

A comparison of methods for the deconvolution of isothermal DSC data

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Abstract

Isothermal reaction rate DSC data from a visible-light-cured (VLC) resin composite were deconvolved using basic time and frequency domain methods, optimised frequency domain methods and iterative methods. The performance of the different methods varied considerably. The constrained iterative method, in conjunction with low pass noise filtering, proved to be the most suitable, requiring minimum user intervention to yield corrected heat flow data that can be used for subsequent kinetic analysis. The validity of this deconvolution method was verified by re-convolving the deconvolved data, which gave a good approximation to the original experimental heat flow curves. © 1998 Elsevier Science B.V.

Keywords: Deconvolution; VLC; DSC; Reaction kinetics; Dental polymers

1. Introduction

The reactions of photo-initiated polymerization systems, such as those used in commercial dental resin composites, are characterised by very short setting times, usually in the range of 30–40 s [1]. Of considerable interest to dental materials scientists is the modelling of the degree (or extent) of reaction within the restoration cavity under non-isothermal conditions, as the final degree of polymerization affects the mechanical properties and hence the performance of the restoration in vivo. It has recently been shown [2,3] that the degree of reaction of dental resin composites can be modelled by integrating the following rate equation:

$$\frac{d\alpha}{dt} = k\alpha^m(\alpha_{\max} - \alpha)^n \quad (1)$$

where α is the degree of reaction, t is time, k is the Arrhenius rate constant, α_{\max} is the maximum degree of reaction attained at a particular temperature, and m , n are temperature independent parameters. The reaction diffusion control effects are accounted for by the use of the α_{\max} term.

The parameters in the above model can be evaluated by performing isothermal photo-DSC studies at a range of temperatures [2,4]. These measurements provide the dependence of the degree of reaction on the isothermal temperature by direct integration of each DSC trace, to produce:

$$\alpha(t, T_{\text{iso}}) = \frac{H(t, T_{\text{iso}})}{H_{\text{tot}}} \quad (2)$$

where $H(t, T_{\text{iso}})$ is the heat developed during the reaction at a given time t and at a particular isothermal temperature T_{iso} , and H_{tot} is the heat developed during cure when full conversion is attained. Regression analysis is then used to determine the remaining kinetic parameters [2].

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Although DSC is a reliable method for monitoring enthalpic changes, the response time of the instrument, the thermal properties of the sample and the possible miscontact of the sample pan with the measuring furnace can all have a significant effect on the measurements. A deconvolution process (see Section 3) can be applied to the isothermal DSC data to correct for these factors. Indeed, several studies have shown that the evaluation of fast-occurring reactions can be erroneous without applying prior deconvolution, particularly in cases where a knowledge of the timing of the reaction is of prime importance [5–7]. This underlines the need for the application of deconvolution to all isothermal DSC data from visible-light-cured (VLC) materials prior to their kinetic evaluation, so that the reaction rate model shown in Eq. (1) reflects the true shape and timing of the reaction.

Flammersheim et al. [6,7] have shown that, for the case of isothermal photo-DSC data, the impulse response of the DSC system that is used to deconvolve the data differs for every specimen investigated. More specifically, each specimen has unique properties (thermal conductivity, capacity and coupling to the sample holder), so the impulse response should be measured on each occasion. This can be achieved either by measuring the step response [6] or by applying the flash technique [7]. Both techniques have been shown to be extremely sensitive to the presence of signal noise, which can result in reconstructed thermograms that are so distorted that kinetic evaluation of the isothermal data cannot be performed.

In this paper, several iterative deconvolution techniques that so far have not been applied to DSC data are examined and evaluated for their ability to provide useful desmeared signals for subsequent kinetic analysis. The most suitable technique found is then applied to a set of isothermal DSC data from a commercially available dental resin composite and the original and reconstructed data are compared.

2. Photo-DSC experimentation

The material investigated was a dental VLC resin composite, XRV-Herculite (universal shade) (Kerr UK Ltd., Peterborough, UK). Isothermal photo-DSC experiments were carried out using a DSC-7 apparatus (Perkin Elmer Corp., Norwalk, Ct., USA) and a VLC

dental light curing unit (Luxor Light 4000, RFJ Electronics, Winsford, Cheshire, UK) with a blue light source (peak output at ≈ 470 nm) and equipped with a fibre optic light guide. Photopolymerization was achieved using a custom-made DSC cell cover, which allowed for the irradiation of the sample cell while at the same time providing the necessary thermal insulation within the furnace. The duration of the light exposures was controlled by the DSC-7 computer, which provided triggering pulses at predefined time instants to open and close a high-speed electromagnetic shutter system (Compur-Electronic GmbH, Köln, Germany), which had an opening time of 4 ms. This configuration, similar to those found in commercially available photocalorimetric accessories, enabled accurate and repeatable application of the desired light exposure times [8].

