Journal of Thermal Analysis, Vol. 31 (1986) 875–881

MODIFICATION OF THERMAL TECHNIQUES: DERIVATIVE, DIGITAL FILTER, FOURIER TRANSFORM

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(Received March 19, 1985; in revised form October 28, 1985)

Continued efforts to identify compatible or incompatible blends have demonstrated a need to separate overlapping curves or peaks in a thermal trace. One way to do this is by using the derivatives of these curves. While the function is available on most modern thermal analysis units, its usefulness is often limited by noise in the system. Two techniques which can help to greatly reduce noise are digital filtering and Fourier transformation of the data. Both approaches have been used on identical sets of noisy data. The FT method appears to offer greater potential for producing useful derivatives from noisy composite curves.

The past few years have seen an increased interest in the utilization of polymer blends. One of the more pragmatic ways of characterizing compatibility in these blends is through the use of thermal techniques, primarily, DSC or DTA. Indeed, utilization of DSC to measure the glass temperature (T_g) of a mixed system is often how compatibility is defined. If there are a number of overlapping T_g's in a system then difficulty is associated with identifying and separating out the individual components.

Based on the above observations there is a clear need to develop techniques which will assist in separating "*s*-shaped" curves. One of the obvious approaches would be to take the derivative of the thermograms; this function is often available on many modern machines. In practice, however, with real systems, the data needs to be smoothed. Taking the derivative of a set of consecutive data points multiplies the high frequency component and the result is often a jumble of noise. One method recently developed for smoothing data is the use of digital filters. This effectively modifies the signal on a point by point basis, so that no one point is allowed to deviate too far from its neighbors. An alternative approach is to attempt to remove the high frequency components (or the noise) by using the Fourier transform of the data [1]. The Fourier transform (FT) of a data set produces a frequency spectrum

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which can be examined, and the high frequency components discarded. The frequency components may then be converted back to the temperature scale through use of the inverse transform.

Experimental

Model s-shaped curves are generated from a normal Gaussian distribution and represent cumulative areas for such a distribution. The total area is assumed to be contained within $\pm 4\,\sigma$. The "width of the curve" is taken as the separation in "x" from one base line portion of the s-shape to the next i.e. it is approximately $8\,\sigma$. When "noise" is introduced into the thermogram a random number generator is used to determine some random fraction of 5% of the maximum "y" value of the s-shape. This fraction is then added to the y value at the current data point as we step through the curve.

Digital filtering is achieved by the following manipulation. An array of consecutive data points $A_1 \ldots A_n$ is taken at equal x intervals. A "B" array is then defined such that $B_i = KA_i + (1-K)A_{(i-1)}$, where K is some fraction, that is typically 0.5 to 0.9, set by the operator. Once a "B" array is obtained a "C" array can be similarly generated, for any number of desired passes of the filter. Needless to say a number of alternatives can be used and optimized for the users particular application. This rather simple method has been widely used by electrical engineers in electronic filter circuits.

The Fourier Transform method used by the author is nominally labelled as "fast", however I choose to use a modification of a Basic version of an FT method in order to be better able to manipulate the components [2]. The number of data points taken was 256, these were derived from the s-shaped curves, which were folded about the last "x" value to produce a continuous "discrete" curve. In effect the s-shaped curve was sampled 128 times. After generating the frequency spectrum, the relatively low intensity but high frequency terms were set to zero, and a new s-shaped curve generated by inverse transformation of the modified frequency spectrum. All programing was carried out on a 48 K Apple II +, in Basic (Applesoft).

Results and discussion

The problems associated with separating out s-shaped curves can be seen in Fig. 1. Here we plot a combination of two s-shaped curves. The numbers on the right refer to the separation versus the "width" of the curve. If two curves of this type are

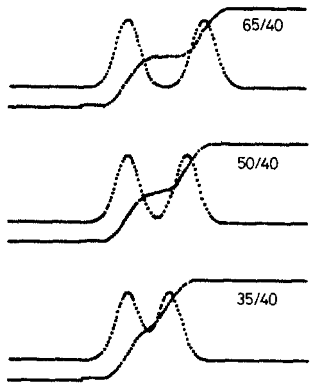

Fig. 1 Plots of idealized DSC traces and their derivatives; mixture with no interaction between components. Various ratios of separation of inflection points for the two components *vs.* width of a transition region are shown a) 65/40, b) 50/40, c) 35/40

combined then a complex "double *s*" is obtained. One can still easily determine that there are two curves involved provided that the separation is significantly larger than the width of these curves, Fig. 1a. However, when separation and width are approximately the same, for example in Fig. 1c, it is more difficult to identify that there are two curves involved. However, in this case, the derivative of these curves clearly shows two peaks and can be used to identify the inflection points of the curves. If separation gets closer than shown in Fig. 1c; then even taking the derivative is of little value. For example, if separation to width ratio is on the order of 20/40 then only a single flat topped peak is obtained.

