

Thermal Analysis by a Constant Heat Flow

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Synopsis

A new method of and apparatus for thermal analysis is described, whereby the heat flow fed by the oven to the sample is kept constant as a function of time. The measurement gives the change of enthalpy in heating or cooling the sample. From this enthalpy-temperature relationship quantitative thermodynamic results are easily obtained. Transitions of first and second order in polymers can be measured in one run.

Introduction

The first experiments on thermal analysis were carried out by Le Chatelier.¹ The influence of fluctuations in the oven's heating rate can be eliminated by measuring the temperature difference between the sample and an inert body,² as is usually done in the differential thermal analysis DTA.^{3,4}

Instead of measuring the temperature difference between two bodies, another solution can be given to this problem, namely by feeding a constant heat flow to the sample. The thermal behavior of the sample is then given by recording its temperature as a function of time. In this paper the method of the constant heat-flow thermal analysis (CFTA) and its applications to some polymers are briefly described.

Principle

The arrangement of a constant heat flow to the sample can be obtained by having a cylindrical oven in which the center of the sample is located. The heat then flows through an air layer of equal thickness from the walls of the oven to the sample. The temperature difference between the oven's inner wall and the sample is proportional to the heat input.

If this temperature difference is kept constant, the heat input will be constant, provided the conductivity of the air remains independent of temperature. As this is not the case, it is necessary to compensate for this phenomenon by a regulating system.

Apparatus

An apparatus based on this principle was designed. The oven (Fig. 1) consists of a copper pipe, which can be heated electrically and cooled by an external circuit. Chips of the polymer to be examined are mixed with aluminum foil, in order to ensure a good heat conductivity in the sample,

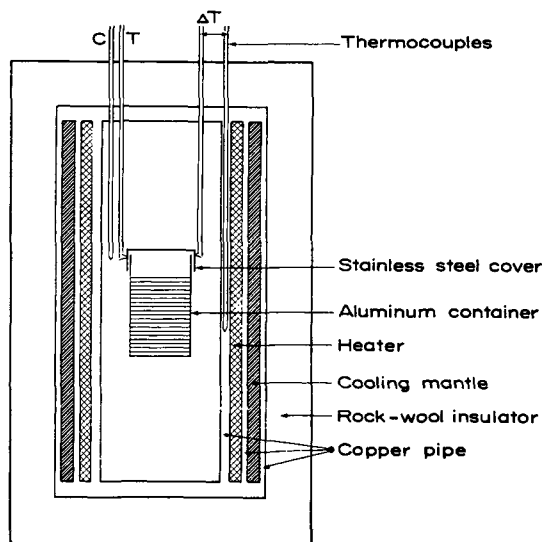


Figure 1.

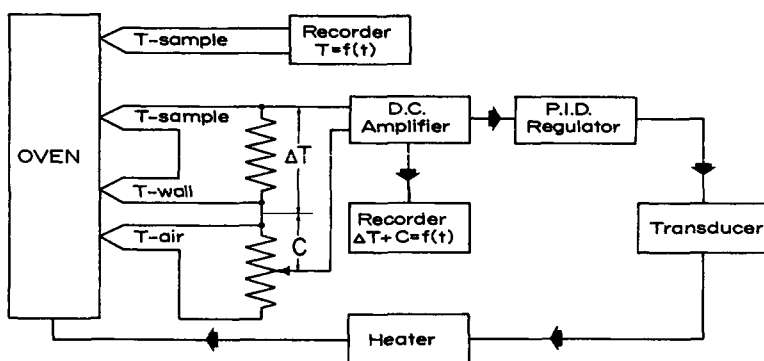


Figure 2.

and are placed in an aluminum tube (a packaging can for 35-mm film cartridge). Normally a sample consists of 10 g of polymer and 9 g of aluminum, tube included. As the heat conductivity in the sample is ensured by the aluminum, the state of the polymer (crystalline, amorphous, powder chips) is of minor importance. The advantages of a relatively large sample are that a good average is reached and that no pulverization is necessary.

The regulating system (Fig. 2) ensures a constant heat flow from the oven to the sample. A pair of thermocouples measures the temperature difference (ΔT) between oven wall and sample and generates the driving signal. To this signal is added a signal proportional to the air temperature (C), so that changes in the air conductivity are compensated. The sum of both signals is preamplified and fed to a proportional-integral-differential

(PID) regulator, which drives the magnetic transducer that regulates the heating current, so that the input signal remains constant.

The temperature of the sample measured by a thermocouple (T) is recorded on a potentiometric recorder (Fig. 2). From this plot a thermograph can be worked out, from which the thermal behavior can be read. Analogously, the behavior of the sample on cooling can be studied in combination with the cooling circuit.

