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DSC kinetic study of the transitions involved in the thermal treatment of polymers. Methodological considerations

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Abstract

The transitions and reactions involved in the thermal treatment of polyethylene (PE) and EVA at a heating rate of 10°C min^{-1} in an inert atmosphere (N_2), have been studied by differential scanning calorimetry (DSC).

A brief discussion on the methodology related to the mathematical treatment of the DSC data is presented. The physical meaning of the kinetic parameters and the objectives of the DSC data reduction procedures are also commented on, emphasising the necessity of complex models in order to explain complex behaviours in detail. Different kinetic models have been suggested and applied involving one or two fractions susceptible of undergoing transitions or reactions. In addition, the variation of the heat capacities of the different fractions has been considered yielding a remarkable improvement in the fitting of the whole of DSC curves. The models applied are capable of representing the different processes observed and can be of great interest in the understanding of such phenomena, as well as in modelling the heat involved in the processing of these type of products. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer; Polyethylene; Polyethylene vinyl acetate copolymer

1. Introduction

Differential scanning calorimetry (DSC) is a commonly used technique in the study of polymer transitions, in which the energy absorbed or evolved by the sample is compensated by adding or subtracting an equivalent amount of electrical energy to a heater located in the sample holder. In this way, continuous and automatic adjustments of the heater power are necessary in order to keep the sample holder temperature identical to that of the reference holder. This adjustment provides a varying electrical signal equivalent to the varying thermal behaviour of the sample. DSC provides information such as the melting point (T_M), the melting enthalpies and the crystallinity of the sample. This technique can also be used for the identification of different polymers in a blend and to determine their properties.

The kinetic study of the different processes involved in polymer processing is becoming a very important way to characterise and to optimise their behaviour. Celina et al. [1] studied the characterisation and degradation of peroxide and silane crosslinked polyethylene (PE) and determined via DSC the melting peak and the specific melting enthalpies (endothermic) of all silane and peroxide XLDPE samples. Rodríguez-Pérez et al. [2,3] applied DSC in order to determine the morphology of the extruded foam profiles of LDPE/EVA blends and also to obtain the melting point and the crystallinity of crosslinked closed-cell PE foams. Braun et al. [4] studied the effect of the crosslinking agent (peroxide) in the melting peaks and the heat of melting (ΔH_M) in PP–PE blends. In a similar way, Shieh et al. [5] used DSC curves to investigate the thermal properties of both silane-grafted and silane-grafted water-crosslinked LDPE.

Therefore, the accurate knowledge of the effect of the different variables (processing and product variables) on the processes involved in thermal heating of polymers (transitions, melting, grafting, crosslinking…) is very important.

Several articles, such as Munteanu and Turcu [6], Marcilla and Beltrán [7] and Conesa et al. [8], have been published related to the kinetic study of the thermal decomposition (TGA) of polyolefins, emphasising the need for adequate models and adequate data reduction procedures in order to obtain sets of representative kinetic parameters. However, there are a few articles such as Sen et al. [9,10], dealing with the kinetic study of the processes involved in polyolefin crosslinking and/or polyolefin foaming, by DSC studies. Sen et al. [11] also studied the kinetics of grafting

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Nomenclature

a, b, c	Parameters of heat capacity
C_p	Heat capacity
DSC	Differential scanning calorimetry
E_a	Activation energy
EVA	Polyethylene vinyl acetate copolymer
k	Rate constant
k_0	Pre-exponential factor
k_{373}	Pre-exponential factor at 373 K
M	Melt state
N	Number of experimental points
n	Reaction order
OF	Objective function
P	Number of parameters to be fitted
PE	Polyethylene or polyethylene domains in EVA
R	Perfect gas constant
S	Solid state
T	Temperature
T_i	Temperature at a given time
t_i	Time (s)
VC	Variation coefficient
w	Mass fraction of non-transformed polymer
XLDPE	Crosslinked Low Density Polyethylene

Greek Symbols

α	Mass fraction of polymer transformed
β	Fraction of EVA(1) in the EVA sample (model 1 for EVA)
γ	EVA(1) + EVA(2) (model 1 for EVA), EVA fraction (model 2 for EVA)

onto PE with vinyl trymetoxy silane (VTMO) by differential scanning calorimetry evaluating the influence of several parameters such as the structure of the catalyst, its concentration, temperature and rate of crosslinking.

