APPLICATION NOTE

Differential Scanning Calorimetry

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Glass Transition Measurement of Undried Fish Gelatin with Fast Scan DSC Technique

Background

Glass transition (Tg) measurement of undried bio-polymers is challenging using the conventional DSC technique. The glass transition (Tg) is frequently masked by the moisture vaporization event. This is particularly troublesome in biomaterial where transitions near 100 ˚C and 0 ˚C are common. HyperDSC® separates two overlapping events with different kinetic properties, therefore Fast Scan DSC techniques (HyperDSC) allow measurements beyond the range of conventional DSC. Double Furnace DSC has superior performance, such as extremely short equilibration time, high sensitivity and high resolution. These support the HyperDSC technique. HyperDSC expands the DSC capabilities beyond the limitations of the conventional slow scan DSC technique by allowing us to separate the overlapping events with different kinetics and to amplify weak thermal events. In this paper, we demonstrate the HyperDSC capability to measure the Tg event of the undried fish gelatin samples with a very short test cycle time.

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Analysis/Methodology

Instrument configurations: PerkinElmer® Double Furnace DSC 8000 with the Intercooler 2P cooling device

Samples

1) Pure fish gelatin

2) Blended fish gelatin (labeled as 25 Sorb-3, 25 Sorb-4 and 25 Sorb-5), each contains unknown amount of sorbitol, starch and some plasticizers as additives.

Sample Preparation Pure and blended gelatin were crushed or cut with a knife into similar, small sized pieces. All samples were crimped in a standard Al solid pan – samples not hermetically sealed (at approximate weight of 8 mg).

Test Method Parameters Scan from -50 ˚C to 200 ˚C, at 10 ˚C/min (slow scan).

Scan from -60 ˚C to 200 ˚C, at 100 ˚C/min (HyperDSC).

Results and Discussion

Running the samples in the conventional DSC slow scan at 10 ˚C/min gave a broad endothermic peak that is observed from approximately 40 ˚C up to 190 ˚C in all fish gelatin samples (Figure 1). This peak is predominately due to the volatile vaporization which masks the relatively weak Tg of the fish gelatin compounds. Due to the overlapping of these two events, it is difficult to determine the Tg with conventional DSC techniques. Other researchers have used conventional DSC with hermetically sealed volatile pans for a similar study.[1] In their work, the Tg was detected by suppressing the vaporization event. This has the disadvantage of exposing the fish gelatin to elevated pressure and may cause changes in the material. Other techniques such as Dynamic Mechanical Analysis can detect the Tg, but required a special sample preparation to allow successful handling of a delicate sample and often takes a long time to run the test.

Figure 2 shows the TGA weight change profile for undried fish gelatin. Note the temperature of the volatile loss step which coincides with the volatile vaporization endothermic peak in Figure 1. This suggests the endothermic event is vaporization.

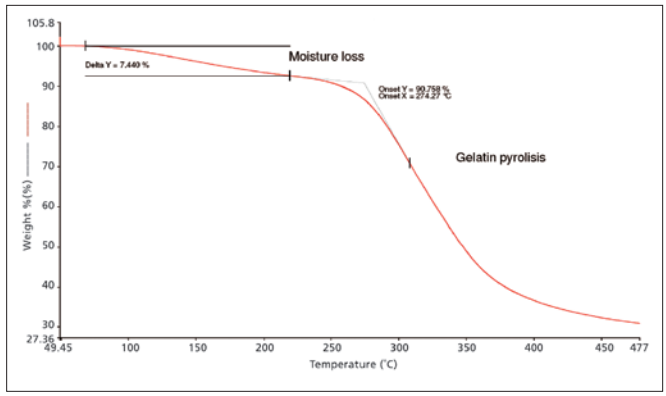

Figure 2. TGA thermogram of pure fish gelatin sample shows a weight loss step which is due to the volatile vaporization.

HyperDSC is capable of separating the overlapping Tg and volatile vaporization events as the latter is a time-dependent kinetic event by pushing the latter to higher temperature. The fish gelatin samples were scanned at 100 ˚C/min and the gelatin Tg is now clearly observed in all samples as shown in Figure 3. Similar work with HyperDSC has been used to separate the Tg and moisture vaporization in other systems. It has been reported in the study of wheat gluten, heparin, proteins, and polyamides[2,3] to name a few. This ability to measure concealed events is important for the study of biopolymers since the Tg is highly dependent on the moisture content[4,5] and water volatilization often masks the transitions.

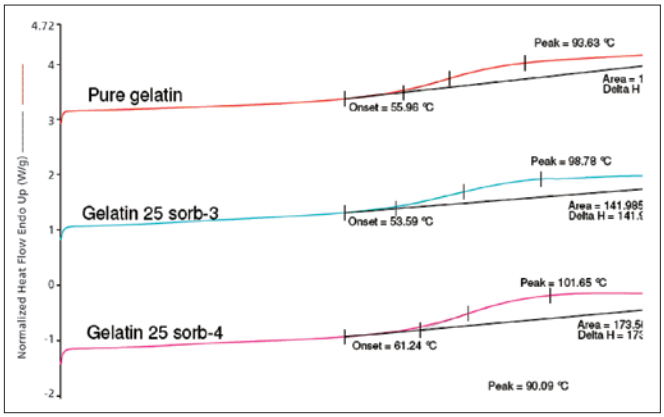

Figure 1. DSC thermograms of pure and blended fish gelatin samples at conventional 10 ˚C/min. Volatile vaporization produces a broad endothermic peak which masks the Tg event. Beside the endothermic peak, there is no evidence of other thermal events.

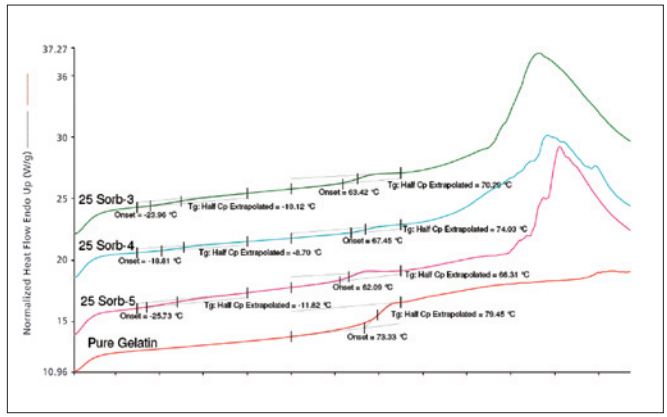

Figure 3. DSC theromgrams of the same fish gelatin sample using HyperDSC at 100 ˚C/min. HyperDSC exposes the Tg event after the moisture vaporization is pushed to a higher temperature.

In addition to the gelatin Tg, HyperDSC reveals a weak sub-ambient Tg, between -30 ˚C and -10 ˚C in all blended samples at 100 ˚C/min. This sub-ambient Tg, shown in Figure 3, is not visible with the conventional 10 ˚C/min slow scan. HyperDSC amplifies the weak signal. Similar works relating to the amplification of weak thermal events by the HyperDSC technique have been reported in graphite composite, sucrose and lactose studies.[6,7,8] In this case, the weak sub-ambient Tg is believed to be related to either the sorbitol or plasticizer used in these blended samples.

Conclusions

This case study shows that Fast Scan DSC (HyperDSC) is capable of detecting the water masked Tg in the undried fish gelatin biopolymer. In addition, it reveals a previously undetected weak Tg. The measurements using HyperDSC were carried out in a few minutes, making HyperDSC an ideal approach for faster analysis and screening.

References

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