

Changes in particles of coffee powder and extensions to caking

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Abstract

Changes in the projected area (PA) of particles of an instant coffee powder were followed in real time by videomicroscopy and image analysis. Particles were placed inside a transparent acrylic chamber ($7 \times 7 \times 3$ cm) where the relative humidity RH (43%, 52%, 67% and 74%) and temperature T (20, 25 and 30 °C) were controlled and measured in the head space. A “caking index”, ϕ , was defined as the change in PA at any time t with respect to the initial PA. At any temperature, there was an increasing effect in ϕ as RH increased and the shape of ϕ versus time curves closely followed that of caking, measured by sieving techniques. The exponential kinetic model adequately fitted the data. The PA method could be used as a first approximation to predict the tendency to caking of amorphous particles.

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1. Introduction

Caking is a deleterious phenomenon in which particles of an amorphous powder are progressively deformed until they stick to each other, eventually forming large agglomerates. Caking kinetics depend on relative humidity (RH), temperature (T) and time (Aguilera, del Valle, & Karel, 1995; Peleg, 1993).

Hygroscopicity and size appear to be the most important properties of particles leading to caking (Provent, Chulia, & Cary, 1993). Thus, the study of particle deformation under gravity, as a function of time and under controlled environmental conditions, should give an indication of the caking tendency. Other factors related to caking have to do with bulk properties of the powders, such as diffusion of moisture to the deeper layers and stress caused by pressure of the material at the top (Tardos, 1996).

Methods used to assess the caking tendency of a powder in bulk have been reviewed by Aguilera et al. (1995). Most

of them are adaptations of tests that measure the flowability of a powder sample under gravity, require a relatively large sample and the equilibration process in the prevailing relative humidity may be uneven and extended in time.

In the initial stages of caking, interparticle bridging appears to be the preponderant mechanism. Bridging may occur due to flow of the outer material in particles under reduced viscosity, induced by moisture adsorption or condensation (Downton, Flores-Luna, & King, 1982). Thus, the study of particle deformation under gravity, as a function of relative humidity or moisture content, should give an insight of the tendency of particles to undergo bridging.

Performing experiments in real time under the lens of a microscope in a stage capable of controlling the main variables of the process has been advocated as a way of “miniaturizing” conditions during processing and storage and to study their effects (Aguilera & Lillford, 1996). Processes such as frying and drying have already been miniaturized, and critical parameters (e.g. cell shrinkage) have been quantified with minimal intrusion (Bouchon & Aguilera, 2001). In the case of caking, data acquired by videomicroscopy can be image-processed to get quantitative information (e.g., projected areas of particles) and to develop a

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kinetic model with virtually no-intrusion. The objective of this work was to follow structural changes in amorphous particles of coffee powder in real time using videomicroscopy, to assess the effect of T and RH on the projected area (PA) of particles and to develop a “Caking Index” based on changes of the PA.

2. Materials and methods

2.1. Samples

Samples of instant coffee powder (Nescafe, Nestlé-Chile) were obtained directly from a new can (originally sealed with an aluminium membrane). The product was prepared commercially by spray-drying and showed signs of slight agglomeration. Thus a uniform sample was obtained by sieving below 100 mesh. The “anhydrous” state was achieved by storing a sample in a desiccator with P_2O_5 for one week until constant weight was obtained.

2.2. Glass transition temperature and adsorption isotherm

Glass transition temperatures of powder samples were determined in a differential scanning calorimeter (Mettler DSC 820, Mettler Instruments AG, Volkestwil, Switzerland) after equilibration over saturated salt solutions in desiccators. Similarly, the adsorption isotherm was constructed by exposing anhydrous samples to different RH in desiccators until constant weight was achieved.

