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A SYSTEMATIC SOLUTION TO THE PROBLEM OF SAMPLE BACKGROUND CORRECTION IN DSC CURVES

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The problem of sample background correction in differential scanning calorimetric curves is addressed in this paper. An equation is derived for the heat capacity of the system, which corresponds to the sample background. Thereby, it is assumed that during the thermal event the system is a two-component mixture of the initial substance and the final product. According to this model, the variation in heat capacity of the system is due both to the increase in the partial concentration of the product at the expense of the initial substance and to the physical change in the specific heats of the two components, resulting from the temperature increase. The final result of the derivation is an integral equation which can be solved by means of a numerical technique. The algorithm used is presented in detail. The model is general, and can be applied to diverse exothermic or endothermic processes. The melting of a semi-crystalline polymer and the cure process of a thermoset are given as demonstrative examples. The method improves the reliability and the reproducibility of the data.

With the advent of on-line data processing with microcomputers, differential scanning calorimetry (DSC) is becoming increasingly popular in both scientific and industrial routine applications. The main areas of interests are the cure kinetics of thermosets and the melting (crystallization) of thermoplastics. Without computers, a kinetic analysis with chart operation for a thermoset cure, for example, is very time-consuming. A microcomputer working on-line with a differential scanning calorimeter requires less than a minute to do a more extensive analysis. The high speed of data processing allows the workers in this field to apply sophisticated numerical techniques to improve the quality of results. This paper reports a numerical computation technique which can be applied to separate the DSC data from the sample background in a systematic manner. The theory presented here is general, and can be applied to many exothermic or endothermic transitions studied by means of DSC.

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The problem of sample background correction in DSC

The problem of sample background correction arises from the fact that the specific heat of the system continuously changes during the thermal event (e.g. curing, melting, etc.) from the level of the initial substance(s) to that of the final product. To obtain the net effect due to the thermal event, the course of the heat capacity change, which we call the sample background, should be subtracted from the data corrected for the instrumental baseline. (Correction of data for the instrumental baseline is usually done by subtracting the blank curve from the direct data.) Though the sample background correction is a severe problem which affects the quality and the reproducibility of the data, very little attention is paid in the literature to the solution of the problem. In the prevailing standard methods to be found in the literature, the initial and the final levels of the specific heats are merely connected by straight lines or sigmoidal curves without any rationale. In the case of a thermoset cure, the DSC curve obtained by repeating the heating cycle on the cured sample is also taken as the sample background. Straight lines or sigmoidal curves may not necessarily represent the real sample background, because the specific heat of the system during the thermal transition depends on both the current degree of conversion and the temperature. At the same time, the repeat cycle used in the thermoset cure represents the real sample background only at the extreme end of the cure process. It poorly represents the sample background at the starting side of the cure process, which is also the most decisive part of the thermogram in the kinetic analysis.

Theoretical considerations

In this section, we shall develop a simple theory with the aim of calculating the heat capacity of the system, which is variable during the thermal event. To do this, we make the following assumption: during the thermal event the system is a two-component mixture of the initial substance(s) and the final product, and the overall heat capacity of the system is determined additively by the instantaneous partial composition of the individual components. It is emphasized here that we recognize not only the gradual change in partial composition of the individual components during the event, i.e. from zero to unity for the product, but also the physical changes in specific heat of the two components due to the temperature increase. This is extremely important, because the thermal events for polymers take place in a temperature range which is wide enough to bring about physical specific heat changes. In the case of thermoplastic melting, the two components are the solid polymer and the polymer melt. In the case of a thermoset cure, they are the uncured resin system and the final cured material.

