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EVALUATING THE LOGISTIC MIXTURE MODEL ON REAL AND SIMULATED TG CURVES

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The aim of this paper is to evaluate and explain the fitting of dynamic TG curves by a mixture of logistic functions. This model assumes that more than one physical process may be involved in each mass loss step and that each physical process may extend along all the experiment. One of the main sources of difficulties in TG is that, very often, different stages of decomposition substantially overlap each other. Several real and simulated TG curves were analysed in this paper. An optimal fitting of the TG curves was obtained by a mixture of logistics. In many cases the optimal fitting reproduces accurately the TG curve. Accordingly, the TG curve can be understood as a sum of parallel reactions, where each single reaction is represented by one or a small number of logistic components. Additionally, making use of the analytical derivative of the fitting, a mixture of Arrhenius reaction order equations was applied to the same curves. In all the cases, the fitting obtained with the mixture of Arrhenius was worse than the obtained with the mixture of logistics. A software was developed to automatically perform these tasks. The physical meaning of the fitting was explained.

Keywords: *Arrhenius, logistic mixture, TG*

Introduction

Thermogravimetric analysis (TG) is widely used to determine kinetic parameters for polymer decomposition. Both isothermal and dynamic heating experiments can be used to evaluate kinetic parameters. Each has advantages and disadvantages. In dynamic thermogravimetric analysis, the mass of the sample is continuously monitored while the sample is subjected, in a controlled atmosphere, to a thermal program, where the temperature is ramped at a constant heating rate. Degradation of polymers is usually a complex process involving combinations of different mechanisms [1]. TG is usually employed to assess thermal stability by determination of the temperature of initial mass loss, which can be viewed as the onset of degradation [2]. The mass loss steps observed in a TG curve can help to identify components in a sample. In some cases the percentages of the components cannot be determined directly from a TG curve because several decomposition processes occur simultaneously [3]. Isothermal methods and controlled rate thermal analysis can help to separate partially overlapping. Both isothermal and dynamic heating experiments can be used to evaluate kinetic parameters [4]. In dynamic thermogravimetric analysis, the mass of the sample is continuously monitored while the sample is subjected to a thermal program, in a controlled atmosphere, where the temperature is ramped at a constant heating rate. The fitting to different models allows for obtention of kinetic parameters. The usual practice consists in fitting sections of the TG curves containing the area of interest, but not entire curves. Multiple heating rate methods are considered more appropriate to obtain kinetic parameters than the single heating rate ones [5–7]. The isoconversional methods such as Ozawa [8] or Friedman [9] are generally recommended. Different processes with different dependence on the heating rate may be overlapping. For example, diffusion controlled processes such as evaporation, do not follow the typical single activation energy Arrhenius model. Chemically controlled mass losses may have different activation energy and thus different heating rate dependence. Overlapping reactions could be detected looking at the dependence of the activation energy on the conversion. Still, problem of separation of overlapping processes remains unsolved. It was reported that determination of kinetic parameters for additively overlapping TG steps is only possible by fitting model equations to the non-standardized mass step by means of non-linear optimization. In practice, to obtain a successful separation of the peaks it is necessary the existence of an overlapping-free interval including the maximum for only one of the overlapping partial reaction steps [10]. Unfortunately, a very common situation is that different stages of decomposition substantially overlap each other. It was mentioned to be the main source of difficulties in the thermal analysis [11]. The most difficult situation would be when decomposition progresses as a multistage process, but the derivative curve presents only one peak. If different stages are not separated, a proof that

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the decomposition under study is really a multistage process, and not a one-stage process, becomes an independent serious problem. The model-free method was proposed to solve this problem, allowing for calculation of the activation energy in the absence of a kinetic model of the process. The method is based on calculation of the integral of Arrhenius exponential over time for a set of isoconversional levels on normalized kinetic curves. It is also possible to calculate the activation energy from a single curve of a derivative of mass loss perturbed by a sinusoidal modulation of a temperature–time relationship [11]. Cao *et al*. proposed a method to fit dynamic TG data to a mixture of logistic functions [12]. It can be applied to an overall TG curve, overcoming the restriction consisting in the need of an overlapping-free interval. Instead of Arrhenius based models, the method assumes a logistic like behaviour of the single ovelapping processes. The fitting gives the amount of sample involved in each single process as well as a central point indicating where each single process is centered on the time or temperature axis. In this paper, the authors went deep on the mixture of logistics model, developing an algorithm for the fitting and extended the method, for comparison, to a mixture of Arrhenius functions.

