Characterisation of Powders

Keywords: DMA, powder holder, thermal transitions, coffee whitener, α-lactose monohydrate TA403

INTRODUCTION

A sample of α-Lactose Monohydrate and a commercial coffee whitener manufactured by Tate and Lyle (Original Coffeemate) were tested with the powder holder on the DMA to determine the mechanical properties of powder as a function of temperature. Original Coffeemate is a complex material and consists of milk protein, hydrogenated fats and stabilisers in its formulation. The aim of this study was to determine transitions that could be detected by DMA and to compare the results for this material with results from other techniques, namely Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

EXPERIMENTAL

The experiments were performed on the Discovery DMA 850 Dynamic Mechanical Analyzer. The powder sample was loaded into the tray of the holder to a depth of approximately 1 mm. Excess sample was removed using a spatula. The lid of the holder was placed onto the top of the powder and the holder then loaded into the dual cantilever frame of the DMA.

For the Original Coffeemate, which contains hydrogenated fats, the sample holder was only lightly clamped (to finger tightness only). The sample was then cooled to the start temperature (-100 °C) and held isothermally at this temperature for five minutes. The drive motor was "Off" during the cool-down period to allow the fats present in the material to fully solidify. After the five minute on hold at the start temperature, the furnace was opened and the clamps tightened to a pressure of 4 PSI. This ensures that the sample holder is secured at the start temperature. By freezing the fats before tightening the clamps ensures that maximum sensitivity for the detection of the fat melting processes is achieved on heating the sample upwards in temperature. After the furnace was closed, the temperature re-equilibrated at the start temperature, the motor was switched on to deform the sample at the pre-requested strain as the heating program was initiated.

To aid in the interpretation of the DMA data, Differential Scanning Calorimeter and Thermogravimetric Analyser were also conducted.

SAMPLE RESULTS

α-Lactose Monohydrate

The α-Lactose Monohydrate sample was loaded into the tray of the holder which was then inserted into the dual cantilever fixture of the DMA.

At a first glance the results in figure 1 look somewhat complex in nature. As the sample is heated there is initially a decline in sample stiffness between 123 and 140 °C. Above 140 °C the stiffness increases until a temperature of 144 °C is reached. Heating above this temperature shows a second decline in the sample stiffness up to a temperature of 151 °C. Further heating showed a gradual decline in sample stiffness up to 213 °C where a dramatic change in stiffness took place. This rapid decline at high temperature was most likely due to the melting or decomposition of the lactose sample. The loss modulus and tan δ signals both show a sharp peak in the transition region which are identical in temperature at 145 °C. Additional tests were performed using DSC and TGA to help in the interpretation of the DMA data generated for this material. DSC measurements on α-Lactose Monohydrate were done in a crimped aluminium pan to simulate the sample preparation in the DMA holder. The heating rate was 3 °C/ min.

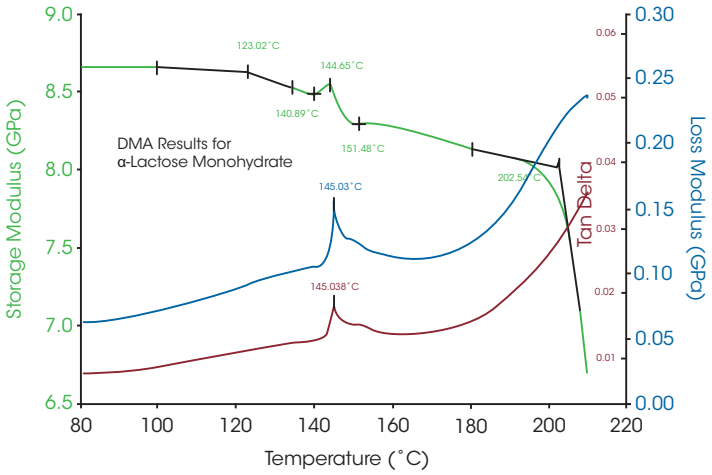

Figure 1: α-Lactose Monohydrate tested with the powder holder on the DMA. Heating rate 3 °C/min, Test frequency 1 Hz.