Although the basis for the decomposition of complex or overleaped peaks as well as the consideration of varying specific heat capacities, are already studied (Mathot [12]), no references have been found in literature where the treatment of these peaks had been attempted.

On the other hand, significant errors could be produced when trying to apply conventional kinetic analysis to complex peaks even at the initial stages of the process, as was shown by Marcilla and Beltrán [13] when studying the application of different methods to the thermogravimetrical data of PVC decomposition.

Finally, certain aspects concerning the number of parameters of a kinetic model and their physical significance are not always taken into account. Thus, the main objectives of the present work are:

1. to analyse the different aspects related with the interpretation of the results from DSC, both for simple and complex systems;
2. to suggest, apply and adapt kinetic models to the analysis and correlation of the DSC data. To discuss the effect of the type of the model, the effect and physical meaning of each parameter, the effect of the number of parameters and their interrelation, in order to represent and correlate the whole curves obtained by the DSC, even those including complex peaks and complex base line behaviours;
3. to apply the methodology developed to the study of the behaviour in DSC of samples of EVA, PE.

2. Equipment and experimental procedure

2.1. DSC

Runs were performed in a Perkin–Elmer® DSC, model DSC 7, controlled by a PC AT compatible system. Samples of 8–9 mg were encapsulated in aluminium pans and treated at a heating rate of 10°C min^{-1}. The temperature range was 40–300°C. The atmosphere used was nitrogen with a flow rate of 45 ml min^{-1}. The main characteristics of the samples used in this paper are shown in Table 1.

The experimental data presented in this paper corresponding to the pure components are the mean values of runs carried out three times. The results obtained in all these cases were very similar.

2.2. Kinetic model and mathematical treatment of the data

The apparent kinetic law of the reaction processes of many materials can be generalised as:

$$\frac{d\alpha}{dt} = kg(\alpha) = k_0 g(\alpha)\exp(-E_a/RT) \qquad (1)$$

where α is the fraction of reacted material and $g(\alpha)$ is a given function of α that depends on the controlling mechanism.

nth-order kinetics is a widely accepted law for TG pyrolysis of polymeric materials and has also been used for DSC,

Table 1
Main characteristics of the samples used

Sample	Commercial name	Manufacturer	Main characteristics	
A	LDPE 003	Repsol QuÍmica®	Density: 920 kg/m^3	MFI: 2 g (10 min)$^{-1}$
B	Alcudia® (EVA 628)	Repsol QuÍmica®	VA content: 28%	MFI: 6 g (10 min)$^{-1}$

Sen et al. [11]. The kinetic law can be expressed as:

$$\frac{d\alpha}{dt} = k_0(1-\alpha)^n \exp(-E_a/RT) = k_{373}(1-\alpha)^n \exp\left(\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{373.15}\right)\right) \quad (2)$$

where k_0 is the pre-exponential factor, k_{373} is the pre-exponential factor at 373 K, E_a is the apparent activation energy, R is the universal gas constant, T is the temperature of the sample at a given time, n is the reaction order and t is the time. In this case we have assumed the same kinetic law to represent the rate of the different transitions observed in the samples, which can be associated with melting processes and chemical reactions, depending on the material under study. We use k_{373} instead of k_0, in order to improve the quality of the fitting [14].

For a melting process, considering that the weight fraction of the non-melted sample is $w = 1 - \alpha$, it can be written that:

$$\frac{dw}{dt} = -k_{373}w^n \exp\left(\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{373.15}\right)\right) \quad (3)$$

Considering a constant latent heat of melting (ΔH_M), the differential heat flow measured by the DSC apparatus could be written as:

$$\frac{dQ_{DSC}}{dt} = -\Delta H_M\frac{dw}{dt} = \Delta H_M k_{373}w^n \exp\left(\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{373.15}\right)\right) \quad (4)$$

In order to calculate the derivative with temperature instead of time, Eq. (4) can be multiplied by the inverse of the heating rate, v_H; to yield:

$$\frac{dQ_{DSC}}{dT} = \frac{-1}{v_H}\Delta H_M\frac{dw}{dt} = \Delta H_M k'_{373}w^n \exp\left(\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{373.15}\right)\right) \quad (5)$$

where $k'_{373} = (1/v_H)k_{373}$.

