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SIMULTANEOUS TG–DSC: A NEW TECHNIQUE FOR THERMAL ANALYSIS *

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ABSTRACT

The combination of a heat flux differential scanning calorimeter with a symmetrical microbalance is described, and the advantages of such a TG–DSC combination are discussed. Various types of applications, previously run separately on TG and DSC equipment, can now be investigated on a single TG–DSC instrument, using only one sample. Examples of applications are given.

INTRODUCTION

Many developments have been seen recently in combined techniques for thermal analysis investigations. Most combinations are built around thermogravimetric equipment, and the most well known and also the oldest is TG–DTA. Many different commercial instruments have been or are still working according to the TG–DTA combination [1,2].

The TG–DTA method is widely used over a large range of temperatures, even at very high temperatures. Inorganic products (minerals, raw materials) are often investigated using such a method [3]. Mass variations of the sample during heating are associated with thermal effects. However, with the rapid growth of the DSC technique, quantitative measurements are required in various fields, especially for polymeric and organic materials. So the question is, why not a TG–DSC combination?

The advantages to be obtained with such a new method are clear: work on the same sample, reliable TG and DSC data, combination with evolved

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* As a young thermal analyst, working in a company manufacturing thermal analysis equipment, the author was introduced to applications by reading the different editions of Thermal Methods of Analysis edited by Prof. W.W. Wendlandt. So it is a pleasure for him to thank Prof. Wendlandt for all his efforts in promoting thermal analysis, particularly in the younger generation of scientists. As Prof. Wendlandt is very much interested in promoting new techniques in the field of thermal analysis, this paper presents a new TG–DSC technique.

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gas analysis. But the problems are how to maintain the proper characteristics of the balance and the DSC when combining the two instruments and will the combination affect the sensitivity and the limit of detection of the balance and the DSC?

The answer to these questions is that the two measuring parts, the balance and the DSC, have to be mechanically separated in the combined set-up in order to have the same measuring characteristics when the balance and the DSC are used alone or combined.

Such a combination, using the original structure of the DSC 111 (Setaram) [4] and a symmetrical microbalance, has already been described [5,6].

DESCRIPTION OF THE NEW TG–DSC COMBINATION

Most of the TG–DSC instruments that are marketed today are derived from the TG–DTA principle. The DSC (disc plate) at the end of a rod is attached to the balance, and located in a furnace.

A completely new approach of the TG–DSC combination is proposed with the TG–DSC 111 (Setaram): the balance and the DSC are two different instruments, coupled for TG–DSC measurements, but they can also be used separately as regular DSC and TG equipment only. The original structure of the DSC 111 makes this type of combination possible (Fig. 1) [4].

The DSC 111 is built around two open refractory tubes crossing the heating furnace. Two identical transducers, designed according to the Calvet principle, are heated in the center of the block. The calorimetric heat flux transducers are located around the refractory tubes. With such a design the sample, contained in a cylindrical crucible, is entirely surrounded by the

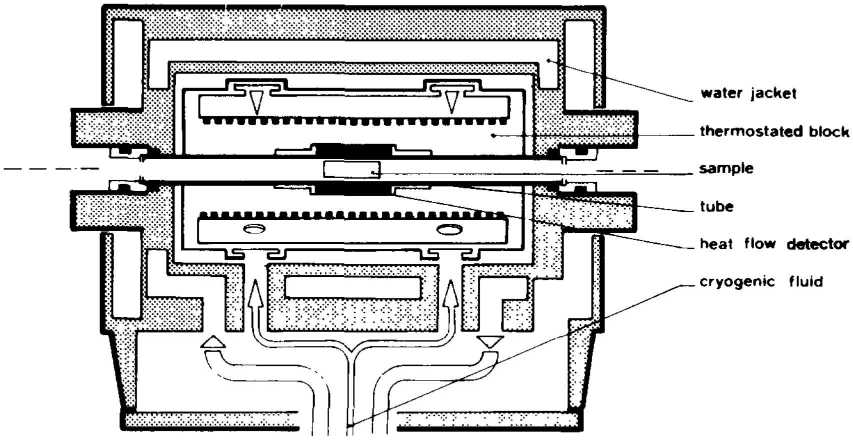

Fig. 1. Cross-section of the DSC 111 calorimetric block.

calorimetric detector, which measures all heat exchanged with very good accuracy and precision ($< 1\%$ in both cases).

The DSC operates equally well horizontally or vertically according to the type of experiment. The vertical configuration of the DSC 111 is especially attractive for combination with a balance. A symmetrical microbalance has been designed to be adapted above the DSC [6]. In such a TG–DSC combination, the DSC instrument supplies the DSC detection unit and the furnace (Fig. 2). After adjusting the balance above the DSC, the suspensions hung at each end of the balance beam are brought into line with the axis of each DSC tube. The crucibles, hooked at the ends of the suspensions, are centered by sliding the balance in the DSC tubes without touching the walls of the tubes. Though the crucibles are not in contact with the DSC tubes, the surrounding structure of the heat flux transducer allows a good integration of the heat exchanged between the sample and the block as for the DSC 111 alone.