The validity of our assumption is unquestionable for the usual thermoplastic melting (or crystallization) processes, because it is improbable that there is a third intermediate phase involved in the transition, whose specific heat is completely different from the other two. As for the thermoset cure, however, we must impose some restrictions, because the degree of crosslinking of the "product" increases gradually until the final degree of crosslinking is attained. This is equivalent to saying that there are an infinite number of intermediates with different chemical structures involved in the cure process. For this reason a single product cannot be defined and the assumption appears to lose its validity for the case of a thermoset cure. We discuss this problem in Section 3 with some details. For the present, let us continue with the theory for the case where the chemical structures of the two individual components in the transient mixture do not change, and there is no third phase involved in the event.

It follows from the above assumption that the sample background, $F(t)$, which is directly proportional to the heat capacity of the transient mixture with the proportionality constant being the heating rate, can be written as

$$F(t) = \alpha\{P_2(t)-P_1(t)\}+P_1(t) \tag{1}$$

where t = the time coordinate, which is proportional to temperature for constant heating rates; α = the partial concentration of the product, which is by definition equal to the current degree of conversion; $P_2(t)$ = the DSC signal for the product alone, which can be estimated through linear extrapolation of the portion of the total curve after the thermal event (for a thermoset cure this is approximately equal to the signal for a repeat cycle); $P_1(t)$ = the DSC signal for the initial substance(s) in the absence of the event, which can be estimated through linear extrapolation of the portion of the total curve prior to the thermal event; and $F(t)$ is the sample background which is to be calculated. The linear extrapolations applied to estimate P_1 and P_2 are justified for the reason that the specific heats of most inorganic and organic materials vary linearly with the temperature. Exceptions are temperature ranges in which third-order type transitions, such as the glass transition, are involved. It is very seldom the case that the glass transition of polymers takes place just prior to the melting of thermoplastics.

The current degree of conversion, α, is given by definition as

$$\alpha = \frac{\int_0^t \{G(t)-F(t)\}\,\mathrm{d}t}{\int_0^{t_n} \{G(t)-F(t)\}\,\mathrm{d}t} \tag{2}$$

where $G(t)$ = the total signal corrected for the instrumental background; and t_n = the time of termination of the thermal event. Figure 1 shows $G(t)$, $P_1(t)$, and

$P_2(t)$ for a typical situation which arises in the case of thermoplastic melting, while Fig. 2 explains the meaning of Eq. 1 graphically. Substitution of Eq. 2 into Eq. 1 yields

$$F(t) = \frac{\int_0^t \{G(t)-F(t)\}\,dt}{\int_0^{t_n} \{G(t)-F(t)\}\,dt}\{P_2(t)-P_1(t)\}+P_1(t) \tag{3}$$

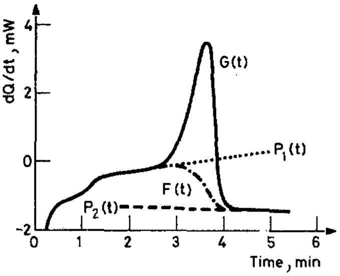

Fig. 1 Typical shapes of the functions $G(t)$, $P_1(t)$, $P_2(t)$ and $F(t)$ for the melting of low-density poly(ethylene). $F(t)$ was calculated via Eq. 3

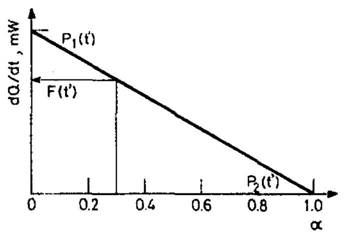

Fig. 2 Diagram showing the relation between $P_1(t)$, $P_2(t)$ and α at a specific time t'

