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# Detection of obscured glass transitions by QiDSC

**L. Judovits · R. Gupta**

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**Abstract** Determination of compatibility in the amorphous phase for a two component blend is usually accomplished by analyzing for whether one notes one or two glass transitions. This can be complicated when one of the components is semicrystalline and its melting peak obscures the second glass transition. Quasi-isothermal differential scanning calorimetry (QiDSC) can be used to detect an obscured glass transition by allowing the semicrystalline component to melt and relax revealing the underlying glass transition of the other component. QiDSC is accomplished by performing a modulated temperature DSC experiment at a particular temperature and step ramping through the transitions of interest. For this study two systems are investigated. The first system is a model system based on a blend of polystyrene (PS) and a copolymer of vinylidene fluoride and hexafluoropropylene, P($VF_2$/HFP). The glass transition for the PS occurs at the same temperature as the melting point for the fluorocopolymer. The second system is a fluoro-copolymer/acrylic dried latex. In both cases the hidden glass transition can be noted in the reversing heat capacity of the QiDSC analysis.

**Keywords** Quasi-isothermal DSC · QiDSC · Glass transition · Acrylic · Polyvinylidene fluoride · Hexafluoropropylene

## Introduction

Poly(vinylidene fluoride) ($PVF_2$) based coatings are widely used as an exterior architectural coatings due to good long-term weathering and superior resistance to color fade. Conventional fluoropolymer coatings are solvent based and typically require high bake temperatures to form homogenous films having necessary properties such as adhesion and hardness. Owing to a shift in the coatings market toward environmentally friendly systems with less energy intensive processing, water-based systems are becoming popular. Advances in emulsion polymerization techniques have enabled the development of new fluoropolymer-based waterborne emulsions to meet the current needs of exterior architectural coatings. The new water-based systems can be formulated into coatings and applied in-field and in low temperature applications. Such latex systems are synthesized through a seeded fluoropolymer emulsion polymerization forming latex particles demonstrating an intimate blend of fluoropolymer and acrylic copolymers. Durability and outdoor weathering performance is dependent on the homogeneous blend of the two copolymers [1]. So, investigative analytical tools are required to study the affect of synthesis parameters and polymer compositions on the final morphology of the latex particles.

Modulated differential scanning calorimetry (MDSC) is part of the modulated temperature differential scanning calorimetry (MTDSC) family and allows the separation of the total heat flow into its reversing and nonreversing components [2]. The reversing signal represents a signal associated with the underlying heat capacity whereas the nonreversing heat flow is associated with the kinetic effects. This allows one to separate overlapping transitions when one transition goes into the reversing signal and the other into the nonreversing signal. But what if both go into the reversing signal such as a melting transition overlapping a glass transition due to a phase separation?

Quasi-isothermal DSC (QiDSC), unlike the typical MDSC experiment where the sample is ramped, modulates

L. Judovits (✉) · R. Gupta
Arkema, Inc., 900 First Avenue, King of Prussia,
PA 19406, USA
e-mail: larry.judovits@hotmail.com

around a set temperature, hence quasi-isothermal, usually with sequential steps. A property of the quasi-isothermal mode is that it allows a material to relax at a given temperature, which should allow further differentiation. In MDSC a sinusoidal modulation is overlaid on a linear ramp. By doing this the reversing heat capacity can be separated. The reversing heat capacity is obtained by a Fourier analysis of the ratio of the amplitudes of the modulated heat flow over the modulated temperature multiplied by the cell constant. The nonreversing component is determined by subtracting the reversing heat flow from the total heat flow. In order to convert from reversing heat capacity to reversing heat flow, the signal needs to be multiplied by the heating rate. Since the heating rate for the QiDSC mode is zero, the nonreversing component cannot be determined as noted in the MDSC diagram (Fig. 1). Therefore, only the reversing heat capacity was analyzed for this study.

For this study two systems were studied. The first system is a blend of polystyrene (PS) and a copolymer of vinylidene fluoride and hexafluoropropylene, P($VF_2$/HFP), having a peak melting temperature of between 100 and 125 °C. The glass transition for the PS occurs at the same temperature as the melting point for the fluoro-copolymer. The second system is a fluoro-copolymer/acrylic dried latex where the acrylic glass transition is obscured by the melting of the second component. The fluoro-copolymer for both systems is similar in monomer composition.

