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Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

INVESTIGATIONS OF THE SUB-AMBIENT TRANSITIONS IN FROZEN SUCROSE BY MODULATED DIFFERENTIAL SCANNING CALORIMETRY (MDSC®)

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Abstract

40% w/w sucrose/water solutions were analyzed by Modulated Differential Scanning Calorimetry [1] in the sub-ambient temperature region. At these temperatures, the solutions exhibit a complex, two-step thermal event. The lower-temperature event is believed to be the glass transition of the amorphous sucrose phase. The nature of the higher-temperature event is the subject of controversy. This event has been shown to have distinct second-order characteristics, and as such is believed to be a second T_g. Others feel that this event is the onset of melting. The temperature region between these events contains a devitrification exotherm. Through the use of MDSC, both in scanning and stepwise quasi-isothermal modes, improved sensitivity and resolution of MDSC provides new insight into the nature of these transitions.

Keywords: frozen sucrose, glass transition, MDSC, MT-DSC, TM-DSC

Introduction

Whereas Modulated DSC®, (also known as modulated-temperature DSC and temperature-modulated DSC) is a relatively new technique, it has been the subject of much research and discussion over the last few years. In addition, many papers have been published which illustrate the benefit of MDSC in the analysis of complex systems [2]. As thermal analysis and MDSC are prevalent in the polymer industry, most of the published literature to date has involved the analysis of synthetic polymeric systems. With regard to complex polymeric systems such as blends and copolymers, the utility of MDSC has been in the ability to separate overlapping transitions. MDSC deconvolutes total heat flow into two main components: that which is due to heat capacity and the component due to kinetically controlled events. Glass transitions are resolved into the former component (designated 'reversing heat flow') and crystallizations occur in the latter, or 'Nonreversing' component. The ability to perform this separation provides for the reso-

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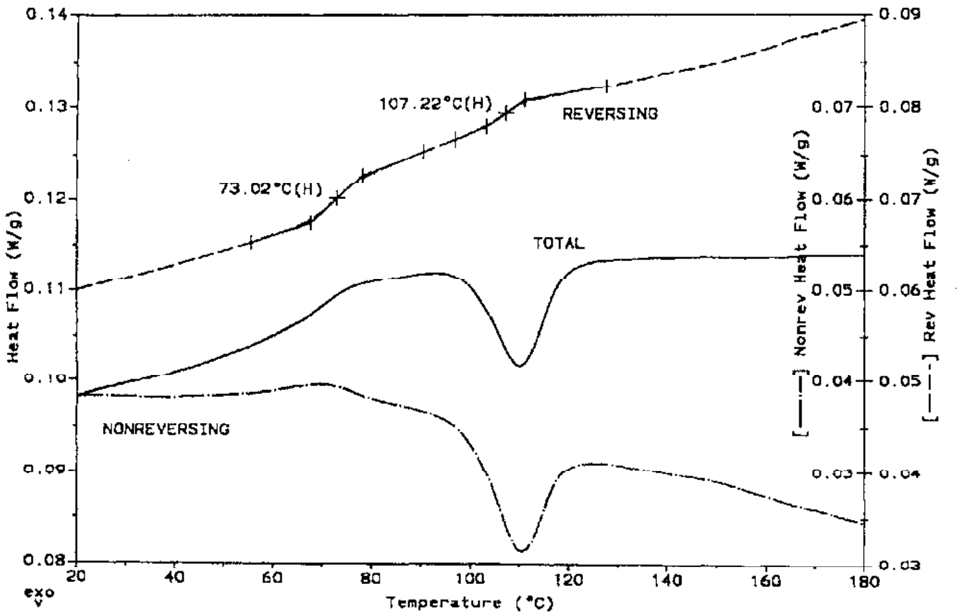

Fig. 1 MDSC results for PET/ABS Blend. The PET cold crystallization occurs simultaneous with the glass transition of the ABS

lution of the glass transition, even when kinetic event are occurring simultaneously such as shown in Fig. 1. This figure contains the MDSC analysis of a poly(thyleneterephthalate) (PET) /acrylonitrile-butadiene-styrene (ABS) blend in which the T_g of ABS occurs at the same temperature as the cold crystallization of PET. Since MDSC separates the glass transition into the reversing component and the cold crystallization into the nonreversing component, the resolution of the T_g is accomplished in one experiment.