In the TG–DSC 111 combination, DSC and TG detection units are mechanically separated. Moreover, the TG measurement is run symmetrically, as sample and reference are located in different tubes on each side of the beam of the balance. This symmetrical set-up allows perturbations

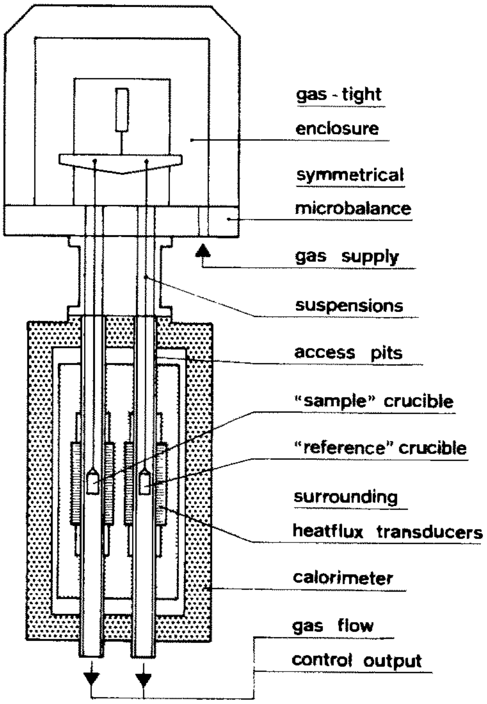

Fig. 2. Cross-section of the TG–DSC 111.

generated by heating to be cancelled (buoyancy effect) and measurements with very small mass variations to be obtained (down to 1 μg). The connection between the balance and the DSC is gas tight thus providing an instrument which can work under gas flow or vacuum. A special set-up can be introduced into the DSC (silica tubes) for working under corrosive atmospheres. Since the DSC is open at both ends, the evolved gases can be collected at the bottom of the DSC and sent on-line to a gas analyzer.

The temperature range of the TG–DSC 111 is from −123 to 827°C; TG–DSC measurements can be run easily at very low or relatively high temperatures.

APPLICATIONS FOR THE TG–DSC METHOD

Measurements are performed in an open crucible which permits flow of both the reacting and evolved gases. Applications with evolved gases are among the best known experiments: dehydration, dehydroxylation, decomposition and pyrolysis. An example is given for the decomposition of $CuSO_4 \cdot 5H_2O$ from 20 to 820°C (Fig. 3). Successive mass losses (H_2O, SO_2, O_2) are associated with the different endothermic effects and their corresponding heats due to different steps of the decomposition. Evaporation of

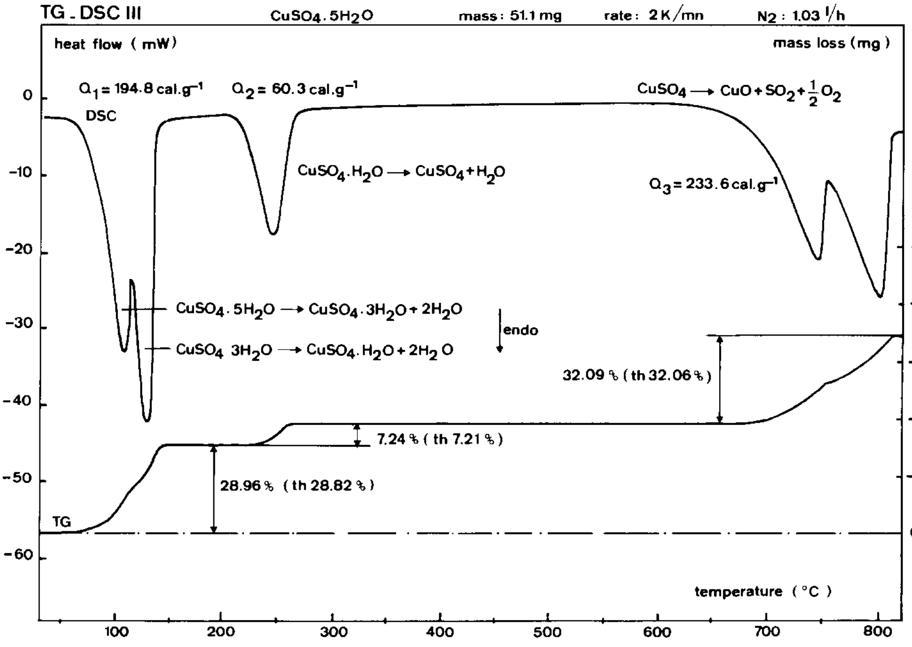

Fig. 3. Dehydration and decomposition of copper sulfate, $CuSO_4 \cdot 5H_2O$.

solvents can also be measured, especially in organic or polymeric materials.

The TG–DSC method is particularly interesting when investigating heterogeneous samples. If the analysis has to be run on two different instruments (DSC and TG), i.e. with two different samples, reproducibility of sampling is generally not achieved. In the TG–DSC mode, with only one sample, reliable DSC and TG data are obtained. This is the case when investigating the decomposition of polymeric materials, powders and explosives.

When investigating the reaction of a gas with a solid or powdered sample, different parameters have to be well defined, e.g. the surface of the sample and its grain size. Depending on the size of the grains or the size of the pores, the TG and DSC data obtained for different samples can vary. In such an experiment, the reacting gas also has to be well controlled, especially its flow rate.

It is clear that the use of a single sample will provide the most accurate measurement of the gas adsorbed on the sample with the corresponding heat of adsorption. This specificity of the TG–DSC method is especially useful for catalysis studies and all types of gas adsorption and surface reactivity investigations.

Physisorption at low temperature can also be measured. Additionally, the gas can react chemically and give rise to other types of reactions such as

