Using Temperature to Control Quality

Thermal analysis helps manufacturers respond to demands for quality.

BY ROBERT L. HASSEL

Manufacturers have been listening. In growing numbers, they have been hearing the rising voices of dissatisfied customers, outspoken consumer advocates, government watchdogs, and litigious lawyers. The message: The public wants products that work, that last a reasonable length of time, and that are safe to use.

American industry is responding to this increasing demand for product quality and performance. One significant indicator is the number of manufacturers that have turned to analytical techniques such as thermal analysis (TA) to evaluate and control product quality. Thermal analysis is being used as a quality control tool in three principal areas:

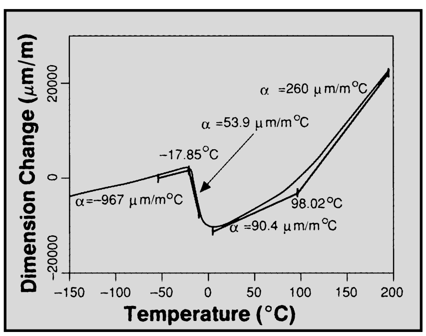
- Materials: TA is providing basic criteria for vendor certification and "fingerprinting" of incoming/outgoing materials. In fact, many industry standards and company specifications use TA tests as criteria for the acceptability of materials and the performance of finished products. The list is global, including accepted standards organizations such as ASTM (American Society for Testing Materials), SAE (Society of Automotive Engineers), UL (Underwriters Laboratories), DIN (Deutsches Institut fur Normung), and British Telecommunications.
- Processing: TA is used to optimize and monitor processing conditions, and to troubleshoot problems when they arise. Many manufacturers of thermoplastic, thermoset, and elastomeric products rely on TA to establish processing parameters—blend ratios, additive content, heating rate, dwell time, and extrusion rate—to achieve maximum product quality, cost effectiveness, and productivity.
- Building in quality: TA helps scientists and engineers understand the behavior of materials, select materials and design criteria, and predict long-term product performance. This use represents a growing conviction within industry that the best QA/QC takes place at the conceptual stage, "building in quality" when a product is designed.

Why thermal analysis?

Why the increasing reliance on thermal analysis? There are several reasons:

- The use of polymeric materials—particularly in the automotive and aerospace industries to replace metals—is growing, for which TA is a particularly well-suited analytical technique.
- TA is growing in its acceptance and availability because it is a fast, dependable, easy-to-use, cost-effective means of monitoring the quality of both the materials and manufacturing processes. Results are accurate, reproducible, and generally free of operator influence.
- TA technology and instrumentation are continuously improving.

Basically, thermal analysis is a series of techniques that measure changes in the physical or chemical properties of materials as a function of temperature. Why temperature as the basic criterion? Because it is the most important and ubiquitous parameter influencing the efficacy and performance of materials.



TMA curve identifies glass transition at −17.85°C and quantifies the coefficient of thermal expansion for various temperatures.

In a typical TA evaluation, a sample is subjected to programmed heating and/or cooling in a controlled atmosphere. Resulting property changes are monitored, analyzed, and reported through a readout device. Put more simply, these techniques determine what happens to a material when it is heated or cooled: Does it melt? Get brittle? Decompose? Expand? How much? And at what rate?

