



Quantification of Polybutadiene in an Elastomeric Blend by Tzero™ DSC and Modulated DSC®

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ABSTRACT

Polybutadiene is an elastomer widely used in industry (tires, belts, hoses, gaskets or seals) because of its mechanical and thermal properties, especially at low temperatures. It is very often used in combination with other elastomers or chemical compounds, and in blends at various percentages.

Polybutadiene is a diene polymer, made from a monomer containing two carbon-carbon double bonds, specifically butadiene, and is an amorphous material. Differential Scanning Calorimetry (DSC) is used to detect the glass transition temperature (1) as a change in heat capacity. In the case of a small amount of polybutadiene in the compound, traditional DSC may not have enough sensitivity to detect the glass transition temperature. Traditional limitations of DSC are overcome by the new Tzero™ technology (2) with its improvements in sensitivity, quality of baseline, resolution, and wider modulation conditions in modulated DSC® experiments.

INTRODUCTION

Differential Scanning Calorimetry (DSC) is used widely to characterize polymeric materials. Typical observed transitions include the glass transition of the amorphous phase, melting and crystallization processes, onset of oxidation, and heat capacity. Tzero DSC technology, with its attendant sensitivity and resolution, is ideal for examining the low energy processes which are generally associated with low content of an amorphous sample in a compound. Modulated DSC is another useful tool that helps in the determination and interpretation of the complex experiments, and is more sensitive.

EXPERIMENTAL

Two samples containing polybutadiene were characterized using Tzero DSC and Modulated DSC, to identify and quantify the components. The expected glass transition temperature is about $-100\text{ }^{\circ}\text{C}$ (3). To examine the materials for the glass transition, standard DSC at $20\text{ }^{\circ}\text{C}/\text{min}$ or Modulated DSC are applied. The DSC instrument is run in standard Tzero mode, with an automated liquid nitrogen cooling system. The

instrument is first calibrated with indium and cyclohexane for temperature, indium for heat flow, and sapphire for heat capacity.

The first sample is 100 % polybutadiene. The liquid nitrogen cooling system brings the sample from room temperature to $-170\text{ }^{\circ}\text{C}$ in less than eight minutes, and then the sample is heated at $20\text{ }^{\circ}\text{C}/\text{min}$. The glass transition temperature is clearly seen in Fig. 1 at $-104.5\text{ }^{\circ}\text{C}$, determined as the mid-point of extrapolated tangents. From the experiment, the step in heat capacity can be quantified as $0.336\text{ J}/(\text{g }^{\circ}\text{C})$. At a higher temperature, the amorphous material crystallizes and finally melts at $-17\text{ }^{\circ}\text{C}$ (3).

A second sample, known to contain a small amount of polybutadiene in a blend with another elastomer, is run under the same conditions in order to detect the glass transition and, if possible, calculate the step change in heat capacity. The Modulated DSC experiment is also performed to increase the sensitivity. The modulated DSC experiment is conducted at $3\text{ }^{\circ}\text{C}/\text{min}$ average heating rate with a amplitude of $\pm 1.5\text{ }^{\circ}\text{C}$ and a period of 60 s. These conditions give a high exchange of heat flow inside and outside of the sample, with a wide range of modulated heating and cooling rates in each cycle.

RESULTS AND DISCUSSION

Figure 1 shows the DSC thermal curve for 100 % polybutadiene sample. The glass transition involves an increase in heat capacity of $0.336\text{ J}/(\text{g }^{\circ}\text{C})$. This value is used as a calibration function for the quantification of amorphous polybutadiene.

