Journal of Thermal Analysis, Vol. 38 (1992) 391-396

HIGH-SPEED VERSATILE DEVICE FOR INVESTIGATING THERMAL DECOMPOSITION PROCESSES

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A new method and technique of TA-experiment are suggested for investigating thermal decomposition processes, as well as for determining kinetic and thermophysical characteristics of solid and liquid substances under conditions of intensive heating or cooling.

Keywords: intensive heating and cooling method and technique, kinetics

Introduction

Most industrial devices used in thermal analysis and calorimetric investigations have certain limitations in respect of the range of linear heating rates: approx. 2–20 deg·min^{-1}. Very often an experiment lasts too long for the successful use of such equipment. For example, if it takes for a sample maximum 500 and minimum 50 minutes to reach 1000°C, rapid chemical reactions and physical transformations are completed before the set temperature is reached.

Therefore, a process with a characteristic time of about one second may escape the attention of the investigator. This often takes place if the investigator contents himself with traditional methods and equipment for thermal analysis.

Rapid chemical processes by themselves also present a practical interest, because of the intensification of various technological processes and development of machines that operate at high temperatures and pressures. In some new technological processes heating and transformation of substances take place within a fraction of a second (the rates of heating being approx. 100–1000 deg·s^{-1} and more). Such processes include, for example, high frequency heating, plasma processing, laser technology and others. The ap-

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pearance of these technologies have stimulated the development of new methods for rapid thermal analysis.

There is another problem since the interpretation of thermal curves and kinetic curves obtained by the methods based on scanning the temperature (TGA, DTA, DTG, etc.) presents certain difficulties as there are no mathematically accurate methods for solving the inverse problems of non-isothermal kinetics.

Experimental details

The proposed technique of TA-experiment makes it possible to overcome these shortcomings. The technique is based on an entirely new method – the method of contact heating with the aid of a metal heat carrier [1]. In this case the rates of heating (or cooling) are within the range of 100–10000 deg·s^{-1}. After quick response heating the sample temperature for good heat conductors reaches a constant level. Thus the interpretation of kinetic curves does not present great difficulties. At the same time, measurements can be carried out under standard conditions, with the rates of heating lying in the range of 2–20 deg·min^{-1} for ordinary thermal analysis and calorimetry. The method under consideration is based on quick response heating of a sample in contact with a heat carrier at a constant elevated temperature. This is the main feature which distinguishes the method of contact heating under consideration from the standard methods of convective and filament heating. Although among the known methods some may ensure rapid heating of a sample (infrared and laser methods a.o.) they cannot always produce a record of kinetic curves for the sample kept at a constant temperature with any great degree of accuracy, and do not permit to

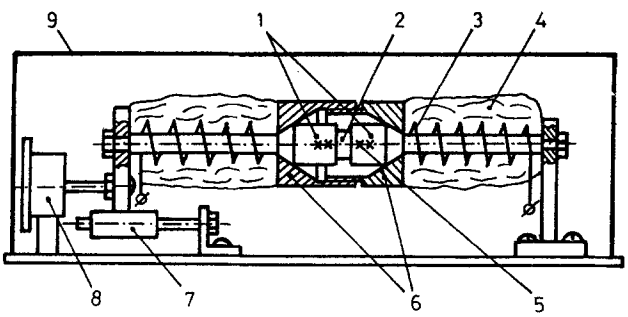

Fig. 1 Diagram of the contact heating device: 1 – metallic rods with nickel plating, 2 – sample, 3 – heater winding or high frequency induction heater, 4 – thermal insulator, 5 – microthermocouples (fluxmeter), 6 – heat insulator rings, 7 – moving rod holder, 8 – electromagnetic drive, 9 – bonnet

calculate the exact kinetic characteristics, such as activation energy, frequency factor, number of stages, etc.

Several new devices are based on the contact method, making use of its advantages. Figure 1 shows a diagram of such a device (most simple in design) based on the method under consideration.

In order to protect the samples from the environment and make them more tractable they are placed in metallic foil up to 0.01 mm thick. Such packing makes it possible to test good thermal conductor powders. As to films and monolayers of plastics from 0.01 to 0.1 mm thick and weighing from 1.0 to 60 mg, it is possible to test them without foil packing. The test samples are weighed on an analytical balance before and after heating.

The electric heater consists of 2 metal rods (1). The left one may move towards the other when heated. The tablet prepared with the sample (2) is fastened between the ends of metal rods preheated to the necessary temperature which is kept constant throughout the test by the electric heater (3). For protracted experiments the heater is supplied with an automatic temperature regulator. The sample is gripped between the rods by an electric drive with a force of about 20 N. The space between the rods ends is the action zone of thermal transformations. The sample is kept in position during the necessary exposure time. The clamping force can be changed to reduce the gap (the sample thickness) in order to decrease the temperature difference between the rod and the specimen surface to the acceptable value. This may drastically reduce the time necessary to establish isothermal conditions.

After a specified time the rods are moved apart and the foil-wrapped specimen is transferred to another environment (cryogenic liquid or water) or exposed to a flow of an inert gas for cooling.

Tests and calculations of heat conduction have revealed that a 0.2 mm thick polymer sample reaches the temperature of the heating of cooling environment within 1 s, with 3–5% error. The tests also show that heat conduction equalizes the temperature of the sample and the rods within 0.9–1 s.