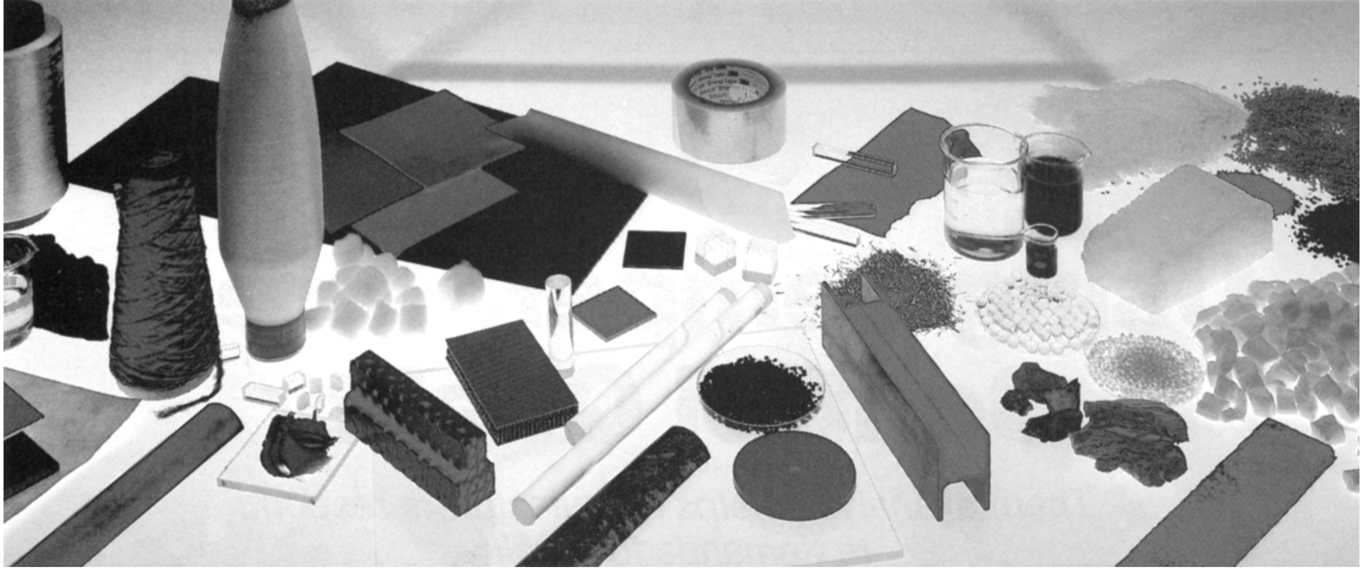
Using thermal analysis for QC

The typical TA system consists of an analysis module—a heat source and measuring apparatus specific to the type of material—and a device for reporting the results, usually an XY plotter. It also needs a computer or other device for programming/controlling the procedure, analyzing, and storing the results.

There are several commonly used thermal analysis techniques for QA/QC:

- Differential scanning calorimetry (DSC) measures the heat flows and temperatures associated with chemical transitions and reactions. DSC provides valuable information on curing kinetics, glass transition, melting point, specific heat, crystallinity, vitrification, and oxidative degradation.
- Thermogravimetric analysis (TGA) measures weight changes as a function of temperature. Typical applications include compositional analysis, thermal and oxidative stability studies, and reaction kinetics to predict estimated lifetimes.
- Thermomechanical analysis (TMA) measures changes in sample dimensions as a function of temperature and time.

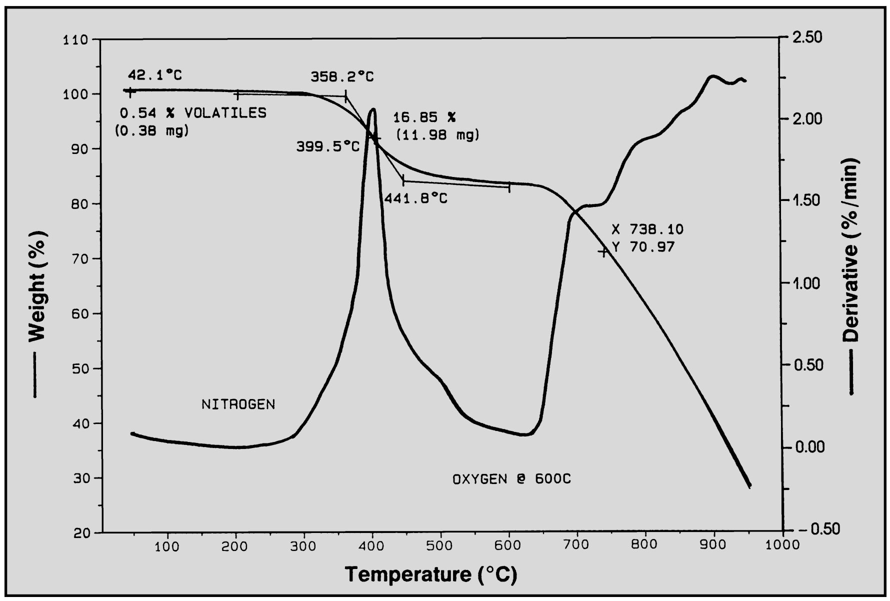
Reprinted from Second Quarter 1991 issue of PI Quality



