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Comparison of Melting Behaviors of Edible Oils Using Conventional and Hyper Differential Scanning Calorimetric Scan Rates

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Abstract: HyperDSC™ (fast scan rate) was used to study the melting behavior of canola (CLO), sunflower (SFO), palm olein (PO), rice bran oils (RBO), and cocoa butter (CB), and was compared to the melting behaviors using conventional DSC. There was an increase in sensitivity with increase in scan rate. Slow scan rate (5 to 20C / min) gave low sensitivity, which increased when the scan rates were increased to 50, 100 and 200C / min. Peak resolution was affected by scan rate depending on the sample weight. Increase in the size of sample coupled with the use of fast scan rate decreased the peak resolution. Generally small sample sizes gave better peak resolution. Results of the effect of scan rate on glass transition (Tg) shows that Tg, which is a weak transition especially in crystalline and low amorphous materials was not detected using conventional scan rates (5 to 20°C / min). It was however detected using of hyperDSC™ scan rates (100 to 200°C / min). Increasing the scan rate resulted in an increase in the peak temperature and the elimination of shoulder peaks, which were caused due to the polymorphic behavior of the triacylglycerols in the oils. The increase in peak temperature caused a shift in the peak position towards a higher temperature value. There is a positive correlation between the peak temperature and scan rate. The correlation coefficients (r) for CLO, SFO, PO, RBO and CB were 0.96, 0.95, 0.97, 0.96 and 0.96 respectively.

Keywords: HyperDSC™, melting behavior

INTRODUCTION

The most important aspect of the physical properties of oils and fats is related to the solid-liquid and liquid-solid phase changes. In other words, melting and crystallization in edible oils and fats are two important properties for functionality in many prepared food products. Thermal analysis methods such as differential scanning calorimetry (DSC) can be used to investigate these thermal behaviors. DSC is a thermo analytical technique for monitoring changes in physical or chemical properties of materials as a function of temperature by detecting the heat changes associated with such processes (Lutton, 1972).

In DSC, the measuring principle is to compare the rate of heat flow to the sample and to an inert material that are heated or cooled at the same rate. Changes in the samples associated with absorption or evolution of heat cause a change in the differential heat flow, which is then recorded as a peak. The area under the peak is directly proportional to the enthalpic change and its direction indicates whether the thermal event

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is endothermic or exothermic. Improvements in the sensitivity of commercially available calorimeters during the last 25 years have made DSC a popular tool for thermodynamic characterization of food components such as edible oils and fats (Dollimore, 1996). The rapid growth in popularity can be attributed in part to the availability of instruments of higher sensitivity and greater ease-of-use, as well as to software which provides rigorous analysis of experimental data, even for the non-expert (Ma *et al.* , 1990). Since the pioneering works in modern thermal analysis were published, it has been well known that scan rates have a strong effect on the thermal behavior of a given substance (Herrera *et al*., 1992). Determination of the temperature boundaries and the weak transitions such as glass transition (Tg) of materials with low amorphous content can be very difficult using the conventional DSC with 5 to 20°C / min scan rate. Such scan rates allows for changes to take place in the original sample during analysis.

Recently, a DSC technique has been shown to give increased sensitivity of DSC measurements (Ford and Mann 2002). HyperDSC™ allows the clear characterization of weak transitions and provides the ability to make measurements of the thermal properties of a sample at very fast scan rates. The fast heating and cooling rates associated with the method, from 100°C / min to as fast as 500°C / min lead to increased heat flow signal and therefore dramatically increased sensitivity. This allows extremely low-energy transitions to be identified and measured with ease. With this technique, sample changes such as recrystallization during melting which is a common phenomenon in oils and fats, decomposition after melting, or possible structural changes that occur during slow heating with conventional DSC can be eliminated or reduced. The benefits that are realized when using this technique include greater sensitivity which allows the measurement of much smaller samples, down to few micrograms. The fast measurement rates allow users to increase sample throughput from the handful of samples often analyzed by conventional DSC to 100 or more runs per day using automated DSC systems that can apply the HyperDSC™ method. In this paper, the effect of using HyperDSC™ on the melting behavior of selected oils was studied and compared to those obtained using conventional DSC.

MATERIALS AND METHODS

Materials

Four different types of edible oils namely; refined bleached and deodorized (RBD) palm olein, canola, rice bran, sunflower oils and cocoa butter, all obtained from a local super market were used in this study.

