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POLYMER THERMODECOMPOSITION.CHARACTERISTIC FEATURES OF NON-ISOTHERMAL KINETICS BY RAPID HEATING

Shlensky O.F., Mendeleev Institute of
chemical technology, Moscow, USSR

ABSTRACT

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

INTRODUCTION

The thermal decomposition kinetics of polymers and natural coals have been studied in the wide range of heating rates from 0,01 to 50000 degree/s (ref.1-3). They demonstrated that each investigated material has a characteristic temperature range in which the thermal decomposition process takes place. Figure 1 (A,B) represents the typical position of TG groups in these ranges.The lower limit $m_{\infty}(T)$ corresponds to condition 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 sample residuum M/M_0.

The curve m_{∞} (T) characterizes the observation results at the lowest heating rates allowing to establish the chemical equilibrium between the material and the decomposition products. When heating rate is increased, the TG curves will be shifted irregularly towards the right side. They show a tendency of clustering in the vicinity of the other extreme position, that is the upper limit $m_{mom}(T)$. Each ordinate of the curve $m_{mom}(T)$, at fixed temperature T, corresponds to $m_{mom}(T) = \lim_{t \to 0} m(T,t) = \lim_{b \to \infty} m(T,t)$, $b = dT/dt$. The ordinates of curve m_{mom} correspond to the shortest ones which are possible, quasimomentaneous heating rates.However, heating time must be sufficient to establish the temperature within the sample, and to remove decomposition products. To

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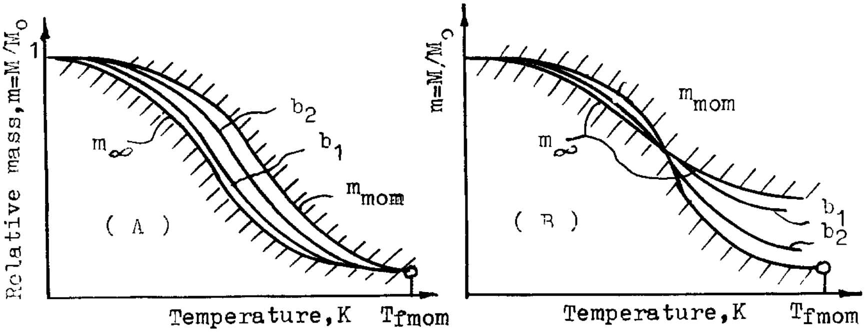

Fig.1. Characteristic position of TG curves for thermoplastic polymers (A) and natural coals (B). Heating rate $b_2 > b_1$. The lines mark the range of thermal decomposition.

accomplish the latter condition - which is great importance - the examples shoud have dimension as small as possible. Details of such experiments are described in ref.2.

It is equally justified to formulate rules for determining the sets of points for the limit of thermal decomposition in another manner. Let us consider the horizontal intersecting line at some fixed value m=const. Then we obtain the following limit values:

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

The limit temperatures T_{mom} and T_∞ are determined graphically. In the case of natural coals and thermoreactive polymers, intersecting of the limiting curves was observed.

MEASURING METHODS

Slow heating rates investigations were being made with use of Paulic-Erdey and Percin-Elmer derivatographs. The rapid heating rates were achieved with employment of special DTA and TGA eqipments. The examples were being prepared in form of films by means of sprayer (or powders) with initial mass about 2 mg, and they were being heated with use of exellent heat conductionly contact metallical heater. Signals from the thermocouples placed in the examples and heater we are registred with use of oscillograph.

RESULTS AND DISCUSSION

Temperature interval of decomposition did not go further then upper limit temperarires: $T_{f\ mom}$ =520°C (PMMA), 530°C (PS), ETC , see fig.2. Fugure 2 represents the dependence $\ln W = f(1/T)$, where $W = 1/t$ - average rate of decomposition, t - the time.