It should be noted that Eq. 3 accounts for the heat capacity variation of the system due to both the conversion and the temperature (or time) increase. The equation also satisfies the following two boundary conditions; at zero conversion, i.e. $\alpha = 0$, the sample background tends to take the form of $P_1(t)$; and at complete conversion, i.e. $\alpha = 1$, it tends to take the form of $P_2(t)$. We must now solve this equation for $F(t)$ so as to obtain the sample background which we are looking for. An analytical solution would be difficult, even if simple analytical expressions are available for the functions involved. However, we could develop an iterative algorithm on a personal computer to find a numerical solution for $F(t)$. The algorithm can be outlined as follows: at first, $P_1(t)$ itself is treated as an approximate solution to $F(t)$, and the right-hand side of Eq. 3 is evaluated with this to find $F(t)$. The outcoming solution for $F(t)$ is a better approximation than the initial input. In the next iteration the new value of $F(t)$ becomes the input. In this way four iterations are done. In practice, four iterations are sufficient to get a fair solution which does not change in further iterations. In the Appendix some programming hints are given in detail. The technique can be applied in different situations involving polymers.

Demonstrative examples

Thermoplastic melting

As a typical example for non-isothermal thermoplastic melting, a low-density poly(ethylene) sample was taken. This polymer has markedly different specific heats in the melt and the solid phase. Figure 1 shows the calculated sample background, together with the functions involved in Eq. 3. $P_1(t)$ is the linear extrapolation of $G(t)$ prior to the melting process, while $P_2(t)$ is that of the melt. In Fig. 3, the calculated $F(t)$ is plotted as a function of α for this case. By interchanging $P_1(t)$ and $P_2(t)$, we could have applied the same computation of $F(t)$ for non-isothermal crystallization of the polymer.

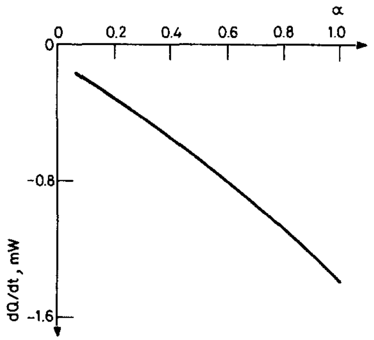

Fig. 3 Diagram showing the relation between the calculated sample background, which is directly proportional to the heat capacity of the system, and the degree of conversion. The data correspond to those in Fig. 1

Thermoset cure

Figure 4 shows the sample background correction for a commercially available epoxy-phenolic resin. $P_1(t)$ is taken as the linear extrapolation of $G(t)$ prior to the cure process, while $P_2(t)$ is the repeat cycle. As in the case of thermoplastic melting demonstrated above, the calculated sample background satisfies the boundary conditions at zero and complete conversion. It goes over smoothly from $P_1(t)$ to $P_2(t)$. However, as pointed out earlier, the assumption of an additive relation for

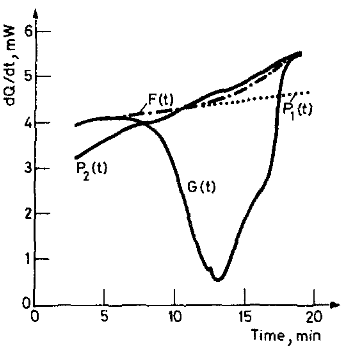

Fig. 4 Typical shapes of the functions $G(t)$, $P_1(t)$, $P_2(t)$ and $F(t)$ for the cure of epoxy resin. $P_2(t)$ was obtained from a repeat cycle after the cure. $F(t)$ was calculated via Eq. 3

the heat capacity (Eq. 1) is not strictly valid in this case. This is because we cannot define a single product, for the reason that the degree of crosslinking is continuously changing until the final cured material is obtained, i.e. there is an infinite number of intermediates. In other words, we are making an error by taking the repeat cycle as $P_2(t)$. To be strict, we must substitute $P_2(t)$ by the actual DSC signal for the cured fraction of resin with the current crosslink density, say $P'(t)$, which is in fact impossible to estimate. It is now argued that the impact of the error on the final result is not serious: the magnitude of the deviation of $P'_2(t)$ from the repeat cycle, $P_2(t)$, is maximum at the beginning of the reaction ($\alpha = 0$), and it is zero at the end ($\alpha = 1$). However, Eq. 1 tells us that for small values of α the function $F(t)$ is contributed to largely by $P_1(t)$, no matter how large the values of $P_2(t)$ may be. Therefore, any error in $P_2(t)$ in this range has a small impact on the final result of $F(t)$. At the same time, the function $F(t)$ is contributed to largely by $P_2(t)$ in the terminating range of the cure process, i.e. for higher values of α. However, the