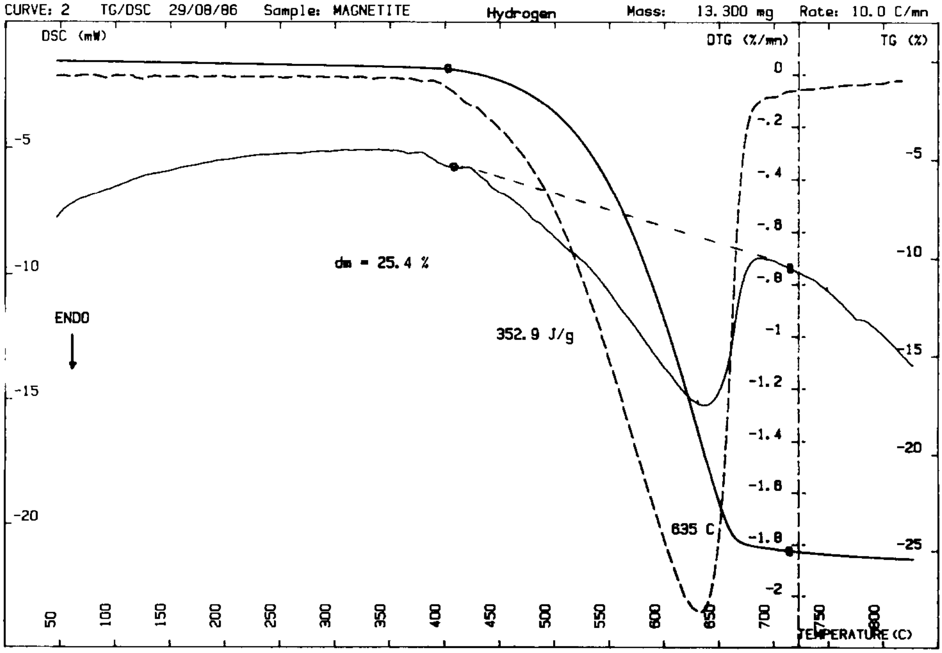

Fig. 4. Reduction of magnetite in hydrogen.

oxidation or reduction. The reduction of magnetite (Fe_3O_4) by hydrogen with the formation of Fe and H_2O (Fig. 4) is an example of using the TG–DSC for this type of application. Gas interaction with liquids, like oils, can also be investigated, especially for evaluating their oxidative stability.

FURTHER EXAMPLES OF TG–DSC APPLICATIONS

Polymers

The characterization of polymeric materials has created a very wide range of applications for the thermal analysis methods, especially DSC and TG [2], each of which has specific applications. Degradation and combustion are the two main applications of a TG system. TG curves can give the content of polymers and fillers. DSC is primarily used to characterize the thermal effects occurring in a polymeric sample without a change in mass, e.g. melting, crystallization, glass transition and cross-linking reactions. Polymers are frequently not pure compounds, but formulations with plasticizers, fillers, stabilizers, lubricants, antioxidants, fire retardants, blowing agents, etc. Some of these compounds are introduced in very small amounts. With the TG–DSC method, it is now possible to detect and measure precisely

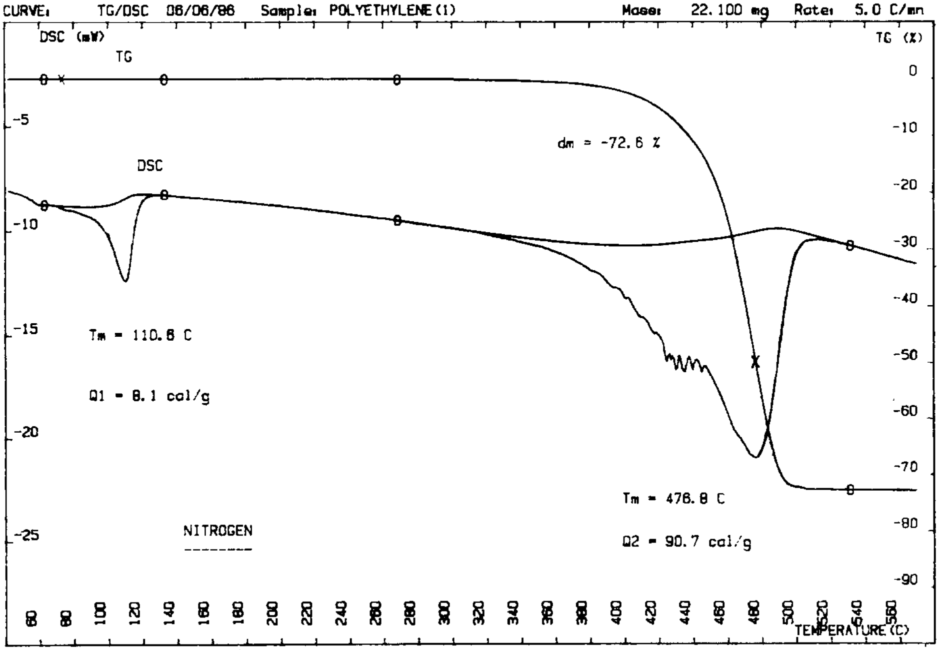

Fig. 5. Degradation of polyethylene in nitrogen.

thermal transformations with or without mass change using only one sample and a single instrument, as shown with the investigation of polyethylene containing carbon black. During the first heating period under nitrogen (Fig. 5), polyethylene is pyrolytically decomposed as seen from the TG curve. The mass change (72.6%) gives the percentage of polymer in the sample, as this type of polyethylene is known not to leave any char.

The DSC curve shows the melting of the polyethylene before the endothermic effect of polymer pyrolysis. The melting temperature (T_m = 110.6 ° C) indicates that the sample is a low-density type polyethylene.

As the amount of polymer is precisely known from the TG curve, it is possible to relate the heat of melting to the real polyethylene percentage (11.2 cal g^{-1} of polyethylene) and determine the percent crystallinity, by reference to the estimated heat of melting for a 100% crystalline polyethylene. The heat of pyrolysis can also be related to the exact mass of polymer (124.9 cal g^{-1} of polyethylene). Some noise peaks are seen during the pyrolysis probably due to the exhaust of gas from inside the sample.

By switching from nitrogen to oxygen, the carbon black is combusted (Fig. 6). The percentage of carbon black (13.1%) is measured from the TG curve. The heat of combustion of carbon black (9160 cal g^{-1} of carbon black) is obtained by integration of the DSC exothermic peak. At the end of the test, the amount of remaining inert fillers (14.3%) is measured.

