Caking development in lemon juice powder

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Abstract

Spray dried fruit juice powders are produced around the world. These powders contain fruit sugars and acids that make them impossible to dry without the addition of a drying aid such as maltodextrin which is added to raise the glass transition of the mixture. Thus, prediction of the glass transition temperature of mixtures is important when working out how much maltodextrin to add and at what conditions to run the spray drier. Even with maltodextrin added, the powders have a strong tendency to cake. This paper compares the glass transition temperature as measured over a range of water activities with a DSC with predictions based on a simple additive model that uses the Gordon Taylor approach for predicting the effect of water of individual component glass transition temperatures and the Fox equation. It demonstrates the development of caking between spray dried lemon juice particles with time when the temperature of the powder is raised above the glass transition temperature using two techniques.

The predicted glass transition temperatures for powder made from juice, using the initial analysis were typically 29 °C too high compared to the measured values over a range of water activities. This was reduced to 22 °C when the compositional analysis for the juice was obtained and used. An artificial powder was made using the same ratio of maltodextrin to food sugars and acids and the Tg was measured at 23.4 °C at a water activity of 0.28 which corresponds to a predicted Tg of 33.2 °C.

The powder was put into 28 mm diameter by 4 mm deep dishes and then placed in a constant RH and temperature cabinet (RH = 26% to match the water activity of the powder, with the temperature set at 7, 12 and 22 °C above the measured Tg of 18°C). The level of caking was measured by the blow tester and by penetration force measurement. Both methods showed the linear development of caking strength with time and that the rate of caking was a strong function of T-Tg.

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Only a single measurement per sample was possible with the blow tester as it tended to destroy the small sample cakes. Multiple readings were not possible due to the limited supply of powder. With the penetration method 6 to 8 readings were taken per sample. It was found that small lumps affected the penetration measurement and less scatter occurred when these were sieved out. The penetration method was also able to follow the caking to higher caking strengths, although there was more scatter in the data for the more strongly caked samples.

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1. Introduction

Worldwide there is an effort being made to spray dry fruit juices. It is now well understood that the combination of fruit sugars (fructose, maltose, sucrose and glucose) and fruit acids (citric acid and malic acid) leads to a powder which cannot be dried in a spray drier due to the low glass transition temperature (Tg) of the amorphous mixture that results from the rapid drying of the juices. To overcome this problem, the common solution is to add a drying aid, such as maltodextrin, to raise the glass transition temperature to a point where the mixture can be spray dried. This is usually tackled by trial and error methods although Bhandari et al (1997) (1) used a semi-empirical approach. These powders are also known to be extremely hydroscopic and cake easily.

A lemon juice powder was produced by first predicting the glass transition temperature of the mixture (Tg mix) by using a simple weighted additive method of the individual Tg values using the Gordon Taylor approach to estimate individual Tg values from moisture contents determined by their adsorption isotherms. Where experimental isotherms for individual components could not be found, as a first approximation, the adsorption isotherm for lactose was used. The predicted Tg mix for the surface of the powder particles was calculated from the outlet air temperature and relative humidity conditions which were estimated by a mass and energy balance around the spray drier which was calibrated for heat losses by running the drier with pure water. This initial work was followed up by drying a second batch of lemon juice obtained much later in the season. For reasons of availability of the spray drier, it was necessary to conduct the spray drying runs before it was possible to check the composition of the new batch, so it was assumed that the composition was the same as the first batch.

This paper characterises the powder obtained from the spray drier in terms of the actual Tg mix as measured on a DSC compared to the predicted Tg mix values using both the method outlined above and using the Fox equation, and its tendency to cake when the glass transition temperature is exceeded. It also quantifies the caking behaviour of the lemon juice powder with time using both the blow test method (2) and a penetration test method (3).

Nomenclature

| Symbol | Description |
|--------|-------------|
| k      | Gordon Taylor constant |
| Tgi    | glass transition temperature of the ith component |
| Tg mix | glass transition temperature of mixture |
| wi     | weight fraction of ith component |

1.1. Theory

The Gordon Taylor equation [1] (4) is primarily used to predict the effect of moisture content on the glass transition point of a substance. In order to use this equation the moisture content of the material must also be known. In most cases when a new juice is going to be produced, the moisture adsorption isotherm for the mixture, and often even for the individual components, is not known. Thus, in order to proceed some gross approximations must be
made. The approach taken here was to use known adsorption isotherms where they exist to predict the moisture content associated with a particular component. If no adsorption isotherm could be found, then the adsorption isotherm for amorphous lactose was used as a first approximation. The total moisture content was found by summing all the moisture contents associated with each component, including those components thought not to have a glass transition temperature, such as soluble fibre. In some cases equations relating the glass transition temperature directly to the water activity of the component were found and in these cases these equations were used directly in estimating the glass transition temperature of the component at a given water activity. The glass transition temperature of the mixture was then calculated by taking a weighted average of the individual glass transition temperatures as estimated at a given water activity.

\[ T_{g_{\text{mix}}} = \frac{w_1 T_{g_1} + k w_2 T_{g_2}}{w_1 + k w_2} \]

