Non-parametric kinetic analysis of thermogravimetric data for the thermal degradation of poly(tetrafluorethylene)

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Abstract: Thermal degradation of Teflon was investigated by thermoanalytical methods (TG and DTA). In the kinetic analysis of the experimental data, the NPK method proves to be a valuable tool, allowing for some new kinetic aspects of the degradation process to be obtained. Analysis of the computed isothermal and isoconversional vectors provided some insight into the reaction kinetics. Two different initiation pathways were suggested to control the global degradation kinetics, their relative contribution being temperature-dependant.

Keywords: Non-parametric kinetics, thermal analysis, TG, thermal degradation, Teflon.

Introduction

Kinetic modeling in thermal analysis comprises two essentially different approaches. The first one, mechanistic modeling, aims at obtaining
information regarding the reaction mechanism of the investigated process and determining the values of some reference parameters, such as activation energies of elementary reactions involved. The second one, operational or empirical modeling, is directed towards constructing an operational model capable of accurate predictions for the real process. To this purpose, the processing of experimental data focuses on the estimation of a number of model parameters large enough for accurate temporal extrapolations to be made.¹

Classical methods of thermal analysis, also known as model-fitting methods, postulate a kinetic model and estimate the values of model parameters by fitting on experimental data.² Some of the most used such methods include Freeman-Carroll³, Coats-Redfern⁴, Fătu⁵, Reich-Levi or the initial rate method⁶. The kinetic models employed are empirical or semi-empirical⁷ and in literature there is a collection of so-called “recommended” equations used to describe a wide variety of processes⁸ such as nucleation and crystal growth, interfacial, diffusion controlled, power-law or chemical reaction models. It has been shown that this approach is a strictly operational one and the obtained kinetic parameters have in general no physical meaning.⁹⁻¹¹

Isoconversional methods, also known as model-free methods¹², manage to overcome the necessity to postulate a kinetic model by relying on thermo-analytical experimental data obtained at various heating rates, allowing for an estimation of the kinetic parameters to be made before the model is identified. Thus, the errors implied by misidentification of the “correct” kinetic model on the kinetic parameters are avoided. Still, they rely on several drastic approximations,¹³ that narrows down their applicability, such as the “single step kinetics approximation” that requires
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all the kinetic parameters (activation energies and pre-exponential factors included), as well as the conversion function, to be invariants over the whole experimental range of temperature and conversion degree. This leads to a logical trap, since these methods often outputs “variable activation energies” that varies with the conversion degree, leading to questions about the mathematical validity of this approach.

Non-parametric kinetic analysis (NPK) represents a completely different approach on kinetic modeling of thermo-analytical data. It does not involve any a priori model, but instead it uses a system of submatrices obtained from a set of thermogravimetric curves recorded at various heating rates. It allows, by algebraic manipulation of the experimental data matrix, the decoupling of the two variables: temperature and conversion degree, without any assumption on the form of the reaction rate dependence on these variables. This allows for a superior generalization degree, since it does not require any approximation to be made. NPK also allows reconstructing isothermal data from non-isothermal experiments. Despite its obvious advantages, the method is presently seldom used in analyzing thermoanalytical data, due to its complexity and the volume of calculation involved.

In the present paper, the NPK algorithm is used for a kinetic analysis of thermogravimetric data recorded at various heating rates for the thermal degradation of poly(tetrafluorethylene). Thermogravimetric studies on the thermal degradation of this polymer have been reported since 1947, and various methods of classical kinetic analysis have been used, with varying and sometimes contradictory results. We’d like to point out a series of papers on this subject by Lucia Odochian and co-workers. Never used before for this polymer, NPK allows for some new kinetic aspects of the
degradation process to be obtained and provides an accurate description of the process, that can be relied upon in a subsequent mechanistic modeling of the degradation reactions.

**Results and discussions**

TG and DTA analyses were performed simultaneously at several heating rates, and the obtained curves are presented in Figure 1.

![Thermograms recorded for PTFE degradation at 1, 2, 4, 10, 15 and 20 K/min (from left to right).](image)

By analyzing the DTA recordings, the melting process can be observed between 300 and 400 °C, followed by an endothermic single stage degradation process starting at around 480 °C. This corresponds to the single stage mass losses from the TG curves. A marked inflexion point is noted in each DTA degradation peak, suggesting a change in the reaction mechanism before maximum degradation rate is attained, without any
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correspondence in the TG curves. As DTA and TG measurements are based on different fundamentals, this apparent disagreement does not necessarily have a physical significance. DTA is much more sensitive than TG and the inflexion could indicate a change in the degradation mechanism, as it is also observed in DTG (Figure 3) and, as will be shown later, in the variation of the apparent activation energy with temperature.

