

## Kinetic analysis of pyrolysis of cross-linked polymers

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### Abstract

Decomposition of cross-linked polymers in an inert atmosphere occurs in such a way that they tend to conserve the structure of their matrix. Bond breaking inside the polymer matrix requires a large amount of energy. That is why decomposition of cross-linked polymers preferentially takes place via a chemical conversion of side chains. Probably, to a first approximation, the side chains can be considered as being almost independent during the decomposition. In other words, the overall decomposition can be described as a set of parallel processes. In such a case, the final residue of the polymer after decomposition can be described as a substance with certain properties independent of the way of obtaining this residue. The accuracy of approximation of kinetic information by using such assumptions is exemplified in four-stage decomposition of cross-linked (rigid) polyurethane in nitrogen. As shown, the set of four activation energies, obtained as a result of the approximation, can be used for sufficiently accurate prediction of the decomposition under arbitrary thermal conditions.

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### 1. Introduction

As a rule, decomposition of polymers occurs as a result of a multitude of physical and chemical processes, and not one single process. Study of polymer decomposition is particularly difficult when a polymer is a multifunctional compound able to decompose with formation of various gaseous products, such as polyurethanes [1,2].

Classical thermogravimetry (TG) allows one to trace the overall change of mass of a material under precisely controlled temperature–time relationships.

Stages of polymer degradation, which are detected at different times in TG experiments, correspond to certain spatial regions under burning of the polymer. Each layer

of the polymer undergoes heating in conformity with certain temperature–time relationship and usually passes first through the melting and then through the stages of thermal degradation. One can expect that polymers with a high thermal stability will have good fire retardant properties, although it is not the only factor. The flow of fuel gases under degradation is also important for the prediction of fire retardancy [3]. Classical TG study of polymer degradation makes it possible to evaluate the rate of fuel production. Such calculations are of interest for thermophysical models of decomposition and can be useful for chemical technology. However, for laboratory practice, the main purpose of the simulation of decomposition kinetics is a comparison of kinetic data with a current chemical content of decomposition products in a polymer. This problem concerns all investigations on thermal stability.

In some devices, gas analysers are combined with thermobalances (GC, MS) [1]. This simplifies chemical

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analysis of decomposition products. However, at present, analysis of substances in a condensed phase (NMR, FTIR) is impossible without interruption of decomposition. As a general rule, the chemical analysis requires larger portions of a substance than the TG experiment. That is why the thermal experiment is typically repeated twice. Kinetics of decomposition is studied under heating with a constant rate, whereas the chemical analysis is implemented by using other samples decomposed under isothermal conditions. Obviously, the stages of degradation in these parallel experiments should strictly correspond to each other.

The simulation of multistage kinetics encounters a number of serious difficulties and requires simplifying assumptions [4]. In general, processes of decomposition of different functional fragments of a polymer are conjugated. However, as shown for highly cross-linked rigid polyurethane used as an example in this article, at least for cross-linked polymers and at least for inert atmosphere (nitrogen) and within the range of comparatively small heating rates (1–7 °C/min) these processes can be considered, at a first approximation, as independent (parallel).

One can imagine that an original polymer consists of a multitude of functional groups of different kind that are able to decompose with evolution of pyrolysis gases. The products of decomposition will themselves decompose, but the stages corresponding to the primary decomposition and the secondary one are sharply divided on scale of time (or of temperature). For example, the first stage is decomposition at a moderate temperature whereas the second one is decomposition at higher temperature in the course of deep carbonisation. In other words, the first stage of degradation and the carbonisation are independent processes.

The purpose of the present article is to illustrate the accuracy of approximation of kinetic data by using the hypothesis of stage independence.

The use of rigid polyurethane for the purposes of fire retardancy is described in a number of publications [5–7]. Mechanisms of its thermal degradation are being investigated [8–10] but still need additional elucidation. This paper is directed to the development of a methodology for investigation of decomposition of cross-linked polymers similar to rigid polyurethane.

## 2. Experimental

### 2.1. Material

Raw material was rigid polyurethane foam supplied by ICI (Belgium). This foam is a highly cross-linked polymer with a closed cell structure. Pentane gas is usually contained within these cells.

### 2.2. Thermogravimetric analyses

TG experiments were carried out at four heating rates (1.02, 2.51, 5.04 and 7.59 °C/min) under nitrogen (Air Liquid grade N45 at  $5 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$ ; flow rates measured in standard conditions) using Setaram 92-16.18 apparatus. Samples (about 10 mg rigid polyurethane ground to an average particle size of  $\sim 40 \mu\text{m}$ ) were positioned in open vitreous silica pans. The precision of the temperature measurement is  $\pm 1.5 \text{ }^\circ\text{C}$  over the whole range of temperature.

## 3. Numerical method

The method used [11–13] determines activation energies and pre-exponential factors by means of minimization of the average square of deviation,  $\Delta$ , between computed and experimental kinetic curves on scale of logarithm of reduced time (the integral of the Arrhenius exponential over time). Eighteen known models corresponding to different physical and chemical processes are included as the basic set in the algorithm (see Table 1). In case of a two-stage process, sequential analysis of  $18^2 = 324$  variants and arrangement of values of  $\Delta^{1/2}$  in ascending order allow the selection of the best models for each of the stages. The lower  $\Delta^{1/2}$  is, the nearer is the calculated activation energies to correct values.

The idea of handling kinetic data for three-stage decomposition (Fig. 1) consists of reduction of the computational procedure to the algorithm for a two-stage decomposition.

After rough determination of positions of  $x_1$  and  $x_2$  points (respectively, the point separating the first and second stages and the point separating the second and third stages), the algorithm first approximates the two last stages (stage 2 and stage 3). It refines the point separating these two stages and searches for the corresponding activation energies and pre-exponential factors. In doing so, the program proposes the best models associated to each corresponding step of degradation. Then the same computation is done for the two first stages (stage 1 and stage 2). The model proposed before for the second stage is considered as the best one during this cycle of computations. Thus, as a final result, the algorithm selects the best models corresponding to each of three stages and calculates corresponding activation energies  $E_1, E_2, E_3$  and the pre-exponential factors  $A_1, A_2$  and  $A_3$ .

If the stages of decomposition are independent, the kinetics can be generally described by the following differential equation for each  $i$ -th stage

$$d\alpha_i^{(v)}/dt = A_i f_i(\alpha_i^{(v)}) \exp[-E_i/RT_v(t)] \quad (1 \leq v \leq M)$$

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