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PECULIARITIES OF DECOMPOSITION KINETICS INDICATED DURING THE PROCESS OF NON-ISOTHERMAL HEATING

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ABSTRACT

General conclusions based on the results of experimental and theoretical investigations of the decomposition kinetics of various polymeric materials over a wide range of heating rates are made. It was found that the decomposition process of the materials investigated proceeds within confined temperature intervals. Kinetic equations to describe the thermal decomposition processes of polymers and natural coals are suggested.

INTRODUCTION

The thermal decomposition kinetics of polymers and natural coals have been studied over a wide range of heating rates from 0.01 to 50000° s^{-1} [1–3]. They demonstrate that each material investigated has a characteristic temperature range in which the thermal decomposition process takes place. Figure 1 represents the typical position of TG curve groups in these ranges. The lower limit, $m_\infty(T)$ (marked by shading), corresponds to the condition

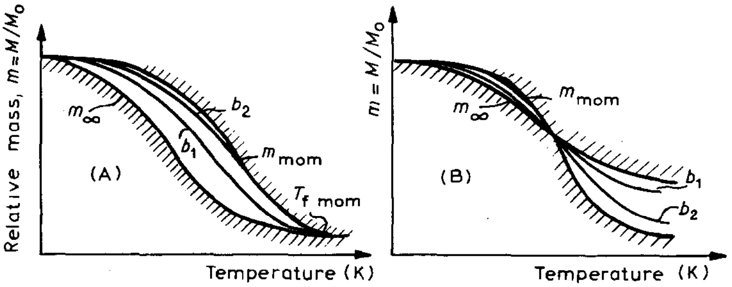

Fig. 1. Characteristic position of TG curves for thermoplastic polymers (A) and natural coals (B). Heating rate $b_2 > b_1$. The shaded areas mark the range of thermal decomposition.

of equilibrium heating. For each fixed temperature T

$$m_\infty(T) = \lim_{t\to\infty} m(T, t)$$

where m is the relative mass of the sample residue $= M/M_0$.

The curve $m_\infty(T)$ characterizes the results observed at the lowest heating rates, allowing chemical equilibrium between the material and the decomposition products to be established. When the heating rate is increased, the TG curves will be irregularly shifted towards the right-hand side. They show a tendency to cluster in the vicinity of the other extreme position, that is, the upper limit, $m_{\text{mom}}(T)$. Each ordinate of the curve $m_{\text{mom}}(T)$, at fixed temperature T, corresponds to $m_{\text{mom}}(T) = \lim_{t\to 0} m(T, t)$.

Since time and heating rate are interrelated, the condition $t \to 0$ is equivalent to the condition $b = \mathrm{d}T/\mathrm{d}t \to \infty$. The ordinates of the curve $m_{\text{mom}}(T)$ correspond to the shortest possible, quasi-instantaneous heating rates. Heating time must, however, be sufficient to establish the temperature in question within the sample, and to remove decomposition products. To accomplish the latter condition, which is of great importance, the specimens should have dimensions as small as possible. Details of such experiments are described in ref. 2.

It is justified to formulate rules for determining sets of points for the limits of thermal decomposition in another manner. Let us consider the horizontal intersecting line at some fixed value m(const.). One then obtains the following limit values

$$T_\infty = \lim_{t\to\infty} T(M, t) \qquad \text{and} \qquad T_{\text{mom}} = \lim_{t\to 0} T(\dot{m}, t)$$

The limit temperatures $T_{i\,\text{mom}}$ and $T_{f\,\text{mom}}$ are determined graphically. In the case of natural coals and thermoreactive polymers, inversion of the limiting curves $m_\infty(T)$ and $m_{\text{mom}}(T)$ was observed.

Figure 2 represents examples of graphically determined limit temperatures from the data of ref. 4. As seen from the figure, the limit temperatures are reached with the polymers in the examples at heating rates as low as 2–6° s^{-1}.

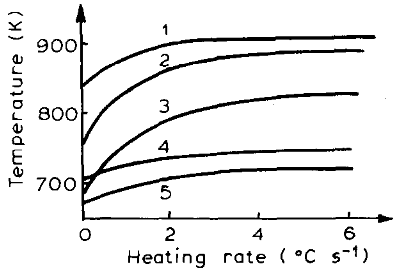

Fig. 2. Characteristic temperatures of decomposition for linear polymers vs. heating rate. (1) $T_{50\%}$ polyamide, (2) T_f polycarbonate, (3) T_i polycarbonate, (4) $T_{50\%}$ polystyrene, (5) T_i resol (resin DBS-1).

EXPERIMENTAL

Slow heating rate investigations were made with the use of Paulik–Erdey and Perkin-Elmer derivatographs. The rapid heating rates were achieved with special DTA and TG equipment. The samples were prepared in the form of films or powders with an initial mass of about 2 mg, which were heated with a contact metallic heater of excellent heat conduction. Signals from the thermocouples placed in the samples were registered with an oscillograph. The temperature interval of decomposition did not go beyond the maximum upper limit temperatures: 520 ± 6°C, PMMA; 530 ± 6°C, PS, etc., see Fig 3. Figure 3 represents the dependence $\ln W = f(1/T)$, where $W = 1/t$ and t is the time of thermal decomposition of the polymer film.

The interpretation of the detected effect is given in terms of the breakdown of Van der Waals bonds at $T = T_{\mathrm{mom}}$ [5,6].

CONCLUSION

The traditional kinetic equation for one-stage chemical reactions of order n combined with the Arrhenius law do not give an adequate description of the TG curves $m_{\infty}(T)$ and $m_{\mathrm{mom}}(T)$ of polymeric materials and natural coals. Accuracy in describing TG reults of such materials is greatly increased by introducing into their kinetic equation the experimentally found limits of

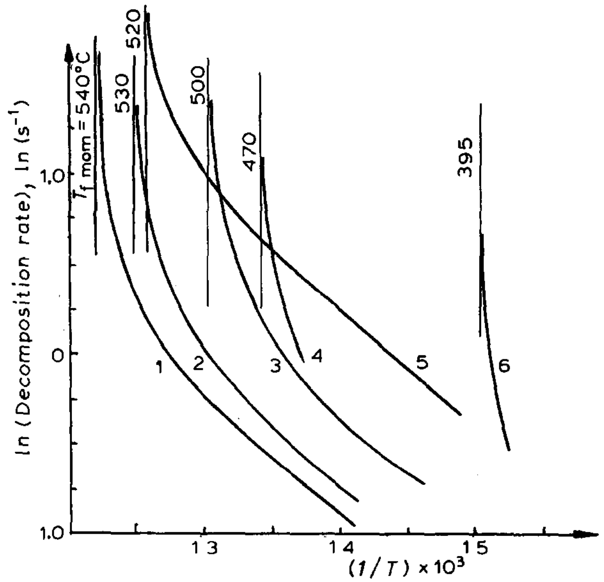

Fig. 3. Characteristic temperatures of thermal decomposition for linear polymers at high heating rates. (1) PS(st), (2) PS(bl), (3) PETF, (4) PVCh, (5) PMMA, (6) Colemanite (mineral).

the thermal decomposition range, $m_{\infty}(T)$ and $m_{\text{mom}}(T)$, and the temperature $T_{\text{f mom}}$.

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