Mixture models

The mixture of logistics proved to give a good fitting in many cases. In this work, a constant was added to the model in order to reproduce the asymptotic value at the end of many TG traces. Just for comparison, it was also proposed a mixture of Arrhenius equations. In this model, mathematically, the reactions are considered to be parallel. Nevertheless, theoretically a good fitting could be obtained with the proposed model even in the case of consecutive reactions.

Mixture of logistics

This model proposes decomposition of the TG trace into several logistic functions, assuming that the degradation kinetics of each component of the sample is represented by one or the sum of few functions. Even in the case of homogeneous materials, it is supposed that several different structures may exist, each one following its specific kinetics that may be different from the others. In this model, it is assumed that a TG trace may be fitted by a combination of logistic functions.

In order to separate the overlapping processes, the TG curves were fitted by a combination of logistic functions and a constant, *K*, that represents the remainder from the mass loss processes. The model proposed by Cao [12] will remain:

$$Y(t)=\sum_{\mathrm{i}=1}^{\mathrm{k}} w_{\mathrm{i}} f(a_{\mathrm{i}}+b_{\mathrm{i}}t)+K$$

$$f(t)=\frac{e^{\mathrm{t}}}{1+e^{\mathrm{t}}}$$

where i=1,2,...,k represent the logistic components (LC) in the model that are related to physical processes taking place in the sample.

TG curve may be expressed as a sum of $Y_{\mathrm{i}}(t)$ functions like

$$Y_{\mathrm{i}}(t)=w_{\mathrm{i}}f(a_{\mathrm{i}}+b_{\mathrm{i}}t)+K$$

where the values b_{i} represent the slope of the trace steps and the change of scale comes from the $a_{\mathrm{i}}/b_{\mathrm{i}}$ rates. The w_{i} parameters account for the amount of the response variable that is represented by each logistic component.

In order to perform the fitting, a similar scale is desirable for all the parameters, so the previous equation can be rewritten as:

$$Y(t)=\sum_{\mathrm{i}=1}^{\mathrm{k}}\left[\frac{w_{\mathrm{i}}\exp\left(\frac{c-x_{\mathrm{i}}}{d}\right)}{1+\exp\left(\frac{c-x_{\mathrm{i}}}{d}\right)}\right]+K \tag{1}$$

where *c* represents the position on the time axis of the inflection point of each logistic component and *d* is related to the slope.

Arrhenius mixture

Although many kinetic models exist, one of the most classical and explained models is the reaction order, based in the Arrhenius equation. A mixture of reaction order function was modelled, assuming parallel reactions. Even in the case the reactions are consecutive or simply do not follow the reaction order model, the curve could be fitted by this model and the results would indicate how the reactions fit to the model. The fitting can be compared with the obtained by the mixture of logistics.

Each single reaction can be modelled as

$$\frac{\mathrm{d}w_{\mathrm{A}}}{\mathrm{d}t}=k_1 w_{\mathrm{A}}^{\mathrm{n1}}=A_1\exp(-E_1/RT)w_{\mathrm{A}}^{\mathrm{n1}}$$

$$\frac{\mathrm{d}w_{\mathrm{B}}}{\mathrm{d}t}=k_2 w_{\mathrm{B}}^{\mathrm{n2}}=A_2\exp(-E_2/RT)w_{\mathrm{B}}^{\mathrm{n2}}$$

$$\vdots$$

$$\frac{\mathrm{d}w_{\mathrm{j}}}{\mathrm{d}t}=k_{\mathrm{j}} w_{\mathrm{C}}^{\mathrm{nj}}=A_{\mathrm{j}}\exp(-E_{\mathrm{j}}/RT)w_{\mathrm{j}}^{\mathrm{nj}}$$