Methods

The thermal properties of the oil samples were investigated by differential scanning calorimetry using a Perkins-Elmer Diamond DSC (Shelton, Connecticut, USA). The instrument was calibrated using indium and zinc. The purge gas used was 99.99% nitrogen with a flow rate of 100 mL / min and a pressure of 20 psi. Sample weights ranged from 2.0-2.9 mg and were subjected to a temperature program. Frozen oil samples were melted at 60°C and were placed in individual aluminum volatile pans and sealed using the pan covers. An empty sealed pan served as the reference. Each sample was cooled to -70°C and held for 2 min, it was then heated from -70°C to 40°C at the rates of 5, 10, 20, and 50°C / min (conventional DSC scan rates), (Tan and Che Man, 2002), and at 100 and 200°C / min (HyperDSC™ scan rates) (Ford and Mann, 2002). The heating thermograms for the conventional and the HyperDSC™ scanning rates were recorded and peak, onset and offset temperatures were tabulated.

RESULTS AND DISCUSSION

Effect of Scan Rate on Sensitivity and Peak Resolution

Figures 1a, 2a, 3a, 4a, and 5a show the heating profiles of canola, sunflower, palm olein, rice bran oils, and cocoa butter, respectively using scan rates of 5, 10, 20, 50, 100, and 200°C/min. There was an increase in sensitivity with increase in scan rate. At a slow scan rate (5 to 20°C/min), the sensitivity was low but was found to increase when the scan rate was increased to 50, 100 and 200°C/min. This was shown by the increase in the size of the peak when the scan rate was increased, even though the same sample size was used. The increased sensitivity is derived from the basic principle of the DSC measurement: DSC output is measured in mW (J/sec). As a DSC experiment is accelerated in the HyperDSC™ method, the same heat flow occurs over a shorter time frame and therefore the thermal event becomes larger. Because of the high sensitivity associated with fast scan rate, sample size can be greatly reduced without compromising on the peak size and sensitivity. Slow scan rates require a larger sample size to maintain the sensitivity and obtain big enough peaks to obtain data. However increasing the amount of sample increases sensitivity, can greatly reduce the peak resolution and particularly when fast scan rates are used. Peak resolution is affected by scan rate depending on the sample weight. Smaller sample weight gives a better peak resolution. Large amounts of samples give huge peaks that are less resolved. It is better to use a smaller sample size (1 mg or less) when fast scan rates (HyperDSC™) are used in order to maintain the peak resolution. The use of a smaller sample size in HyperDSC™ compared to the required larger sample size of about 5-7 mg in conventional DSC is advantageous because samples that are difficult to obtain in large quantities can also be analyzed. It also conserves the samples used because little amounts are needed for any one analysis.

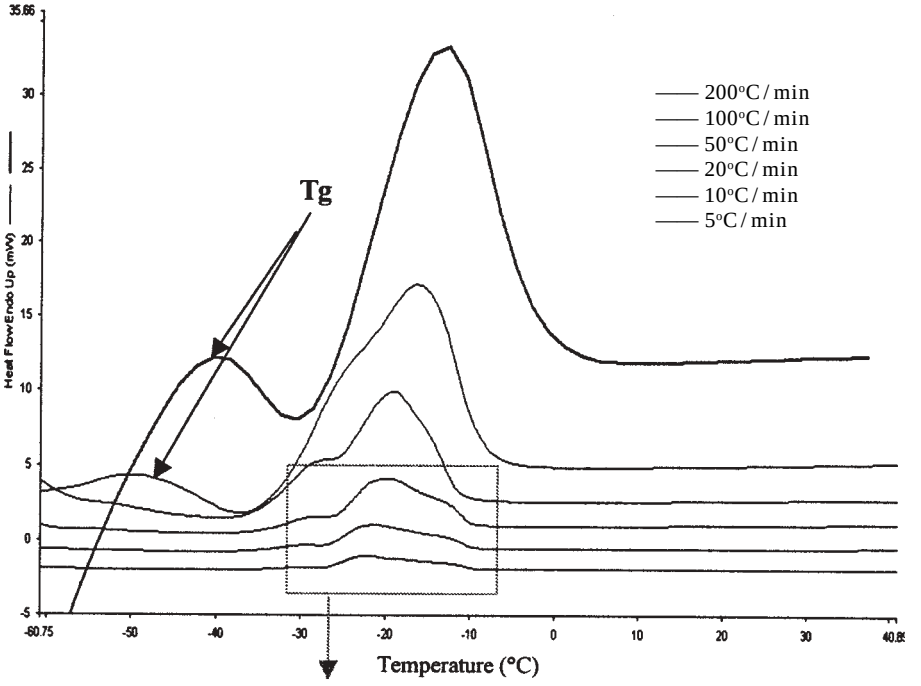
Effect of Scan Rate on the Detection of Glass Transition (Tg)

