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A NEW SYMMETRICAL MICRO-THERMOBALANCE

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A new symmetrical micro-thermogravimetric analyzer has been developed. The symmetrical design of this instrument allows determination of very small mass changes over a wide range of temperatures. The utility of the instrument was demonstrated by studying the decomposition characteristics of $CaC_2O_4 \cdot H_2O$ and the curing and decomposition kinetics of a glass filled polymer composite.

There is a wide range of different thermobalance models available on the market. State-of-the-art instruments use electronic analytical or microbalances with electromagnetic compensation for mass changes which can be as low as micrograms. The arrangement of the balance in relation to the furnace is usually unsymmetrical and contains arrangements to measure sample temperature and to change the atmosphere. The user is, therefore, confronted with a balance signal which is influenced by changes in atmosphere and affected by buoyancy as well as the temperature gradient between the sample and the measuring point.

Beam balances with knife-edges or torsion systems have found general application in thermobalances. With the first type of system a high load can be used, compared to microbalances using the torsion principle. The sample weights are in a range 1 mg to approximately 20 g. Operating principles of the balances are load compensation systems with optical, inductive or capacitive zero-load detection or inclination balances. The relative readability of the systems—maximum load divided by readability—are in a range 10^5 to 10^6.

The arrangement of the sample and the furnace relative to the balance system is treated differently. Whilst a spring balance (e.g. quartz spring) leaves no flexibility for the furnace arrangement, balances with horizontal beams allow the sample carrier to be mounted above or hanging from the beam. The hanging arrangement is inherently more stable, but it demands a better screening of the balance from the radiation heat of the furnace. The top-loading arrangement requires, in order to be mechanically stable, a compensation weight mounted beneath the balance beam and for this reason the design is taller with high balance load. For balance beams with knife-edges it is often possible to connect the thermocouple wires without influencing the weight signal, so that the temperature measurement can be carried

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out directly on the sample or other temperature measurements in more positions as is necessary for simultaneous TG–DTA-measurements.

Thermogravimetric results in different atmospheres are superimposed by the so-called buoyancy effect. Due to the reduction in density of the atmosphere inside the furnace during heating, influenced by the volume of sample and sample holder system inside the hot zone of the furnace, an apparent weight increase results.

The buoyancy effect can only be determined empirically, as the temperature gradients in a furnace and the effective sample carrier volume are not constant; or compensated for by the technically demanding method of totally symmetric design.

Instrumentation

For the newly introduced NETZSCH-Micro-Thermobalance TG 439 a totally symmetrical arrangement of the balance, furnace and gas flows are used as design principle. Two identical hang-downs are mounted on the quartz beam of a symmetrical, totally electronic micro-balance.

A similar quantity, identical volume of sample material and reference material up to 1 g each can be supported in platinum or aluminium oxide pans. Generally the sample weight lies in the submilligram range and is measured in the thermobalance.

For the sensitive determination of small mass changes two compensation ranges are available, 10 mg and 100 mg, so that using an analog recorder TG steps $\geqslant 0.1$ μg can be evaluated (measuring ranges 10 μg to 100 mg). When operating with a computer the digital balance electronics offers a resolution of 0.1 μg with measuring ranges from 100 μg to 100 mg. The relative readability is 10^7, i.e. on the upper boundary of the capabilities of balance systems.

Two identical furnaces with temperature range 25 to 1000° can be raised electrically over the sample carrier. By using modern low thermal mass materials for construction of the furnaces, heating rates up to 100 deg min are achieved. Additional water cooling ensures optimum protection from heat transfer for the balance system and also enables fast cooling rates to be used. The large dimensioned low power furnaces are controlled by a microprocessor temperature programmer. The sample area is separated from the heating elements by a quartz-glass protective tube. The sample and balance areas are evacuable to 10^{-2} mbar to allow exact atmosphere control and gas changes and the system is fitted with a sophisticated gas control system. The principle of total symmetry is also used for the gas flow paths and the vacuum connections. A schematic of the system is shown in Figure 1.

The volume of gas flow is controlled and exactly maintained by a stepwise electronic push button control. The automatic change between two gases can be

