THERMAL ANALYSIS IN THE PLASTICS WORKS LABORATORY

A. MANDEL

*Robert Bosch GmbH, Abteilung Stoffe und Verfahren Nichtmetalle,
D-7050 Waiblingen (Germany)*

(Received 23 May 1975)

ABSTRACT

Almost all the physical and chemical phenomena which occur during a rise in temperature can be recognized, and therefore materials identified, by the use of thermoanalysis. The simple and rapid thermoanalysis procedures described are applicable to the testing of batches of material as well as to the examination of the material-dependent workability and application properties of plastics parts. They are therefore an important aid to quality control in the plastics works laboratory.

1. INTRODUCTION

Thermal analysis as a method of examination of organic high polymers is being applied increasingly and its use extended, as is evidenced by the abundance of new work in this field[1–4]. Equipment and examination procedures are numerous, which often makes a comparison of results and exchange of experience difficult. In order to improve this state of affairs it is therefore all the more desirable that emphasis should be laid on proved procedures and that they should be made public. The findings resulting from thermal analysis often bear a close relationship to the properties required for applications of plastics parts and we have available here a convenient aid to quality control in the laboratory which does not result in destruction of the specimen.

2. APPARATUS

It has proved very favorable, for the purposes of high-polymer thermo-analysis in the laboratory, to combine the methods of differential thermal analysis (DTA) with thermogravimetry (TG) and differential thermogravimetry (DTG). One of the commercially available equipments which afford these three test methods is the Mettler thermal analyser 1 (MTA)[5]. It is capable of recording weight (TG), changes of weight (DTG) and exchanges of quantities of heat or changes in the specific heat (DTA), whilst still enabling the vacuum and the gas, which flows round the sample during heating, to be freely selected. A block diagram of the MTA is shown in Fig. 1. The heat change (DTA) is determined as a function of the temperature of the reference
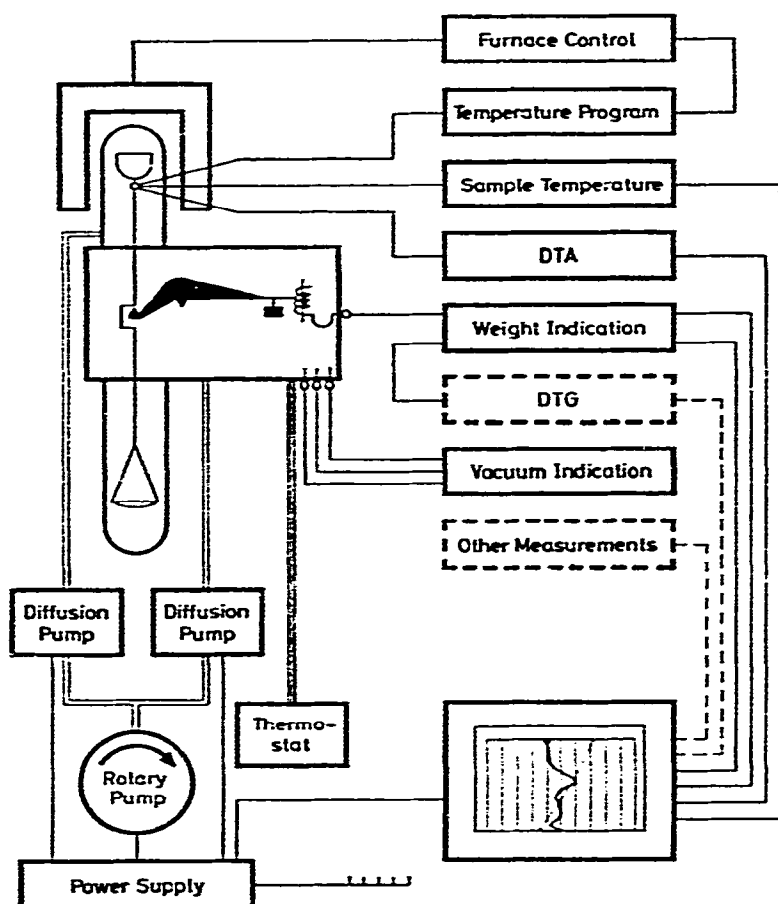
Fig. 1. Block diagram of the Mettler thermal balance.

substance by measuring with platinum–platinum/rhodium thermocouples the difference in temperature between the test substance and the inert reference substance which are heated together, but in separate crucibles, in the furnace and simultaneously weighed. The MTA records on a chart as a function of time, the temperature of the reference substance, the total weight (sample and reference substance), the temperature difference sample/reference substance (DTA) and the differential weight (DTG).