At slow scan rates, as in conventional DSC, weak thermal transitions are difficult to detect. However, increasing the scan rate as in HyperDSC™ (100 to 200°C/min) dramatically increases the sensitivity and thermal events are blown up allowing easier detection and separation of thermal transitions. Glass transition (Tg) is the temperature at which an amorphous polymer (or the amorphous regions in a partially crystalline polymer) changes from a hard and relatively brittle condition to a viscous or rubbery condition, it is a point or narrow region on the temperature scale where the thermal expansion coefficient, ±, undergoes a discontinuity and below which configurational rearrangements of polymer chain backbones are extremely slow (Ferry, 1970). Tg is a weak transition especially in crystalline and low amorphous materials. It is often not detected at all during thermal analysis using conventional scan rates. But due to the increase in sensitivity associated with the use of hyperDSC™ scan rates, this weak transition can be detected even in low amorphous and crystalline materials as shown in Figure 1a, 2a, 3a, and 5a. In the thermograms obtained using 100 and 200°C/min, Tg was clearly defined. However at a low scan rate of 5 to 20°C/min, no Tg was detected.

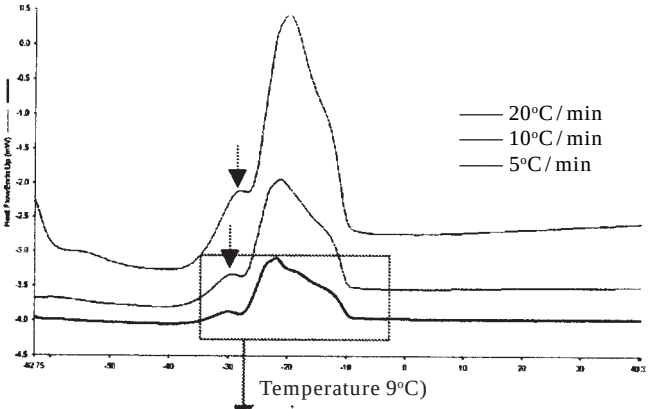
Effect of Scan Rate on Peak Position

Table 1 shows the peak temperature of different oils at various scan rates. Increase in the scan rate increases the peak temperature. The increase in the peak temperature causes a shift in the peak position towards a higher temperature value. There is a positive correlation between the peak temperature and scan rate. The correlation coefficients (r) for CLO, SFO, PO, RBO and CB were 0.96, 0.95, 0.97, 0.96, and 0.96, respectively. The change in peak position indicates a change in melting behavior. Though the complete melting temperature remains the same when different scan rates are used, the polymorphic behavior of the triglyceride species (i.e. they solidify in

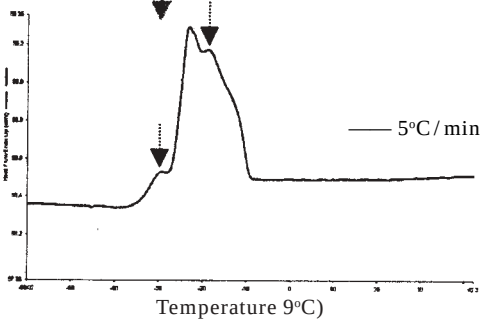
(a)



(b)