Levine and Slade [3, 4] have elucidated upon the kinetic similarities between complex carbohydrate systems and polycrystalline or amorphous polymers. In addition, the importance of T_g as a physicochemical parameter in the preparation and storage stability of foods is well know. To this end, much work has been accomplished in the investigation of frozen polysaccharide systems, and the complex transitions found in the glass transition region [5, 6]. However, the nature of the events which occur in the subambient temperature region of sucrose/water systems is the subject of controversy. Depending on the thermal history, frozen sucrose solutions can exhibit a multi-step transition just prior to the melting transition of the aqueous phase (Fig. 2). The nature of this transition is the controversial topic.

It is known that the lower temperature step-change (T_{TR1}) is the primary glass transition of the amorphous sucrose phase. The temperature and intensity of this transition will change with thermal history and sucrose concentration [7]. It is

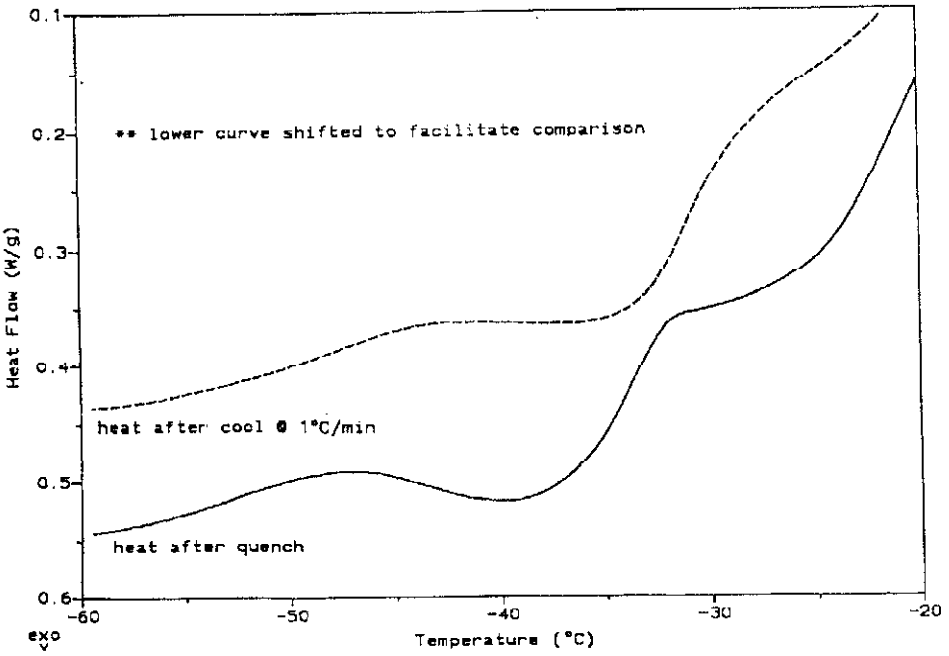

Fig. 2 Standard DSC (10°C min^{-1}) results for 40% w/w sucrose/water solution after quenching in liquid N_2 (top curve) and cooling at 1°C min^{-1} (bottom curve)

the nature of the higher temperature step-change (T_{TR2}) which generates dissent. This transition has been ascribed as a secondary glass transition [8], the onset of melting [5], a combination melt and T_g known as the 'softening temperature' [9], or the ice-dissolution transition [7], among other interpretations. Between these two endothermic transitions is often found an exotherm, attributed to devitrification of the solution, and subsequent ice crystallization.

Recently, Goff [10] has reported on the potential of MDSC in the analysis of frozen sucrose systems. Subsequently, Izzard *et al.* [7] reported on the use of MDSC to examine the sub-ambient transition region in frozen sucrose. They reported on the improved resolution capability of the transition region using MDSC, and attributed T_{TR2} to ice dissolution. In addition, they reported this ice-dissolution peak as having both reversing and nonreversing characteristics, which was thought to occur due to the non-equilibrium condition of the process.

