Journal of Thermal Analysis, Vol. 35 (1989) 1067–1072

RECENT ADVANTAGES IN THERMAL ANALYSIS INSTRUMENTATION

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Curing and decomposition of a phenolic resin is studied by simultaneous thermal analysis (STA) and mass spectrometry (MS) to get quantitative and qualitative information on the reactions. The influence of the heating rate and the curing mass loss of the same material is measured with a symmetrical micro thermobalance. A high temperature DSC apparatus is used to determine the specific heat of a glass ceramic. Poco graphite is used for expansion calibration measurements with a new dilatometer up to 2000 °C.

During the past several years there has been an increasing demand for materials which can be used under a variety of unique operating conditions. This demand has led to the development of a large number of new materials such as technical ceramics, advanced polymers, etc. The development of these materials has been accompanied by the need to quantitatively characterize their behaviour. This, in turn has resulted in the rapid development of a new generation of thermal analysis instrumentation.

The purpose of this paper is to review current state-of-the-art thermal analysis instrumentation. Four of the most modern and important commercially available thermal analysis instruments are the simultaneous thermal analyzer (STA) coupled with a mass-spectrometer (MS), a micro thermogravimetric analyzer (TGA), a differential thermal analyzer (DTA), and dilatometer/thermomechanical analyzer (TMA). Each of these instruments, along with application examples and current limitations such as temperature range and sensitivity, will be discussed.

Instrumentation

STA/MS

The Netzsch model STA 429 allows simultaneous determinations of mass loss (TG) and energetics (DTA). With this particular instrument measurements can be conducted on solid or liquid samples over the temperature range of − 160 to 2400°.

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Samples can be tested under a high vacuum or in a static or dynamic gas atmosphere. The high temperature furnace is constructed with a tungsten heating element mounted in a water-cooled housing and is capable of operation to 2400°. When coupled with an MS system the STA 429 allows simultaneous TG/DTA/MS measurements to be conducted at temperatures up to 2400°. The MS system yields information regarding the atomic or molecular structure of an evolved gas and up to 16 different mass numbers can be evaluated simultaneously. Finally the STA 429 is available with a sophisticated 16/32 bit computer control and data acquisition and the appropriate software for data evaluation. Figure 1 shows the curing decomposition behaviour of a glass-filled phenolic resin at temperatures up to 1600°. As can be seen the curing mass loss is about 9.01% and occurs in the temperature range of approximately 100 to 350°.

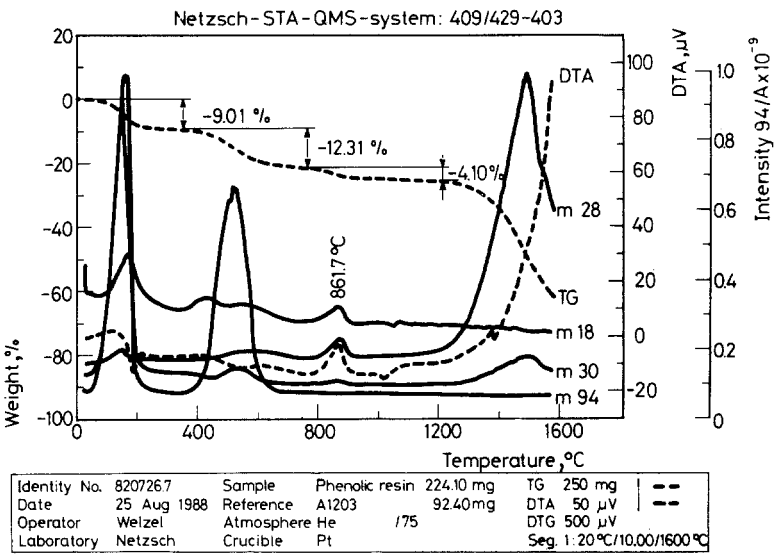

Fig. 1 Mass loss and evolved gases of a polymer during curing and decomposition

The onset of resin decomposition (pyrolysis) occurs at about 380° and results in an additional mass loss of about 16.41%. Finally the weight loss associated with the carbon-silica reactions starting at about 1200° is obvious. Also depicted in Fig. 1 are some of the evolved gases associated with the curing and decomposition. As can be seen significant quantities of gases with mass number of 18, 28, 30 and 94 are evolved during the curing and decomposition process. It must be pointed out here that other gases were evolved, but are not shown due to space limitations.

