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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

INTEGRATED CIRCUIT THERMAL ANALYSIS
A new thermal technique for polymer characterization

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Abstract

Polymer characterization has largely helped in the development of thermal analyzers and calorimeters, based mainly on the thermocouple technology, or more recently the semiconductor technology. With the use of an integrated silicon thermopile as a detector, a new thermal technique is appearing, to give more possibilities of investigations in the field of polymeric materials. Combining high sensitivity and use of small amount of sample, the originality of the new design comes from its low power consumption, giving rise to a portable version of the instrument. With such a concept, the thermal analysis technique is carried on the industrial site, to perform online measurements.

Melting and crystallization, glass transition, control of reticulation are a promising field of applications for the characterization of polymeric materials on industrial sites.

Keywords: calorimetry, integrated circuit, polymer, portable

Introduction

The discovery of Le Chatelier on the thermocouple technology has originated the modern development of the thermal analysis techniques, firstly with DTA (differential thermal analysis) followed with DSC (differential scanning calorimetry). Different types of DTA, described in the books of MacKenzie [1] and Wendlandt [2], have been designed, but are not very well adapted for the characterization of polymers. With the introduction of the DSC technique, this field of application has grown very quickly and Turi [3] in her book described all types of investigations on polymeric materials. Other types of DSC, based on the Boersma theory, power compensation concept and the Calvet principle, are described in different books [4–6]. More recently, the semiconductor technology has been introduced to improve the sensitivity of the instrument, particularly for the detection of very weak thermal transitions [7, 8].

However, this very high sensitivity calorimetric technique requires a larger amount of sample and has a limited range of temperature.

As a new jump in the calorimetric technique, the technology of micro-sized silicon chips is used to develop a so-called integrated circuit thermal analyzer operating with a

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small sample mass, exhibiting a high sensitivity and a very short response time [9–11]. All such characteristics are in well accordance with the thermal characterization of polymers and related materials. The sample in any form (solid, powder, liquid, film, fiber, etc.) can be directly placed on the chip without any crucible. Due to the miniaturized heat flow transducer and the low power consumption, the analyzer is very compact and easy to carry. A portable version of the thermal analyzer will allow the direct investigation of polymeric materials on the industrial site. Fast information from the experimental runs will give indication to quickly interact on the industrial process or on the quality control. The new thermal analyzer is mostly designed for quality control and routine analysis.

Description of the integrated circuit detector

The new integrated circuit detector is constructed on the basis of micro-sized silicon chips, issued from the microelectronic technology. The thermopile, used as a detector, consists of an array of 160 *p*-type silicon/aluminum thermocouples which are connected in series and integrated in an *n*-type silicon epitaxy layer, grown on the silicon wafer. The silicon chip (size: 28×28 mm) is fixed in a conventional integrated circuit chip carrier (PGA) (Fig. 1).

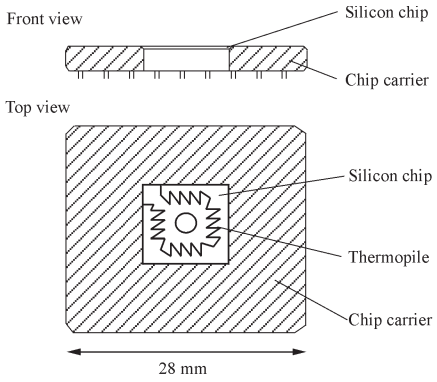

Fig. 1 Schematic description of the integrated circuit detector

The Si-chip is a planar structure with a self-supporting membrane. The sensitive sphere for the heat detection is in the middle of the membrane. The remaining rim serves as a mechanical suspension as well as a heat sink to thermally isolate the hot junctions from the cold junctions. The device operates according to the Seebeck effect, the same principle on which thermocouples are based. Between the sensitive sphere and the rim, the thermopile, integrated in the membrane, measures the temperature difference given as a consequence of the heat flow through the membrane with the thermocouples. For the use of an integrated circuit as a heat detector, it is essential that the heat flow is mainly evolved through the membrane.

The integrated circuit calorimetric device also contains a heater resistance. This resistance is suitable for calibration purposes, using the Joule effect principle (Fig. 2). A

known power is dissipated through the resistance to heat up the silicium membrane. The corresponding calorimetric signal is recorded.