In this work we examine the transition region of a 40% w/w sucrose/water solution using MDSC. Common to Izzard *et al.*, we report on the reversing and nonreversing nature of the various components of the complex transition. In addition, novel work centers on the use of stepwise quasi-isothermal MDSC to examine the heat capacity response of the system, free of any time-dependent effects. Additional information with regard to the second-order nature of the T_{TR2} is reported.

Theory

The theory of the MDSC measurement has been extensively addressed in the literature [11–32], and will not be repeated herein.

A modification of the classical MDSC experiment has recently come to fore as a valuable technique in the analysis of complex transitions. Known as stepwise quasi-isothermal MDSC (SQI-MDSC), this technique involves performing the MDSC experiment with an underlying heating rate equal to zero ($\beta = 0$). The only temperature perturbation is generated by the small modulation amplitude, thus the term 'quasi-isothermal'. The sample is held at a particular temperature until all time-dependent processes are apparently satisfied. At this point, the equilibrium heat-capacity is measured, free from kinetic effects. The temperature of the sample is incremented slightly, and the process repeated. Using this technique, it is possible to step through a transition region very slowly, measuring equilibrium heat capacity at each incremental temperature. The underlying heating rate across the transition approaches zero, providing for extremely high resolution. The utility of SQI-MDSC has been shown in the analysis of the polystyrene glass transition, in which time-dependence is prevalent [33]. SQI-MDSC results showing this transition are contained in Fig. 3.

In addition, SQI-MDSC has been recently used to analyze the melting of indium [34] and tin [35], in experiments based on work performed by Cantor and O'Reilly [36].

As stepwise quasi-isothermal MDSC is useful examining the heat capacity response of complex transition, it was theorized that this technique would be

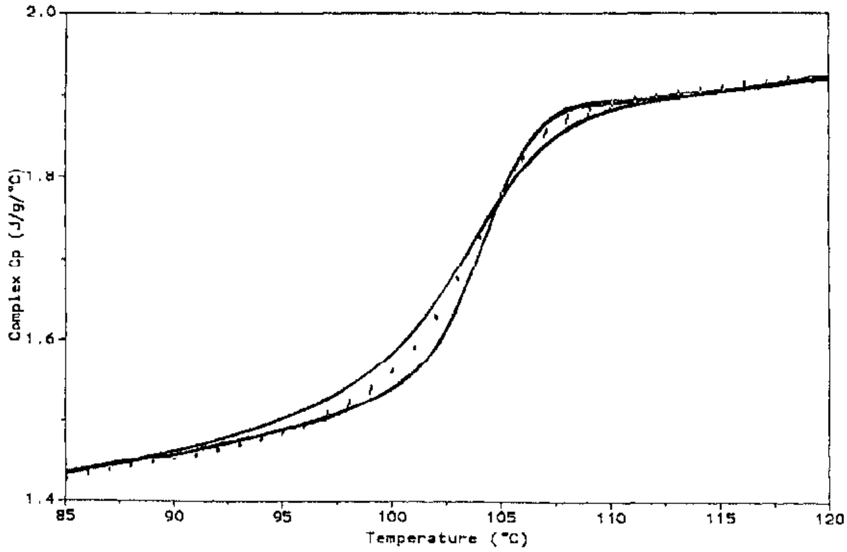

Fig. 3 Modulated DSC data for the glass transition of polystyrene. The solid lines are heating and cooling at 1°C min^{-1}, the dots represent the stepwise quasi-isothermal experiment

valuable in the analysis of the sub-ambient transitions in sucrose solutions. In particular, it was thought that the nature of the higher-temperature transition could be elucidated using SQI-MDSC.

Materials and methods

All modulated DSC measurements were performed on a TA Instruments DSC 2920, equipped with a refrigerated cooling system (RCS). The purge gas used was helium, flowing at 25 ml min^{-1}. The DSC heat flow was initially calibrated using a traceable indium standard ($\Delta H_f = 28.3$ J g^{-1}), and the heat capacity response was calibrated using a sapphire standard. Sucrose (analytical grade) solution (40% w/w) were prepared in the manner reported in [6]. All samples were analyzed in hermetically sealed aluminum DSC pans. The reference was an empty hermetically sealed aluminum DSC pan. The temperature programs used are discussed in the next section.