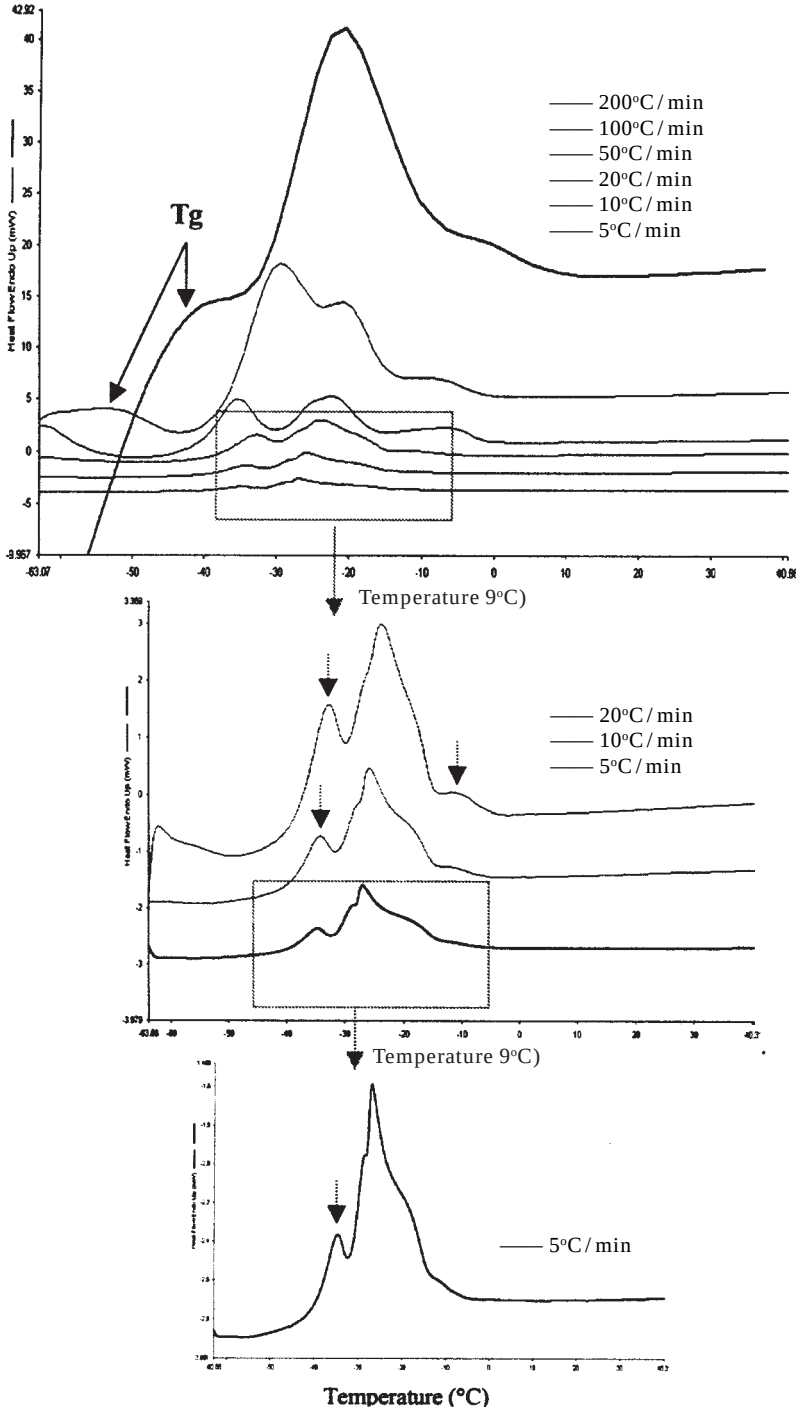


(c)



: Presence of shoulder peaks at slow scan rate, which disappeared at fast scan rates

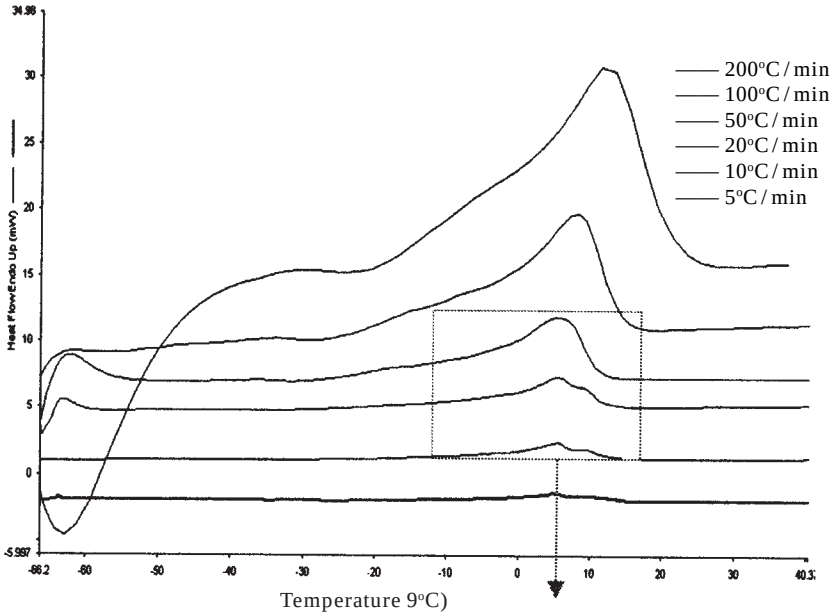
Figure 1: Heating thermogram of Canola oil at various scan rates