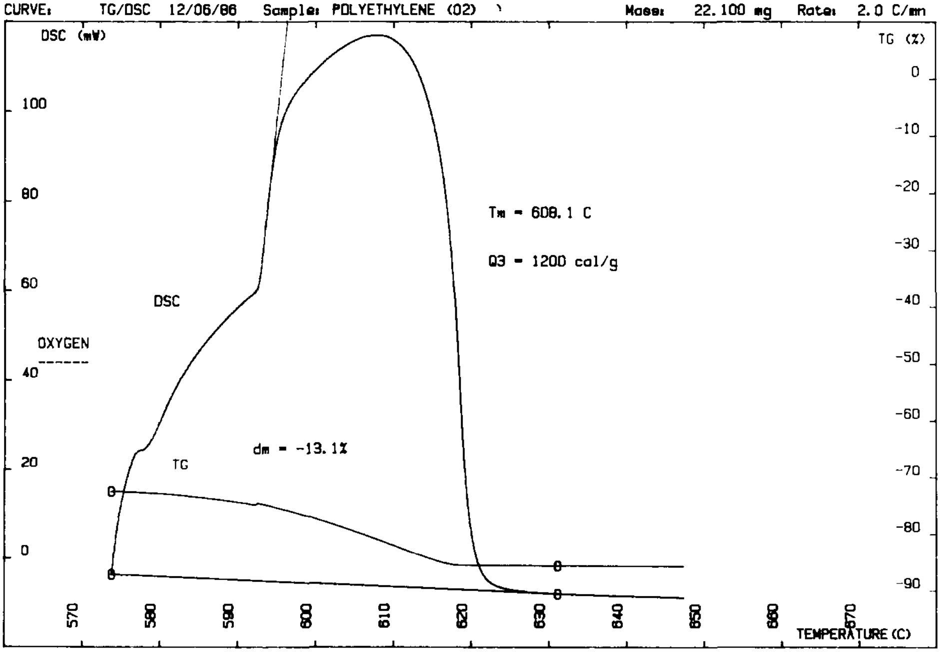

Fig. 6. Burning of carbon black (polyethylene).

In a single experiment, it has been possible to get a variety of information: type of polyethylene sample, temperature of melting, percent crystallinity, temperature of degradation, polymer content, heat of pyrolysis, carbon black content, heat of combustion and inert filler content.

Resins

Like polymers, resins are also complex mixtures. Most of them are impregnated on supports (glass fibers, graphite fibers, etc.). DSC is used to follow the curing of the resin, or to control the curing by measuring the glass transition temperature of the resin [2]. The amount of resin on the support is measured by TG. A problem with this technique is how to correlate precisely the heat of curing with the amount of resin when only 10 mg of sample, including resin and support, are separately investigated on two different instruments. With the TG–DSC method, the sampling is no longer a problem, especially if a sample of printed circuit board has to be investigated. When testing an epoxy PC board sample with the TG–DSC 111, most of the epoxy resin is first decomposed under nitrogen, as seen on the TG curve (Fig. 7). In addition to the mass loss (27.2%), the heat of decomposition is measured by integration of the DSC exothermic peak (60.2 cal g^{-1}). Prior to the decomposition, it is possible to detect the glass

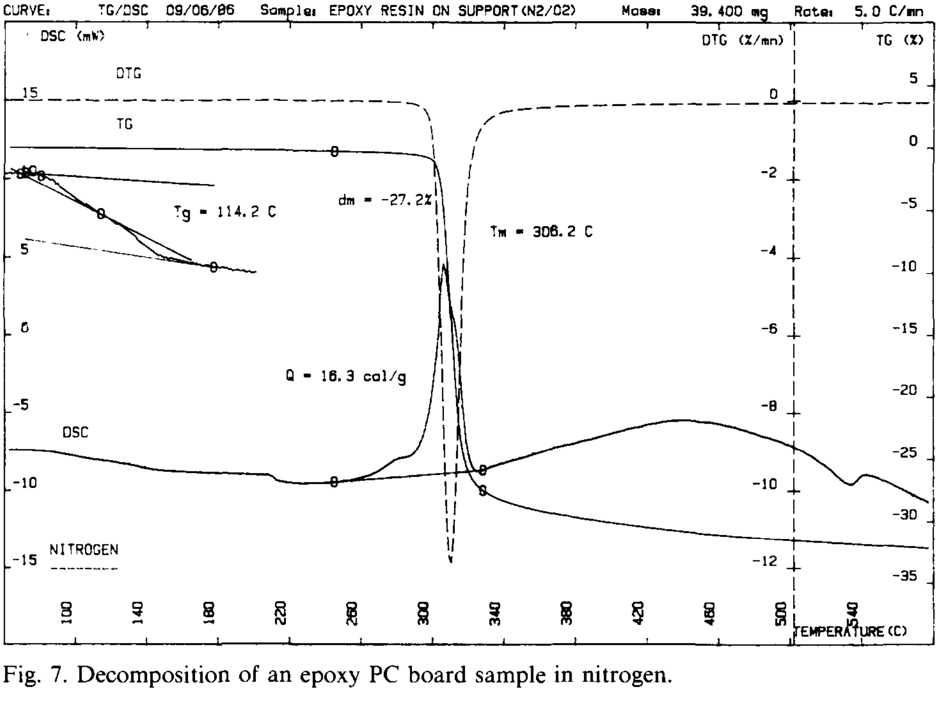

Fig. 7. Decomposition of an epoxy PC board sample in nitrogen.