2.3. Experimental setup

The experimental setup is presented in Fig. 1. An acrylic chamber with an open bottom was constructed with dimensions $7 \times 7 \times 3$ cm (length–width–height), so that a small

head space was over the coverslip containing the sample. Dehydrated particles were sprinkled on the coverslip to have as many individual units as possible and observed with a stereomicroscope Nikon model SMZ 2B-2T (Nikon, Japan). Control of relative humidity (RH) in the chamber was achieved by bubbling air through a saturated salt solution by means of a small aquarium pump. Saturated solutions had the following RH values (in parentheses): K_2CO_3 (42–44%); $Mg(NO_3)_2 \cdot 6H_2O$ (52%); $CuCl$ (67–68%) and $NaCl$ (74%). Humidified air at constant temperature (20, 25 and 30 °C) was brought into the chamber after submerging the Tygon tubing in a controlled temperature water bath (see Fig. 1). Both, air RH and temperature, were checked inside the acrylic chamber with a HM 34 C humidity and temperature meter (Vaisala, Finland) placed over the sample. Further control of the temperature was achieved by placing the coverslip over a Linkham hot stage model TMS 92 (Linkham Scientific, Surrey, UK) set at the same temperature as the circulating air.

2.4. Image analysis

Images were captured with a JVC videocamera, model TK-128E (JVC Europe Ltd., London, United Kingdom), connected to a JVC videorecorder (model HR-57100 U, JVC, New Jersey, USA). Subsequently, the recorded images were transferred to a PC using Vidpress 1.23 software (Matrox Electronic Systems Ltd., Stoke poges, UK) and processed employing Image Tool 3.0 software (University of Texas Health Science Center, San Antonio, USA). Large differences in grey level between coffee particles and the background were found. The obtained bimodal histogram allowed easy segmentation by thresholding. That is, grey levels that fell below an intensity limit (threshold) were arbitrarily set to equal 0 (black) and all other values were set to 255 (white). Selection of the proper threshold was carried out by trial and error, guided by visual observation of the result. Finally, several geometrical parameters, such as area, roundness (i.e. $Perimeter^2 / (4 * \pi * Area)$), mean Feret diameter (i.e. average caliper or Feret length, where the Feret length is the distance between pairs of parallel tangents to the projected outline of the particle in a fixed direction), were obtained, using the object analysis option of the software.

2.5. The kinetic model

A caking index was defined as (Eq. (1))

$$\phi(t) = \frac{PA(t) - PA(0)}{PA(0)} \quad (1)$$

where $PA(0)$ and $PA(t)$ are the values (mm^2) of the mean projected area of particles at the initiation of the experiment and at any time t thereafter. At least 10 particles were analysed for each experimental run, and average values are presented. The ratio of standard deviation to the mean value was in all cases less than 10%. A first order kinetic

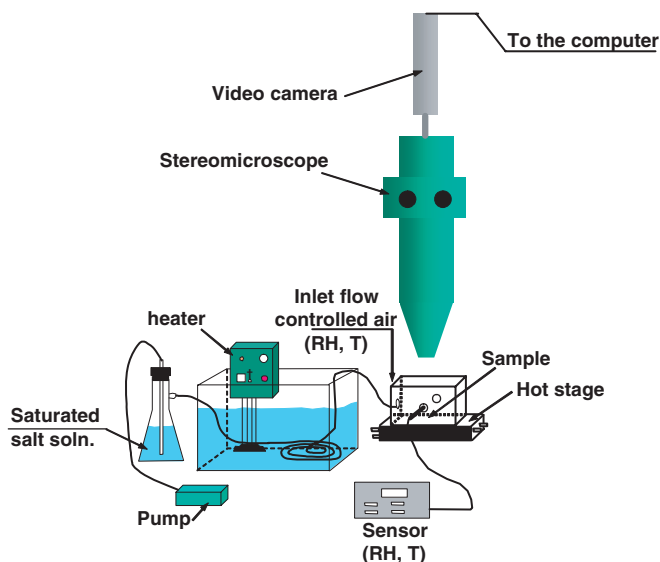


Fig. 1. Experimental setup used to determine the projected area of particles by video microscopy under controlled relative humidity and temperature conditions.

model with retardation time t_d (Aguilera et al., 1995) was adjusted to all experimental data for ϕ , using Solver from Excel (Eq. (2)). The programme minimises the sum of the quadratic error between experimental and predicted values.

$$\phi(t) = \phi_{\infty} \left[1 - \exp\left(-\frac{t + t_d}{\tau}\right) \right] \quad (2)$$

where ϕ_{∞} is the equilibrium caking index and the relaxation time τ was adjusted according to a Williams-Landel-Ferry (WLF) type expression (Eq. (3))

$$\log\left(\frac{\tau}{\tau_g}\right) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (3)$$

where T_g is the glass transition temperature, T is the temperature of the experiment and τ_g is the relaxation time at T_g .