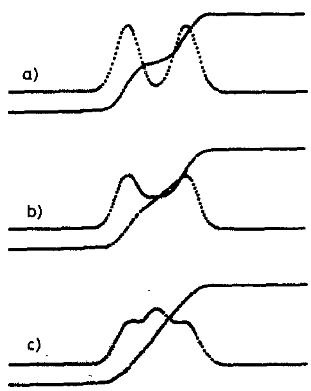

Fig. 2 Plots of idealized DSC traces and derivatives for a 2 component mixture in which various amounts of "compatibility" are envisioned. a) No compatibility—simple mixture; S/W = 50/40. b) 20% of each components mixes to form a compatible system; the remaining 80% unperturbed. c) 40% of each component mixes to form a compatible system

Further problems are encountered when we move to compatible systems. In this particular case (Fig. 2) we are allowing the two components to blend to varying degrees. For example, in curve 2b we have allowed 20% of each of the individual components to blend together. In this way we have generated a complex T_g due to 80% of original material 1, plus 80% of original material 2, and a blend of 20% of each of the two components. In Fig. 2c we see from the derivative that a 40% blend produces 3 separate peaks. The blend peak is clearly identified, and "shoulders" of the original components can be seen on the derivative plot. However, if we examine the original co-added *s*-shaped curve we would be hard pressed to identify anything more than a single transition.

The latter two figures have been associated with idealized systems, in any real system noise exists. Noise has been introduced into the idealized system by adding a random signal to each data point. The signal is no greater than 5% of the maximum signal seen in the system. If we simply take the derivative of this noisy spectrum, no discernable features can be seen, Fig. 3a. One of the properties of derivatives is that the high frequency components, the noise components, are enhanced relative to low frequency terms. One way in which we can remove these high frequency terms is to use a digital filter technique. This technique effectively damps out random fluctuations by allowing a particular data point to be modified, to some degree, by the position of its neighbors. This technique is much faster than a floating 5 point or 3 point smoothing technique, where points are fit to a curve.

Another advantage of the digital filter technique is that the process can be easily repeated until the operator determines that "sufficient smoothness" has been

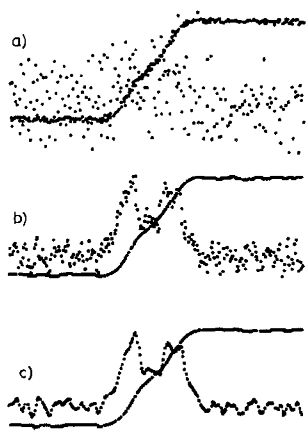

Fig. 3 Plots of deliberately noisy DSC traces and the derivatives, smoothed using a digital filter method. a) No noise removal; 5% noise; S/W = 35/40. b) 5 passes with a digital filter. c) 10 passes with a digital filter

obtained. Once the original curves have been smoothed then the derivatives, while still noisy, clearly show that two peaks can be resolved, Fig. 3b. After 10 passes of the digital filter a somewhat smoother spectrum is obtained (Fig. 3c) and one can discern two peaks in the derivative. However, one would be hard pressed to clearly fix the position of the inflection points on the basis of the derivative.

If we attempt this approach with a "blend" system then, after five passes, one can just discern a peak maximum Fig. 4b. After ten passes one can still not identify the number of components in the filtered spectrum, let alone the positions of these components, Fig. 4c. While the digital filter technique may have some utility for readily separated peaks, it clearly is of limited value when the component peaks exist as shoulders, or as closely overlapping peaks, in a thermal curve.

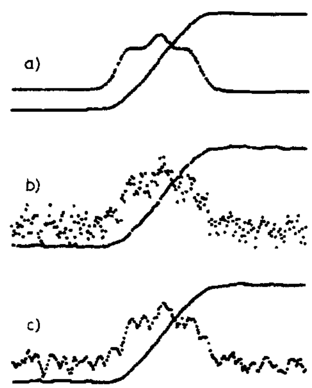

Fig. 4 A 40% "compatible" system with noise introduced and smoothed using a digital filter to various degrees. a) No noise or smoothing; S/W = 50/40; blend = 40%. b) With 5% noise and 5 passes of a digital filter. c) With 5% noise and 10 passes of a digital filter

As an alternative to the digital filter technique a Fourier transform method has been developed. In Fig. 5 we see a comparison for a non-blended system between digitally filtered data and Fourier transformed data. In both cases 5% noise was added to the original curve. The data was filtered 5 times using the appropriate digital techniques. One can clearly discern two peaks once the derivative is taken. The FT-DSC system shows a much superior separation and smoothness in the derivative, although we do introduce a slight amount of undulation in the background.

