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CALCULATION OF SMOOTHING FACTORS FOR THE COMPARISON OF DSC RESULTS

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Complex mixtures of long chain organic compounds often show overlapping glass transition temperatures (T_gs) when analyzed by differential scanning calorimetry (DSC) or modulated DSC (MDSC). In such cases, subjective and inconsistent smoothing of data acquired under different conditions can lead to the misinterpretation of results. A quantitative method for the selection of smoothing factors for the analysis and comparison of (M)DSC results is presented. The method is most useful for the analysis of the derivative of the heat capacity, dC_p/dt or dC_p/dT, plots which best highlight overlapping T_gs. Four equations are shown to relate the heating rate and the smoothing factor. The equations allow a comparison of data acquired *i*) at different heating rates and plotted *vs.* temperature, *ii*) at a single heating rate and plotted *vs.* both time and temperature, i.e., dC_p/dt *vs.* dC_p/dT, *iii*) at different heating rates and plotted *vs.* both time and temperature, and *iv*) at different heating rates, and shown exclusively in the time domain. Examples of the use of the equations are provided for the analysis of bitumen, a complex mixture of natural origin.

Keywords: *bitumen, data analysis, differential scanning calorimetry (DSC), modulated differential scanning calorimetry (MDSC), smoothing*

Introduction

Differential scanning calorimetry (DSC) and modulated DSC (MDSC) are used to measure the enthalpy of transitions and the heat capacity of materials [1–5]. DSC has a long history [3, 4], with its foundation in thermodynamics firmly established by the turn of the 20th century [6]. MDSC is more recent [5]. Despite the long history of calorimetry and the widespread use of (M)DSC, it can be difficult to acquire the knowledge for their proper use. Formal training is possible at less than 4% of science and engineering departments in the USA [4], and day- or week-long courses are often limited to basic techniques and analysis. The identification of artefacts is seldom discussed in the literature [7], and the issue of smoothing is absent from textbooks [2, 3].

In scanning calorimetry, the heat flow from the sample is superimposed with a random signal, best described as noise. Generally, the removal of noise (smoothing) requires filtering, or digital processing, of the signal either in the time or the frequency domain [8]. In the frequency domain, smoothing is applied to the Fourier transform of the signal, a common method to filter spectroscopic data [9]. In calorimetry, heat flow is monitored against time and temperature, and smoothing is done in the time or temperature domains on data acquired at regular intervals, where the most common methods of smoothing are the *n*-point moving average and the method of least squares [10, 11].

The choice of smoothing factors in (M)DSC analysis is operator dependent and, most often, very subjective. In DSC, the level of smoothing is often unimportant, but with MDSC [5] it can have a much greater effect on interpretation. A case in point is the study of glass transition temperatures (T_g) in complex mixtures such as bitumen [12, 13], where several, and sometimes overlapping, T_gs show as maxima in the derivative curves of the heat capacity, dC_p/dt or dC_p/dT. Figure 1 shows that bitumens have 2 to 4 strong T_gs and possibly several small ones. For insightful comparisons of the underlying material struc-

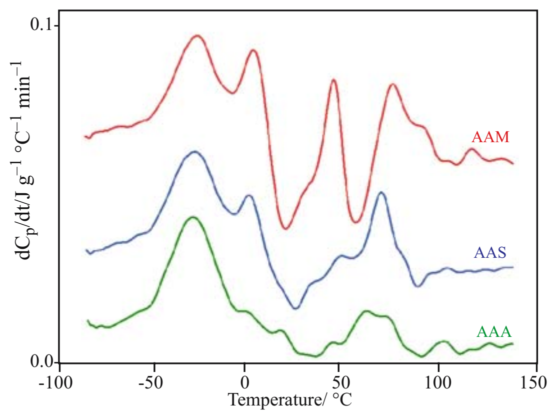

Fig. 1 Derivative curves of the heat capacity for three bitumens after a first heat run at 5°C min^{-1}. Curves are offset for better display

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tures that give rise to the T_gs, smoothing must not affect interpretation.

The problem with the subjective selection of smoothing factors is especially acute when data acquired under different conditions must be compared, or when results are acquired at different times in the year, sometimes by different operators. To the authors' knowledge, there is no method that allows for the selection of smoothing factors such that the effects of different experimental conditions on the results are unambiguous and void of effects due to inconsistent smoothing.