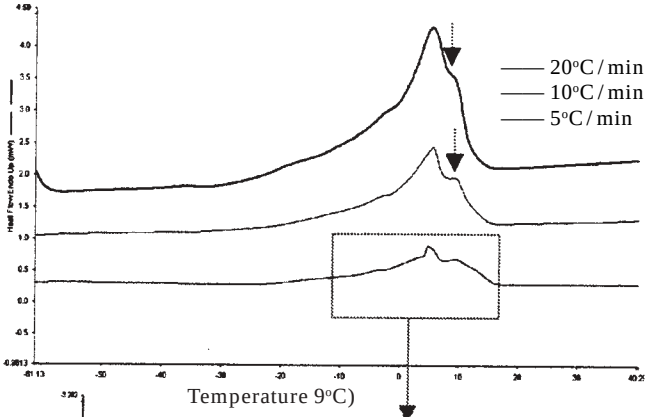
= Presence of shoulder peaks at slow scan rate, which disappeared at fast scan rates

Figure 2: Heating thermogram of Sunflower oil at various scan rates

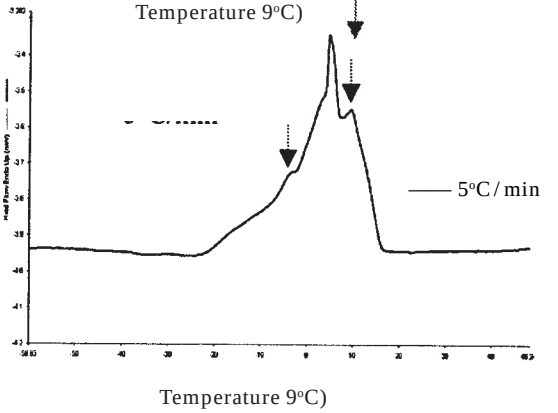
(a)



(b)



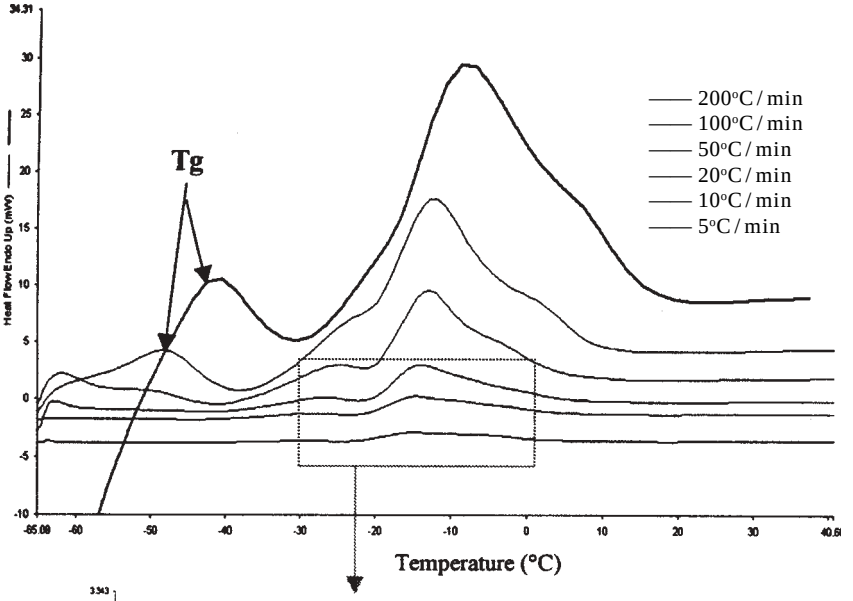
(c)



