AAN030

Characterisation of Frozen Liquids by DMA using a Liquid Sample Holder

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INTRODUCTION

There has been considerable interest in recent years on the characterisation of the viscoelastic properties of liquids/solutions/ pastes in the frozen state. Dynamic Mechanical Analysis testing has, until recently been a technique that has been utilised for the investigation of materials in the solid state. A novel sample container has been developed that enables liquids to be frozen in a Dynamic Mechanical Analyser and then heated to characterise the viscoelastic properties of the frozen structure. Although qualitative in nature, the technique is able to identify the glass transition and other smaller relaxation processes (such as β and γ relaxations) of frozen liquids/solutions/ pastes. Furthermore it is anticipated that this holder could be used for the monitoring of cross-linking of thermosets and adhesives from the liquid to the vitrified glassy state.

EXPERIMENTAL

The sample holder to contain the liquid is the same, used for powder testing*). The liquid is loaded into the holder and the holder inserted into the standard 35 mm Dual cantilever frame of the DMA. The holder is then clamped to a pressure of 4 PSI. The sample, when cooled down below the freezing poin, forms a solid in the container. Typically samples are loaded at ambient temperature, cooled down at a controlled cooling rate to a start temperature and then heated at the desired heating rate back to ambient temperature. Cross-linking reactions can be measured at elevated temperatures and strain induced re-crystallisation of thermoplastic materials could be investigated from the liquid to the solid state by performing cooling experiments from a temperature above the melt to the point of re-crystallisation.

The following experimental conditions were employed for the analysis of the liquid samples.

Measurement frequencies : 1 Hz

Clamp pressure : 4 PSI

Heating rate : 2°C/min & 3°C/min

Mode : 35 mm Dual cantilever.

A number of samples have been investigated to evaluate the suitability of the liquid holder for the characterisation of the frozen state of a liquid. These sample are:

- Water to identify the melting of ice.
- A 40wt% Sucrose solution
- A commercial shower gel
- Golden Syrup

*) Product note APN023

RESULTS

Analysis of Water by DSC and DMA

Water was transferred into the liquid holder with a pipette. The holder then inserted into the 35 mm Dual cantilever frame and clamped to a pressure of 4 PSI. Next the sample was cooled down to -80°C forming ice in the holder while the water was freezing . During the cooling process the sample was not subjected to any deformation, it was simply held still in the dual cantilever rig until the start temperature of -80°C was reached. The sample was tested at a heating rate of 2°C/min.

DSC measurements had been performed at the same heating rate so that results could be compared between the DSC and DMA. The results are represented in figure 1. The DMA detects the ice melt as a large step decline in the storage modulus. As the ice melts, the stiffness of the holder decreases significantly due to the phase change that the ice passes through. DSC gives a large endothermic peak for the ice melt over a very similar temperature range.

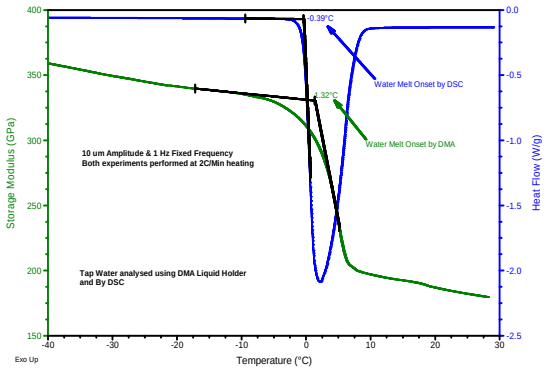

Figure 1: Graph showing DMA and DSC analysis of ice

The melting onset was determined at 1.32°C when investigated by the DMA and was identified at -0.39°C by DSC. The agreement is excellent between the techniques which, to a large extent are expected because the stainless steel holder will ensure excellent heat transfer to the sample and largely eliminate thermal gradients within the sample and help improve the resolution of transitions as a consequence. With DSC this is not an issue because of the small sample mass used in the analysis and the fact that the pan which contains the sample is heated conductively and not radiantly as is the case with DMA experiments. It can be seen that the width of the ice melt as measured by the DMA is similar to that observed by the DSC, an indication that resolution is on a similar level to the data generated by DSC.

DSC & DMA analysis of 40wt% Sucrose solution.

A sucrose solution was made up using warm water and commercial sucrose. Once the sucrose had completely dissolved in the water, the solution was transferred with a pipette into the holder and loaded into the dual cantilever rig of the DMA. The holder was tightened in the dual cantilever clamps to a pressure of 4 PSI. It was then cooled down to the start temperature and heated at a rate of 3 °C per minute up to 30 °C in order to characterise the viscoelastic changes taking place in the frozen state of this solution. Figure 2 shows the results from the DMA measurement and figure 3 an overlay of the DSC and DMA results obtained on the sucrose solutions.