Nevertheless, it has been observed that this kinetic equation is not sufficient to fit all the experimental data of the whole DSC curve, even for simple DSC curves with a single peak, due to the base line variation. Thus, in order to obtain better correlation, the heat capacity (C_P) dependence with the temperature of each state — solid (S) and melt (M) — has been introduced in the model as a second degree polynomial. Thus, the new equation could be written as follows:

$$\frac{dQ_{DSC}}{dT} = wC_{PS} + \Delta H_M k'_{373}w^n \exp\left(\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{373.15}\right)\right) + (1-w)C_{PM} \quad (6)$$

where T is the temperature at any time and the first and last term of the equation are the variation of the solid and melt heat capacities, respectively:

$$C_{PS} = (a_S T^2 + b_S T + c_S) \quad (7)$$

$$C_{PM} = (a_M T^2 + b_M T + c_M) \quad (8)$$

These kinetic parameters have been optimised using the tool “Solver” included in the spreadsheet Excel 7.0 for Windows. In all the calculations, the objective function (OF) considered was:

$$OF = \sum_{i=1}^{N}\left[\left(\frac{dQ_{DSC}}{dT}\right)_{exp} - \left(\frac{dQ_{DSC}}{dT}\right)_{calc}\right]^2 \quad (9)$$

where i represents the experimental data at temperature T_i and at time t_i, $(dQ_{DSC})/(dT)_{exp}$ represents the experimental heat derivative with respect to the temperature as obtained from the DSC apparatus, and $(dQ_{DSC})/(dT)_{cal}$ is the calculated value from Eq. (6).

In order to compare different kinetic models a variation coefficient is introduced:

$$VC(\%) = \left|\frac{\frac{\sqrt{OF}}{N-P}}{D_{exp\ av}}\right|100 \quad (10)$$

where N is the number of experimental points, P is the number of parameters to be fitted and $D_{exp\ av}$. is the average of the experimental derivatives. The integration of the kinetic equations was carried out using the Euler method.

2.3. Comments on the data reduction procedure

Before applying the proposed kinetic models for DSC it is worth considering different aspects concerning the usual and widely accepted data reduction procedures:

1. Normally DSC equipments include a data reduction system that provides the heats involved in the process studied and the peak temperatures. These two parameters are normally reported and compared. Therefore, this would imply two parameters per peak observed in the dynamic DSC curve. Nevertheless, to obtain such parameters other parameters are required, i.e.: the initial and final temperature for integration (2 parameters), the type of integration selected and the parameters to correct the base line (2 parameters in the simple case of linear correction), representing an additional set of 4 parameters per peak plus a decision with respect to the type of base line correction. Therefore, in the traditional treatment of the data, a total of 6 parameters are required to characterise a single peak with their corresponding reaction heat and temperature. But the later four parameters are normally not considered, discussed nor reported and any possibility of reproducing the complete DSC curve and its detailed shape is lost with this practice.
2. In the case of two or more overlapping peaks the

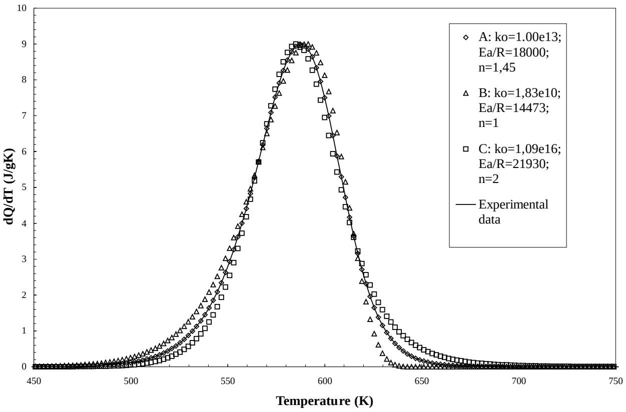


Fig. 1. Comparison of the fitting provided by three different sets of kinetic parameters.

additional problem of determining where the different peaks end or begin arises.