From this experiment, two important data are obtained:

– the sensitivity of the detector
– the time of response of the calorimetric device

The sensitivity of the detector can reach values as high as 1000 up to 2000 microvolt per milliwatt, $\mu V\ mW^{-1}$, to be compared with 10 $\mu V\ mW^{-1}$ for DSC based on thermocouple technology and 100 $\mu V\ mW^{-1}$ for calorimeters based on semiconductor technology. A very small time of response, in the range of one second, is obtained with such a device. Associated with the small time constant for the heat exchange between the sample and the heat sink, is the small heat capacity value of the active, sample holding place on the membrane, compared to the classical DSC and calorimeters.

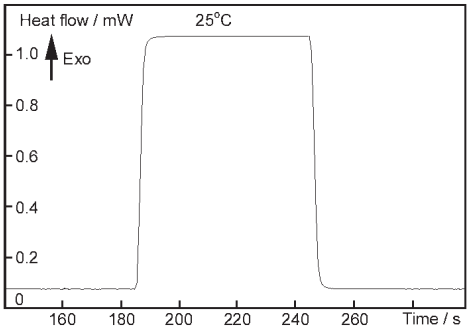

Fig. 2 Joule effect calibration curve

As a result of these different characteristics, the integrated circuit detector is to provide its highest sensitivity when a small sample mass is used and when the experiment is run without a container.

As a positive effect of the low heat capacity of the calorimetric set-up, the influence of external temperature disturbances is very weak, that makes easier and simpler the thermostatisation of the instrument. In the same type, relatively high scanning rates are available, reducing the experiment time.

Presentation of the new analyzer

Based on the performances of the integrated circuit detector, described in the previous chapter, a scanning thermal analyzer, called SETline, is built.

By contrast with the conventional scanning calorimeters, a twin system is not necessary for the compensation of parasitic heat flow, since the heat capacity of the calorimetric set-up is very small. This makes easier the construction of such a scanning thermal analyzer. The IC-detector is set in a thermoregulated block (Fig. 3), made of aluminum. A

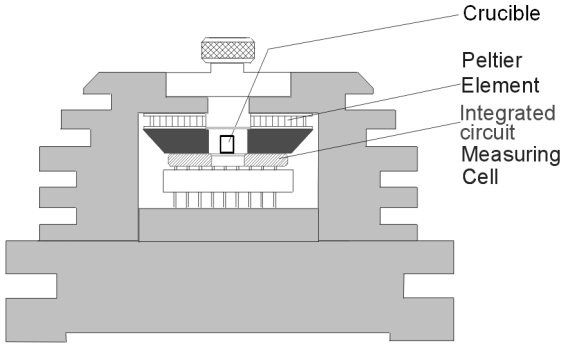

Fig. 3 Cross section of the integrated circuit thermal analyzer

good thermostatisation of the experimental chamber is reached through two Peltier elements located closed to the detector.

Heating and cooling, in the range of –10 to 120°C, is easily performed. The temperature, in the experimental chamber, is measured by means of a platinum resistance located under the integrated circuit. In order to reach the lower temperature of operation (down to –25°C), a water circulation is used through the metallic block.

Scanning rates, as high as 20°C min^{-1}, are available with such a set-up.

Scanning up and down is performed without any external coolant, except the water circulation in the calorimetric block, when the minimum temperature has to be reached.

Due to the low thermal inertia of the detector, the time of thermal stabilisation before starting an experiment is very short. Within 5 min, the thermal analyzer is operational.

The mass of the sample, as indicated previously, has to be as small as possible, to get the highest sensitivity from the detector. Usually the mass ranges from less than one mg to some mg.

The sample is placed in the center of the chip, without any crucible. If there is a risk of contamination of the detector or if the cleaning of the detector after the test is too difficult, an aluminum container can be used. In such a situation, the wall of the container has to be as thin as possible.

Any type of sample (solid, liquid, fiber, film, etc.) is investigated without container. In the special case of film and fiber, it is well known that the sampling of such materials with conventional DSC is not easy. The thermal contact for such samples between the DSC pans and detectors is not very good. With the IC detector, the film or fiber sample is laid on the chip, providing an optimized thermal contact.

The portability is becoming more and more popular in the field of analytical instrumentation. In the last decade, portable gas chromatographs and spectrometers have been developed and introduced on the market. One of the main interests of this new type of instruments is the sample analysis on the field. The sampling of the material, to be sent to a central laboratory, is no more required. Up to now, the thermal analyzers require different supplies only found in the analytical laboratories: electricity, water and gas supplies, weighing. The main limitation for the portability is the power

needed for the electrical supply of the thermal analyzer, particularly for the furnace heating. With the new concept of the integrated circuit detector, this problem is now overcome. A maximum power of 10 watt, supplied through batteries, is only needed to work with the new thermal analyzer.