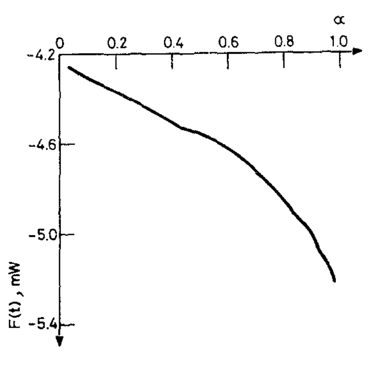

Fig. 5 Diagram showing the relation between a calculated sample background and the degree of conversion. The data correspond to those in Fig. 4

impact on $F(t)$ is again small, because the deviation of $P'_2(t)$ from $P_2(t)$ itself is small. It follows that the error associated with $F(t)$ is maximum in the neighbourhood of $\alpha = 0.5$. The worst case of this error can be estimated if we recognize that $P'(t)$ should always lie between $P_1(t)$, and therefore the deviation of $P'_2(t)$ from $P_2(t)$ is always smaller than that of $P_1(t)$ from $P_2(t)$. For the example shown in Fig. 3, the latter mentioned deviation is about 0.16 mW. This value times α (0.5) is equal to about 0.02% of the total DSC signal in this range. In Fig. 5, the calculated $F(t)$ is plotted as a function of α for this case.

Figure 6 shows DSC curves for the isothermal cure of an epoxy-phenolic resin. The sample background can be computed with similar arguments given above for the non-isothermal case. It may be noted that $P_1(t)$ and $P_2(t)$ are parallel to the time coordinate in the isothermal part in Fig. 4. This is a consequence of our assumption that the specific heats of the two components in the mixture depend on the temperature.

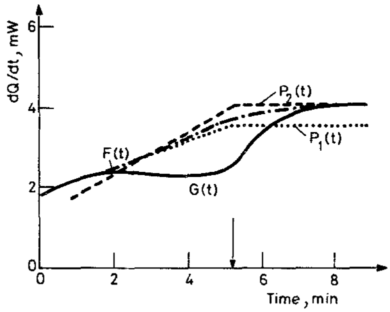

Fig. 6 Typical shapes of the functions $G(t)$, $P_1(t)$, $P_2(t)$ and $F(t)$ for a thermoset under isothermal cure. $F(t)$ was calculated via Eq. 3

Experimental

The chemistry of the materials which served as examples in Section 3 has no relevance in the context of this work. They are merely typical classical examples, and are not described here.

For the experiments reported here, a Perkin–Elmer DSC 4 apparatus was used, which was operated in conjunction with a Perkin–Elmer Thermal Analysis Data Station 3600. The data collected in the data station were transferred to an IBM personal computer via the auxiliary communication port of the data station (RS232). To acquire and process data, programs were written in IBM PC APL. The personal computer took 50 seconds to perform the numerical evaluation of the sample background when the number of data points in $G(t)$ was 512 and the number of iterations was 4.

Concluding remarks

Throughout the above discussion it was assumed that the total DSC curve has been corrected for the instrumental baseline. This is usually done by subtracting a blank curve from the direct DSC signal. According to Eq. 3, an instrumental baseline correction is not necessary if the baseline is parallel to the time axis within the range of the thermal event.

Application of the reported method in the construction of the sample background leads to reproducible results, as we have experienced in the laboratory. The reproducibility of the measurements is much better than if the sample background is assumed to be a straight line or a sigmoidal curve.