The most important data relating to the MTA are:

Range of weight: 0 to 16 g, on the most sensitive range 1 scale division = 0.01 mg; range of temperature: 25 to 1600°C, rates of rise and fall 0.5 to 25°C min^{-1}, accuracy 1°C; vacuum: $5 \cdot 10^{-2}$ Torr (rotary pump); gases: dry air, N_2, CO_2, etc. and also corrosive gases, flow-rate 1 to 30 l h^{-1}; DTA: measuring ranges, 20, 100, 500 μV (1 V $\cong$ 0.1°C); DTG: measuring ranges 5, 10, 20 mg min^{-1}.

When using combinations of equipment, the DTA sensitivity cannnot always be fully exploited. However, by adapting sample weight and test conditions to the problem in question, partial compensation can be achieved.

3. STANDARD METHOD OF EXAMINATION

As the data for the MTA show, there is a choice of a wide range of test conditions. A very important guide in evaluating thermograms, however, is the comparison of curves recorded under identical conditions. It is therefore expedient to keep the test constant unless there are special reasons for not doing so. This "standard programme" is so chosen that the advantages of the thermoanalytical procedure are utilised. This means that the weight of the sample is 5 to 10 mg (grain size $\leqq 80\ \mu$), that is, in most cases an almost non-destructive test is possible, the heating rate is $10\,°C\ min^{-1}$ up to about $900°C$ (1.5 h after the start of testing the thermograph can be evaluated), DTA sensitivity is $500\ \mu V$ (without changing the measuring range, for example, the melting and setting processes as well as combustion with strong exothermic reactions can be recorded on one chart, greatly facilitating comparison of the graphs) and DTG sensitivity $10\ mg\ min^{-1}$.

The physical and chemical phenomena by the use of differential thermal analysis (DTA) and thermogravimetry (TG) are described in Table 1.

TABLE 1

DTA	TG
Melting behaviour	Decomposition
Reaction	Identification
Identification	Drying
Crystallinity	Combustion
Recrystallisation	Oxidation
Glass transformation	Corrosion
Ignition	Evaporation
Setting	Carbonisation
Phase change	Type of filler
	Thermal stability

Simultaneous measurement DTA/TG has the great advantage that the interpretation of the graphs is facilitated; for example, it is very instructive to know whether a particular transformation takes place with or without change of weight. For reactions with change of weight quantitative interpretation through the TG curve is often simpler than through the DTA curve.

