

Solutions for Polymer Analysis & Development

Explore a number of different lab-scale techniques for both the chemical, elemental and structural analysis of polymers, rheological analysis and approaches for polymer compound extrusion and testing.

 Learn more at **[thermofisher.com](https://www.thermofisher.com)**

TABLE OF CONTENTS

- 5** ARTICLE
Investigative Failure Analysis of Plastic Using FTIR Spectrometry
- 14** ARTICLE
FTIR Reflectance Spectroscopy for the Analysis of Polymer Samples
- 19** INSIGHTS FROM INDUSTRY
Fundamentals of Polymer Analysis with X-Ray Fluorescence (XRF)
- 31** ARTICLE
How to Measure Polymer Materials with X-Ray Diffraction (XRD)
- 38** ARTICLE
Optimizing Polymeric Materials with Rheological Analysis
- 56** ARTICLE
Producing Master Curves for Polymeric Materials
- 67** INSIGHTS FROM INDUSTRY
Torque Rheometers Bring Advantages in Polymer Development
- 74** ARTICLE
Preparing and Analyzing PET with Additives



Introduction to Polymer Research and Development

Polymers are ubiquitous in the modern world for their fantastic tunable properties. Changing either the chemical composition, average molecular weights, or the curing process of polymers makes it possible to completely modify the material behavior of the final polymer. With advanced machining techniques making it possible to easily make highly complex structures from polymers, it is hard to find many modern objects that do not have at least one polymer component.



This eBook covers a number of different lab-scale techniques for both the chemical, elemental and structural analysis of polymers, rheological analysis and approaches for polymer compound extrusion and testing. Together, a comprehensive understanding of these techniques provides a way of fully understanding polymer materials for polymer design or manufacturing applications.

In this eBook we will explore:

- Chemical Analysis of Polymers
- Elemental Analysis of Polymers
- Structural Analysis of Polymers
- Rheological Analysis of Polymers
- Lab-scale Polymer Compounding, Extrusion and Testing



Follow our **Advancing Materials blog** to learn about our latest polymers and plastics applications and instruments.

Chemical Analysis of Polymers

Examine the chemical composition of polymers and constituents to improve the development, quality and performance of parts and products.

Investigative Failure Analysis of Plastic Using FTIR Spectrometry

A routine challenge faced by manufacturers employing plastic parts is analyzing failed parts to determine the root cause of the failure. This article studies how several techniques can be used to analyze and confirm why a plastic part failed.

A manufacturer of precision optical equipment developed a plastic cover for a device with specifications for color and optical transmission, surface texture, and chemical composition.

In short, the cover was to be created from a polycarbonate – acrylonitrile butadiene styrene (PC-ABS) blend with enough titanium dioxide to give a marginally off-white color and an optical transmissivity of less than 0.01% T over a broad spectral range, from the UV into the near-infrared.

The opacity was needed to block ambient (room) light from reaching the optical device and hindering low light level measurements. Originally, each of the supplied parts fulfilled the specifications and the product delivered a satisfactory performance

A re-engineering project commenced to lessen costs and increase the competitiveness of the product. Quotations were then requested from different suppliers of various parts.

An alternative supplier underbid the earlier cover supplier, and the test parts satisfied all the requirements for opacity. As a result of this, the production was changed to include this new supplier.

After a short period of time, the product was failing serious performance tests. The failures were quickly traced to ambient light creating elevated backgrounds which strongly affected the low level optical measurements.

A visual inspection of the covers did not show obvious variations from the original, but different control experiments led to the failure being traced back to the new cover. A root cause analysis utilizing several techniques was carried out to efficiently discover and limit the issue.

Experimental Results

UV-Visible Spectroscopy

Diffuse transmission measurements of the earlier cover and failed cover were taken utilizing a [Thermo Scientific™ Evolution™ 220 UV-Visible Spectrophotometer*](#) and integrating sphere, as shown in Figure 1.



Figure 1. Evolution 220 UV-Visible Spectrophotometer (left), and sample compartment integrating sphere accessory (right).*

The cover by design included high quantities of particulates, which would quickly scatter any transmitted light. Due to this, transmittance was analyzed with an integrating sphere.

Parts of covers from both good and failing devices were positioned at the transmittance port of the sphere and spectra were gathered from 220 to 800 nm, resulting in the spectra demonstrated in Figure 2.

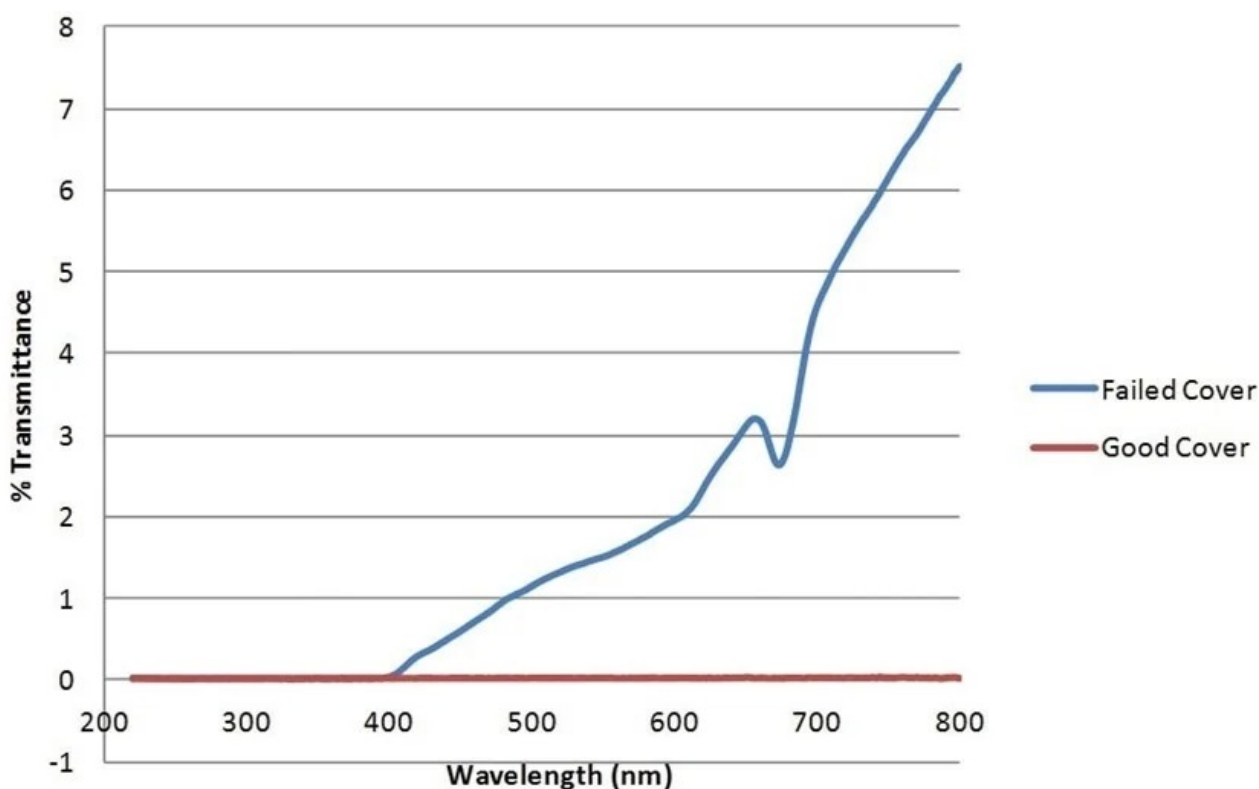


Figure 2. Diffuse Transmittance UV-Visible spectra of the failed cover (blue) and good cover (red), gathered with an Evolution 220 UV-Visible Spectrophotometer and integrating sphere accessory.

Virtually no transmittance was quantifiable through the good cover. In contrast to the failing cover, where a notable amount of transmittance through the visible part of the spectrum,

greater than 7% T, was measured.

This evidently provided an explanation for the poor performance, - the light leak of the device under ambient conditions - but did not explain the root cause.

Thermogravimetric Analysis (TGA)

Small parts of both covers were then inspected with a TA Instruments™ thermogravimetric analyzer to discern bulk composition, with the results displayed in Figure 3.¹

The samples were heated from ambient to 650 °C at 20 °C per minute under N₂ purge, then cooled to 550 °C, and heated again to 1000 °C at 20 °C per minute with air purge.

The first heating ramp under nitrogen pyrolyzes the organic component of the covers, and the last temperature ramp in air burns the rest of the organic components with only oxides of the inorganic content remaining.

The organic decomposition profiles of both covers were almost the same, showing that each one had the same plastic composition.

Although, the good cover contained leftover inorganic components representing 5.4% by weight, whereas the failed cover had an inorganic component of just 2.2% by weight. This showed an extensive variation in the amounts of inorganic filler between the covers and gave a strong hint as to the origin of the light leak.

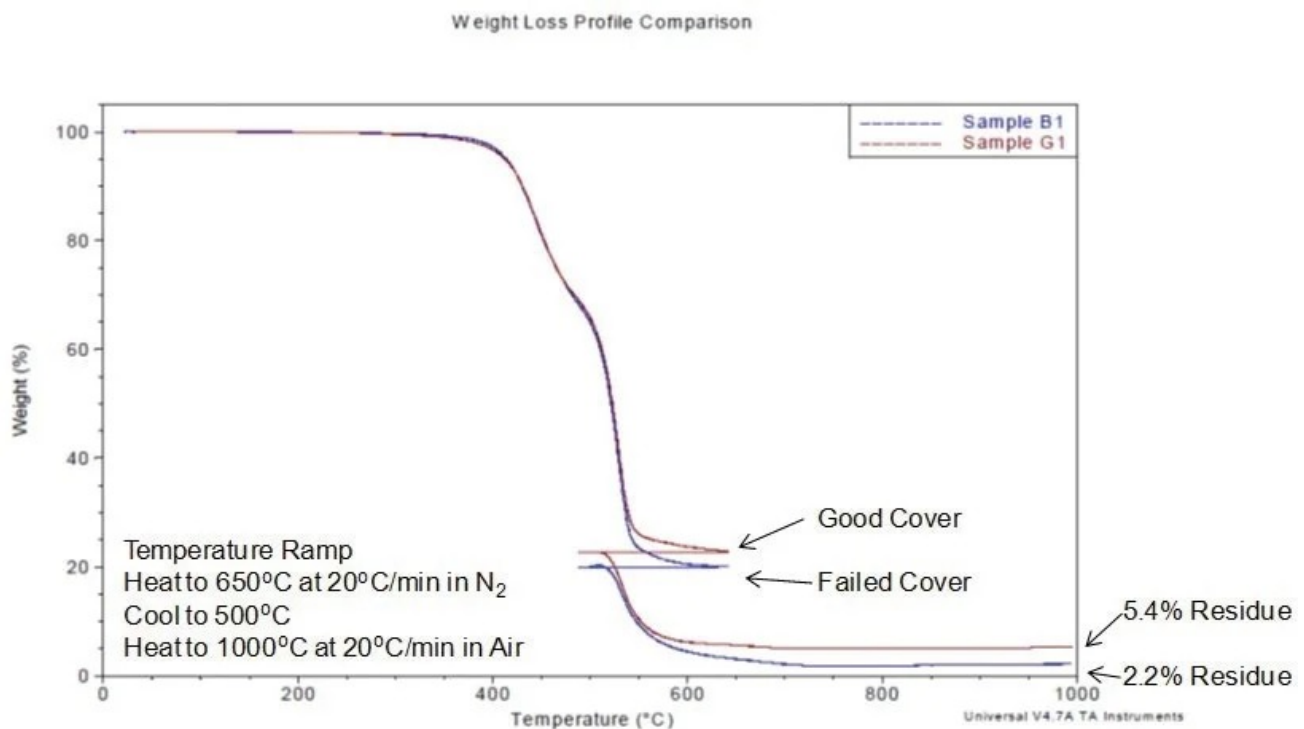


Figure 3. Thermogravimetric analysis weight loss curves for the good cover (red) and failed cover (blue), demonstrating that the good cover has extensively higher inorganic content

compared to the failed cover.

Infrared Analysis

Infrared spectra of small pieces of each cover were collected with the integrated diamond iS50 ATR on a [Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer](#), displayed in Figure 4.

The built-in iS50 ATR on the Nicolet iS50 has an exclusive detector which allows the collection of combined mid- and far-IR ATR spectra down to 100 cm^{-1} . The capability of the iS50 ATR to gather spectra in the far-IR creates the simple measurement and discovery of inorganic fillers in plastic parts.



Figure 4. Nicolet iS50 FT-IR spectrometer with built-in diamond iS50 ATR, iS50 ABX Automated Beamsplitter exchanger, and sample compartment iS50 Raman accessory.

When integrated with the iS50 ABX Automated Beamsplitter exchanger on the Nicolet iS50 Spectrometer, mid and far-IR spectra can be immediately collected and stitched together utilizing a Thermo Scientific™ OMNIC™ Macros\Pro™ Visual Basic Program to give a single spectrum of a sample from 4000 to 100 cm^{-1} .²

The ATR spectra of the plastic parts, illustrated in Figure 5, were corrected with the advanced ATR correction algorithm³ in Thermo Scientific OMNIC Software.

The advanced ATR correction algorithm explains both relative intensity changes generated by sample penetration depth as a function of wavelength and also for peak shifts in the infrared spectra because of index of refraction variations between the ATR crystal and sample.

An examination of the infrared spectra of each plastic piece reveals the polymer

composition to be similar, however the original plastic part has an elevated baseline below 800 cm^{-1} , and a sharp peak at 360 cm^{-1} , demonstrated in Figure 6, that are missing or very weak in the spectrum of the replacement part.

The peak at 360 cm^{-1} is under the range of a common mid-IR spectrometer combined with a KBr beamsplitter. The iS50 ABX with a solid substrate far-IR beamsplitter allows the far-IR range to be accessible in this analysis, while high performance across the whole range is uncompromised.

There are further differences between the spectra which are highlighted through a spectral subtraction. The difference spectrum (Figure 5, bottom) indicates slight peak shifts in the polymer bands, showing a small polymer composition difference between each part, common when contrasting plastic parts made by alternate suppliers, but a critical spectral difference is also observed below 800 cm^{-1} .

A library search of the difference spectrum against a forensic library of automobile paint pigments and fillers,⁴ displayed in Figure 7, matches rutile, one of the crystalline forms of titanium dioxide, suggesting a formulation difference between both of the covers.

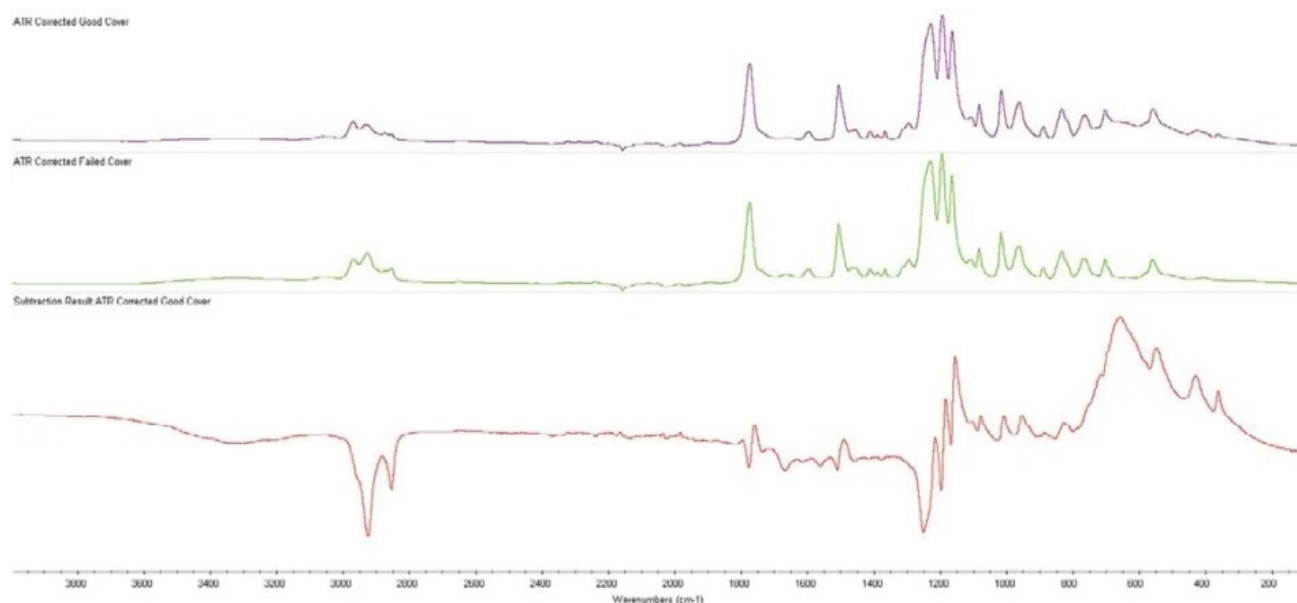


Figure 5. Advance ATR corrected infrared ATR spectra of the good plastic cover (top), failed plastic cover (middle), and difference spectra between the two (bottom).

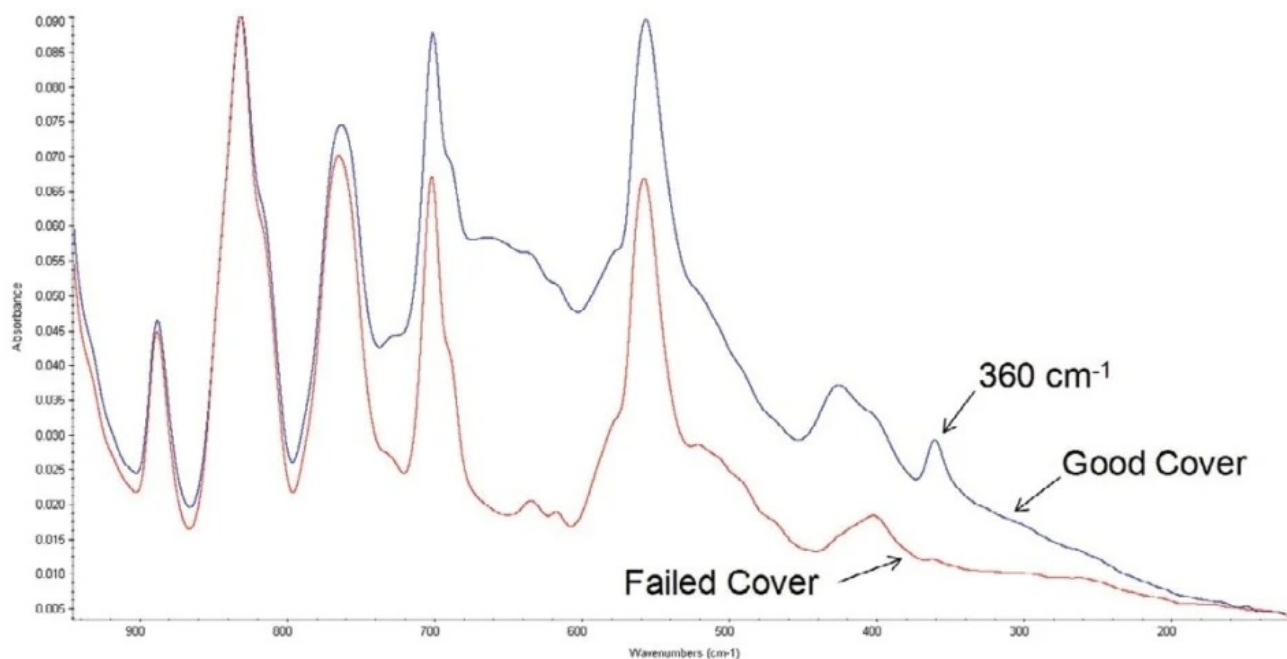


Figure 6. Overlay of the advanced ATR corrected spectra of the good cover (blue) and failed cover (red), over the spectral region from 940 to 100 cm^{-1} . Note the elevated baseline and the absorbance band at 360 cm^{-1} in the spectrum of the good cover that are missing or significantly reduced in the spectrum of the failed cover.

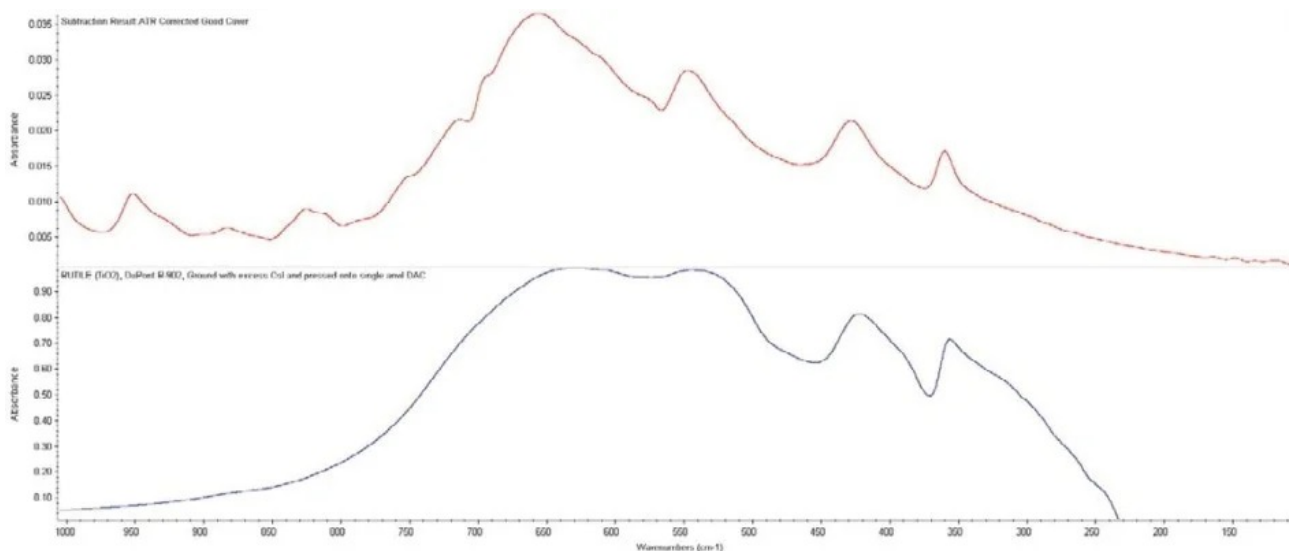


Figure 7. FT-Raman difference spectrum between the good and failed covers (blue), and top match from a library search against a forensic automobile paint pigment and fillers library (red), identifying a higher concentration of rutile (titanium dioxide) in the good cover.