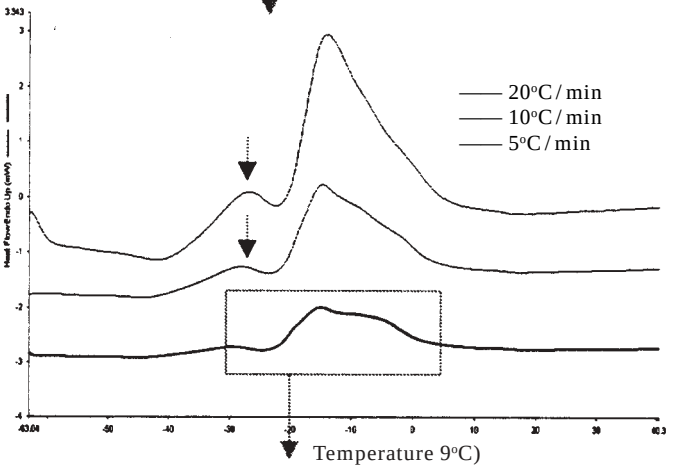
: Presence of shoulder peaks at slow scan rate, which disappeared at fast scan rates

Figure 3: Heating thermogram of Palm super olein at various scan rates

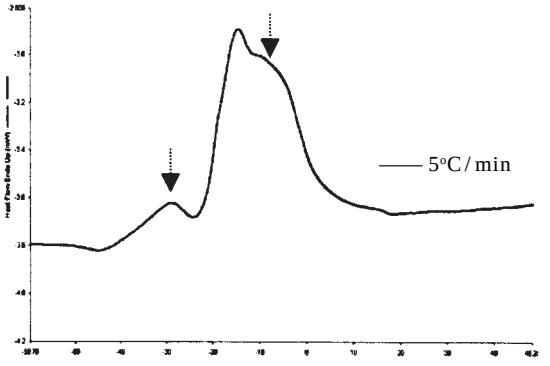
(a)



(b)



(c)



↓ = Presence of shoulder peaks at slow scan rate, which disappeared at fast scan rates

Figure 4: Heating thermogram of Rice bran oil at various scan rates temperature (°C)