3. It is evident that for complex DSC showing two or more processes, a set of at least six parameters per peak is required, plus an additional parameter per peak referring to the concentration related to that peak.
4. The application of kinetic models in an adequate way, such as that presented, has the clear advantage of its ability to fit the whole DSC curve, allowing also the analysis of multiple, overlapping and complex peaks. These models allow the characterisation, reproduction and interpolation of the thermal process undergone by the sample in the whole range of temperature, time and conversion, using a number of parameters equal or similar to that required by the conventional methods included in the equipment.
5. The physical meaning of the parameters normally reported is evident: peak area is related to the heat involved and peak temperature is the temperature of the maximum rate. It is evident that these parameters can be obtained from the data reduction procedure suggested. Additionally, this procedure has the advantage of enabling the reproduction of the whole curve, even the details on the symmetry of the peaks. Nevertheless, the comparison of the kinetic parameters (k_0, k_{373}, E_a and n) must be carefully considered since the three parameters are highly interrelated. The order of reaction is related to the shape and symmetry of the peaks, being almost symmetric for first order reactions. For orders higher than one they present a progressive tail at the higher temperatures, whereas they present a sharp decrease at lower temperatures for orders close to zero. The activation energy and the pre-exponential factor are both related to the peak location (T_{max}) and width. The width of the peak is more sensitive to E_a. Thus it is evident that the three parameters must be considered together when comparing their values from peak to peak. Two similar pre-exponential factors do not mean any similarity in the process if the kinetic model and the other parameters are different, and the same applies for the other parameters. In any case they must be considered as apparent kinetic parameters.

Another aspect to be considered is that the three kinetic parameters are optimised to correlate all the features of the DSC, i.e.: the shape, the symmetry, the peak temperature, etc. If a non-symmetrical curve with a tail at the high temperature end has to be fitted using a simple model, as that suggested, an order higher than one must be allowed, otherwise a bad correlation would be obtained. On the other hand, if a set of kinetic parameters is not able to represent a DSC curve it is obvious that their physical meaning is, at least, doubtful, as the corresponding model they come from. Thus, a necessary but not sufficient condition that a model must fulfil is that it provides a good fitting of the experimental data. Another desirable condition is that it involves the minimum number of parameters. This later condition is, from our point of view, many times not adequately interpreted. Frequently a model is not considered because it involves a large number of parameters and a very simplistic model is preferred only because it involves less number of parameters, despite that it provides only a rough approximation to the experimental data. Thus a compromise must be found between the number of parameters, the physical founding of the model, the reasonable simplifications to be introduced and the use intended for the data and equations obtained.

Fig. 1 shows three possibilities of fitting a hypothetical experiment (solid line) using three different set of parameters k_0, E_a and n. In curves B and C the reaction order has been fixed to 1 and 2, respectively, and the other two parameters have been optimised in order to fit the experimental curve. Curve A has been calculated freely optimising the three parameters. As expected, curve A provides the best fit. Therefore a decision has to be made on whether to accept or not the validity or physical significance of the fractional order obtained in case A. At the same time, it is evident that cases B and C do not properly represent the experimental data, and the first or second order kinetics cannot be accepted.

What we suggest in the present work is to develop a model capable of an adequate fitting of the experimental data and simplify it after its application, depending on the case analysed. Furthermore and with the purpose of validating the model, in a similar way to the case of TG data, we also suggest applying the model to different experiments run under different conditions (i.e.: heating rate, concentration of the reactants…) and correlating the corresponding data simultaneously. The set of parameters and the model capable of correlating all the cases simultaneously is, in principle, more representative of the real process than any other model or set of parameters not capable. Again this fact can be considered only as a necessary but not sufficient condition for the model to represent the process.

After these considerations we suggest the proposed

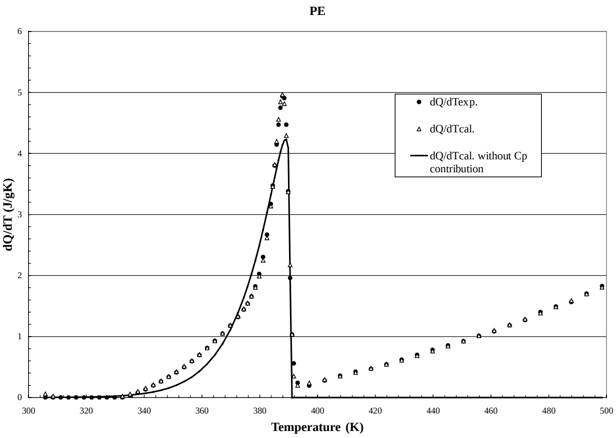


Fig. 2. Experimental and calculated DSC of PE.

kinetic procedure for the study of the DSC data corresponding to polymer systems. In further work we will apply this methodology to the mixtures of these compounds to study the foaming and crosslinking reactions.

