

METHOD OF DIFFERENTIAL THERMAL ANALYSIS FOR DETERMINATION OF SHORT-TERM THERMAL STABILITY OF SOME MATERIALS

O. F. Shlensky, L. N. Aksenov, Yu. V. Zelenev and E. M. Eremenco

Mendeleev University of Chemical Technology of Russia, Moscow

(Received May 20, 1995; in revised form January 2, 1996)

Abstract

The method of DTA and design of two thermoanalytical cells are suggested for high-rate heating of samples at speeds up to $10^3 \text{ }^\circ\text{C s}^{-1}$ and more. Method allows to determine the limiting temperature of attainable superheat during thermolysis processes of melting substances. Some testing results are given.

Keywords: attainable superheat, contact heating methods DTA, thermal stability

Introduction

Usual thermoanalytical tests with standard equipment last for a few decades of minutes. But in some cases there arises a demand for performing sets of tests for determination of short-term thermal stability of a large series of polymeric or other melting material samples (time of heating about some seconds or fractions of second). Standard apparatus are not quite suitable for such purposes. Moreover, not all laboratories could perform a great number of such experiments because of high difficulties and labour consuming of large series of measurements. In this paper we suggest a method of differential thermal analysis of melting polymers which is adapted for ordinary equipment available for many laboratories. At the same time this method makes it possible to glean information on material properties as from short-term tests as from standardized experiments at constant rate of temperature elevation and $T = \text{const}$.

Experimental

Construction of the certain experimental cell is shown on Fig. 1. its main part is a thin strip of stainless steel with two junctions of a differential thermocouple [5, 8] fixed at its surface. To measure absolute temperature either one more

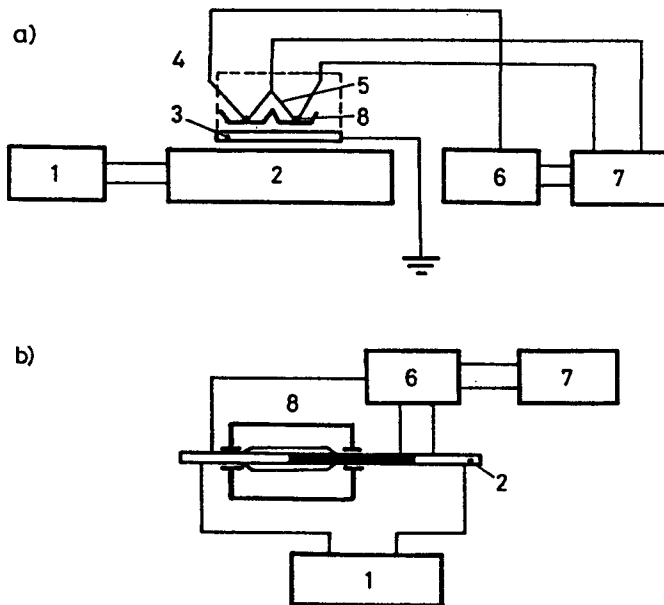


Fig. 1 Principal diagrams of thermoanalytical cell of high-speed DTA. A – variant of positioning a sample on a thin metal support-a screen. B – variant of positioning a film of a sample on a thin filament of a heater. 1 – a power pack with voltage regulator, 2 – a filament heater, 3 – a screen, 4 – a cuvette, 5 – a thermocouple, 6 – an intermediate amplifier of differential thermocouple signal, 7 – two-coordinate recorder, or oscillograph, 8 – a sample mounted on a junction of differential thermocouple

thermocouple is fixed at the surface [5] or one junction of differential thermocouple is used [8]. In the latter case the accuracy of measurements is a bit lower. Metal plate serves as a support for polymeric or another samples under test. A sample in a form of a thin film is mounted on one of differential thermocouple junctions. For meltable polymers preheating of sample together with a support is desirable after which the sample contacts its support tightly (the temperature of preheating has to exceed the melting point of sample's substance).

In contrast with earlier described method of high speed thermoanalysis [1] in which sample is mounted on a massive metal plate with high thermal inertia, in the cell offered, a sample is placed on a stainless steel foil support 0.1 mm thick. For the tests of low viscous liquids such as solutions of polymers, the edges of the foil are bent upwards forming a rigid container.

The foil is heated by the electric filament heater separated from the container with a metal screen, which is earthed to avoid induced currents.

To even temperature field a massive hollow block made of a good heat conducting metal (aluminum) has been used. It's shown on the diagram with a dotted line.