Six specimens of 15–20 mg of the material were deposited into standard aluminium pans and were carefully flattened, producing a layer ≈ 0.5 mm thick, to ensure isothermal conditions during cure. In order to avoid activation prior to measurement, the preparation of the samples was performed at sub-ambient light levels.

The light exposure timing sequence that was followed for each isothermal measurement is shown together with representative DSC traces in Fig. 1. Following the initial 40 s irradiation of a specimen, three additional measurements of equal duration were performed to obtain the average baseline level so that it could be subtracted from the initial trace [2,9]. Finally, the flash technique used required the exposure of the sample to a light pulse of 50 ms in duration [7] in order to determine the impulse response of the system.

The cure of the composite was investigated at six temperatures from 25–50°C at 5 degree intervals. Fig. 2(a) illustrates the exotherms obtained after subtracting the baseline and Fig. 2(b) shows a typical impulse response. Although some small differences were observed in these impulse response data, they were indistinguishable at the scale used in Fig. 2(b).

3. Theoretical aspects of deconvolution

The underlying assumption of desmearing algorithms for performing deconvolution on isothermal

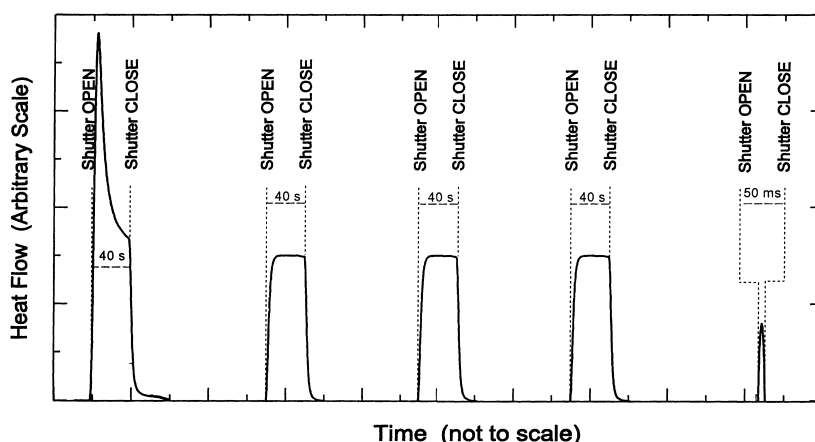


Fig. 1. Shutter-controlled isothermal photo-DSC timing sequence and typical traces.

or dynamic DSC curves is that the recorded signal $y(t)$ is the “true” signal $x(t)$ convolved with the impulse response of the measurement system $h(t)$:

$$y(t) = x(t) * h(t) = \int_0^{\infty} x(t - \tau) \cdot h(\tau) d\tau \quad (3)$$

where “*” denotes the deconvolution operation. For discrete signals of length N , the integral is transformed into a sum:

$$y[n] = \sum_{k=0}^{n-1} x[n-k] \cdot h[k] \quad n = 1, 2, \dots, N \quad (4)$$

where $y[n]$, $x[n]$ and $h[n]$ denote the values of the respective temporal functions $y(n)$, $x(n)$ and $h(n)$ at $t = nT$, where T is the sampling period of the signal.

Solving for $x[n]$ results in the following equation:

$$x[n] = \frac{1}{h[0]} \left(y[n] - \sum_{k=1}^{n-1} x[n-k] \cdot h[k] \right) \quad n = 1, 2, \dots, N \quad (5)$$

The recursive nature of this equation renders it an ill-conditioned problem since even the smallest noise presence in the input signals can produce large errors in the output.

Deconvolution of discrete signals can also be performed in the frequency and z -domains [10]. Using the

Fast Fourier Transform (FFT) to obtain the spectra $Y[f]$ and $H[f]$ of the known signals $y[n]$ and $h[n]$ respectively, the spectrum $X[f]$ of the unknown signal $x[n]$ is expressed simply as the ratio of the spectra of the observed signal and the impulse response function:

$$X[f] = \frac{Y[f]}{H[f]} \quad (6)$$

Taking the Inverse Fast Fourier Transform (IFFT) of $X[f]$ gives the signal $x[n]$. Again, a problem may arise when using this method if the spectrum of the impulse response $H[f]$ has zero or small values, as this renders the solution indefinite or overamplifies the noise.

Similarly, in the z -domain,

$$X[z] = \frac{Y[z]}{H[z]} \quad (7)$$

and, by taking the inverse z -transform of $X[z]$, the deconvolved signal $x[n]$ can be calculated. If, however, any of the roots of $H[z]$ fall outside the unit circle in the z -plane, this results in an unstable system and this method is inappropriate.

