Protecting your brand with thermal analysis of your polymers

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GUIDE

Contents

Purpose of this guide

Thermal analysis is an excellent technique for supporting polymer manufacture and new materials development. It excels at raw material characterization, especially when analyzing a complex mix of materials, or using recycled or reground polymers. It can also give information about the potential performance of the finished product, and there are even thermal analysis techniques that allow you to predict behavior over time. In short, thermal analysis helps to ensure your product always makes the grade your customers expect, and your brand remains one associated with high quality.

This guide sets out to explain and demystify thermal analysis of polymers. We'll cover:

- Why it's so important to analyze polymers during manufacture and materials development
- The specific advantages of thermal analysis as a technique
- How to interpret results for some common ASTM method measurements

At Hitachi High-Tech, we've been designing thermal analysis equipment for the polymer industry for over 45 years. In that time, we've seen the global use of polymers skyrocket, with today's materials far more complex than even a decade ago. It's our aim that with this help of this guide, you can become confident enough with thermal analysis to use it as a central technique in your quality control, ensuring your products always meet the high standards associated with your brand.

Why do we need to analyze polymers?

Polymer analysis should be a key part of a robust production quality control program and thermal analysis (TA) is particularly good at materials characterization and troubleshooting. Here we'll take a detailed look at why it's so important to include polymer analysis in your processes.

1. To follow regulations

Many ASTM D and E committees as well as DIN and ISO methods are related to thermal analysis and as such you'll need TA as part of your standard process. This tends to vary by industry. Even if you're not working within ASTM regulations, your own procedures may well call for routine thermal analysis and you'll have to include it to remain compliant.

2. To show technical expertise

A dedicated materials characterization lab equipped with the right thermal analysis equipment is an excellent way to visibly demonstrate to your customer base that you take product quality seriously. This is especially the case now as supply chains become more complex and the expectation to use recycled material increases.

3. To improve quality control

Polymer specifications are determined by the final application and ensuring the correct material is used in all your production runs helps to ensure the products perform as expected. The more you test, the more likely you are to pick up problems with raw material specification or even in-house processes before they are passed to your customers. This increases yield and reduces waste.

4. To ensure new products perform as expected

Thermal analysis plays an important part of new material development. As well as ensuring the raw material has the right specification, you can use TA to evaluate how a material will perform after years of use by running a simple half hour analysis. This can help to advance your in-house R&D significantly, as well as ensure new products perform as advertised.

5. To protect your brand

Running routine tests on polymers before and during production helps to maintain your reputation for quality and protects your brand in the eyes of your customers. Failing components and product recalls can take years to bounce back from in a highly competitive arena such as plastics production.

How not to cut costs – a cautionary tale

In today's difficult economic climate, many companies look to reduce product costs to maintain a good profit margin. One way to reduce the cost of goods sold is to buy cheaper raw materials. It's standard practice for many companies to constantly seek cheaper materials but it's important that newly-sourced materials are thoroughly tested.

An unfortunate example of what happens if you don't test is from a large humidifier manufacturer. This company sourced cheaper components for their products to lower the manufacturing cost. Unfortunately, these components were produced from non-fire-retardant material, and this was not discovered until several humidifiers caught fire while in use, causing $4.5 million USD in property damage.

The company was fined $15 million USD and was left with a ruined brand reputation. To make matters worse, they were producing white label humidifiers for other companies and those companies also faced problems with brand reputation.

Evaluating additives, such as fire retardants, is something that thermal analysis is designed for, and a simple test would have saved this company's reputation and millions of dollars.

How can we analyze polymers?

There are different ways and techniques to control the quality of your polymer products. With inline/online quality control, you'll have real-time information about your product, but this doesn't work for every type of sample and the detection limits aren't the best always. Offline/atline is the most common way to analyze polymer product. Measurements aren't done in real-time, but you get the best detection limits, and it enables you to follow the standards methods like ASTM. Offline/atline also provides flexibility for the instruments to be used as troubleshooting (e.g., customer complaints) and for research and development.

There are no magic instruments which can do every type of analysis. You need to find out which one or which complementary techniques will be the most suitable for you, and this is where we can help.

Introduction to thermal analysis

Thermal analysis (TA) describes a collection of analytical techniques that measure the change in a material's behavior as a function of time and / or temperature, either when heated, cooled or kept at constant temperature. The sample sizes are usually in the mg range and the material changes detected can be extremely small.

Examples of material behaviors that are monitored are sample weight, stiffness, thermal events temperature changes and sample size. These measurable changes are plotted on an output graph and the characteristics of these thermograms give you precise information on fundamental material properties like melting point, glass transition and crystallization temperature. From this you can determine a material's fundamental characteristics and composition and predict how the material will behave in each application. A simple example is whether the plastic used in a high-temperature application (like a car engine) will have a melting point high enough to remain solid in use.

Advantages of thermal analysis

The main advantage of thermal analysis is that it precisely analyses fundamental bulk material properties. Even for complex materials, you can often tease out the behavior of the constituent polymers to ascertain what's in the mix. It's applicable to a wide range of materials and doesn't need material specific calibration curves, so you can easily investigate novel materials.

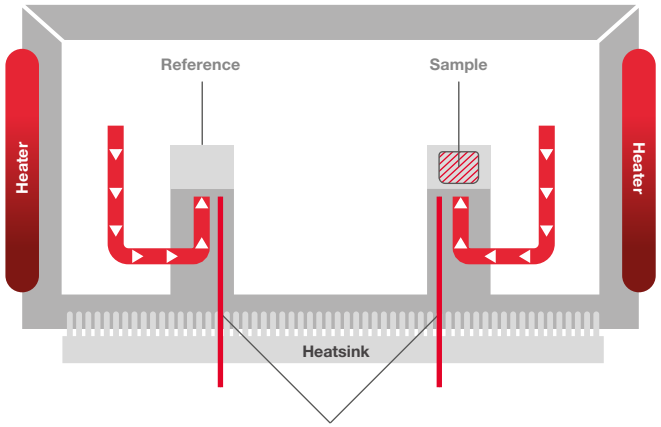
There is very little sample preparation, with no harmful chemicals to contend with and, with a little training, the analyses can be run by anyone, especially with an instrument that has a high degree of automation.

