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Thermal oxidative decomposition estimation combining TGA and DSC as optimization targets for PMMA

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ABSTRACT

Thermal analysis techniques play a key role to determine and characterize solid phase thermal decomposition. In this sense, Simultaneous Thermal Analysis (STA, i.e. TGA and DSC tests carried out simultaneously) are widely employed, since it provides information about how mass is lost and energy released while the temperature of the sample increases. Fire computer models combined with numerical methods are widely used to represent the results from tests and to achieve the values of the kinetic and thermal parameters.

Previous works looked forward achieving those parameters using, as unique optimization target, the mass loss curve (TGA) or its derivative (DTGA). As the study of heat release rate is a decisive element to characterize the material properly, most recent works were adding additional measures. These extra measurements concern the heat transfer and the energy required or released during temperature programmed heating, such as heat rate release, heat of gasification, or the surface temperatures of the samples. The information about the energy is provided by the Differential Scanning Calorimetry curve (DSC).

Despite of the employment of the information provided by the DSC, this information usually is not used as a target to approach the DSC simulated curve to the experimental one as TGA does. Based on the lack of use of the DSC curve as numerical approaching process to set the kinetic properties, we decide to explore the possibility of adding this as a new target in the process. Therefore, kinetic and thermal properties might be achieved fitting experimental and simulated curves simultaneously, which should allow us to take into account the decomposition process and their energy released.

Results obtained in the present work reveal the major challenge of getting a set of parameters, which can fit DSC curve. The level of accuracy reached when only TGA is utilized as target to approach is higher than the level of accuracy of DSC curve. This fact makes increase the value of the errors when both curves are used as targets to approach. In other words, an approach to both curves simultaneously cannot be directly made. With this consideration in mind, this paper proposes an alternative methodology in order to fit TGA curve considering the optimization of the DSC curve.

The methodology proposed in the present work is applied to the analysis of poly(methyl methacrylate) (PMMA).

KEYWORDS:

Thermal decomposition, solid phase chemistry, numerical methods, optimization methods, TGA, DSC, CFD, PMMA.



INTRODUCTION

For fire computer modelling purposes, most of the thermal and kinetic properties cannot be obtained directly from the experimental tests and in order to find the values of these properties it is necessary to make an approach by applying different methods.

Previous works, performed using numerical optimization methods, have claimed their effectiveness to obtain the kinetic and thermal parameters of different materials. The work of Lautenberger and Fernandez-Pello [1] compiles briefly some contributions to this area classified by type of method, scale and laboratory apparatus used and tested material.

Focus on numerical methods applied to thermal analysis, early works employed the variation of TGA exclusively as a target to approach. We can highlight the works of Rein et al. [2], Capote et al. [3] or Hasalová et al. [4].

In order to improve the characterization of the material assessing the energy released, some works were adding this information. There are several ways to include this feature e.g. analysing the heat of gasification which defines the ignition resistance and fire response [5], employing the DSC curve to adjust a numerical model [6] [7], determining the heat transfer basis among other curves in DSC [8], defining the heat transfer or setting the limits of the heat of pyrolysis of the different reactions during pyrolysis process [9], obtaining the values of the enthalpy values for oxidation reactions [10], identifying exothermic or endothermic peaks [11] or determining the enthalpy during the oxidation process [12].

These previous works [6-9] employed the information provided by the DSC curve with the aim to achieve a more comprehensive set of properties that model the thermal decomposition of the material. However, we observed that DSC curve is not used as a target to approach to the experimental one. Based on the lack of treatment of the DSC curve in this way, our work explores adding the DSC curve as a new target to approach, using numerical methods. Therefore, kinetic and thermal parameters may well be achieved fitting experimental and simulated TGA and DSC curves simultaneously. In that way, this methodology should allow us to take into account the decomposition process and their energy released. The material analysed in this work is the polymer poly(methyl methacrylate) (PMMA).