The device presented in this work is a basic version of a device that makes use of the method under consideration. Other modifications of this model have been designed. They are also based on the quick response heating of the sample (with of without foil) in contact with a heat carrier at constant high temperature [1, 2]. Some of them contain transducers and a system for measuring the reaction duration or the sample lifetime. The time measurements are carried out by way of recording acoustic, electric, optic and other signals.

Some modifications of the device make it possible to measure heat capacity, heat conductivity, changes in entropy. Such devices are equipped with two fluxmeters and heat insulator rings (Fig. 1).

Results

Some tests results are shown in diagrams (Figs 2, 3). The characteristic feature of the experimental data is that the starting time of the measurements is 1 s [3].

The new method has made it possible to establish the existence of a whole series of previously unknown rapid reactions and thermolysis processes of explosive nature. Three types of high-rate thermolysis processes have been identified [1–3]:

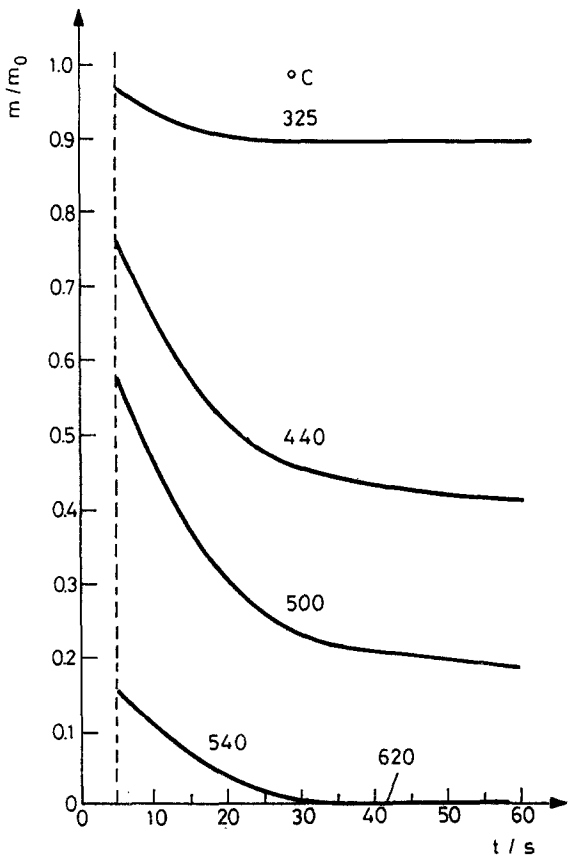

Fig. 2 Kinetic curves of capron

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

– processes characterized by changes in entropy;

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

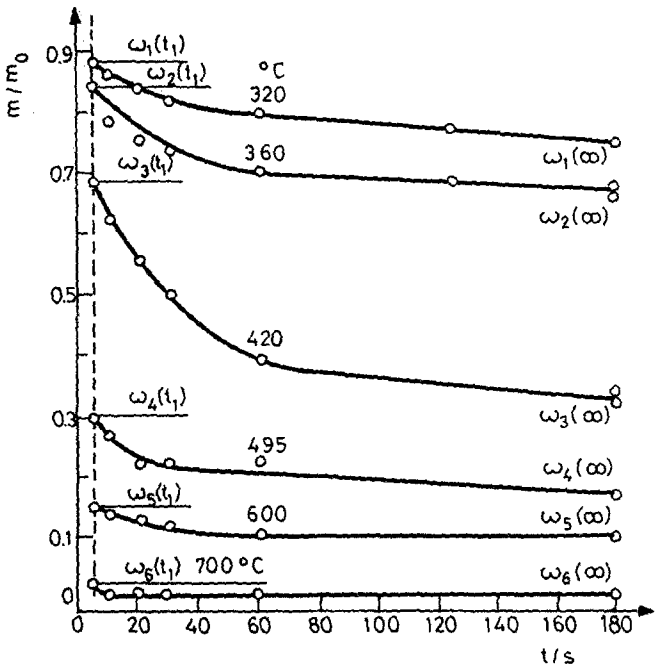

Fig. 3 Kinetic curves of a polymer compound for high temperature protection

Physical and mathematical models of thermolysis have been developed. Some of the results have already been published [1–3], others are due for publication soon.

Application fields

The method under consideration has found application in the following areas:

– studying thermal decomposition of heat-insulating materials and coals;

– simulating full-scale thermal effects on various heat-insulating materials used in fire and explosion prevention;

– studying relaxation processes in the course of instantaneous heating;
– optimizing the composition and quality of components for composite materials;
– working out specification certificates for new composite materials;
– forecasting thermal stability of materials subjected to rapid heating;
– calculating various parameters in design plasmochemical reactors;
– express TA-analysis

Conclusion

The paper presented describes the possibilities of a new TA method which is characterized by a short period of time (1 s and less) necessary to heat samples. Use of the proposed devices makes it possible to extend the range of heating rates and to increase the number of parameters measured both by TA and calorimetry.

References

1 O. F. Shlensky, A. G. Shashkov and L. N. Aksenov, Thermal decomposition of materials, Elsevier 1991.
2 O. F. Shlensky, E. F. Vaynstein and A. A. Matyukhin, J. Thermal Anal., 34 (1988) 645.
3 Poster at ESTAC-5

Zusammenfassung — Es wird eine neue Methode und ein neues Verfahren von thermoanalytischen Versuchen zur Untersuchung thermischer Zersetzungsprozesse sowie auch zur Bestimmung kinetischer und thermophysikalischer Eigenschaften von Feststoffen und Flüssigkeiten bei intensivem Erhitzen oder Abkühlen beschrieben.