The equipment is inexpensive to run, and you don't have to keep the equipment in standby when not in use, cutting electricity and gas consumption.

DSC: Differential Scanning Calorimetry

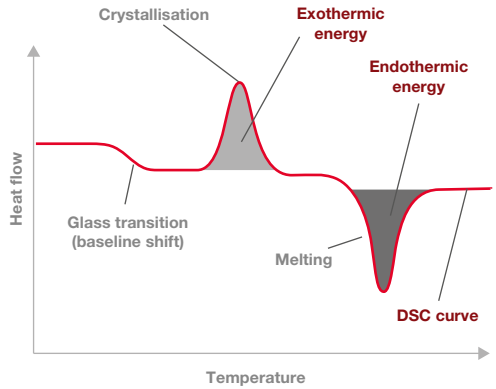
The sample to be analyzed and a referenceare placed in a DSC furnace and the temperature of the furnace is changed under controlled conditions. The temperature difference between the sample and the reference material is measured as a function of the applied temperature.

Differential Scanning Calorimetry (DSC)



The difference in temperature between the sample and the thermally stable reference indicates changes of state within the sample.

DSC thermogram example



This sample output trace above illustrates the typical information from a DSC analysis run and is a plot of the difference in temperature (heat flow: y-axis (mW/mg)) in relation to the rising applied temperature (x-axis).

The baseline shift gives the temperature for the glass transition. The position and spread of the exothermic peak give information on the crystallization temperature and the amount of energy released, and the endothermic peak relates to the melting temperature and energy required to go through this thermal transition. This information allows to you to confirm polymer ID, quality, and purity, and is an excellent raw material quality check.

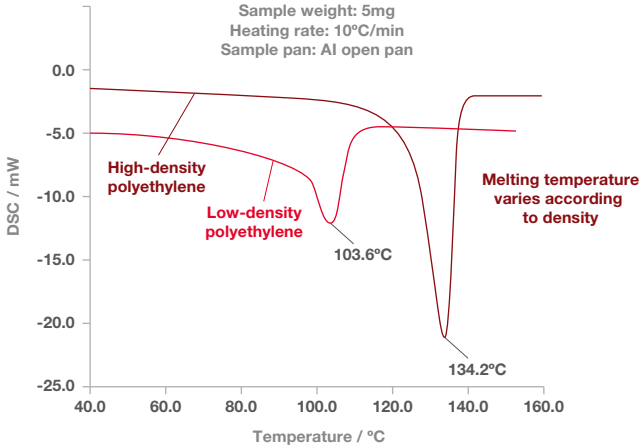
ASTM E794-06(2018) example: standard test method for melting and crystallization temperatures by thermal analysis

This test method describes the determination of melting (and crystallization) temperatures of pure materials by differential scanning calorimetry (DSC) and differential thermal analysis (DTA).

The DSC thermogram on the right shows how this technique can differentiate between different types of polymers. Polymers have different melting temperatures depending on their type, but also to their composition (type or concentration of additives). The example below shows two types of polyethylene (high and low density) which exhibit different melting point temperature. For polymers, the melting temperature is taken at the peak of the melting process.

This measurement can be used to confirm incoming raw materials identification, detect trace of impurities (e.g. polypropylene in polyethylene) as well as final product specifications. It works for powders, films or pellets.

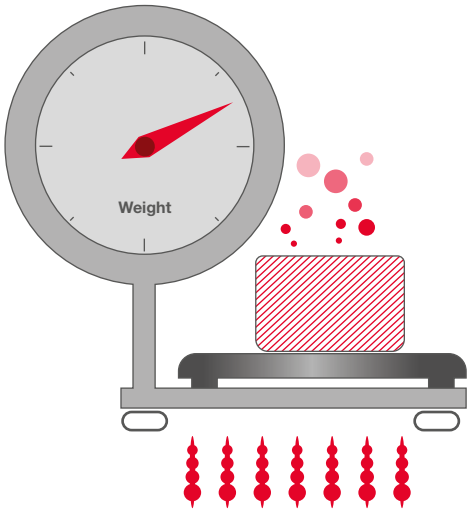
DSC thermograms of different polyethylenes



STA: Simultaneous Thermogravimetric Analysis

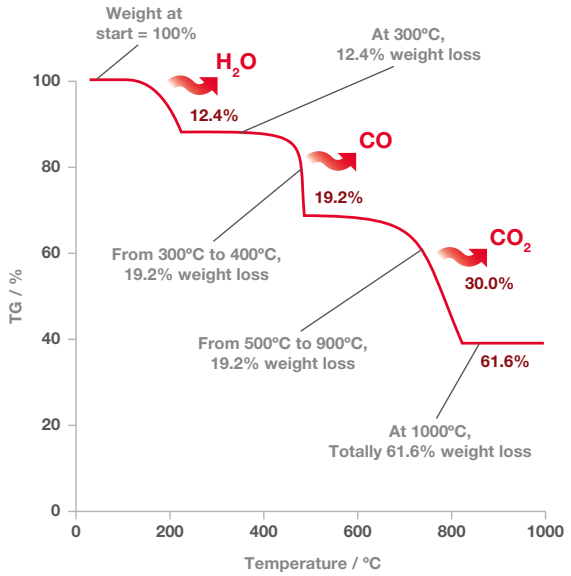
Gravimetric analysis is when sample is placed in a furnace on a highly sensitive balance. The mass of the sample is monitored against time or controlled temperature in oxidative or an inert atmosphere.