FT-Raman Analysis

To verify the judgments taken from the infrared analysis, the two samples were also investigated utilizing the iS50 Raman sample compartment FT-Raman accessory on the Nicolet iS50 Spectrometer (displayed in Figure 4).

The iS50 Raman accessory fits into the sample compartment of the Nicolet iS50 FTIR Spectrometer and does not require an external module frequently seen in alternative FTIR spectrometer systems.

The iS50 Raman accessory allows for the simple gathering of Raman spectra with a near-infrared beamsplitter and an InGaAs detector mounted inside of the spectrometer.

FT-Raman spectra of the good and failed covers, in addition to the spectral difference spectrum between them, are shown in Figure 8. FT-Raman spectroscopy supports the collection of spectra into the far-IR region, accompanying the power of the Nicolet iS50 FTIR Spectrometer with the built-in iS50 ATR and ABX in gaining access to this region.

Again, the two spectra are highly alike, showing a comparable polymer composition, with slight differences in the spectra observable below 800 cm^{-1} , plainly seen in the difference spectrum.

A library search of the difference spectrum using a minerals Raman library⁵ is presented in Figure 9, establishing the difference between both plastic parts as rutile, confirming the identification from infrared analysis.

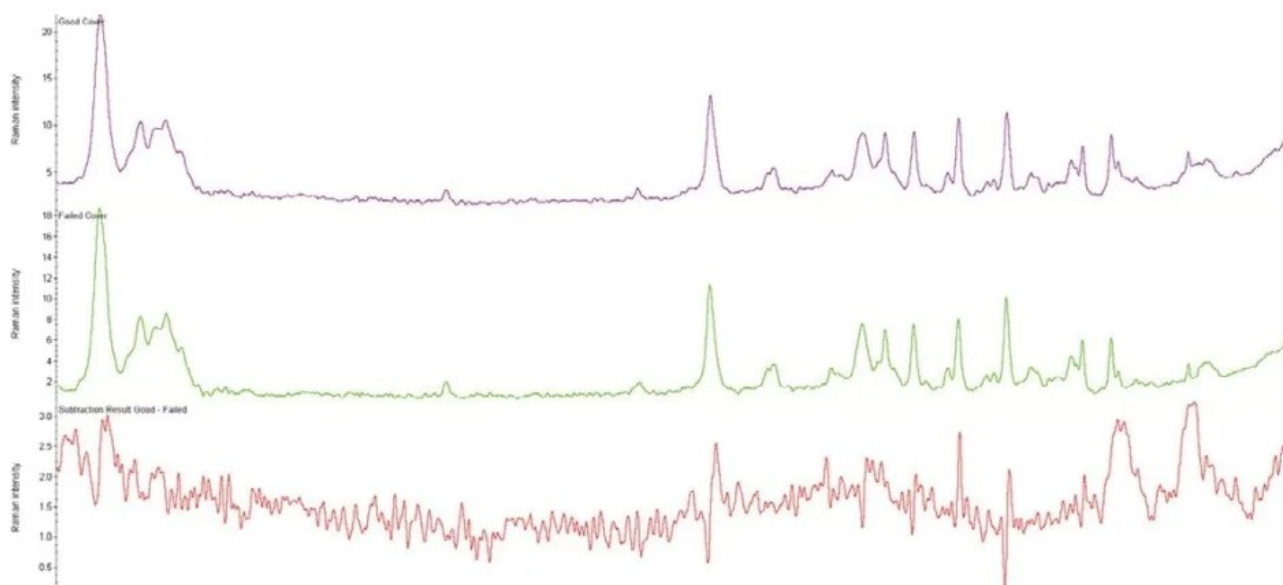


Figure 8. FT-Raman spectra of the good cover (top), failed cover (middle), and subtraction result between the two (bottom).

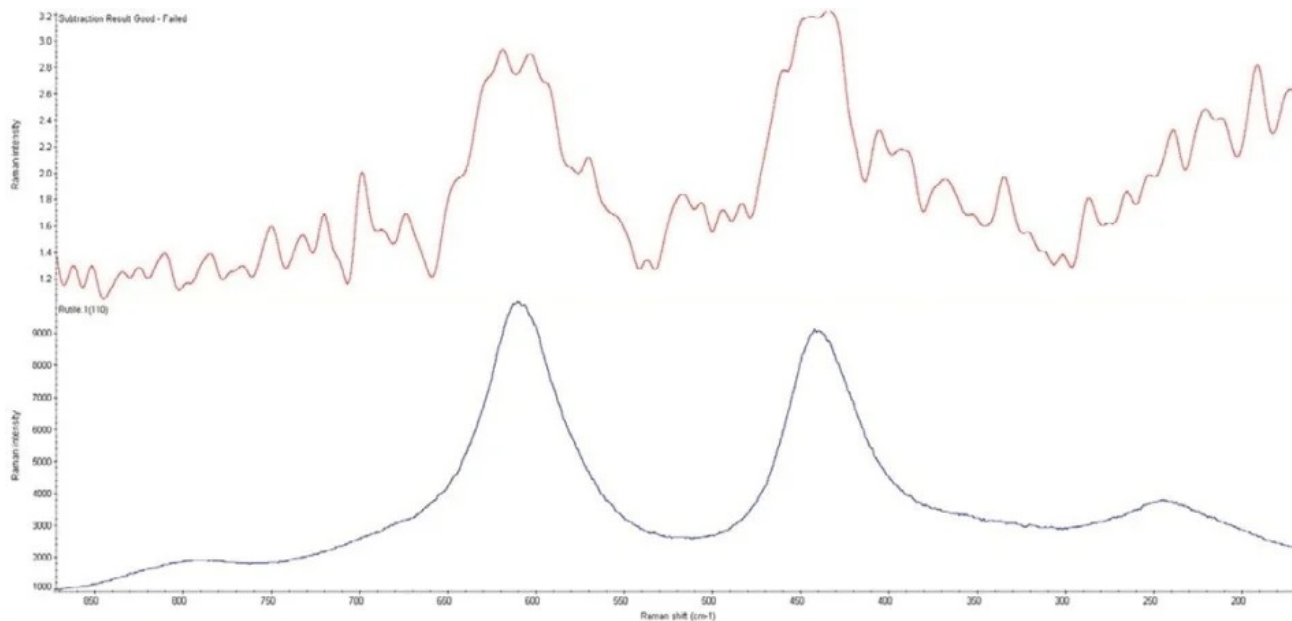


Figure 9. FT-Raman difference spectrum between the good and failed covers (top), and top library search result against a minerals Raman library (bottom), showing a higher concentration of rutile (titanium dioxide) in the good cover.

Summary and Conclusion

Ambient light reaching the device produced incorrect measurements for low light level measurements. Diffuse transmission measurement of the parts by UV-Visible spectroscopy established that the failed cover did not meet the specification for maximum transmittance.

Thermogravimetric analysis showed that the composition of the original cover had around 3% more, by weight, of an inorganic filler in contrast to the replacement cover.

Infrared ATR analysis over the mid and far-IR spectral regions demonstrated that the first cover had an extensively higher rutile (titanium dioxide) content than the second cover. The infrared results were verified by FT-Raman spectroscopy.

This study strongly shows that it is critical to have several tools available for root cause analysis. Most of the tools utilized can be found on the Nicolet iS50 FTIR Spectrometer. The [Nicolet iS50](#) can collect multi-range spectra without compromise using the built-in iS50 ATR and iS50 Raman accessories.

The analyses given by the Thermo Scientific UV-Vis and FTIR instruments, in combination with thermogravimetric analysis, were conclusive in discovering the root cause failure of the plastic cover.

**This is now discontinued and replaced with [Evolution One Plus UV-Vis Spectrophotometer](#). The ISA 220 accessory has not changed and is compatible with Evolution One Plus.*

References and Further Reading

1. Thermogravimetric results provided by Jeff Jansen, The Madison Group, 2615 Research Park Drive, Madison, WI, 53711.
2. Mid-Far ATR iS50 collection program available upon request. Requires Nicolet iS50 FTIR Spectrometer configured with built-in diamond iS50 ATR, and ABX Automated Beamsplitter exchanger with KBr and solid substrate beamsplitter.
3. Thermo Scientific Application Note 50581, Advanced ATR Correction Algorithm.
4. An Infrared Spectral Library of Automobile Paint Pigments ($4000\text{--}250\text{ cm}^{-1}$), developed by Dr. Edward H. Suzuki at the Washington State Police Crime Laboratory, downloadable from the SWGMAT.org website
5. Downs R T (2006) The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. Program and Abstracts of the 19th General Meeting of the International Mineralogical Association in Kobe, Japan. O03-13 Minerals 514 Raman Library



This information has been sourced, reviewed and adapted from materials provided by Thermo Fisher Scientific – Materials & Structural Analysis.

For more information on this source, please visit [Thermo Fisher Scientific – Materials & Structural Analysis](#).

FTIR Reflectance Spectroscopy for the Analysis of Polymer Samples

One of the most popular techniques for material identification is single bounce ATR spectroscopy. However, in some cases, the specular reflectance sampling technique may still be necessary. Much like light hitting a mirror, in a specular reflectance measurement, the infrared light from the spectrometer is reflected directly off the sample.

As it is a useful sampling technique, several ATR accessories can be configured to amass specular reflectance spectra. The Thermo Scientific™ Nicolet™ Summit FTIR Spectrometer with the Everest ATR Accessory is shown in Figure 1. It is possible to configure this with the specular reflection attachment.



Figure 1. Thermo Scientific Nicolet Summit FTIR Spectrometer with the Everest ATR

Very large samples can be measured, for example, paintings, with no contact between the instrument and the artwork using other dedicated reflectance accessories. The distorted spectra that may result from anomalous dispersion, or the possible scattering effect as the light interacts with the sample, are both disadvantages of the specular reflectance sampling technique. It is difficult to get reasonable matches with most spectral libraries when there are distorted spectra, as these are usually collected in transmission.

The specular reflectance spectrum collected with the Everest accessory from a white piece of smooth, white plastic is shown in Figure 2. Here, the collected spectrum, in red, looks quite different from the best match value, in blue. The [Thermo Scientific™ OMNIC™ Paradigm Software](#) calculated a match value of only 52.5. This is very low, suggesting that the two spectra are from different materials.

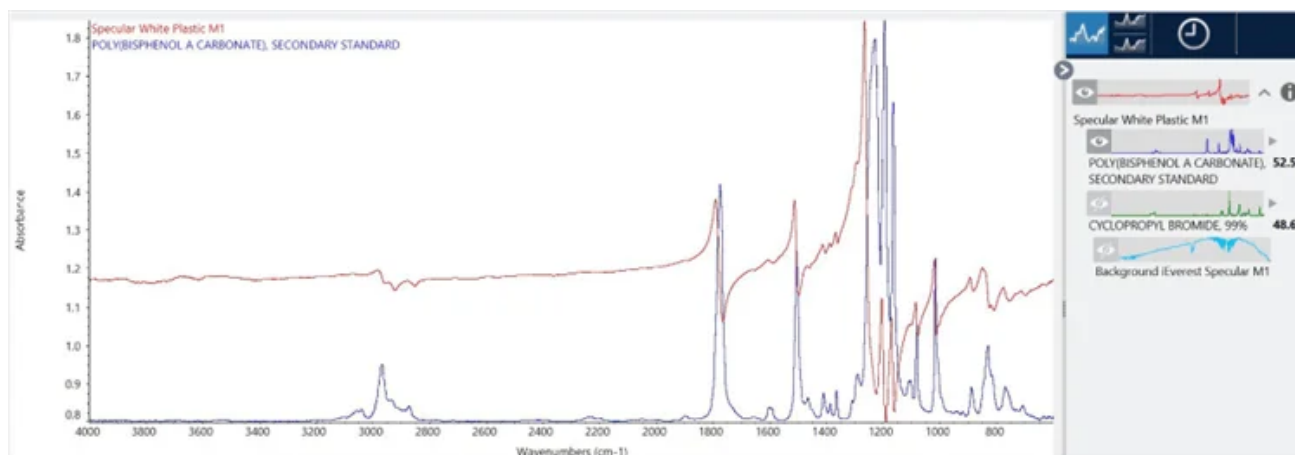


Figure 2. *Specular reflectance spectrum (red) from a white piece of plastic and the library spectrum from the best search result.*

Much of the spectral distortion resulting from the specular reflectance measurement is mathematically eliminated with the Kramers-Kronig correction in the OMNIC Paradigm Software. A spectrum is also created that looks as if it were collected in transmission.

The corrected spectrum, in red, overlaid with the top match value, in purple, is shown in Figure 3. The match value increases dramatically to 93 once the Kramers-Kronig is applied, indicating that the sample is most likely a polycarbonate plastic.

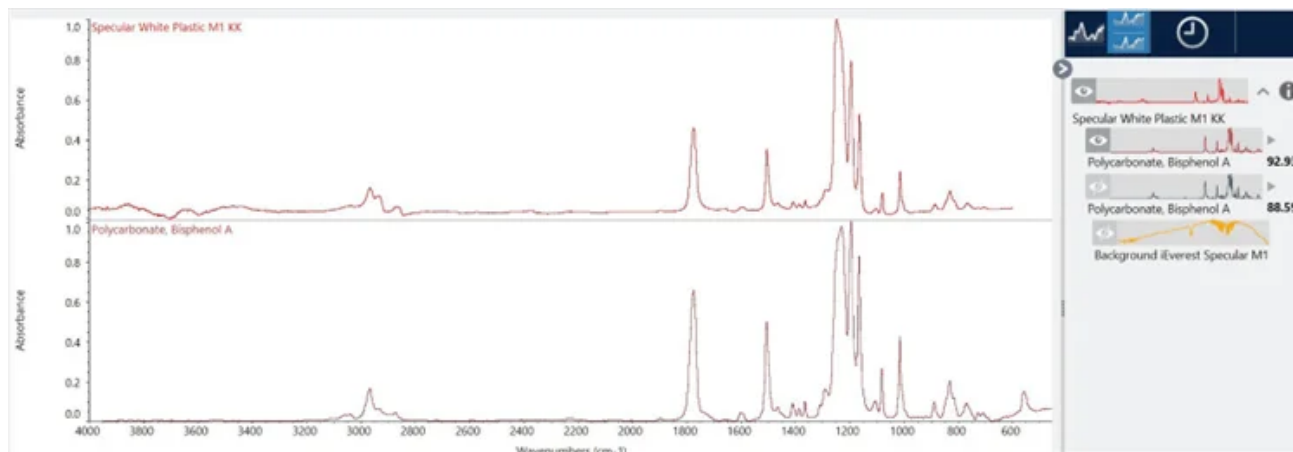


Figure 3. Spectrum after Kramers-Kronig corrections and library spectrum from the best search result.

The OMNIC Paradigm Software can speed up future analyses by automatically creating a workflow, similar to a *Standard Operating Procedure*, ensuring consistent results from one analyst to the next. The actual processing steps completed for the spectral reflectance spectrum, including the Kramers-Kronig correction, are displayed to the right-hand side of Figure 4. The workflow is automatically created for future use (Figure 5) by clicking on the Create Workflow button at the bottom right-hand side of Figure 4.

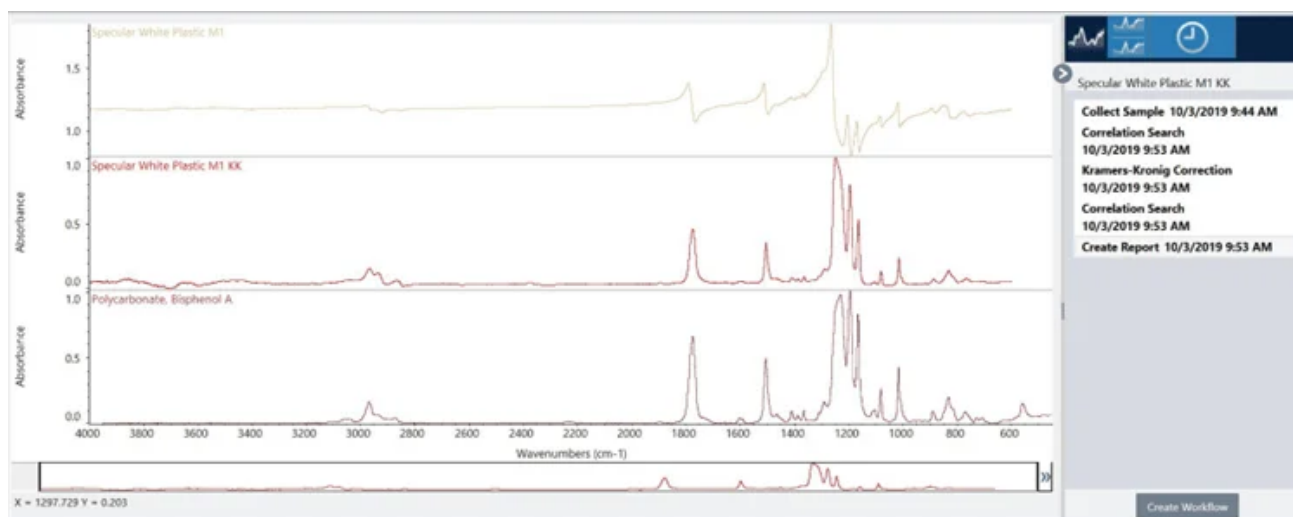


Figure 4. Comparison of the original spectrum from the white plastic, the KK corrected spectrum and the best library match.



Figure 5. The workflow resulting from clicking on “Create Workflow” button.

A fully functional workflow is automatically created by the [OMNIC Paradigm software](#).

Lab managers may sometimes require additional functionality in the workflow in order to improve it. As shown in Figure 6, a more robust workflow is achievable with a few additional features (or Tiles):

1. **Instruction tile** – Sample information, such as the name and batch number, needs to be entered by the operator.
2. **Save Results tile** – The spectra and results are archived to a specified file location
3. **Repeat tile** – A loop is added so that multiple samples can be analyzed at once



Figure 6. Final Workflow with enhancements.

Several useful features are included with OMNIC Paradigm Software to make analysis easy. Spectral distortions can be removed from diffuse reflectance measurements through the application of the Kramers-Kronig correction, which significantly improves the library match value from around 50 to greater than 90. The steps can be simplified for any scientist or technician in the lab as the process of collecting a spectrum, applying the Kramers-Kronig correction, and successfully searching a library can be automated into a Workflow.

ThermoFisher
S C I E N T I F I C

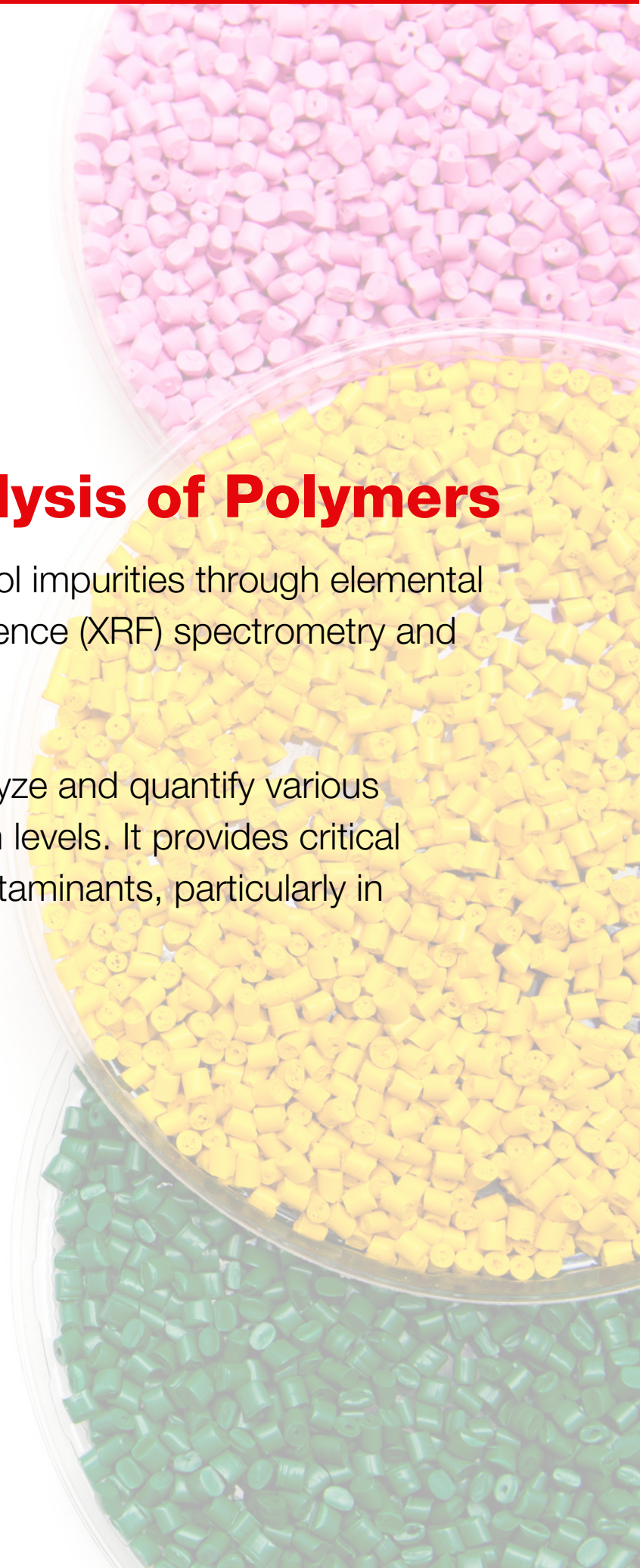
This information has been sourced, reviewed and adapted from materials provided by Thermo Fisher Scientific – Materials & Structural Analysis.