Results and discussion

Figure 2 contains the standard DSC (10°C min^{-1}) curves for a 40% w/w sucrose solution subject to different thermal histories: quench-cooled by rapid immersion in liquid N_2, and control-cooled at 1°C min^{-1} in the DSC cell. The purpose of using two different pre-treatments was to impart different morphology into the sucrose solution. The quench-cooled sample would be expected to con-

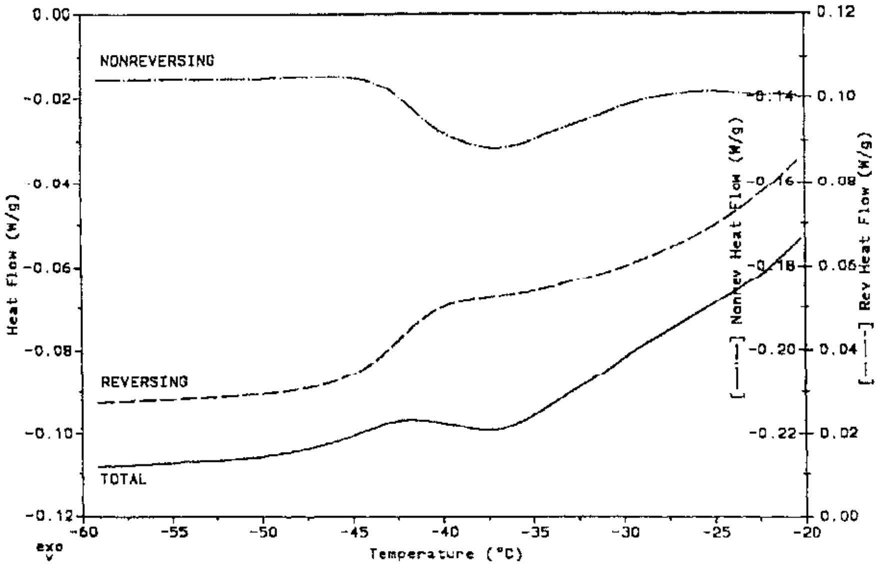

Fig. 4 Modulated DSC results for the minimally freeze-concentrated 40% w/w sucrose/water sample

tain a minimally freeze-concentrated sucrose phase. In other words, during the cooling process water molecules are kinetically 'trapped' into the vitrified sucrose phase. The high viscosity of the sucrose does not allow for the crystallization of the trapped water, so the water is thought of as unfrozen. In addition, the unfrozen water acts to plasticize the sucrose phase, lowering its glass transition temperature. Upon slower-cooling of the system, the water is allowed to transmigrate out of the sucrose phase, allowing for freeze-concentration of the sucrose. Most of the associated water crystallizes upon cooling [37]. The resulting differences in DSC response is illustrated in Fig. 2. Whereas the curves in this figure contain events typical of glass transition, they are somewhat complex and difficult to reliably interpret.

Figure 4 contains an MDSC curve for the quench-cooled sample. In this experiment, the sample was heated at 1°C min^{-1}, with a modulation amplitude of ±0.5°C over a period of 100 s. In this curve, the glass transition of the sucrose (T_{TR1}) is clearly apparent in the reversing heat flow signal at about –43°C. Exothermic activity is seen in the nonreversing heat flow signal, originating near the midpoint of the glass transition. This exotherm can be attributed to devitrification of the amorphous sucrose, and resultant crystallization of the liberated water. This scenario correlates well with phase diagrams recently published by Roos *et al.*[5]. In these diagrams, the glass transition temperature of the sucrose system falls near –45°C, with a region of maximum ice formation between –45 and –35°C.

The curve in Fig. 5 contains the MDSC results for the sucrose solution which was cooled at 1°C min^{-1}. The MDSC conditions were the same as for the previous experiment. The reversing heat flow still contains the primary glass transition (T_{TR1}) of the sucrose near –43°C, however it is much less intense. In addition to this transition, there is a larger step-change (T_{TR2}) centered near –38°C. This step-change is accompanied by an endotherm in the non-reversing heat flow signal. This phenomenon has been addressed by Izzard *et al.* [7], and has been attributed to a non-equilibrium condition occurring during the ice-dissolution process. It is interesting that this process was also seen in non-annealed sucrose solution in [7], but not in the present work. The effect of slow-cooling of the sample is illustrated in the absence of any devitrification exotherm. This suggests that most of the associated water translocated out of the sucrose phase and crystallized during cooling. To this end, the sucrose phase would be freeze-concentrated.