Power pack is connected to a voltage regulator which makes it possible to proceed a desirable rate of heating: either uniform elevation of temperature (linear heating), or isothermal conditions of testing, or exponential law of heating. Using this cell, rates of heating up to $100\text{--}500^\circ\text{C s}^{-1}$ have been attained, dependent on the thickness of the film under tests. Limiting factors of heating rates in the cell described are considerable thermal inertia of the heater with the screen and lagging time of a two-coordinate recording device.

Higher rates of heating of samples (higher than $10000^\circ\text{C s}^{-1}$) were attained in a thermoanalytical cell shown on Fig. 1b, on which a bimetallic wire of a small diameter (less than 0.1 mm) served as a heating element. A current from a power pack was to pass through the wire. To attain high heating rates an electric discharge of a preliminary charged capacitor was used. Compared to well known filament heaters of this type [2], the wire consisted of three conductors made of different metals whose junctions had high thermo-emf: such as Chromel-Alumel-Chromel, Iron-Copper-Iron, etc. A thin film of a tested polymer coated one of the junctions.

For coating a junction with a polymer the latter was preliminarily dissolved in a liquid solvent (dichloroethane) and layer by layer spread over the wire attaining a required thickness (about 0.1 mm). Insoluble polymers were spread in a form of melt. The wire was heated by the current passed through it and at the same time the wire served as a differential thermocouple to measure temperature difference between the free junction and the one coated with a polymer and to measure absolute temperature as well.

To avoid high temperature gradients, maximum thickness of a polymeric film was determined for each of the tested substances dependent on heating rate and thermal properties of the polymer.

If the thickness of a sample is not high, then the error of the experiment can be assessed the tolerance. Method of estimation of a tolerant thickness of a sample at a given heating rate is described in [3, 4]. Flying off of a sample from the support, caused by the untight adhesion; formation of gaseous products of thermal decomposition, etc. can be additional sources of errors in the cell of the considered constructions.

Exfoliation control is performed visually and on the absence of data reproducibility of a series of successive tests.

To avoid the film exfoliation or bubbles formation caused by slow diffusion of gases towards the surface of a sample, the latter must be of a thickness less than allowable. For PE, PS, PMMA the allowable thickness is 5...3 micrometers [4].

Results and discussion

The results of the tests of HDPE samples are presented on Fig. 2. The tests have been performed in a cuvette-like cell. The sample with the cell were heated by setting them in contact with the screen (base) preheated up to 300°C .

Duration of heating was about 1...2 seconds. Ranges of heating (from pt.A to pt.B) and cooling (from pt.B to pt.A) can be clearly seen on the diagram. Direction of motion of a sensitive element is indicated with arrows.

The diagram (Fig.2) makes it possible to determine the melting point of polymer at high speeds of heating and cooling and its dependence on them.

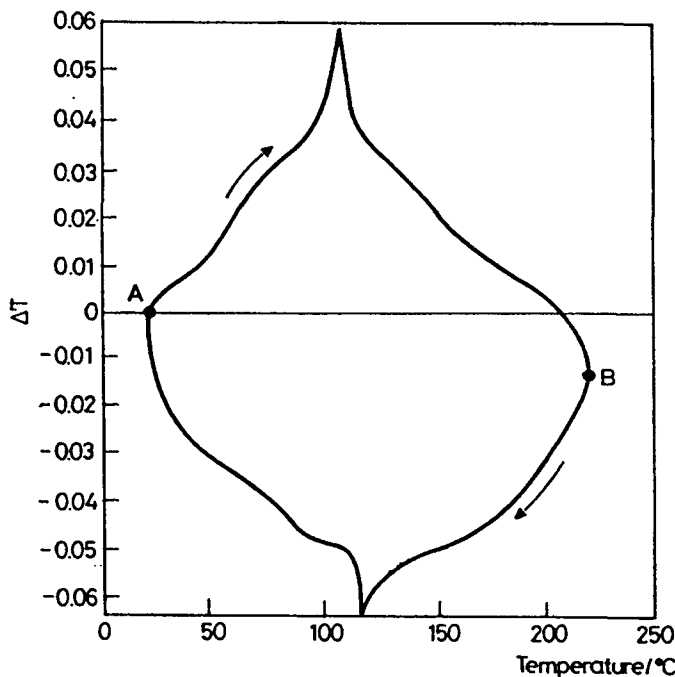


Fig. 2 Heating-cooling (one cycle) thermoanalytical curve; 1 - heating process, 2 - cooling process of a sample (high density polyethylene)

DTA curves of thermal decomposition of block-PS at different heating rates obtained with a filament heater (Fig. 1b) are presented on Fig. 3.