For more information on this source, please visit [Thermo Fisher Scientific – Materials & Structural Analysis](#).

Elemental Analysis of Polymers

Identify polymers and control impurities through elemental analysis with X-ray fluorescence (XRF) spectrometry and elemental analyzers.

XRF is ideally suited to analyze and quantify various elements down to sub-ppm levels. It provides critical insight into additives or contaminants, particularly in regulated environments.



Fundamentals of Polymer Analysis with X-Ray Fluorescence (XRF)

insights from industry

Christopher Shaffer

XRF, XRD, & OES Business Development Manager
Thermo Fisher Scientific



From manufacturing to recycling, industries can benefit a lot from the use of polymer analysis by XRF.

A recent interview with Christopher Shaffer, XRF, XRD, and OES Business Development Manager, from Thermo Fisher Scientific, outlines the uses and benefits of this powerful technique throughout the entire polymer value chain, looking at where XRF fits into these processes and providing a number of example scenarios and applications of this.

Could you give a brief introduction to XRF and the underlying principles of this technique?

XRF is an inorganic elemental analysis technique used on solids, liquids and powders. In XRF, we use an x-ray source to eject an inner electron from an atomic shell, leaving this in a very unstable state.

To become more stable, this outer shell electron will relax, release energy and take the place of that missing electron. This process emits energy known as fluorescence energy, which is what we measure via XRF.

This released energy is unique to an element, so we can use different techniques to quantify and identify that fluorescence energy.

There are two styles of x-ray fluorescence: energy dispersive and wavelength dispersive.

Energy dispersive XRF is a more direct analysis of the fluorescence energy emitted from the sample. We use an x-ray source, an excited sample and a solid-state detector to collect the fluorescence energy. The detector is used for the discrimination and determination of this collected energy.

In wavelength dispersive XRF, we use a combination of crystals and detectors to determine what the collected energy is. This system is known as a goniometer.

Wavelength dispersive XRF takes fluorescence energy and uses a crystal to diffract and divide this into its component wavelengths. Using the detector and the crystal, a 2 theta angle can be determined for that individual element.



How does XRF compare to other techniques in terms of its accuracy and limits of detection?

When we compare X-ray fluorescence to other techniques such as ICP or spark emission, we can see that X-ray fluorescence can accommodate single-digit PPM, all the way up to 100% analysis on many different types of elements.

XRF reaches the detection limits of an ICP, which can be as low as PPP, PPT or even PPQ, but with XRF, there is a lot less sample preparation required. We can typically run a sample, as received, with minimal or no sample preparation, whereas in ICP, we must dissolve the sample into an aqueous solution. Dissolving a sample in this way will lead to different degrees of dilution, potentially impacting ICP's detection limits.

XRF can be used with solids or liquids, but not gases.

How are samples prepared for XRF, and what factors should users bear in mind when looking to work with this technique?

Sample preparation is critical for X-ray analysis. There are many different approaches to sample preparation, depending on the sample we are running.

For liquids, we use disposable films with different films as support. The films we use are determined by what type of solution we are using.

The best way to measure materials depends on what type of solution is being used. For example, gravimetric or volumetric measuring techniques work very well if we have an aqueous solution. If you have a nonaqueous solution - like an oil solution - then gravimetric measuring is the method to use.

We tend to use the same support, films and disposable cells as we do in liquids for loose powders. We simply insert an amount of sample into a cell gravimetrically when working

with this sample type.

Regardless of the loose powder sample type, we tend to use the least absorbing film. This is typically polypropylene.

The advantages of this approach are that it is a quick, inexpensive means of conducting heavy metal analysis. The disadvantages of this method lie in its inability to offer an adequate analysis of light elements, primarily due to the film's absorption rate. There are also issues with inconsistent packing on the sample's surface, prompting differences in detection between particles and creating variation.

When preparing polymers, we tend to use a hot press to heat the polymer and press this under about 10 tons of pressure. This method is ideal for good sample preparation, offering good surface adherence and surface smoothness. It also doesn't require a film and is suitable for elements ranging from carbon to uranium.

The downside to this method of polymer preparation is that this is a more expensive technique requiring a specific hot press to be available in the lab. These presses can only reach 180 °C, and while the process does not need a melt temperature, this does need to sufficiently soften the polymer for pressing this into a solid disc.

What are some of the specific advantages of XRF? Why might users want to implement an XRF setup in their labs?

One of the most significant advantages of XRF is its ability to analyze numerous types of samples. XRF is not restricted to just aqueous samples; it can accommodate solid solutions or suspensions.

The majority of sample preparation with XRF is fast and relatively simple compared to other techniques because we can measure many samples directly. Most techniques also require linear calibrations, but if we are using XRF without standards, we can use semi-quantum fundamental parameters to achieve quick analysis for single or multiple element procedures.

Where can XRF be implemented in the polymer value chain? Are there any particularly representative examples of this?

XRF fits into the polymer value chain at almost every step of the process; everything from exploration, refining and processing, through to polymer production, final product manufacture and finally during the recycling of a product back into either a polymer chain.

XRF is also useful when looking to meet environmental regulations in terms of analyzing the polymer as a waste.

In exploration, we can use XRF for mineral identification and quantification, for example, in blast holes and pouring samples. We can analyze the elements present from PPM to 100% levels, either to look for trace elements that identify the presence or likelihood of oil-rich ores or to just look at the sample's general composition and its major and minor components.

In a typical exploration application, we would take a sample, run the XRF analysis and determine its elemental composition. This would typically be expressed as oxides – a stoichiometric expression of elemental concentrations.

We take that information and use another technique known as [X-ray diffraction](#) (XRD) to determine the phase assembly or any crystalline components in the sample.

When we perform a search on a database for XRD, there will be hundreds of thousands of possible candidates populating our search results. We can use our XRF results to minimize the search criteria by knowing which elements to search for. This aids in the processing and quantification of the XRD data.

The combination of these two techniques allows us to gain a complete picture of the elemental composition and the mineralogy of the samples we are looking at.

What other application areas in the petrochemical industry does XRF see regular use within?

XRF applications vary dramatically in the petrochemical industry. These include everything from environmental regulation, software determination, refinement, analysis of diesel and gasoline, corrosion prevention, process optimization, QA/QC and a full range of other laboratory uses.

Types of samples can range from gasoline to catalysts, additives and everything in between. We often use different ISOs, norms or regulations that dictate which elements we are going to look for and the concentration ranges we need to achieve. Using this information, we can better determine which X-ray will best fit our analysis needs.

For example, when looking at crude oil, we typically monitor sulfur, chloride and other contaminants in the crude oil. Sulfur determination, in particular, can involve very high concentrations, depending on where the crude oil comes from - from thousands of PPM up to 5% or 6% in value.

XRF can easily accommodate these limits using a long-range, linear regression. This can

be achieved with just one calibration, with no need to dilute.

Chloride determination is key to managing corrosion and emission issues in the refinery. We need to monitor this and ensure that chloride concentrations are low enough so that we don't start corroding the refinery pipes or ore.

When working with other heavy metals, such as vanadium and nickel, we need to determine and quantify these because they can poison the catalyst and render this ineffective in the cracking process.

If these metals move through the refinement process and enter oil products, this can create corrosion issues in the engine blocks. Again, XRF is excellent at detecting all of these substances from low PPM to high percentage ranges.



Image Credit: Shutterstock/oilandgasphotographer

What factors should users consider when using XRF for trace element analysis?

Sulfur is the most common target in trace element analysis. Acceptable limits of sulfur are set in regulations, country by country.

For example, in gasoline, the regulations state that sulfur levels must be 10 PPM or less, while in diesel, this is 15 PPM or less. These regulations continue to be set lower and lower,

so we need to be able to measure as low as possible to adhere to these regulations.

Using energy-dispersive XRF, we can reach a detection limit of two PPM of sulfur, while using wavelength dispersive allows us to reach as low as 0.1 PPM - well within even the lowest regulations on either technique.

The other thing we have to consider is repeatability as this determines how reliable our results are. In one example application, we ran the same solution in 20 different cells, measuring an average concentration of 7.3% and a typical variation of less than 0.3 PPM.

This example confirmed very high precision from sample to sample, even using different cells. In fact, the cells were typically where we saw most of the variation.

What is XRF's role in quality control and contaminant analysis?

We can use XRF for quality control as part of oil analysis. There are many different areas where we can do this, such as avoiding wasting fuel or looking for hazardous materials. Oil may be contaminated by anything from wear metals to other environmental contaminants during routine use.

Chrome and nickel are some of the more common wear metals. Their presence in oil can indicate where a part is wearing, how fast it is wearing and where failures could potentially come from.

Contaminants like sulfur and fluoride generally come from environmental conditions. These need to be monitored to help minimize external contaminants in the oil.

Are there any other areas where XRF analysis is used?

There are a few more key areas where we can use **XRF** in the polymer field. For example, lubricating additives are intentionally added inorganic elements designed to enhance the effectiveness of different lubricants. These must be maintained and monitored via a QA/QC process because out-of-specification additives will result in out-of-specification oil materials.

Another essential part of the refinement process is the cracking catalyst – the catalyst used to break down the crude oil into its component hydrocarbons.

One of the main elements we need to monitor in this instance is the total chloride. This should be done in fresh regenerator spent alumina catalyst because the effectiveness of the catalyst may be affected if chlorine levels are too high.

We can also use XRF to evaluate suppliers, undertake R&D on new catalyst formulations, audit controls and evaluate recycling of the bulk catalyst. The best method for preparing

these samples is via what is known as fusion - the addition of lithium tetraborate and metaborate mixtures and fusing this into a solid glass disc. This then creates homogenous samples which offer long dynamic ranges.

Using fusion, we can calibrate different elements from a PPM level up to 100%. This is all done using the same linear regressions, making it very easy to do QA/QC control over a multitude of elements for the catalyst.

Polymer analysis by XRF

*Watch OnDemand
Webinar Here*



Working with polymers and plastics involves more products designed for the end-user, with less focus on refinement and more on plasticizers.

The analysis of polymer additives is another key focus in this area. These additives are inorganic elements added to polymers to give them different properties, such as stabilizers, flame retardants, antioxidants or colorants.

Some polymers also develop undesirable properties as they break down. When organometallics break down, for example, polymers will degrade and start releasing certain elements that are very toxic or environmentally damaging.

We can use XRF to monitor both these aspects - polymer additions and the breakdown of the polymer with respect to the environmental regulations.

When working with polymers, typical elements we can investigate via XRF include magnesium, calcium, iron, zinc, and more. These elements can be easily analyzed by EDXRF or WDXRF, with the best choice of technique depending on which elements are in the concentration range.

What sort of calibration steps are required when using XRF for polymer analysis?

We typically will do a matrix match calibration. This is where we take a calibration standard from a similar type of polymer with known concentrations, create linear regressions and then run our unknown sample against this.

If we don't have an exact matrix match, as long as we can get a liquid with the same density, we can often use those liquids to create different calibrations of our actual polymer samples.

In XRF, we only need to calibrate the system once, and we can maintain these calibrations for the instrument's life using something known as drift correction.

Drift correction uses samples that do not change over time. They are used to monitor the degradation of an X-ray tube or any other components and then factor in that change to ensure the calibration is relevant through the entire lifespan of the instrument.



Image Credit: Shutterstock/XXLPhoto

What role does XRF play in maintaining regulatory compliance when working with polymers?

The most common regulations that we see for hazardous materials or hazardous waste are RoHS and WEEE. These are sets of limitations around products' quantities of certain elements: cadmium, lead, mercury, chrome and bromide.

RoHS and WEEE stipulate that we have to measure different types of chromium and bromides. XRF can only tell us the total amount of chromium or the total amount of bromides, so we regulate to a level below chromium and the bromides, such that even if they were in these forms, they would be below the detection limits.

The US equivalent to RoHS (a European standard) is ASTM F2617. This standard requires monitoring the same elements at the same concentration ranges as RoHS.

We can meet all of these easily with a benchtop XRF system, with limits of detection a factor of a hundred or more, less than their restricted levels. Overall, XRF offers a

straightforward means of quantifying and identifying these toxic materials.

When is it more appropriate to use a WDXRF system in polymer analysis rather than an EDXRF system?

This depends on the elements and the concentration range in question. Once we start moving to lighter elements, results via WDXRF are far superior to EDXRF.

For example, if you want to start looking at fluorine, sodium and magnesium at lower concentration ranges, energy dispersive XRF will not provide that value for you – you should consider moving to a wavelength dispersive XRF instead.

The ASCM6247 standard defines lower and upper limits for many of these elements in process control: fluorine from 100 to 300 PPM, sodium from 25 to 200 PPM, magnesium from 10 to 600 PPM, etc.

These are limits that energy-dispersive XRF will not meet, but wavelength dispersive XRF will. We can still achieve all the limits required for heavy metal analysis in WDXRF.

In general, if an energy dispersive XRF system – which is lower cost and available as a smaller benchtop system – is suitable for the analytical techniques and samples required, this is likely a more appropriate choice. However, if an application requires detection that EDXRF cannot accommodate, then it will be necessary to step up and move to a WDXRF system.

Could you explain a bit about the UniQuant tool and how this fits into an overall polymer analysis workflow?

In wavelength dispersive or energy-dispersive XRF, we can perform analysis using standards. This allows us to do semi-quantitative analysis.

UniQuant is an ideal analysis tool for up to 79 elements in situations where appropriate standards are not available, where samples can only be obtained in a very small quantity, the samples have an irregular shape or you want to undertake coding or layer analysis from a substrate.

UniQuant is a peak-based analysis tool, offering much greater accuracy than a scan-based tool.

In a scan-based tool, we typically only spend fractions of a second at each individual 2 theta angle (or the keV in energy-dispersive XRF). This means that when we are just glancing over each peak or location very quickly, meaning it is likely that we will miss a trace element amount.

In a peak-based tool, we move to the known 2θ location (or keV location), measure this for a set amount of time - from 4 seconds and 12 seconds - and measure on a background position.

Peak to background precision is therefore much better because we are getting much better counting statistics through the analytical time. This 'peak-hopping' method is a much more accurate method for semi-quantitative analysis.

The total count time for these types of techniques is anywhere from 14 to 20 minutes, depending on how many elements we are looking at and what power of system we have. We typically look at elements from fluorine to uranium but using WDXRF; we can add other elements such as carbon, boron and nitrogen.

This calibration is maintained through the use of drift correction. It is also manipulable, meaning we can shrink the total analysis time by eliminating elements we know won't be there.

Alternatively, if we have a particular element that we need to measure with very high precision, we can increase the individual count time on that element without increasing the count time across the board.

What are the benefits of using the ARL QUANT'X tool as part of an XRF workflow, and how does this work?

The **Thermo Scientific ARL QUANT'X** features a 10-position sample changer, or it can analyze a single polymer sample with a specific platform.

With the sample loaded, we can continue to do the analysis. If we don't have a method for the sample, we can use UniQuant - the standard routine. A range of programs are available, including vacuum mode.

The analysis is started with the single press of a button, and the system provides updates at each stage of the analysis.

Once the first condition has been evaluated and elements detected, we can automatically label them and then expand around that with further conditions. As the keV level continues to be increased, further conditions may reveal additional elements present but not currently being excited enough to be displayed.

The system progresses from condition to condition, increasing keV and exciting different elements as it does. The elements immediately to the left of the major excitation pump will be excited most efficiently.

Once the analysis is complete, the user is returned to the main menu to look at the results and perform any calculations that need to be done.

About Christopher Shaffer

Christopher Shaffer is XRF, XRD, and OES Business Development Manager at Thermo Fisher Scientific. After graduating college, Chris started his career at the Ferro Corporation managing an analytical laboratory where he first learned the techniques of X-ray diffraction (XRD) and X-ray fluorescence (XRF). Chris joined Thermo Fisher Scientific in 2007 as an XRF applications specialist for North America and then held different roles in Europe and back to the US in product management and business management.



Thermo Fisher
S C I E N T I F I C

This information has been sourced, reviewed and adapted from materials provided by Thermo Fisher Scientific – Materials & Structural Analysis.

For more information on this source, please visit [Thermo Fisher Scientific – Materials & Structural Analysis](#).

Disclaimer: The views expressed here are those of the interviewee and do not necessarily represent the views of AZoM.com Limited (T/A) AZoNetwork, the owner and operator of this website. This disclaimer forms part of the [Terms and Conditions](#) of use of this website.

Structural Analysis of Polymers

Observing the structure of a material at various scales is key to understanding the performance of polymer-based materials.

How to Measure Polymer Materials with X-Ray Diffraction (XRD)

Polymer materials are employed in a huge array of applications across the various facets of contemporary society, from packaging materials to aerospace engineering. Virtually every application demands specific, often differing, properties. These properties are primarily determined by the structure of the polymer product.

Fast, Dynamic Analysis with Benchtop XRD. Video credit: Thermo Fisher Scientific – Materials & Structural Analysis

Key observables for polymer materials include the type of polymer – for example, polyethylene (PE) or polypropylene (PP) – or its crystallinity. Polymers also exhibit varying microstructures, much like those found in common metal alloys, like steel. These microstructures also influence polymer materials' mechanical properties.

It is widely recognized that the introduction of additives or pigments to polymer matrices facilitates the finetuning of different properties, such as optical or physical properties.

It is important that users and producers in highly industrialized environments are able to rapidly screen products to ensure they possess appropriate properties.

One straightforward and quick way to perform this screening lies in the use of X-ray diffraction (XRD) combined with whole pattern Rietveld refinements. This approach represents an ideal solution for QC/QA or research-related applications.

In a recent study, the [Thermo Scientific™ ARL™ EQUINOX 100 Diffractometer](#) was used to evaluate a number of key polymer properties.



Thermo Scientific ARL EQUINOX 100. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Identification of Type and Polymorphism

After analysis, a comparison of acquired results to the ICDD PDF4+ Organic database clearly confirmed that the results showed high-density Polyethylene (HDPE) and Isotactic Polypropylene.

Additional qualitative phase analyses confirm the presence of Polyethylene (PE) and Polypropylene (PP) type materials.

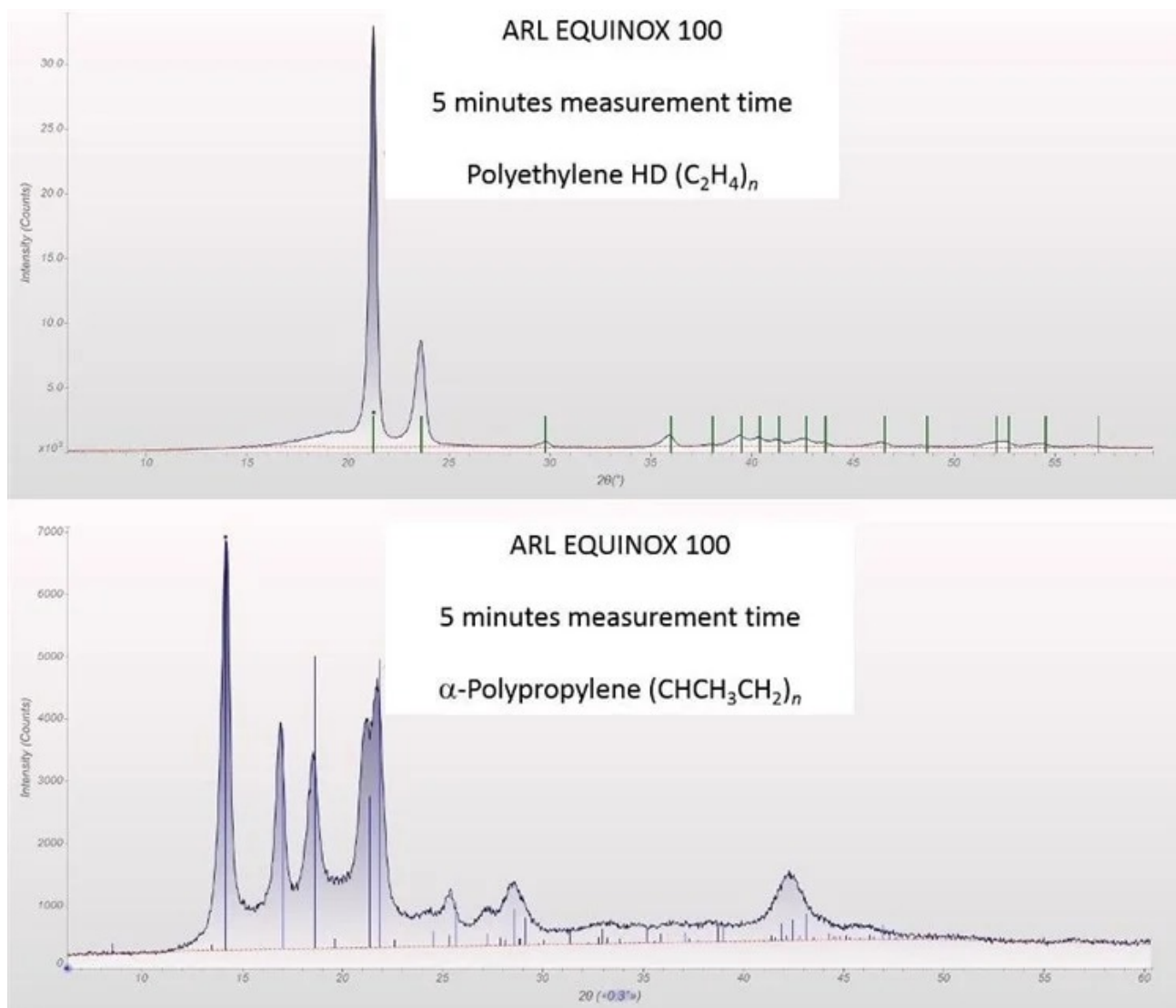


Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Degree of Crystallinity (DOC)

By using [MDI JADE 2010](#), it is possible to directly determine D via a standardless refinement method. This approach involves the intensity of the amorphous contribution being directly determined by deconvoluting the diffraction pattern via Rietveld's method.