THERMAL DECOMPOSITION MODEL

Thermal decomposition and pyrolysis models describe how the material decomposes with the temperature. This work uses the FDS pyrolysis model software [13]. This model is based on the Arrhenius equation Eq. 1 to represent a material that undergoes one or more decomposition reactions. The Arrhenius equation provides the relationship between the reaction rate (r_{ij}) (1/s) and the temperature (T) (K).

$$r_{ij} = \frac{d\alpha}{dt} = A_{ij} f(\alpha) e^{\left(-\frac{E_{a_{ij}}}{RT_s}\right)} \quad (1)$$

The term A is the pre-exponential energy (1/s), E_a is the activation energy (J/mol), ($f(\alpha)$) is the reaction model, coefficient α is the extent of conversion.

The thermal decomposition process usually takes place through multiple reactions. A scheme of these reactions needs to be defined in the model to represent properly the thermal decomposition. PMMA is made by a macromolecule (ethylene and one methyl group replacing one hydrogen atom), and a second hydrogen atom is replaced by an acetyl group, creating the basic monomer unit [14]. Thermal decomposition of PMMA can be simplified and represented with two main reactions: main chain random scission, followed by and the homolytic scission of the methoxycarbonyl side group [15]. Considering this, a reaction scheme made of two consecutive reactions was used to model the thermal decomposition. Eq. 2 and Eq. 3 show the scheme of reaction employed:



To sum up the previous reaction scheme, material A reacts (reaction 1) (Eq. 2) and produces a fictitious amount (v_p^1) of material B and releases an amount of fuel gas (v_f^1). Material B will be the reactive material of reaction 2. Material B reacts (reaction 2) (Eq. 3) and produces an amount of residue (v_f^4) and an amount of fuel gas (v_r^4).

OPTIMIZATION ALGORITHM

This work applies a numerical method to achieve the suitable values of the parameters that characterize the decomposition process, known as Shuffled Complex Evolution (SCE) [16].

Once the reaction scheme is established (Eq. 2, 3) it is necessary to determine which parameters are required to model the decomposition process. In accordance with Eq. 1 the triplet kinetic (A, E_a, n) are needed. Other parameters such as density (ρ), specific heat (C_p), conductivity (k), heat of reaction (H_r) and emissivity (ε) were included in order to determine the effect of each one in the approaching process. The reduced mass and size of the samples may lead to discard the influence of parameters such as C_p , k or ε . Nevertheless, the works of Lázaro et al. [17] and Comesaña et al. [18] exposed the effects of the boundary conditions, particularly the variation of the sample mass and the effect of the thermal lag when STA test is performance. For this reason, C_p , k and ε were also considered. Density (ρ) was included as a factor (v_p^1) i.e. the amount of material that does not react and will become in reactive mass for the next reaction. Density has to be taken into account in this way since the volume of the simulated sample does not change.

SCE algorithm provides to FDS the values of the INPUT parameters that FDS will use to simulate the decomposition process and obtain the TGA and DSC curves. SCE will converge the value of the function towards a global minimum. The function to minimize its value is the Evaluation error function Eq. (6), which assess the error produced in the approach of TGA and DSC signals.

$$\text{Evaluation error function} = \sqrt{(\alpha \cdot X_{TG_{error}})^2 + (\beta \cdot X_{DSC_{error}})^2} \quad (4)$$

The term (x_i) is the mathematical operator used to evaluate the difference between experimental ($x_{i,exp}$) and simulated curves ($x_{i,sim}$). Eq. 5 show this operator:

$$X_{error} = \frac{\sqrt{\sum_i (x_{i,exp} - x_{i,sim})^2}}{\bar{x}_{exp}} \quad (5)$$

The coefficients α and β are used to give relative weight to both signals in overall error, i.e. whether we assume the DSC curve is more relevance or not, and figure out its influence on the global error. Coefficients α and β are linked such as $\alpha + \beta = 1$. In that way, the more influence of DSC curve, the less influence of TGA curve.

SCE algorithm requires an initial range of values for the parameters to start the process. During the process, the algorithm never goes from those values range. The values are collected from the bibliography, increasing and decreasing them a percentage in order to provide a certain degree of flexibility.

Table 1. Range of values of the parameters to start the optimization process.