The DSC results in figure 2 were interesting in that instead of a single endothermic reaction for the loss of the hydrate a double peak was observed. One possible explanation for this could be the presence of two hydrates in different crystalline phases. The easiest way to determine whether this was the case or not, was to perform a thermogravimetric test and determine whether two distinct weight loss processes took place over this temperature region or not.

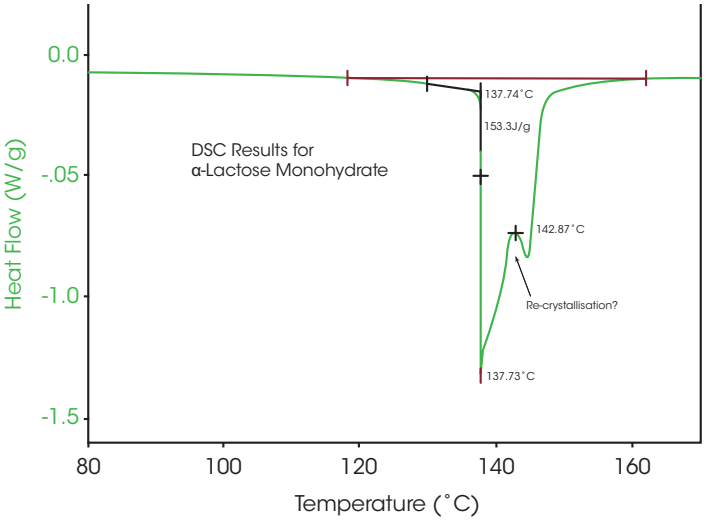

Figure 2: DSC trace of α-Lactose Monohydrate

The TGA results in figure 3 clearly show that the hydrate comes off in a single step which leads to the following explanation of the DMA trace.

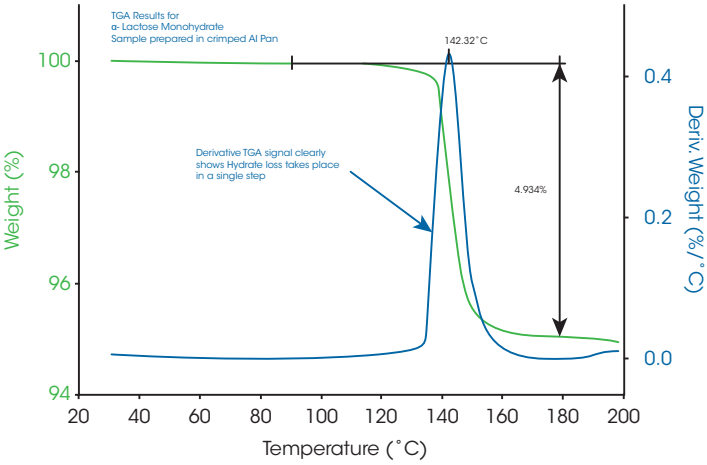

Figure 3: TGA trace of α-Lactose Monohydrate.

The sample stiffness as measured by the DMA initially declines as the hydrate is evolved on heating. This would be expected because as the hydrate comes off, there will be a volume reduction of the sample which will lead to a reduction in pressure being applied to the sample via the top plate of the holder and hence a decline in stiffness will occur.

The loss of the hydrate leads to a re-ordering process. This process takes place simultaneously with the hydrate loss. This is observed in the DSC trace as an exothermic peak midway between the endothermic response observed for the hydrate loss.

The re-ordering process is detected readily by the DMA data and is found to cause an increase in stiffness. This could indicate that re-ordering will lead to an increase of the overall sample volume, which would respond in the DMA as an increase in measured stiffness.

The TGA data clearly show that the hydrate loss takes place as a single step. There is no "double" weight loss observed in the transition region and this therefore gives further evidence that are-crystallisation is taking place within the hydrate loss.

When the DMA, DSC and TGA data are overlaid the interpretation becomes somewhat simpler. The curve overlay in figure 4 gives a clearer insight as to the processes that are taking place within this sample on heating.