Thermogravimetric analysis (TGA)



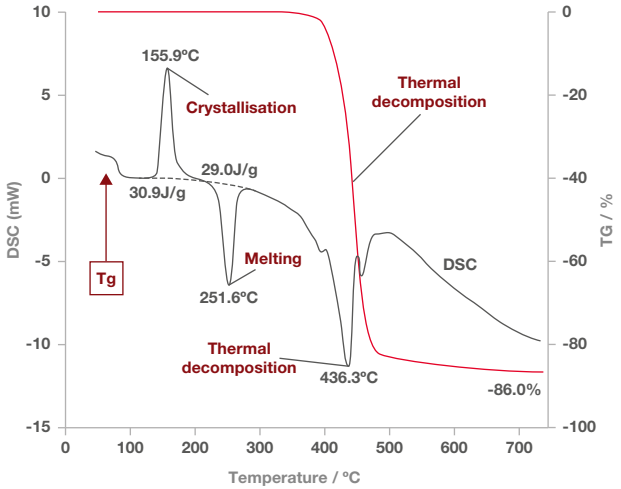
The change in mass of the sample is plotted against time or temperature. The percentage reduction in mass at given temperatures can be clearly seen.

TGA thermogram example



Thermogravimetric analysis (TGA) alone can give you information on moisture content, residual solvents, and the amount of desorbed or decomposed components emitted at given temperatures. However, simultaneous thermogravimetric analysis (STA) is where a DSC and a TGA are run simultaneously, and this gives you more complete thermal information about your sample, including exothermic and endothermic events. A typical STA output trace for PET is shown on the next page.

Typical STA thermograms for PET



The DSC signal is shown in grey and the TGA signal in red. The DSC results shows the calorimetric analyst for crystallization and melting, whereas the TGA signal shows the weight change by thermal decomposition.

ASTM E2550-11: standard test method for thermal stability by thermogravimetry

This test method covers the assessment of material thermal stability through the determination of the temperature at which the materials start to decompose or react and the extent of the mass change using thermogravimetry. The test method uses minimum quantities of material and is applicable over the temperature range from ambient to 800°C.

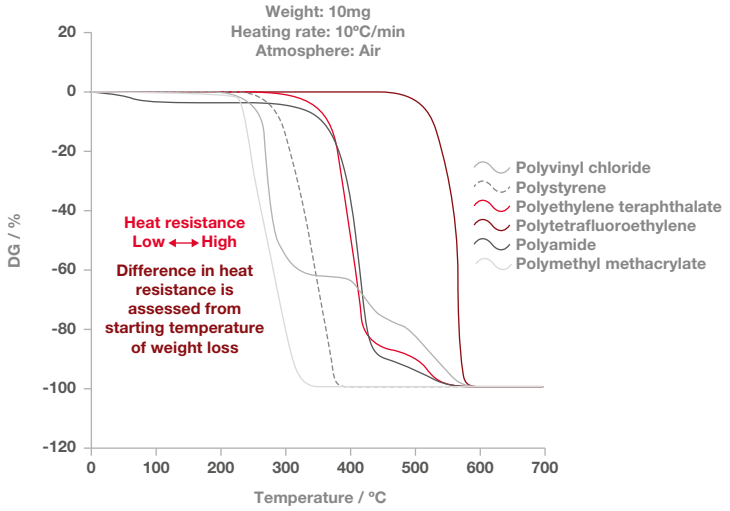
The absence of reaction or decomposition is used as an indication of thermal stability in this test method under the experimental conditions used.

This test method may be performed on solids or liquids, which don't sublime or vaporize in the temperature range of interest.

The TGA thermograms below are showing the thermal stability of different type of polymers. In this example, the stability of the polymer can be observed where there is no weight loss. The temperature at which the polymers lose their thermal stability is measured at the intercept of the baseline and where the weight loss is happening the fastest.

In this example, the most stable polymer is the polytetrafluorethylene (PTFE) and the least stable is the polymethyl methacrylate (PMMA). It's also worth noting that the polyamide weight loss at around 100°C is due to water loss and not due to thermal stability.

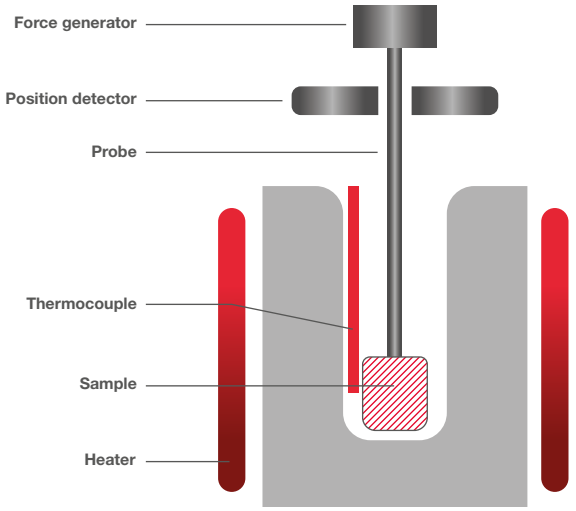
Thermal stability of polymers



TMA: Thermomechanical Analysis

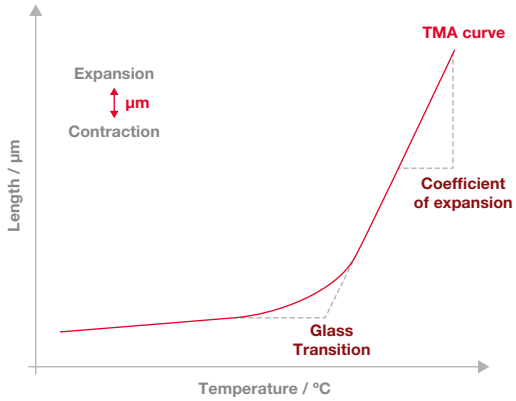
A sample is placed in a TMA furnace where it's subject to constant stress (compression, tension or flexure) while the temperature of the sample is changed in a controlled way. Any deformation of the sample at a specific temperature is detected.