Such a thermogram, which shows TG, DTA, and T curves simultaneously, provides so many indications, which are often characteristic of the materials; that is, an unknown material can be identified or slight changes in the material can be demonstrated. This, it is admitted, assumes that comparative thermograms of the material or a similar material are available. In the examination of plastics, however, a collection of thermograms is quickly built up which contain standard curves of the current thermoplastics, thermosetting moulding plastics, fillers and elastomers and can be made up into an "atlas". Of the reactions quoted in Table 1 an identification or control of "constancy" for thermoplastics is above all made possible by the
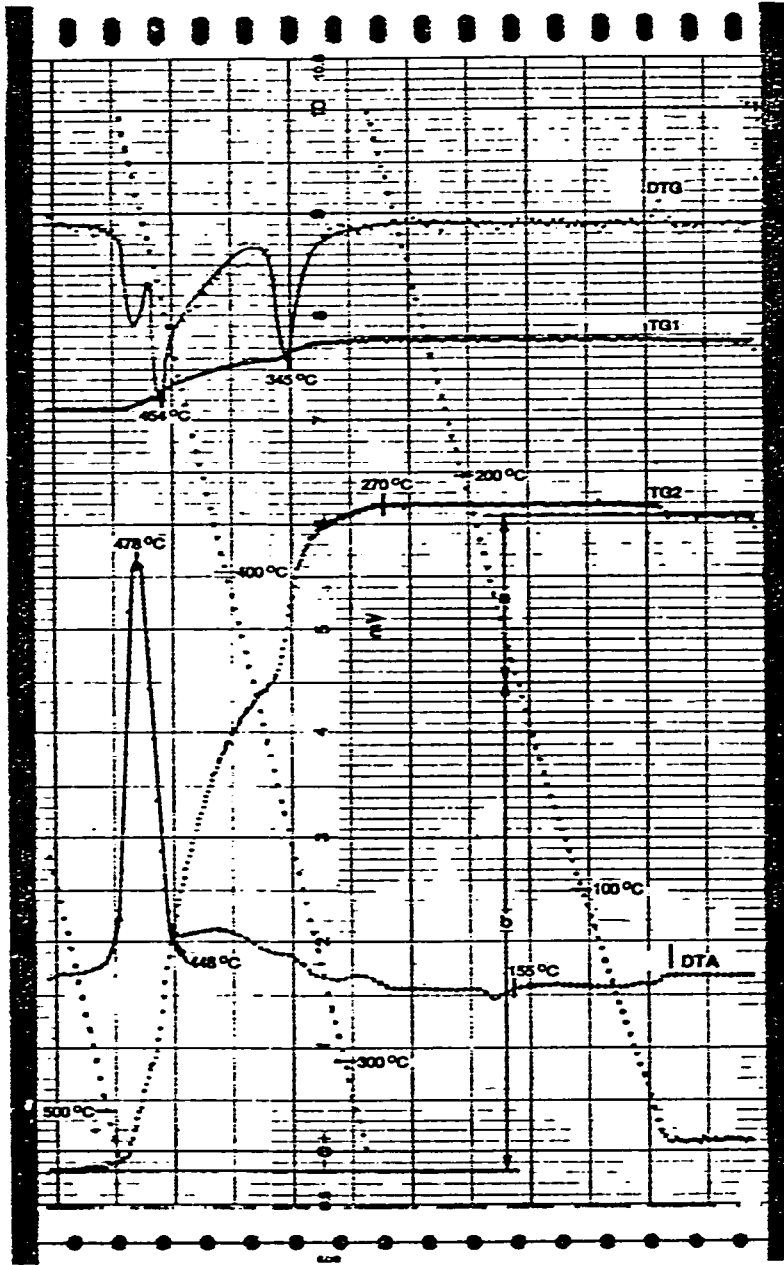
Fig. 2. Thermogram of the standard analysis of a polypropylene (Recorder diagram reduced in size). DTG = differential thermogravimetry TG 1 and TG 2 = thermogravimetry with sensitivity 1 scale division = 1 mg and 1 scale division = 0.1 mg; DTA = Differential thermoanalysis; a = 1st reduction in weight of 1.78 mg; b = 2nd reduction in weight of 4.72 mg; test conditions: Sample weight = 6.9 mg, rate of heating = 10°C min⁻¹, atmosphere = air, velocity of flow = 61 h⁻¹.

melting temperature, start of decomposition, ignition temperature and ash content, whilst for thermosetting moulding plastics the relevant reactions are resin content (weight reduction from 200 to 500°C) weight steps or heat change, fillers, and ash content besides the general shape of the curves.

When no comparative graphs exist or in complicated cases, recourse must be made to other methods of examination (determining the mechanical, electrical and visco-elastic properties of materials, infrared analysis, gas chromatography, etc.). It would be expecting too much of thermal analysis alone to give complete evidence in every case.

Compared with other analytical procedures thermal analysis has, besides the basic requirements of non-destruction of sample, speed and small amount of work entailed, the advantage that not only is identification possible but at the same time, or during a separate test, important data for the application and workability of a material are obtained. Examples are melting temperature, setting temperature, start of decomposition, ignition temperature, slight changes of the material compared with the standard. For application to quality control and improvement of the quality of plastic parts information on these details is indispensible. In the case of thermoplastic and thermosetting moulding compounds, the standard thermogram has often been an indispensible aid in the rapid control of raw materials because of the possibility of differentiating very quickly between "good" and "bad" charges.