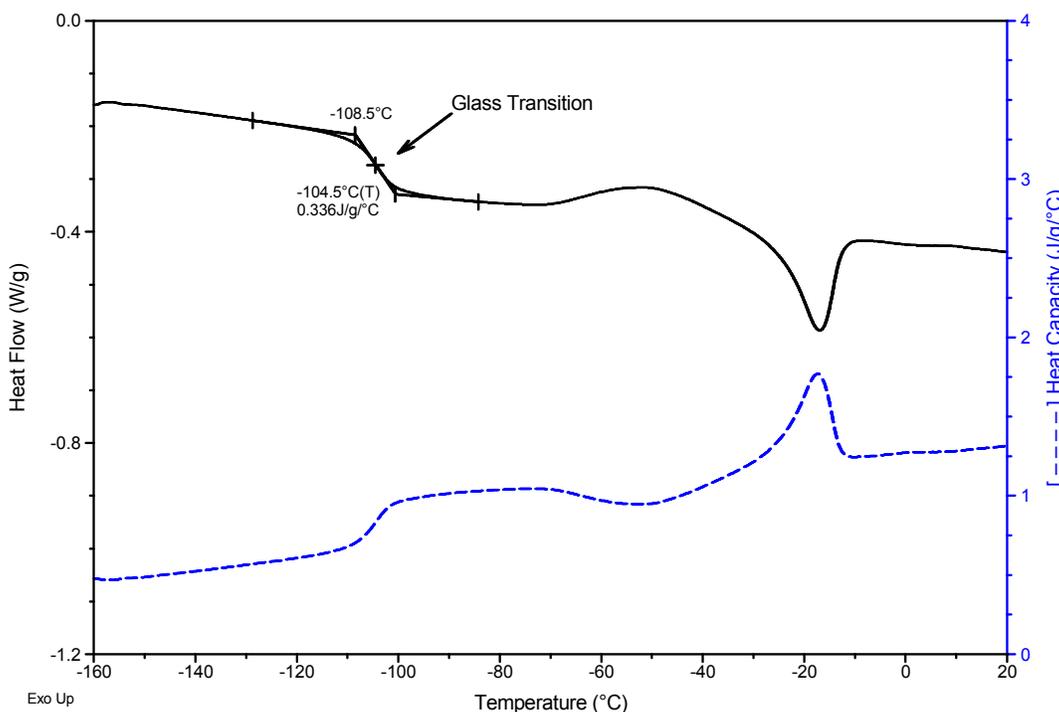


Figure 1 – DSC Curve for 100 % Polybutadiene

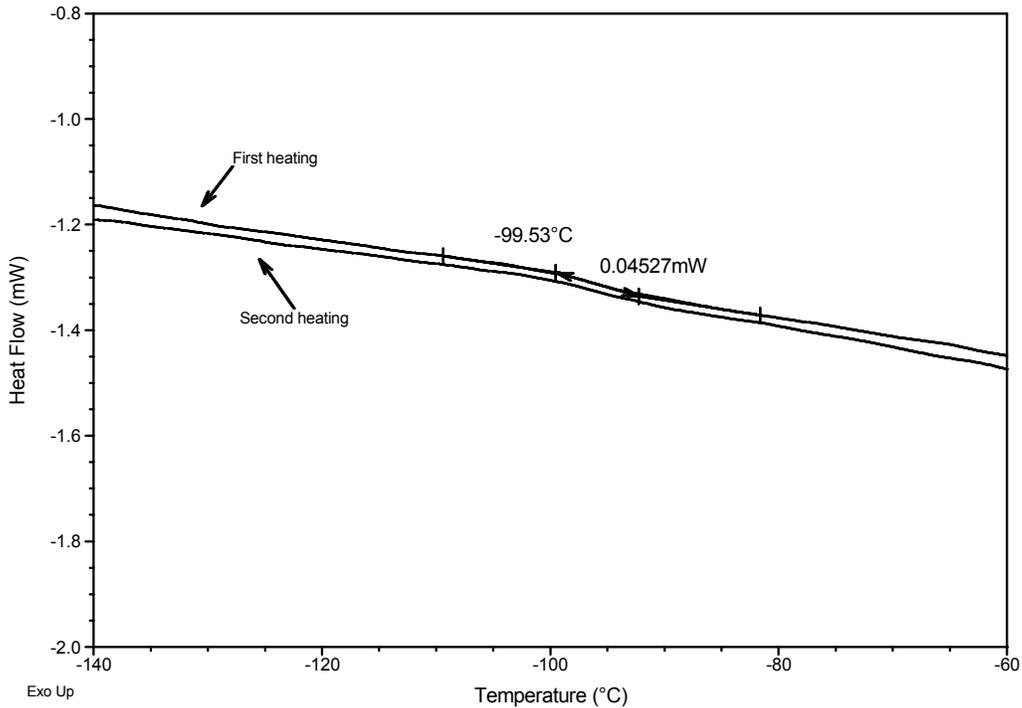


Figure 2 – DSC Curve of the Low Content Polybutadiene Level Sample

Figure 2 shows the traditional DSC result of replicate heating at 20 °C/min of the low polybutadiene co-polymer, the glass transition is visible by standard DSC. The