Thermomechanical Analysis (TMA)

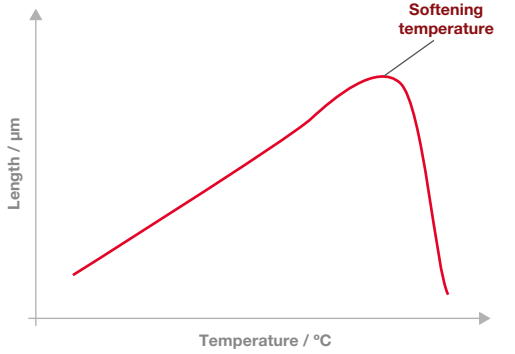


Sample deformation, such as thermal expansion/contraction or softening is detected, and the result is plotted against the applied temperature.

TMA expansion thermogram example



TMA penetration thermogram example



The output traces on the previous page show two different types of measurement. On the top, the coefficient of expansion can be determined by the gradient of the curve above the glass transition. The bottom trace is a penetration measurement, where the softening temperature of the polymer can be determined.

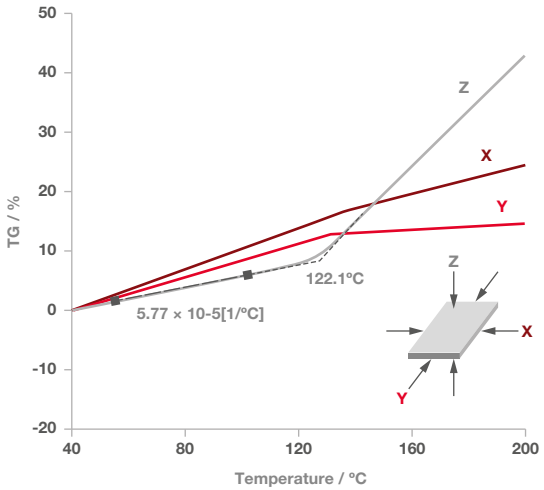
ASTM E831-19: standard test method for linear thermal expansion of solid materials by thermomechanical analysis

This test method determines the technical coefficient of linear thermal expansion of solid materials using thermomechanical analysis techniques.

This test method is applicable to solid materials that exhibit sufficient rigidity over the test temperature range such that the sensing probe does not produce indentation of the specimen.

The TMA thermograms on the right show a classic example of a linear thermal expansion measurement, which is also call coefficient of thermal expansion (CTE). For most polymers with an amorphous phase (i.e. exhibiting a glass transition), the expansion will be lower below the glass transition than after. In this case, we can see that the slope of the linear part before the transition happening at 122.1°C is not as steep as the one after. This is showing that the expansion is bigger at higher temperature. In this example, we can also see that CTE results will vary depending on the axis which the measurement was performed. The CTE is measured by looking at the dimension change between two different temperatures in the linear thermal expansion region and is reported as µm/(m · °C).

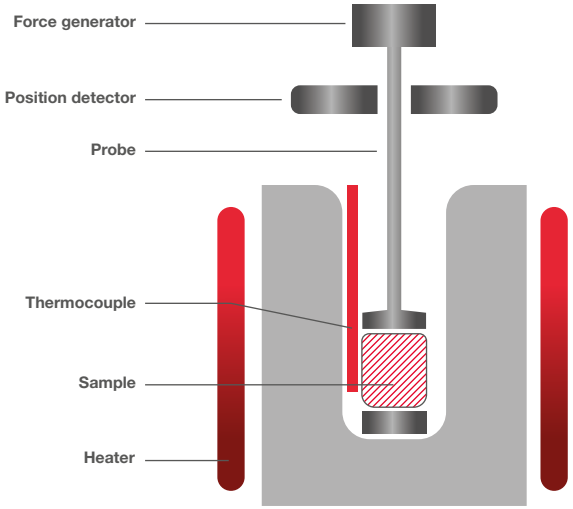
Coefficient of thermal expansion (CTE) of a composite material



DMA: Dynamic mechanical Analysis

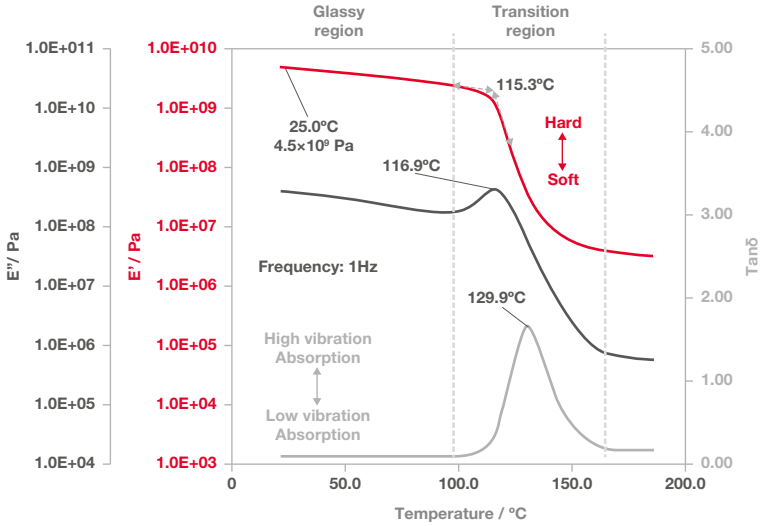
A sample is clamped in the measurement head of the DMA instrument and a sinusoidal force is applied while the temperature of the sample is changed in a controlled way. The relation between the applied force and the resulting deformation is measured.

Dynamic Mechanical Analysis (DMA)



Sample properties such as elasticity and viscosity can be calculated from the applied stress and strain plotted as a function of time or temperature.