Variable	Activation energy (A) (1/s)	Pre-exponential factor (E_a) (kJ/kmol)	Reaction order (n) (-)	Specific heat (C_p) (kJ/kg K)	Conductivity (k) (W/m K)	Emissivity (ε) (-)	Heat of reaction (H_r) (kJ/kg)	(v_p)(-)
Upper value	1.00e+15	200000	5.00	3.00	1.50	1.00	-1000	0.99
Lower value	1.00e+9	90000	0.50	0.20	0.01	0.50	1200	0.01

RESULTS AND DISCUSSION

To begin with, a STA test according the standard ASTM-E1131 was executed with an oxygen concentration of 21%. The heating rate was 30 K/min from 50 °C to 800 °C. Once TGA and DSC curves were obtained, we use several strategies to fit both curves simultaneously. All laboratory tests were repeated 3 times to ensure the repeatability.

The first approach assessed the TGA curve exclusively, i.e. coefficients α and β from Eq. 4 have a value of 1 and 0, respectively. This approach was made in order to test the validity of the scheme reaction model proposed in Eq. 2 and Eq. 3. Results obtained validate the scheme reaction proposed since an accurate TGA simulated curve was obtained.

To check the influence of DSC over the approaching process, three distinct attempts were carried out: #1, the coefficients had a value of $\alpha = 0.5$ and $\beta = 0.5$; #2, $\alpha = 0.7$ and $\beta = 0.3$, and #3, $\alpha = 0.9$ and $\beta = 0.1$. Attempt #1 gives same relevance in the error equation (Eq. 4).

Attempt #1 gives same relevance in the error equation (Eq. 4). The results revealed that the TGA error increased and the DSC error did not improved as it was supposed. These results showed that employment of the DSC curve in numerical approaching process could be not useful as it was expected. Attempts #2 and #3 were executed to verify that in the approaching process, the more influence of the DSC curve, the higher values of the total error.

Due to the effect of the reaction rate (r_{ij}) over both curves, the only parameter in Eq. 6 that allows modifying the energy released or aborted by the sample (DSC curve) without changing the TGA curve is the heat of reaction ($H_{r,ij}$). Hence, a new attempt (#4) was executed changing exclusively the heat of reaction of each reaction, once the TGA curve was fitted properly, as in attempt #1 had been done.

$$\dot{q}_{s,c}'''(x) = -\rho_0 \sum_{i=1}^{N_m} \sum_{j=1}^{N_{r,i}} r_{i,j}(x) H_{r,ij} \quad (6)$$

This attempt #4 reached more accurate results for both curves, than the previous attempts. Next Fig. 1 shows the results obtained using this approaching strategy.

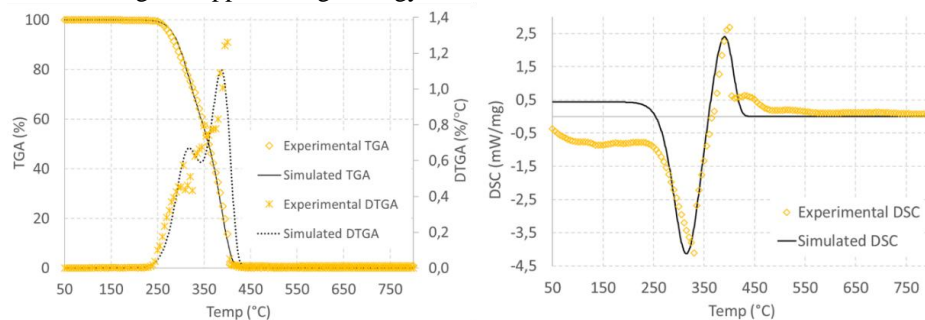


Fig. 1. STA approaching results (attempt #4) (heating rate 30 K/min): left) TGA and DSC curves, right) DSC curves.

As this implies a different approach, Eq. 4 is not expected to assess the errors, because TGA simulated curve is obtained previously and then DSC curve is adjusted. Therefore, Eq. 5 was used to evaluate the errors by replacing in each case the value of mass for the TGA or energy for the DSC. Next table 2 collects the errors obtained.

Table 2. Errors made by the approaching attempt No.4.