So the mixture of Arrhenius functions can be written as:

$$\begin{aligned}\frac{\mathrm{d}w_\mathrm{T}}{\mathrm{d}t} &= \frac{\mathrm{d}w_\mathrm{A}}{\mathrm{d}t}+\frac{\mathrm{d}w_\mathrm{B}}{\mathrm{d}t}+...+\frac{\mathrm{d}w_\mathrm{j}}{\mathrm{d}t}+K= \\ &= A_1\exp(-E_1/RT)w_\mathrm{A}^{\mathrm{n1}}+ \qquad (2) \\ &+A_2\exp(-E_2/RT)w_\mathrm{B}^{\mathrm{n2}}+...+A_\mathrm{j}\exp(-E_\mathrm{j}/RT)w_\mathrm{j}^{\mathrm{nj}}+K\end{aligned}$$

The main problem to perform this fitting comes from the need of an accurate TG derivative curve. Since the numerical estimate of the derivative exhibits important amount of noise, the way chosen in this case consisted in derivating the optimal fitting of the TG curve obtained by the mixture of logistics. Then, the Arrhenius parameter values are calculated by multiple regression, making the following transformation:

$$\ln\left(\frac{\mathrm{d}w}{\mathrm{d}t}\right)=\ln A-\frac{E_\mathrm{a}}{RT}+n\ln w$$

this equation is plotted on the axis $\left[\frac{\ln(\mathrm{d}\alpha/\mathrm{d}t)}{1/T}\right]$.

The data are then fitted to a line of the type

$$y=a_0x'+a_1x''+a_2$$

where

$$\begin{cases} a_0=f(1/T) \\ a_1=f(w) \\ a_2=\text{const.}\end{cases}$$

by solving

$$\left.\begin{aligned} a_0&=-\frac{E_\mathrm{a}}{R} \\ a_1&=n \\ a_2&=\ln A\end{aligned}\right\}\Rightarrow\begin{cases}E_\mathrm{a}=-a_0R \\ n=a_1 \\ A=\exp(a_2)\end{cases}$$

Performing the fitting

For fitting the data to any of the previously described models some estimation of the parameter values in Eqs (1) and (2) is needed. In this case, a software application was developed to perform this task.

It performs a non-linear optimization making use of the maximum descent method, followed by unidimensional optimization of the pass size. It uses the Fletcher–Reeves algorithm, allowing to reach the optimum starting from pilot values very far from the optimum. Intelligent optimisation techniques were used to find for good starting values.

The following non-linear regression model has been considered

$$y_\mathrm{i}=m(x_\mathrm{i},\theta)+\varepsilon_\mathrm{i},\quad i=1,2,...,n$$

where the response variable and the independent variable values are denoted by y_i and x_i, respectively. θ is the parameter vector, that is estimated by least squares, and ε_i is the error, assumed to have normal distribution, zero mean and constant variance.

The residuals of the model are denoted as:

$$\varepsilon_\mathrm{i}(\theta)=y_\mathrm{i}-m(x_\mathrm{i};\theta),\quad i=1,2,...,n$$

The parameters of the model were estimated by the non-linear least squares method. The fundamentals of this method were described by Gay [13].

Figure 1 shows the diagram of the method routine for generation of the approximation sequence to the minimum point. It was used for the calculation of the parameter values that minimize that sum.