Dynamic mechanical properties of a polymetyl metacrylate (PMMA) film



DMA can analyse the dependence of the sample stiffness on the temperature and the glass transition temperature, and also its dependence on the vibration frequency and vibration absorption.

The DMA output trace on the previous page shows the three parameters typically plotted from a DMA measurement.

E' is the storage elastic modulus and shows the elastic property of the sample and the degree of the energy stored and recovered against the applied force.

E'' is the loss elastic modulus and shows the viscous property of the sample and degree of the energy transferred to heat against the applied force.

Tanδ is the loss tangent and shows the ratio of E' to E'' and reflects the vibration absorbability. It is also called the vibration absorption coefficient.

Fundamentally, these parameters give you information about the changes in stiffness and damping of your polymer over a temperature range.

ASTM D4065-20: standard practice for plastics: dynamic mechanical properties: determination and report of procedures

This practice is intended to provide means of determining the transition temperatures, elastic, and loss moduli of plastics over a range of temperatures, frequencies, or time, by free vibration and resonant or nonresonant forced vibration techniques. Plots of elastic and loss moduli are indicative of the viscoelastic characteristics of a plastic. These moduli are functions of temperature or frequency in plastics and change rapidly at particular temperatures or frequencies. The regions of rapid moduli change are normally referred to as transition regions.

Different modes of deformation, such as tensile, bending and shear, are used, as listed in the referenced test methods.

The DMA thermograms on the previous page shows the results for a polymethyl metacrylate (PMMA) film analyzed in tension. The three curves show different information related to the material viscoelastic behaviors. E' is the storage modulus and gives information about the elastic component of the material which related to the material stiffness. The stiffness of the material can be measured at any point, as showed here for the modulus value at 25°C. For amouphous or partly amorphous materials like PMMA, DMA is the perfect technique to detect the glass transition (Tg) as it's extremely sensitive. In this case the glass transition temperature from the storage modulus is detected at 115.3°C.

Glass transition can also be detected using E" which is the loss modulus using the peak which is 116.9°C in this case. Lastly, Tanδ can also be used to where the glass transition is 129.9°C as well as to see how well the material absorb vibration, which is also called damping.

It's normal that E', E" and Tanδ give different values as they are measuring different properties of the polymer. What's important is to compare results obtained with the same type of measurements (E', E" or Tanδ).

Understanding your thermal analysis results

Traditionally, the output of thermal analysis is in the form of the thermograms we've seen in the examples above. For many applications, these give the information needed. Glass transitions, melting points, deformation, lag, etc. can all be seen and there's no potential to misunderstand the results.

However, sometimes you might get anomalies in the output traces, such as a strange artefact in the output graph or the sample looks different when the analysis is complete, and you'd like to know where in the temperature range this change occurred. This is where our unique Real View® image capture feature really helps.

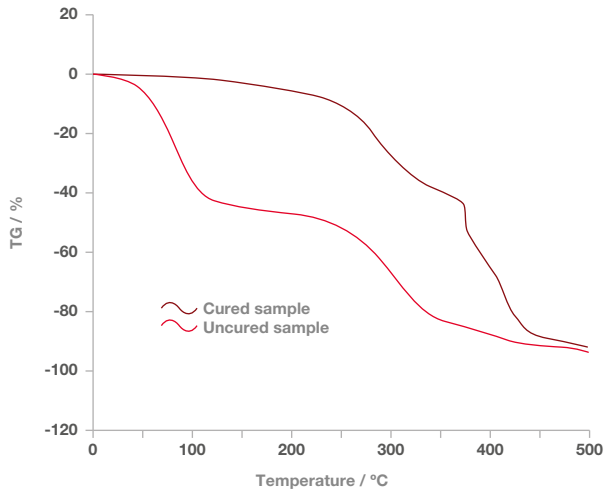
Real View® – Seeing is believing

Our Real View® camera captures images of your sample, allowing you to see visible changes in real-time over the course of the analysis. The system also retains these images for later analysis, allowing you to either bring up a still image at a certain point in the analysis, or watch a video of the whole thing.

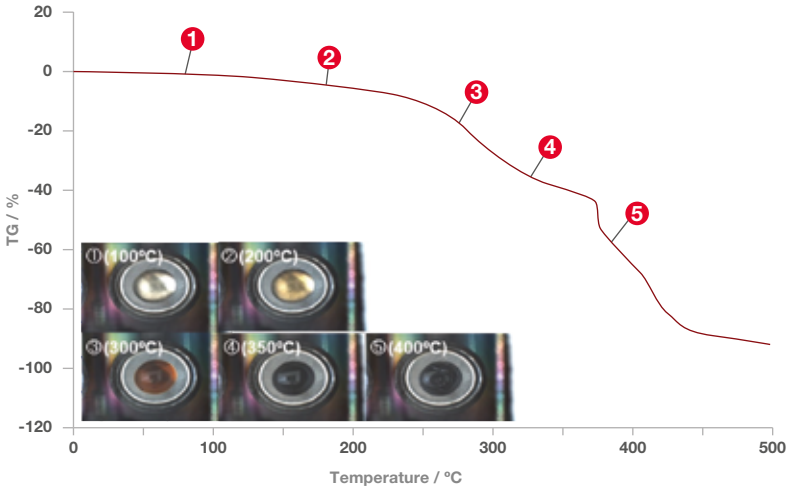
Troubleshooting STA analysis

One area where Real View® helps to understand your results is when you have an unexplained feature in the results as illustrated in the following TGA output trace:

TGA Thermogram of cured and uncured samples



TGA thermogram of cured sample



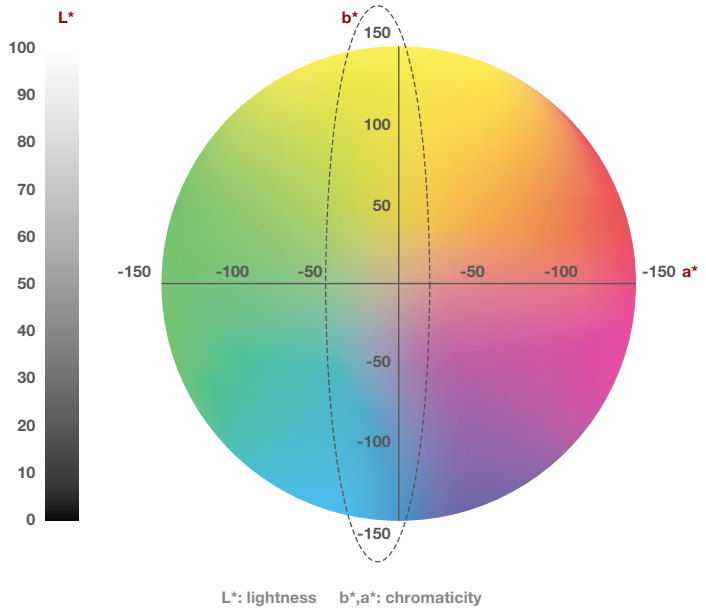
Here we can see two output traces of an uncured and cured epoxy sample. There's an odd 'bump' in the graph at about 375°C that we wouldn't normally expect. Referring to the Real View® images shows that the anomaly is due to a gas bubble trapped in the sample which burst out at this temperature. The mystery is solved, and we don't need to spend time investigating the odd behavior.

True color analysis

Another feature of our Real View® camera is color analysis. This is useful when assessing whether high temperatures will affect the color of a polymer component, or to assess polymer degradation where the main indicator is a color change.

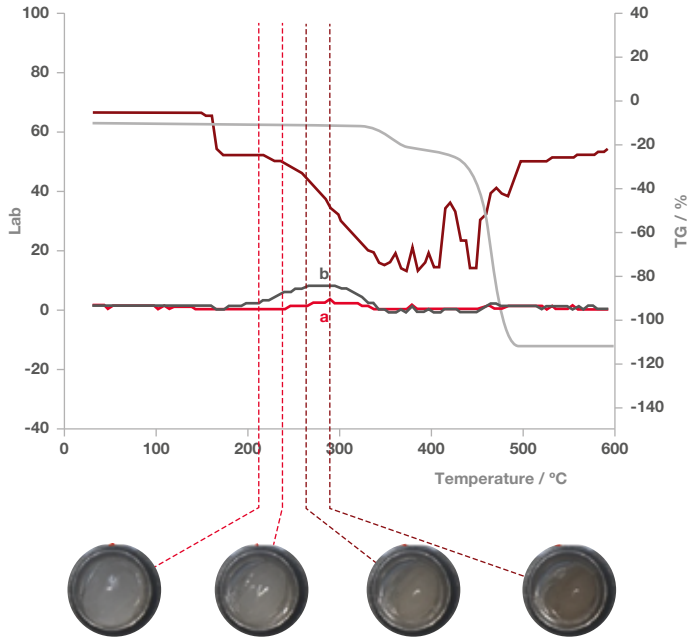
The following graph shows how Real View® can be used to assess polymer degradation, even when there is no weight loss of the sample.

Real View® used to assess polymer degredation



The color change of the sample is quite difficult to make out by eye, but the Real View® software calculates the RGB, CMYK and Lab values, and converts them into a graphic form as shown below:

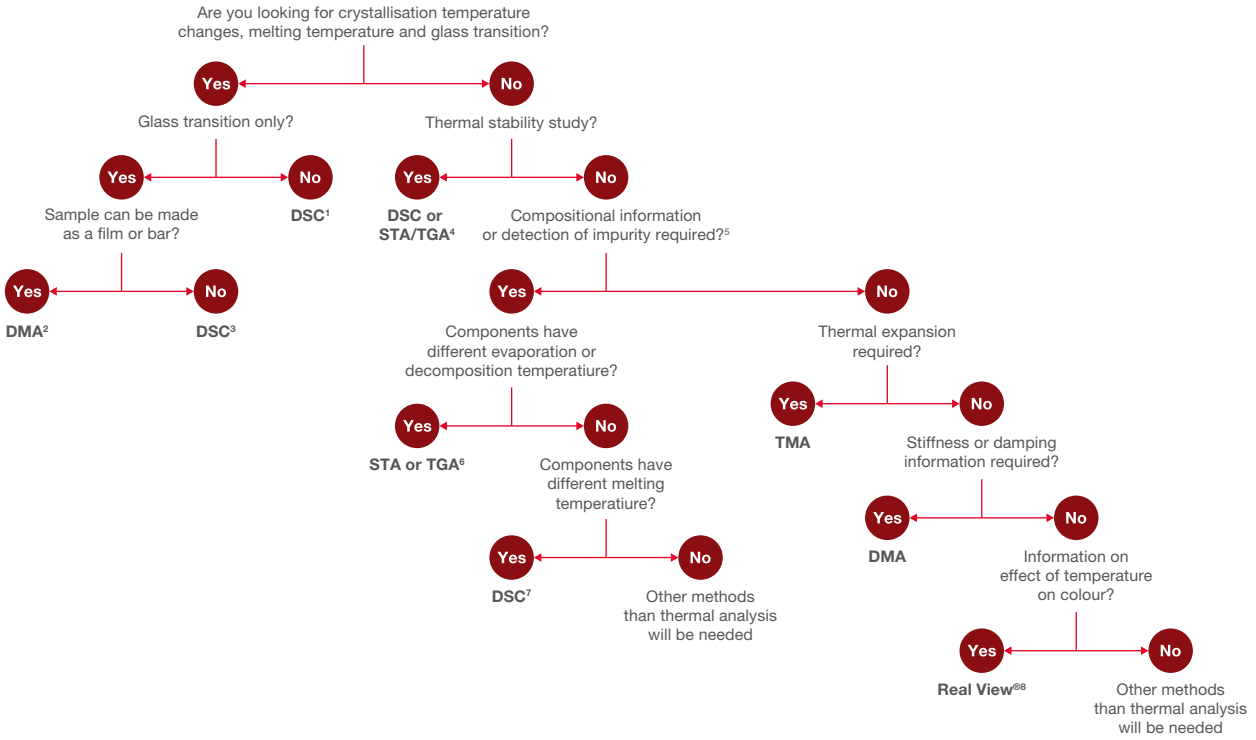
TGA thermogram with Lab colour analysis



From the color analysis graph, you can see that there's an increase in b*, which shows as an increase in yellowness. This is important because this indicates polymer degradation, but there was no associated weight loss on the TGA output. Without Real View®, this result could have been missed.