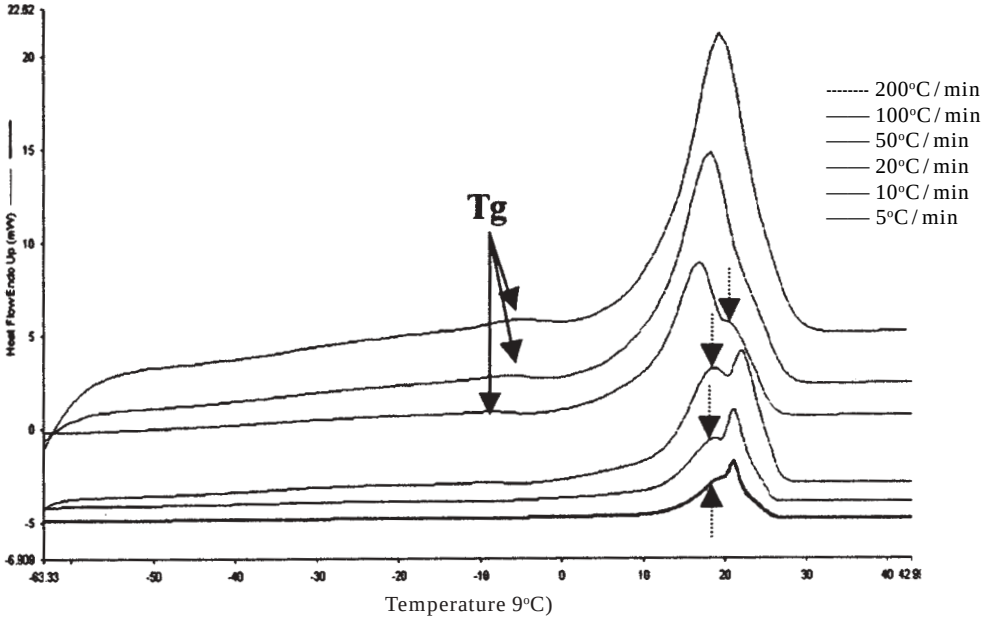


Figure 5a: Heating thermogram of cocoa butter at various scan rates

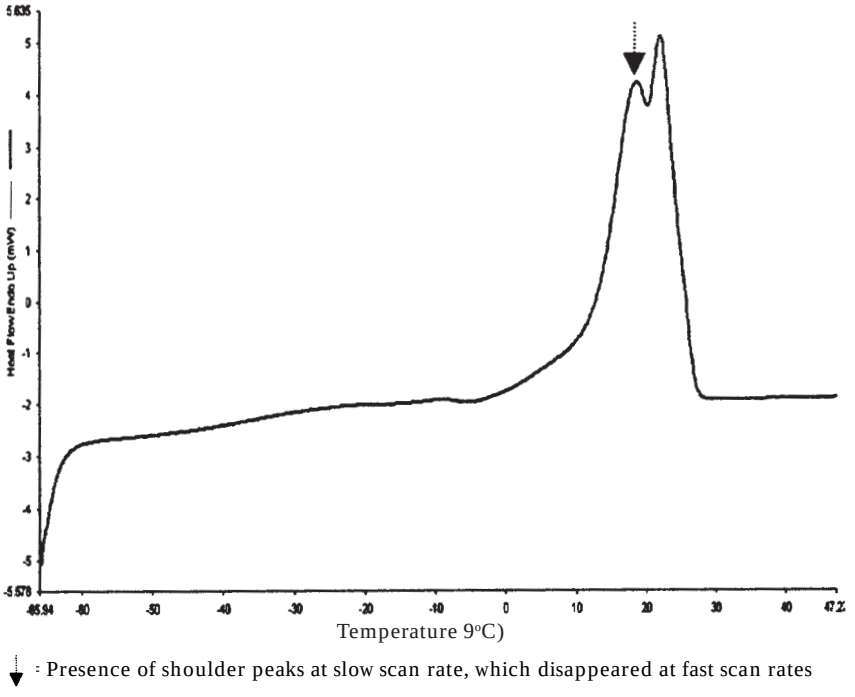


Figure 5b: Heating thermogram of Cocoa butter at 20°C / min

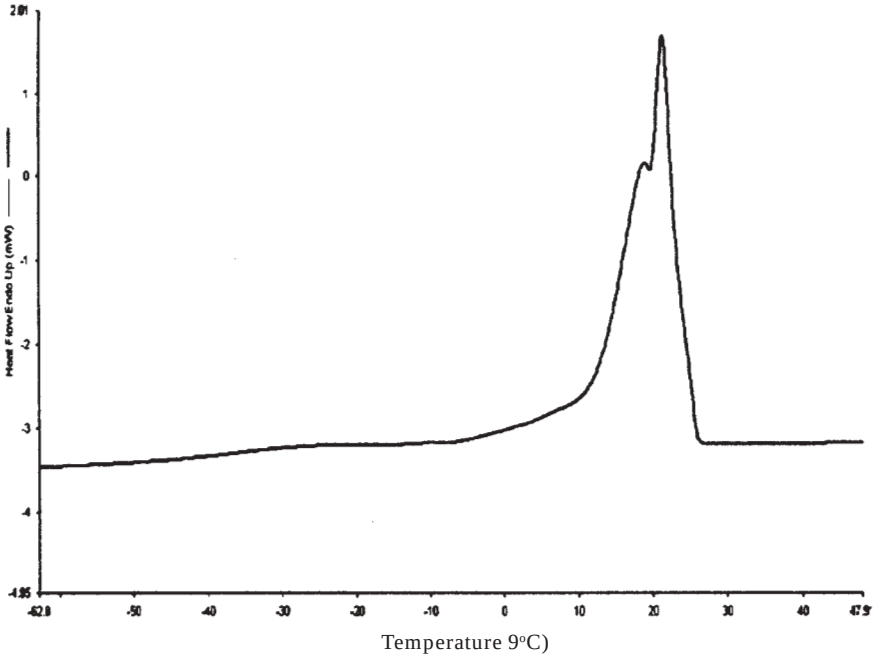


Figure 5c: Heating thermogram of Cocoa butter at 10°C / min

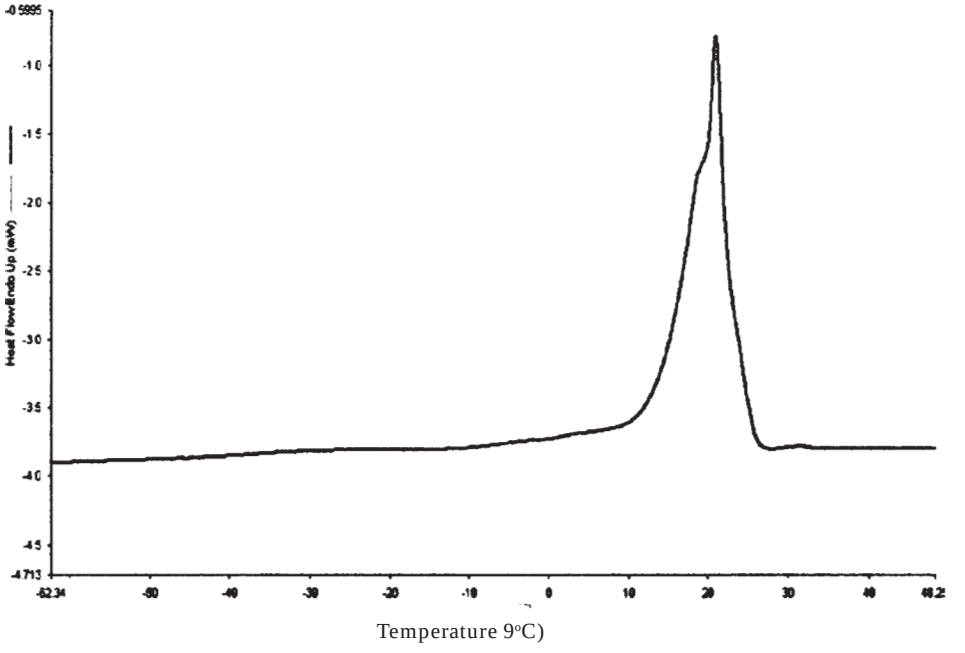


Figure 5d: Heating thermogram of Cocoa butter at 5°C / min

Table 1: Melting characteristics of vegetable oil samples at various scan rates

	CLO			SFO			PO			RBO			CB		
Scan rate (°C/min)	Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)
5	-27.28	- 22.25	62.18	-29.77	-26.09	65.41	-22.41	4.74	71.76	-22.41	-14.88	71.76	14.31	17.46	67.10
10	-26.89	-20.77	62.10	-29.84	-25.88	61.98	-3.54	5.53	67.06	-22.07	-14.62	70.96	12.05	17.76	69.51
20	-26.58	-19.41	62.00	-31.06	-24.92	61.38	-3.01	5.34	67.13	-21.15	-14.14	68.72	10.87	18.04	73.31
50	-28.93	-19.30	58.94	-39.66	-23.79	59.00	-7.06	5.62	64.71	-21.77	-12.88	65.07	11.34	18.46	76.37
100*	-32.91	-16.73	56.02	-38.90	-22.63	49.23	-6.56	8.24	64.82	-23.47	-12.74	59.75	12.55	20.28	73.82
200*	-27.08	-12.71	52.21	-31.98	-20.66	46.42	-8.09	11.30	64.17	-21.16	-8.72	51.28	19.19	24.29	71.36

* HyperDSC™ scan rate
CLO = Canola oil, SFO = Sunflower oil, PO = Palm olein, RBO = Rice bran oil, CB = Cocoa butter

different crystal forms, which are often sufficiently stable to exhibit distinctive melting points, densities, heats of fusion, x-ray diffraction patterns etc, Lutton, 1972) in the oil samples was eliminated. This was noticed by the disappearance of the minor and shoulder peaks which merge into a single peak. This may have caused the shift in the peak positions. Figures 1b, 2b, 3b, and 4b, showed heating thermograms of