The following examples are given in order to make clear the wide range of data which can be obtained with standard analysis:

Figure 2 shows the standard analysis of a polypropylene. The very good linear temperature–time dependence (accuracy ±1°C) can be recognised. Reduction of weight begins at 270°C and occurs in several characteristic steps, which are seen even more distinctly from the peaks of the DTG-curve. At 500°C only inorganic sediment, amounting to about 6%, remains. The start of melting at 155°C can be recognised by an endothermic peak (pointing downwards) in the DTA curve. When combustion begins (448°C) the heat change is strongly exothermic.
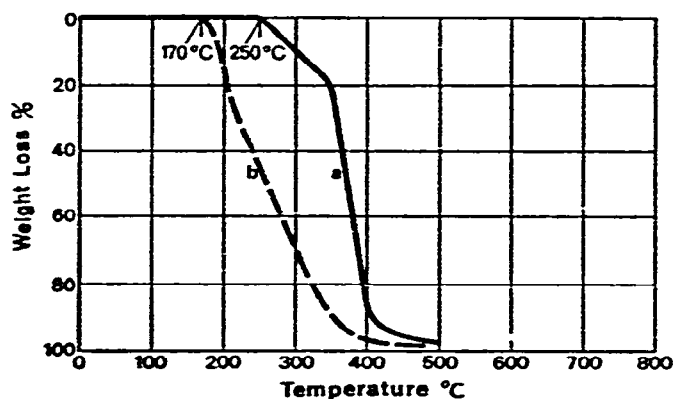

Fig. 3. Resistance to high temperatures of standard polypropylene (a) and PP in a mixture (b) of polypropylene (10%) and barium-ferrite (90%).

Figure 3 shows how thermal stability of plastics can be modified by mixing them with other materials. With magnets with a plastic binding agent the decomposition temperature is lower for a PP–barium–ferrite mixture than for pure PP and this is of decisive importance in workability and application. The reason for the earlier start of decomposition is the oxydation of the plastic by the ferrite.

Figure 4 shows the thermogram of a thermosetting moulding material consisting of polyester resin with a filler of glass fibre and chalk (similar to Type 801 of DIN7708). It permits the content of organic components (39%) to be determined from the decline in weight up to about 550 °C, whilst from a further step between 650 and
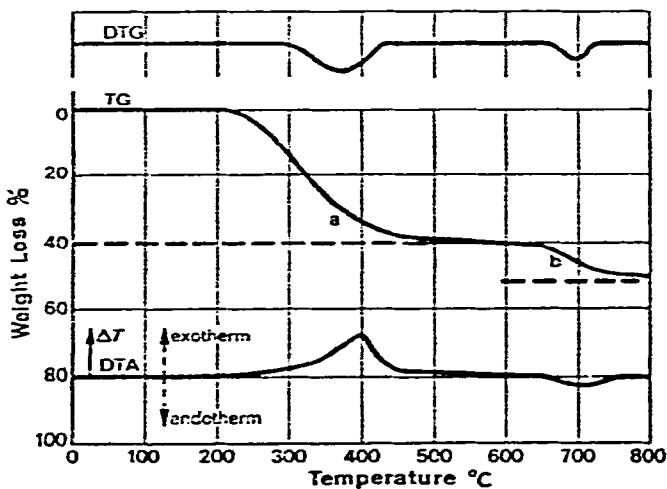

Fig. 4. Thermogram of polyester resin moulding compound with a glass fiber filler (35%) and chalk (20%). DTG = differential thermogravimetry; TG = thermogravimetry; DTA = differential thermoanalysis; a = reduction in weight as a result of volatization of the organic components; b = reduction in weight as a result of decomposition of the chalk ($CaCO_3 \rightarrow CaO + CO_2$).

750 °C with endothermic DTA curve ($CaCO_3 \rightarrow CaO + CO_2$) the chalk content (about 20%) can be calculated. The glass fibres which are still present can be examined on quality under the microscope and their quantity can be found approximately from the weight of ash. A great advantage here is that the analysis can be broken off immediately after combustion of the resin or thermoplastic, and the undestroyed glass-fibre content can be examined microscopically. Commencement of decomposition and form of the exothermic combustion peak are characteristic of the type of resin.