Choosing the right thermal analysis technique

With four different techniques to choose from, we've made it easy for you to figure out which is right for your needs:

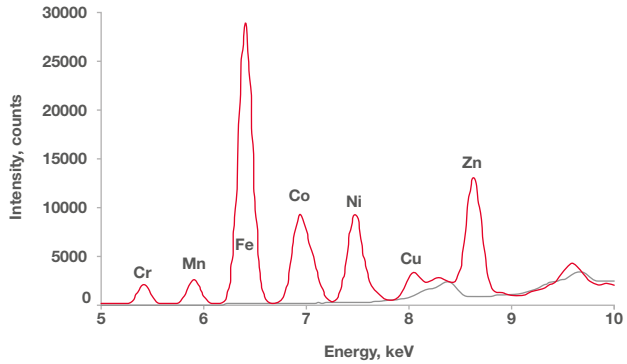


1. DSC will give information on melting, crystallization, exothermic reaction, UV curing heat capacity and more
2. DMA is much more sensitive than DSC to detect glass transition and it can also detect weaker transition such as local motions
3. Although it's possible use a DMA to analyze powders and viscous liquids, it's much easier to do it with a DSC
4. The required technique depends on the type of analysis required. TGA/STA are usually the favoured techniques for thermal stability studies as they are made for these analysis. If oxidative induction time (OIT) is required, a DSC will be the right technique.
5. Compositional analysis includes the measurement of residual solvents, moisture, carbon black, ash content, and quantification of other components that are present within the formulation.
6. TGA or STA will allow determination of concentration (%) of each component as long as they are coming off at different temperature.
7. DSC will detect different components if they have different melting, crystallization or glass transition temperatures.
8. Hitachi's sample observation system is called Real View®. It allows visibility of the samples during a thermal analysis measurement including the observation of color and dimension change. Real View® is compatible with DSC, STA (TGA/DSC) and DMA.

XRF analysis as a supplementary technique

X-ray fluorescence (XRF) can be a useful supplementary technique to thermal analysis for polymers. A fast and non-destructive technique, XRF can analyze and quantify the additives in polymers as a solid, powder, liquid and pellet form, and needs very little sample preparation. As it's completely nondestructive, it can be used on finished components for a final elemental compositional check. It can also be used to measure the thickness and composition of metal coatings, such as metal plating on plastic components.

Typical XRF spectrum



How does XRF work?

XRF works by bombarding the surface of the sample with incident X-rays that 'knock' electrons into higher energy states where they immediately fall back to their ground state. The energy released as the electrons fall back down is in the form of characteristic X-rays that are unique to the elements present. XRF instruments detect these X-rays, and the software determines what elements are present in the sample and in what quantities. It relies on prior calibration with similar materials, but once the equipment is set up, is highly accurate

Conclusions

With the plastics industry driven by fast-paced innovation, quality control of polymers and plastics across the polymer supply chain and lifecycle ensures performance of materials against specifications and customer expectations. Thermal analysis provides the ideal technique for determining material properties, transitions and characterizing polymers to help you protect your brand and deliver key innovations to help you get your job done.

References:

Plastics – the Facts 2021
An analysis of European plastics production, demand and waste data
https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/

Production, use and fate of all plastics ever made.
Geyer et al. 2017.
https://www.science.org/doi/full/10.1126/sciadv.1700782

Conductive Plastics
https://knowledgecenter.mearthane.com/conductiveplastics

A material flow analysis of polymers and plastics in India
https://research.csiro.au/rpwi/wp-content/uploads/sites/412/2021/12/A-material-flow-analysis-of-polymers-and-plastics-in-India-Final-Nov-2021.pdf

The Global Commitment 2021 Progress Report
https://www.unep.org/resources/report/global-commitment-2021-progress-report

About the author

Olivier Savard joined Hitachi High-Tech Analytical Science Ltd. in September 2019 as the thermal analysis sales manager for EMEA. He has since taken the lead on global thermal analysis product management. Before joining Hitachi, Olivier worked as a material characterization application specialist for PerkinElmer U.K. and Canada. He obtained his chemistry B.Sc. from Université Laval (Québec City, Québec) and his M.Sc. working on proton exchange membrane fuel cells at Simon Fraser University (Burnaby, British Columbia).

Our solutions for polymers analysis

We specialize in high-tech analysis solutions, designed to help the polymer industry in both research and development and maintaining high quality standards. For over 45 years, Hitachi High-Tech has pioneered the use of high-performance and reliable analyzers for laboratory and volume production use and has developed a full range of analytical instruments.

NEXTA DSC: High accuracy materials characterization

Designed for accurate determination melting point, glass transition and crystallization temperatures, our range of differential scanning calorimeters delivers excellent sensitivity and baseline flatness.

NEXTA STA: Complete quantitative thermal analysis

Designed for complete thermal analysis of materials, including thermal resistance, decomposition temperature, melting point, and specific heat testing, the NEXTA STA combines DSC and TGA to deliver TGA applications and more within a single analyzer.