In this paper, it is shown that the problem with the proper selection of smoothing factors in (M)DSC can be addressed with four equations that provide for an equal basis of comparison, thus providing for more consistent data treatment and helping to avoid possible misinterpretation. This is demonstrated for dC_p/dt or dC_p/dT curves, but it applies equally well to all (M)DSC results. The equations apply to the analysis of data acquired under different conditions or displayed in different domains (time or temperature). In this respect, the choice of appropriate smoothing factors for three scenarios is presented: a) data acquired at different heating rates; b) data compared across time and temperature domains (dC_p/dt *vs.* dC_p/dT); and combinations of a) and b).

Experimental

The data were acquired with a DSC-2910 from TA Instruments. The data collection rate was 5 points/second, and the heating rates were 1, 3 and 5°C min^{-1}. The results were those for bitumen between –100 and 150°C. The derivative of the heat capacity, dC_p/dT or dC_p/dt, was obtained from the reversing (M)DSC signal [5, 12, 13].

The DSC signals were smoothed with software from TA Instruments, Universal Analysis 2000, version 4.1d, for which smoothing is based on the method of least-squares and where a minimum of five data points are used for calculations. The input for smoothing was the width of the region to be smoothed, either in min or in °C.

Results and discussion

Smoothing for different heating rates in the temperature domain (dC_p/dT)

Figure 2 shows unsmoothed dC_p/dT curves for heating rates of 1, 3 and 5°C min^{-1}. The faster was the heating rate, the smoother was the data. In such a comparison, it is difficult to determine the effect of heating rate on a transition that may be of interest, and to avoid interpreting noise. In Fig. 2, this was especially true away from the main transition at –50 to 20°C. Various smoothing factors could be applied to the curves by trial and error until they appear to have a uniform smoothness, but the results would be operator dependent.

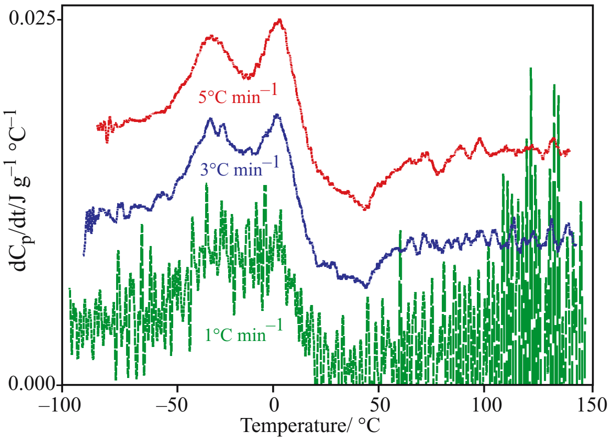

Fig. 2 Unsmoothed temperature derivatives of the heat capacity for a bitumen heated at 1, 3 and 5°C min^{-1}. Curves are offset for better display

To correctly smooth data in the temperature domain acquired at different heating rates (e.g., Fig. 2), there must be an equal basis for comparison after smoothing. In a manner analogous to n-point averaging, a possible basis of comparison might be to select an equal number of data points (N^T) for each curve, as calculated from

$$I/H=G \quad (1)$$

$$GS(T)=N^T \quad (2)$$

where I is the fixed instrument sampling rate in points (pt)/min, H is the heating rate in °C min^{-1}, G is the experimental sampling rate in pt/°C, and $S(T)$ is the smoothing interval in the temperature domain in °C. On the basis of Eq. (2), the number of data points is equal for two different conditions (i, j) if

$$G_iS(T)_i=G_jS(T)_j=N^T \quad (3)$$

Table 1 shows the results obtained from the application of Eq. (3) on the three heating rates in Fig. 2. These results show that an increase in heating rate would require greater smoothing, which is contrary to experience.

Table 1 Calculation of the smoothing factor based on Eq. (3)

H/ °C min^{-1}	I/ pt/min	G/ pt/°C	$S(T)$/ °C	N^T/ pt
1	300	300	3	900
3	300	100	9	900
5	300	60	15	900

The roughness of the curves in Fig. 2 suggest that less smoothing would be required with an increase in heating rate. The dC_p/dT curve obtained at the highest heating rate appears smoother because there are fewer data points. With the instrument sampling rate, I=300 pt/min, Table 1 shows that the number of data points in the temperature domain (G) was 300, 100, and 60 after one minute at the respective rates of 1, 3 and 5°C min^{-1}.