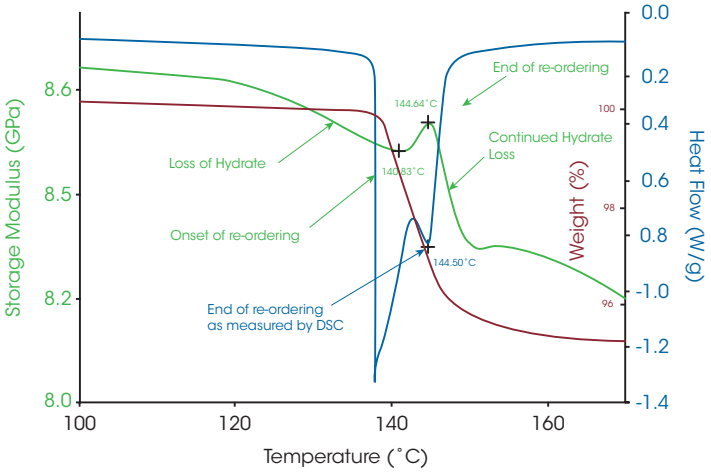

Figure 4: Overlay of DMA, TGA and DSC traces for α-Lactose Monohydrate.

The overlay is conclusive in that it shows the decline in stiffness for the hydrate loss taking place over the same temperature range as that observed by TGA and DSC. There is also excellent agreement between the DSC and DMA data in terms of the measured end point of the re-ordering process which was identified as 144 °C by both techniques. The other interesting point to note is that after the completion of the re-ordering process the rate of decline in the sample stiffness increases, possibly indicating a more rapid loss of hydrate as a consequence of this re-ordering process.

Original Coffeemate

Figure 5 shows the DMA results obtained on the Original Coffeemate powder sample in a temperature ramp.

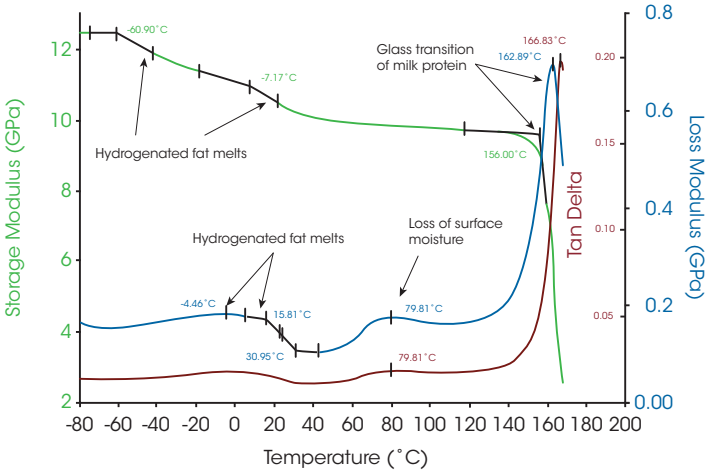

Figure 5: DMA trace of the Original Coffeemate performed at a heating rate of 3 °C/min and a test frequency of 1 Hz.

The storage modulus signal (which is qualitative in nature since it is a combined response of the holder and the loaded powder) shows two distinct softening phases between -60 °C and 40 °C which can be attributed to the melting of the hydrogenated fats on heating. Between 60 °C and 110 °C, peaks are observed in the loss modulus and tan δ signals and the temperature of these peaks are identical which would indicate that the response in this region is most likely due to dehydration or loss of surface water from the powder particles. At approximately 156 °C there is a rapid decline in the measured storage modulus of the powder which could be attributed to the glass transition of the milk protein being passed through. The storage modulus is a measure of stiffness and when a material is heated through its glass transition the stiffness declines significantly as the material transforms from a glassy rigid state to a rubbery soft state. The peaks that are observed in the loss modulus and tan δ signals are significant in magnitude which indicates softening of the main or continuous phase of this product. The fact that the peaks are offset also indicates that this transition is indeed second order in nature, such as a glass transition.

Figure 6 is an expanded view of the region where suspected loss of free surface water from the powder particles is taking place.