In this example, a calculation of the amorphous content (in w%) used a density of 0.85 g/cm³, confidently providing results for both PE and PP samples with high and low D values.

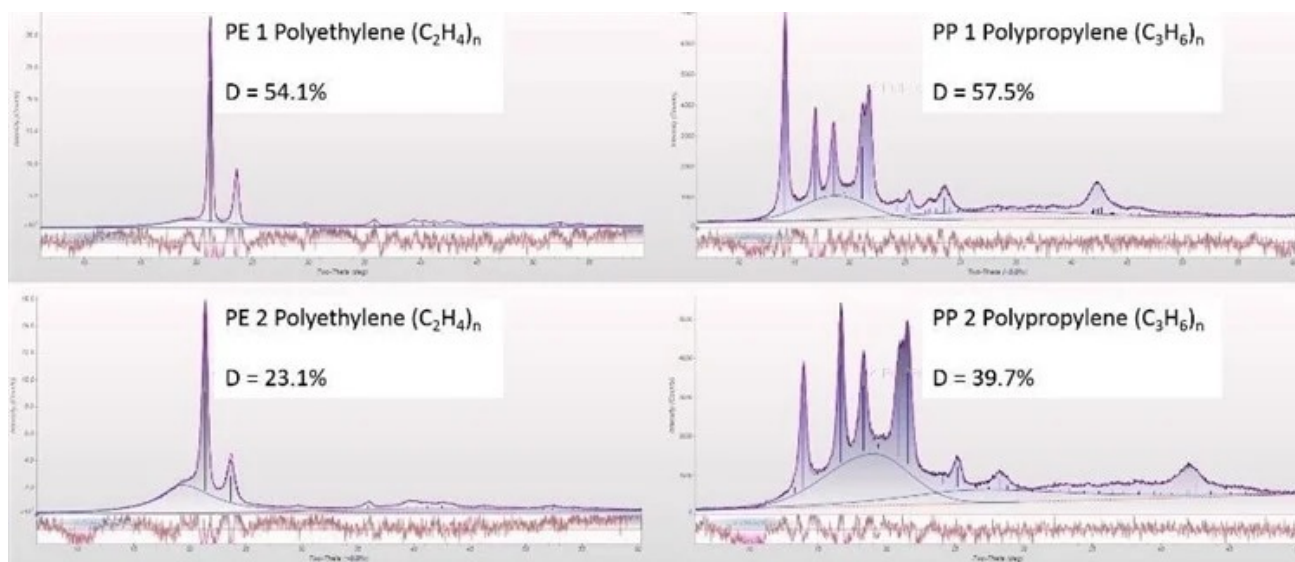


Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Polymorphism and Crystallite Size

A comparison of the acquired data to the ICDD PDF4+ Organic database highlights predominantly β -PP (blue) and traces of α -PP (grey). Domain sizes were found to differ between β -PP (33 nm) and α -PP (10 nm).

It should be noted that the intergrowth structure of α -PP and β -PP is central to the resulting material properties, prompting this observable to be widely used in industrial applications.

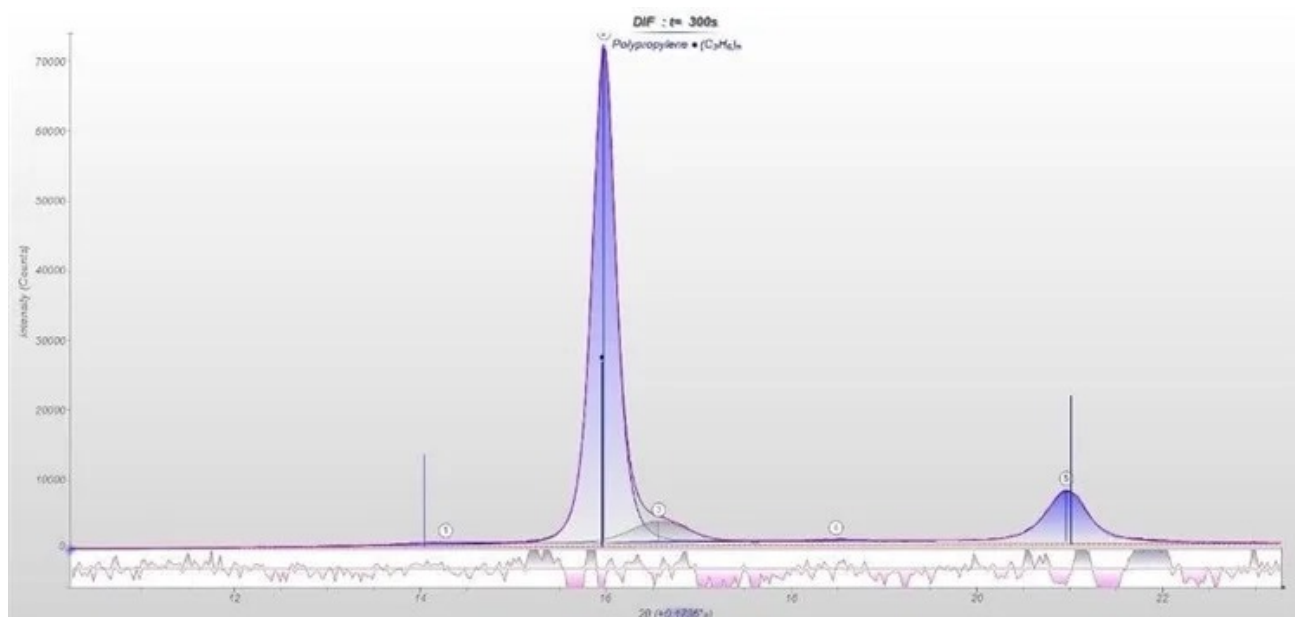


Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Additives and Pigments

In the example presented here, the application of XRD to a resin sample with embedded Al and TiO₂ (rutile) particles quantified an amorphous content of 98% (XRF:98%), 0.9% TiO₂ (XRF: 0.74%) and 1.1% Al (XRF: 1.16%).

These results were achieved via Whole Pattern Rietveld refinement with MDI JADE 2010, which affords users a robust and standardless method for the quantification of amorphous content.

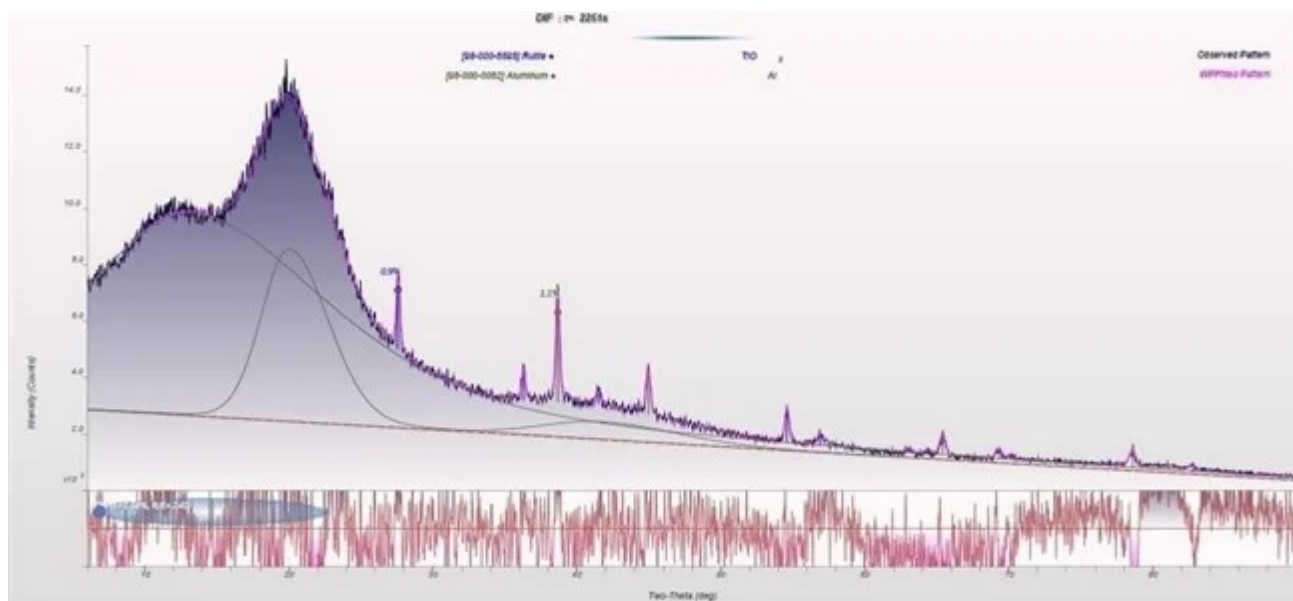


Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Instrumentation and Experimental

The Thermo Scientific™ ARL™ EQUINOX 100 X-ray diffractometer features a custom-designed Cu (50 W) or Co (15 W) micro-focus tube that is equipped with mirror optics.

As the system is low wattage, this does not necessitate the use of an external water chiller or additional peripheral infrastructure. The instrument can therefore be easily transported between laboratories or from the laboratory to the field.

The **ARL™ EQUINOX 100** is highly suited to both reflection and transmission measurements. The instrument also offers rapid data collection

Interested in the instruments highlighted in this article?

time versus other traditional diffractometers. This is due to its unique curved position sensitive detector (CPS), which is able to simultaneously measure all diffraction peaks in real-time.

*Request a quote, demo,
or conversation with an
expert at
[thermofisher.com](https://www.thermofisher.com)*



In the XRD measurements highlighted here, sheet samples of PE (polyethylene) and PP (polypropylene) were measured in transmission geometry for 5 minutes. The resin sample was measured for a total of 38 minutes using Cu-K α radiation.

The obtainable data quality from the benchtop ARL™ EQUINOX 100 is comparable to that of a common high-power floor-standing instrument.

In the example presented here, both qualitative and quantitative analysis was undertaken using MDI JADE 2010 and the ICDD PDF4+ Organic database.

Acknowledgments

Produced from materials originally authored by Ju Weicai, Raphael Yerly and Dr. Simon Welzmueller from Thermo Fisher Scientific.



This information has been sourced, reviewed and adapted from materials provided by Thermo Fisher Scientific – Materials & Structural Analysis.

For more information on this source, please visit [Thermo Fisher Scientific – Materials & Structural Analysis](#).

Rheological Analysis of Polymers

Due to their chemical structure and high molecular weight, polymers exhibit a complex flow and deformation behavior - showing both viscous and elastic properties. Knowing the viscoelastic properties of a polymeric material is therefore essential to optimize formulations and production processes.

Optimizing Polymeric Materials with Rheological Analysis

Plastics are widely used polymeric materials employed in a diverse array of applications and across a wide range of popular consumer products.

Polymers used in the production of plastics are typically processed at higher temperatures, working with these in a molten state. Properly comprehending their melting, deformation and flow is central to effectively processing and transforming these into end products.

Polymers are regarded as viscoelastic materials, meaning that they exhibit both viscous (liquid-like) and elastic (solid-like) properties. Their high molecular weight and chemical structure cause polymer melts to exhibit a complicated flow and deformation behavior.

The ability to optimize blends and formulations is dependent on a good knowledge of a polymeric material's viscoelastic properties. This knowledge is also essential to adapting a process to the properties of a specific material.

A polymer melt's molecular structure, testing conditions or processing conditions will generally determine whether its viscous or elastic behavior is dominant.

Too much elasticity may result in flow anomalies and undesirable effects during a range of common processing steps,¹ for example, a melt stream may swell as it exits the narrow die of an extruder.

Figure 1 displays a series of other examples of flow anomalies resulting from the elastic properties of polymeric fluids.



Figure 1. Typical flow anomalies of viscoelastic polymer fluids. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Two tools frequently employed in the measurement of polymer melt viscosities are capillary

viscometers and melt flow indexers. These instruments do not offer any insight into the viscoelastic properties of the tested sample, however.

In contrast, the use of a rotational rheometer with the capacity to perform rheological tests with small oscillatory mechanical excitations can offer users a robust and comprehensive investigation into these properties.

This article offers an overview of the various rheological tests which can be conducted using rotational rheometers. It also outlines how the results of these tests relate to a range of processing conditions and final product properties.

Rotational Versus Oscillatory Testing – The Cox-Merz Rule

Rheology is widely recognized as an excellent tool for the analysis of polymers' mechanical properties in their various physical states. A number of testing methods can be employed to comprehensively characterize the rheological behavior of polymeric materials.

Rotational steady-state shear experiments offer a means of measuring the non-Newtonian viscosity of dilute and semi-dilute polymer solutions, but the application of an oscillatory shear deformation remains the testing method of choice for polymer melts and solids.

This is because of polymer melts' high elasticity and their tendency to result in edge failures when exposed to the large deformations typical in a rotational rheometer.

The Cox-Merz rule states that when complex viscosity ($|\eta^*|$) is derived from oscillatory frequency sweep measurements plotted against the angular frequency (ω), this will be identical to the steady-state shear viscosity determined via rotational testing plotted against the shear rate.²

The Cox-Merz rule is an empirical rule applicable to a wide range of polymer melts and solutions.

Figure 2 compares viscosity data acquired from rheological tests in rotation versus data acquired in oscillation mode.

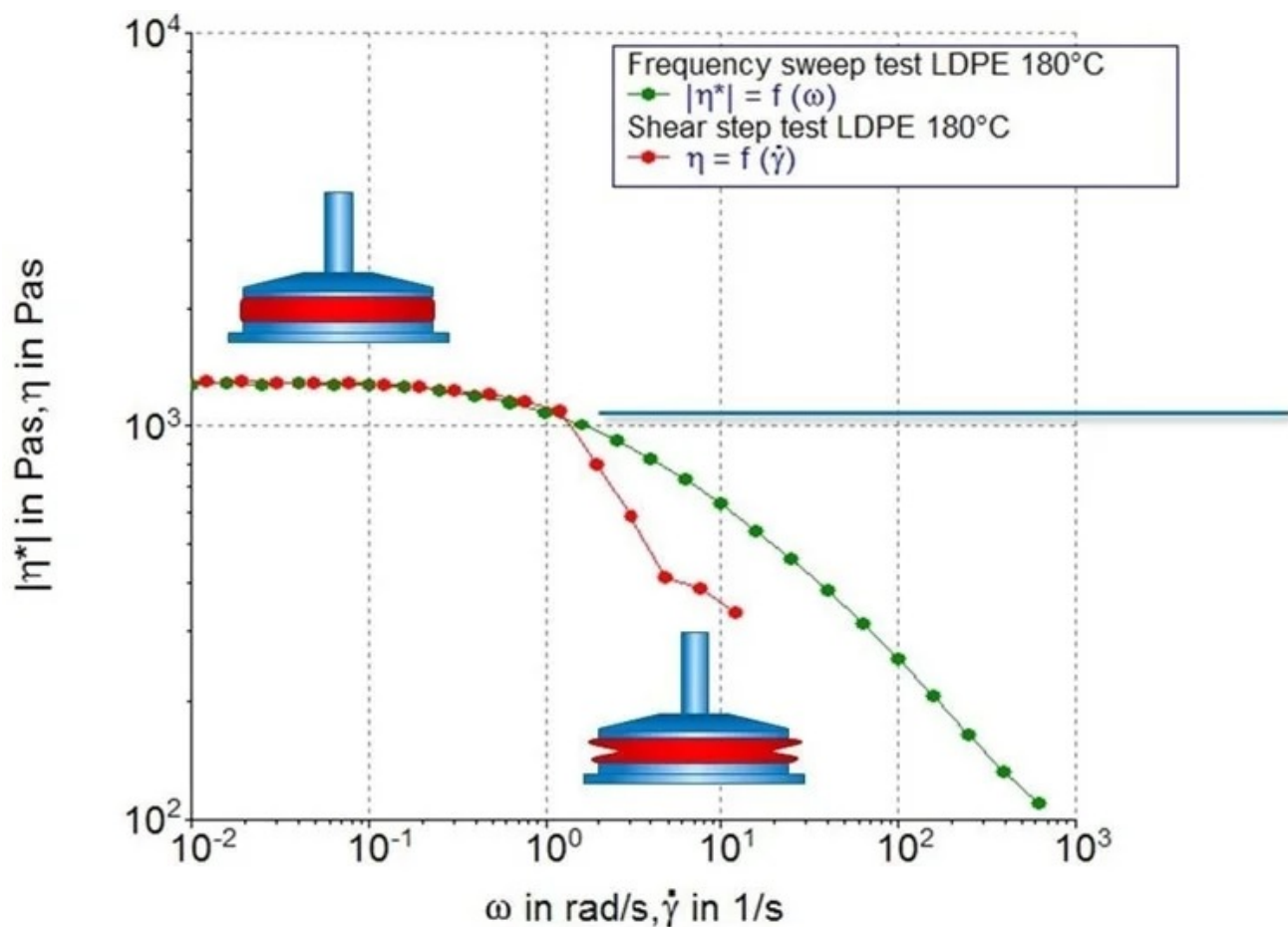


Figure 2. Comparison of viscosity data obtained from a steady state shear (red symbols) and an oscillation frequency sweep test (green symbols). Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Viscosity begins to decrease as the end of the Newtonian (zero shear viscosity) plateau is reached. At this point, the shear viscosity (red symbols) drops abruptly and ceases to display a smooth and continuous progression.

This observable drop is the result of sample fracture at the edge of the measuring geometry, a phenomenon caused by secondary flow fields.¹ It should be noted that the oscillation frequency sweep (green symbols) provides higher data quality and can accommodate a broader frequency range.

The oscillatory frequency sweep's enhanced testing range is due to the small amplitudes of the imposed oscillatory shear. Therefore, conducting an oscillatory frequency sweep and applying the Cox-Merz rule is the method of choice when looking to acquire shear viscosity data for polymeric materials.

Using Amplitude Sweep Tests to Identify Linear-Viscoelastic Range

It is important that the applied sinusoidal oscillatory deformation is relatively small and within a material's linear viscoelastic range (LVR) to ensure that viscosity data from a frequency sweep experiment is comparable.

When maintained within its LVR, the material's microstructure remains unchanged. Its rheological properties will also remain constant and unaffected by the applied stress of deformation; for example, the storage and the loss modulus (G' and G'' , respectively) or the complex viscosity.

Should a critical deformation or stress value be reached, this will prompt the material's microstructure to change, and in turn, its rheological parameters.

To determine the linear viscoelastic range of a material, it is necessary to conduct an oscillation amplitude sweep test. This test must be performed at a constant frequency and involves a gradual increase of the sinusoidal deformation or stress applied by the rheometer.

Results of an amplitude sweep for LDPE at 190 °C are displayed in Figure 2.

In the example presented here, the rheometer software has automatically calculated the end of the linear viscoelastic range of this LDPE melt, determining this to be equal to a deformation of 55%.

It is also advisable to perform additional tests in oscillation mode at a deformation below this critical value, for example, frequency, temperature or time sweep tests. This is unnecessary for tests intended to be outside the LVR, however.

Should it be necessary to perform a frequency sweep test over a wider frequency range of several orders of magnitude, it is advisable to undertake a number of amplitude sweeps at various frequencies to ensure the selected deformation is within the LVR throughout the whole frequency range.

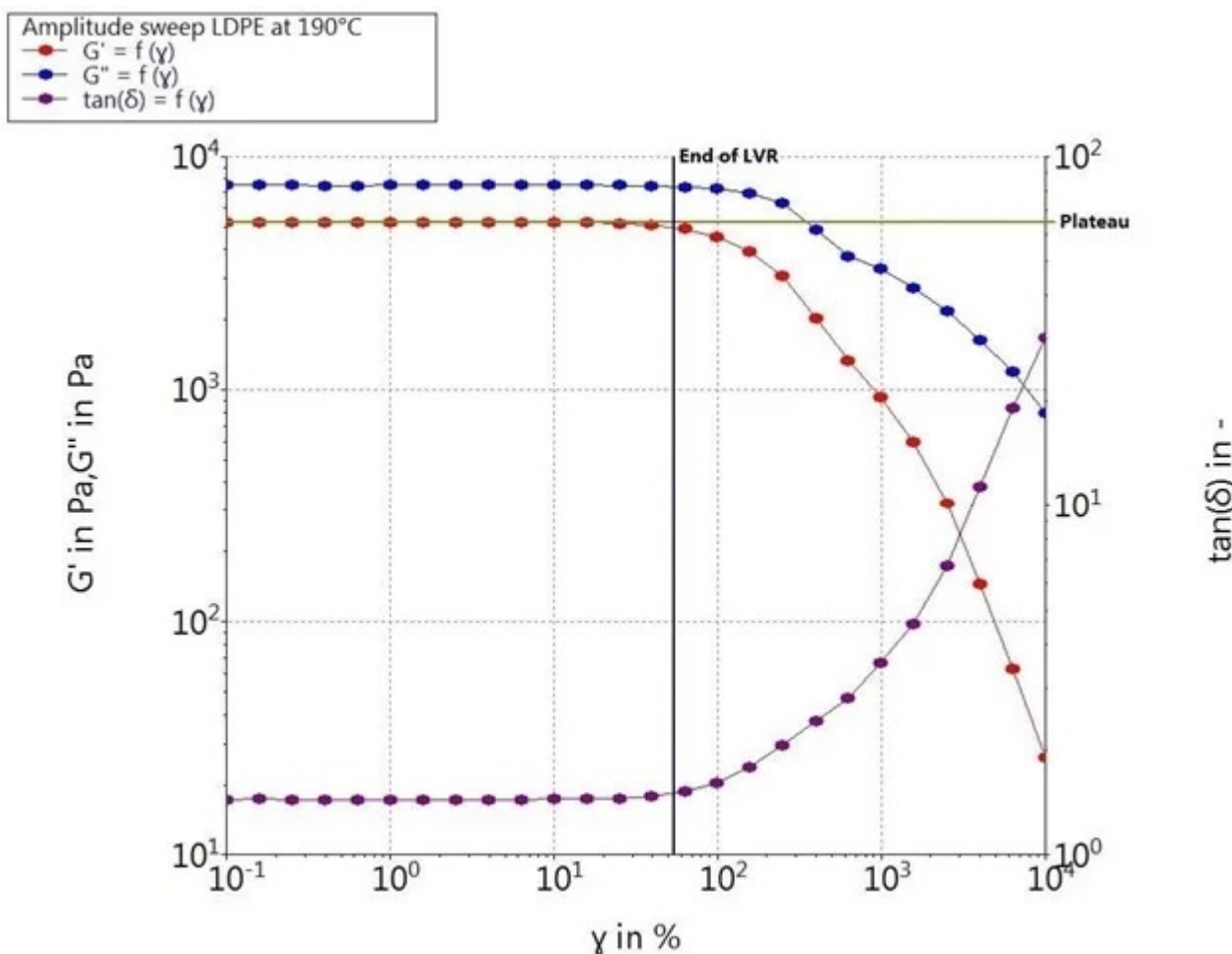


Figure 3. Storage modulus G' , loss modulus G'' and the complex viscosity η^*I as a function of the deformation γ for a LDPE melt at 1 Hz and 190 °C. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Using the Frequency Sweep Test to Determine a Material's Viscoelastic Fingerprint

A diverse array of information can be acquired from performing rheological tests in oscillation mode.