Thermal analysis characterizes many materials, including: thermoplastics, thermosets, composites, elastomers, films, fibers, ceramics, glass, metals, paint, adhesives, lubricants, and food products.

TMA provides data on the coefficient of thermal expansion (CTE), glass transition temperature, gel time and temperature, delamination temperature, resin flow, materials compatibility, and the stability of films and fibers.

- Dynamic mechanical analysis (DMA) measures sample modulus (stiffness) and energy dissipation (damping). DMA provides information about transition temperatures, curing phenomena, and properties such as impact resistance and sound absorption.
- Dielectric analysis (DEA), the newest TA technique, applies an alternating electrical field to measure the permittivity and loss factor. This method is particularly opportune for QC uses because of its on-line applicability.



TGA quantifies resin/reinforcement ratios for a high-temperature epoxy/novolac/amine resin reinforced with carbon fiber.

Who uses thermal analysis?

As might be expected, the leading proponents of advanced quality and process control techniques are high-technology industries such as aerospace, automotive, and electronics. But the companies that develop and produce advanced materials and components—predominantly companies in the process industries—are also becoming more involved.

TA is used for electronics applications to test for dimensional stability, laminate and thermoset curing, gel times, and thermal stability. For example, the key concerns in the manufacture and use of multilayer printed circuit boards are the dimensional stability of individual layers and the degree of cure achieved in the press or bonding cycle.

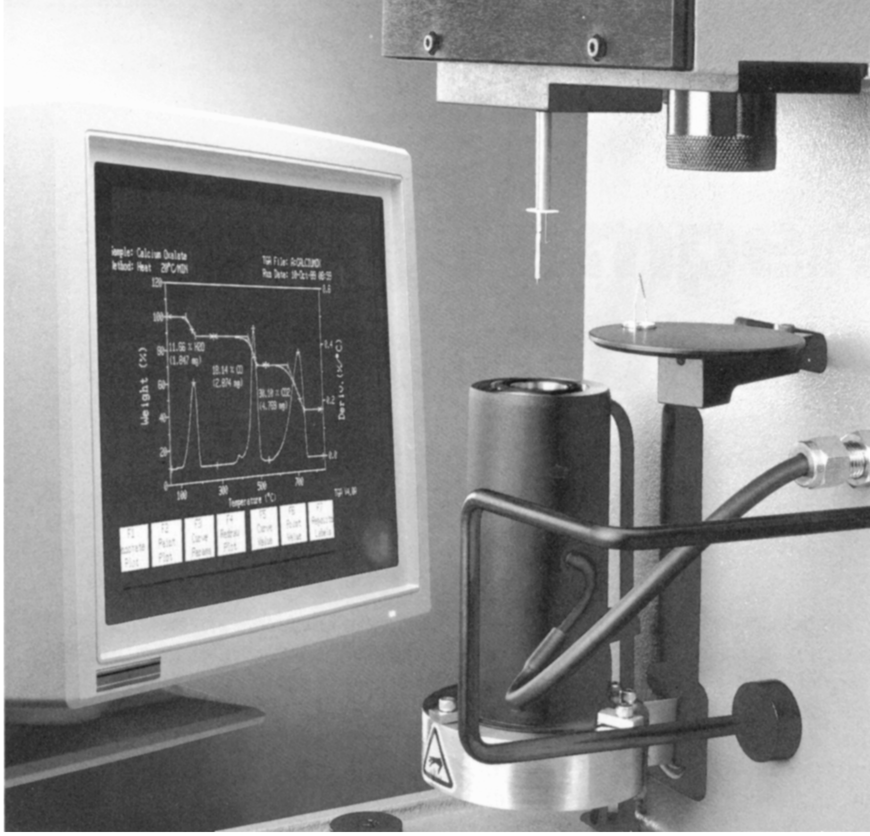
U.S. automobile manufacturers include a variety of thermal analysis tests in specifications for incoming raw materials and components. A number of these were adopted after the easy-to-use thermal test methods were found to correlate closely with cumbersome, time-consuming traditional methods. Many automotive materials are currently evaluated by TA: seals, gaskets, engine and body mounts, belts, bumpers, body panels, lubricants, paints and coatings, and adhesives.