## Experimental

Both the conventional and modulated DSC experiments were performed on a TA Instruments Q1000 differential scanning calorimeter (DSC). A refrigerated cooling attachment was used with a nitrogen purge. The unit was

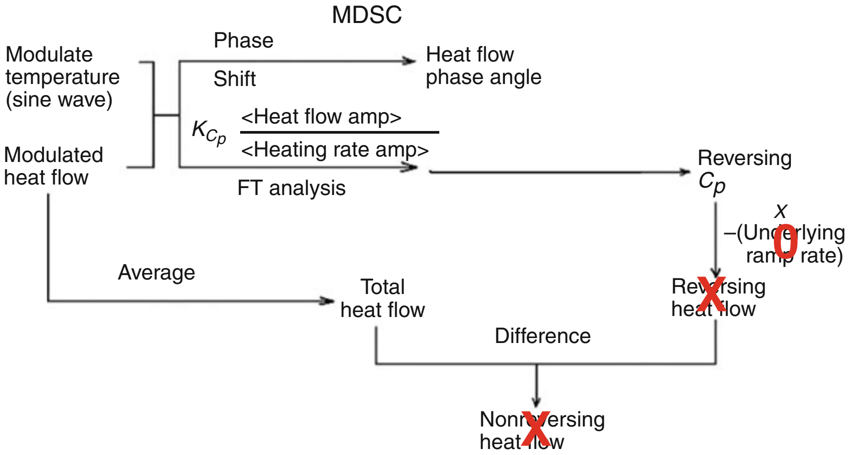


**Fig. 1** MDSC schematic for the quasi-isothermal mode for a TA Instruments 2920 module

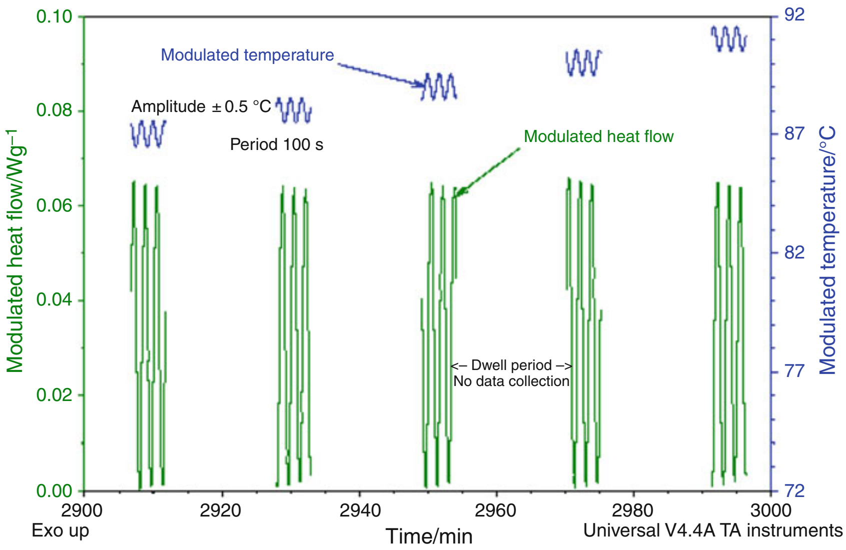


**Fig. 2** Parameter schematic for the QiDSC runs

calibrated with high purity metals (indium, lead, and zinc). A heating or cooling rate of 10 °C $\mathrm{min}^{-1}$ was used for all conventional DSC runs. The quasi-isothermal runs were done in the modulated mode using an amplitude of ±0.50 °C, a period of 100 s, and stepped incrementally every 1 °C. At each temperature step a dwell time where no data was collected of 15 min was used with a 5 min data collection. This can be noted in Fig. 2.

Glass transitions obtained from the reversing heat capacity signal were analyzed. The glass transition temperature, $T_g$, was determined as a midpoint. For quantification, the change in heat capacity, $\Delta C_p$, was determined by taking the heat capacity difference between the solid and liquid baselines at the $T_g$.

## Results and discussion

A property of the quasi-isothermal mode is that it allows a material to relax at a given temperature. For the two systems studied both had overlapping glass transition with a melting transition from the second component. For the first system a blend ratio of 50/50 and 75/25 of fluoro-copolymer to PS was used. Conventional DSC, as seen in Fig. 3, notes the glass transition of the PS at approximately 100 °C, the glass transition of the fluoro-copolymer at about –25 °C, and a broad melting with a peak temperature of approximately 115 °C. The PS glass transition is obscured by the melting transition.