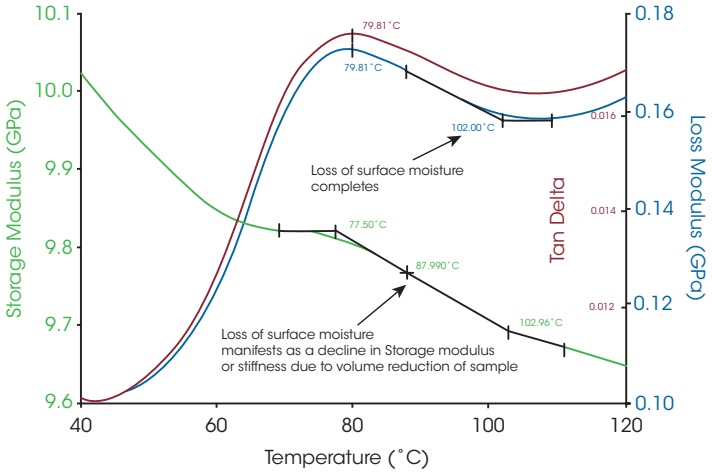

Figure 6: Expanded view of the trace of the Original Coffeemate powder in the region between 40 and 120 °C, where free water loss is expected.

This expanded view shows a step decline in the storage modulus between 77 °C and 103 °C which can be attributed to the loss of surface moisture from the powder. As the water is evolved the sample volume will reduce and this will cause a drop in the pressure exerted on the powder inside the holder leading to the trend observed in figure 6. The peak alignment in the loss modulus and tan δ signals is also indicative of a dehydration process or volatile loss from the powder. In order to prove that this is in fact a response due to volatile loss, a fresh sample of Original Coffeemate was investigated by thermogravimetric analysis. The sample was analysed in an open aluminium DSC crucible. The TGA experiment was performed at the same heating rate as that utilised for the DMA experiment and a flowing Nitrogen purge gas was used to sweep the volatiles evolved to atmosphere. The DMA test was also performed in a flowing gas atmosphere since cold nitrogen gas is driven onto the dual cantilever configuration for cooling purposes. In addition the air supply that is used to drive the air bearing system of the DMA enters the base of the furnace chamber and flows through the measuring region.

Figure 7 shows an overlay of the TGA and DMA experiments performed on the Original Coffeemate powder investigated.

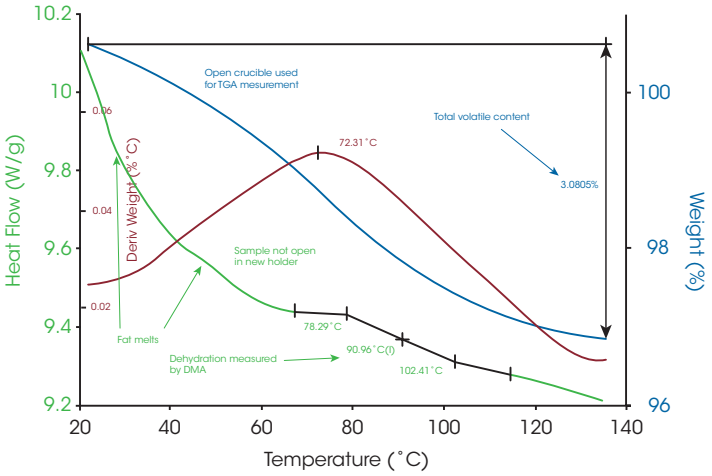

Figure 7: Overlay of the TGA and DMA experiments performed on the Original Coffeemate powder

This result clearly shows that by TGA a volatile content of approximately 3.9% of the starting mass was calculated. The DMA result indicates that the stiffness decline takes place in the region where the rate of volatile loss was most significant (when looking to the TGA data). There is an offset between the volatile loss detection between the two techniques because for the TGA experiment, the sample was run in an open crucible whereas with the DMA holder a lid is used to contain the sample and this will typically cause volatile losses to be driven to higher temperatures because of the restriction in the ability of the volatiles to evolve freely. However, the TGA conclusively shows that there is a volatile component to the material and the effects of this can be detected by DMA as a drop in the measured sample stiffness because of the volume reduction that takes place during this reaction.