Figure 6 compares the measured heat capacity results for the quench-cooled and slow-cooled samples. The glass transition (T_{TR1}) is obvious in the quench-cooled sample, and occurs at a similar temperature, but is less intense in the slow-cooled sample. Unique to the slow-cooled sample is the higher temperature step-change, T_{TR2}. Note that the combination of the step-changes attributed to T_{TR1} and T_{TR2} in the slow-cooled sample is approximately equal to the step change in T_{TR1} in the quench-cooled sample.

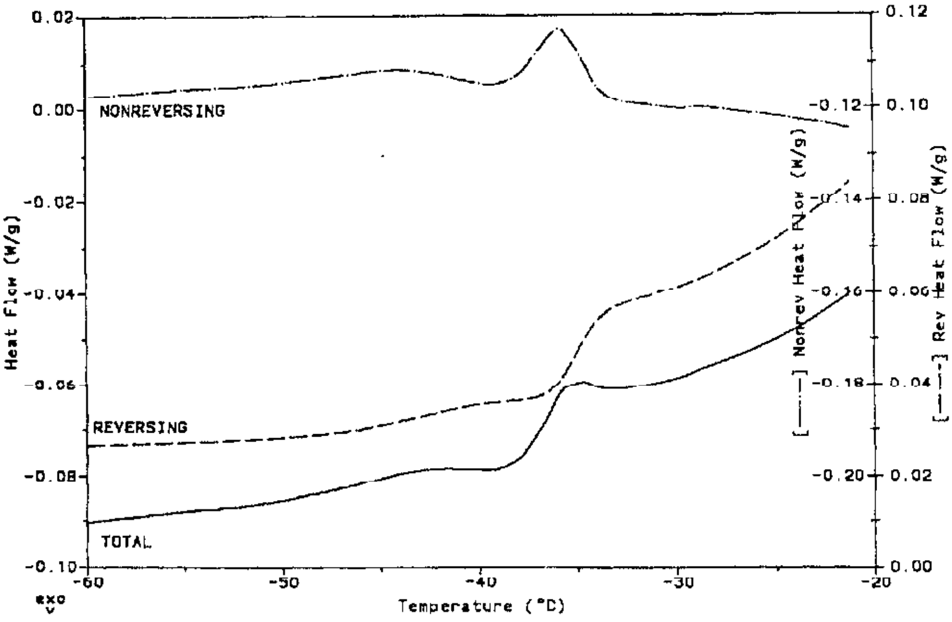

Fig. 5 Modulated DSC results for the maximally freeze-concentrated 40% w/w sucrose/water sample

