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A NOVEL APPROACH TO STUDY THE ISOTHERMAL BEHAVIOUR OF SUBSTANCES AFTER 0.01–1 s FROM THE CHEMICAL PROCESS INITIATION

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New modifications of a contact heater are suggested for investigating thermal decomposition processes, as well as for determining kinetic characteristics of substances under conditions of intense heating to a fixed constant temperature.

Keywords: contact heating methods and technique, isothermal behaviour, kinetics

Introduction

Most existing industrial and laboratory TA devices are not entirely suitable for studing short-term stages of kinetic processes of thermolysis. Those based on convective heating are only capable of registering processes of thermolysis which last from several minutes to several hours. The samples are usually placed in open crucibles or in crucible with non-sealed lids.

We have developed new experimental devices and methods of contact thermal analysis. The methods under consideration are based on quick-response heating of the sample in contact with a heat source at a constant elevated temperature [1–3]. This factor distinguishes our contact method of heating from existing convective and filament methods of heating the sample. Although some existing methods are capable of extremely rapid rates of heating (e.g. infrared and laser methods), they cannot record the kinetic characteristics of a sample maintained at constant temperature after 0.01 ... 1 s from initiation of the thermal process.

It is necessary to mention a characteristic of thermolysis of materials placed in an open crucible. The mass-transfer in the reaction zone has an influence on the thermolysis rate [1]. It should be noted that the kinetics of the mass loss of the substance in the open crucible can be described by following equation [4]:

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$$\frac{d\alpha}{dt} = Z f(\alpha)\left(1 - \frac{p_i}{p_\infty}\right) e^{-E_{ef}/RT} \tag{1}$$

where Z = pre-exponential factor, E_{ef} = activation energy, p_i = partial pressure of evaporating component, and p_∞ = equilibrium vapour pressure over the sample. By substituting for the partial pressure and p_∞ [5] in equation (1) we obtain:

$$\frac{d\alpha}{dt} = Z f(\alpha)\left(1 - \frac{p_1 - \frac{q\,h}{D\,\rho} p_a}{A_{exp}\left(-\frac{\Delta H}{RT}\right)}\right) \exp\left(-\frac{E_{ef}}{RT}\right) \tag{2}$$

where h = height of crucible, ρ = density, D = diffusion coefficient, $f(\alpha)$ is a geometrical factor, p_a, p_1 = atmospheric and partial pressures at the edge of the crucible, and ΔH = enthalpy.

From the above equation it follows:

$$-E_{ef} = RT \ln\left(\frac{\frac{d\alpha}{dt}}{Z f(\alpha)}\right)\left(1 - \frac{p_1 + \frac{M_o\,h}{S\,D\,\rho} p_a \frac{d\alpha}{dt}}{A \exp\left(-\frac{\Delta H}{RT}\right)}\right) \tag{3}$$

Equation (3) shows, that the obtained effective activation energy is dependent on the diffusion coefficient and the dimensions of the crucible.

Many experiments have shown [1, 6] that kinetic curves depend on the shape of crucible and lid design. The highest temperatures of chemical processes are obtained from samples examined in closed crucibles and the lowest temperatures from experiments conducted using open crucibles. The labyrinth sealed crucible makes it possible to study true microkinetic processes without a mass-transfer complication and thus to obtain the most exact values for activation energy.

On the other hand, under extremely rapid heating the temperature of the decomposing sample can be greater than the equilibrium temperature. Then $p_\infty >> p_i$, $1 - \frac{p_i}{p_\infty} \approx 1$ and according to Eq. (1) the kinetics of mass loss are independent of mass-transfer and geometrical properties of the sample container. The correct results from the experiment may therefore be obtained. The contact method fulfils these conditions. In addition, the time delay in following the thermoanalytical signal is small in comparison with ordinary TA instruments (line D on Fig. 1) because there is no thermobalance or other inserted devices.

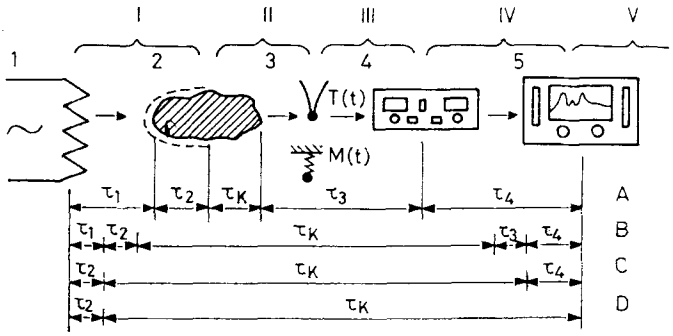

Fig. 1 Delays in the passage of the TA signal in various designs
I — environment of a sample, II — measuring means, III — measurement
IV — registering system, V — interpretation; 1 — heater, 2 — sample,
3 — transducers, $T(t)$ and $M(t)$, 4 — transformer (detector), 5 — recorder (oscillograph). Characteristic times: τ_1 crucible heating, τ_2 sample heating, τ_k reaction time, τ_3 time of measurement, τ_4 is recording time.
Horizontal lines: A — complet chain, B — TG-technique, C — ITG-technique, D — contact heating of the sample

Experimental details

The contact TA device includes two different types of heating arrangement: one-sided heating of the sample and two-sided heating of the sample. In the first variant one side of the sample has free access.