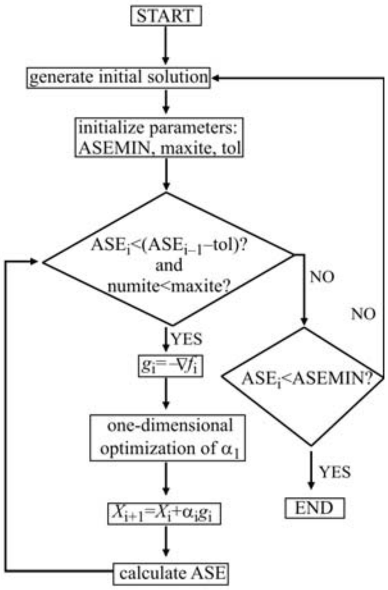

Fig. 1 Diagram of the method routine for generation of the approximation sequence to the minimum point

Application to a simulated TG curve

A TG curve was simulated to check the ability of the method to separate single components from a mixture. The simulated curve was composed of 6 logistic components, some of them overlapping strongly. An optimal fitting was obtained with ASE=0.0000032123. Figure 2 shows an overlay of the row data, the fitting and the single logistic components obtained by the fitting. A numerical comparison of the real and estimated parameter is shown in Table 1, where the *c* parameters represent the inflection point of each logistic component, that is, where each logistic component is 'centered'.

Application to a polyurethane curve

A TG curve was obtained from a polyurethane sample using a heating ramp of 10°C min^{-1} and a purge

Table 1 Real and estimated parameter values obtained by the fitting in the case of the simulated curve

Components	*w*		*c*		*d*	
	real	estimated	real	estimated	real	estimated
1	12	11.9992482801	15.2	15.1998656623	1	0.9999180816
2	18.5	18.5012676056	23.5	23.4999645572	1.5	1.5002079647
3	20	19.9582960274	45.23	45.2271085739	0.95	0.9477790344
4	13.5	13.5491875626	53.23	53.2169514856	2.12	2.1308890131
5	19	18.9857108622	70.23	70.2304259215	1.76	1.7576634345
6	17	17.0061042347	80.3	80.2989820052	1.23	1.2305602057
Constant	0	0.0000548175				

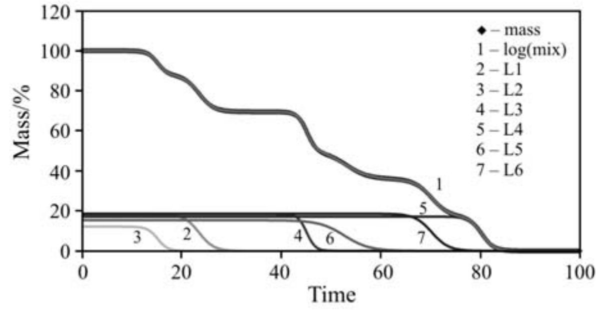

Fig. 2 Overlay of the simulated TG data, the fitting by the logistic mixture method and the single logistic components obtained by the fitting

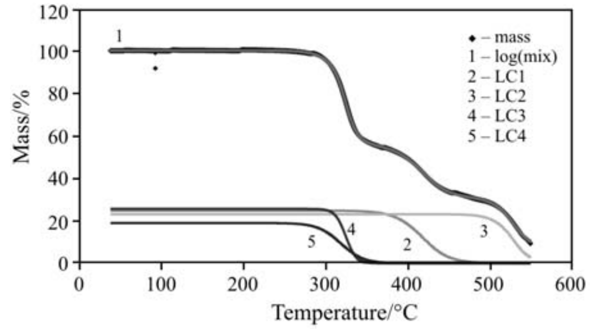

Fig. 4 Polyurethane TG curve fitting obtained by a mixture of four logistic components and a constant

of 50 mL min^{-1} of argon. The curve, shown in Fig. 3, presents 3 degradation steps separated enough to be visually distinguished. In order to explain the relation between physical and mathematical components, two fittings were performed. In the first case, Fig. 3, three logistic components were used. Each logistic component resulted to represent one degradation step giving an ASE value of 0.0967430472. Although the fitting was performed on the time axis, the results were plotted on the temperature axis, which is more normal to represent dynamic TG curves.