To provide for a proper normalization of the data sets with the application of smoothing in accordance with experiment, G must be divided by S such that

$$G_i/S(T)_i=G_j/S(T)_j=\nu \quad (4)$$

where ν is the normalized number of data points per °C, with units of *pt*/°C^2. With a substitution for G from Eq. (1), (4) is conveniently written in terms of heating rate as

$$H_iS(T)_i=H_jS(T)_j \text{ (units of °C}^2\text{ min}^{-1}) \quad (5)$$

This equation can be used to calculate the smoothing factors for the proper comparison of any (M)DSC data in the temperature domain and obtained at different heating rates (Table 2). Figure 3 shows examples of the application of Eq. (5). Two sets of S(T) values are shown based on the unsmoothed dC_p/dT curves in Fig 2. In Fig. 3, only data within a set can be compared, in this instance, to reveal the effect of heating rate on the amorphous phases that give rise to glass transition temperatures. The upper set in Fig. 3 shows that an increase in heating rate affects the ratio of the two main phases that give rise to the twin transitions between –50 and 20°C. The figure also shows that an increase in $S(T)$, say from 6.7 to 13.3°C, to flatten the apparent noisy curve of the data acquired at 3°C min^{-1} between 40 and 150°C, would not provide for a proper comparison of the main transitions as it blends the twin transitions into one. With the proper smoothing, it could be argued that the weak but multiple maxima between 40 and 150°C arise from secondary amorphous phases, also affected by the heating rate, but this argument could not be made with greater smoothing.

Table 2 Calculation of smoothing factors based on Eqs (4) and (5)

H/ °C min^{-1}	G/ pt/°C	$S(T)$/ °C	ν/ pt/°C^2
1	300	5.0	60
3	100	1.6	60
5	60	1.0	60

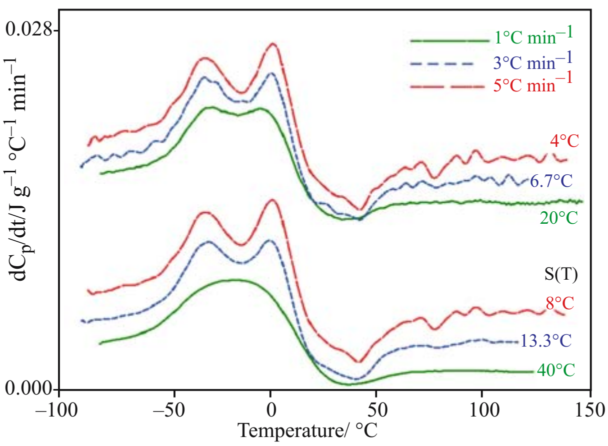

Fig. 3 Smoothed curves from Fig. 2. The smoothing factors $S(T)$ were calculated with Eq. (5). Curves are offset for better display

Comparison across the time and temperature domains (dC_p/dt vs. dC_p/dT)

In some cases, it might be necessary to compare two DSC curves, one represented in the time domain and the other in the temperature domain. Most often the tendency is to use the same smoothing factor for each curve, but then the smoothness of the curves are different (top of Fig. 4). To compare data from one heating rate across time and temperature domains, the number of data points in both domains must be equal, $N^T=N^t$, or

$$GS(T)=IS(t) \quad (6)$$

With a substitution for G from Eq. (1), (6) can be written

$$H=S(T)/S(t) \quad (7)$$

Equation (7) allows for the selection of proper smoothing factors to compare data from a single heating rate across the time and temperature domains. The bottom curves in Fig. 4 shows dC_p/dt *vs.* dC_p/dT

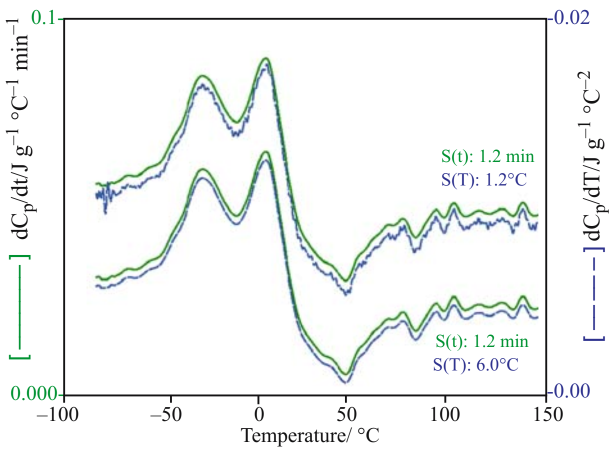

Fig. 4 Time and temperature derivatives of the heat capacity. The smoothing factors were calculated with Eq. (7). Curves are offset for better display

curves with respective $S(t)$ and $S(T)$ factors calculated based on Eq. (7). The curves are identical in shape and smoothness.