For elastomeric and polymeric materials, TMA measurements of dimensional changes, such as expansion and penetration, can help define optimum processing conditions as well as end-use properties and operating temperature ranges. For example, a manufacturer determines that the glass transition of its rubber compound is at −17.85°C, the point at which the material becomes rigid and loses its damping characteristics. TMA techniques can generate a curve to quantify the coefficient of thermal expansion (alpha) for various segments of the temperature range. This provides clues on the rubber's compatibility with adjacent components, and its ability to maintain a seal.

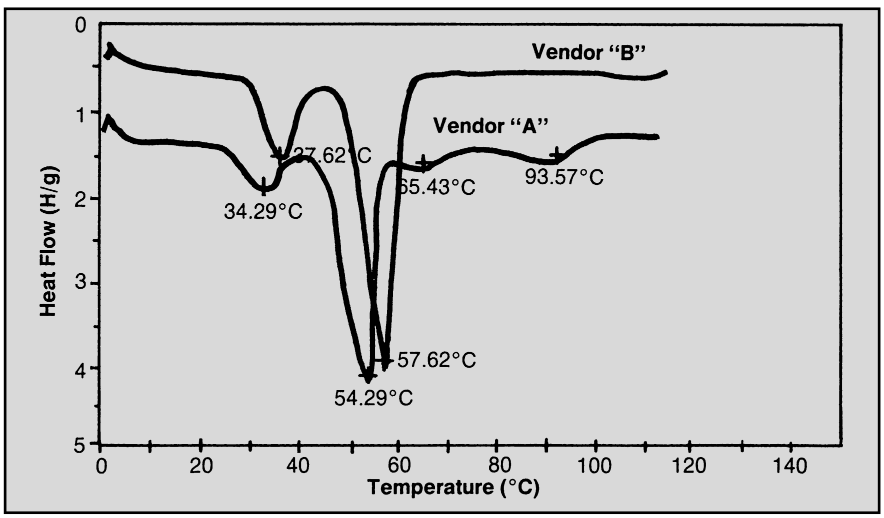
In another application, DSC curves provide information about the melting point and range—key processing parameters for thermoplastics—and the heat of fusion. Using suitable reference materials, the heat of fusion can be converted to percent crystallinity, an important end-use parameter.

With photosensitive and photocurable materials, differential photocalorimetry (DPC) can measure transitions and reactions. Hercules Research Center (Wilmington, Del.) uses DPC (a DSC accessory) as a QC tool to determine the polymerization kinetics of its liquid photopolymers according to sample thickness, UV exposure, and ambient process-