Figure 5 shows the thermogram of thermosetting moulding material consisting of polyester resin (approx. 35%), aluminum oxyhydrate (45–50%), glass-fibre (15–20%) and chalk (7%). The release of water by the aluminium oxyhydrate is indicated by the weight step and endothermic peak, the exothermic peak at 360 °C reveals that gases are ignited, at about 500 °C the cinder consisting of organic substances ignites and at 650–750 °C (weight step, endothermic peak) the chalk decomposes.
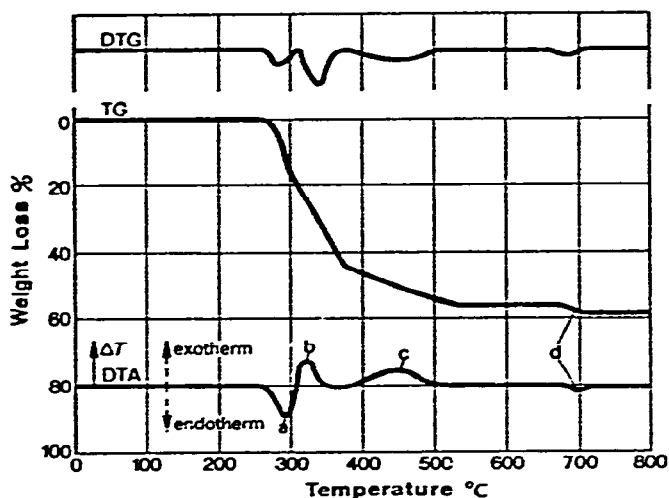
Fig. 5. Thermogram of a thermosetting moulding compound composed of polyester resin (33%), aluminiumhydroxide (45%), glass fiber (15%), chalk (7%). DTG = differential thermogravimetry; TG = thermogravimetry; DTA = differential thermoanalysis; a = release of water from the aluminum hydroxide; b = combustion of the gases; c = combustion of coke; d = decomposition of the chalk.

These examples have shown that fillers can also be examined by thermal analysis. Aluminum hydrate and china clay, for example, serve to improve the resistance to tracking of plastics with poor anti-tacking qualities. Their performance can be ascertained through thermal analysis. Release of water vapour and gas at low temperatures leads to the suppression of sparks on the surface of the insulation. Other fillers which can be examined qualitatively and quantitatively, by means of the splitting-off of water of crystallization and/or combustion, are asbestos and wood flour.

4. SPECIAL METHODS

4.1 Thermal stability

By suitable selection of test conditions, thermal analysis offers the possibility of maintaining a standard above that of the results obtained by standard analysis and of attaining higher accuracy.

A problem frequently encountered in the examination of plastics is the determination or monitoring of the thermal stability of thermoplastic moulding compounds and checking parts for aging or damage by heat during fabrication. Whilst by chemical analysis the type and concentration of stabiliser can be ascertained, thermal analysis can tell us directly what degree of thermal stability (still) exists. As a value for comparison a characteristic temperature (T_5) for 5% loss of weight in the sample under defined volume/surface ratio at a heating rate of $2\,^\circ C\,min^{-1}$ or a characteristic time t_5 needed for 5% weight reduction at a temperature a little below the melting temperature is taken[6]. For identical test conditions and material compositions (molecular weight) T_5 is 10 to 50°C higher for stabilized than for non-

stabilized materials. That, for instance, an examined material has already aged before, can be demonstrated by the lower value T_5 or t_5 compared with that of the new material. For the easy flowing PA we prefer the isothermal method below the melting point, because the volume/surface ratio is better defined and held constant during the whole process.

Table 2 shows two examples: T_5 for heat stabilized polypropylene and polypropylene highly thermally stressed and t_5 at 245°C for 6.6 polyamide of different melt viscosity at 290°C (measured with an oscillating type rheometer (Contraves balance) at a frequency of $w = 1 \sec^{-1}$) heat stabilisation and aging. This method is also applied to plastics for wire insulation, fluoride plastics, etc.