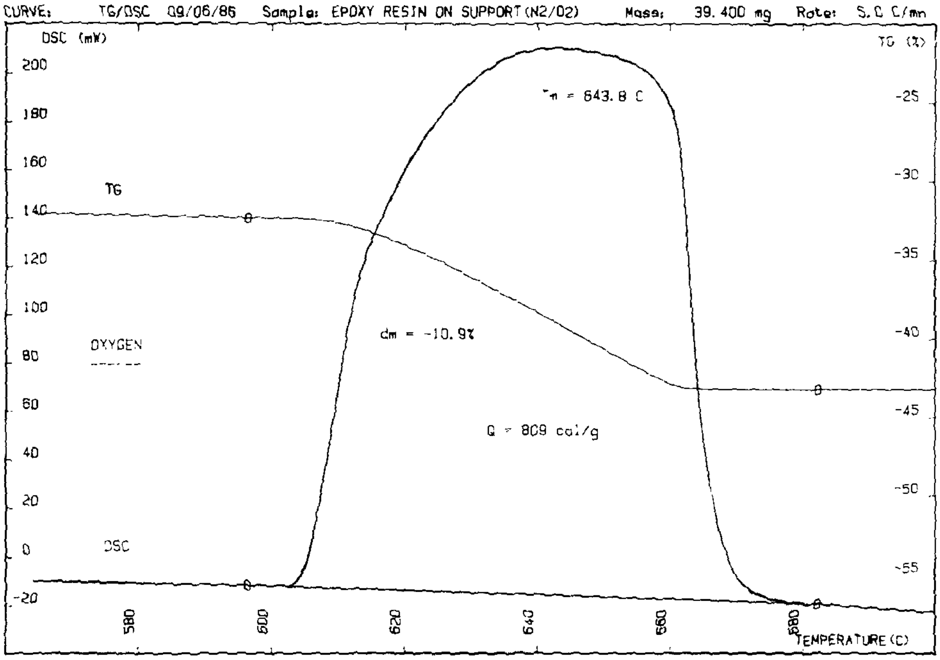

Fig. 8. Burning of the carbonaceous residue of the epoxy PC board sample.

transition temperature of the epoxy sample (114.2° C), characterizing the state of curing.

At 560° C (Fig. 8), switching from nitrogen to oxygen produces burning of the carbonaceous residue (10.9%). The DSC curve provides the amount of heat evolved by the combustion (7422 cal g^{-1} of carbon residue). At the end of the experiment (700° C), the amount of glass fiber is measured precisely (56.8%).

On a single epoxy PC board sample, the following information is obtained using the TG–DSC method: glass transition of the cured sample, temperature of degradation, heat of degradation, organic matter and carbon residue content, heat of combustion and glass fiber content. The same test can be run on uncured samples, in order to correlate precisely the heat of curing with the real resin content.

Fibers

Thermal analysis is an accurate and convenient tool for studying fibers, including physical transformations, thermal decomposition, effects of chemical or physical pretreatments, etc. [2].

The biggest problem presented by fibers for thermal analysis investigations is the geometry of fibers, especially their long length. Sampling and

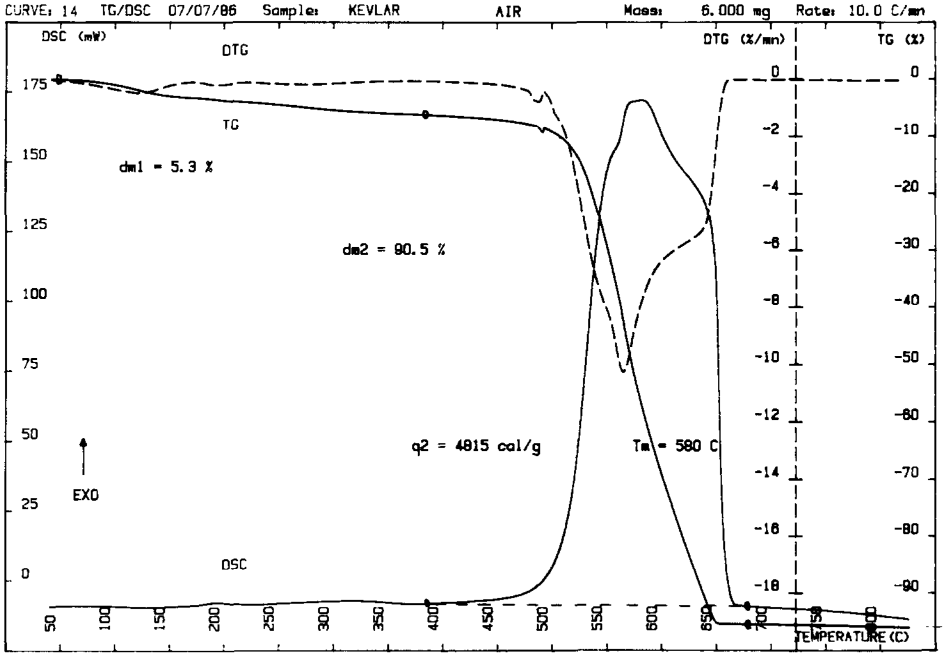

Fig. 9. Oxidation and decomposition of Kevlar.

introduction into the DSC or TG crucible are not easy. Using the TG–DSC method, this problem is reduced since only one sample is needed.

For the example shown (Fig. 9), a Kevlar sample is heated in air. Before the combustion of the fiber, moisture is detected on the TG curve. The combustion of Kevlar occurs in three steps, as seen on the DTG curve. The heat of combustion can be related to the fiber content measured on the TG curve.