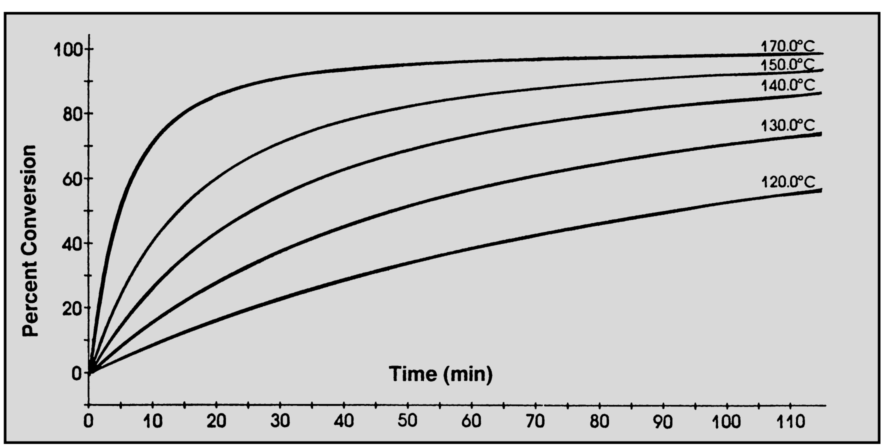
Reprinted from Second Quarter 1991 issue of PI Quality



Thermogravimetric analysis (TGA) measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures to 1000°C.



Evaluating paraffin waxes from two suppliers, DSC is used to test for melting points and heats of fusion.



DSC predicts the degree of cure for an epoxy/fiberglass composite at various time/temperature combinations.

ing conditions. Data obtained using this method are related to photo speed and degree of cure of the photopolymer.

TGA is widely used to characterize the constituents in compounds such as oil-extended elastomers. A single TGA test can quantify these constituents—oil, polymer, carbon black, and residual ash—as well as their decompositon temperatures. The TGA derivative curve, which often can resolve weight losses that are obscured or overlapping in the parent curve, is useful as a fingerprint of the compound. And it can be the basis for compliance with specifications.

Examining composites

The aerospace industry, a leading user of advanced composites, looks to TA methods to help understand, select, process, and monitor the performance of such materials. TGA can rapidly quantify the ratio of resin to reinforcement in, for example, a high-temperature epoxy/novolac/amine resin reinforced with carbon fiber. To determine the ratio, purge the system with nitrogen, then decompose the reinforcement under oxygen. The TGA curve shows the ratio of volatiles to resin. Programming automatic switching of the purge gas into the analysis minimizes operator attention.

DSC gives the composites processor an easy-to-use technique for establishing optimum curing conditions for sheet molding compounds (SMC), and for monitoring finished product quality. Data from a single DSC experiment are analyzed using software applying the Borchardt and Daniels method for curing kinetics. Curves produced predict the degree of cure at various time/temperature combinations. This method uses short-term experiments to derive kinetics data, which are used to project long-term results.

Of the several methods available for evaluating cure rates, DSC or TMA measurements of glass transition temperatures (T_g) are the most common. They are useful for determining the degree of cure at any processing stage, since the T_g moves to progressively higher temperatures as the thermoset advances from prepreg through finished laminate. However, TMA often follows the T_g better in highly filled or reinforced materials, such as PC boards, because the dimensional change at the glass transition temperature is greater than the specific heat change measured by DSC.

Reprinted from Second Quarter 1991 issue of PI Quality

Improving reliability

One of the advantages of TA is that it is not an elitist technique applicable only at the frontiers of science. TA's greatest service probably is in supporting more mundane, day-to-day applications. It helps countless producers of commodity chemicals and plastics keep their products reliable and their manufacturing processes out of trouble.

For example, Mastic Corp. (South Bend, Ind.) recently adopted DSC to solve production problems that "could not be solved by traditional vinyl siding analysis methods," according to a paper presented by J. B. Williams, of Mastic's QC laboratory, at the SPE/ANTEC '89 meeting. [1]

Mastic had experienced problems with PVC extrusion line speeds when it switched sources of its paraffin wax lubricants. When torque rheology showed "no significant difference" between the wax lubricants from the two suppliers, Williams tested the materials by DSC. The resulting curves "showed clearly that one wax contained two higher-tem-

TRENDS IN TA

BY RICHARD L. FYANS

The automation of thermal analysis (TA) instruments in recent years has made it easier to use, increased the precision and accuracy of data, aided test reproducibility, and increased both the speed of operation and sample throughput capacity. Because of these changes, plastics companies and other industries have found it expedient to add TA instruments to their QA/QC operations. While polymer R&D laboratories are still a major application area for TA, much of the new growth in TA instrumentation is occurring on, or near, the production line.