Increase of heating speed has caused decomposition peak shift right up to the higher temperatures of thermal decomposition of PS, that corresponds to experimental results obtained by other methods [3, 4]. At the same time the heating rate in fact did not effect the melting point of the substance.

The suggested method has been used for thermolysis kinetic parameters determination. One junction of differential thermocouple was used to determine the time of thermal decomposition of substances t_d which is connected with average reaction rate $k:k=1/t_d$. During the thermal decomposition the temperature of sample junction is lower then temperature of free junction. The curves $\log(1/t)=F(T)$ as well allow [3, 4] to determine limiting temperatures of thermal decomposition. The results of some isothermal tests are presented on Figs 3 and 4. The values of limiting temperatures obtained correspond to another experimental data given in [4].

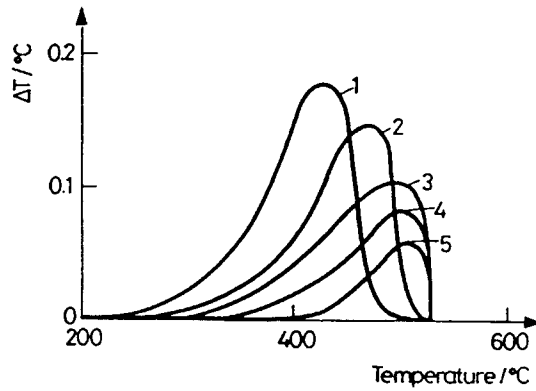


Fig. 3 Differential thermoanalyses of thermal decomposition of block polystyrol at different heating rates (b). 1 - $b = 10^{-1} \text{ }^\circ\text{C s}^{-1}$, 2 - $b = 1.0 \text{ }^\circ\text{C s}^{-1}$, 3 - $b = 10^1 \text{ }^\circ\text{C s}^{-1}$, 4 - $b = 10^2 \text{ }^\circ\text{C s}^{-1}$, 5 - $b = 10^3 \text{ }^\circ\text{C s}^{-1}$

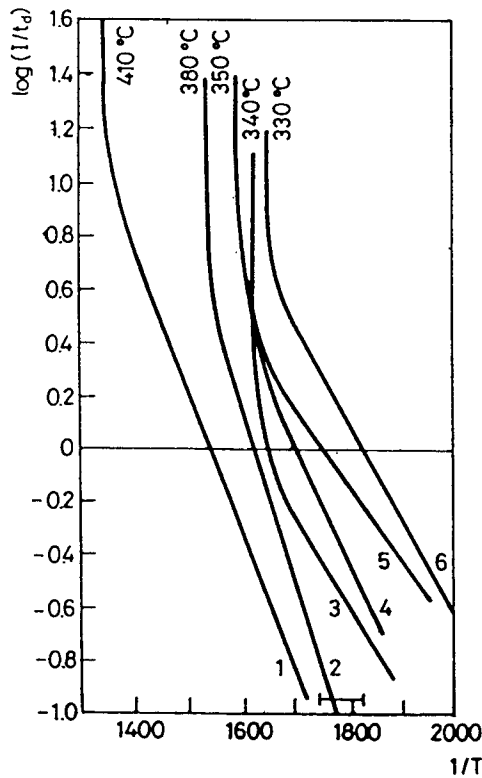


Fig. 4 Temperature dependences of the thermal decomposition reaction duration of some melting substances. 1 - polydiethylsilane, 2 - α -alanine, 3 - ammonium nitrate, 4 - pimeline acid, 5 - oktogen, 6 - trotil (TNT)

Conclusion

1. Application of high-speed DTA allows to reduce considerably the duration of testing time at quite sufficient resolving power; temperature drop ΔT , dependent on the size of a sample, can be measured either with two-coordinate recorder or any oscillograph.

2. Method of heating in which a filament heater is simultaneously used to measure absolute temperature and DTA signal has the least thermal inertia.

3. It was determined that for different classes of linear polymers (both crystalline and noncrystalline) transient processes of thermal decomposition take place at temperatures not exceeding some limiting value, dependent on chemical composition of samples.

References

- 1 O. F. Shlensky and G. E. Vishnevsky, *Doklady Akademii Nauk USSR*, 279 (1984) 105.
- 2 I. Shestak, *Thermophysical properties of solids*, Academia, Prague 1984.
- 3 O. F. Shlensky, L. N. Aksenov and A. G. Shashkov, *Thermal Decomposition of Materials*, Elsevier, Amsterdam 1991.
- 4 O. F. Shlensky and D. N. Yundev, *Teplofis. Vysok. Temp.*, 31 (1993) 685.