Calculating Method

The heat quantities put into the sample are proportional to the time. When replacing the polymer by aluminum chips, the proportionality constant between the delivered heat quantity and the time—the heat current—can be determined. The heat capacity of aluminum is indeed relatively constant and well determined in the temperature range considered (0–300°C). By this calibration the time coordinate can be replaced by a heat coordinate, expressed in calories. The heat absorbed by the aluminum ballast of the sample can be determined by making a plot only for the ballast. The heat taken up by the polymer needed to reach a certain temperature is calculated by making the difference between the heat of the sample and that of the aluminum ballast needed to reach the same temperature. Dividing this value by the polymer weight results in the heat needed for 1 weight unit of polymer.

In practice, the enthalpy (H) of the polymer as a function of temperature is obtained by taking the differences in heat quantity between the two

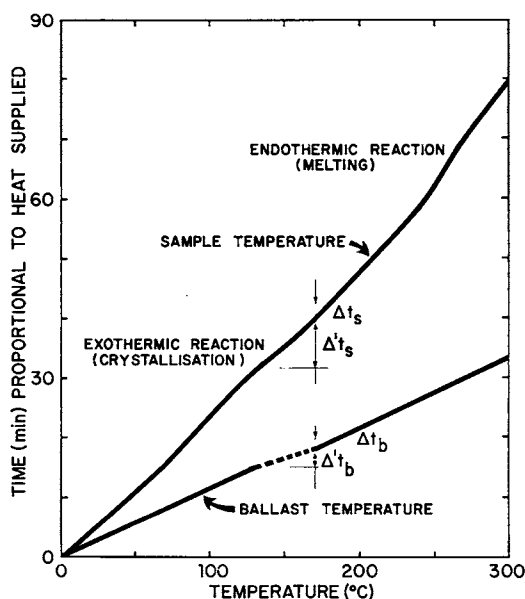


Figure 3.

curves (Fig. 3) and dividing this value by the polymer weight, taking into account the proportionality factor between time and heat delivered (Fig. 4).

An endothermic reaction, as a sharp melting, appears as a vertical line in the thermogram. Since polymers have no sharp melting point, however, the increase of enthalpy is spread over a certain temperature range. The molten fraction may be derived for any temperature in the melting range, even as the degree of crystallinity. The difference in ordinates between the end and the beginning of the melting process is a measure of the melt enthalpy (Q_m), but since the polymer takes a whole range to melt, this difference is the sum of the melt enthalpy and the heat taken up by the heat capacity in warming up the polymer throughout this whole temperature

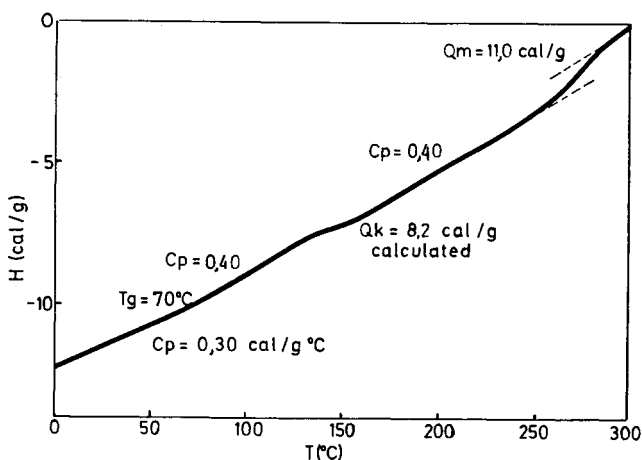


Figure 4.

range. The melt enthalpy can be derived graphically by prolonging the slope of the graph before and after the melt range towards the middle of the temperature range, where the enthalpy difference is read. So the average value of the specific heat in this range is taken into account.

Determining that the reaction heat of an exothermic reaction is a crystallization (Q_k) is more complicated, since in this case the reaction is no longer controlled by the regulating system. The increase in temperature is due not only to the heat current of the furnace but also to the heat provided by the reaction itself. From this point of view an exothermic reaction is not the inverse of an endothermic reaction. In an endothermic reaction only the polymer absorbs a greater amount of heat, whereas in an exothermic reaction the polymer delivers heat to itself and to the ballast. So the temperature of the ballast rises faster than during the calibration procedure, where the oven heat only was at disposal. This difficulty can be eliminated, because the heat absorbed by the ballast and the sample is proportional to their respective heat capacities.

A method of calculating the heat quantities connected with an exothermic reaction can be derived from these considerations, as shown in Figure 3.

$$\Delta t_s / \Delta t_b = C_s / C_b \quad (1)$$

$$\Delta' t_s / \Delta' t_b = C_s / C_b \quad (2)$$

In these equations Δt_s and Δt_b are the gain in time during the exothermic reaction of the sample and of the ballast, $\Delta' t_s$ and $\Delta' t_b$ are the times for passing through the reaction interval taken by the sample and the ballast, and C_s and C_b are the heat capacities of the sample and of the ballast.