TG

The Netzsch model TG 439 allows the determination of the mass loss of substances over a wide range of temperatures. The TG 439 is a micro thermogravimetric analyzer which employs a totally symmetrical arrangement with a microbalance as the central element [1]. Both the sample and reference crucibles are suspended symmetrically from the balance arm. Also both sides of the system are heated uniformly by separate furnaces and are exposed to equal purge gas flow. This design virtually eliminates buoyancy effects and allows accurate detection of very small mass changes over the entire temperature range of the instrument. The furnace design employs a platinum wound heating element mounted in a water-cooled housing. The instrument is currently capable of operation to 1500° at heating rates changing from 0.1 to 100 deg/min. The same data acquisition/control system used with the STA 429 is also available for the TG 439.

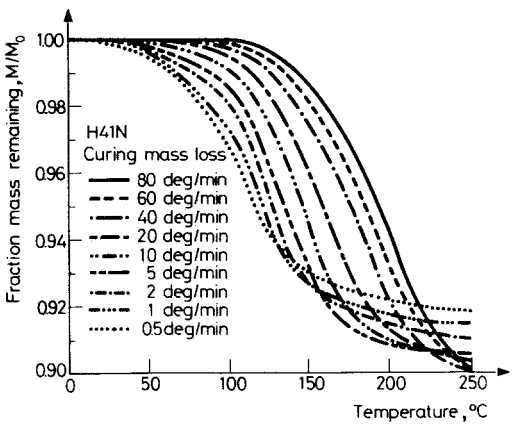

Fig. 2 Curing mass loss of polymer *vs.* temperature at several heating rates

Figure 2 shows the curing mass loss of the same glass-filled phenolic resin as a function of temperature and heating rate. Clearly shown is the heating rate dependence of the curing kinetics as well as the consistent increase in the mass loss with heating rate.

Notice that the 9.0% mass loss for the 10 deg/min heating rate agrees well with the 9.01% curing mass loss measured for the same material with the STA 429. It is also interesting that the TG 439 consistently detects differences in the final mass loss as small as 0.07%.

Fig. 3 DSC 404 with control cabinet and computer

DTA

The Netzsch model DSC 404 (heat flux) can be used for evaluation of reaction onset and peak temperatures, enthalpy determinations, and quantitative determination of the specific heat for a wide variety of materials [2]. This instrument (Fig. 3) comes equipped with a new platinum furnace and platinum/rhodium sample carrier. The platinum furnace produces a consistent and uniform heat flux to the sample carrier. Hence, the baseline drift is quite small and the reproducibility is excellent, making quantitative specific heat measurements possible [3].

The measuring probe consists of a platinum/rhodium sample carrier head mounted on an alumina support stem. The sample carrier head functions both as a holder for the sample and reference crucibles and as the platinum/rhodium leg of the monitoring thermocouple. The sample crucibles and lids are constructed of a platinum/rhodium alloy and are approximately 6.0 mm in diameter and 3.0 mm deep. The large contact area between the crucibles and sample carrier results in excellent sensitivity. Both the furnace and sample carrier are capable of operation to over 1500° at heating rates changing from 0.1 to 100 deg/min. Experiments can be conducted under a vacuum or in a static or dynamic gas atmosphere. The data acquisition/control system is the same as that previously described. Also software for complete evaluation of the DSC results has been developed.

The specific heat of pyroceram 9606, a glass ceramic, was calculated from experimental data obtained with the DSC 404 using the well-known ratio method. A comparison of the published and measured values of the specific heat in the

temperature range of 50 to 1080° is shown in Fig. 4. Clearly the results are quite good. The maximum deviation between the measured and the published values is approximately 1.5% and the average deviation over the entire temperature range is about 0.6%.

