Characterization of Bitumen by Modulated Differential Scanning Calorimetry and High Resolution Thermogravimetric Analysis

Els Verdonck, Ph. D.
TA Instruments-Waters LLC, Brusselsesteenweg 500, 1731 Zellik, Belgium

ABSTRACT

This paper discusses the characterization of the glass transition (Tg) of bitumen by MDSC®, as well as a method allowing quick fingerprinting of bitumen by using Hi-Res™ TGA.

INTRODUCTION

Bitumen is a viscous hydrocarbon used in numerous building applications, *e.g.* paving of roads and waterproof sealing of roofs.

It is important to characterize the glass transition of the bitumen, as the mechanical properties of the material undergo a significant change at this temperature. In general, DSC is very suitable to detect even weak glass transitions. However, in cases where other thermal events occur in the same temperature range as the Tg, Modulated DSC® provides the capability for separation. This will be shown to be required for the Tg detection of bitumen.

A constant chemical composition of the bitumen is often required for its applications. TGA is useful in obtaining quick fingerprinting of composition of various samples. In addition, TGA allows determination of the composition of materials if the various constituents decompose in a different temperature range. In cases where there is overlap between the degradation of the components of a complex mixture, High-Resolution TGA techniques are often necessary for accurate fingerprinting of the material.

EXPERIMENTAL

A TA Instruments Q2000 DSC equipped with a refrigerated cooling system (RCS90) was used in this study to measure the Tg of the bitumen. The Q2000 DSC is based on Tzero™ technology[1]. Tzero technology takes into account the intrinsic asymmetry between sample and reference sensor in a DSC. As a result, the instrument baseline is extremely flat and the resolution is improved dramatically. Baseline flatness allows for easier interpretation of broad and weak transitions such as the Tg of bitumen. Modulated DSC technology allows the separation of difficult-to-interpret and complex heat flow into reversing and nonreversing components. This is achieved by superimposing a sine wave modulation on the linear heating profile[2]. The reversing heat flow mainly contains heat capacity events such as the Tg, while the nonreversing heat flow includes kinetic effects such as enthalpy recovery, crystallization, and evaporation.

Temperature and enthalpy calibration of the DSC were performed with an indium standard; the heat capacity calibration was performed with a sapphire sample. The DSC was purged with nitrogen gas (50 ml/min). A 10 mg sample was sealed into an aluminum pan and a heating rate of 4°C/min was applied with a modulation amplitude of 0.5°C and a period of 40 sec.

Fingerprinting of the bitumen was performed with a TA Instruments Q5000IR TGA. Among many other features, the Q5000IR boasts extremely tight temperature control of the balance chamber, ensuring baseline flatness to within 10 micrograms[3]. A flat baseline is indispensable for accurate quantification of very small weight losses. Furnace heating is provided with infrared light, allowing for very fast controlled heating rates up to 500°C/min. The incorporated Hi-Res TGA™ technique accommodates better separation of overlapping decomposition events and therefore easier fingerprinting. With Hi-Res TGA, the heating rate is continuously changing in response to changes in the rate of decomposition of the sample[4]. There are multiple modes of operation available. In the dynamic rate mode the heating rate is continuously varied between a fixed minimum (>0°C/min) and the specified maximum, according to an algorithm that depends upon the resolution and sensitivity settings. In the constant reaction rate mode the heating rate is changed (and even cooling can occur) in order to keep the rate of decomposition constant. The stepwise isothermal approach consists of heating at constant rate until a weight change begins (defined by an operator chosen rate) and then holding isothermally until the weight change is complete (again defined by an operator chosen rate).

Temperature calibration of the TGA was performed with Curie point standards (alumel and nickel). The TGA balance was purged with nitrogen gas, and the furnace purged with air. A sample weight of 4 to 6 mg was loaded in a platinum TGA pan. Standard TGA runs were measured at a heating rate of 10°C/min. For the experiments in constant reaction rate mode a threshold of 0.316%/min was used. In the dynamic rate mode the maximum heating rate was 50°C/min, with a resolution setting 3 and sensitivity 5. An excellent overview of the optimization of these parameter settings for similar materials as the ones in this study is found in Reference 5.

RESULTS & DISCUSSION

Figure 1 contains the MDSC heating results of a bitumen sample. From the Total Heat Flow signal (green curve) it is difficult to determine the sample's Tg, as there are multiple overlapping transitions. However, the Reversing Heat Flow (blue curve) clearly shows the very broad (~40) Tg of the bitumen around –18°C. In the Nonreversing Heat Flow component (red curve) a small cold crystallization peak (2.7 J/g) is visible near –16°C and melting at about 50°C. The cold crystallization probably results from the wax fraction that was unable to crystallize during the relative fast cooling because of mobility restrictions. On heating, this fraction acquires the necessary mobility for crystallization at the moment that the bitumen devitrifies. Closer inspection of the broad Tg region is accomplished by looking at the derivative of the Reversing Heat Flow. This signal shows two peaks (Figure 2), indicating that instead of a single Tg there are actually two Tg's in this region: one around -27°C and a second one around -7°C.