3. Results and discussion

Fig. 2 shows the simple case of a typical PE DSC curve involving a single process at 115°C (both experimental and calculated) corresponding to the fusion of the crystalline domains of the thermoplastic. A noticeable variation of the base line can also be observed. If the variation of the heat capacity with temperature is not considered and only the melting is taken into account a very poor fitting can be obtained (see Fig. 2) along the whole range of temperatures (especially at the initial and final slopes), though the PE peak is satisfactorily located. In this case the model has only four parameters (the pre-exponential factor, the activation energy, reaction order and the heat involved). Furthermore if we set the reaction order to 1 the model has three parameters, and the correlation is, obviously, worse. Another practice could be to subtract the base line and fit the resulting data. This would require, for instance, selection of two temperatures: one at the beginning and another at the end of the peak and consider the base line as a straight line. In this case the fitting is improved, but we have added four additional parameters to enable this calculation, though they are not normally considered as parameters of the model. If contrarily we accept a variation of the heat capacity of the solid and liquid PE with temperature there is no need to select the initial and final temperatures or to consider the base line as a straight line (though the dependence of the heat capacity must be formulated). In this case, if we consider a parabolic variation of the heat capacities with temperature, the model will have ten (4 + 6) parameters. In the previous (traditional) case the number of parameters was 8 and four of them, the initial and final temperatures and the type of line connecting them, are somewhat subjectively selected.

Table 2
Kinetic parameters obtained from the fit of experimental data to the DSC of PE

Kinetic parameters		Optimised values
PE	ΔH (J kg^{-1})	24,710
	k$'_{373}$ (K^{-1})	6.92×10^{-4}
	E_a/R (K)	60,365
	n	0.88
C_{PS}	a_S (J kg^{-1} K^{-3})	0.508
	b_S (J kg^{-1} K^{-2})	−325.9
	c_S (J kg^{-1} K^{-1})	52,120
C_{PM}	a_M (J kg^{-1} K^{-3})	5.43×10^{-2}
	b_M (J kg^{-1} K^{-2})	−33.2
	c_M (J kg^{-1} K^{-1})	4842
VC (%)	0.11	
		Calculated values
T_{max}	K	387.9
k' at T_{max}	(K^{-1})	0.340

Therefore, the kinetic model used for the single peak of this case is that given by Eq. (1).

Table 2 shows the corresponding kinetic parameters as well as the value of the variation coefficient obtained. We have included the rate constant at the peak temperature as well as the peak temperature as calculated from the model. This latter parameter in addition to the heat of reaction (i.e.: the peak area) are those normally reported in DSC experiments and can be used for comparison.

In the above discussion only one process has been _considered. Obviously, when more processes are observed, i.e.: more peaks, the model must be consequently completed adding the corresponding terms to the equations, increasing the number of parameters accordingly. For instance a DSC with two peaks must involve two reactions occurring consecutively or from different fractions in the sample, and the model must be formulated accordingly. If the DSC curve is to be completely represented a large number of parameters is thus unavoidable.

In the case of the EVA DSC curves (Fig. 3) three different peaks can be observed. Therefore, if the kinetic model has to contemplate these three different processes, three different kinetic terms must be used. The first two peaks are closely overlapped, at 49°C and 72°C, respectively, and the third peak appears at 114°C. This last peak could be associated to the fusion of the PE domains of the EVA. The origin of the first two peaks is more uncertain and they could probably be explained by different mechanisms, associated with the softening of the vinylacetate segments of the EVA [15]. In this work, two different possibilities have been considered to model these two peaks:

Model 1. Two different EVA fractions may exist (i.e.