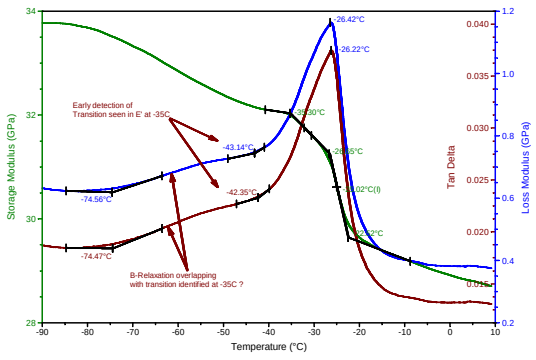

Figure 2: Dynamic Mechanical Analysis of 40% w/w Sucrose solution

The DMA data show a possible β relaxation having an onset temperature around -75°C. This is also observed as a drop in the storage modulus (which is qualitative and a

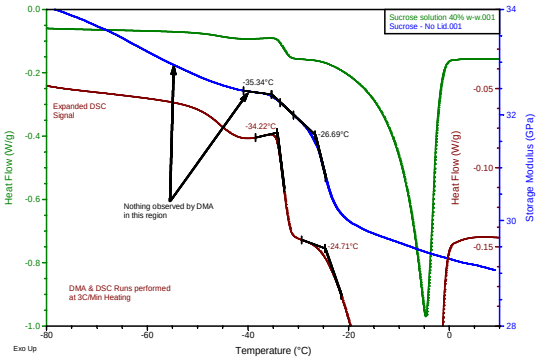

Figure 3: Overlay of DSC and DMA data for 40wt% sucrose solution

measure of the combined stiffness of the Holder and the frozen structure contained in the holder) between -80°C and -40°C. Between -35°C and -26°C there is then a rapid decline in the measured storage modulus which possibly relates to ice dissolution. Between -26°C and -22°C a rapid decline in storage modulus is identified which is most likely to be due to the melting of the frozen structure remaining in the holder. Peaks are observed in the loss modulus and tan δ signals at approximately -26°C which will be due to the melting of the ice structure.

The DSC data generated for this sample are superposed with the qualitative storage modulus measured by DMA. The endothermic step change observed in the DSC heat flow signal between -55°C and -40°C shows no significant change in the measured stiffness over this same temperature range when investigated by DMA. Between -34°C and -25°C there is a sharp endothermic response in the DSC data for this sample which is possibly due to ice dissolution. A decline in the storage modulus was also observed over this temperature range indicating that in terms of stiffness, the frozen sucrose solution softens during this possible ice dissolution process. At -26 C the DMA detects a large and rapid decline in the measured storage modulus due to the onset of melting of the frozen sucrose solution. This compared well with the onset of melting detected by the DSC.

DMA Analysis of shower gel

A commercially available shower gel was investigated using the liquid holder and by DSC for comparative reasons. The shower gel was loaded into the holder and the holder then clamped in the dual cantilever configuration. The sample was cooled down to a start temperature of -80°C and held there for a few minutes before deformation of the sample was initiated. It was then heated at a rate of 3°C per minute.

Figure 4 shows that on heating by DMA a glass transition is observed as a step decline in the storage modulus and peaks are clearly observed in the loss modulus and tan δ signals for the glass transition. The DMA detects the glass transition between -47°C and -30°C. Peaks in loss modulus and tan δ were observed at -39.9 and -38.7°C respectively. When looking at the DSC for this sample, it is obvious that a transition is taking place in the frozen state which begins at a temperature of -50°C but it is not clear from these data that it is in fact a glass transition. The DMA data clearly shows the presence of a glass transition in the frozen state which demonstrates the increased sensitivity that DMA as a technique has over DSC.

Analysis of Golden Syrup by DMA and DSC

Golden Syrup is a viscous liquid at ambient temperature. It is used for cooking purposes and on freezing, converts to an amorphous glass. This material was analysed using the DMA liquid holder and by Differential Scanning Calorimetry to characterise the glass transition. For the DMA measurements some golden syrup was loaded into the liquid holder and then the holder was loaded into the dual cantilever fixture of the DMA. The holder was tightened in the clamps to a pressure of 4 PSI. The sample was cooled down to a start temperature of -80°C with no deformation applied to the sample on cooling i.e. the holder was held in a static position down to the start tem-