Organic compounds

The application of DSC and TG techniques to organic compounds is very diverse [1]. Purity determination is the most important application in the pharmaceutical industry. Fusion, crystallization, decomposition, oxidation and vaporization are among the known measurements in the field of organic compounds. Some thermal transformations occur without mass change (fusion, crystallization and polymorphism) and others with a mass change (decomposition, vaporization, oxidation, etc). TG–DSC is a very useful tool for investigating organic compounds by combining all these different characterizations in a single run. As seen for the investigation of a granule of chlorpropamide (Fig. 10), the TG curve first shows a mass loss, corresponding to the vaporization of moisture, before melting of the sample, seen on the DSC curve. The melting is immediately followed by decomposition of

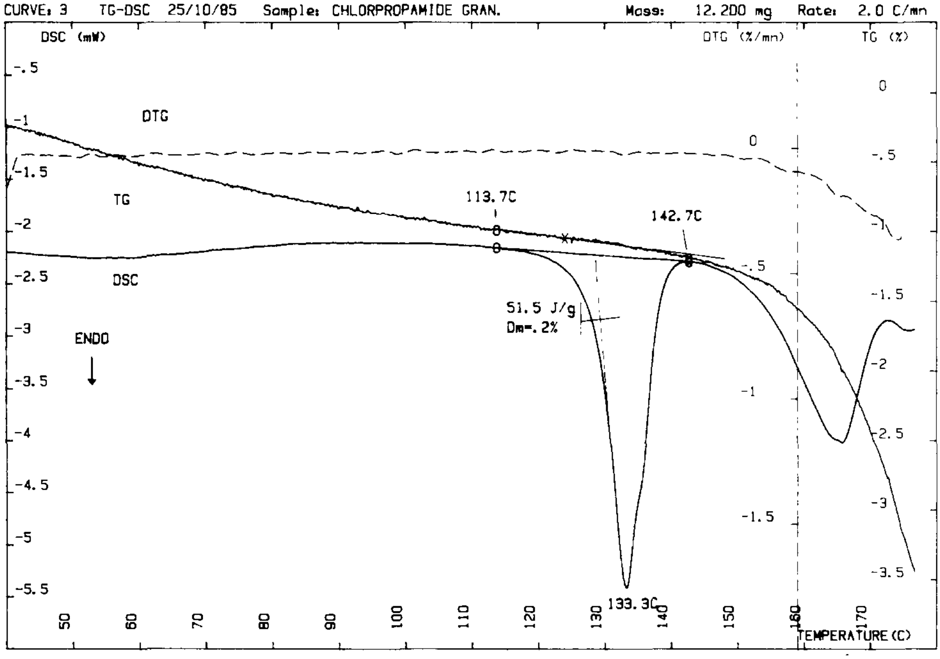

Fig. 10. Melting and decomposition of chlorpropamide.

the sample as detected on both DSC and TG curves. This test gives the moisture content, the temperature of melting, the heat of melting and the temperature of degradation. Purity determination can also be made using the melting peak.

Using the TG–DSC method for the organic compounds, enthalpic changes and thermal stability are investigated at the same time on the same sample. The TG–DSC test is also useful in evaluating the oxidative stability of an organic sample, e.g. lubricating oils (Fig. 11). According to the TG curve, a large mass loss starts below 100 ° C. This indicates that the oil starts to evaporate at low temperature. The simultaneous DSC curve allows a clear distinction between the effect of oil vaporization (endo peak) and the effect of oil oxidation (exo peak). On the DTG curve, the two different effects are also detected, but not so clearly.

Decomposition of organic compounds, and particularly hazardous products, is also a specific application for the TG–DSC instrument. The sample, the stability of which has to be controlled, is usually a heterogeneous industrial product. For such an application, the amount of sample to be investigated by DSC or TG is generally very small (~ 1 mg). Sampling reproducibility is not achieved in such a case. Again, TG–DSC can easily solve this problem of sampling for comparative purposes. The DSC peak indicates the temperature and the heat of decomposition. The corresponding mass loss on the TG curve gives the real organic matter content. A kinetic

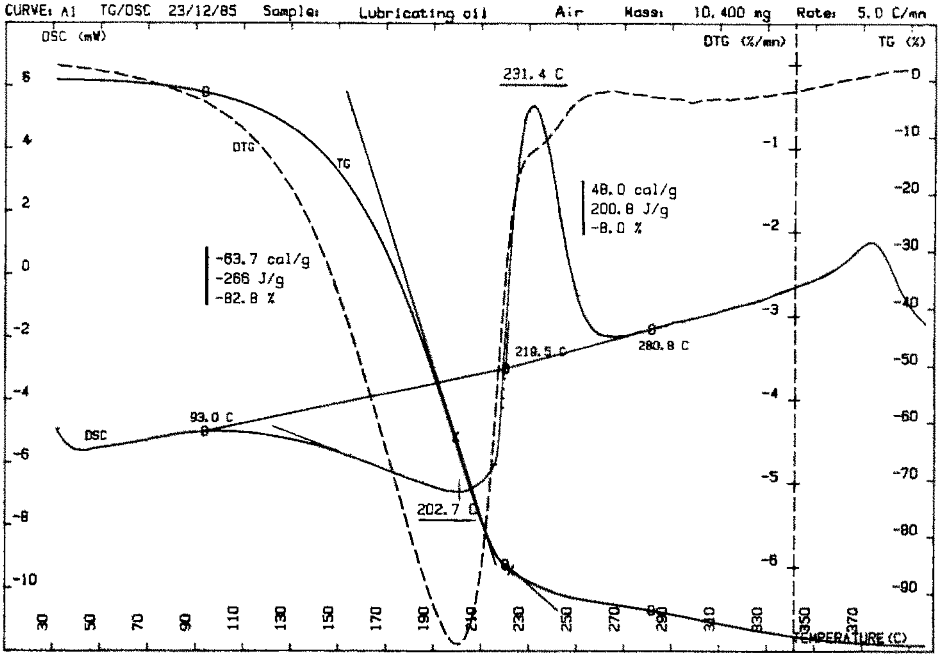

Fig. 11. Oxidation of a lubricating oil.

study of the decomposition reaction can be done using either the DSC or the DTG peak.

Clays, minerals and ceramics

The birth of thermal analysis was mainly due to early thermal investigations on clays and minerals [7]. Nowadays, the techniques have been improved and the number of applications in this field has also been increased to a large range of temperatures [1,3]. DSC is mainly used for characterizing thermal transformations (dehydration, dehydroxylation, solid–solid transition, decomposition, etc.). As in many cases, vapors (H_2O, CO, CO_2, etc.) are emitted from the sample; the combination with a TG measurement provides additional information on the mass transfer.

