maximum perimeter and Feret diameter of particles, decreased steadily with their size. The shape factor presented rather similar values for all sizes, except for the smallest and the largest ones. Liquid on top of sample, presented characteristic recoiling during contact until liquid evaporated and the contact angles had values of 0°. Surface texture was rougher for tablet than for the wetting mark as evaluated by FDT and ASM. No clear tendency of the effect of particle size on these parameters was observed.

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