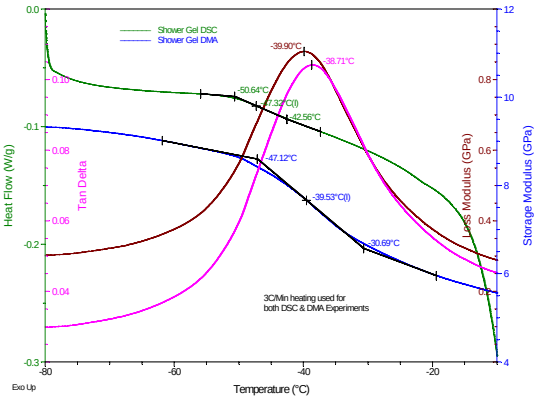

Figure 4: Storage Modulus and heat flow determined for a shower gel from -80 °C to room temperature

perature to allow the material to convert to a glassy form without any mechanical disturbance of the sample. Once at the start temperature the motor was switched on and the sample heated at 3°C per minute up to ambient temperature. An experiment was also performed on the Golden Syrup by DSC where a small sample mass was loaded into a hermetic sample pan, cooled down to the start temperature of -80°C and then heated at a rate of 3°C/min up to ambient temperature. The results of the DMA and DSC experiments on this sample are shown in figure 5.

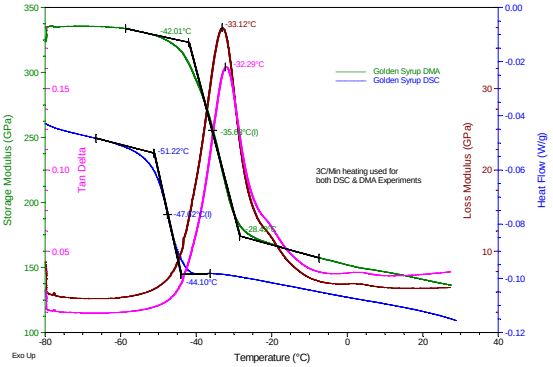

Figure 5: Graph showing overlay of DSC and DMA data on Golden Syrup

The results above clearly show that the DMA is able to determine the glass transition of the Golden Syrup as a large step decline in the storage modulus (which is a qualitative signal and comprises the combined stiffness of the stainless steel holder and the sample in question) as would be expected. Peaks are observed in the loss modulus and tan δ signals at -33 and -32°C respectively as would be expected at the Tg. A shoulder is observed in the loss modulus and tan δ peaks at around -25°C indicating the presence of a possible further transition. Nothing was observed in this region when the sample was investigated by DSC. The DSC identifies the Tg as a step decline in the measured heat flow response and this has been analysed to give an onset, mid-point and end-set temperature for the Tg at -51°C, -47°C and -44°C respectively. There is a shift in the position of the Tg when comparing the DSC and DMA data which will be in part a consequence of the difference in the measurement frequencies used for the Tg determination (1Hz with DMA and 0Hz for DSC measurement). The difference may also be due to the thermal conductivity of the Golden Syrup which may lead to a shift upwards when evaluated by DMA because of the significantly larger sample mass used. If the Golden Syrup has poor thermal conductivity (which is highly possible as it is completely amorphous in nature) then this will have the effect of artificially "pushing" the Tg to a higher temperature. Perhaps a slower heating rate for the DMA experiment would reduce the difference observed between the DSC and DMA Tg position with respect to temperature.

Discussion and Conclusions

The liquid holder has proved a useful tool for the characterisation of the frozen state of liquids. It has shown many benefits which include:

- The ability to measure the melting of water gives an excellent temperature calibration procedure for the liquid holder. It also enables melting transitions to be readily detected by DMA.

- The investigation on the sucrose solution shows that there is no glassy state formed when cooled under the conditions employed for this sample. The presence/absence of a glassy state for such solutions has been the subject of considerable academic debate over recent years but has proved largely inconclusive because of no facility to measure the mechanical properties of such frozen solutions. This is an important area for the food industry and is likely to lead to considerable interest in this approach to clarify the structure of frozen structures. A rheometer is unable to characterise the frozen state of such solutions because of the stiffness of the frozen sample of water based systems (compliance becomes significant in the frozen state).

- The analysis of the shower gel has important implications. Complex healthcare formulations are commonly investigated by rheological techniques for quality control etc but results are often inconclusive. By having a technique that is able to characterise formulation sensitive transitions (such as the Tg) a more reliable and methodical approach to research and development and quality control can be utilised with the liquid holder.

Further areas for which this holder would become useful include, but are not limited to the following :

- Investigating curing of Aerospace resins and adhesives
- Characterising frozen foodstuffs – Ice creams, Sucrose solutions, sauces etc…
- Determining the glass transition temperature of solutions which are to be freeze dried. Many food and pharmaceutical products are freeze dried and to determine the Tg temperature of such solutions is critical so that when freeze drying, the Tg temperature is not exceeded otherwise “Product collapse” would occur.