For example, the acquisition of shear rate-dependent viscosity data via oscillatory frequency sweep experiments can be processed using the Cox-Merz rule to quantify a material's flow resistance during high shear processing applications such as injection molding or extrusion.

In contrast, low frequency/shear data (for example, zero shear viscosity / η_0) can be employed to calculate the average molecular weight (Mw) of a polymer melt. This is achieved via the following formula:

$$\eta_0 = K \cdot M_w^{3.4} \quad (1)$$

Within this equation, the prefactor (k) is dependent on the polymer's molecular structure.³ Equation 1 is applicable to polymers with a linear chain structure and a molecular weight above a critical value (M_c).

Figure 4 displays an example viscosity curve of a polystyrene melt, highlighting the corresponding shear rate ranges encountered in several routine processing applications.

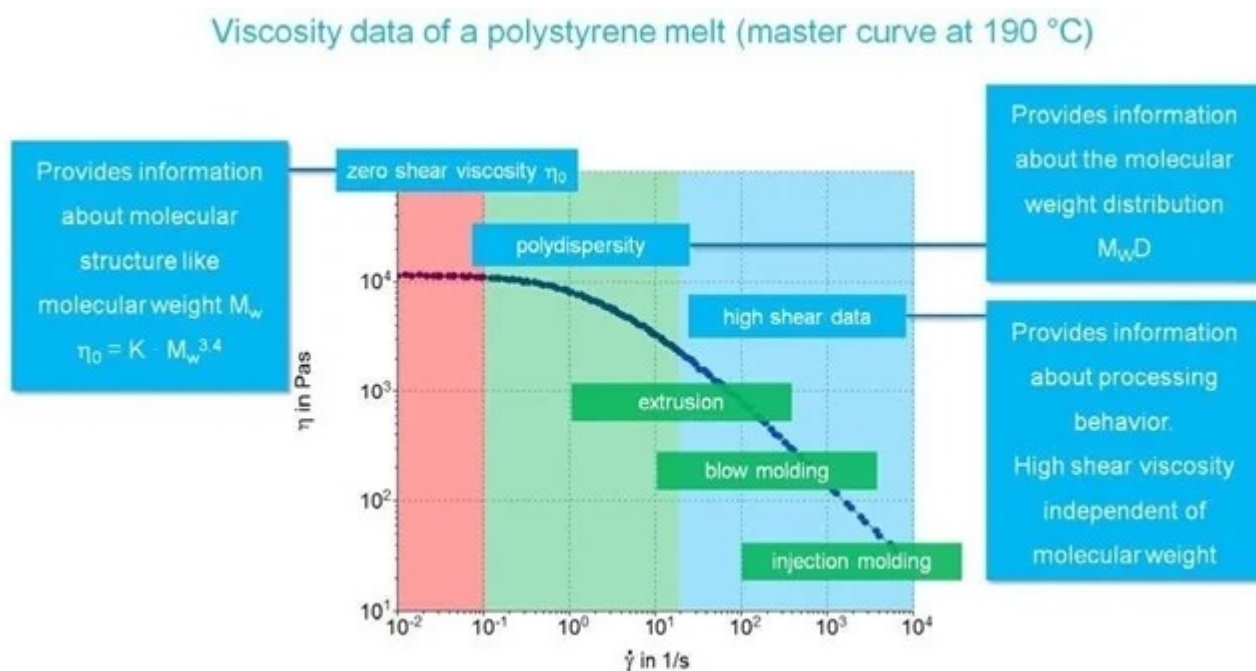


Figure 4. Shear rate depending viscosity of a polystyrene melt and typical applications.

Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Frequency sweep data also offers a means of directly measuring a polymer's viscous and elastic properties. These properties are represented by the storage and the loss moduli (G' and G'' , respectively) and are generally measured at varying frequencies and timescales.

Data from these measurements can illustrate the general structure of a material, alongside valuable information on its molecular weight (M_w) and molecular weight distribution (MWD).

It is possible to employ repetitive frequency sweep measurements over a narrow frequency range to capture the crossover point. This, therefore, enables the detection of thermal degradation, triggering alterations to the MW and MWD.

Figure 5 illustrates an example of this crossover point shifting, highlighting where $G' = G''$ and the MW or MWD differ for an otherwise identical polymer melt.

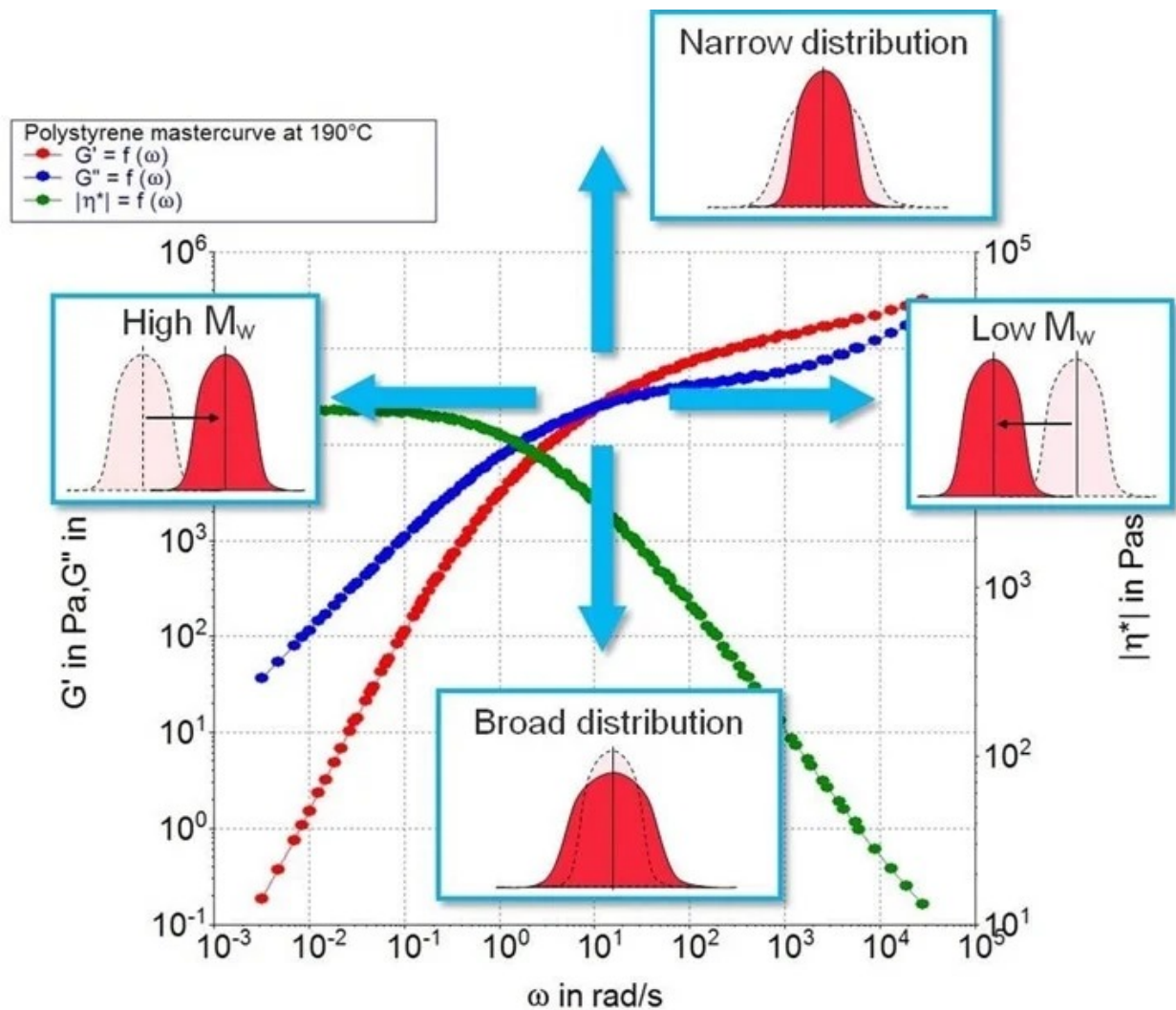


Figure 5. Storage modulus G' , loss modulus G'' and the complex viscosity $|\eta^*|$ as a function of the angular frequency ω for a polystyrene melt at 190 °C. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Flow anomalies caused by the elasticity of polymer melts may adversely affect product quality in extrusion and other polymer processing applications.

Figure 6 compares storage modulus data as a function of the applied frequency for a number of polyethylene samples with differing Melt Flow Indices (MFI).

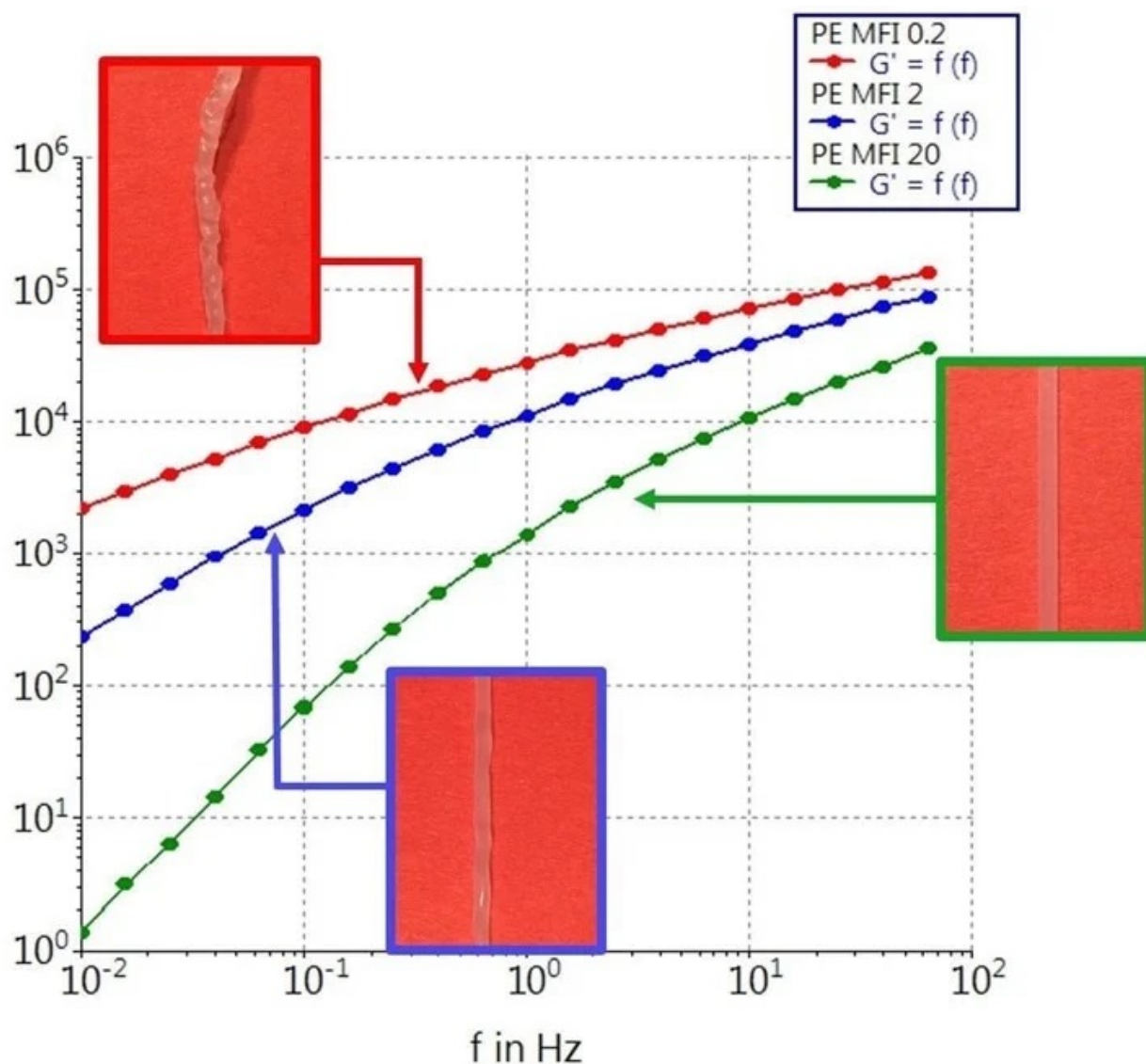


Figure 6. Storage modulus G' as a function of the angular frequency ω for polyethylene melts with different MFI at $190\text{ }^\circ\text{C}$. The images show the extrusion strands that were prepared with the melts in a twin screw extrusion process. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Each of these three PE samples was processed under identical conditions using a 16 mm parallel twin screw extruder.

Once they reached the end of the extruder barrel, the melts were forced through a vertical rod capillary die with a diameter of 1 mm and an L/D ratio of 10. A laser micrometer was employed to measure the die swell of the extrudate.

A die-swell of 0.5 mm was found to result in a total strand diameter of 1.5 mm for the PE with the lowest molecular weight and highest MFI (~ 20). The strand exited the extrusion line as an even strand with no observable surface defects (Figure 6).

The PE sample exhibiting medium MFI (~2) displayed an uneven surface structure with a changing diameter, while the PE sample exhibiting the lowest MFI (~0.2) and highest molecular weight displayed obvious indications of melt fracture under the extrusion conditions also utilized for the other samples.

An examination of the rheological data highlights that the three samples are notably different in terms of their elasticity (G'). This is particularly prevalent at the lowest frequency (10^{-2} Hz), where the values in G' differ in one or more orders of magnitude.

Storage modulus also offers a sensitive indicator of the elasticity incorporated by a high molecular weight tail.

Figure 7 compares the results of a total of three frequency sweeps performed on a low molecular weight LDPE and two blends of an identical LDPE that also featured a small weight fraction of a high molecular weight PE.

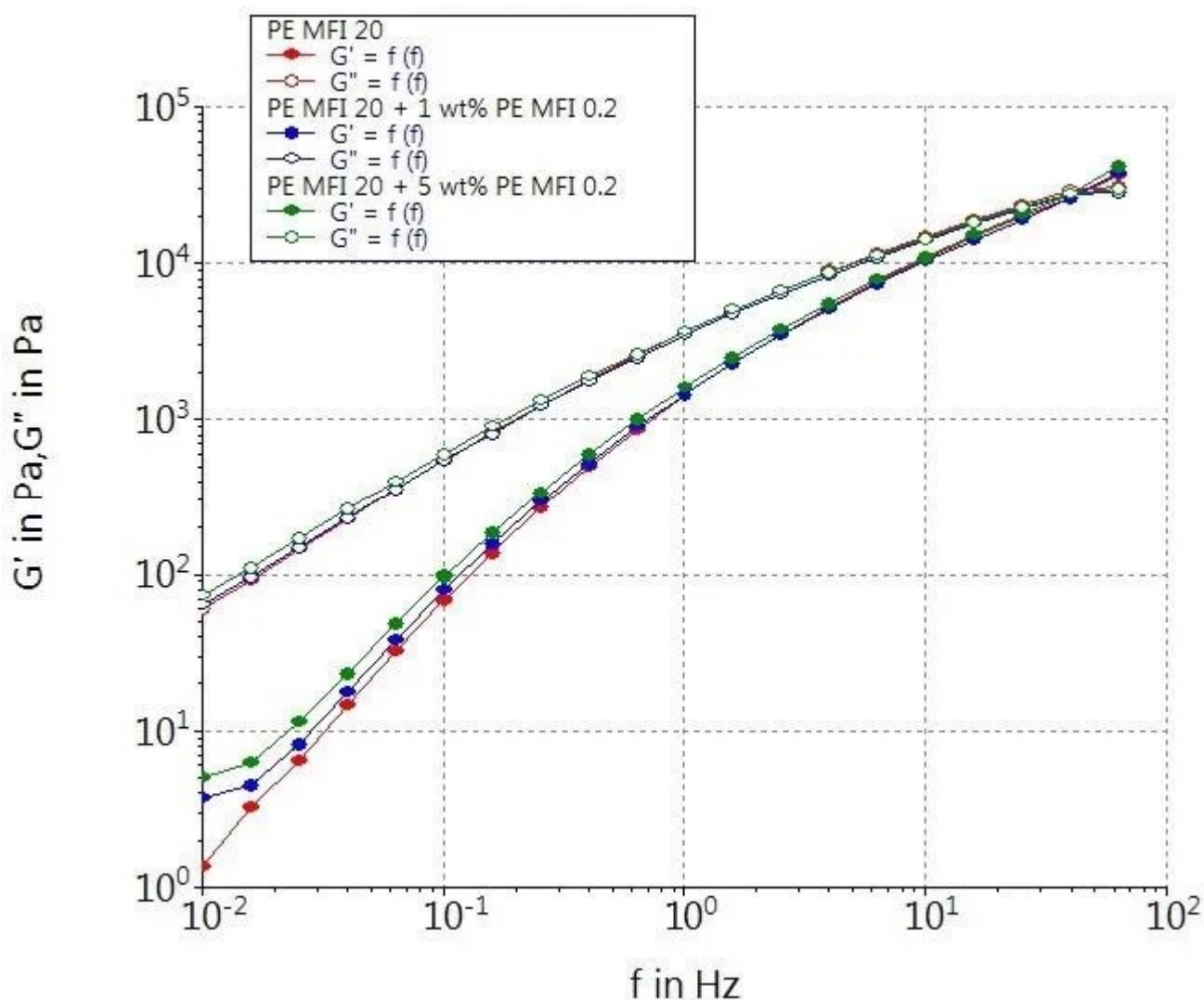


Figure 7. Storage modulus G' and loss modulus G'' as a function of the angular frequency

ω for a low molecular weight polyethylene melt and two blends at 190 °C. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

G' shows clear differences for these three melts in the low frequency range, and a small fraction of 1 wt% of high molecular weight PE can also be detected.

It should be noted that it is rarely possible to view these small differences when employing [Gel Permeation Chromatography](#) (GPC) or related techniques to ascertain molecular weight distribution.

MFI results achieved via a capillary viscometer would also fail to reveal differences between the three samples.

Storage modulus data acquired via oscillatory frequency sweep experiments remains the most sensitive indicator of a high molecular weight tail in a polymer melt.

It is important to acquire this data because even small amounts of high molecular weight fraction can lead to flow anomalies that negatively impact final polymer strand quality.

Figure 5 displays rheological data obtained over an angular frequency range from less than 10^{-2} rad/s to over 104 rad/s. Acquiring rheological data over such a wide range requires more than a single frequency sweep test.

Both the low and high frequency regions are limited by time issues (for example, duration of a single oscillation) or rheometer specifications (for example, maximum frequency).

These limitations can be overcome using the time-temperature superposition principle, however.

Using the Time-Temperature Superposition Principle to Extend Measurement Range

A single frequency sweep test will generally cover between 2 and 4 orders of magnitude. Application of the Time-Temperature Superposition (TTS) principle can effectively extend the data range beyond the low- and high-end frequencies.

TTS leverages the principle that both temperature and frequency (time) affect the viscoelastic behavior of polymer melts in similar ways,³ meaning that it is possible to perform a number of frequency sweeps over a smaller range at different temperatures.

A data set (at one temperature) is selected as a reference, allowing a master curve to be generated by shifting other results towards the reference curve.

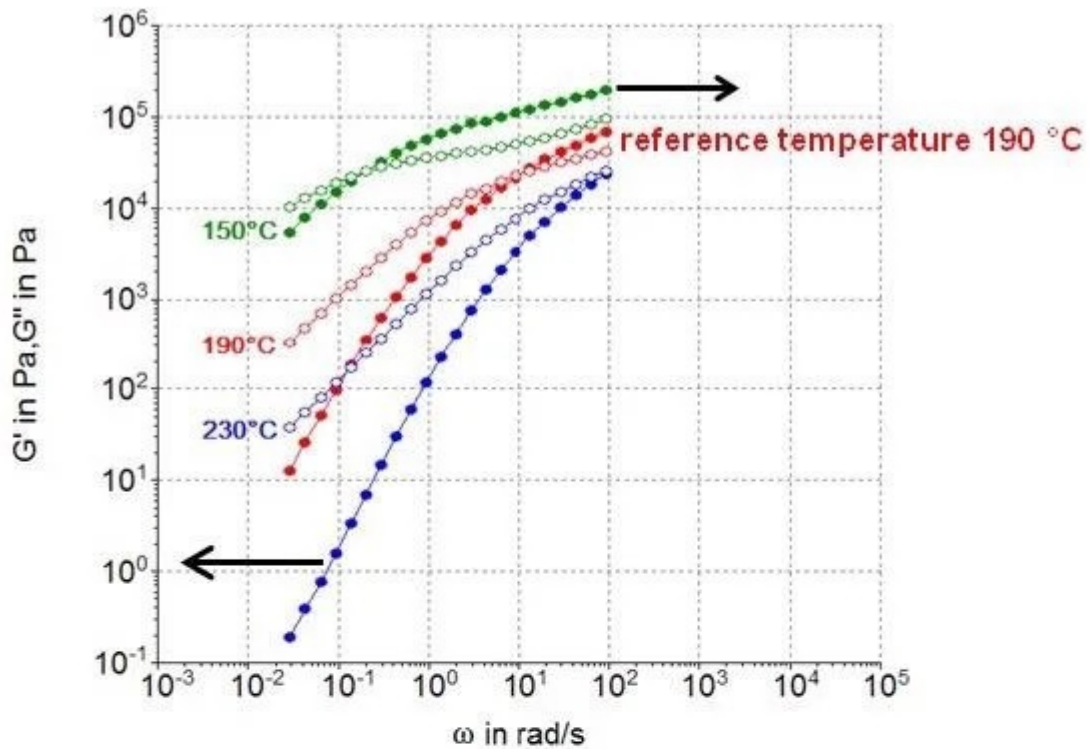
It is, therefore, possible to acquire rheological data over a much wider frequency range when using the TTS principle, particularly when compared to a single frequency sweep experiment.