Figure 3 contains the standard TGA measurement of two different bitumen samples. From the weight loss curves it is difficult to distinguish between these samples. There seems to be three characteristic decomposition regions: from 200-350°C, 350-475°C, and above 475°C. Very good fingerprinting of these different regions can be obtained with Hi-Res TGA, using different modes for the different regions[5]. Figure 4 shows that for the lower temperature region excellent separation and fingerprinting is obtained in constant reaction rate mode (threshold 0.316 %/min). For Sample 1 a duplicate test is shown, illustrating the excellent reproducibility of this hi-res TGA technique. For the middle and higher temperature region the best fingerprinting is obtained in dynamic rate mode (Figure 5).

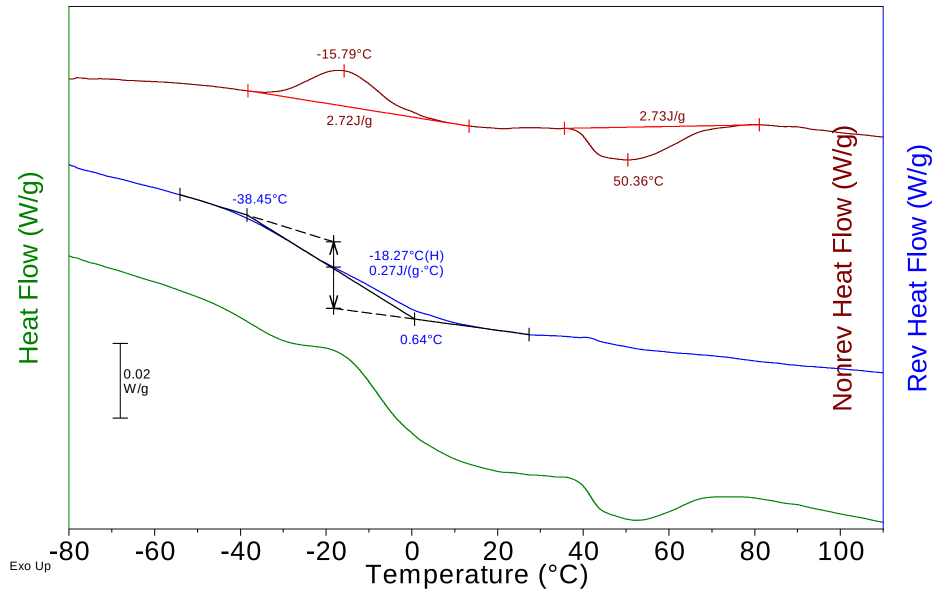

Figure 1: MDSC heating run of bitumen sample after cooling at 20°C/min

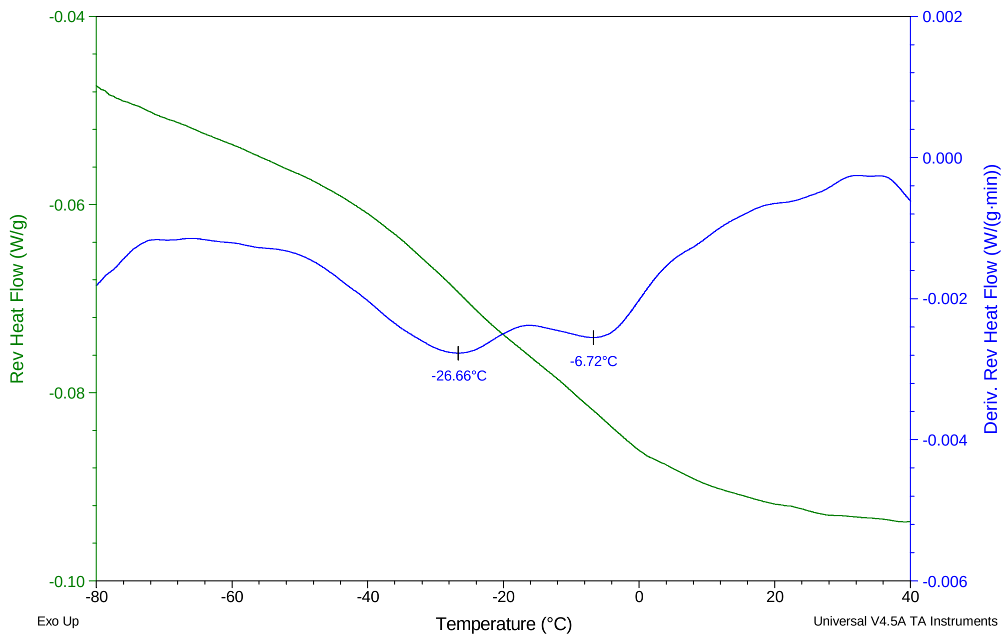

Figure 2: Reversing heat flow and its derivative of bitumen sample

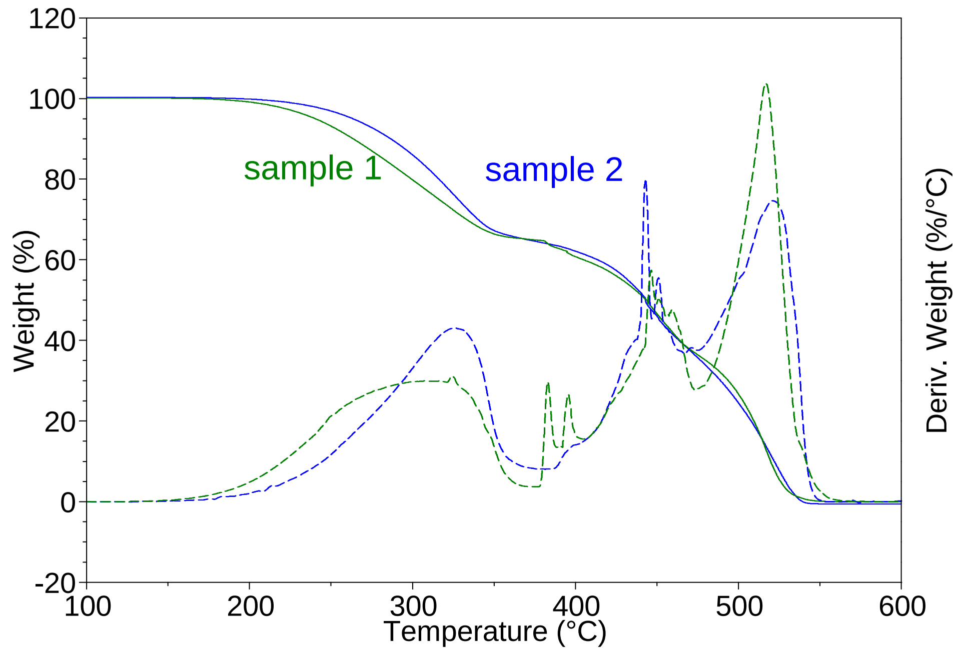

Figure 3: TGA runs at 10°C/min of 2 different bitumen samples

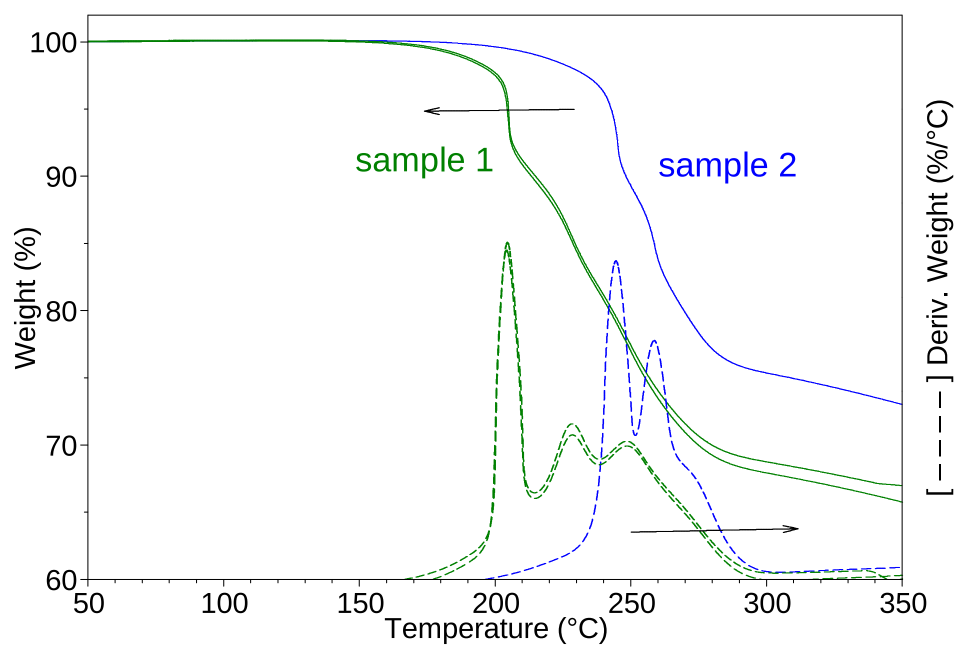

Figure 4: TGA runs (constant reaction rate) of the same bitumen samples as in Figure 3 (lower temperature range only)