Replacing Eq. (3) in Eq. (2), it is possible to determine parameters ϕ_{∞} , t_d and τ through estimation of parameters C_1 and C_2 , for the whole set of experimental conditions.

3. Results and discussion

In caking, two important parameters related to the material are the dependence of T_g on equilibrium relative humidity (ERH) and the adsorption moisture isotherm, which relates ERH and moisture content (Aguilera et al., 1995). T_g is an important predictor of the mobility of the system and it has been observed that, when a system is above its T_g , the kinetics of structural events vary as $10^{\Delta T}$ where $\Delta T = T - T_g$ (Roos, 1995). This dependence has been observed in caking and related phenomena, such as collapse and stickiness (Aguilera et al., 1995; Roos, 1995). Values of T_g of powdered coffee as a function of water activity, a_w (ERH/100) are shown in Fig. 2. T_g versus a_w data were correlated according to the Gordon–Taylor equation (Eq. (4))

$$T_g = \frac{T_{g1} + 4852 \cdot T_{g2} \cdot w}{1 + 4852 \cdot w} \quad (4)$$

where T_{g1} and T_{g2} are the glass transition temperatures of anhydrous coffee (79.4 °C) and water (−135 °C), respectively, and w is the moisture content on a dry basis (g water/g dry matter).

It can be observed that a large depressing effect on T_g occurred as a_w increased. For example, at 50% ERH, a T_g close to 20 °C (that is, close to “ambient temperature”, T_a) was attained, meaning that an amorphous material in equilibrium with a RH > 50% presents a $T_g < T_a$ and will thus be prone to structural changes in actual times.

The second important parameter related to caking is the moisture sorption isotherm. Experimental data points of powdered coffee at 25 °C are also shown in Fig. 2. Results compare well with those reported by Chirife, Timmermann, Iglesias, and Boquet (1992) for instant coffee (plain curve).

As shown in Fig. 3, videomicroscopy, followed by image processing, provides binarized images that can easily be quantified. Digital isolation and quantitative characterisation of single particles, to determine geometrical parame-

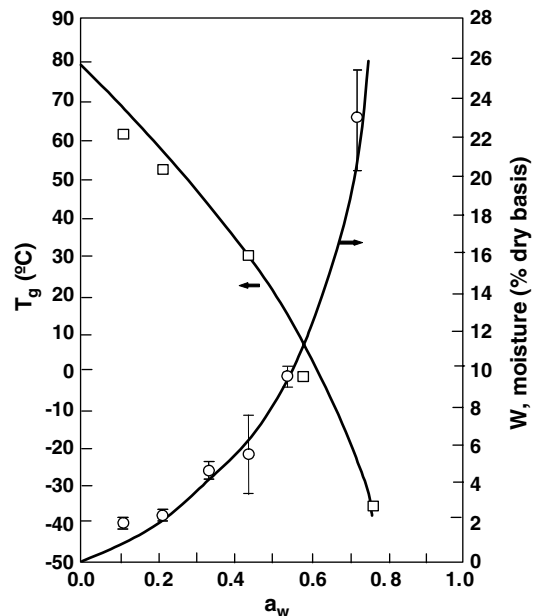
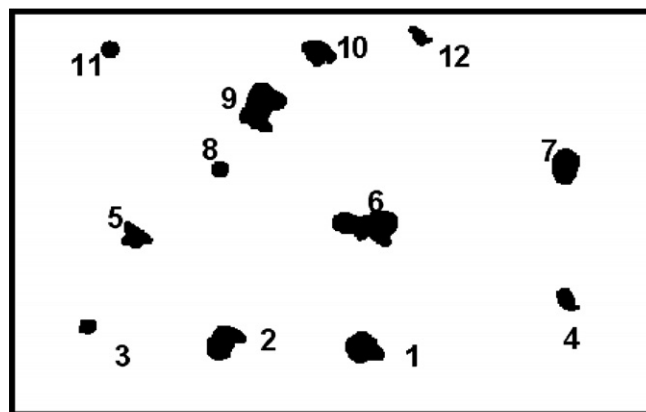