TABLE 2

CHARACTERISTIC TEMPERATURE T_5 OR TIME t_5 FOR POLYAMIDE (PA) AND POLYPROPYLENE (PP)

Material		T_5 (°C)
PP (copolymer) heat stabilized		256
PP (copolymer) heat stabilized highly thermally stressed (from welding seam)		242
		t_5 (min)
PA 6.6 not stabilized 5·10^2 poise		37
PA 6.6 not stabilized 1.6·10^3 poise		50
PA 6.6 not stabilized 6·10^3 poise		68
PA 6.6 heat stabilized 5·10^2 poise		55
PA 6.6 heat stabilized 1.6·10^3 poise		245
PA 6.6 heat stabilized 1.6·10^3 poise	aged 100 h/170°C	179
	aged 100 h/190°C	80

4.2 Nucleus formation

The setting temperature of partly crystalline thermoplastics is as a rule much lower than the melting temperature (sub-cooling) and this is of importance in the fabrication, for example, of injection moulded products. Large subcooling due to slow setting speed necessitates a long time cycle and can lead to deformation difficulties. On the other hand small sub-cooling (high setting temperature) can in certain circumstances increase the risk of cracks appearing in parts. By nucleus formation or through definite distribution of molecular weight of the material concerned, the manufacturers of thermoplastics try to adapt the setting temperature and speed as well as possible to the given requirements.

For determination of the setting temperature the sensitivity of the indication is increased compared with the standard method by using higher weights of the sample and increased DTA sensitivity (100 μV). After heating up to about 30°C above the melting temperature (endothermic melting peak), cooling down at the rate of 25°C min^{-1} takes place. The appearance of the exothermic setting peak gives the setting temperature, comparison with the melting temperature the sub-cooling, the area of the peak gives the heat of setting and the shape leads to conclusions about the setting speed.

When the results of such measurements (Table 3) are compared with the workability and the quality of the parts, it becomes evident that differences in the sub-cooling of even a few degrees have a large effect on the cycle time; that is, deviations in the setting temperature of different charges of the same material can greatly affect the speed of fabrication and dimension accuracy of the parts.

The extent to which a filler can influence the sub-cooling is shown by the example of polypropylene in Table 3. The talcum filler reduces the sub-cooling by 13°C.

TABLE 3

SUBCOOLING OF THERMOPLASTIC MELTS

Material	Melting temp. (°C)	Setting temp. (°C)	Sub-cooling (°C)
Polyamide 6.6 molecular weight distribution 1	254	218	36
Polyamide 6.6 molecular weight distribution 2	254	223	31
Polyacetal copolymer, standard	170	144	26
Polyacetal copolymer, "nucleus formed"	170	146	24
Polypropylene, standard	157	118	39
Polypropylene with 37% talcum	159	133	26

4.3 Thermal analysis of carbon brushes

Figure 6 shows the thermogram of a carbon brush. Essential constituents of brushes such as binding coke and graphite, which as carbon are hardly distinguishable in a chemical analysis, can easily be determined, frequently even quantitatively, in thermal analysis from the various combustion temperatures (exothermic peaks) through the steps in weight associated with the peaks. Since changes in composition or manufacturing process are made evident by a changed thermogram, thermal analysis is used with advantage for carbon brush quality control.