CLO, SFO, PO, and RBO, respectively at 5, 10, and 20°C / min scan rates and the heating thermograms of CB at 5, 10, and 20°C / min are shown in Figures 5b, 5c, and 5d, respectively. In these thermograms, multiple peaks and / or shoulder peaks can be seen which are due to either the melting of different triglyceride species in the oil sample or their polymorphs. When compared to the thermogram obtained with 100 and 200°C / min scan rates, the multiple and shoulder peaks were absent. Due to this reason, fast scan rates typical of hyperDSC™ cannot be used to study polymorphic behavior of crystals as it is eliminated. At fast scan rates, high temperatures are attained in a very short time and this causes two or more triglycerides to melt simultaneously even though their melting temperatures are different (Tan and Che Man, 2002), which results in broader peaks.

CONCLUSIONS

HyperDSC™ provides true information of the sample without introducing any additional interference, such as recrystallization or decomposition. HyperDSC™ eliminates misinterpretation of material behavior and helps to improve product quality. The past scan rates allow users to increase sample throughput easily up to 100 or more runs per day. Increased sensitivity which is available with this new technique enhances the ability to identify weak transitions often missed with conventional DSC. Accurate interpretation of results and fast scanning makes HyperDSC™ the new and preferred tool for the pharmaceutical and polymer industries to reduce time-to-market for new product and increase manufacturing efficiency. Other industries like the food industry will soon begin to discover the benefits of HyperDSC™.

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