	Error in TGA	Error in DTGA	Error in DSC
Attempt #4	0.351	14.933	25.272

Fig 1. and Table 2 reveal the errors obtained for the curves related to the variation of the mass have less values, so the approach of the TGA or DTGA curves is more accurate than the approach of the DSC. The errors of the Table 2 are the best errors (lowest values) obtained for all approaching attempts explained in this section.

To validate the set of parameters obtained in the approaching process, we employed this set to simulate two new decomposition process under different heating rates (10 K/min and 50 K/min). Then the simulated results were compared with their corresponding STA experimental tests. Next Fig 2. shows the comparison for a heating rate of 10 K/min and Fig. 3 for 50 K/min. Table 3 displays the errors for both heating rates.

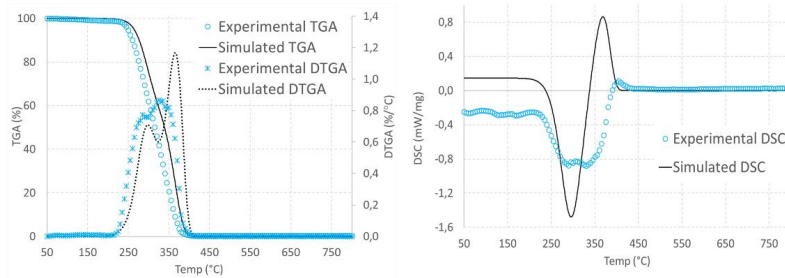


Fig. 2 STA validation results (heating rate 10 K/min): left) TGA and DTGA curves, right) DSC curves.

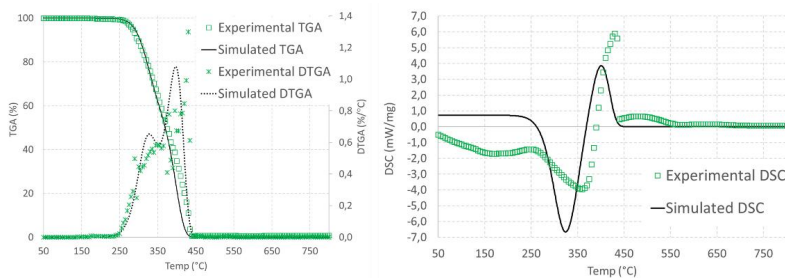


Fig. 3. STA validation results (heating rate 50 K/min): left) TGA and DTGA curves, right) DSC curves.

Table 3. Errors for the validation results.

Heating rate (K/min)	Error in TGA	Error in DTGA	Error in DSC
10	1.962	23.924	25.889
50	0.892	16.540	44.107

In general, it would appear that the set of parameters obtained is valid to simulate other heating rates, especially when TGA curves are compared. However, the variability of the values of the DSC curve makes the approach to these curves has less accuracy. The errors produced are higher when the set is applied at 10 K/min.

Next Table 4 collects the values of the parameters obtained in the best approaching (attempt #4)

Table 4. Parameters obtained by the approaching process

Parameter	Material A	Material B	Residue
Emissivity (ϵ)	1.00	1.00	1.00
Conductivity (k)	0.94	0.21	0.04
Specific heat (C_p)	0.87	0.98	0.38
Reaction order (n)	1.92	0.87	
Activation energy $\text{Log}_{10}(A)$	11.66	11.75	
Pre-exponential factor (E_a)	149459	169647	
Heat of reaction (H_r)	-643	500	
v_p	0.55	0.00	

CONCLUSIONS

As far as including energy in optimization process is concerned, DSC curve was considered as objective to optimize simultaneously with TGA curve. According to the results, DSC simulated curve cannot be fitted as the same quantity as TGA curve since DSC approaching makes unfit the TGA approaching. The more influence of DSC is taken into account in the numerical method and in the Eq. (5) the more error is produced in the approaching of the TGA curves. To obtain the DSC curve without unfit the TGA one, the best method is

to achieve first a proper adjustment to the TGA curve, without considering the DSC curve, and then adjust the values of the heat of reaction of each reaction.

This reached such an accurate approximation to the TGA curve from other heating rates are used. These findings cannot be extrapolated to the comparison of DSC curves, and more investigation is need regarding this issue.

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