The problems associated with the use of deconvolution techniques in calorimetric systems have previously been examined in the z -domain, by using a technique that involves the theoretical determination of the system transfer function [11,12]. Once this is achieved, appropriate filtering techniques in the frequency domain [13] or the time domain [14] can be

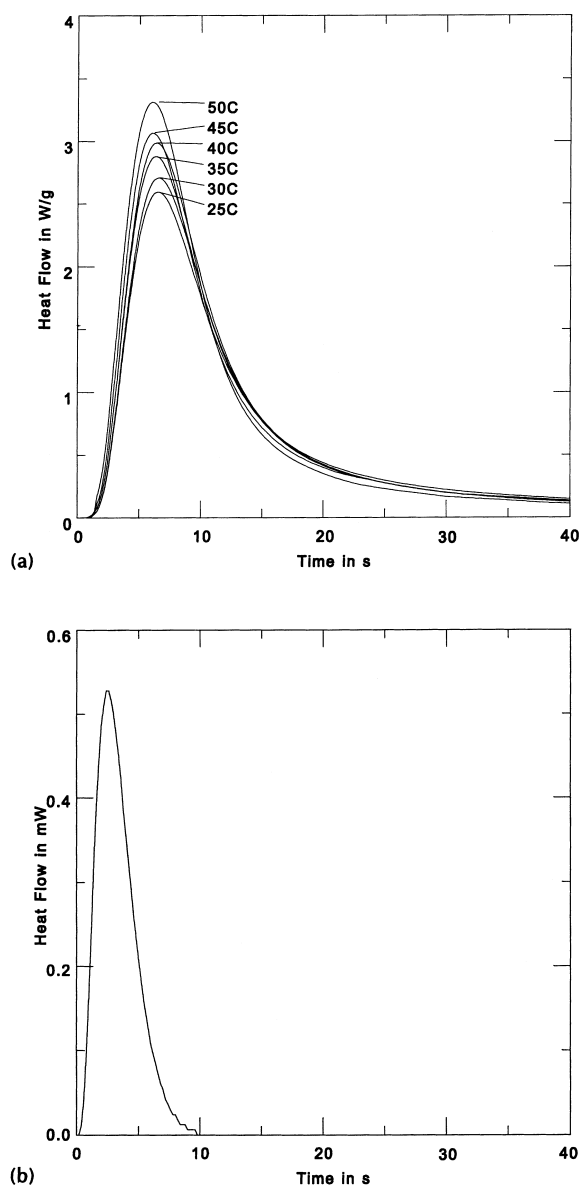


Fig. 2. (a): Isothermal DSC thermograms obtained at six different temperatures for the VLC dental resin composite XRV-Herculite. (b): Impulse response of the DSC apparatus to a light pulse of 50 ms in duration for the sample cured isothermally at 25°C.

applied to eliminate the strong noise presence in the deconvolved signal. Research in several other fields, including electronic system design [15–17], chromatography and spectrophotometry [18–21], where again the knowledge of the precise timing and shape of the acquired data are required, has resulted in the devel-

opment of a plethora of alternative techniques. These are based either on the methods just described or on iterative methods. Several of these methods will be examined, with an emphasis on those that are iterative, as these usually require the least user intervention to obtain the desired signal.

4. Optimisation based deconvolution techniques

Riad [22] in his review outlined a category of frequency domain techniques that included a regularization function $R[f]$ into Eq. (6):

$$X[f] = \frac{Y[f]}{H[f]} \cdot R[f] \quad (8)$$

Several attempts have been made to find an optimum form of $R[f]$. For example, Nahman and Guillaume [23] suggested the following:

$$R[f] = \frac{|H[f]|^2}{|H[f]|^2 + \gamma f^4}, \forall \gamma > 0 \quad (9)$$

Parruck and Riad [24] proposed a similar expression:

$$R[f] = \frac{|H[f]|^2}{|H[f]|^2 + \lambda}, \forall \lambda > 0 \quad (10)$$

and Gans [15] used the following:

$$R[f] = \frac{|H[f]|^2}{|H[f]|^2 + \delta |C[f]|^2}, \forall \delta > 0 \quad (11)$$

where $|C[f]|^2$ is the squared magnitude of the FFT of the second difference operator.

The parameters γ , λ or δ in the above equations are introduced in order to increase the magnitude of the frequency terms of the impulse response of the system in order to avoid spurious solutions. Their optimum values however cannot be easily determined, so they are usually “subjectively” optimised [16,22]. Clearly, if any of γ , λ or δ equal zero, Eq. (8) reduces to Eq. (6), as $R[f] = 1$. If, on the other hand, any are chosen to be very large, then $x[k] \rightarrow 0$.

Other researchers have proposed more intricate expressions for the regularization function that involve the use of two [25,26] or three parameters [17]. Although these functions have been shown to be superior to those given in Eq. (9), (10) and (11), they are also more involved in terms of the optimisation procedure used to determine their regularization parameters.