TTS is applicable to many polymer melts and blends, but this is generally only a viable tool when used over a limited temperature range.⁴

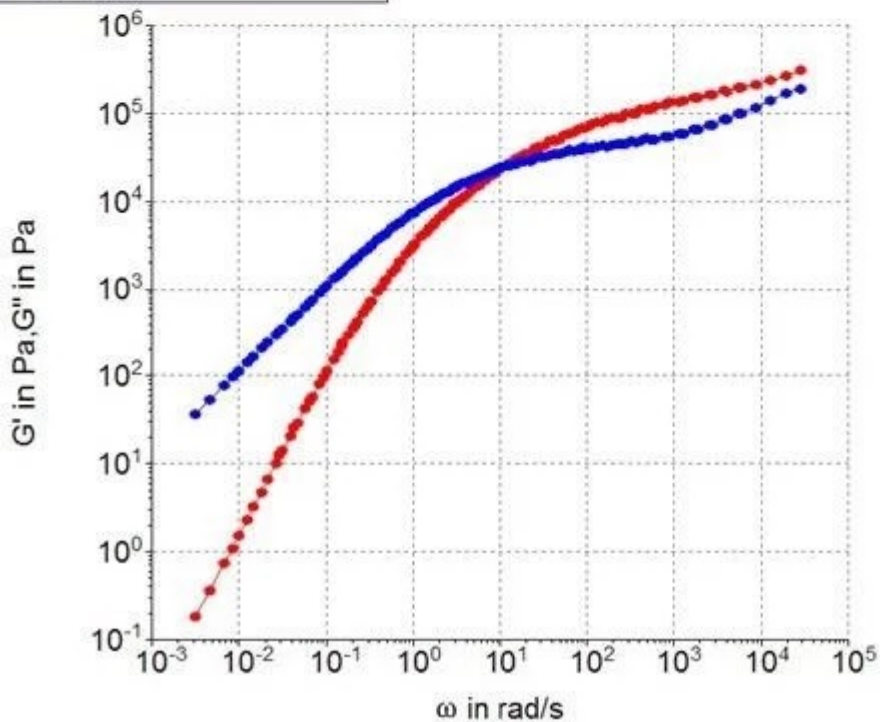
Figure 8a displays results from a number of frequency sweep tests conducted at various temperatures.

The TTS principle was applied to these results, with 190 °C chosen as a reference temperature, generating a master curve (Figure 8b) which includes viscoelastic data over almost 8 orders of magnitude in frequency.

8a



Polystyrene mastercurve at 190°C
 ● $G' = f(\omega)$
 ● $G'' = f(\omega)$



8b

Figure 8. Application of the Time-Temperature-Superposition principle with a polystyrene melt. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

It is possible to divide the master curve into three regions. At low frequencies, the sample is in the terminal region prompting the polymer melt to exhibit predominantly viscous behavior.

Material behavior in the terminal region is controlled by long molecule chain relaxation processes, while G' and G'' typically have slopes of 2 and 1 in a double logarithmic plot in this region.

At medium frequencies, however, a transition takes place with a crossover between G' and G'' . In this scenario, viscoelastic behavior is primarily driven by the polymer's molecular weight distribution.

At the highest frequencies, the sample exhibits predominantly elastic behavior, with G' larger than G'' . In this scenario, the polymer's behavior is controlled by the rapid relaxation motion of the shortest polymer chains.

G' and G'' data obtained over a wide frequency range can also be employed in the calculation of molecular weight and molecular weight distribution for a significant number of linear thermoplastic homopolymers.

This is achieved by ensuring that the tested frequency range includes data from the low frequency terminal region to the end of the high frequency plateau region.

Using Dynamic Mechanical Thermal Analysis to Investigate Final Product Properties

It is also possible to utilize rotational rheometers in [Dynamic Mechanical Thermal Analysis \(DMTA\)](#), applying this technique to solid, rectangular-shaped polymer specimens.

DMTA testing involves a material being exposed to oscillatory mechanical excitation while its temperature is continuously altered.

Data acquired throughout this process can be used to identify characteristic phase transitions, for example, glass transition, melting and/or crystallization within the polymer matrix.

DMTA can also be used to evaluate final product performance and to investigate the robustness of specific application-based properties, such as brittleness, stiffness, damping or impact resistance.

Figure 9 displays an example DMTA test performed on a semi-crystalline polyetheretherketone (PEEK) sample.

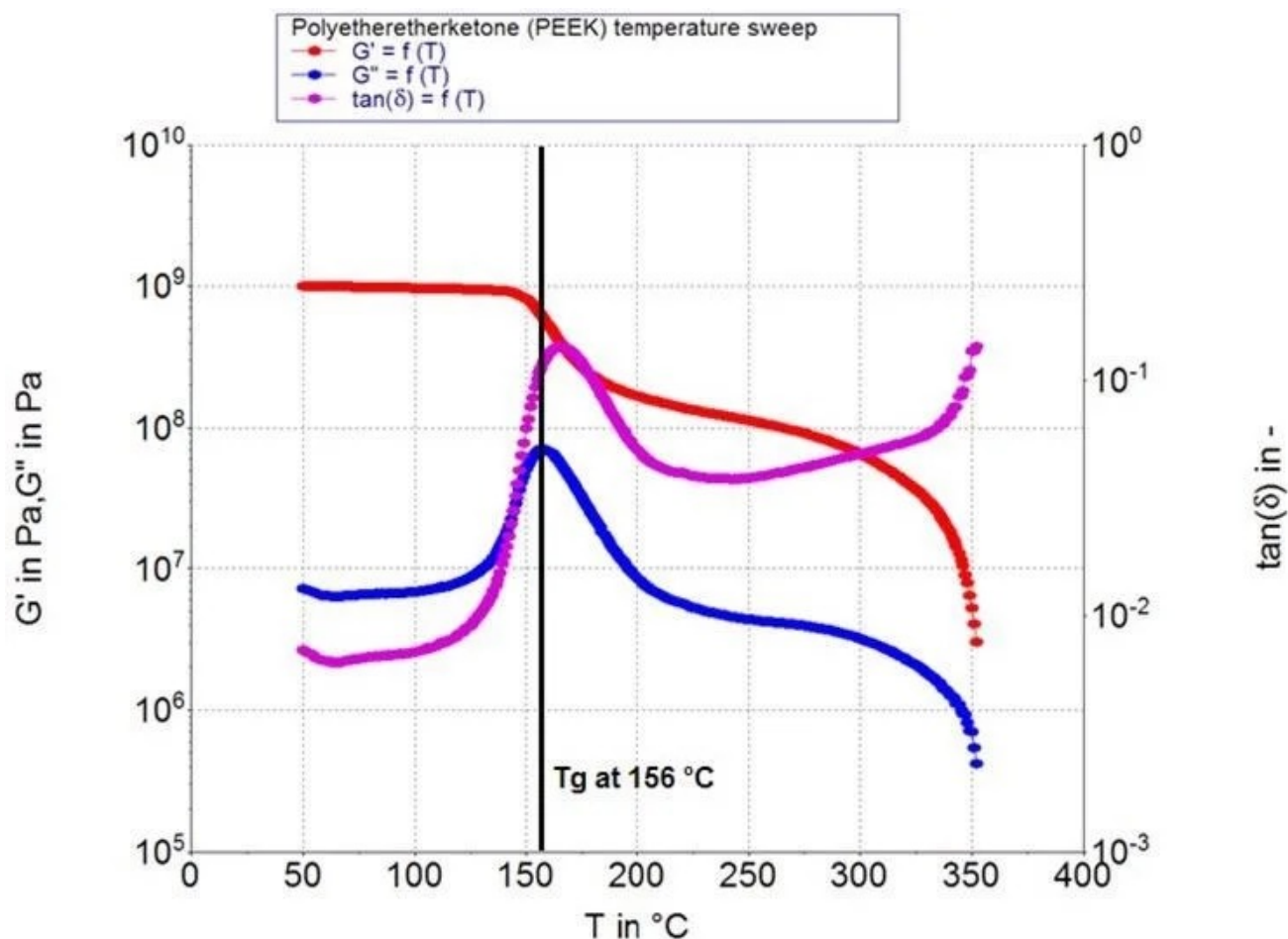


Figure 9. Storage modulus G' , loss modulus G'' and $\tan\delta$ as a function of temperature for a polyetheretherketone. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

This was tested from below its glass transition to slightly under its melting temperature, supported by the use of a specialized solids clamping tool designed for rotational rheometers.⁵

A lab scale injection molding system was used to prepare the rectangular sample.⁶ A material's glass transition can be identified using different metrics under rheological testing, with the most common metric utilizing the maximum in the loss modulus G'' .

The initial decrease in the storage modulus G' or the maximum in the $\tan\delta$ (G''/G') can also be used to highlight glass transition.

In the example presented in Figure 9, the maximum in G'' is found in the center of a wider transition range, while the onset of the G' decrease is close to the beginning of the transition. The maximum in $\tan\delta$ is found close to the end of this range.

Figure 10 showcases the generalized behavior of a polymeric sample during a temperature

sweep test.

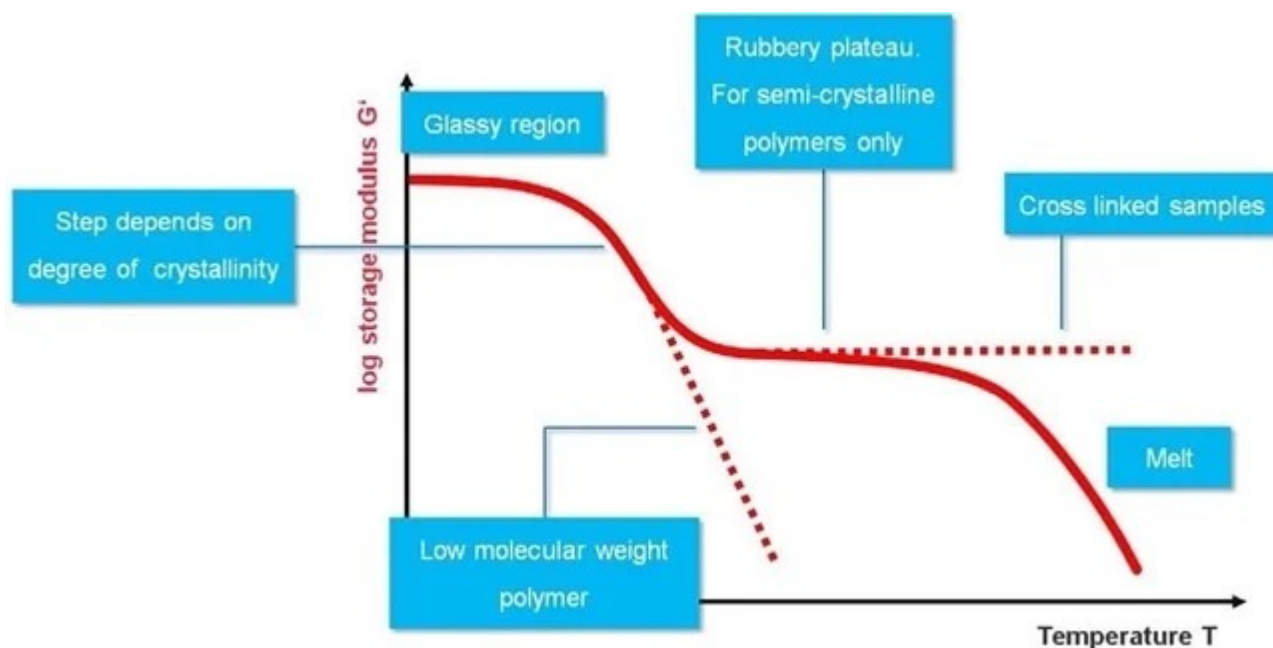


Figure 10. Generalized behavior of polymer sample in a DMTA test. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Semi-crystalline polymers will always transition from a glassy region at low temperatures, shifting to a rubbery plateau and ultimately into their melt state when subjected to higher temperatures.

The step height from the glassy region to the rubbery plateau is dependent on the polymer's degree of crystallinity - as the degree of crystalline domains in the polymer increases, this, in turn, causes a decrease in step height between the two regions.

It should also be noted that low molecular weight polymers do not exhibit a rubbery plateau. In these examples, once the glass transition is complete, the material will change to a soft melt with G' decreasing in line with increasing temperature.

Cross-linked polymers do not melt at all, however. These remain in a rubbery state until the onset of thermal decomposition.

Benefits of Extensional Testing

Extension is the third primary flow type that can be investigated rheologically. Extensional flows occur in processes such as spraying and vessel filling, but these are not very common for polymer melts.

Rather, extensional flows tend to occur in polymer melt processes in the form of film blowing, fiber spinning, injection molding or foam extrusion.

Figure 11 illustrates transient extensional viscosity at a range of extensional deformation rates for two different polyethylene samples.

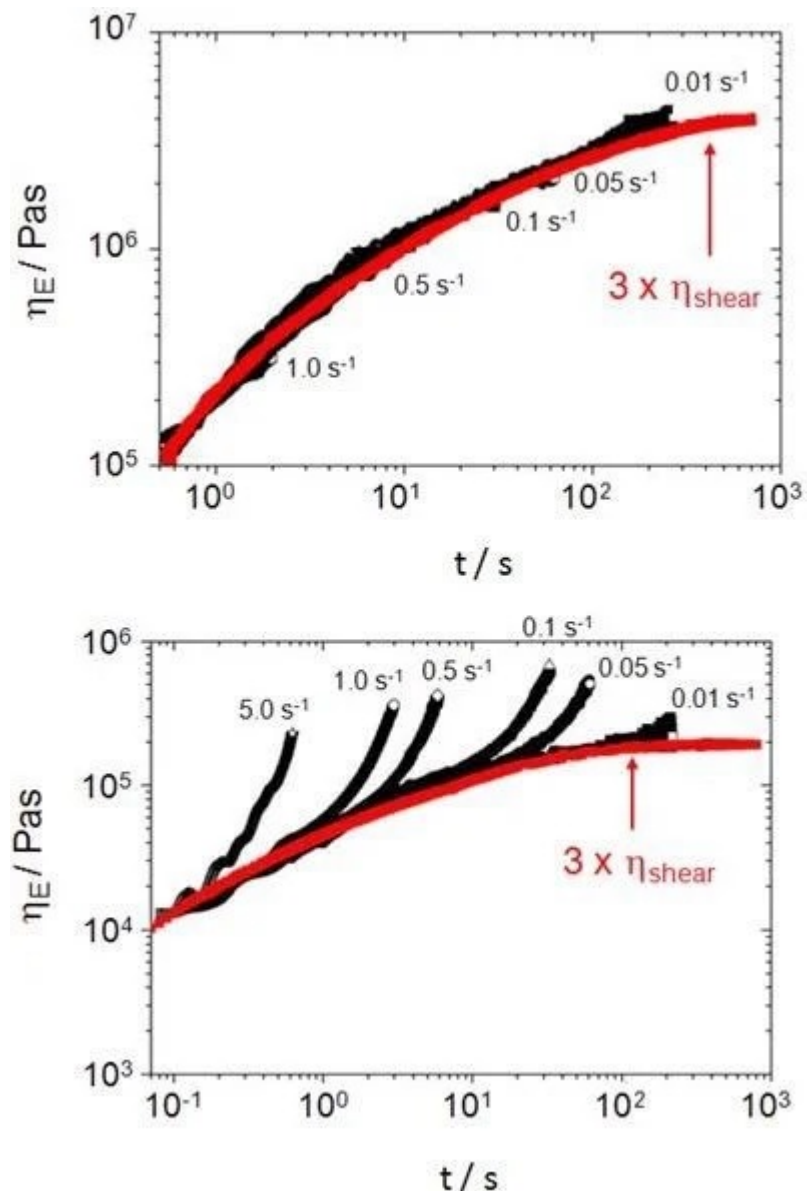


Figure 11. Extensional viscosity as a function of strain rate for a non-branched HDPE (top) and highly branched LDPE (bottom). All tests were performed at 150 °C. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

These tests were conducted using the Sentmanant Extensional Rheometer (SER) fixture designed for use with rotational rheometers.⁷

The plot on the left displays the extensional behavior of a non-branched high-density polyethylene (HDPE) sample - no observable strain hardening occurred for this type of

material.

The plot on the right displays the results of identical experiments and was performed with a highly branched low-density polyethylene (LDPE) sample.

The red curves in the images indicate transient shear viscosities multiplied by three according to the Trouton ratio for uniaxial extension.⁸ This shear viscosity data was acquired via rotational step experiments.

The extensional behavior of the branched LDPE sample was notably different from the behavior observed in shear flow, unlike the linear HDPE sample. The LDPE sample displayed shear hardening behavior throughout extensional testing, particularly at higher deformation rates.

Strain hardening behavior offers advantages to polymer processing techniques, including film blowing or fiber spinning. A comprehensive understanding of a polymeric material's extensional behavior is a key factor in optimizing its final product properties.

This behavior cannot be measured and evaluated using standard rotational rheological measurements.

Conclusion

Knowledge of a polymeric material's viscoelastic properties is key to optimizing formulations and blends, adapting a process to accommodate the properties of a specific material, and minimizing the risk of flow anomalies.

The use of rotational rheometers to perform appropriate [rheological tests](#) facilitates the investigation of a polymers' viscoelastic behavior; from the melt-state to the solid-state and all points in between.

Acquired data can be utilized in the optimization of processing conditions and final product performance, as well as for establishing structural property relationships.

Their usefulness and applicability are major drivers in rheological tests' wide use in the analysis of polymeric fluids, both in industry and academia.

Interested in the instruments highlighted in this article?

Request a quote, demo, or conversation with an expert at thermofisher.com



References

1. C.W. Macosko, *Rheology: Principles, Measurements, and Applications*, Wiley-VCH; New York (1994).
2. W.P. Cox and E.H. Merz, *Journal of Polymer Science*, 28, 619 (1958).
3. J.D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., John Wiley & Sons, N.Y. (1980).
4. J. Dealy, D. Plazek, *Time-Temperature Superposition – A Users Guide*, *Rheology Bulletin*, 78(2), (2009).
5. C. Küchenmeister-Lehrheuser, K. Oldörp, F. Meyer, *Solids clamping tool for Dynamic Mechanical Analysis (DMTA) with HAAKE MARS rheometers*, Thermo Fisher Scientific Product Information P004 (2016).
6. *Thermo Scientific HAAKE MiniJet Pro*, Thermo Fisher Scientific Specification Sheet (2014).
7. C. Küchenmeister-Lehrheuser, F. Meyer, *Sentmanat Extensional Rheometer (SER) for the Thermo Scientific HAAKE MARS*, Thermo Fisher Scientific Product Information P019 (2016).
8. F. T. Trouton, *Proc. R. Soc. A77*, 426–440 (1906).

Acknowledgments

Produced from materials originally authored by Fabian Meyer and Nate Crawford from Thermo Scientific.



This information has been sourced, reviewed and adapted from materials provided by Thermo Fisher Scientific – Materials & Structural Analysis.

For more information on this source, please visit [Thermo Fisher Scientific – Materials & Structural Analysis](#).

Producing Master Curves for Polymeric Materials

Thermoplastics are used to make a variety of everyday items. These polymers are distinguished by their ability to soften when heated and harden when cooled. In their molten state, they can be fashioned into various shapes using extrusion, injection molding, and blow molding, among others.

Polymethyl methacrylate (PMMA) is an example of a commonly used thermoplastic. Due to its high transparency, it is frequently used in optical applications such as shatterproof glazing.¹

Polymers comprise repetitive units of smaller molecules known as monomers that combine to form long chains. These polymer chains in a molten state or solution include random coils with strong intermolecular interactions through entanglements. As a result, the flow and deformation behavior is complex. Rotational rheometers are commonly used to characterize flow behavior and assess the processability of various plastics.

Polymer melts have a high elasticity due to their structure, which often restricts rheological measurements in a rotational mode where secondary flows and edge fractures can occur. As a result, frequency-controlled oscillatory tests are used to gain insight into the rheological properties of various processing parameters.

According to the equation, Cox and Merz discovered that for linear, unfilled polymers, the dynamic viscosity η as a function of the shear rate $\dot{\gamma}$ can be correlated with the complex viscosity $|\eta^*|$ as a function of the angular frequency ω according to the equation (1).²

However, the so-called Cox-Merz rule does not apply to multiphase liquids, such as suspensions or chemically crosslinked and gelled systems.³

$$\eta(\dot{\gamma}) = |\eta^*|(\omega) \quad \text{Equation 1}$$

To apply this relationship to polymer processing, certain boundary conditions concerning the measurement technique, as well as rheometer performance, must be taken into account. On the one hand, the time needed to pass through one period at a given deformation amplitude defines an oscillatory movement.