TMA7000: Versatile thermal analysis of mechanical characteristics

The TMA7000 range can carry out a range of measurements within a single instrument – from precise TMA analysis, including thermal expansion, glass transition and softening, to DMA testing and creep measurement.

DMA7100: Ultra-sensitive mechanical characterization

Our dynamic mechanical analyzer range is engineered for ultra-low noise and high sensitivity, making it ideal for precise viscoelastic measurements of polymers, rubbers and thin films within a production or research environment.

Real View® Camera

Real View® is available as an option on our NEXTA DSC series, NEXTA STA series and DMA7100 instruments. The camera and lighting system have been optimized for both still images and video. It's possible to capture images from -50°C to 300°C thanks to a localized heating system that keeps the viewing window free from ice.

LAB-X5000 benchtop XRF analyzer

Flexible and powerful XRF analysis for rapid quality assurance and process control of polymers. Ideal for analyzing additive levels and screening for unwanted elements.

X-MET8000 handheld XRF analyzer

Ideal for checking raw polymers as well as finished products for chlorine content, to give an indication of the presence of PVC (and potentially phthalates) in the materials being used. You can also use it to determine bromine content in polystyrene waste. X-MET also makes it easy to measure metal content in plastics.

TM4000 Tabletop SEM

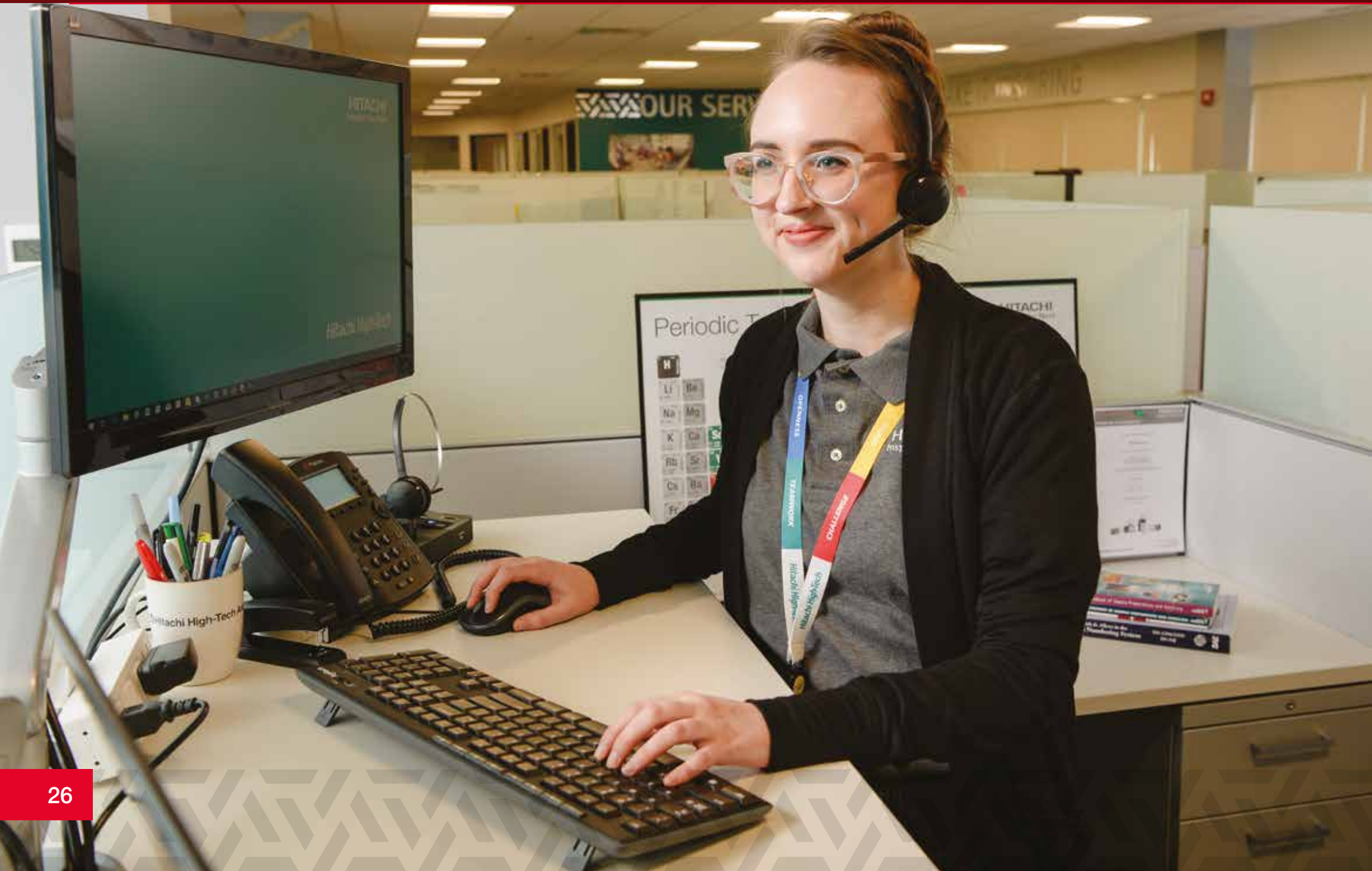
This tabletop scanning electron microscope is easy to use and requires no specialist installation and is ideal for a visual inspection of ultra-minute features and surface characteristics on polymers.

HM1000A spectrometer for phthalates

This thermal desorption mass spectrometer aids rapid phthalate screening for RoHS directives, separating samples that fall within the overall phthalate limit and those that will need further testing.

UH4150 UV-Vis/NIR spectrophotometers

Advanced spectrophotometers operating in the ultraviolet, visible and near infrared regions for the characterization of polymers.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From the moment your Hitachi analyser is installed, you'll receive expert-level support from our services team to ensure you get the best from your Hitachi equipment. Our aim is to provide consistent, high-quality support that keeps your costs low and your uptime high.

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