Fig. 2. Relationship of water activity a_w (ERH/100) to T_g and moisture content, W , for powdered coffee. Symbols represent experimental data. Curves are fitted by the Gordon–Taylor equation (a_w versus T_g) and GAB equation reported by Chirife et al. (1992).



Object	Area (μm^2)	Roundness (n.d.)	Feret Diam. (μm)	Compactness (n.d.)
1	92900	0.85	343.9	0.84
2	93200	0.72	344.5	0.83
3	22700	0.97	170.0	0.90
4	35800	0.75	213.5	0.77
5	55100	0.63	264.9	0.77
6	162600	0.56	455.0	0.69
7	81500	0.88	322.1	0.86
8	24700	0.96	177.3	0.96
9	149200	0.63	435.9	0.83
10	65700	0.76	289.2	0.79
11	26800	0.94	184.7	0.98
12	26300	0.58	182.9	0.75
Mean	69708	0.77	282.0	0.83
St. Dev.	48163	0.15	100.3	0.09

Fig. 3. Binary image of coffee particles, showing some of the geometrical parameters that can be quantified.

ters of interest, such as projected area (PA), roundness, Feret diameter and compactness, can be carried out, hence mean values and standard deviations are calculated. Eventually, other geometrical and shape features could be used to characterize particle deformation.

Deformation and flow of material, due to a decrease in viscosity in the rubbery state (above T_g), led to a progressive increase in projected area with time. Data for caking index, ϕ , with time for each of the selected temperatures (20, 25 and 30 °C) as a function of ERH, at 43%, 52%, 67% and 74%, which are typical ambient conditions for storage of powdered coffee, are presented in Fig. 4. All samples held at 74% RH approached a value of ϕ close to 1.2 after 4 h, while samples held at 67% RH had not yet reached the asymptotic value. To corroborate that $\phi = 1.2$ was the “true” equilibrium value, samples kept at lower RHs (43%, 52%, 67%) and 20 °C for 1 h were instantaneously brought to 74% RH inside the chamber. Results shown in Fig. 5 reveal that all samples reached $\phi = 1.2$. However, the time required to achieve this equilibrium value, after the step change, increased as the initial RH of the sample decreased.

A major effect of RH was observed at each temperature, particularly when RH was changed from 52% to 67% RH.