**Fig. 3** Conventional DSC of the model system

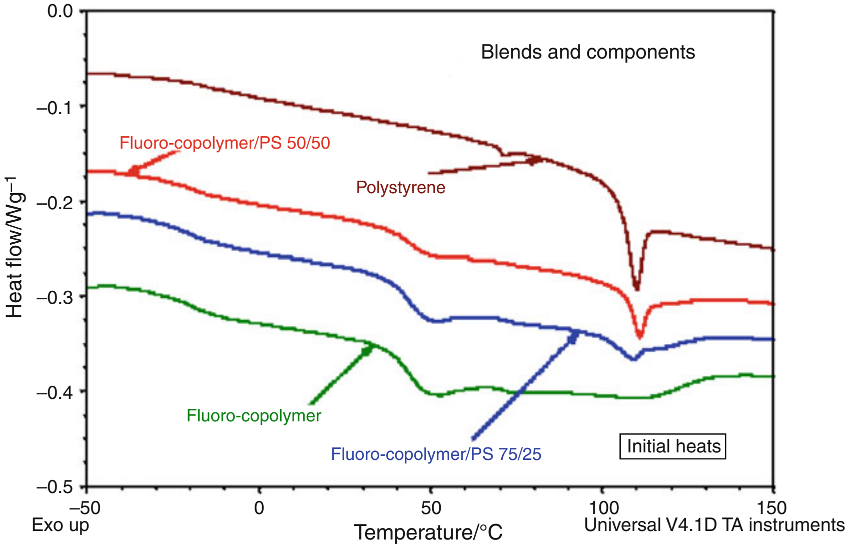


**Fig. 4** QiDSC of the model system. The *y*-axis is not in absolute heat capacity values but relative values for scaling

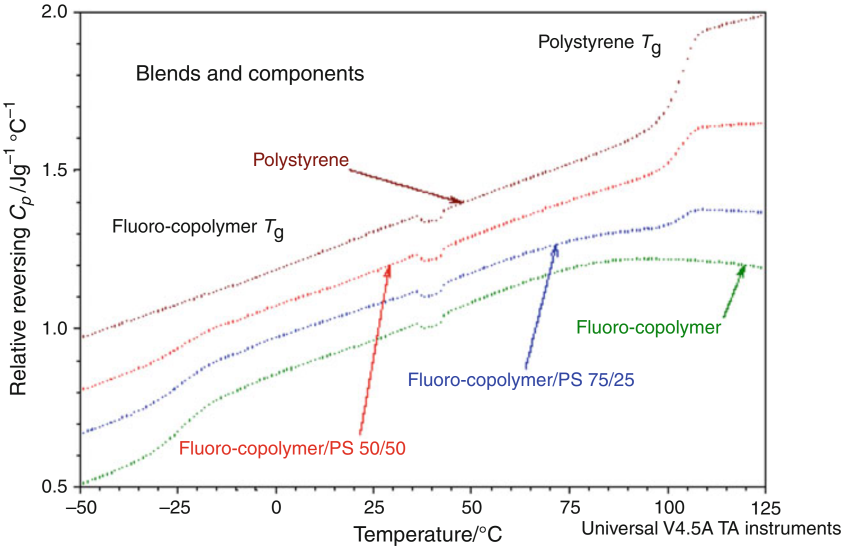


**Table 1** QiDSC Data for the lower and upper glass transitions

| Type | $T_{gL}$/ °C | $\Delta C_{pL}$/ J g$^{-1}$ °C$^{-1}$ | $T_{gU}$/ °C | $\Delta C_{pU}$/ J g$^{-1}$ °C$^{-1}$ |
|---|---|---|---|---|
| Polystyrene | | | 102.5 | 0.27 |
| Fluoro-copolymer/PS 75/25 (first blend) | −24.0 | 0.09 | 101.6 | 0.05 |
| Fluoro-copolymer/PS 50/50 (second blend) | −26.8 | 0.05 | 102.8 | 0.12 |
| Fluoro-copolymer | −22.4 | 0.12 | | |