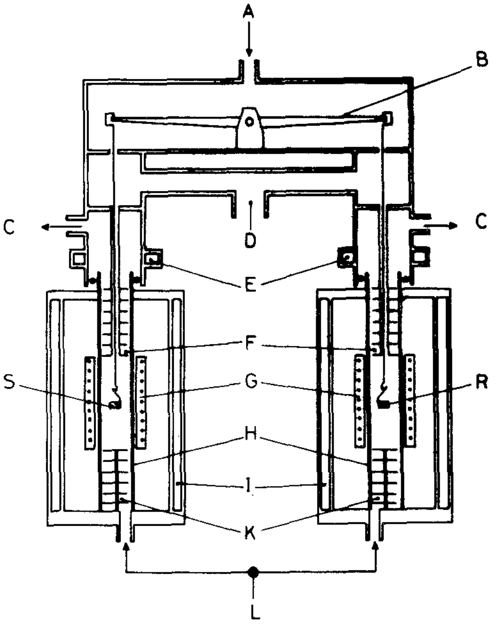

Fig. 1 Schematic of micro thermogravimetric analyzer. A: protective gas inlet, B: balance, C: gas exhaust, D: vacuum connection, E: temperature control water channels, F: radiation shields, G: heating elements, H: protective tubes, I: cooling water channels, K: radiation shields, L: purge gas inlet, S: sample crucible, R: reference crucible

programmed and automatically carried out by either the microprocessor temperature programmer or alternatively the computer.

Mechanical aids are fitted to allow easy loading of the sample and reference material together with an automatic closing of the furnace chambers during loading. These features allow easy and fast operation of the instrument.

Results and discussion

Using sample quantities in the microgram range results, in most applications, in a dramatic reduction in the reaction interval (the temperature difference between start and end of a TG-step) when compared with the results from a larger sample weight. This is clearly shown by $CaC_2O_4.H_2O$ in Figure 2.

Table 1 shows the reaction steps compared with the TG results using a 50 mg sample in a simultaneous TG–DTA system (STA 429) where all other measurement parameters are nearly identical.

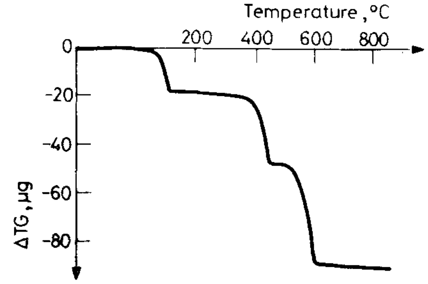

Fig. 2 Decomposition of $CaC_2O_4.H_2O$ in a nitrogen atmosphere. Sample: calcium oxalate.H_2O, weight: 137 µg, measuring range: 100 µg/250 mm, heating rate: 20 deg/min, atmosphere: N_2, 50 cm^3/min

Table 1 Reaction intervals, $CaC_2O_4.H_2O$

Instrument	TG 439	STA 429
sample mass	137 µg	50 mg
purge gas flow rate	50 ml/min	100 ml/min
evolved gas	interval, °C	interval, °C
H_2O	24 °C	103 °C
CO	34 °C	85 °C
CO_2	62 °C	105 °C

The fraction of mass remaining, m/m_0, as a function of temperature and heating rate for the curing cycle of a glass-filled polymer is shown in Figure 3. As can be seen, the curing mass loss for this particular polymer is complete by 250° for all of the heating rates studied. This indicates 100% cure and was confirmed by a combination of differential scanning calorimetry and mass spectrometry experiments which showed no additional curing energetics or release of volatile components above 250°. Also, as expected, the curing kinetics are strongly dependent on the heating rate. For example, the difference between the temperatures corresponding to $m/m_0 = 0.95$ is over 75° for 0.5 and 80 deg/min heating rates. In addition, it is clear from Figure 3 that the curing kinetics change with temperature for each of the heating rates studied. Finally, it is important to note that there is a clear and consistent increase in the curing mass loss with heating rate. As can be seen, the mass loss at 250° increases from about 8.12% for the 0.5 deg/min heating rate to approximately 9.9% for the 80 deg/min heating rate. This results in a different microstructure, and hence different decomposition kinetics, for each heating rate, even though in each case the polymer is fully cured.