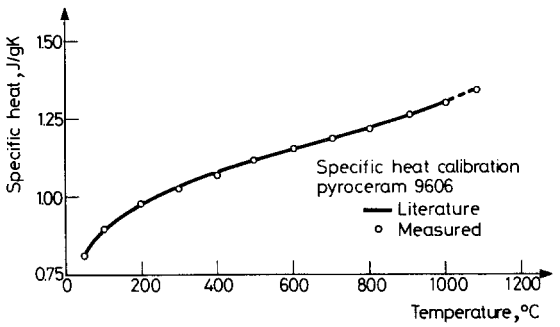

Fig. 4 Measured and published c_p values of pyroceram 9606

Dilatometer/TMA

The newly introduced Netzsch model 402 E/7 low-spring-tension, ball-bearing dilatometer can be used to determine sintering expansion and onset temperatures, expansion during binder burn out, coefficients of expansion, etc. The measuring range of the instrument is 50 to 5000 μm with a resolution of 0.1 μm. The dilatometer furnace consists of a bifilar, graphite heating element mounted in a water-cooled housing. The pushrod and sample carrier are constructed from high purity graphite. The instrument is currently capable of operation to 2000° at heating rates ranging from 0.1 to 50 deg/min. Also, because of the water-cooled housing, the cooling rate of the unit is quite high. These fast heating and cooling rates are unique for high temperature dilatometers and are possible because of the high degree of thermal stability of the graphite components. Samples can be tested in a vacuum or in a static or dynamic gas atmosphere. A data acquisition system and the associated software are available for the 402 E/7.

Figure 5 shows the results of expansion calibration measurements made with the new dilatometer for Poco AXM 501 graphite. The excellent agreement between the measured and published values is obvious. The maximum difference between these values over the temperature range of 100 to 1925° is only about 2.0%, while the average difference over this temperature range is approximately 0.8%.

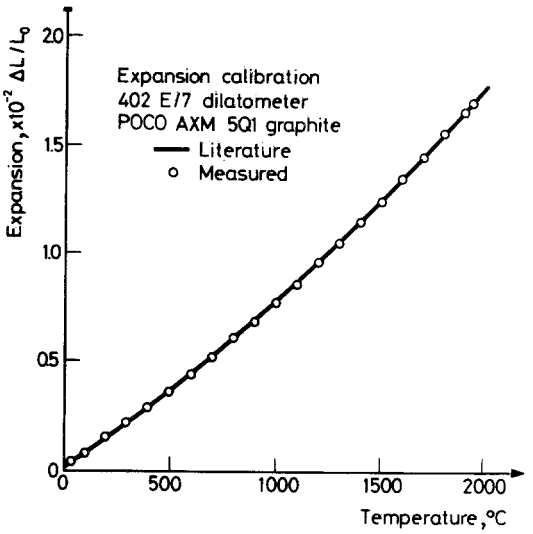

Fig. 5 Measured and published expansion values of Poco AXM 501 graphite

References

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Zusammenfassung — Mittels simultaner Thermoanalyse (STA) und Massenspektroskopie (MS) wurden Vernetzung und Zersetzung von Phenolharzen untersucht, um so quantitative und qualitative Erkenntnisse über die entsprechenden Reaktionen zu erlangen. Der Einfluß der Aufheizgeschwindigkeit und des Vernetzungsmassenverlustes desselben Stoffes wurde mit einer Mikrothermowaage gemessen. Zur Bestimmung der specifischen Wärme einer Glaskeramik wurde ein Hochtemperatur-DSC Gerät verwendet. Zu Ausdehnungskalibrationsmessungen bis zu 2000° mit einem neuen Dilatometer wurde Pocographit verwendet.

Резюме — Совмещенный метод термического анализа и масс-спектрометрии был использован для получения качественной и количественной информации о реакции отверждения и разложения фенольной смолы. Влияние скорости нагрева на потерю веса при отверждении одного и того же образца было измерено с помощью симметричных микротермовесов. Высокотемпературная ДСК была использована для определения удельной теплоемкости стеклообразной керамики. Градуировка нового дилатометра была проведена до 2000 °C с использованием графита.