During the late 1970s and early 1980s, computer technology was first applied to thermal instruments. Operations changed from an instrument attached to an analog recorder and a Ph.D. scientist doing manual calculations to an instrument attached to a microcomputer and automated calculation of results. But, during the last five years, the picture has changed dramatically. Automation has made instruments less user-intensive. Operation and interpretation of data are greatly simplified. Thermal instruments typically have no manual controls at all since they are controlled by the attached microcomputer. Both the instrument functions and the calculation of results are fully automated.

The following examples help illustrate some of the major changes that have taken place in TA during the last 10 to 15 years.

- *Speed of TA analysis*: Ten years ago, it wasn't practical to use DSC (differential scanning calorimetry) for quality control to analyze the kinetic reaction of a thermoset as it cures. Typically, a scientist would run the thermoset sample through a manually controlled DSC attached to a strip-chart recorder. Upon completion, the scientist would take the data from the strip chart and use manual methods to calculate results. One analysis required about half a day to perform.

Today, one analysis takes 20 seconds. The automated DSC is preprogrammed to perform all the calculations previously done by the scientist. Moreover, the computer's calculations are far more precise and reliable. Manual techniques rarely produced the same number twice. A computer's calculation of peak area never varies. This means that the performance of TA no longer requires someone with an advanced degree; more and more technicians are running routine QA/QC tests.

- *Throughput*: Companies today typically run 20 samples a day where they could previously analyze only a few. Fifteen years ago, a scientist or production manager asking for a sample analysis could expect to wait several days to get the results; today the answer is available in hours or minutes. This high-volume capability has contributed significantly to the trend toward using TA at the production line as a QC tool.

Because the various types of thermal analysis measure either different physical properties or the same property differently, it is common practice to use several TA techniques to get a complete "profile" or characterization of a sample.

- *Sensitivity of analysis*: Manufacturers of TA instruments are pushing the sensitivity of thermal analysis to the limit. Thermal instruments today are much more sensitive than their counterparts of the 1970s, primarily as a result of advances in electronics and materials. This increased sensitivity allows laboratories to detect materials at much lower levels.

For example, one major application of TA in the plastics industry is to measure the percentage of various fillers, extenders, reinforcement agents, and other additives (see the main text for more on this application). Slight changes in the mix of additives will alter the physical properties of the polymer material. Once a company defines the exact properties it wants for a particular polymer, it uses various analytical techniques, including TA, to test additive configurations.

After a basic configuration is defined, polymer scientists can use TA to determine the optimal level of each additive down to 0.01 percent. This level of analysis can save a plastics company millions of dollars a year in additive supplies.

- *Analytical precision*: Although the precision of detection technology has improved in recent years, providing wider dynamic range and faster heating and cooling, the major contribution to higher precision is again attributable to digital computer technology. High-end TA instruments not only can store data, but they can also compare these data with previous runs or an established standard, look for patterns, and manipulate them in a number of other ways. Equally important, the computerized thermal analysis systems available today eliminate the human error in tasks such as calculating peak area.

Ten to twenty years from now, it may be possible for a production line worker to remove a polymer pellet from the line, drop it into an integrated, discrete thermal analysis instrument, push a button, and seconds later receive a printout of DSC, TMA (thermomechanical analysis), TGA (thermogravimetric analysis), and DMA (dynamic mechanical analysis) that indicates whether the process is operating within specification. Because thermal analysis includes so many different techniques, this theoretical "thermal answer machine" is many years from becoming a reality, but this is ultimately where the industry is heading.

Companies such as Perkin-Elmer have already begun to make strides toward that goal. The introduction of the SCO Unix operating system at the 1991 Pittsburgh Conference represents a big step. The system runs three independent tasks in real time. Tasks can consist of any three analyzers operating at the same time, with each performing different tests.