This is especially important for investigations on raw materials transformed in an industrial process. The heat and mass balances have to be established to adapt the energy consumption, as in the cement industry. A sample of cement containing some oil traces, heated in air, gives much important information when investigated by the TG–DSC method (Fig. 12). The amount of water produced by the different dehydrations up to 200 °C is known, and the corresponding heats of dehydration are evaluated. At 300 °C, the oil starts to burn, and the heat produced by the burning is

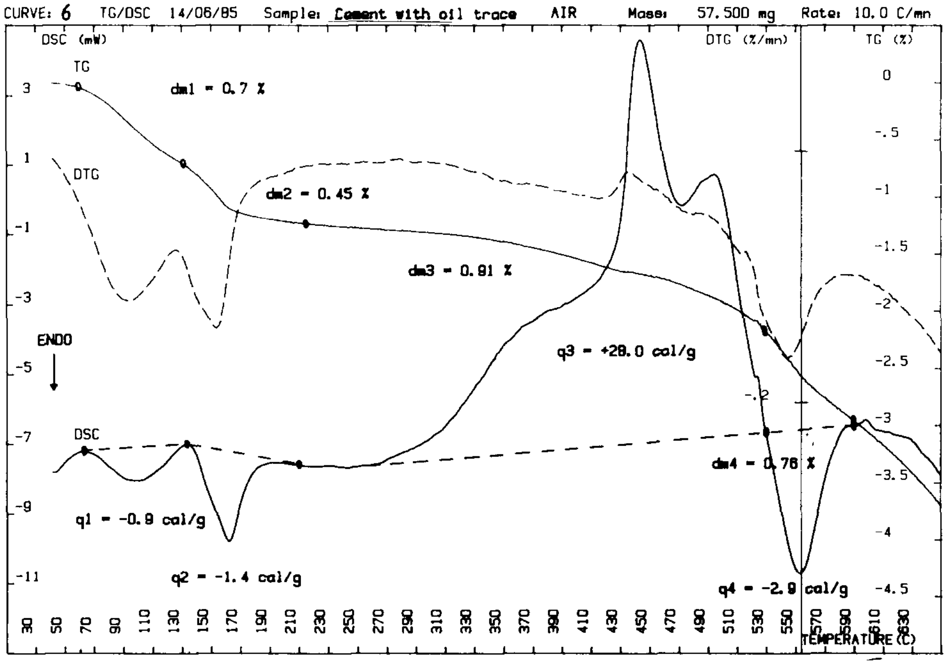

Fig. 12. Thermal investigation of a cement containing oil traces.

evaluated. At the same time dehydroxylation of some products and decomposition of carbonates occur.

The same data are needed for the firing process of ceramics, as shown by the investigation of an alumina–zirconia powder in air (Fig. 13). Between 250 and 350 ° C, the amount of solvents and the corresponding heat of vaporization are measured. Above 400 ° C, the DTG and DSC peaks indicate the combustion of solvents and the decomposition of acetates introduced as an additive to the alumina–zirconia powder. The TG curve indicates the mass of the sample after densification. Above 700 ° C, crystallization of the new densified product is detected on the DSC curve. With such a test, the different thermal effects and mass transfers occurring during the firing process of the ceramic powder are precisely characterized.

Catalysts and zeolites

For a long time, the use of thermal analysis, especially DTA and DSC, has been limited to establishing the phase composition of catalysts or to identifying catalysts [8]. Very few applications have been developed for adsorption or reaction measurements, mainly because the measuring heads suffer from limitations due to gas flow. These experiments are primarily determined using TG. The use of the heat flux principle of the DSC 111 has

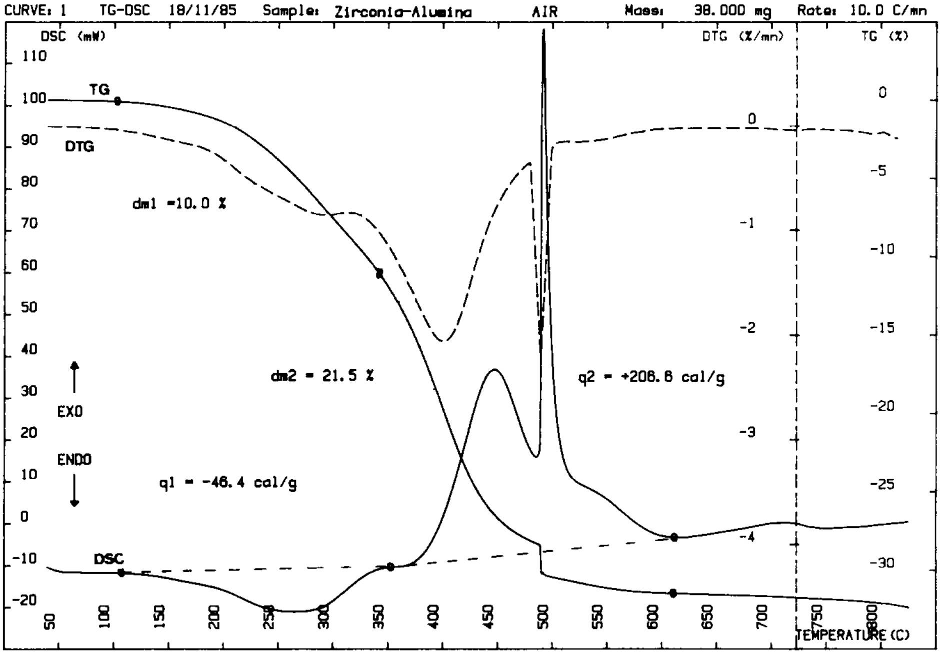

Fig. 13. Firing of a zirconia–alumina powder in air.

shown that adsorption and reaction measurements can be run precisely with various types of gas without limiting the detection [9].