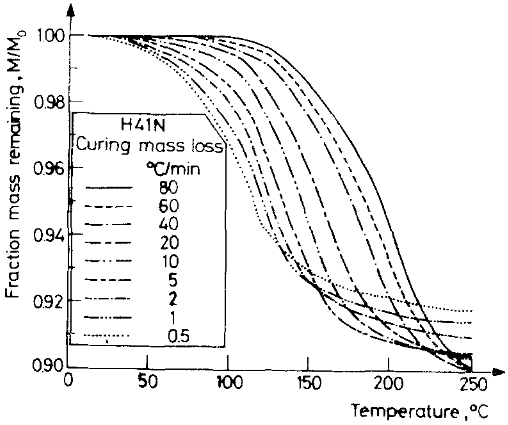

Fig. 3 Curing mass loss *vs.* temperature at several heating rates

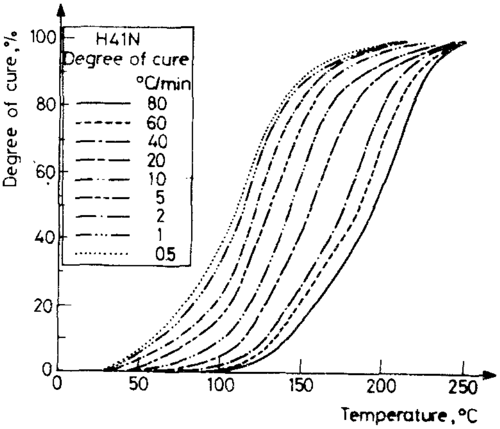

Fig. 4 Degree of cure *vs.* temperature at several heating rates

The mass loss data presented in Figure 3 were also used to calculate the degree of cure as a function of temperature and heating rate. The results of these computations are shown in Figure 4. It should be pointed out that the final fraction of mass remaining, m_f/m_0, at 250° was used to compute the mass loss at 100% cure. Therefore a different value of m_f/m_0 was used for each of the nine curing rates. This produced an ultimate degree of cure of 100% for each rate. The data presented in Figures 3 and 4 display, of course, the same general behaviour.

Figure 5 depicts the decomposition mass loss as a function of temperature at a heating rate of 40 deg/min for the samples cured at rates of 80, and 1, and 0.5 deg/min. As shown, a decrease in the curing rate results in a consistent shift in the

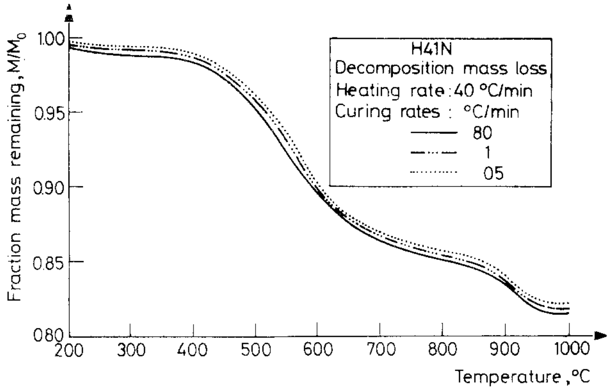

Fig. 5 Decomposition mass loss *vs.* temperature for three curing rates

mass loss curves to higher temperatures. In addition, the mass loss at 1000° increases with the curing rate. For example, the mass loss increases by about 0.7% as the curing heating rate is increased from 0.5 to 80 deg/min. The increase in material performance which accompanies the slower curing rates is a result of the higher degree of cross linking. A more complete discussion of the effects of curing on the decomposition kinetics has been given by Henderson and Emmerich [1]. Also details of the general behaviour of this material have been given by Henderson, Tant, Doherty and O'Brien [2].

Concluding comments

Using a fully electronic symmetrical microbalance, a thermobalance was constructed that, with "state of the art" technology and a symmetrical design principle, using two identical furnaces, and a specially constructed gas flow system allows the exact evaluation of TG-plateaus and extremely good long term stability with exceptionally low long term drift. Sample weights in the microgram range result in reaction intervals which are considerably shorter than those for a conventional TG-system.

In addition, the results of this work show that the rate of cure significantly affects the decomposition kinetics of phenolic composites. Increasing the curing rate not only increases the mass loss during the curing cycle, but shifts the mass loss curves to lower temperatures and increases the total mass loss during the decomposition cycle. Decreasing the degree of cure shifts the decomposition mass loss curves to lower temperatures and increases the total mass loss. This behaviour clearly demonstrates that the curing cycle is of paramount importance for composites used in high temperature thermal protection applications. Finally, the micro thermogravimetric analyzer proved to be an invaluable tool for resolving the small differences in the mass loss at high temperatures.

References

1 J. B. Henderson and W.-D. Emmerich, accepted for presentation at the 16th Annual North American Thermal Analysis Society Conference, Washington, D. C., USA, September 1987.

2 J. B. Henderson, M. R. Tant, M. P. Doherty and E. F. O'Brien, Composites, Vol. 18, No. 3, 1987, 205.

Zusammenfassung — Ein neuer symmetrische mikrothermogravimetrischer Analyser wurde entwickelt. Die symmetrische Gestaltung dieses Instruments ermöglicht die Bestimmung sehr geringer, sich über weite Temperaturbereiche hinziehender Massenveränderungen. Die Brauchbarkeit des Instruments wird demonstriert, in dem die Zersetzungscharakteristik von $CaC_2O_4.H_2O$ und die Kinetik der Härtung und Zersetzung von glassverstärkten Polymerverbundstoffen untersucht wird.

Резюме — Разработан новый симметричный микро-термогравиметрический анализатор. Симметричное решение этого прибора позволяет определять очень малые изменения массы в широкой области температур. Эффективность прибора показана на примере изучения реакции разложения $CaC_2O_4.H_2O$, а также кинетики отверждения и разложения стеклонаполненного полимерного композита.