As emerging microprocessor technology is applied to TA instruments, they will continue to become more automated, faster, more sensitive, and more reliable. Most new product development is likely to be aimed at the QA/QC market as production managers take advantage of the increasingly accessible TA technology.

RICHARD L. FYANS is director, worldwide thermal and elemental analysis marketing and development at Perkin-Elmer Corp., Norwalk, Conn.

Table 1. What Thermal Analysis Reveals About Materials

Characterization	Analysis Technique	Characterization	Analysis Technique
Polymeric materials		**Electronic materials**	
Composition	TGA	PC boards, prepregs	DSC, TGA, TMA
Blend compatibility	TMA	Solder masks, photoresists	DSC, TMA, DPC*
Polymer/reinforcement ratio	TGA	Liquid crystals	DSC
Additive content, effectiveness	DSC, TGA	Encapsulants	DSC, TGA, TMA
Flow, bleed, extrudability	TMA	Optical fibers	DSC, TMA
Polymer crystallinity	DSC	Insulating materials	DSC, TGA, TMA
Curing kinetics	DSC	**Pharmaceuticals and fine chemicals**	
Degree and rate of cure	DSC, TMA	Calorimetric purity	DSC
Thermal stability	TGA/Kinetics	**Edible oils**	
Estimated lifetime	TGA/Kinetics	Oxidative stability, shelf life	DSC/Pressure DSC
Oxidative stability	DSC/Pressure DSC	**Lubricants**	
Dimensional stability	TMA	Oxidative stability	DSC/Pressure DSC
Coefficient of thermal expansion	TMA	Cloud point, pour point	DSC
Delamination time, temperature	TMA	Thermal stability	TGA
Additives, compounding agents		Wax content	DSC
Curing agents	DSC, TGA, TMA		
Reinforcers, blends	DSC, TGA, TMA		
Plasticizers, modifiers	DSC, TGA, TMA		

*DPC (differential photocalorimeter) is a module operated as a DSC accessory to measure transitions and reactions in photosensitive and photocurable materials.

Laboratory professionals develop new applications methods, and provide technical support for customers.

perature components that were not present in the other wax," he reported.

Mastic has since modified its raw material specifications to include DSC tests for melting points and heats of fusion, as defined by ASTM standard test methods.

In another example, George Dugan, research supervisor of the polymer characterization/thermal analysis laboratories at the Hercules Research Center, explains several ways that his company uses thermal analysis for day-to-day QC and production support. According to Dugan, TA helps Hercules predict product end-use performance, solve production problems, and assure the safe production of an unstable material:

- In polypropylene fiber production, the oxidation of the resin starting material is an important processing factor. Process stabilizer is added to minimize degradation during high temperature extrusion of the resin. High-pressure DSC methods help determine anti-oxidant levels and ensure that the stabilizer is added at the proper concentration.
- In packaging films, melting and crystallization of the starting materials affects the processing operating window. It also affects end-use performance of the final product, especially in copolymeric films. Hercules uses DSC and TMA methods to characterize the flow properties of both the resin and film. In films used for overwrap packaging applications, shrinkage of 2 percent or less must be maintained to guarantee high-quality graphics; TMA provides the high sensitivity required to measure this shrinkage under different loads.
- Liquid hydroperoxides, used primarily as polymerization initiators, decompose exothermically and some are autocatalytic. Using DSC methods to study the kinetic factors involved in the catalysis and decomposition of these materials, Hercules has established safe processing, shipping, and storage procedures.

Thermal analysis techniques are gaining ground in the quality arena as manufacturers continue to search for faster, less costly methods of analysis. TA's predictive abilities help establish a framework for large-scale production ventures, further ensuring that quality is built in as the product is designed. ■

ROBERT L. HASSEL is vice president of planning for TA Instruments, New Castle, Del.

References

1. J. B. Williams, "Use of DSC as a Quality Control Tool," Society of Plastics Engineers, Analytical and Technical Conference (SPE/ANTEC), 1989.

Reprinted from Second Quarter 1991 issue of PI Quality