Even a lower value of the ASE, 0.0303626123, was obtained using one more logistic component. Figure 4 shows the single logistic components and the inflection points. It is quite obvious that LC3, in the case of a mixture of 3 components, was splitted in 2 logistic components in the case of a 4 components mixture. In fact, the inflection points of these two components are very close: 317 and 324°C on the temperature axis. Admitting that only three degradation processes exist, one of them needed two LCs to be accurately fitted. A clue to identify LCs belonging to the same physical process is the relative distance between the inflection points.

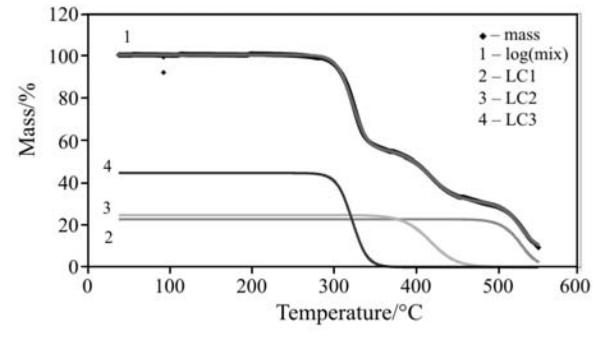

Fig. 3 The fitting of a polyurethane TG curve by a mixture of 3 logistics and a constant

Application to a wood curve

A relatively complex TG curve was obtained from an oak sample using a heating rate of 10°C min^{-1} and purge of 50 mL min^{-1} of argon. An optimal fitting was obtained with 5 LC and a constant. Figure 5 shows the

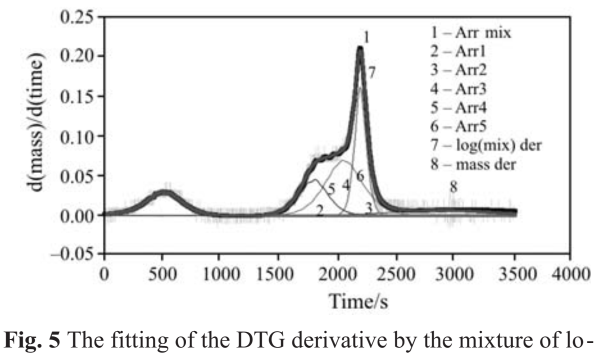

Fig. 5 The fitting of the DTG derivative by the mixture of logistics and the mixture of Arrhenius functions

Table 2 Logistic mixture parameter values obtained in the case of oak

LC	*w*	*c*	*d*
1	12.4239726229	511.9600563984	102.2409761784
2	7.8735187685	2909.3795873350	282.8797921562
3	20.9012065874	2197.8752353917	33.1508665353
4	14.2771121874	1800.0761454308	80.2733022364
5	29.2327278586	2057.1500819734	106.7308602699
Constant	15.1772154218		

Table 3 Reaction order mixture parameter values obtained in the case of oak

Function no.	E_a/kJ mol^{-1}	*n*	*A*
1	27605.4696336972	1.18049400264054	1243358.4
2	33020.5716105606	7.47508236880776E-02	51.9205723
3	267098.983470073	1.15364595354885	2.75091E+44
4	98862.3024829048	1.2759294017526	5.38211E+11
5	79360.4157430996	1.192881243205	344452247.4

fitting of the TG derivative by the mixture of logistics and the mixture of Arrhenius functions. Tables 2 and 3 show the parameter values obtained with each model. In case some values do not make sense from the physical point of view, it would mean that those components do not follow a reaction order model.

Finding the optimal number of components

The way to find the optimal number of logistic components is to use a relatively high number of them and to analyse the results. The components having a mass parameter *w*=0 do not exist. In case of components having a *w* value close to 0, they are minoritary components. They can represent a small amount of the sample or can be understood as a mathematical component to compensate some deviation from the model. The fitting can be performed again, after removing the superfluous components, with the optimal number of logistic components.

Conclusions

The proposed method allows to optimize the fitting of TG curves by mixtures of logistics and mixtures of Arrhenius functions.

The logistic mixture gave better fittings than the Arrhenius mixture in all the cases considered.

Mathematical components centered at the same or close points on the time axis seem to correspond to the same physical component.

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