From both equations it can be concluded that the ratio of the heat capacities of sample and ballast is the proportionality factor for the gain in their heating time [eq.(1)] and for the time necessary to heat them up to a certain temperature [eq.(2)]. So the first equation is a parameter for the distribution of the heat of reaction, and the second allows an easier calculation of the thermogram. Now that the heating time of the ballast is known, the

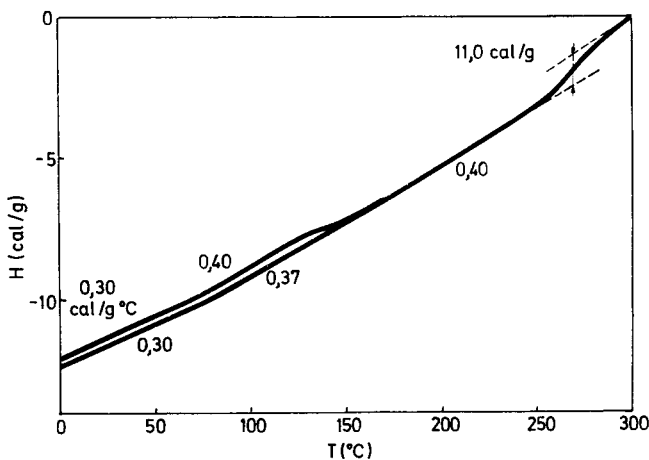


Figure 5.

calculation of the thermogram can proceed as sketched above. However, this implies that the response time of the regulating system is small enough to ensure continuously a constant temperature difference between sample and oven. It is also to be noted that, because a part of the reaction heat is absorbed by the ballast, the resulting thermogram does not give graphically the heat of reaction (Q_k) as in the case of an endothermic reaction, but only the heat that stays in the polymer.

The slope of the enthalpy curve (Fig. 4) gives the specific heat at constant pressure, $c_p = dH/dT$. This specific heat changes at the glass transition temperature (T_g). This temperature is thus indicated by an inflection of the slope of the thermogram.

Advantages

As seen above, quantitative results are easily obtained, and the progress of a reaction can directly be read on the graph. This makes the method very suitable for plastics, which have mostly a large melting and crystallization range.

Another advantage of the method is that effects of first and second order are measured in one run: the first ones are translated by a jump in the graph, the second ones by a difference in slope.

The temperature difference in the sample is less than 1°C , and the measurement of the temperature has the accuracy of the thermocouple used. The error in the enthalpy is about 5% and depends on the variation

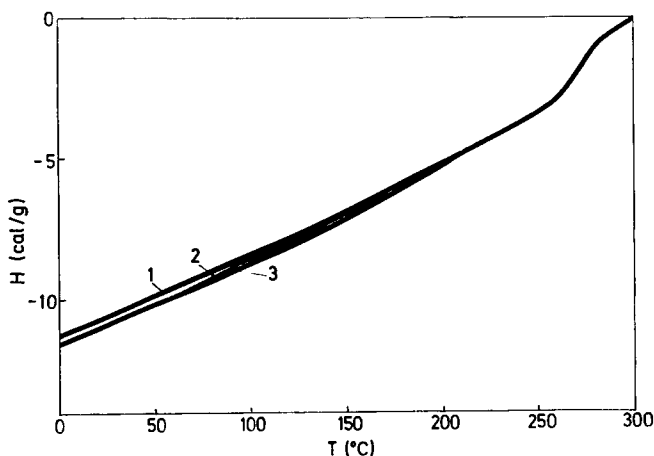


Figure 6.

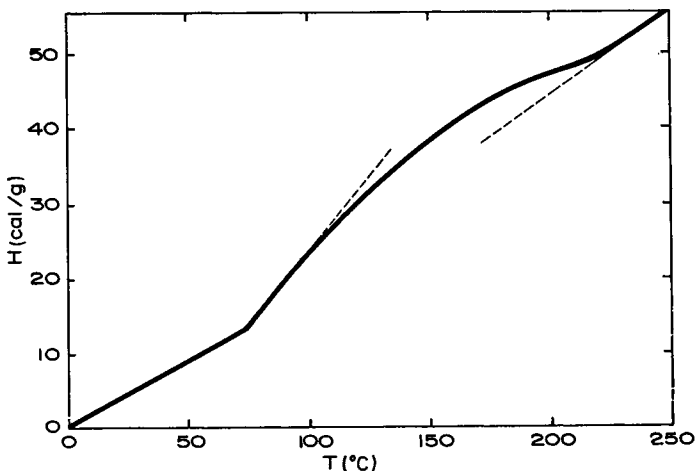


Figure 7.