By suitably choosing the test conditions, thermal analysis can supply information additional to the results obtained from the standard curve: The carbonisation of a "green" carbon brush under protective gas is an essential process in carbon brush manufacture. This process can be simulated on the balance, whereby an unknown carbonised brush is pulverised (80 μ grain size) and the powder (approx. 250 mg) is heated under protective gas. It is possible to determine the carbonisation
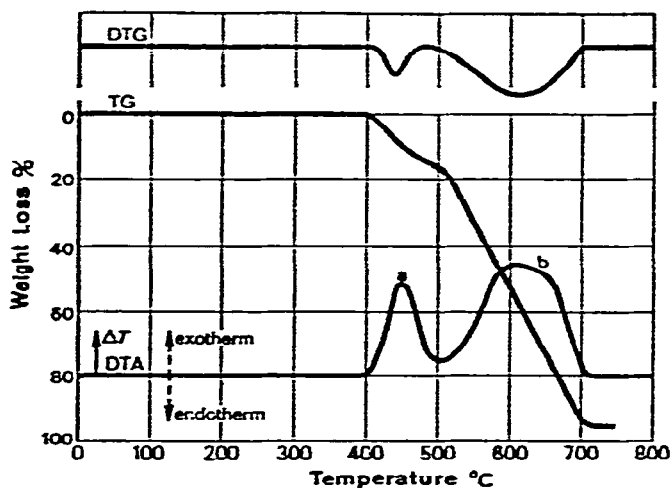
Fig. 6. Thermogram of a carbon brush. DTG = differential thermogravimetry; TG = thermogravimetry; DTA = differential thermoanalysis; a = combustion of coke; b = combustion of graphite.

temperature, since when this temperature is exceeded an increasing reduction in weight takes places, being initiated by the advance of the carbonisation.

In a similar manner impregnation of a carbon brush can be qualitatively and quantitatively examined in a special test by suitable choice of weight and volume/surface ratio of the sample.

4.4 Determination of crystallinity

Several thermoplastics polymers, for example polyamide, polyolefine, polyoxymethylene (POM) and thermoplastic polyester, contain, side by side, at room temperature both crystalline and amorphous regions. By applying heat, melting of crystalline parts (endothermic) and crystallisation (exothermic), as well as glass conversion of the amorphous regions (step) can be demonstrated by DTA. The area of the DTA peak is a measure of the degree of crystallinity. Questions on the correct fabrication, different crystallisation of the interior and the region bordering on the surface of a part or the effectiveness of annealing can thereby often be answered.

4.5 Further examination procedures

DTA is also suitable to measure curing properties of thermosetting systems. Only small quantities of the substance are required (≤ 1 g). The DTA curve gives the temperature at a start of cure and heat change and when the DTA is sufficiently sensitive the degree of cure. With polycondensing moulding compounds the measurement is more difficult, since the endothermic heat change of evaporating constituents and the exothermic curing reaction take place at roughly the same time. According to Knappe and others[7] it is possible using a pressurized crucible to prevent evaporation and thus to follow the exothermic reaction exactly.

Because suspended samples can be weighed, the use of the thermal analyzer described permits measurement to be extended to include magnetism and sedimentation analysis. By weighing a sample, which is attracted by a constant magnetic field (Gouy method), the mass susceptibility down to $5 \cdot 10^{-9} \, cm^3 \, g^{-1}$ can be determined. Sedimentation analysis enables both particle size and size distribution to be determined.

5. CONCLUSION

The object of this article has been to describe practical methods of thermal analysis in the industrial plastics laboratory. More emphasis has therefore been placed on describing simple, rapid and inexpensive procedures which lead to useful results in everyday practice, than in giving details of procedures which lead to very precise and, from a theoretical viewpoint, more interesting results.

To summarize, it may be said that thermal analysis can contribute to the solution of many common problems; for example, identification of an unknown material, clarification when confusion exists regarding the identity of a material, checking the charge, examination of thermal stability and aging of parts, workability difficulties due to the material, monitoring the composition and manufacturing process of carbon brushes.

REFERENCES

1 D. Schultze, *Differentialthermoanalyse*, Verlag Chemie, Weinheim/Berstraße, 1969.
2 W. J. Smothers, *Handbook of Differential Thermal Analysis*, Chemical Publishing Company, New York, 1966.
3 H. G. Wiedemann, *Thermal Analysis, Proc. III, ICTA, Davos, 1971*, Birkhäuser Verlag, Stuttgart, 1972.
4 C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 1963.
5 H. G. Wiedemann, *Chem. Ing. Tech.*, 36 (1964) 1105.
6 T. J. Miranda, *Proc. 1971 Int. Conf. on Mech. Beh. of Mat.*, Vol. III, pp. 392–404.
7 W. Knappe, G. Nachtrab and G. Weber, *Angew. Makromol. Chem.*, 18 (1971) 169.