Portable IC calorimeter for polymer characterization

The thermal characterization of polymeric materials has offered thermal analysis with a very large field of applications [3]. Taking into account the temperature range of the new portable IC thermal analyzer (–10 to 120°C), many investigations can be performed out of the analytical laboratory, mainly on the industrial site in a routine way.

Thermoplastics

Thermoplastics cover a very wide range of materials, including polyolefins, polyvinylchloride, polystyrene, polyesters and polyamides. The DSC technique has been widely used to characterize such polymers, especially for the determination of their glass transition temperature T_g, melting point T_m and crystallinity according to their state (amorphous, semicrystalline, crystalline).

The glass transition is detected either in amorphous or semicrystalline polymer. The temperature of glass transition varies with the composition, the structure of the polymer. The chemical structure, molecular mass, diluents may affect this transition. The thermal and processing history is also another important parameter to be controlled. As all these factors have an influence on the properties of the polymer, the determination of the glass transition temperature is an essential test to be performed. This operation can be easily run on the field by picking a sample from the production line or from the product storage area. An example is given with the determination of the glass transition of a sample of polyethyleneterephthalate (PET) (Fig. 4).

A small piece of PET is placed on the detector without container. Weighing the sample is not needed, as only the information of the glass transition temperature is needed. The sample is heated from 20 to 100°C at 5°C min^{-1}. Within 20 min, the glass transition temperature of the PET sample is precisely measured.

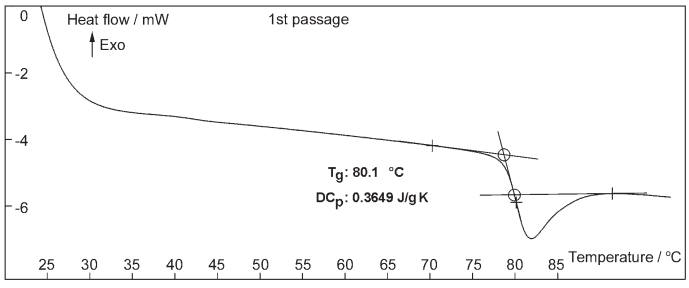

Fig. 4 Glass transition of a PET sample

According to the range of temperature of the portable thermal analyzer, same glass transition determinations can be carried out on polyamides such as aliphatic nylons, polystyrene, polyvinylchloride [12].

For semicrystalline and crystalline polymers, the melting point T_m is an important parameter to be precisely defined. The heat value associated with the melting peak is related to the crystallinity of the polymer. Chemical structure, crystallization temperature, molecular mass affect the value of the melting point. The portable thermal analyzer is adapted for measuring melting points below 120°C, such as polyethyleneoxide (PEO) or polyetheretherketone (PEEK) for its low melting endotherm [13].

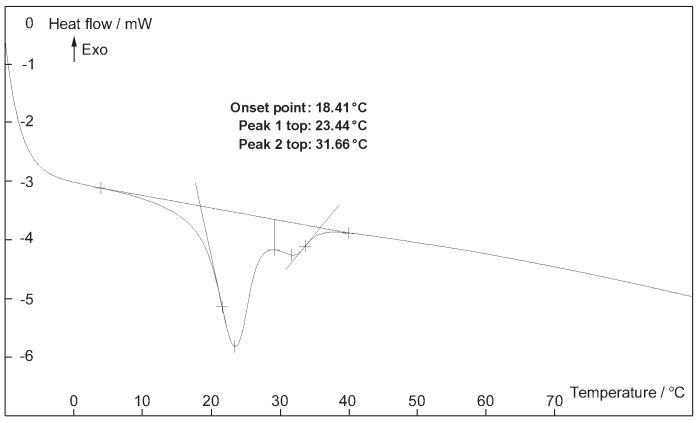

Fig. 5 Relaxation in PTFE

Below the melting point, except the glass transition, other viscoelastic relaxations are detectable. In polytetrafluoroethylene (PTFE), the β relaxation, near room temperature, is associated with two first-order crystalline phase transitions occurring around 10 and 30°C. The analyzer clearly identifies the two-phase transitions (Fig. 5). It is important to notice that for such a test, no external coolant is needed even if the experiment starts at –10°C.