This approach was used as it assumes that only the water content associated with a particular component is important in determining the glass transition temperature of that component. An alternative equation often used in the literature to estimate the glass transition temperature of a mixture of substances with different glass transition temperatures is the Fox equation. \[ T_{g_{\text{mix}}} = \frac{T_{g_1}}{1 + \frac{T_{g_2} - T_{g_1}}{T_{g_1}}} \]

2. Materials and methods

The lemon juice was supplied as filtered and pasteurised juice from St.Andrews Limes, Hawkes Bay, New Zealand in two batches. The sugar and fruit acid composition was analysed using a Dionex Summit HPLC system; the sugars and maltodextrin with a Waters Sugarpak1 column and an RI detector, while the acids used a Varion Meta carb H column with a UV detector. Maltodextrin D10 was sourced from Hawkins Watts, Auckland, NZ. and it was added to the juice at a ratio of 1.5 to 1 maltodextrin to sugars plus acids using the analysis from the first batch of juice for both batches as the analysis could not be run until after the spray drying had to be completed.

The original spray dried lemon juice powder was ground for 6 to 8 seconds in a coffee grinder (IKA A10 lab mill) to break down the larger agglomerates that were observed under a microscope. The water activity was measured on an AquaLab 4TE water activity meter and this was confirmed as being unchanged after the grinding by using a calibrated combined temperature and humidity sensor (Rotronic HC2-S). The glass transition temperature was measured by using a Mettler-Toledo DSC 1 using a gradient from -25 to 75 °C at a rate of 10 °C/min, followed by cooling back to -25 °C and then repeating the run. After further cooling to -25, two repeat runs at a rate of 5 °C/min were also completed.

The powder was loaded into petri style dishes that were 28 mm in diameter and 4 mm deep. These were placed into controlled temperature and RH climatic boxes. Two different boxes were used due to availability. The first was a custom built climate glove box that controlled temperature to within ±0.2 °C and RH to within ±1% (6). The second box was a Binder G14 which controlled temperature within ±1°C and RH to within ±2%.

The blow tester has been described in (7, 8). It is shown in Figure 1. It consists of a 1 mm diameter stainless steel tube mounted at 45 degrees and placed 2 mm above the bed. The air flow was increased until a channel was blown in the powder bed. The rotameter reading was recorded on a cam recorder so that the air could be shut down as soon as a channel appeared in the cake. The pressure at the rotameter was also recorded from a pressure gauge. The rotameter reading was then corrected for air pressure to give the flow rate in litres per minute at atmospheric pressure.
Figure 1. Blow tester

The penetration equipment was custom built according the method described by Knight and Johnson (1988) (3). The probe used had a 2 mm diameter flat tip and it was set to penetrate 2 mm into the bed at a speed of 12.5 mm per second. The force was measured with a HBM S2 s-beam load cell and recorded via a Labview program on a computer. The maximum force experienced was determined and this is the metric that was used to determine the strength of the cake.

3. Results and discussion

The compositional analysis of the two batches of raw filtered lemon juice as determined by HPLC is shown in Table 1.

| Component          | Concentration (g/l) B1 | Concentration (g/l) B2 | Dry wt. fraction | Dry wt. fraction |
|--------------------|------------------------|------------------------|------------------|------------------|
| Citric Acid        | 17.19                  | 23.02                  | 0.256            | 0.343            |
| Malic Acid         | 4.25                   | 2                      | 0.063            | 0.030            |
| Glucose            | 6.85                   | 11.76                  | 0.102            | 0.175            |
| Fructose           | 8.04                   | 12.45                  | 0.120            | 0.185            |
| Sucrose            | 0.00                   | 1.74                   | 0.000            | 0.026            |
| Other (Taken as soluble fibre) | 41.69           | 16.23                  | 0.459            | 0.241            |
| Total solids       | 78.02                  | 67.2                   | 1.000            | 1.000            |

It has been assumed that the density was close to that of water and that the difference between the sugars and the food acids are soluble fibre material of unknown composition. Maltodextrin was added to the batch 2 juice so that the ratio of maltodextrin DE 10 to the sum of the sugars plus acids was 1.5 to 1 based on the assumption that the second batch had the same composition as the first batch and the resultant mixture was spray dried in a Niro FSD Pilot Plant spray drier. It is obvious, looking at Table 1, that the assumption that the two juices (B1 and B2) had the same composition was wrong, with the second sample having a completely different sugar and acid profile.
Fig. 2 shows the predicted T-Tg of the surface of the powder as it exits the spray drier for various inlet air and production flow rates based on the composition of the B1 juice. The predicted optimum conditions are clearly shown with a T-Tg at the optimum being 6.8 °C. The conditions used for the spray drier were a chamber inlet air temperature of 160 °C, a fluid bed inlet air temperature of 80 °C and an outlet air temperature of 92 °C, resulting in an average feed flow rate of 12.71 l.h⁻¹.

When the second batch of juice was processed through the spray drier, the powder did not come out of the spray drier, with most of the powder forming agglomerates on the walls of the spray drier and the powder had a burnt look.
A second run was conducted with a lower outlet air temperature. These were brushed off and collected at the end of the run. They had a measured water activity of 0.256.