For a kinetic analysis of the TG data, the $T(t)$ and $m(T)$ dependencies provided by the thermobalance were normalized as $\alpha(T)$, where $T$ is sample temperature, $t$ is the time passed since the beginning of the degradation, $m$ is sample mass and $\alpha$ is the conversion degree, defined as:

$$\alpha(T) = \frac{(m_0 - m_\alpha) - (m(T) - m_\alpha)}{m_0 - m_\alpha} = \frac{m_0 - m(T)}{m_0 - m_\alpha}$$ (1)

where $m_0$ is initial sample mass and $m_\infty$ is the residue (sample mass after complete degradation).

We shall define the reaction rate $\nu$ as the first time derivative of $\alpha$:

$$\nu = \frac{d\alpha}{dt} = -\frac{1}{m_0 - m_\alpha} \frac{dm}{dt}$$ (2)

Obviously, the reaction rate is a two-variable function, as it depends on temperature and on conversion degree.

The reaction rate dependence on the temperature and on the conversion degree along the experimental TG curves is depicted in Figures 2 and 3, respectively.
The NPK algorithm starts from the well-known equation relating the reaction rate to its variables $T$ and $\alpha$:

$$\frac{d\alpha}{dt} = F(T, \alpha)$$  \hspace{1cm} (3)
The separability of the two variables, an essential condition in any other method of non-isothermal kinetic analysis, expressed as:

\[ F(T, a) = k(T)f(a) \]  \hspace{1cm} (4)

does not have to be postulated here. If the condition is met, this fact arises naturally from calculation, and the NPK method allows testing the validity of the above equation point by point, along the entire course of the degradation process.

Based on equation 3, the reaction rate can be represented as a three-dimensional surface with variables \( T \) and \( \alpha \), that can be discretized as a matrix \( M \) whose elements are the reaction rate for constant \( \alpha \) (on rows) and for constant \( T \) (on columns).

\[
M = \begin{pmatrix}
F(\alpha_1, T_1) & F(\alpha_1, T_2) & \ldots & F(\alpha_1, T_M) \\
F(\alpha_2, T_1) & F(\alpha_2, T_2) & \ldots & F(\alpha_2, T_M) \\
\vdots & \vdots & \ddots & \vdots \\
F(\alpha_N, T_1) & F(\alpha_N, T_2) & \ldots & F(\alpha_N, T_N)
\end{pmatrix}; \quad M \in \mathbb{R}^{N \times M} \hspace{1cm} (5)
\]

Singular value decomposition (SVD) of \( M \) provides a set of three matrices: \( U \) (\( M \times N \) orthogonal), \( W \) (\( N \times N \) diagonal, whose elements are the singular values of \( M \)) and \( V \) (\( N \times N \) orthogonal) that allows the original matrix to be reconstructed:

\[ M = U \cdot W \cdot V^T \] \hspace{1cm} (6)

If the conversion and temperature functions are independent, the matrix \( M \) is the scalar product of two vectors, \( f(\alpha) \) and \( k(T) \). As a result, only the first columns of the matrices \( U \) and \( V \), namely \( u \) (isothermal vector) and \( v \) (isoconversional vector), are needed to reconstruct the original matrix \( M \). In this case, only the first singular value of \( M \), respectively the first element of the diagonal matrix \( W \), will be different from zero.

\[ M = u \cdot w \cdot v^T \] \hspace{1cm} (7)
So, the NPK algorithm allows testing the validity of the condition in equation 4 by analyzing the singular values of $M$. The isothermal and isoconversional vectors express the influence of the variables $\alpha$ and $T$, respectively, over the reaction rate. The values of the conversion and temperature functions, $f(\alpha)$ and $k(T)$, at the grid points $(\alpha_i, T_j)$ where the discretization expressed in equation 5 has been made and can be directly computed from the two vectors provided by SVD:

$$f(\alpha) = [u_1, u_2, \ldots u_N]$$  \hspace{1cm} (8)

$$k(T) = [w_1v_1, w_1v_2, \ldots w_1v_N]$$  \hspace{1cm} (9)

where $w_1$ represents the first singular value of $M$.

After computing the isothermal and isoconversional vectors, the nature of the $f(\alpha)$ and $k(T)$ functions can be investigated directly. They can also be used for fitting in mechanistic kinetic modeling.

Following this procedure, the experimental data in Figures 2 and 3 were used to construct the three-dimensional surface representing the reaction rate. As it can be seen from Figure 4, experimental data is available on a restricted range of temperature and conversion degree. The reaction rate surface was constructed by localized nonlinear multivariate regression in the area bordered by the lowest, respectively the highest experimental curve in Figure 4. That is, to avoid erroneous results, no extrapolation of the experimental data has been made.
Figure 4. Experimental data used in constructing the three dimensional surface of the reaction rate.