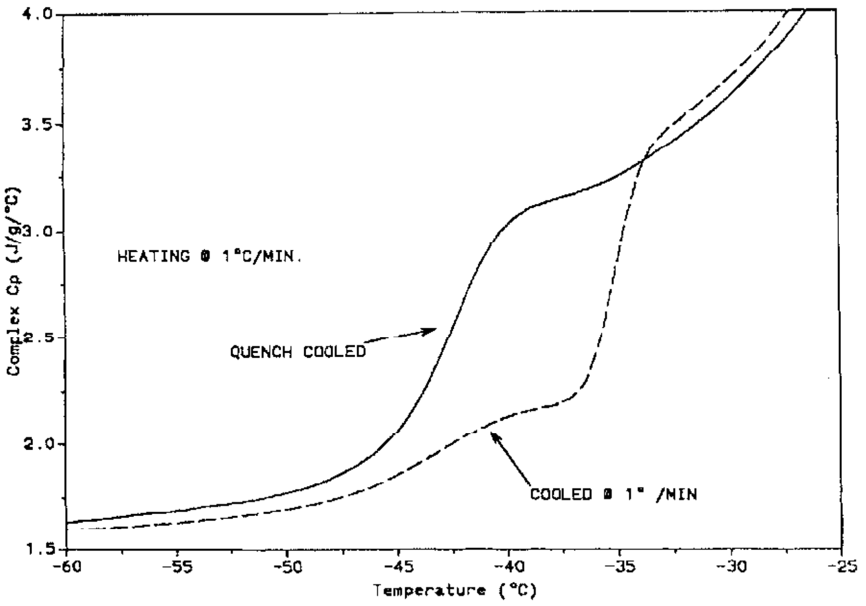

Fig. 6 Comparison plot showing the complex heat capacity signals of the minimally freeze-concentrated (quench-cooled) and maximally freeze-concentrated (cooled @ 1°C min^{-1}) sucrose solutions

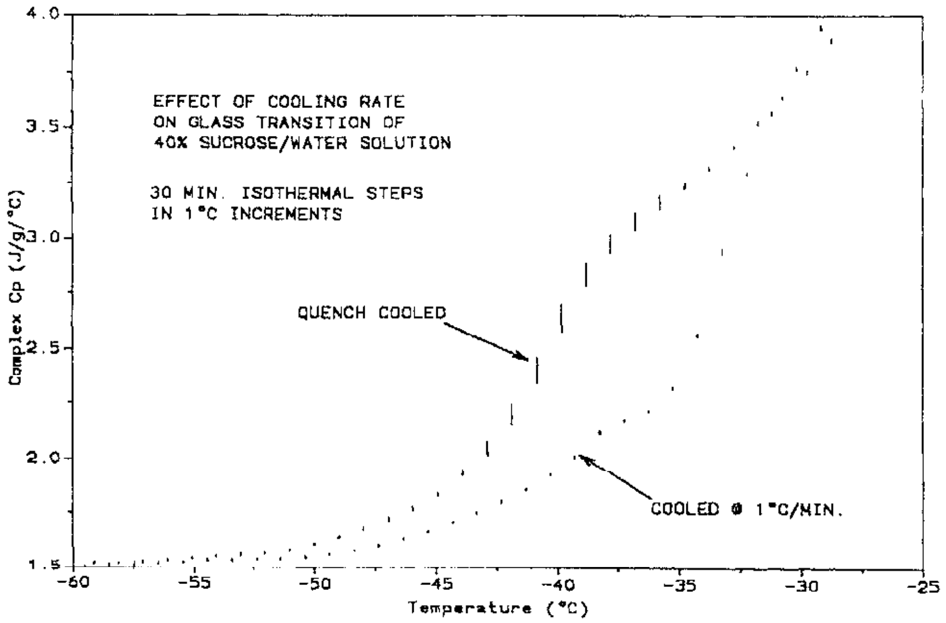

Fig. 7 Stepwise quasi-isothermal data for the minimally freeze-concentrated (quench-cooled) and maximally freeze-concentrated (cooled @ 1°C min^{-1}) sucrose solutions

Figure 7 contains the stepwise quasi-isothermal data for both samples. In these experiments, the samples were held isothermally for 30 min, with a superimposed temperature modulation of ±0.5°C over a period of 100 s. Only the last 20 min of data is saved, which eliminates noise early in the isothermal period arising from non-steady-state conditions. An interesting difference is seen between the two samples. The quench-cooled sample is seen to have a dynamic heat capacity during the glass transition region, whereas the freeze-concentrated sample displays stable heat capacity throughout.

The dynamic heat capacity is manifested as vertical lines as opposed to dots in the SQI-MDSC data. The vertical lines indicate that the value of the heat capacity is changing as the sample's temperature is held constant. In this case, the change is due to a decrease in heat capacity as devitrification occurs, and liberated water crystallizes. A similar phenomenon is seen during the SQI-MDSC experiment of quench-cooled poly(ethyleneterephthalate). During the cold crystallization process of this polymer, the vertical lines are present in the heat capacity signal (Fig. 8). The absence of these vertical lines in the slow-cooled sucrose sample attests to the freeze-concentration of this sample.