Fig. 3 shows the glass transition temperature results from the two DSC runs done at 10 °C min⁻¹ and the two at 5 °C min⁻¹ against the water activity of the powder. The slower scanning rate gave Tg values typically 3 °C less than the faster scanning rate. These were typically 28 °C below what had been predicted based on the composition of the first batch of juice and the predicted minus 28 degree line is shown in Fig. 3 to show that the effect of water has been correctly predicted, but that the actual values at all water activities are much lower. This explains why the powder did not come out of the spray drier as with a Tgmax being 28 °C below the predicted value, the surfaces of the powder would have been over 35 °C above the Tg and hence the powder would be very sticky resulting in the powder particles sticking together and to the walls of the drier.

An alternative method (Fox equation) of predicting the glass transition of mixtures was investigated. This equation predicted slightly lower Tg values for the mixture, but because the predicted Tg of the mixture was a function of the total moisture in the sample, the predicted Tg value becomes a function of the soluble fibre content and the associated water content. As an example, at a water activity of 0.26 the Fox equation predicts a Tgmax of 36.1 °C when the fibre and water associated with the fibre are included but 60.4 °C when the fibre content with its associated water is removed. The weighted average method stays constant with a prediction of 42.2 °C.

Four explanations are possible as to why the predicted Tg values are so much higher than those measured; firstly, the soluble fibre component may have significant amounts of material that have Tg values, where it has been assumed that this material is inert from a Tg perspective. Secondly, the food acids maybe having an additional synergistic effect meaning that using a simple weighted additive approach is not appropriate. The third reason is that the composition of the juice could be significantly different to that assumed in the predictions. The fourth possibility is that the moisture contents assumed to be associated with each component is grossly out. The first can be tested by producing an artificial lemon juice powder without the fibre component and this was done on a smaller GEA Niro Mobile minor Model H spray drier. The resulting powder had a water activity of 0.28 and a measured Tg of 23.4 °C compared to the predicted Tg of 33.2 °C for this composition. A sample of the powder was equilibrated to a different water activity and the glass transition measured. These results are presented in Fig.3 as well.

The composition of the second batch of juice, B2 was analysed by HPLC and it was found to be significantly different to the previous batch as seen in Table 2. Using this composition new predictions were made which are 7°C lower than those predicted for the B1 composition. (See Fig.3) The compositional change accounts for about one third of the original difference between the B2 powder measured Tg and the measured Tg value. Since no soluble fibre was present in the artificial lemon juice powder and there is still a significant difference between the predicted and measured Tg values, about 9.5 °C, we must conclude that the effect of the fruit acids is significantly greater than predicted and or that the prediction of the moisture content associated with each of the sugar components is significantly different to the assumed adsorption values. Indications of the total water content are that it is significantly less than that predicted for the mixture which is the wrong way for the prediction of Tg. This points to a difference in plasticising effect of the fruit acids as being greater than that predicted by their weight fraction alone. Much more work will be needed in this area to confirm this. The results also show the importance of measuring the actual composition of the juice before deciding how much maltodextrin to add and before doing the spray drying.

The fact that the measured Tg values for the artificial juice made up to the same composition as the B2 powder are above the actual B2 powder at the same water activity indicates that there are components in the fibre or soluble solids fraction that are having an effect on the glass transition temperature of the final powder. More work is required to investigate the cause of this effect.

The results of the blow test caking investigation, (Fig.4) show that the powder is very susceptible to caking with the rate of caking being a linear function with time and is also a function of the degree that the glass transition temperature is exceeded. At a T-Tg of 7 °C the rate is relatively slow with the maximum blow test range not being reached for 7 hours, while only 1.25 hours was required at a T-Tg of 12 °C showing a dramatic increase in the rate of caking formation with only a 5 °C increase in temperature. This is similar to the increases seen with time and T-Tg with the caking of amorphous lactose in (2).
Fig. 4. Caking strength development with time as measured by the blow tester at two different T-Tg values.

Fig. 5 shows the same trends in the development of caking with time and T-Tg but where the caking strength has been measured by a penetrometer as described in the methods section above. The penetrometer method has the advantage of being able to follow the caking process to a higher level and hence a couple of data points at a T-Tg value of 22 °C were collected and are shown.

Fig. 5. Caking strength development with time as measured by the penetrometer at three different T-Tg values.
4. Conclusions

The importance of having accurate compositional data for the juice has been highlighted by the practical applications of this work where the wrong compositional data lead to an error of 10 °C in the predicted Tg of the powder. It was also demonstrated that even when correct compositional data is available the current prediction methods for predicting Tg are not adequate and hence the prediction of the best operating conditions for the spray dryer cannot be accurately forecast. Even with the errors in Tg prediction, the methodology for finding the best conditions for running a spray dryer has been demonstrated to work as the prediction method does correctly follow the effect of water activity on Tg.

Both the blow test and the penetrometer tests showed the development of caking strength with time and that the rate of caking strength with time is also a function of the amount the powder is above its glass transition temperature.

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