Figures 3 and 5 indicate that the heat capacity of the system is nearly directly proportional to the degree of conversion. This is evidence of the correctness of the solution we have found for Eq. 3. The small deviation from direct proportionality is due to the accompanying physical specific heat change due to the temperature increase, i.e. the variation of the slope $(P_2(t)-P_1(t))$ and the intercept $(P_1(t))$ of the straight line in Fig. 2. The smooth transition of $F(t)$ from $P_1(t)$ to $P_2(t)$ indicates that the calculated sample background is at least closer to reality than the straight line or sigmoidal type sample background curves which are constructed without any underlying law.

Appendix

To solve Eq. 3 in the text numerically, the following programming steps are recommended.

1. Define the vectors, $G(t)$, $P_1(t)$ and $P_2(t)$, so that all have an equal number of elements. The corresponding time vector, t, contains the same number of elements, which are equidistant. P_1 should contain the values given by'$P_1(t) = mt+c$, where m and c are the slope and intercept, respectively, of the linear part of $G(t)$ prior to the thermal event. For thermal events such as thermoplastic melting, $P_2(t)$ is similar to $P_1(t)$, but contains values corresponding to the linear part of $G(t)$ after the thermal event. For a thermoset cure, P_2 should be the repeat cycle.

2. Set $F(t)$ equal to $P_1(t)$ and evaluate the right-hand side of Eq. 3. To do this, each element of $P_1(t)$ and $P_2(t)$ is considered. The corresponding current degree of conversion, α, is determined by dividing the integral $G(t)-F(t)$, with the integration limits being given by the beginning of the event and t, which

corresponds to the current elements of $P_1(t)$ (or $P_2(t)$), by the integral $G(t) - F(t)$ for the whole range.

3. Set the evaluated $F(t)$ equal to the input $F(t)$ and perform step 2 again. Repeat this procedure until $F(t)$ does not change further when the output of the preceding iteration is put equal to the input of the next.

Zusammenfassung — Diese Arbeit spricht das Problem der Probenuntergrundkorrektur an, das bei den Thermogrammen der Dynamischen Differenzkalorimetrie auftritt. Es wird eine Gleichung für die Wärmekapazität der Probe bzw. den Probenuntergrund hergeleitet. Dabei wird angenommen, daß das System während des thermischen Geschehens eine Zweikomponenten-Mischung darstellt. Laut diesem Modell findet eine Aenderung der Wärmekapazität deswegen statt, weil die partielle Konzentration der Probe auf Kosten des Ausgangsmaterials zunimmt, und weil die Temperaturerhöhung eine physikalische Aenderung der spezifischen Wärme der zwei Komponenten herbeiführt. Das Resultat der Herleitung ist eine Integralgleichung, die mit Hilfe eines numerischen Verfahrens gelöst werden kann. Der dabei angewandte Algorithmus wird beschrieben. Das Modell ist allgemein gültig und auf verschiedenartige thermische Prozesse anwendbar. Als Beispiele dienen das Schmelzen eines teilkristallinen Polymers und der Aushärtungsvorgang eines Harzsystems. Das Verfahren verbessert die Reproduzierbarkeit und die Verläßlichkeit der Daten.

Резюме — В статье обсуждена проблема коррекции фона пробы для кривых ДСК. Выведено уравнение теплоемкости системы, которое соответствует фону пробы. При этом предполагалось, что во время термического события система является двухкомпонентной, состоящей из исходного и конечного веществ. Согласно этой модели изменение теплоемкости системы обусловлено как увеличением парциальной концентрации продукта за счет исходного вещества, так и физическим изменением, вследствии увеличения температуры, удельной теплоемкости двух компонентов. Конечным результатом дифференцирования является интегральное уравнение, решаемое числовым методом. Подробно описан используемый для этой цели алгоритм. Представленная модель является общей и может быть применена к различным экзо- и эндотермическим процессам. В качестве примеров приведено плавление полукристаллического полимера и процесс отверждения термопластика. Метод увеличивает надежность и воспроизводимость получаемых данных.