**Table 2** Comparing expected values to experimentally determined values

| | Fluoro-copolymer Expected (%) | Fluoro-copolymer Calculated (%) | Polystyrene Expected (%) | Polystyrene Calculated (%) |
|---|---|---|---|---|
| First blend | 75 | 75 | 25 | 18 |
| Second blend | 50 | 42 | 50 | 44 |

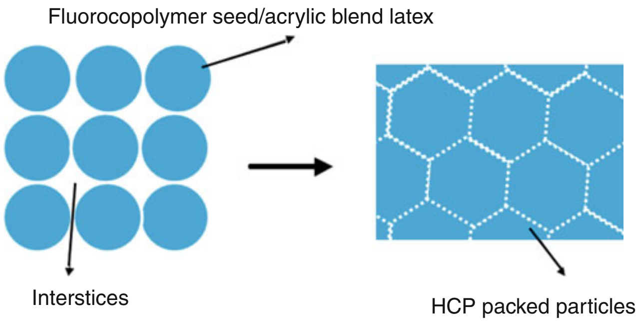


**Fig. 5** Pictorial representation of the latex film formation process. The *round spheres* can be noted by atomic force microscopy. During initial stages as water evaporates, latex particles come into irreversible contact. At a later stage osmotic pressure packs particles in hexagonal close packing (HCP) with clear boundaries, which become less defined as polymer chains reptate across boundaries shown by *dotted lines*

However, using QiDSC, the PS glass transition is now observable as noted in Fig. 4. Analyzing and quantifying the lower (L) and upper (U) glass transitions we can note that the experimental ratios from the $\Delta C_p$ determinations (normalized by the PS homopolymer or Fluoro-copolymer $\Delta C_p$ at $T_g$) are close to the expected formulated values. This is summarized in Tables 1 and 2.

The second system studied was of a fluoro-copolymer acrylic blend where the exact composition of the acrylic is uncertain since it was polymerized around a fluoro-copolymer seed. The morphology of the latex after air drying is that of a fluoro-copolymer particle embedded in an amorphous matrix as observed by atomic force microscopy, as illustrated in Fig. 5.

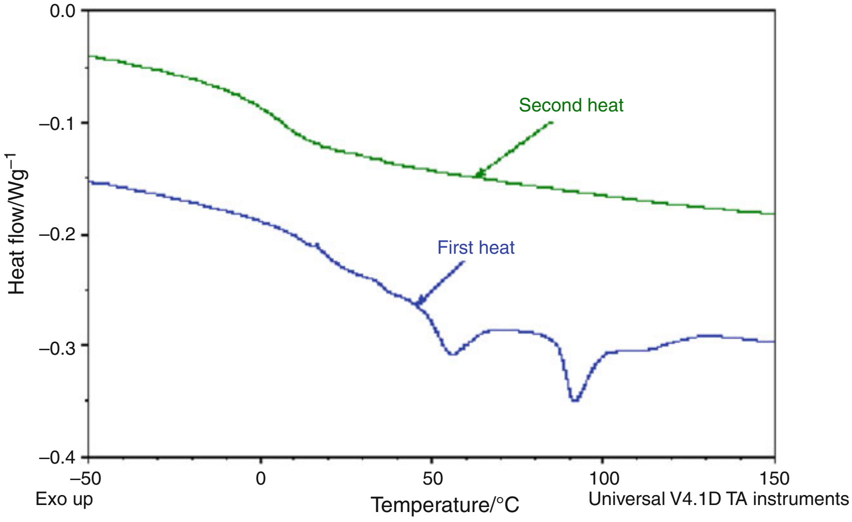
Determination of the degree of intermixing between the fluoro-copolymer and the acrylic phase is limited due to the semicrystalline melting peak. Reheating of the sample results in the loss of the crystallinity and only a single glass transition is noted (see Fig. 6).

Three ratios of fluoro-copolymer to acrylic were investigated: 50/50, 70/30, and 90/10. Conventional DSC shows not only the upper glass transition overlapping but for some blend compositions, the lower glass transition also overlaps, as noted in Fig. 7.

Using QiDSC, the glass transitions for both the fluoro-copolymer rich and the acrylic rich regions can now be clearly noted. The lower fluoropolymer rich glass transitions increase with acrylic content while the upper glass transition increases in magnitude with decreasing acrylic content as noted in Fig. 8.