An alternative category of methods that help to overcome the problems associated with the subjective determination of the regularization function parameters are the so-called iterative deconvolution methods. Of these, perhaps the most widely used is

the Van-Cittert technique [27] and its variants [28]. This provides a solution for the desmeared signal $x[n]$ by performing successive approximations, using the convolution equation. Described by Eqs. (12a) and (12b), the estimated sequence of $x_{i+1}[n]$ is continuously updated by adding an error correction term to the result of the previous iteration $x_i[n]$:

$$x_{i+1}[n] = x_i[n] + (y[n] - h[n] \cdot x_i[n]) \quad (12a)$$

where x_i is the i th estimate of $x[n]$, i is the iteration number and

$$x_0[n] = y[n] \quad (12b)$$

Ideally, this process should terminate when $h[n] * x_i[n] = y[n]$, which implies that $x_{i+1}[n] = x_i[n]$. However, this is not always possible without introducing additional parameters into Eq. (12a)[27,28]. Two variations of this method have been proposed, namely the constrained and the relaxation-based iterative methods.

Constrained methods work by limiting the i th solution estimate to non-negative values, provided that it is known a priori that the corrected signals do not include negative terms. This assumption is valid for the isothermal DSC data considered here as they describe exothermic events produced during the course of the radical chain polymerization reactions. The non-negativity constraint is incorporated into Van-Cittert's method as follows [29]:

$$x_{i+1}[n] = p[n]x_i[n](y[n] - h[n] \cdot p[n] \cdot x_i[n]) \quad (13a)$$

where

$$p[n] = \begin{cases} 1, & x_i[n] \geq 0 \\ 0, & x_i[n] < 0 \end{cases} \quad (13b)$$

The role of the vector $p[n]$ is to constrain the negative solutions of each of the i th estimates of $x[n]$ so that the subsequent solutions are free from spurious components.

Other iterative methods modify the value of the correction factor in Van-Cittert's equation to improve the estimate by using a relaxation function $r\{x_i[n]\}$ [18]. Both of these methods work by truncating the part of the temporal solution containing undesired negative values [28]. Several other relaxation functions have been proposed [18,30] but these require a heuristic determination of their parameters.

5. Evaluation of the deconvolution methods on VLC data

In order to make a comparison of the methods presented above, a representative thermogram of XRV-Herculite obtained at 25°C and the corresponding impulse response were used.

Fig. 3(a) shows the deconvolved signal calculated using the time domain algorithm of Eq. (5), Fig. 3(b) the IFFT of the desmeared signal $X[f]$ using Eq. (6) and Fig. 3(c) the deconvolved signal from the z -domain using Eq. (7). From these, it is apparent that the desmeared data cannot be utilised for kinetic work, as they are severely affected by distortion and noise. Flammerheim et al. [7] dealt with this problem by starting the deconvolution using Eq. (5) at a later time instant, thereby ignoring the first few initial points of the DSC data. Fig. 4 shows that, by starting the deconvolution at time $t=1$ s all three methods produce noise-free signals, because the initial value of the impulse response is now well above zero. However, by ignoring these initial points an integration of the isothermal data, which is required in order to perform

any subsequent kinetic evaluation, would produce erroneous values for the reaction enthalpies.

Of the three regularization methods given in Eqs. (9)–(11), the last offers a non-subjective criterion that can be used to effect an optimum balance between the noise presence and the value of the estimate $x[n]$. Gans [15] noted that as δ increases from zero, the Root Mean Square (RMS) value of the imaginary part of $x[n]$ first decreases, then passes through a minimum and subsequently increases. The minimum RMS value signifies the value of δ at which a good compromise between noise removal and signal information can be achieved.

Fig. 5 shows that this technique can also be applied to the DSC data of VLC materials, in this case for the XVR-Herculite. The changes in the RMS value are small as δ increases above its minimum value. Fig. 6 shows the effect of three different values of δ on the deconvolved signal. For small values, the signal is most distorted, while for δ corresponding to the minimum imaginary part of $x[n]$, distortion is reduced. However, the initial value at $t=0$ does not start from the baseline, indicating erroneously that the onset of the reaction has occurred prior to its activation. Even

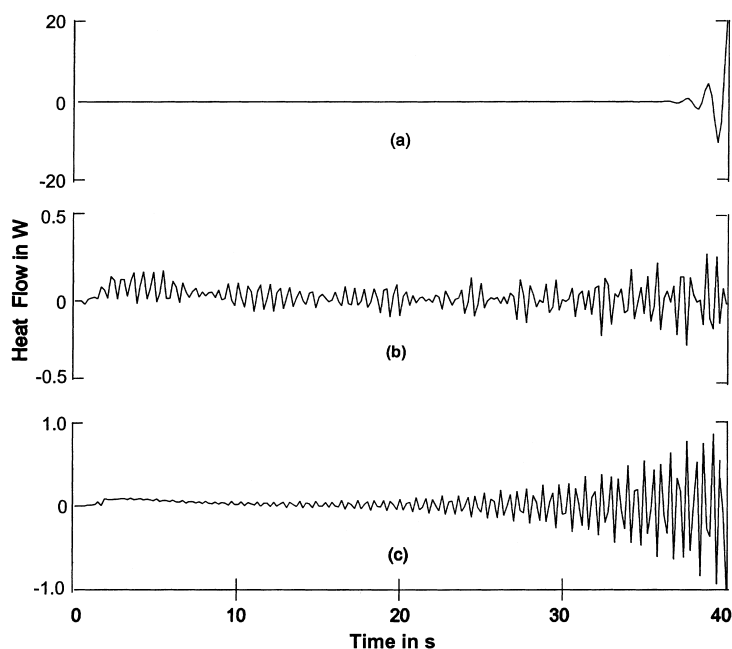


Fig. 3. Deconvolution of the isothermal signal obtained at 25°C, using all the data points. (a): The time domain; (b): the frequency domain; c: the z -domain.