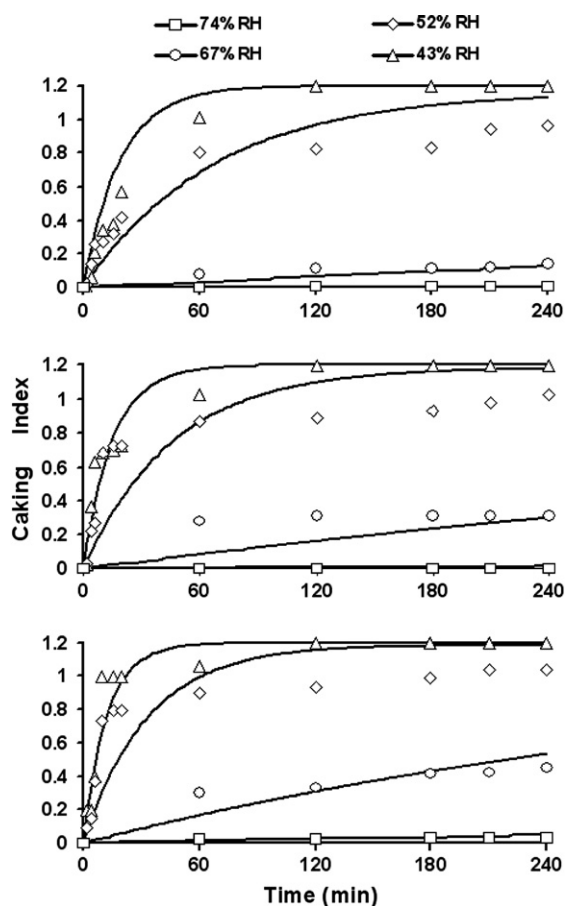


Fig. 4. Caking index as a function of time, when maintaining powder coffee at 20 (top), 25 (middle) and 30 °C (bottom). Symbols represent experimental data; curves are the model, according to Eq. (5).

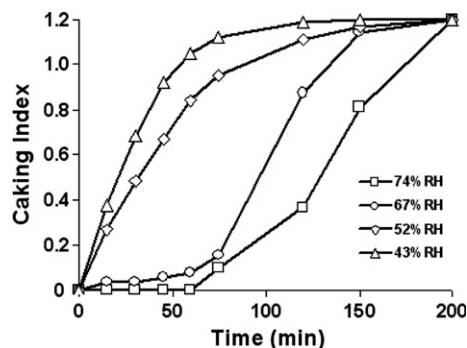


Fig. 5. Caking index as a function of time for powdered coffee held at 20 °C and various RH for 1 h, and then brought to 74% RH until the asymptotic value was reached.

For all temperatures a relative humidity of 43% did not induce significant changes in particle area after 4 h of observation. Since the T_g of the powder at 43% RH is around 29 °C, it is expected that mobility of the system is achieved only for storage temperatures above this temperature. At the other extreme, a RH of 74% produced a fast change in the projected area of particles for all the studied temperatures, as should be the case, since the corresponding T_g is about -35 °C. The kinetic behaviour (i.e., shape of curves ϕ versus time) observed for particles is quite similar to that reported for caking (determined by sieving techniques) of amorphous powders (Aguilera & del Valle, 1995).

The kinetic model obtained was (Eq. (5))

$$\phi(t) = 1.2 \left[1 - \exp\left(\frac{-t}{\tau}\right) \right] \quad (5)$$

The calculated value of ϕ_∞ , which is the asymptotic value of ϕ for long times, was 1.2, as the value experimentally observed for the sample (Fig. 5). The predicted retardation time, which can be regarded as an equilibration period of the sample to the environmental conditions, was nil. The constants for the Williams–Landel–Ferry (WLF) model for τ were $C_1 = 4.47$ and $C_2 = 33.09$ °C, which are quite different from the universal constants of the WLF equation. However, these values are not uncommon for polymers, ranging from 13.7 to 34 for C_1 and from 24 to 80 °C for C_2 (Peleg, 1992). The adjusted model predicted a relaxation time of over 10,000 min (167 h) at T_g , a considerably high value, as expected at the glassy state.

Predicted values of ϕ are shown as plain curves in Fig. 4. Given that the fitting procedure involved all the experimental data, predicted values are quite satisfactory ($R^2 = 0.84$), except for the experiments held at 67% RH, where values were overestimated.

4. Conclusions

Following the changes in projected area of particles by videomicroscopy is a simple, fast and non-intrusive method of evaluating deformation of a material under gravity at different T and RH conditions. Images can be analysed to determine geometrical parameters of interest, particu-

larly projected area (PA), from which a caking index, ϕ , can be derived. The shape of ϕ versus time curves is similar to that of caking measured by screening techniques; thus its potential value as a “caking index” should be considered. Similarly, changes in formulation (e.g., addition of fat) to reduce the tendency to caking can be rapidly evaluated. It has to be kept in mind though that caking of powders in bulk is a more complex phenomenon, involving diffusion of moisture between particles and a compacting effect due to the weight of top layers of material (Tardos, 1996). However, the former technique, notwithstanding its limitations in reproducing actual process conditions, opens a promising area of miniaturisation of experiments.

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