To increase accuracy, the surface was constructed on several partially overlapping domains until the whole experimental range was covered. For illustration purposes, the results obtained for temperatures in the range 750-860 K and conversion degree in the range 0-0.4 are presented in Figure 5.

Figure 5. Experimental data and the interpolated three dimensional surface.
The grid density was chosen to 0.5 K/point for temperature and 0.001/point for conversion degree, so that for example, the surface in Figure 5 had 88000 points.

The obtained surfaces were used to construct sets of partially overlapped submatrices that were then submitted to SVD, each matrix providing a pair of individual vectors \((u, v)\). Because SVD is unique up to a multiplication scalar, the individual vectors obtained were shifted vertically with respect to each other. The results are presented in Figure 6.

**Figure 6.** Individual isothermal (left) and isoconversional (right) vectors for PTFE degradation.

**Figure 7.** Complete isothermal (left) and isoconversional (right) vectors for PTFE degradation.
After testing their superposability, the individual vectors were scaled based on a continuity criterion, allowing the isothermal, respectively the isoconversional vectors to be obtained over the whole experimental range, as depicted in Figure 7.

An analysis of the isoconversional vector (the temperature function, \( k(T) \)) allows the calculation of the global activation energy of the degradation process, assuming the temperature dependence to be of Arrhenius type. The results are depicted in Figure 8.

As it can be seen from Figure 8, the apparent activation energy varies with temperature. There are two temperature domains where it remains constant: 765-795 K, where the value is 321 KJ/mol, and 830-890 K, where the value is 293 KJ/mol. The transition from one regime to the other is continuous, between 795 and 830 K, where the apparent activation energy is continuously varying. These observations indicate that competitive reaction pathways coexist, with different contributions to the global kinetics of the degradation.

![Figure 8. Apparent activation energy as a function of temperature for PTFE thermal degradation.](image-url)
The balance between the contributions of parallel reactions to global kinetics is expected to shift with temperature since the effective rate constant is a linear combination of the rate constants of the individual pathways, and the temperature dependence of the degradation process could be modelled as a sum of contributions, each of them being of Arrhenius type:

\[
k_{\text{effective}}(T) = f_1 A_1 \exp\left(-\frac{E_{a1}}{RT}\right) + f_2 A_2 \exp\left(-\frac{E_{a2}}{RT}\right)
\]

where \(f_1\) and \(f_2\) represent the probability of each pathway, respectively, depending on temperature and composition.

An analysis of the conversion function reveals similar behaviour, with two different reaction regimes separated by a transition range between 0.5 and 0.6 conversion degree values. A detailed analysis of the nature of the isothermal vector is however beyond the scope of this study.

The same conclusion of a reaction mechanism comprising two concurrent pathways is also supported by the inflexion points in DTA curves.

As PTFE degradation occurs through a straight chain mechanism, these findings can be explained by the coexistence of two possible initiation processes that control the global kinetics. At lower temperatures (the beginning of the degradation process), due to the high viscosity of the molten polymer and the low radical concentration, initiation by random scission of the macromolecular chain is dominant. With increasing temperature and as the degradation advances, the viscosity decreases and the total radical concentration increases, promoting initiation by intermolecular chain transfer. Having lower activation energy, this pathway eventually takes control over the global kinetics of the degradation.\(^{26}\)
These conclusions are supported by the remarkable agreement between the values of the activation energies experimentally obtained in this study and the ones corresponding to the two proposed parallel pathways, as will be shown in a subsequent paper.

**Experimental**

PTFE was supplied by Hoechst, Germany as granular polymer (under the commercial name Hostaflon TF 1645), with an average molecular mass of $10^6$ g/mol and granule diameter between 0.1 and 0.5 mm.

TG and DTA analyses were carried out on a Diamond Pyris TG-DTA thermobalance (Perkin-Elmer) under nitrogen flow and at heating rates varying between 1 and 20 K/min. Temperature and heat flow calibration were done with Perkin-Elmer calibration reference materials.

**Conclusions**

Thermal degradation of Teflon was investigated by thermoanalytical methods (TG and DTA). In the kinetic analysis of the experimental data, the NPK method proves to be a valuable tool, allowing for some new kinetic aspects of the degradation process to be obtained. The temperature and the conversion functions were separated and computed. The results suggested that, even if the degradation occurs in a single step, the reaction mechanism modifies as the degradation advances. Two different initiation pathways were suggested to control the global degradation kinetics, their relative contribution to the global kinetics of the degradation being temperature-depndant.

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