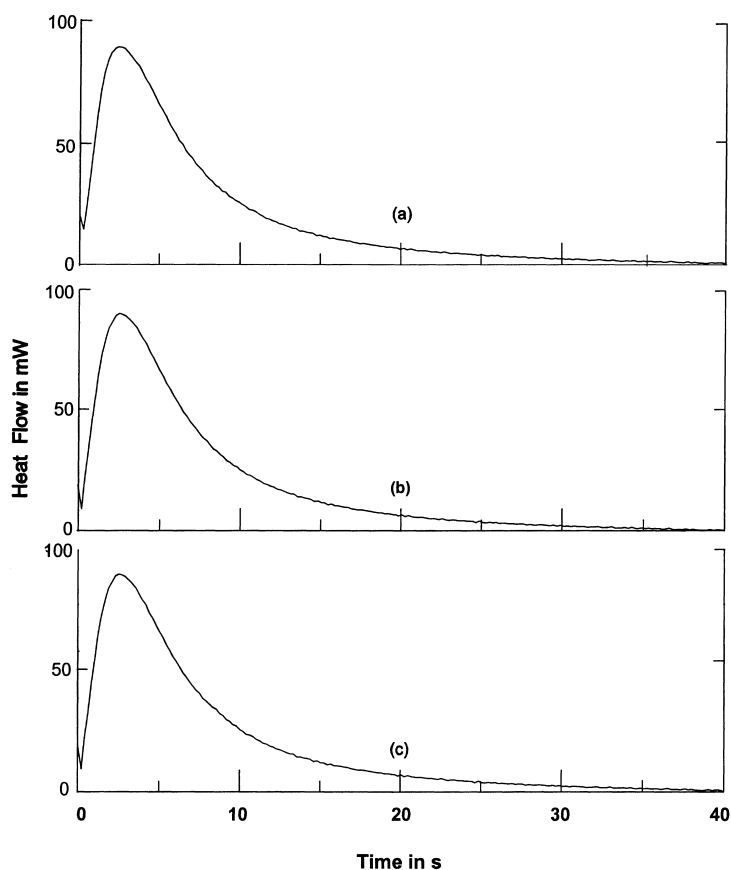


Fig. 4. Deconvolution of the isothermal signal obtained at 25°C, using data points starting at time $t=1$ s. (a): The time domain; (b): the frequency domain; (c): the z -domain.

smoother features are obtained for $\delta=5000$, but there is more error at the initial values. Eq. (9) and (10) produce similar effects on the deconvolved signal by varying the regularization parameters and are not suitable for an accurate kinetic evaluation.

Van-Cittert's iterative technique produced the signal shown in Fig. 7. To achieve this, a convergence monitor based on the RMS value of the error correction term was used [18]. In a similar fashion, the constrained iterative method produced the desmeared signal illustrated in Fig. 8. The estimated signal using the constrained method is the least affected by noise, as the applied constraint cropped the negative values and therefore prevented the oscillatory behaviour observed when using the former method.

The question remaining is whether the data obtained from the constrained iterative method are

appropriate for subsequent kinetic evaluation. The power spectrum of the deconvolved data, shown in Fig. 9, shows little signal content above 0.3 Hz and the presence of noise at higher frequencies. The low pass filtering of frequencies higher than 0.3 Hz, in this case using a dual pass (zero phase) fourth-order Butterworth filter, can greatly improve the signal characteristics, as demonstrated in Fig. 10. The validity of the above operations can be examined by re-convolving the deconvolved data with the impulse response. Fig. 11 shows that the resulting curve is almost identical to the experimental curve.

Similar deconvolved results were obtained by applying the constrained iterative method to the data obtained at the five other tested temperatures, using the corresponding impulse responses. Fig. 12 illustrates the resulting curves. These differ substantially