The Original Coffeemate sample was also investigated using the DSC to see what level of correlation could be observed between the DMA and DSC data. The sample was run in an open crucible in the DSC at the same heating rate used for the DMA measurement and with a flowing nitrogen atmosphere through the DSC cell.

Figure 8 shows the DSC data and an overlay with the DMA data for the Original Coffeemate.

The fat melts are clearly detected by both the holder and the DSC. The main fat melt corresponds well with the significant step decline observed in the storage modulus and the signal drop observed in the loss modulus and tan δ signals. The peaks observed in the loss modulus and tan δ signals at around 80 °C correspond to the loss of surface moisture and compares well with the maximum seen in the DSC endotherm for this volatile loss process.

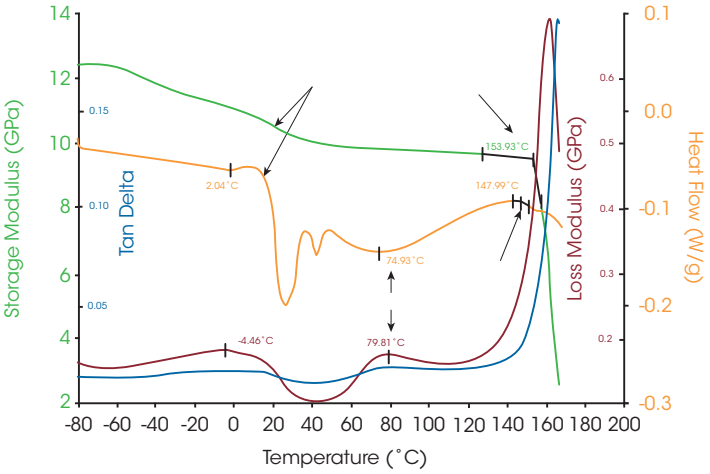

Figure 8: Overlay of the DSC data with the DMA data for the Original Coffeemate

The glass transition for the milk protein is observed in the DSC data with an onset temperature of 148 °C. However this Tg is distorted somewhat because it is observed at the tail end of the endothermic loss of surface moisture from the sample. The Tg is identified at a higher temperature with the holder (obviously due to the effects of frequency) and involves a large decline in stiffness and associated peaks in loss modulus and tan δ.

SUMMARY AND CONCLUSIONS

The dehydration mechanism of α-lactose monohydrate was thoroughly investigated here and interpretations made on the basis of comparing the data from DSC, DMA and TGA techniques. Heating the sample leads to the departure of water molecules from the lactose which subsequently causes a re-organization of the crystal phase causing a change in the packing of the lactose molecules (The hygroscopic metastable form, L αH is formed under heating). The DMA results clearly demonstrate the excellent sensitivity of the holder to determine processes such as dehydration and re-ordering, processes which cannot simultaneously be identified by DSC or TGA techniques alone. Furthermore the loss modulus and tan δ signals show sharp peaks in the transition region which most likely represent the onset of the re-ordering process. Reactions such as dehydration or solid transformations are typically 1st order in nature and therefore do not exhibit a time (or frequency) dependence. The fact that the loss modulus and tan δ peaks are identical in temperature indicate that a first order transition is occurring.

For the Original Coffeemate, the DMA data agree well with the data generated for this sample using Differential Scanning Calorimetry and Thermogravimetric Analysis. Many different transitions are identified with the holder which include fat melts, dehydration and a main glass transition. The main Tg was easily identified with the holder and confirmed what was possibly identified as a Tg by DSC.

To summarise, the main conclusions from the study are the following:

- This study has shown the importance of using a range of techniques to gain a real understanding of complex processes that are taking place in this material on heating.
- It has been demonstrated that the ability to overlay data from different thermal instruments gives a "synergy" effect with respect to theinterpretation of measured transitions.
- The holder can be used to evaluate many other types of other materials, such as Starch powders, milk powders, powdered sugars/sweetners and food additives for example.

For more information or to place an order, go to http://www.tainstruments.com/ to locate your local sales office information.