EVA(1) and EVA(2)) that undergo the fusion or transition process at different temperatures:

$$\mathrm{EVA(1)} \xrightarrow{k_1} \mathrm{EVA(M)} \tag{11}$$

$$\mathrm{EVA(2)} \xrightarrow{k_2} \mathrm{EVA(M)}$$

$$\mathrm{PE} \xrightarrow{k_3} \mathrm{PE(M)}$$

where EVA(M) and PE(M) are the melted EVA and PE. Thus, the heat derivative with respect to temperature would be:

$$\frac{\mathrm{d}Q}{\mathrm{d}T} = w_\mathrm{S} C_\mathrm{PS} - \left(\Delta H_{\mathrm{EVA(1)}} \frac{\mathrm{d}w_{\mathrm{EVA(1)}}}{\mathrm{d}T} + \Delta H_{\mathrm{EVA(2)}} \frac{\mathrm{d}w_{\mathrm{EVA(2)}}}{\mathrm{d}T}\right)\gamma - \Delta H_\mathrm{PE} \frac{\mathrm{d}w_\mathrm{PE}}{\mathrm{d}T}(1-\gamma) + (1-w_\mathrm{S})C_\mathrm{PM} \tag{12}$$

taking into account that:

$$w_\mathrm{S} = (w_{\mathrm{EVA(1)}}\beta + w_{\mathrm{EVA(2)}}(1-\beta))\gamma + w_\mathrm{PE}(1-\gamma) \tag{13a}$$

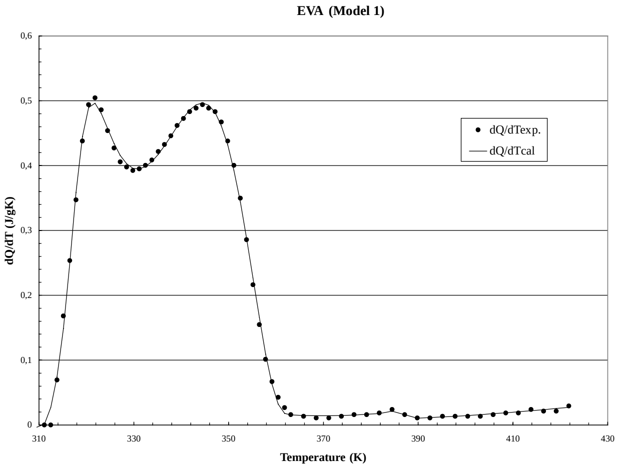
$$\frac{\mathrm{d}w_{\mathrm{EVA(1)}}}{\mathrm{d}T} = -k'_1 w_{\mathrm{EVA(1)}}^{n_1}\beta = -k'_{373,1} w_{\mathrm{EVA(1)}}^{n_1}\beta \exp\left(\frac{-E_\mathrm{a1}}{\mathrm{R}}\left(\frac{1}{T} - \frac{1}{373.15}\right)\right) \tag{13b}$$

$$\frac{\mathrm{d}w_{\mathrm{EVA(2)}}}{\mathrm{d}T} = -k'_2 w_{\mathrm{EVA(2)}}^{n_2}(1-\beta) = -k'_{373,2} w_{\mathrm{EVA(2)}}^{n_2}(1-\beta) \times \exp\left(\frac{-E_\mathrm{a2}}{\mathrm{R}}\left(\frac{1}{T} - \frac{1}{373.15}\right)\right) \tag{13c}$$

$$\frac{\mathrm{d}w_\mathrm{PE}}{\mathrm{d}T} = -k'_3 w_\mathrm{PE}^{n_3} = -k'_{373,3} w_\mathrm{PE}^{n_3} \exp\left(\frac{-E_\mathrm{a3}}{\mathrm{R}}\left(\frac{1}{T} - \frac{1}{373.15}\right)\right) \tag{13d}$$

where, β is the fraction of EVA(1) in the EVA sample, and γ is the sum of EVA(1) and EVA(2), and 1-γ the PE domains. Note that in order to reduce the number of parameters, and besides there exist different solid and melt species along the melting process, their contribution to the heat capacities has been grouped into two different terms only, corresponding to the initial and final slopes of the DSC curve.

This model has 20 parameters to be optimised to explain the complexity of the curve considered and the number of processes involved. Table 3 shows the corresponding kinetic parameters as well as the value of the variation coefficient obtained; the peak temperature and the corresponding rate are also included.