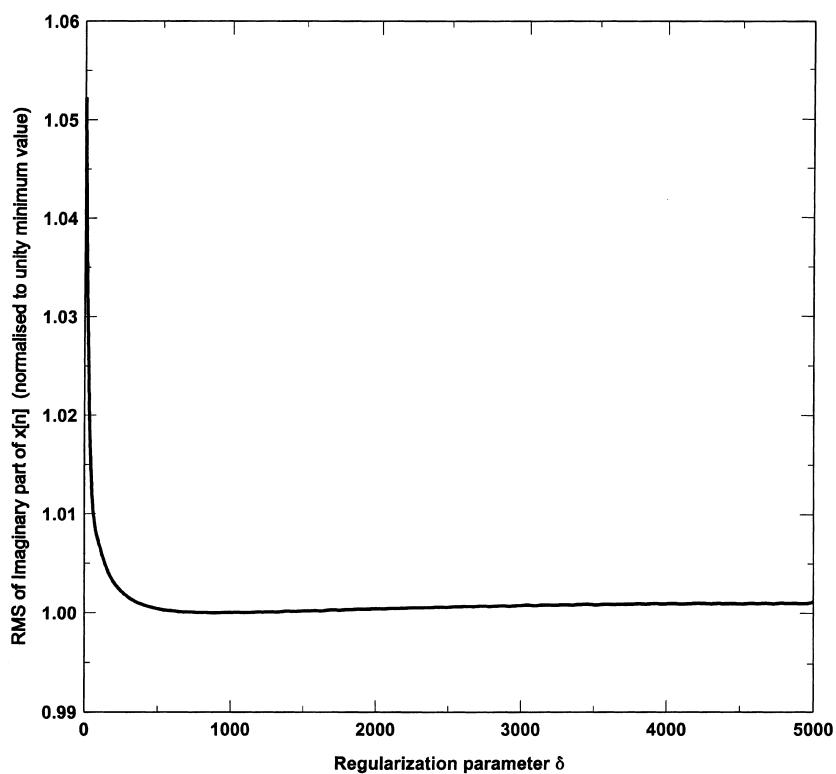


Fig. 5. Variation of the RMS of the imaginary part of the deconvolved signal with the regularization parameter δ .

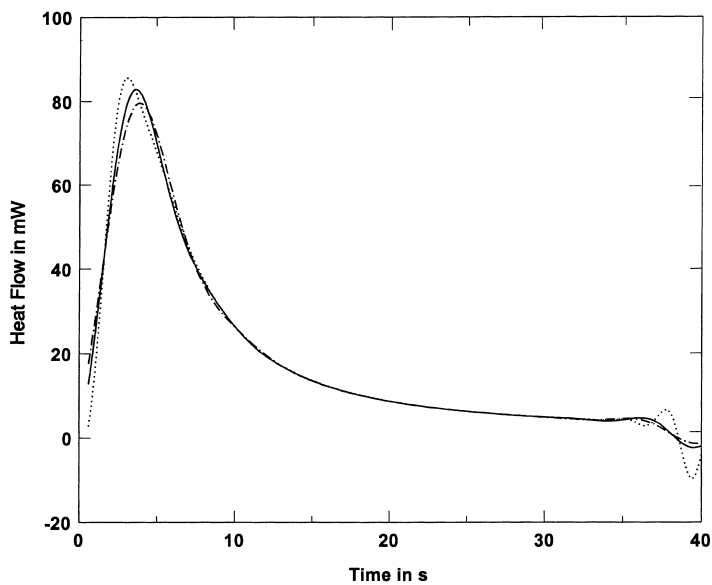


Fig. 6. Deconvolution of the isothermal DSC signal obtained at 25°C using different values of the regularization parameter δ : $\delta=5$ (\cdots); $\delta=900$ (—) and $\delta=5000$ (---).

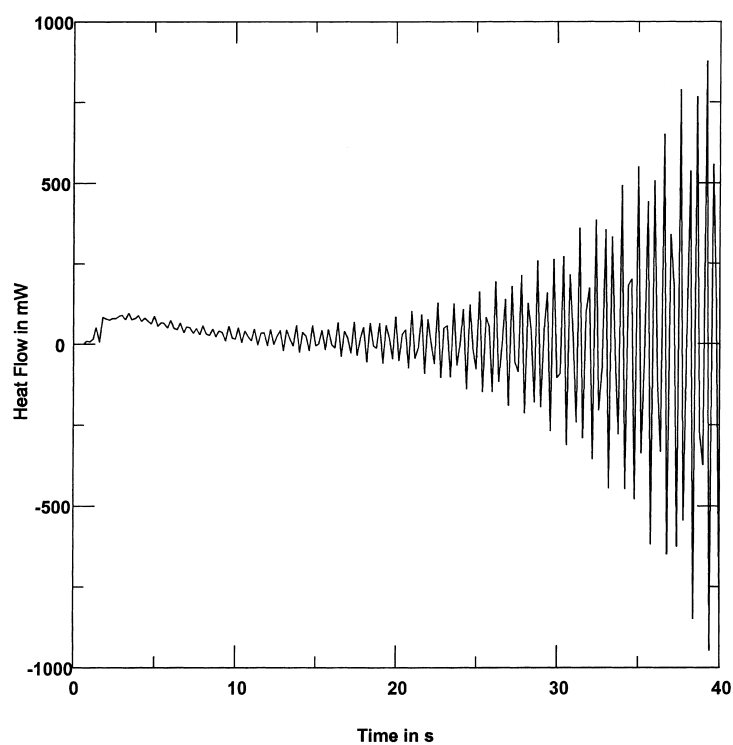


Fig. 7. Deconvolution of the isothermal DSC signal obtained at 25°C using Van-Cittert's iterative method.

