THERMAL ANALYSIS

DESCRIPTION OF TECHNIQUES

Thermal analysis measures physical or chemical changes in a material as a function of temperature. Two common complimentary techniques in this category are differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These methods are typically used to determine the material properties of organic polymers as the sample is heated or cooled in a controlled manner or held isothermally for a specified time. Differential thermal analysis (DTA) is a method similar to DSC, but performed at higher temperatures for metals, minerals, ceramics, and glasses.

DSC - Differential scanning calorimetry measures heat flow to or from a sample as a function of temperature and time. A small portion of a sample is placed in an aluminum pan and heated and/or cooled in a controlled manner. A reference material (usually an empty aluminum pan) simultaneously undergoes the same programmed time/temperature routine. Calorimetric measurements are made during the heating/cooling cycle.

Two methods can be used for the calorimetric measurements. Differences in temperature between the sample and reference material can be measured as the same amount of heat energy (calories) is added to both. Or, differences in the amount of heat energy added to both are measured as the temperature for both the sample and reference are kept constant. In both cases, the heat flow and temperature of the sample are monitored in comparison to the reference material. The analysis is usually performed in an inert gas atmosphere, such as nitrogen. The amount of energy absorbed (endotherm) or evolved (exotherm) as the sample undergoes physical or chemical changes (e.g. melting, crystallization, curing) is measured in calories as a function of the temperature change. Any material reactions involving changes in heat capacity (e.g. glass transition) are also detected.

The thermal cycle for DSC typically can range from less than -50°C to 300°C or greater. The principals for differential thermal analysis (DTA) are similar to DSC, but the temperature range for DTA can reach temperatures greater than 1500°C.

TGA - Thermogravimetric analysis continuously measures the weight of a sample as a function of temperature and time. The sample is placed in a small pan connected to a microbalance and heated in a controlled manner and/or held isothermally for a specified time. The atmosphere around the sample may consist of an inert gas, such as nitrogen, or a reactive gas, such as air or oxygen. The heating program may start in an inert atmosphere and then be switched to air at a certain point to complete the analysis. Weight changes observed at specific temperatures correlate to volatilization of sample components, decomposition, oxidation/reduction reactions, or other reactions or changes. Fourier transform infrared spectroscopy (FTIR) or mass spectroscopy (MS) may be used in conjunction with TGA to analyze and identify the evolved gases from constituents volatilized from the sample at specific temperatures. (See the FTIR and GC/MS sections of this handbook for more details about these analytical techniques.)

ANALYTICAL INFORMATION

DSC - By closely monitoring the heat flow and temperature, DSC can provide abundant information regarding a polymer material including: melting temperature, heat of fusion, glass transition temperature, curing temperature, heat of reaction, thermal history, and others. DSC is ideal for studying reversible reactions of thermoplastics such as melting-crystallization points and glass transition temperature. It is also used in the study of the kinetics of thermoset curing reactions, purity, heat capacities, and the effects of additives. Similarly, DTA analysis is used for determining the temperatures for melting and solid state phase transformations in metals, minerals, and ceramics.

TGA - As the TGA instrument measures the temperature and weight of the sample, thermally activated events are recorded. These events are expressed as weight loss or weight change for a given time or temperature. They may also be expressed as a rate of weight loss. The onset temperature for the weight loss is also recorded. These data correlate to and give information about such properties as: thermal stability, moisture or solvent content, additive or filler content, oxidation or decomposition temperatures and rate. Thermal events such as melting, glass transition, and other changes are not detected because there is no change in sample mass associated with these events. Identification of the constituents driven off as evolved gases may be obtained when the TGA is used in conjunction with FTIR or mass spectroscopy.

TYPICAL APPLICATIONS

DSC (or DTA)

- Determination of melting temperature, heat of fusion, and glass transition temperatures
- Analysis of polymer blends and copolymers
- Comparison of two lots of similar polymers
- Determination of cure temperatures/times for epoxies or other thermally-cured polymers
- Reaction rate and temperature evaluation
- Determination of thermal history, e.g. annealing, etc.

TGA

- Volatile compound concentration
- Plasticizer content
- Inorganic filler content
- Polymer thermal degradation profiles
- Polymer thermal and/or oxidative stability
- Identification of volatile components or thermal degradation products (with FTIR or MS)

SAMPLE REQUIREMENTS

DSC - Typically requires six to ten milligrams of sample. Samples may solids or liquids.

TGA - Typically requires twenty to thirty milligrams of sample. Samples may be solids or liquids.