In the second variant both surfaces of the sample are enclosed between two plates or rods. A sample may be wrapped in a metallic foil up to 0.01 mm thick. Such packing makes it possible to test powders, films or fibres. Samples are weighed on an analytical balance and secured between the end faces of metal rods preheated to a desired temperature which is kept constant throughout the test by an electric heater. The high thermal conductivity of metals makes it possible to heat samples to the desired temperature in about 1 s. This heating technique has the advantage of excluding specimen exposure to the environment due to protection by the foil, which does not hinder evacuation of decomposition products from the reaction zone. Wrapping of the samples simulates the labyrinth seal. Due to the high thermal conductivity of the metal heating elements, the average rate of heating is 200–800 degrees per second. Instead of the metal rods suggested in [1] molten tin, lead and aluminium were tried as heat transfer agents to test foil-wrapped samples immersed in them. To prevent any chemical interaction of the foil with either samples or medium, the foil material was selected from the following: aluminium, stainless steel, nickel, titanium and gold. Some modifications

of such devices are discussed in [1, 3]. After cooling, the foil-wrapped samples are re-weighed on the same analytical balance.

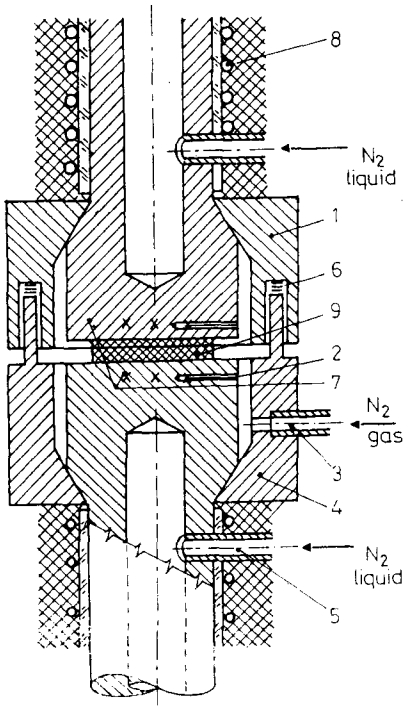

Fig. 2 Construction of the calorimetric cell 1 – Upper heat insulating ring, 2 – Hole for thermocouples, 3 – Tube for inert gas, 4 – Lower heat insulating ring, 5 – Tube for cryogenic liquid, 6 – Insulation layers, 7 – Metal rods, 8 – Electric nickel-chromium wire, 9 – Sample

Modification of the heating cell (Fig. 2) makes it possible to measure heat capacity and conductivity (average values). Such a device is equipped with two fluxmeters and heat insulating rings [3]. To enlarge the temperature range in the low-temperature field in the rods they are supplied with two cooling cavities for a cryogenic liquid. This device allows electric conduction analysis (ECA) and radio-frequency thermal analysis (RFTA).

The highest heating rates are obtained with the aid of one-sided and all-round heating. Some methods of construction of the heaters are shown in Fig. 3. The devices are distinguished from each other by the various ways of presenting the sample to the pre-heated metallic surface of the heat carrier [1, 2].

The time of the thermolysis reaction is obtained in the following manner:

$$t = \frac{V_o^v}{l}$$

where V_o is the speed of relative motion, and l is the length of the imprint. The following are various methods for measuring TA–signals which can be used in contact heating devices: 1. temperature, 2. thermal flow, 3. life-time, 4. electric capacity or inductance, 5. dielectric loss, 6. sound emission, 7. rate or pressure of gas flow 8. weight of the sample.