Model 2. The EVA undergoes an initial transition followed by the real fusion, i.e.:

$$\mathrm{EVA} \xrightarrow{k_1} \mathrm{EVA(T)} \xrightarrow{k_2} \mathrm{EVA(M)} \tag{14}$$

$$\mathrm{PE} \xrightarrow{k_3} \mathrm{PE(M)}$$

where EVA(T) is the intermediate specimen (i.e. which has undergone the transition process) and EVA(M) and PE(M) are the melted EVA and PE domains, respectively. In this case, the heat derivative with respect to temperature would be:

$$\frac{\mathrm{d}Q}{\mathrm{d}T} = w_\mathrm{S} C_\mathrm{PS} - \left(\Delta H_\mathrm{EVA} \frac{\mathrm{d}w_\mathrm{EVA}}{\mathrm{d}T} + \Delta H_{\mathrm{EVA(T)}} \frac{\mathrm{d}w_{\mathrm{EVA(M)}}}{\mathrm{d}T}\right)\gamma - \Delta H_\mathrm{PE} \frac{\mathrm{d}w_\mathrm{PE}}{\mathrm{d}T}(1-\gamma) + (1-w_\mathrm{S})C_\mathrm{PM} \tag{15}$$

taking into account that:

$$w_\mathrm{S} = w_\mathrm{EVA}\gamma + w_\mathrm{PE}(1-\gamma) \tag{16a}$$

$$\frac{\mathrm{d}w_\mathrm{EVA}}{\mathrm{d}T} = -k'_1 w_\mathrm{EVA}^{n_1}\beta = -k'_{373,1} w_\mathrm{EVA}^{n_1}\beta \exp\left(\frac{-E_\mathrm{a1}}{\mathrm{R}}\left(\frac{1}{T} - \frac{1}{373.15}\right)\right) \tag{16b}$$

$$\frac{\mathrm{d}w_{\mathrm{EVA(T)}}}{\mathrm{d}T} = k'_1 w_\mathrm{EVA}^{n_1} - k'_2 w_{\mathrm{EVA(T)}}^{n_2} = k'_{373,1} w_\mathrm{EVA}^{n_1} \exp\left(\frac{-E_\mathrm{a1}}{\mathrm{R}}\left(\frac{1}{T} - \frac{1}{373.15}\right)\right) - k'_{373,2} w_{\mathrm{EVA(T)}}^{n_2} \exp\left(\frac{-E_\mathrm{a2}}{\mathrm{R}}\left(\frac{1}{T} - \frac{1}{373.15}\right)\right) \tag{16c}$$

Table 3
Kinetic parameters obtained from the fit of experimental data to the DSC of EVA using model 1

Kinetic parameters		Optimised values
EVA-1	ΔH (J kg^{-1})	17,750
	k'_{373} (K^{-1})	7.14×10^8
	E_a/R (K)	48,601
	N	5.42
EVA-2	ΔH (J kg^{-1})	17,750
	k'_{373} (K^{-1})	0.759
	E_a/R (K)	10,291
	N	0.78
β (%)	43.55	
γ (%)	99.49	
PE	ΔH (J kg^{-1})	5050
	k'_{373} (K^{-1})	2.17×10^{-3}
	E_a/R (K)	53,915
	n	0.38
C_{PS}	a_S (J kg^{-1} K^{-3})	0.444
	b_S (J kg^{-1} K^{-2})	−280.3
	c_S (J kg^{-1} K^{-1})	44,142
C_{PM}	a_M (J kg^{-1} K^{-3})	3.47×10^{-3}
	b_M (J kg^{-1} K^{-2})	−2.24
	c_M (J kg^{-1} K^{-1})	351.9
VC (%)	0.18	
		Calculated values
EVA-1	T_{max} K	321.5
	k' at T_{max} (K^{-1})	0.601
EVA-2	T_{max} K	344.5
	k' at T_{max} (K^{-1})	0.077
PE	T_{max} K	387
	k' at T_{max} (K^{-1})	0.397

$$\frac{dw_{EVA(M)}}{dT} = k'_2 w_{EVA(M)}^{n_2} = k'_{373,2} w_{EVA(M)}^{n_2} \exp\left(\frac{-E_{a2}}{R}\left(\frac{1}{T} - \frac{1}{373.15}\right)\right) \tag{16d}$$

$$\frac{dw_{PE}}{dT} = k'_3 w_{PE}^{n_3} = k'_{373,3} w_{PE}^{n_1} \exp\left(\frac{-E_{a3}}{R}\left(\frac{1}{T} - \frac{1}{373.15}\right)\right) \tag{16e}$$