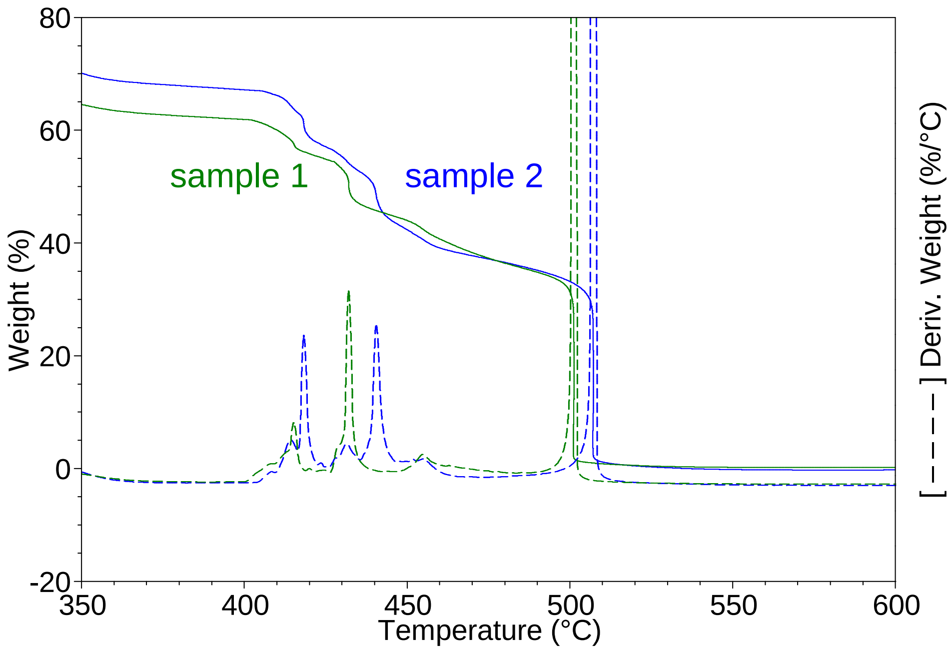

Figure 5: TGA runs (dynamic rate) of the same bitumen samples as in Figure 3 (middle and higher temperature range only)

CONCLUSIONS

The data presented illustrate the ease of determination of the Tg of bitumen with MDSC, despite an overlapping cold crystallization effect. Closer observation reveals a double Tg instead of a single broad Tg.

By using different modes of Hi-Res TGA™ excellent fingerprinting of different bitumen can be accomplished. For these bitumen samples the mode giving the best results depends upon the decomposition temperature range that is studied.

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KEY WORDS

DSC, MDSC, TGA, Hi-Res TGA, Bitumen, Glass transition temperature

TA Instruments

United States
109 Lukens Drive, New Castle, DE 19720 • Phone: 1-302-427-4000 • E-mail: info@tainstruments.com

Canada
Phone: 1-905-309-5387 • E-mail: shunt@tainstruments.com.

Mexico
Phone: 52-55-5200-1860 • E-mail: mdominguez@tainstruments.com

Spain
Phone: 34-93-600-9300 • E-mail: spain@tainstruments.com

United Kingdom
Phone: 44-1-293-658-900 • E-mail: uk@tainstruments.com

Belgium/Luxembourg
Phone: 32-2-706-0080 • E-mail: belgium@tainstruments.com

Netherlands
Phone: 31-76-508-7270 • E-mail: netherlands@tainstruments.com

Germany
Phone: 49-6196-400-7060 • E-mail: germany@tainstruments.com

France
Phone: 33-1-304-89460 • E-mail: france@tainstruments.com

Italy
Phone: 39-02-2742-11 • E-mail: italia@tainstruments.com

Sweden/Norway
Phone: 46-8-555-11-521 • E-mail: sweden@tainstruments.com

Japan
Phone: 813-5479-8418 • E-mail: j-marketing@tainstruments.com

Australia
Phone: 613-9553-0813 • E-mail: sshamis@tainstruments.com

India
Phone: 91-80-2839-8963 • E-mail: india@tainstrument.com

China
Phone: 8610-8586-8899 • E-mail: info@tainstruments.com.cn

Taiwan
Phone: 886-2-2563-8880 • E-mail: skuo@tainstruments.com

Korea
Phone: 82.2.3415.1500 • E-mail: dhrhee@tainstruments.com

To contact your local TA Instruments representative visit our website at www.tainstruments.com