The marked superiority of the FT-DSC system is further demonstrated in Fig. 6. A clear resolution of three overlapping derivative peaks is obtained, and the positions of these peaks are close to their original values. The major disadvantage, if indeed it is a disadvantage of the method, is that it does require some operator input to balance resultant signal versus the sinusoidal character of the background. We

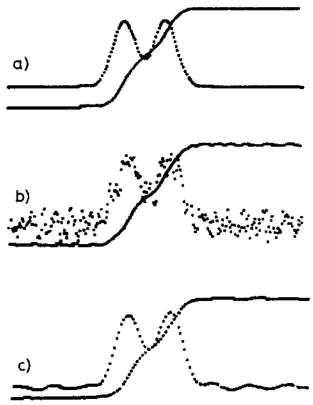

Fig. 5 A comparison of digital filter methods versus the FT-DSC approach. a) No noise, 2 components with no compatibility; S/W = 35/40. b) As above with 5% noise and 5 passes of a digital filter. c) As in (a) with 5% noise which has been transformed, high frequency terms removed and the inverse transform used to regenerate the curve

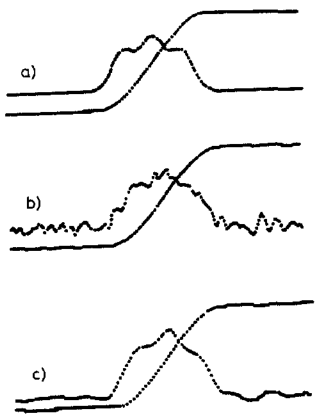

Fig. 6 A comparison of digital filter methods versus the FT-DSC approach for semi-compatible systems. a) A 40% blend with no noise; S/W = 50/40. b) As above with 5% noise and 10 passes with a digital filter. c) As in (a) with 5% noise which has been transformed, high frequency terms removed and the inverse transform used to regenerate the curve

might also note that in order to carry out any of these smoothing procedures the operator has to have access to the raw data. Unfortunately this is often very difficult to do with commercial units. Manufacturers of these units have in general made it near impossible for the average user to access generated experimental data. Only recently has it been possible to examine original data and allow the operator to develop his or her own programs.

Conclusions

Based on continuing work on blends, particularly in efforts to determine if we have compatible or incompatible blends, there is a clear need to be able to derivatize DSC data. While this function is available on most instruments, what is missing is an ability to smooth the data. We have looked at two techniques both of which effectively smooth data. The digital filter technique is fast, is easily used and, can be repeated until an appropriately smooth curve is obtained. The Fourier transform technique can be at least as fast, and has the apparent advantage that it will be more readily able to separate out overlapping peaks. The derivative can be obtained directly from the Fourier transform or from the regenerated noise free thermogram.

I feel that the FT-DSC approach offers a number of advantages to the researcher. The obvious potential for smoothing and obtaining useful derivatives has been demonstrated for idealized composite curves. It remains to test this approach on "real" data where contributions can be made to our understanding of blended systems. Other options exist in terms of data treatment after the FT has been obtained [3]. One that may prove useful in thermal analysis is the ability to remove "instrumental broadening" through deconvolution procedures.

References

1 E. O. Brigham, The Fast Fourier Transform, Prentice Hall, New Jersey 1974.
2 P. C. Emerson, Creative Comp., July (1980) 58.
3 G. Horlick, Analyt. Chem., 44 (1972) 943.

Zusammenfassung — Ständige Versuche zur Identifizierung kompatibler und nichtkompatibler Gemische haben die Notwendigkeit mit sich gebracht, sich überlappende Kurven oder Peaks in thermischen Kurvenverläufen zu trennen. Eine Möglichkeit dafür bietet die Registrierung differenzieller Kurven. Diese können mit den meisten modernen Geräten aufgenommen werden, ihre Brauchbarkeit wird aber oft durch den Geräuschpegel im System limitiert. Der Geräuschpegel kann durch digitale Filterung und durch Fourier-Transformation der Daten herabgesetzt werden. Beide Methoden wurden unter Verwendung identischer Datenserien geprüft. Die FT-Methode scheint bessere Möglichkeiten zu bieten, geeignete Differentialkurven aus starkes Rauschen aufweisenden Kurvenverläufen zu erhalten.

Резюме — Продолжающиеся попытки идентифицировать совмещающиеся и несовмещающиеся смеси показали необходимость разделения в термическом анализе накладывающихся друг на друга кривых или пиков. Одним из способов решения этой задачи является дифференцирование таких кривых. Хотя такая возможность имеется в самых современных термических аналитических системах, однако полезность ее ограничивается наличием больших шумов. Методами, которые могут помочь значительно уменьшить шум, являются математическая фильтрация и фурье-преобразование данных. Оба метода были использованы для данных с одинаковым уровнем шума. Метод фурье-преобразования обладает большими возможностями для получения требуемых производных кривых.