The increase in glass transition temperature would confirm that the acrylic content is increasing. So it would be unexpected to see the acrylic rich glass transition to decrease in $\Delta C_p$ with increasing acrylic content. This may be related to how the blend was prepared or to the

**Fig. 6** Cycled DSC of a dried latex blend. No crystallinity is noted on the reheat



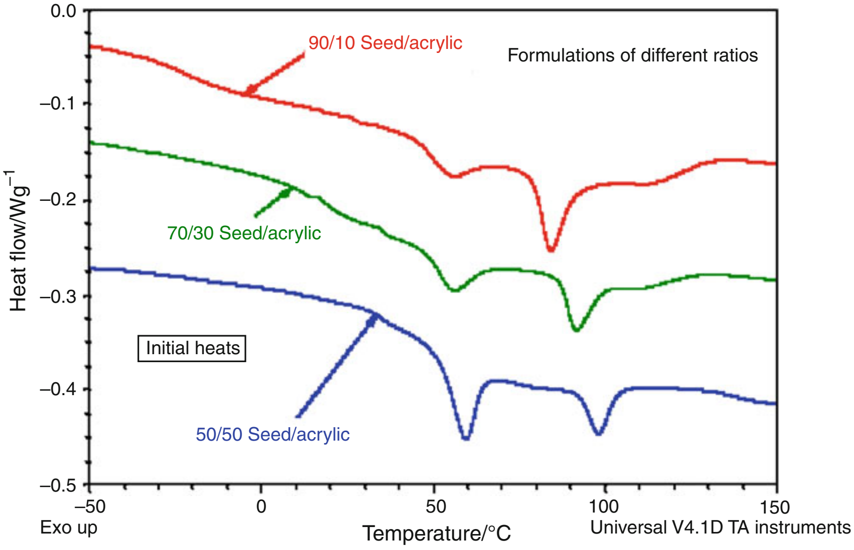


**Fig. 7** Conventional DSC of a dried fluoro-copolymer/acrylic latex

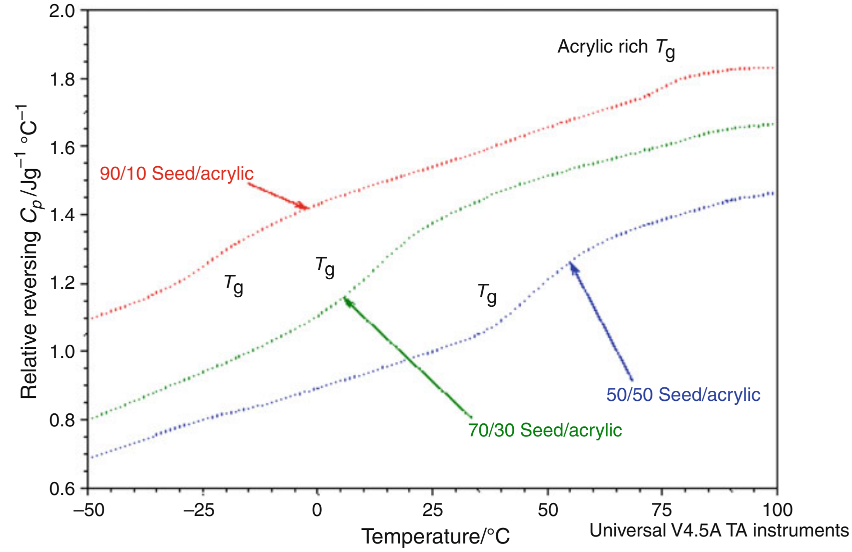


**Fig. 8** QiDSC of a dried fluoro-copolymer/acrylic latex. The *y*-axis is not in absolute heat capacity values but relative values for scaling

polymerization of the acrylic causing the percent incorporation of the acrylic to differ.

## Conclusions

Through the use of QiDSC, glass transitions that overlapped with melting transitions are now visible. This is preformed by allowing sufficient time for the material to melt revealing the underlying glass transition in the reversing heat capacity. The $\Delta C_p$ at the glass transition follows a dilution effect for a model system based on a fluoro-copolymer and polystyrene blends. Glass transitions for a fluoro-copolymer/acrylic can be noted in the QiDSC mode though also obscured by melting transitions. The acrylic rich glass transition for these blends increased in magnitude with decreasing acrylic content though the blend glass transition increased in temperature. This may indicate a difference in blending due to the preparation of the blend.

## References

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