The combination of TG and heat flux DSC now gives access to a larger range of applications in the field of catalyst and zeolite investigations, e.g catalyst evaluation and preparation, surface reactivity, pulse adsorption, reduction, chemisorption and physisorption. An example of catalyst preparation is given by the reduction of nickel oxide deposited on a silica support (Fig. 14). After the evaporation of adsorbed water, the nickel oxide is reduced by hydrogen to metallic nickel. The TG curve allows the evaluation of the amount of metallic nickel on the support according to the reduction reaction. By coupling a mass spectrometer to the TG–DSC 111, through a capillary tube, analysis of the evolved gas clearly shows evaporation of water in the first step, and the formation of water during the subsequent reduction process.

As the TG–DSC instrument is also easily used below room temperature, it is possible to characterize the specific area and pore volume of a catalyst or a zeolite by adsorption of gas with increasing pressure, to simulate the BET method.

Using the TG–DSC method, as shown for the adsorption of CO_2 on a molecular sieve at $-20.5\,^{\circ}C$ (Fig. 15), the variation of the amount of gas adsorbed on the molecular sieve is recorded with increasing pressure, but also the corresponding heat of adsorption is evaluated. A precise correlation

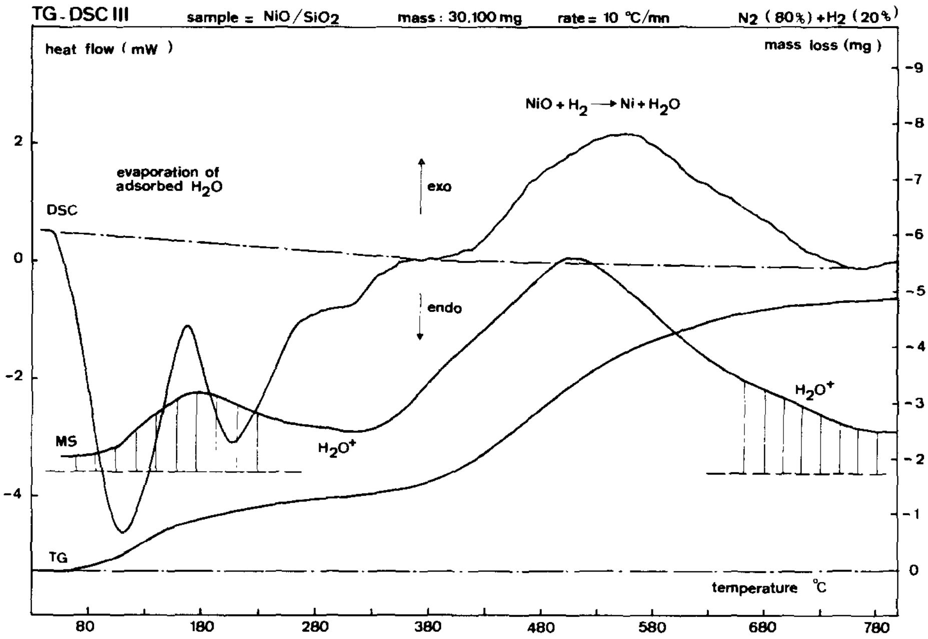

Fig. 14. Reduction of an NiO/SiO_2 catalyst in hydrogen.

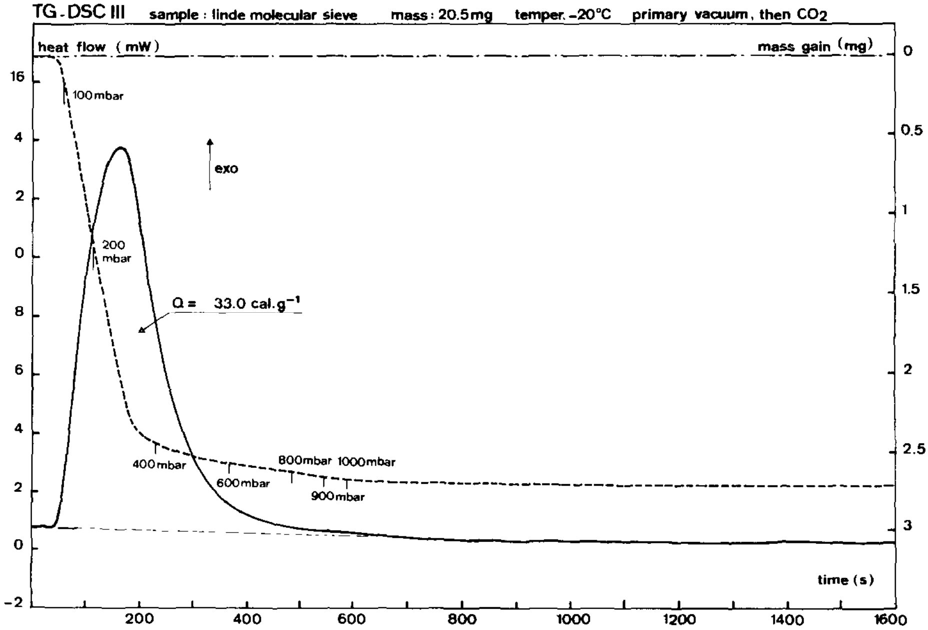

Fig. 15. Adsorption of CO_2 on a molecular sieve at low temperature (−20 °C).

between the amount of gas adsorbed and the heat of adsorption can be done.

CONCLUSION

The TG–DSC method offers new investigation possibilities for thermal analysts interested in DSC and TG measurements. In many cases, combination of the two methods on the same sample greatly improves the correlation between TG and DSC data, especially for transformations with evolved gases, for reactions with gas interactions and for investigations of heterogeneous compounds.

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