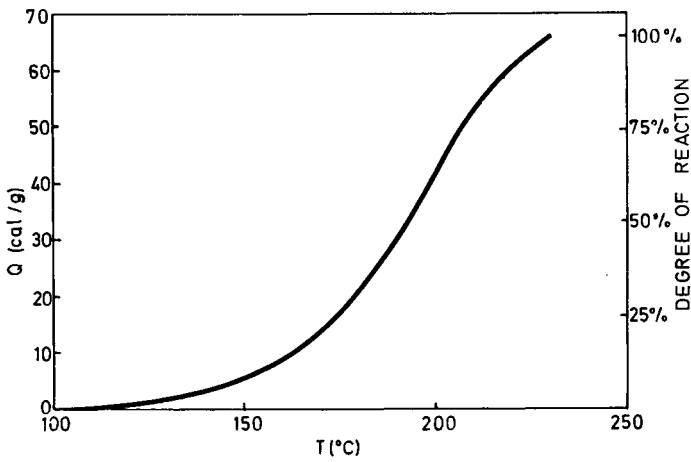


Figure 8.

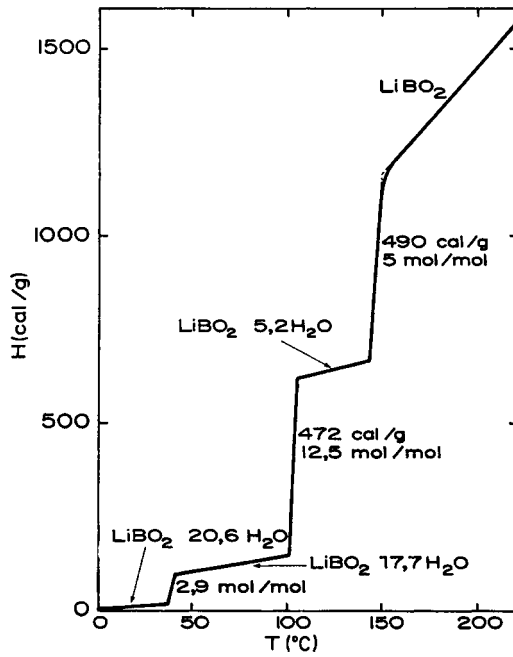


Figure 9.

of the four between the calibrating run and the measuring of the sample. For reducing this variation an oven in stainless steel will be built.

Remark

By another route of reasoning Kumanin⁵ discovered a similar method. He noticed that during an endothermic process the temperature difference

between oven and sample becomes greater, as the sample receives more heat, which results in a decrease of the deviation of the thermogram from the baseline. In order to increase the sensitivity, he held the temperature difference constant.

Examples

As an illustration of the constant heat-flow thermal analysis (CFTA) a number of thermograms are depicted in the following illustrations.

The behaviors of amorphous and crystalline polyethylene terephthalate (PETP) are compared in Figure 5. The amorphous samples (1.7% degree of crystallinity) crystallize during the heating in the oven. The crystalline one underwent a preliminary treatment at 200°C during 15 min, so that this degree of crystallinity reached 42.4%, determined by the density gradient method.

Orientation of the PET samples favors the crystallization (Fig. 6). Curve 1 corresponds to a sample that was oriented without crystallization. In this case the crystallization starts immediately at the glass transition temperature. Samples 2 and 3 were oriented at 80°C to a different degree. The crystallization starts at a lower temperature than in the case of an unoriented sample (Fig. 5, curve 1).

In Figure 7 a crosslinking reaction occurs in phenoxy-8-substituted metasulfonazidobenzoic acid, and the course of the reaction can be derived (Fig. 8).

Figure 9 demonstrates a method of determining the water amount during the dehydration of a sample $\text{LiBO}_2 \cdot x\text{H}_2\text{O}$. With the CFTA method this amount was found to be 20.6 mol per mol of LiBO_2 . The Carl Fisher method gives a value of $\text{LiBO}_2 \cdot 21 \text{H}_2\text{O}$.

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References

1. H. Le Chatelier, *Bull. Soc. Franc. Minéral*, **10**, 204 (1887).
2. W. C. Roberts-Austen, *Proc. Inst. Mech. Engrs. (London)*, **1**, 35 (1899).
3. W. J. Smothers and Y. Chiang, *D.T.A., Theory and Practice*, Chemical Publishing, New York, 1958.
4. B. Ke, in J. Mitchell, Ed., *Organic Analysis*, Interscience, New York, 1960, p. 361.
5. K. G. Kumanin, *J. Appl. Chem. USSR*, **10**, 1242 (1947).

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