The results provided by this model are shown in Fig. 4. This model has 19 parameters to be optimised and Table 4 shows the corresponding kinetic parameters and VC (Eq. 10). The peak temperature and the corresponding rate constant are also shown. Comparing with Table 3 it can be observed that the parameters for the third process are very similar, as well as the rate constant at the peak temperature. The parameters corresponding to the peaks ascribed to EVA are different in the two cases as corresponds to the different kinetic models tested. In both cases the correlation of the experimental results is excellent. It is important to note that in the case of EVA DSC curves, the contribution of the heat capacity variation

Table 4
Kinetic parameters obtained from the fit of experimental data to the DSC of EVA using model 2

Kinetic parameters		Optimised values
EVA-Transition	ΔH (J kg^{-1})	7180
	k'_{373} (K^{-1})	1.75×10^8
	E_a/R (K)	45,404
	n	4.41
EVA-Melt	ΔH (J kg^{-1})	11,230
	k'_{373} (K^{-1})	0.721
	E_a/R (K)	9611
	N	0.77
γ (%)	99.36	
PE	ΔH (J kg^{-1})	4990
	k'_{373} (K^{-1})	2.15×10^{-3}
	E_a/R (K)	55,336
	n	0.40
C_{PS}	a_S (J kg^{-1} K^{-3})	0.383
	b_S (J kg^{-1} K^{-2})	−242.2
	c_S (J kg^{-1} K^{-1})	38,057
C_{PM}	a_M (J kg^{-1} K^{-3})	3.58×10^{-3}
	b_M (J kg^{-1} K^{-2})	−2.31
	c_M (J kg^{-1} K^{-1})	365.4
VC (%)	0.17	
		Calculated values
EVA-Transition	T_{max} K	321.5
	k' at T_{max} (K^{-1})	0.582
EVA-Melt	T_{max} K	344.5
	k' at T_{max} (K^{-1})	0.085
PE	T_{max} K	387
	k' at T_{max} (K^{-1})	0.452

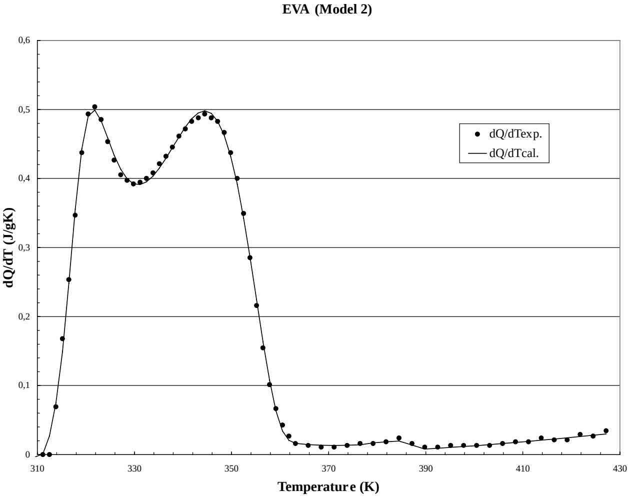


Fig. 4. Experimental and calculated DSC of EVA using model 2.

is less than in the case of PE, as can be seen by the absence of important slopes before and after the corresponding EVA peaks. These two models have been considered in order to show that different models can provide a good representation of the data, and obviously one, at least, is not correct from the mechanistic point of view. This feature illustrates the idea that a good fitting is only a necessity but not a sufficient condition for a model to represent a process. The discrimination of the real model can be a difficult task. The combination of this type of data reduction procedure with other experimental techniques is the only way to solve this type of problem. Nevertheless, the suggested procedure for handling the DSC data has the advantages of avoiding the subjectivity in the quantification of the features of the DSC curves and allows the interpolation of the data and the reproduction of the whole DSC curve.

4. Conclusions

The models proposed satisfactory fit the different calorific processes that occur in the different materials studied by the DSC technique even when complex peaks are present.

The fact of adding the variation of the heat capacities with temperature improves the quality of the correlation and can be considered as an objective type of base line correction in order to completely fit the entire DSC curves.

From these results it is evident that different models can provide excellent fitting of the experimental data. The physical significance of the parameters obtained must be carefully considered, and the type of model and the interrelation among the parameters must be taken into account.

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