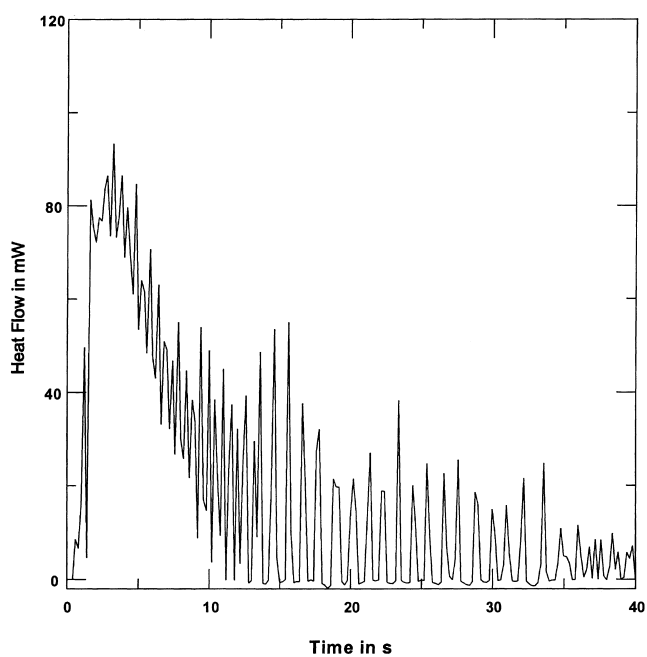


Fig. 8. Deconvolution of the isothermal DSC signal obtained at 25°C using the constrained iterative method.

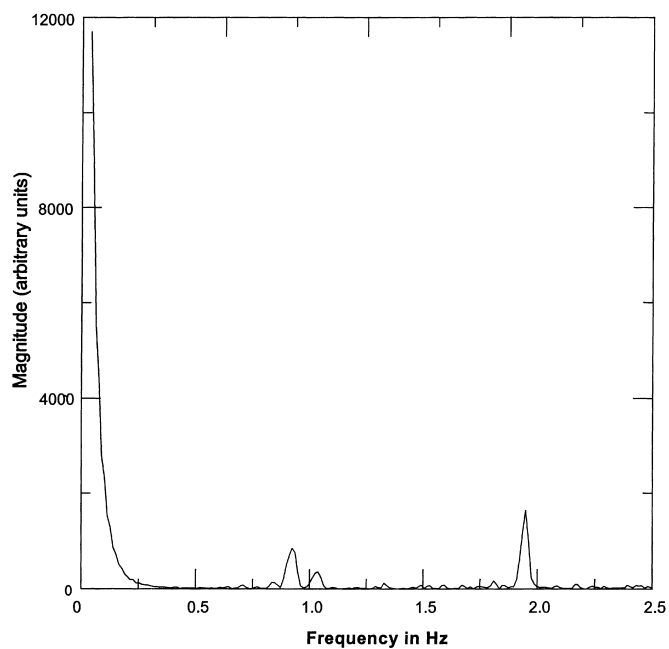


Fig. 9. Power spectrum of the signal illustrated in Fig. 8, indicating little signal content at frequencies above 0.3 Hz and noise components at higher frequencies.

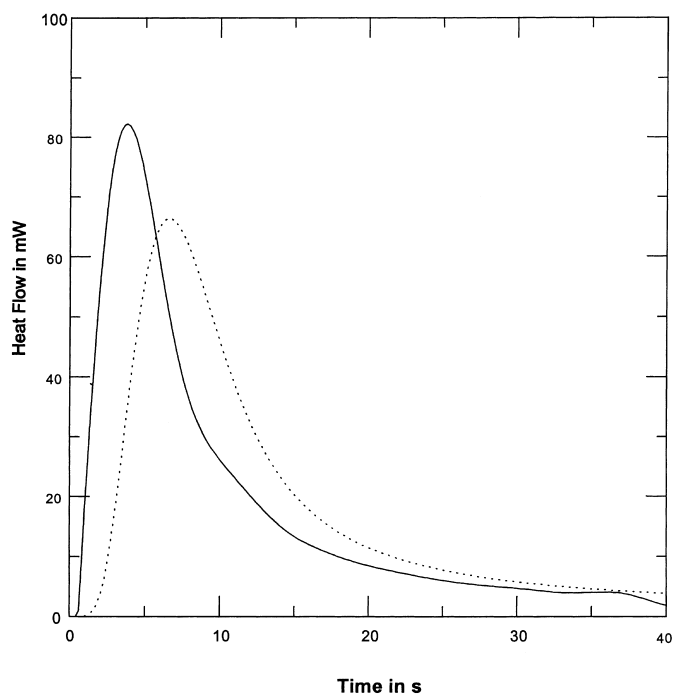


Fig. 10. Filtered deconvolved data of Fig. 8 (—) and the original isothermal DSC data obtained at 25°C (···).