Therefore, acquiring rheological data in oscillation could take less than a second, minutes,

or even days or weeks, based on the chosen frequency. On the other hand, the maximum frequency of commercially available rheometers is usually limited to around 100 Hz (628 rad/s) by the inertia of the measuring system itself.

To address this problem, the time–temperature superposition (TTS) principle can generate master curves with a broader frequency range. This article offers a guideline for the generation of master curves. It also verifies whether the TTS principle can be applied to a data set by employing the van Gorp-Palmen plot.

Materials and Methods

A [Thermo Scientific™ HAAKE™ MARS™ iQ Air Rheometer](#) with temperature chamber TM-CR-O450 was used for this research. A polymethyl methacrylate (PMMA) sample was the subject of the investigation. Figure 1 depicts the measurement procedure. All rheological measurements were taken with a parallel-plate geometry with a 15 mm diameter and a 1 mm measuring gap.

A deformation amplitude γ of 0.5 % was chosen within the sample's linear viscoelastic range. At 180, 200, 220, 240, 260, and 280 °C, frequency sweeps were performed from 300 rad/s to 1 rad/s. Each frequency sweep was performed with a fresh sample to ensure no thermal degradation occurred. Matching sample discs were prepared in advance for all rheological measurements using a HAAKE Minijet Pro Mini Injection Molding System.

Results and Discussion

In an oscillatory shear experiment, the excitation frequency and temperature have a similar effect on the viscoelastic properties of polymers, which means that their behavior at higher temperatures equals their behavior at lower frequencies and vice versa. Figure 2 depicts this phenomenon for the storage modulus G' and loss modulus G'' as a function of angular frequency for a PMMA melt at 180 °C, 220 °C, and 280 °C.

G' and G'' intersect at an angular frequency of 1.78 rad/s at the chosen reference temperature of 220 °C. PMMA exhibits this crossover at a much higher frequency of 144 rad/s at 280 °C. PMMA, on the other hand, shows no crossover of G' and G'' at 180 °C. G' and G'' appear to be different parts of the same curve depending on the temperature.

This observation is used when implementing the TTS principle. The individual frequency sweep data sets are shifted horizontally and vertically towards a reference temperature T_0 to generate a master curve covering a frequency range much larger than the limited range

of a single sweep experiment.

As a result, frequency measurements at different temperatures can gather information about a material's viscoelastic properties over a wide range of time scales.

The TTS employs temperature-dependent horizontal and vertical shift factors, a_T and b_T , respectively.⁵ The horizontal shift factor a_T specifies the shift of the measured moduli data along the x (frequency)-axis towards the data set acquired at the reference temperature T_0 .

The temperature dependence of a_T is most commonly described by either the empirical Arrhenius or the William-Landel-Ferry (WLF) models, depending on the polymer's glass transition.⁴ Measurement data can also be transitioned towards reference temperatures for which no experimental data is available using these two models.

The vertical shift factor b_T is characterized by the density $\rho(T)$ of the polymeric material at a given temperature in comparison to the reference $\rho_0(T_0)$, as shown in equation (2).⁵

$$b_T = \frac{T_0 \cdot \rho_0(T_0)}{T \cdot \rho(T)}$$

Equation 2

The temperature-density dependence of entangled polymers is quite small. As a result, vertical shift factors are typically around 1. Even so, data sets can be integrated using b_T in such a sense that the optical appearance of the master curve can be impacted, and probable experimental errors can be covered up.⁵

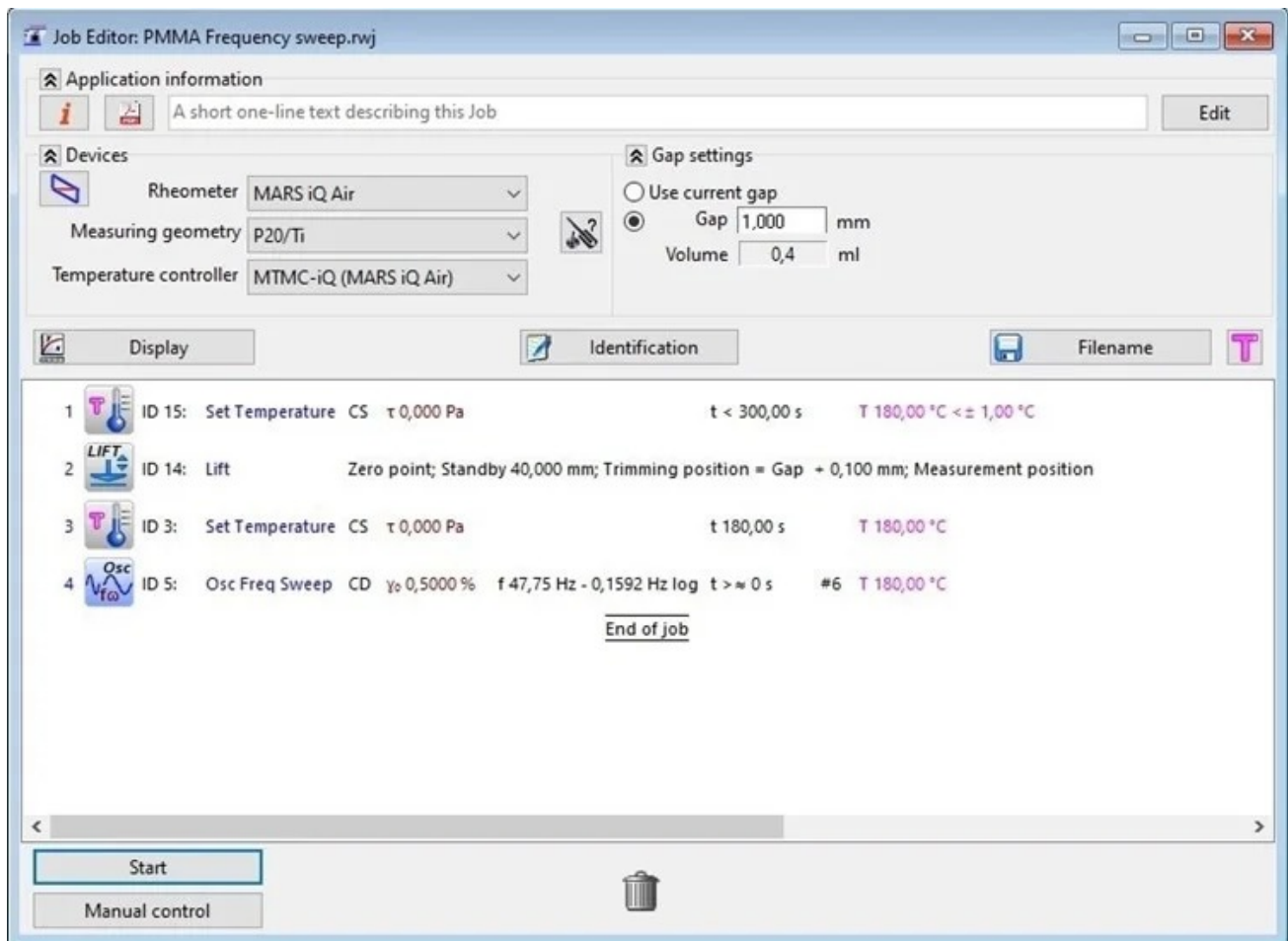


Figure 1. Measurement routine for performing a frequency sweep measurement in the HAAKE RheoWin Software. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

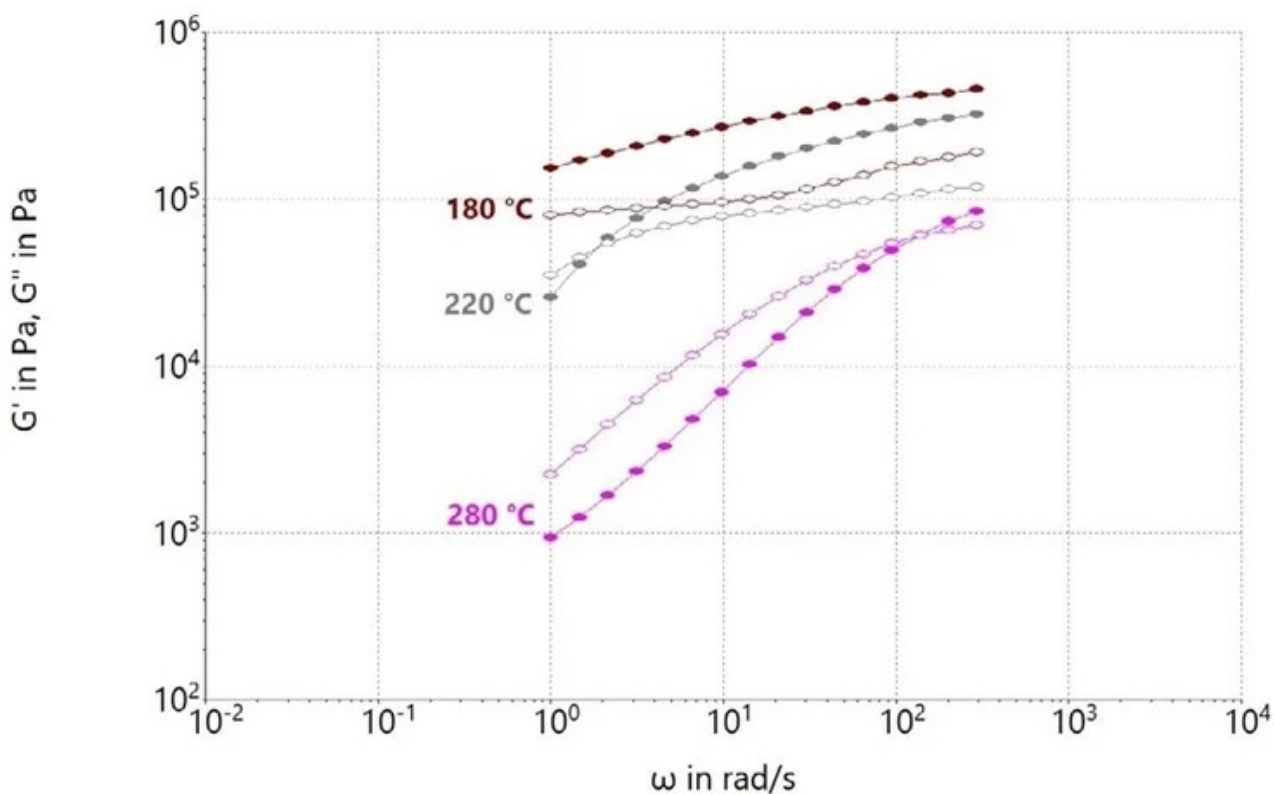


Figure 2. Rheological frequency sweep data at temperatures of 180 °C, 220 °C, and 280 °C for PMMA. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Modern rheometer software, such as the [HAAKE RheoWin™ Rheometer Control Software](#), shifts rheological data and generates master curves to obtain information about viscoelastic properties over a wide frequency range. The TTS principle cannot be applied to thermorheologically complex materials in which two or more relaxation mechanisms have different temperature dependencies.⁵

The rheological data in Figure 2 were used to generate the PMMA master curve in Figure 3. Additional measurement data was collected at 200 °C, 240 °C, and 260 °C to allow for more overlap and higher precision. The reference temperature was set at 220 °C.

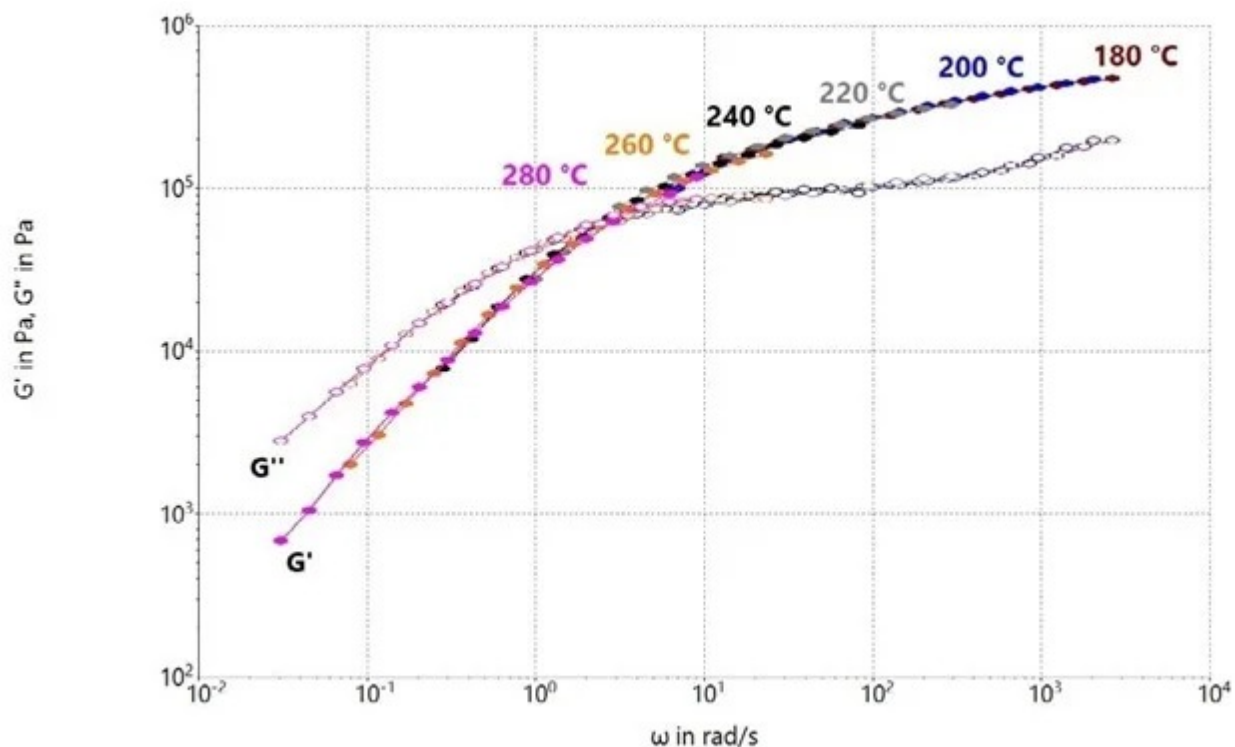


Figure 3. G' and G'' master curve at a reference temperature of 220 °C obtained from frequency sweep data at 180 °C, 200 °C, 220 °C, 240 °C, 260 °C and 280 °C for a PMMA melt. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

TTS was used to prolong the original angular frequency range of each measurement data set (1 to 300 rad/s) to 0.03 to 2600 rad/s. This range is broad enough to include shear rates encountered in many standard polymer processing techniques, such as extrusion (1...1.000 s⁻¹) and injection molding (10...10.000 s⁻¹).⁶

The master curve could be lengthened to even higher frequencies/shear rates with additional frequency sweeps at temperatures below 180 °C.

Van Gorp–Palmen disclosed that the phase angle δ as a function of complex shear modulus $|G^*|$ for each isothermal frequency sweep used to develop a master curve must superpose into a single continuous curve to ascertain the applicability of the TTS principle for a given polymer fluid.⁷ Figure 4 depicts the van Gorp–Palmen plot of the individual PMMA frequency sweep measurements.

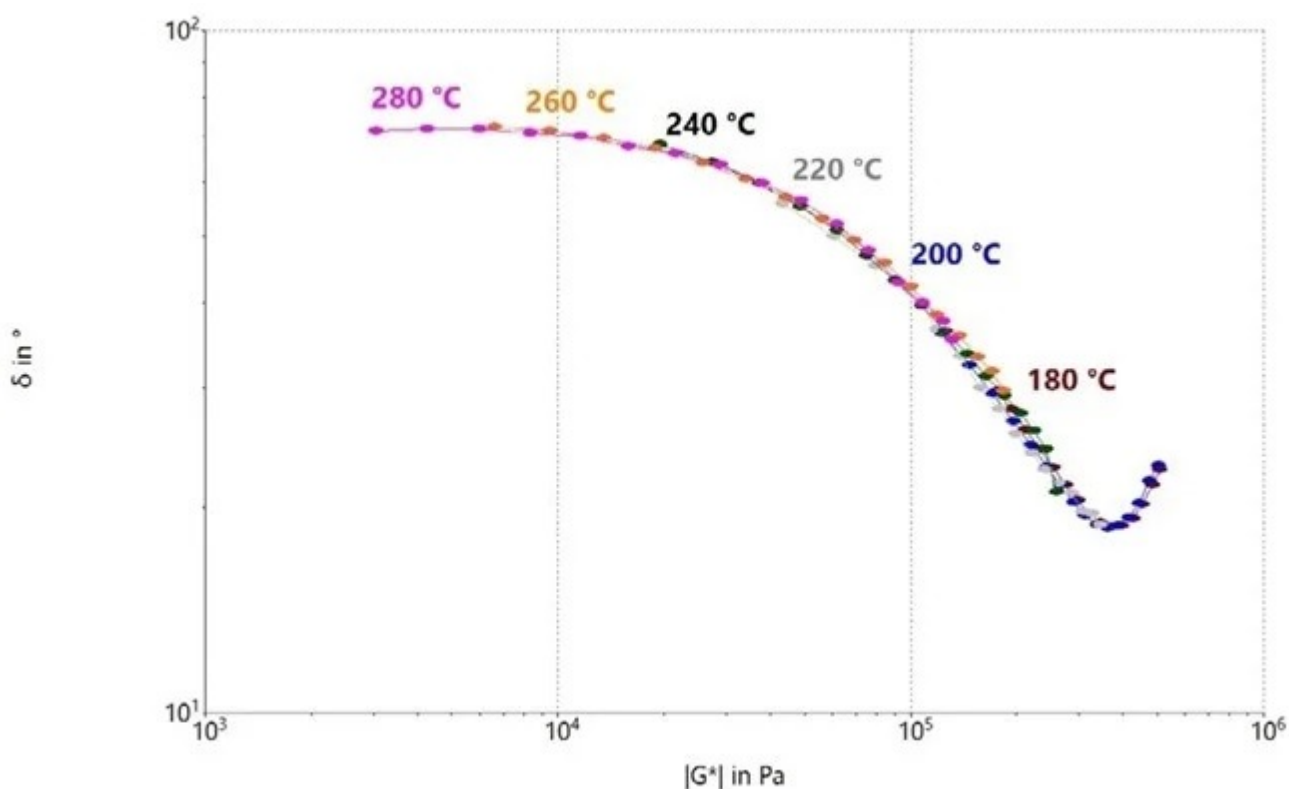


Figure 4. van Gorp-Palmen plot for the single PMMA frequency sweep tests performed at different temperatures. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

The van Gorp–Palmen plot can be used to determine whether a polymer sample, such as the PMMA grade used in this study, is thermorheologically simple.

The rheometer software automatically obtains information on the complex viscosity $|\eta^*|$ of the sample based on the G' and G'' master curves (3).

$$|\eta^*| = \frac{\sqrt{G'^2 + G''^2}}{\omega} \quad \text{Equation 3}$$

Numerous material-dependent parameters can be acquired from a master curve for the complex viscosity, using a suitable model fitting, such as the Carreau–Yasuda curve fit described in equation.(4).⁸

$$|\eta^*|(\omega) = \frac{\eta_\infty + (\eta_0 - \eta_\infty)}{(1 + (\lambda\omega)^a)^{\frac{1-n}{a}}} \quad \text{Equation 4}$$

In Equation 4, η_{∞} is the viscosity at an infinite shear rate, η_0 is the zero-shear viscosity, and λ is a time constant that represents a characteristic relaxation time of the sample. The power law index n describes shear thinning behavior at high shear rates, whereas the transition factor a refers to the process of polymer chain disentanglement within the polymer network, and the transition from the Newtonian plateau to the material's shear thinning behavior.

Figure 5 depicts the various Carreau–Yasuda curve fit parameters on an example master curve.

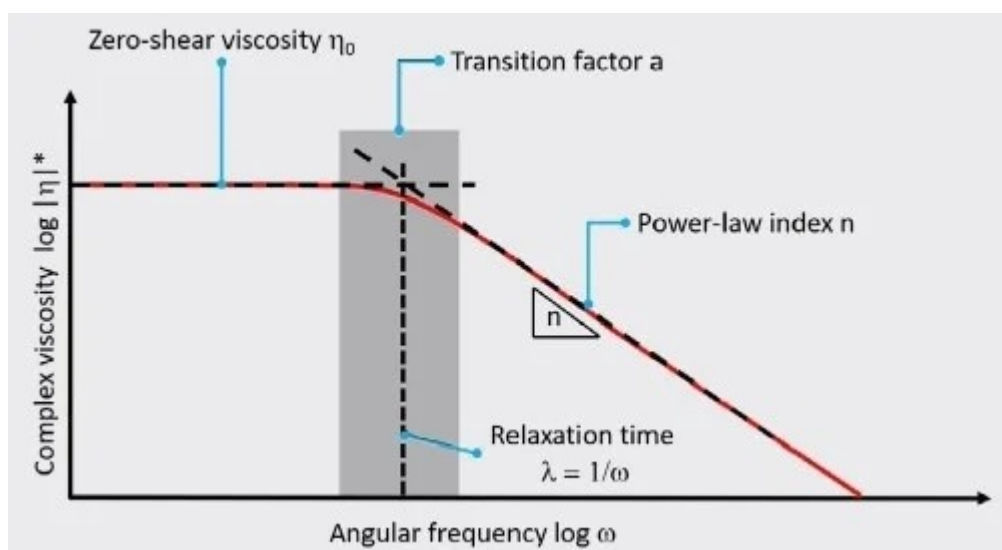


Figure 5. Carreau–Yasuda curve fit parameters illustrated at an example master curve. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

A Carreau-Yasuda curve fitting was executed on the complex viscosity data of the master curve to acquire these material-specific parameters for the examined PMMA sample. The master curve was generated, and the curve fitting was performed using the respective HAAKE RheoWin Software functionalities.

The HAAKE RheoWin Software calculated the Carreau–Yasuda parameters for the PMMA master curve at 220 °C, as shown in Table 1.