Thermosets

Thermal analysis plays a major role in the characterization of thermosetting materials and processes. The processing of thermosets includes polymerization or cure. The curing reaction is complex and involves several steps: gelation and vitrification. The determination of the glass transition temperature of the thermoset at different stages of the curing is an easy way to follow the polymerization [14]. According to the curing state, the glass transition temperature varies from a minimum value corresponding to the unreacted material to a maximum value when the material is fully cured. For a selected thermoset, the determination of its glass transition temperature allows to know the degree of cure.

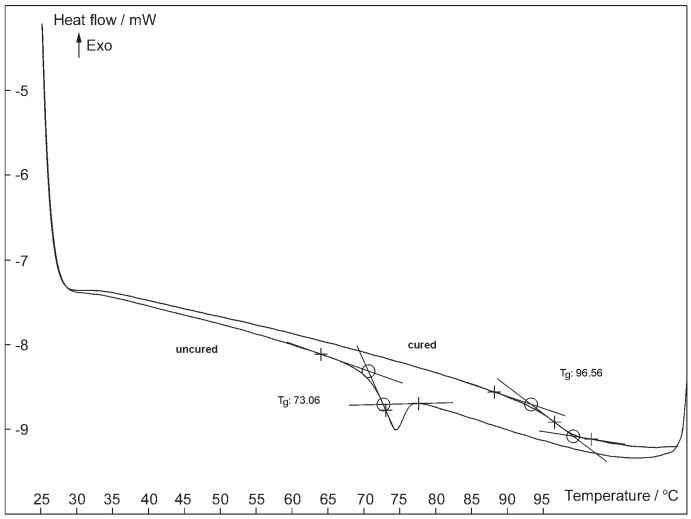

Fig. 6 Glass transition determination on uncured and cured epoxy resin

With the portable analyzer, this information is quickly obtained, by running the test in the industrial polymerization hall. According to the measurement, fast decision can be taken to adjust the curing process. An example is given with uncured and cured epoxy resin (Fig. 6).

The T_g temperature varies from 73 to 96.5°C depending on the curing state. A new information on the reaction is obtained every 30 min. For such a test, a container is used to prevent the damage of the detector.

The portable analyzer is also adapted to monitor the curing reaction in the isothermal mode. For such an operation, the temperature of the instrument is fixed at the

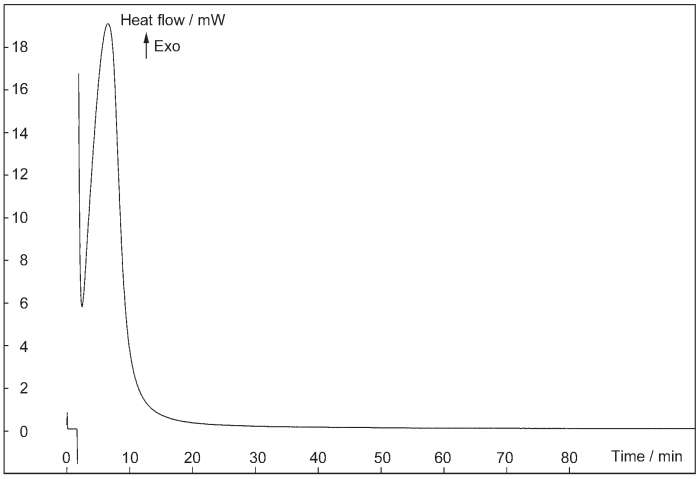

Fig. 7 Isothermal curing of an adhesive

desired value. The sample, in the container, is quickly placed on the IC detector. As the thermal stabilisation of the experimental chamber is fast, it is easy to record the whole heat corresponding to the isothermal reaction, as shown in the following example, corresponding to the hardening of an adhesive (Fig. 7).

The easy access to the experimental chamber and the configuration of the IC detector allow to predict the combination with an UV source to investigate photopolymerization of thermosets.

Conclusions

Some examples of polymer characterization using a portable thermal analyzer are given to illustrate the new possibilities of development offered in this field. Get quickly information on the industrial site to monitor the industrial process or to control the quality of the material is one of the major goals of the new technique. The shape of the integrated circuit detector makes also easier the investigation of fibers and films of PET or Nylon, of composites without the need of a container. The combination of integrated circuit detector and portability is a new opening for the development of the thermal analysis techniques .

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