It is interesting that T_{TR2} is also apparent in the SQI-MDSC data, and that the heat capacity values are stable during this transition. This stability is similar to the data during T_{TR1} in the same sample. Both of these transitions behave simi-

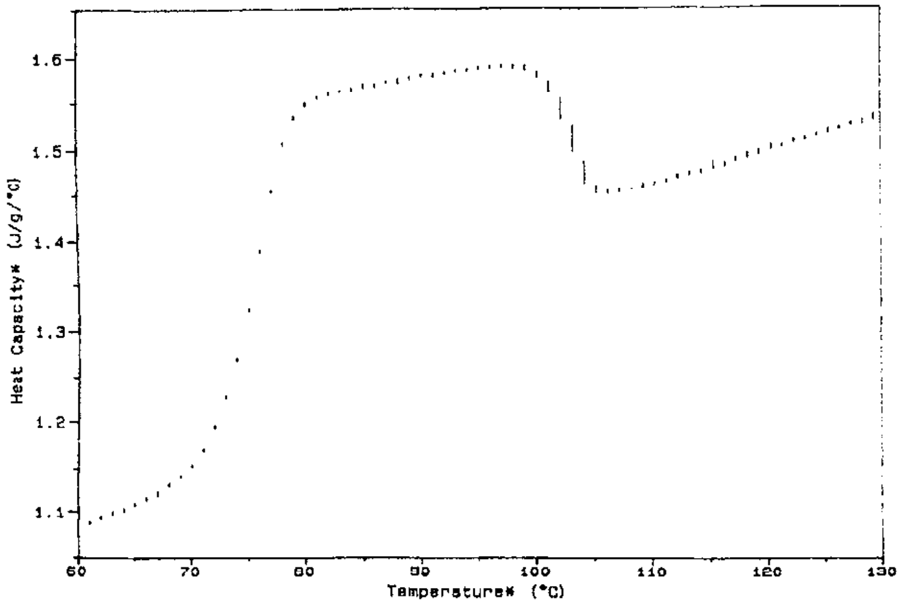

Fig. 8 Stepwise quasi-isothermal data of the glass transition and cold crystallization region of poly(ethyleneterephthalate)

larly to the SQI-MDSC data of the polystyrene glass transition reported in [33]. The stability of the heat capacity signal during T_{TR2} suggests that there is no latent heat associated with this transition, which implies second-order characteristics. However, it has been shown that materials can also exhibit reversible first-order melting [38, 39], in which a melt-recrystallization equilibrium is achieved. This phenomenon exists when the melting of at least part of a sample can occur during one half of a modulation cycle. Subsequently, the recrystallization of the melted phase must occur during the subsequent half of the cycle. The latent heat associated with this reversing process adds to the amplitude of the modulated heat flow, increasing the apparent heat capacity of the sample above the classical vibrational C_{p}. As long as no supercooling occurs, and/or nucleation sites are available, this scenario seems plausible for the sucrose/water system.

A method used to investigate the melt-crystallization equilibrium involves the use of Lissajous analysis [34]. In this technique, the modulated heat flow during an SQI-MDSC experiment is plotted *vs.* the modulated heating rate. When no latent heat flow is present in the modulation cycle, the resulting curve is an ellipse. When melt-recrystallization equilibria are present, the ellipse is distorted (Fig. 9). This phenomenon was initially reported by Cantor and O'Reilly [36], and has recently been measured and reported during the melting transitions of indium [34] and tin [35]. During the melts of these materials, considerable distortion of the Lissajous curves were encountered. It is interesting that Lissajous

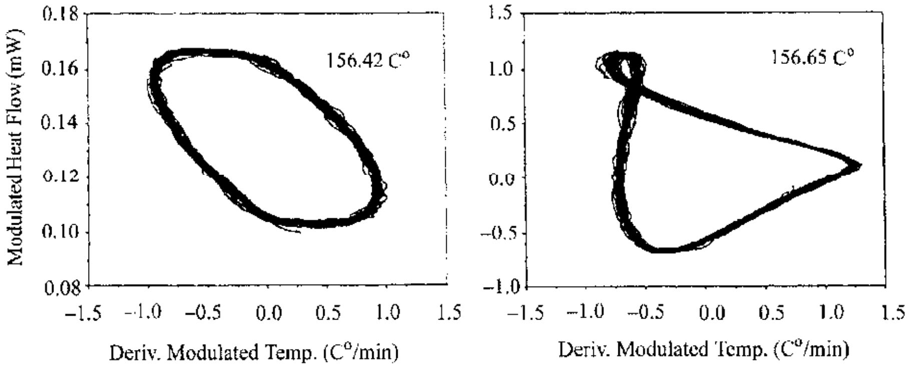

Fig. 9 Lissajous figures showing quasi-isothermal data for temperatures below the melt (left curve) and in the melting region (right curve) of indium metal