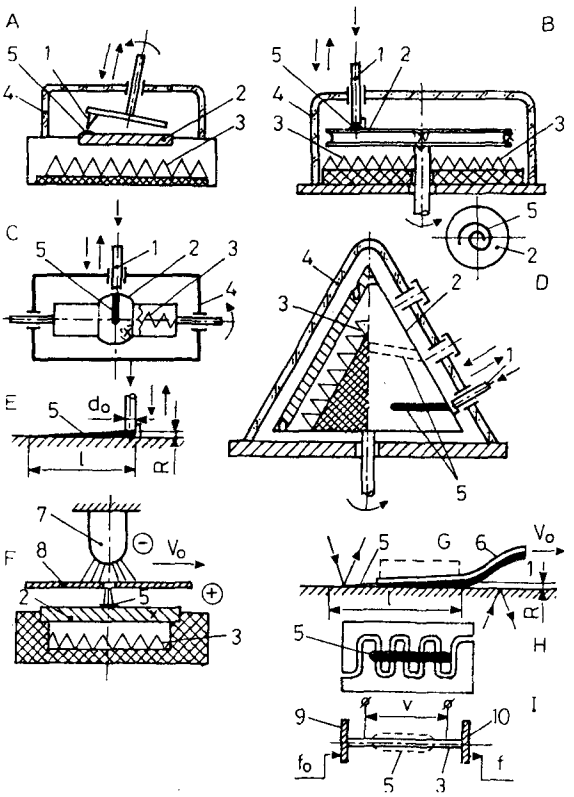

Fig. 3 Various methods of application of films (solution or melt) on the pre-heated metallic surface of the heater. 1 — Specimen, 2 — Metallic surface, 3 — Electric wire coil, 4 — Transparent cover, 5 — Imprint melting film, 6 — Plastic tape, 7 — Pulveriser, 8 — Screen, 9, 10 — Source and receiver of ultrasound signal. A, E, F, G, H, I — motionless metallic heat carrier (sample moving). B, C, D — mobile metallic heat carrier (sample immovable).B — revolving disc, D — revolving cone, C — revolving cylinder, E, G — dimensions of samples, * — thermocouples

Among contact TA-instruments the most precise are based on detection of electrical (Fig. 3 H) or acoustic (Fig. 3 I) signals with the aid of corresponding transducers. They contain a system for measuring relaxation of the signal or the life-time of the samples. All-round heating of samples is carried out through immersion of the sample in a melt of the metallic heat carrier without the foil. The acoustic signal from the transducer placed on the sample holder is registered.

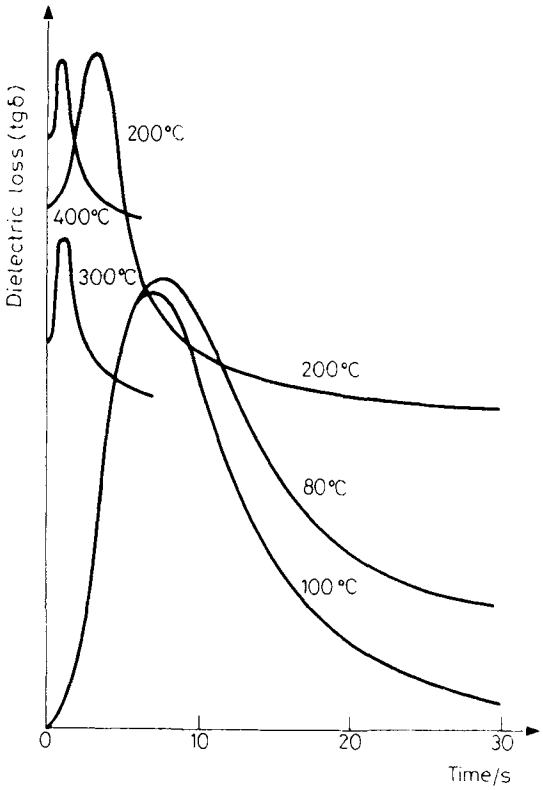

Fig. 4 Phase and kinetic transformation of PMMA at different temperature

Results

Experimental results based on weighing the samples are given in [1, 2, 8, 9]. The contact method of sample heating has made it possible to establish the existence of a whole series of previously unexplored rapid reactions and pre-spinodal processes of an explosive nature. Three types of high-rate thermolysis processes have been identified:

– processes caused by weakening of intermolecular bonds and phase transition,

– processes characterised by changes in entropy (polymers),

– processes involving the loss of stability in some clusters of oscillators in condensed substances.

Physical and mathematical models of thermolysis have been developed. The paper presents some tests obtained with the aid of the RFTA-technique. Figure 4 presents the change of $\tan\delta$ (dielectric loss) during the pyrolysis, phase and kinetic transformation in polymethylmethacrylate. It may be seen that the width of the peak characterises the duration of the heating process in the sample.

Conclusion

New modifications of contact heater devices are given. They allow the possibility of resting various condensed materials under very high heating rates and heating condition, including kinetic and calorimetric investigations.

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Zusammenfassung — Zur Untersuchung von thermischen Zersetzungsprozessen und der Bestimmung der Reaktionskinetik von Substanzen bei intensivem Erhitzen auf vorgegebene konstante Temperaturen wird eine neue Abart von Kontakterhitzern beschrieben.