In a more complex scenario, where data from different heating rates are compared across the time and temperature domains, one smoothing factor in Eq. (5) is substituted for its equivalent in Eq. (7) to give

$$H_iS(T)_i=(H_j)^2S(t)_j \quad (8)$$

Equation (8) allows for the comparison of dC_p/dt *vs.* dC_p/dT curves for data acquired at different heating rates. Figure 5 shows an example of its use where the dC_p/dt curve was obtained at 3°C min^{-1} and the dC_p/dT curve was obtained at 5°C min^{-1}.

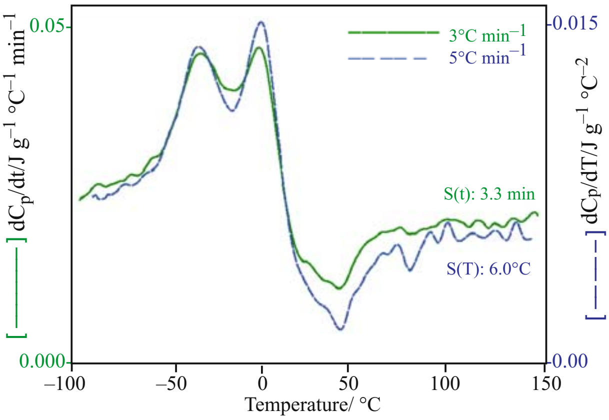

Fig. 5 Time and temperature derivatives of heat capacity acquired at 3 and 5°C min^{-1}. The smoothing factors were calculated with Eq. (8)

Comparison of derivative curves in the time domain (dC_p/dt)

Given Eq. (5) for the temperature domain (dC_p/dT), one might assume that it could apply equally well to the time domain, but this is not the case. The substitution of the remaining $S(T)_i$ in Eq. (8) for its equivalent in Eq. (7), leads to an equation expressed exclusively in the time domain

$$(H_i)^2S(t)_i=(H_j)^2S(t)_j \quad (9)$$

This equation is analogous to Eq. (5) except that the heating rates are squared. As with the other equations, Eq. (9) may be used to compare the time domain for any (M)DSC results acquired at different heating rates, but it is most useful to compare the dC_p/dt derivatives. Figure 6 shows two examples of $S(t)$ for yet another bitumen heated at two different heating rates. With equal smoothness, the effect of the different experimental conditions becomes unambiguous. It the case of bitumen, a higher heating rate highlights the weaker transitions.

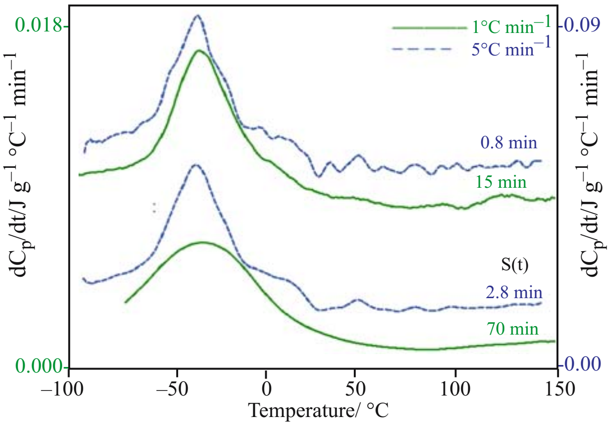

Fig. 6 Time derivatives of heat capacity acquired at 1 and 5°C min^{-1}. The smoothing factors $S(t)$ were calculated with Eq. (9)

Table 3 Representative sets of smoothing factors for various heating rates

H/°C min^{-1}	$S(T)$/°C	$S(t)$/min
1	10	10
2	5	2.5
3	3.3	1.1
4	2.5	0.7
5	2	0.4

As shown above, there are four key equations to select appropriate smoothing factors. With the factors in Table 3, for instance, Eqs (5) and (9) are used to move vertically in the temperature and time domains, respectively. Equation (7) is used to move horizontally from $S(T)$ to $S(t)$ and vice-versa, whereas Eq. (8) is used to move diagonally from one column to the next.

Conclusions

(M)DSC results acquired at different heating rates and represented in the time or the temperature domains are generally compared after a trial and error selection of smoothing factors. To circumvent the subjectivity of this process, four equations that relate the heating rate and the smoothing factor were developed. These equations allow an easy conversion of the results from the temperature to the time domain, and vice-versa, and provide for an equal basis to compare data acquired at different heating rates. The equations are especially useful in the comparison of dC_p/dT and dC_p/dt derivatives used to highlight T_gs in complex mixtures.

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