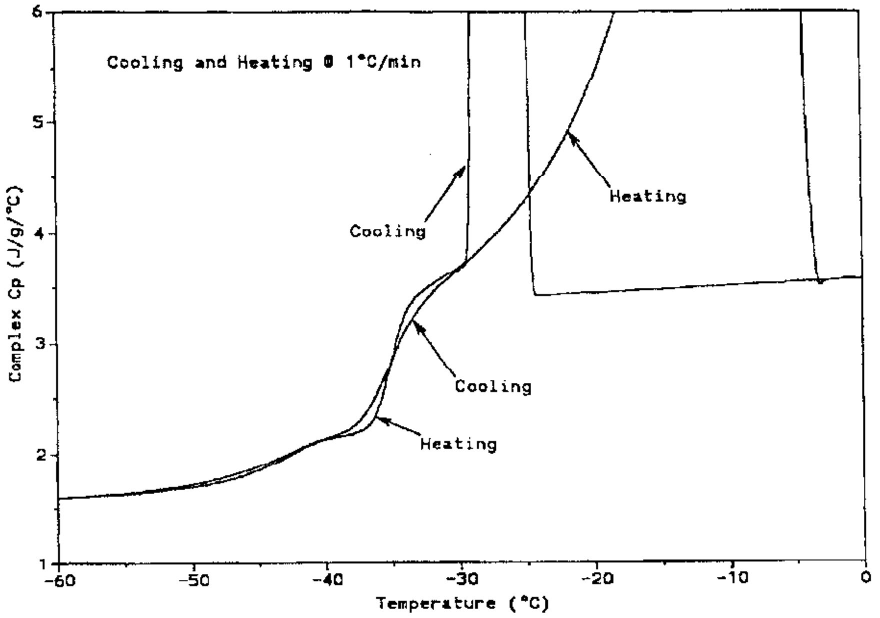

Fig. 10 MDSC data (heating and cooling at 1°C $\min^{-1}$) for the subambient transition region of the maximally freeze-concentrated sucrose solution

analyses of the SQI-MDSC data during T_{TR2} exhibited no distortion whatsoever, suggesting second-order behavior once again.

The final evidence for second-order behavior at T_{TR2} is shown in Fig. 10. The curve in this figure contains the MDSC data from heating through the transition at 1°C, with modulation of ±0.5°C every 100 s, and cooling through the transition region at 1°C $\min^{-1}$ with the same modulation parameters. At higher temperatures in the heating and cooling scan, the respective melting and bulk crystallization processes are clearly evident. The transition T_{TR2} is also apparent near –35°C. However, this transition is exhibiting a hysteresis effect, in that the scan on cooling is not identical in shape to the scan on heating. This type of hysteresis is common at the T_g of a polymer, as shown in the polystyrene glass transition in Fig. 3.

Summary

Modulated DSC has been used to analyze the sub-ambient transition region in a 40% w/w sucrose solution. The sample was pretreated to invoke minimal and maximal freeze-concentration. In the minimally freeze-concentrated sample, the T_g (T_{TR1}) is clearly evident, as is devitrification and subsequent crystallization of liberated water. The maximally freeze-concentrated sample also exhibits T_{TR1}, however, it is comparatively less intense. The freeze-concentrated sample also exhibits a second transition, labeled T_{TR2}. Both classical MDSC experiments in heating and cooling modes, and stepwise quasi-isothermal data suggest that this transition exhibits strong second-order behavior, similar to the glass transition of a polymer.

Clearly the data presented herein is not irrefutably conclusive. More experiments need to be performed to examine the kinetics of T_{TR2} so that the nature of this transition can be confirmed. Modulated DSC is shown to be a valuable tool in the analysis of this transition, and more research into the applicability of MDSC in this area is clearly justified.

References

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