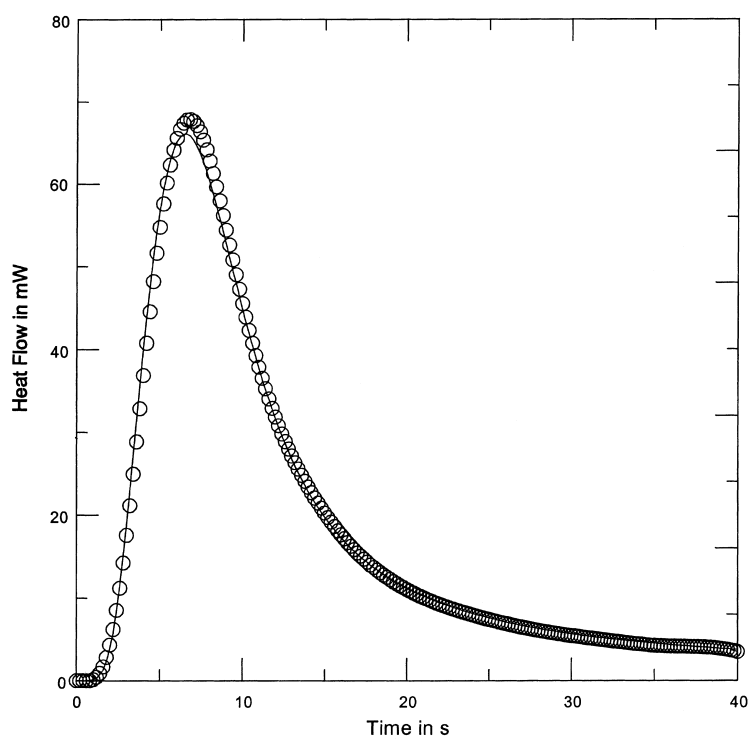


Fig. 11. Original isothermal DSC data obtained at 25°C (—) and the re-convolved deconvolved data of Fig. 10 (○).

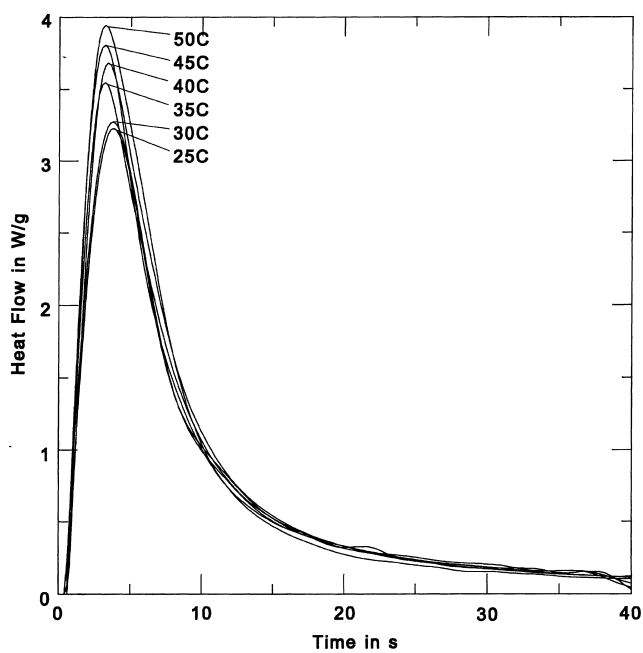


Fig. 12. Deconvolution of the isothermal DSC data illustrated in Fig. 2(a) obtained by applying the filtered constrained iterative method.

from the original data (Fig. 2(a)) in many aspects, such as the peak height, time to reach to peak and the width at half maximum, confirming other investigations on isothermal DSC data [7]. Their kinetic evaluation will consequently yield different values for the parameters (k , m , n) of Eq. (1) describing the dependence of the degree and rate of reaction.

6. Conclusions

The deconvolution of isothermal DSC data is an essential operation when monitoring fast reaction curves, but cannot be implemented satisfactorily considering only the defining equations in the time, frequency or the z -domain. Several alternative expressions for the determination of the desmeared signal were considered, including those attempting to regularize the frequency spectra of the input data. The rather heuristic approach required for the determination of their parameters suggests that these methods should be treated with caution when applied to isothermal DSC data. This does not necessarily imply that their successors, which use more intricate expressions for the regularization function will suffer from the same problems. More experimentation is therefore essential to establish how effective these are for the case of DSC data.

Iterative methods and the constrained Van-Cittert method in particular have clearly demonstrated their ability to produce more meaningful results, but do require appropriate filtering techniques to render their output usable. In this work, the useful frequency range of the deconvolved data was found to be below 0.3 Hz, allowing the filtering of noise components at higher frequencies. The deconvolution of the convolved data allowed an accurate reconstruction of the original experimental curve, confirming that the constrained iterative technique with filtering could prove to be useful for applying to DSC data that are to be used to investigate reaction rate kinetics.

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