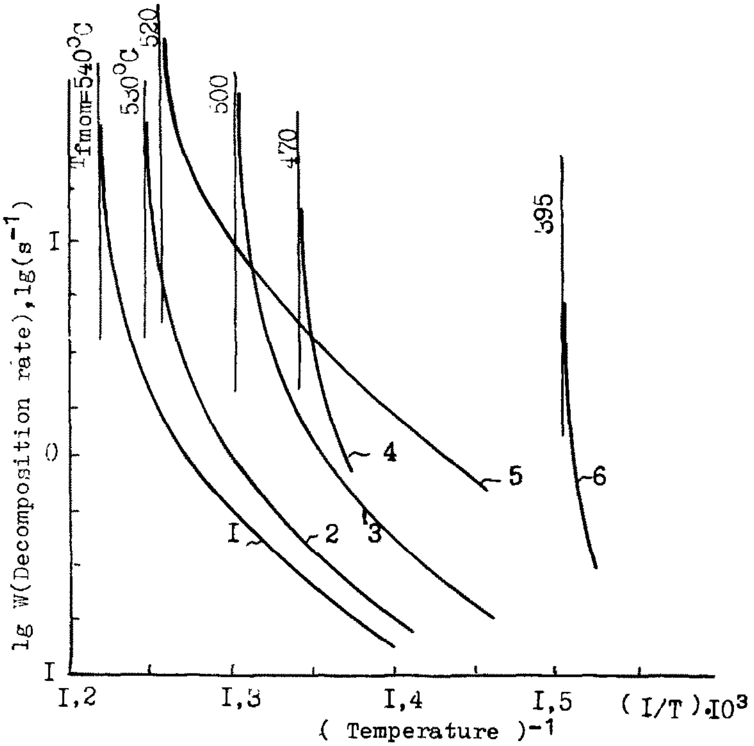

Fig.2. Characteristic temperatures of thermal decomposition and decomposition rates for linear polymers.1- PS (St),2-PS (Bl), 3-PETF, 4-PVCh, 5- PMMA, 6 - mineral kolemanit.

The following empirical expression is proposed for the decomposition rate constant of investigated polymers:

$$k = k_o \exp\left(- \frac{E}{RT} + \frac{A}{1/T - 1/T_{f\ mom} + d}\right)$$

where k_o, E, A, d - are parameters, f.e. for PMMA $A = 2{,}6 \cdot 10^{-5}$ 1/gr, $E/R = 1{,}7 \cdot 10^{4}$ grad, $k_o = 2{,}4 \cdot 10^{10}$ 1/s, $d = 1 \cdot 10^{-6}$ 1/grad , $T_{f\ mom} = 793$K e.g. The experimental results for mineral colemanit were obtained in ref.4.

It appears reasonable to apply, in order to obtain exact kinetic relationships, to Hinshelwood's theory, in which the behaviour of reactant is modelled by a set of 2s oscillators whose energy does not exceed a maximum value $\mathcal{E}_m$. The rate constant of the dissociation of the system of oscillators will depend on temperature:

$$k = k_o \ e^{\theta} \left(j_{s-1} + j_{s-2} + \dots + 1 \right)$$

where $j_{s-1} = \theta^{s-1}/(s-1)$, $j_{s-2} = \theta^{s-2}/(s-2)$ ... are the terms of the polynomial $\theta = \mathcal{E}_m/kT$.

Only the first factor in eq. corresponds to the Arrenius equation. Owing to the factor in brackets, the rate constant "k" will grow more rapidly with temperature than according to the Arrenius equation, since in macromolecules, the number "s" will increase with temperature rise which results in higher mobility of the kinetic units (atom groups, segments) and simultaneously in lower viscosity of the polymer. The interpretation of detected effect is given (ref. 5) in the terms of break-down Van Der Waals (intermolecular) bonds at the limit temperature $T = T_{f\ mom}$,

$T_{f\ mom} = D_m/R$, where D_m - is energy of intermol. bonds.

CONCLUSION

The traditional kinetic eqution for one-stage chemical reaction of order "n" combined with Arrenius aquation not allou to obtain an adequate description of the TG curves m_{∞} (T) and T_{mom}(T) of polymeric materials and natural coals. Accuracy in describing TGA results is largely increased by introducing into kinetic eqation the limits of the thermal decomposition range m_{∞} (T) and m_{mom}(T) and temperatures $T_{f\ mom}$.

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