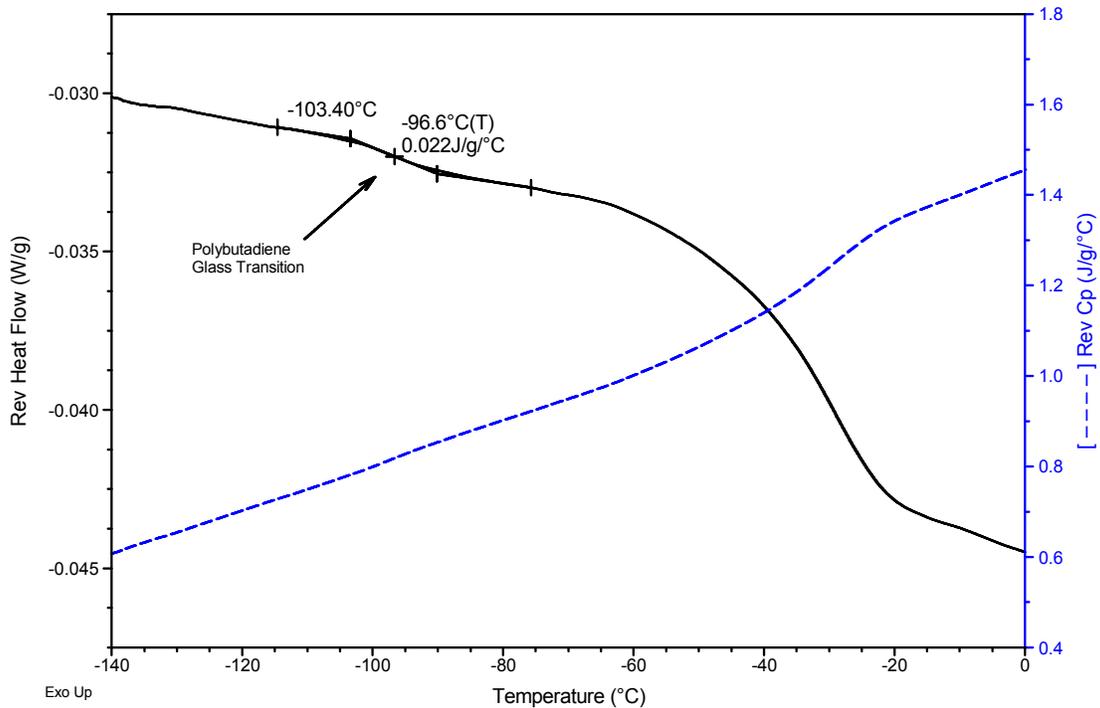


Figure 3 – Modulated DSC of Low Content Polybutadiene Sample

change in heat flow is only 45 μ W, and although it can be detected by the DSC experiment, the determination of the glass transition is difficult.

Figure 3 shows the reversing heatflow and heat capacity the modulated DSC experiment. The glass transition is clearly seen in both signals, and the change in heat capacity is calculated as 0.022 J/(g °C). To quantify the amount of polybutadiene in the blend sample, this result is divided by the heat capacity change for 100 % polybutadiene yielding $(0.022 \text{ J/(g °C)} / 0.336 \text{ J/(g °C)}) \times 100 \% = 6.6 \% \text{ polybutadiene}$.

CONCLUSION

The weak glass transition of elastomers and the amount of each component in blends are easily determined and quantified using the high sensitivity of Tzero and Modulated DSC.

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KEYWORDS

differential scanning calorimetry, elastomers, glass transition, modulated differential scanning calorimetry, polybutadiene

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