Table 1. Carreau–Yasuda curve fit parameters for a PMMA master curve at a reference temperature of 220 °C. Source: Thermo Fisher Scientific – Materials & Structural Analysis

Parameter	Value
η_0	100.200 Pas
λ	0.81

a	0.74
n	0.20

The zero-shear viscosity η_0 and the transition factor are essential parameters for polymer processing. It is well known that η_0 is proportional to a polymer's average chain length. The distribution of different chain lengths relates to the transition factor. As a result, changes in zero-shear viscosity after processing or recycling can be directly correlated with a polymer's molecular mass or polydispersity.

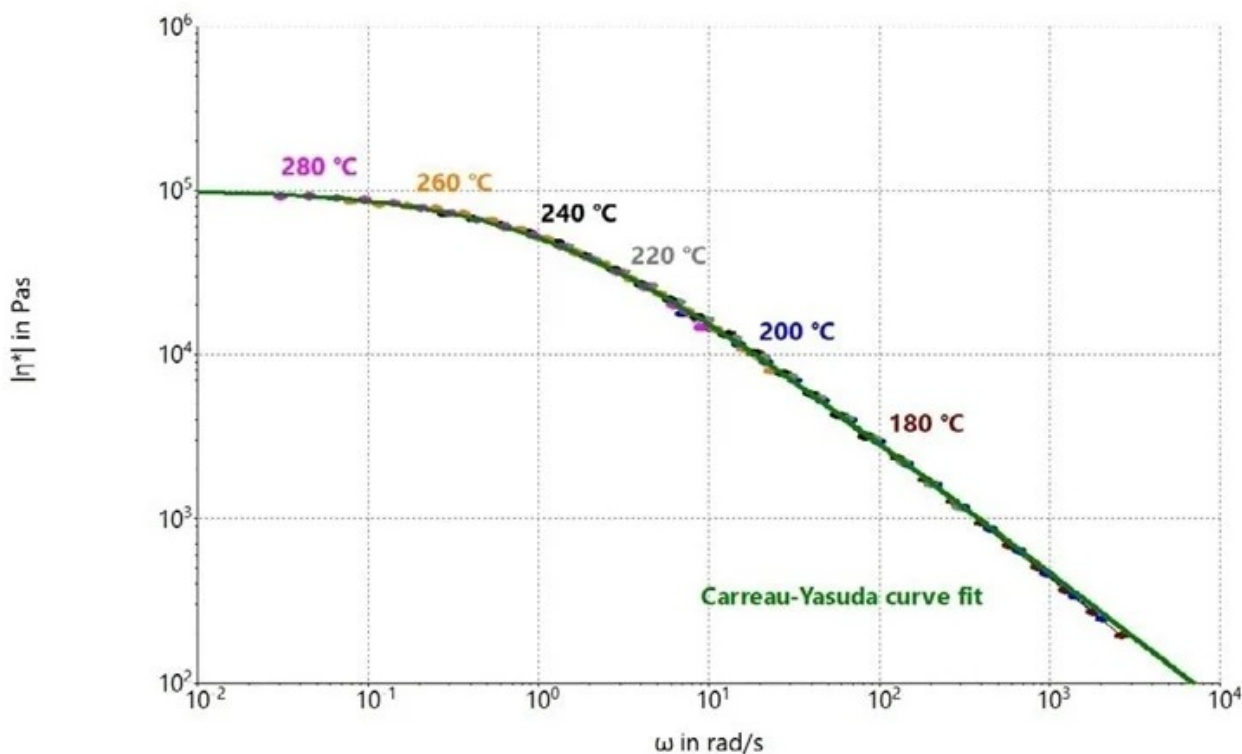


Figure 6. Complex viscosity master curve at a reference temperature of 220 °C obtained out of frequency sweep data at 180 °C, 200 °C, 220 °C, 240 °C, 260 °C and 280 °C for a PMMA melt including Carreau–Yasuda curve fit. Image Credit: Thermo Fisher Scientific – Materials & Structural Analysis

Conclusion

The creation of a master curve from frequency sweep data collected at different temperatures and using the TTS principle for a PMMA sample was outlined in this article. The van Gurp-Palmen plot was developed to provide a quick and easy way to determine whether a set of frequency sweep data is suitable for TTS shifting.

The Carreau–Yasuda curve fitting model was discussed as a method for obtaining various polymer-specific parameters from master curves, which can be used to characterize the

effects of different processing techniques or recycling steps on a polymer material's average molecular mass or molecular mass distribution.

References

1. Alger, M–Polymer Science Dictionary (2017)
2. Cox, W. P. and Merz, E.H.–Correlation of Dynamic and Steady flow Viscosities–*J. Polym. Sci.* (1958)
3. Geissle, W. and Hochstein, B.–Validity of the Cox-Merz rule for concentrated suspensions–*J. Rheol.* 47 (4) (2013)
4. Dealy, J.M. , Read, D.J., Larson, R.G.–Structure and Rheology of Molten Polymers– 2nd edition (2018)
5. Plazek, D.–Time-temperature superposition–A users guide – *Rheol. Bul.* 78 (2) (2009)
6. Carnicer, V. et al.–Microfluidic rheology: A new approach to measure viscosity of ceramic suspensions at extremely high shear rates–*J. Oceram* 5 (2021)
7. Van Gorp, M., Palmen, J.–Time-temperature superposition for polymeric blends– *Rheol. Bul.* 67 (1) (1998)
8. Malkin, A. and Isayev, A.–Rheology–Concepts, Methods, and Applications–3rd edition (2017)



This information has been sourced, reviewed and adapted from materials provided by Thermo Fisher Scientific – Materials & Structural Analysis.

For more information on this source, please visit [Thermo Fisher Scientific – Materials & Structural Analysis](#).

Lab-scale Polymer Compounding, Extrusion, and Testing

Compounding is employed to mix a polymer matrix with different additives to achieve a specific material behavior. Extrusion is used to determine the final form of polymers and plastics, from small sample amounts during initial product development through to full-scale manufacturing processes.



Torque Rheometers Bring Advantages in Polymer Development

insights from industry

Dirk Leister
Leader, Technical Marketing
Thermo Fisher Scientific



In this interview, AZoM talks to Dirk Leister from Thermo Fisher Scientific about the role of torque rheometers in the field of polymer compound development.

To start, could you give a brief overview of Thermo Fisher Scientific and the role that you play in the field of polymers?

Our company, Thermo Fisher Scientific, is a global leader in serving science. I work in the business that delivers twin-screw compounders, torque and rotational rheometer solutions to the polymer

industry to optimize new processes and material development.

Rheology and compounding are particularly important in the field of new polymeric materials.

Our customers are working every day to make life better in packaging materials, aerospace and automotive components, cosmetics and healthcare products, and almost every other area of daily life by developing new polymer compounds with specific properties. We provide them with the systems to do that.

R&D customers in the sectors of novel polymer compounds or polymer additives are often limited by the amount of material available to develop formulations or do pilot-scale production. Our standalone twin-screw compounders offer flexible compounding configurations for small sample amounts making them particularly well-suited for R&D work. They are also available in different grades of steel for the product contact parts so they can be used in more regulated environments such as pharmaceuticals, cosmetics and food applications.

*Compendium Download:
Flexible Solutions for
Advanced Material
Development*



Our rheometer solutions help to characterize polymer compounds in a melt or in their final shape to optimize processing or ensure quality requirements.

One instrument in particular, the Thermo Scientific™ HAAKE™ PolyLab™ Torque Rheometer combines both worlds of compounding and rheological material testing in one instrument. That's why it's like a hidden gem for polymer development and processing; just this one instrument serves many needs in both R&D and QC.

What types of work/applications are done in new polymer compound/material development?

It's amazing what our customers are doing today and working to accomplish for tomorrow with polymers. They are trying to make polymers and products so they are safer, more economical, more lightweight, more heat resistant, longer lasting, and much, much more.

For example, some recent work went into the area of “green tires” to increase fuel efficiency for automobiles. The goal was to develop new rubber compounds from ecologically friendly resources with the aim to reduce roll-resistance and wear; the reduction in resistance helps save fuel and make the tires themselves last longer.

Another hot research topic involves novel battery technologies for electric cars. The focus here is on battery separator films and electrode materials. Both critical battery components can be manufactured using a twin-screw extruder. The lab-scale size of our equipment makes production of those materials fast and resource efficient.

In both examples, it's important that the new materials are thoroughly compounded at the start. Then, after compounding, extensive testing of the material properties is required. This is where the unique modularity of the HAAKE PolyLab Torque Rheometer comes into play; it can handle both kinds of tasks.

How does the HAAKE PolyLab Torque Rheometer assist in the development of new compound materials?

Our customer's daily work in polymer development is to create and test a large number of new polymer formulations to find the optimal material properties. But daily work changes and evolves over time. Having a modular system really helps to keep up with not only today's tasks but future demands as well.

As I said before, the HAAKE PolyLab Torque Rheometer blends the worlds of compounding and rheological material testing into one instrument. That's how the platform can serve multiple research and quality control tasks. The modular design allows it to combine four instrument capabilities in one system solution.

The HAAKE PolyLab Torque Rheometer has a strong, reliable drive and measuring unit, and it's flexible enough to combine with different processing devices. These are batch mixers, single screw extruders, twin-screw compounders, and rheological testing solutions under process-relevant conditions. That means the same system can be used to compound new materials and, with just a few set-up changes, test those same new materials for relevant material properties.

This flexibility helps customers to establish workflows specific to their needs and to rapidly adapt to changing requirements in the future. By utilizing different modules, customers can leverage their workflows in both R&D and QC environments. For example, the batch mixers can be used for recipe development in R&D and quality determinations in QC. The mixers also help to understand important material properties like melting, degradation and flow behavior to optimize final products. Single screw extruders can be used to produce test-specimen like sheets and films to test additive dispersion in a final product.

The HAAKE PolyLab Torque Rheometer system's continuously operating twin-screw compounder is a lab-scale instrument that delivers results comparable to its production sibling, but the customer needs only a fraction of the material and time to achieve results. With a wide range of up- and downstream accessories and a modular screw design, this torque rheometer is a very useful tool in R&D.

The last, but not least of the four applications is rheological testing under process-relevant conditions. Different capillary dies are available depending on the material to be tested and the desired shear rate range; these allow the customer to reliably determine rheological behavior. This is of prime importance for machine and tool design, as well as for the optimization of final product.

What's the real benefit of your torque rheometer system for the user?

The single biggest benefit of the HAAKE PolyLab Torque Rheometer is its modularity which helps users successfully produce and characterize a large number of samples in a minimal amount of time.

For example, the HAAKE PolyLab Torque Rheometer saves time and reduces operating errors as users learn just one software system to perform many different activities. That makes it faster and easier for users to learn how to use the software and do the different tasks. It also reduces the chance for error by not having to operate different software packages for standalone mixers, extruders and rheometers.

Often software methods developed in the R&D lab are complex and involve multiple steps until a full compounding or mixer test is conducted. The HAAKE PolyLab Torque Rheometer provides consistency from R&D to QC with a mode of software operation that guides users in QC to set up the system correctly and run pre-programmed methods by pressing a single button. The software system is also available in multiple languages for businesses and processes that span location sites in multiple countries.

Another way the HAAKE PolyLab Torque Rheometer saves time is through its ability to work with small sample volumes. It not only saves on material costs, but also allows the customer to produce and characterize more samples in less time.



The flexibility of the HAAKE PolyLab Torque Rheometer shows through when it comes to transferring work from the lab to the production environment. With an extremely broad range of available downstream equipment, such as feeders for liquid and solid materials, dies and take-off devices, users can set up entire compounding lines in the lab that have the same functionality as real-world production environments. Because the HAAKE PolyLab Torque Rheometer allows users to do all work under the conditions of the process

environment, the results obtained initially allow for easy scale-up to the production area. In fact, the HAAKE PolyLab Torque Rheometer provides data from the analysis of material properties that can be used directly for quality control purposes.

And of course, the HAAKE PolyLab Torque Rheometer is an open system – different sensors can be attached to it to get additional information. For example, conductivity measurements in the mixer can help to analyze the dispersion of carbon black in rubber compounds in an online process. Plug-and-play functionality means the system automatically detects attached accessories and helps to minimize set-up errors. So it's faster to do multiple applications on one instrument, and the changeover from one application to the next is quick and easy.

In what other applications can the HAAKE PolyLab Torque Rheometer be used?

The HAAKE PolyLab Torque Rheometer has applications in many different fields including extensions of the polymers industry itself. More and more customers are deviating from standard polymers to those modified for different applications.

Powder injection molding (PIM) is one field where the HAAKE PolyLab Torque Rheometer is deployed frequently. For PIM feedstock, polymers are compounded with a high load of metal or ceramic powders (80% or more). The HAAKE PolyLab Torque Rheometer enables efficient compounding of those materials.

Additive manufacturing, which includes 3D printing, makes up another field where we have seen a steep rise in interest for specialized material in the form of polymer filament to be used with 3D printers.

Many customers have asked to explore possibilities with the HAAKE PolyLab Torque Rheometer beyond polymers. For example, we are working with industry partners and universities in the areas of food extrusion and cosmetics formulation where the system is used as a continuous mixing device.

Such demand encourages us to continue developing the capabilities of the HAAKE PolyLab Torque Rheometer; we're always developing new accessories and enhancements to ensure the system can meet future market demands. In fact, we just published an application compendium that shows many specific applications for the HAAKE PolyLab Torque Rheometer; it can be found on our website and even on your AZO Materials web pages. It's called Flexible solutions for advanced material development.



[Download the Free Compendium on Flexible Solutions for Advanced Material Development](#)



We plan to grow the capabilities of the flexible torque rheometer system. There are many new applications to come for the HAAKE PolyLab Torque Rheometer. As an open system, we may develop different sensors to provide users with additional information during operation. For example, simultaneous conductivity measurements while compounding new rubber compounds would give users a quality measurement of the homogeneity of the rubber compound. What are the plans for the future of torque rheometers and related polymer instruments at Thermo Fisher Scientific?

We're always striving to increase the range of our equipment. As another example, additional die designs can help in setting up a small-scale production system to more effectively mimic a large-scale system. And those are just a few ideas of what can be done with the HAAKE PolyLab Torque Rheometer.

About Dirk Leister

Dirk Leister holds an Engineering degree (Dipl.-Ing.) in Biotechnology from University of Applied Science in Giessen, Germany. He also has a bachelor's degree in Sales and Marketing from the University of Applied Science in Karlsruhe, Germany.

Dirk has over 20 years of experience in Sales and Marketing for laboratory and manufacturing equipment especially in the pharmaceutical and life sciences industries.



Disclaimer: The views expressed here are those of the interviewee and do not necessarily represent the views of AZoM.com Limited (T/A) AZoNetwork, the owner and operator of this website. This disclaimer forms part of the [Terms and Conditions](#) of use of this website.

Preparing and Analyzing PET with Additives

PET samples with several additives and plain resin were mixed for a specific amount of time. While the mixing took place, the composition/decomposition was measured in the integrated slit capillary. The mixture was then transferred to a micro injection molding machine so as to prepare disc-shaped test specimens. With these discs, rheological tests of the polymer melt were conducted later on a rotational rheometer. The aim was to demonstrate that a test in a micro compounder with just 7 g of sample can be used for a rapid screening of PET and additives and to provide an indication for the chemical recycling of the polymer.



[Request a Quote](#)



Methods

Sample Preparation

The [Thermo Scientific™ HAAKE™ MiniLab Micro Compounder](#) with co-rotating screws (Figure 1) was used to prepare the mixtures of PET with additives at 270 °C with a screw speed of 50 rpm. For 15 minutes, the sample was mixed by re-circulating. During the mixing process the pressure drop was monitored in the slit capillary of the backflow channel (Figure 2).



Figure 1. HAAKE MiniLab Micro Compounder.

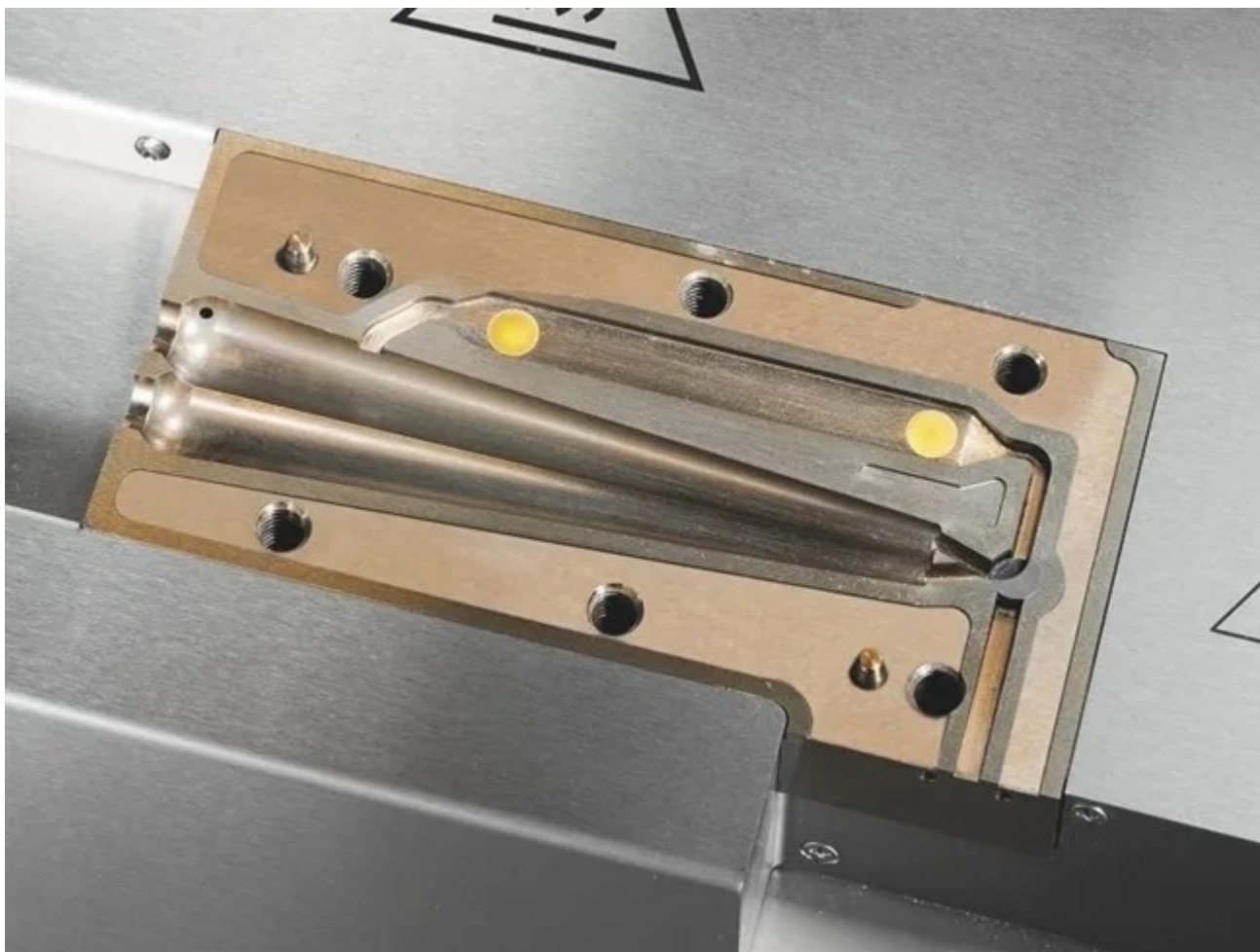


Figure 2. HAAKE MiniLab Micro Compounder backflow channel built as slit capillary with two pressure sensors.

Injection Molding of the Test Specimens

After the mixing process was completed, the polymer was directly extruded into the heated cylinder of the Thermo Scientific™ HAAKE™ MiniJet Pro System (Figure 3) for injection molding of test specimens (20 mm Ø and 1.5 mm thickness) for additional rheological tests. The heated cylinder's temperature was 270 °C and the mold was heated to 80 °C. The samples had been injected with 500 bar for five seconds and post pressure of 300 bar for five seconds.



Figure 3. HAAKE MiniJet System and molds.

Rheological Test

The rheological tests were performed using 20 mm parallel plates and a gap of 1.4 mm on a Thermo Scientific™ HAAKE™ MARS™ Rheometer with an electrical heated oven at 270 °C under nitrogen atmosphere. All samples had been primarily tested in an amplitude sweep to determine the linear viscoelastic range. New test specimens were used for frequency sweeps from 0.1 to 46 Hz. The deformation for all tests was 0.5%, thus in a safe

regime of the linear viscoelastic range for all samples.



Figure 4. Thermo Scientific™ HAAKE™ MARS™ Rheometer

Results

In the recirculation mode, the pressure profile can be monitored over a period of time by the pressure difference of the two pressure sensors, built in backflow channel (see Figure 2). At the start of the test, material is filled into the micro compounder. This causes a pressure peak. After all the material is filled in and the temperature equilibrated, the pressure profile over time can refer to a reaction of the polymer. A decrease of the pressure over time shows an alteration of the material. For plain PET, for instance, this can be a reaction of the polymer with water (moisture) where the polymer degrades. A reduction of the pressure is in line with a lower viscosity of the PET. When the pressure increases over time it is a sign of a condensation reaction of the PET increase in the chain length or branching which results in a higher viscosity. The samples for the rheological test were prepared with material that had been recirculated for 15 minutes in the HAAKE MiniLab Micro Compounder. The final pressure value can be correlated with complex viscosity $|\eta^*|$ of a dynamic oscillatory test done with a rheometer. For the plain PET illustrated in Figure 5 after the loading peak, the pressure drop shows a decomposition of the PET. After 15 minutes, pressure is nearly constant with a value of approximately 18 bar. In Figure 6, the frequency sweep for the same sample indicates that the loss modulus G'' is significantly higher than the storage modulus G' . The slight bumpy curve of G'' is because of the fact that the phase shift δ is nearly 90° and the smallest changes have big influences on G'' . The complex zero shear viscosity $|\eta^*|$ is 200 Pas.

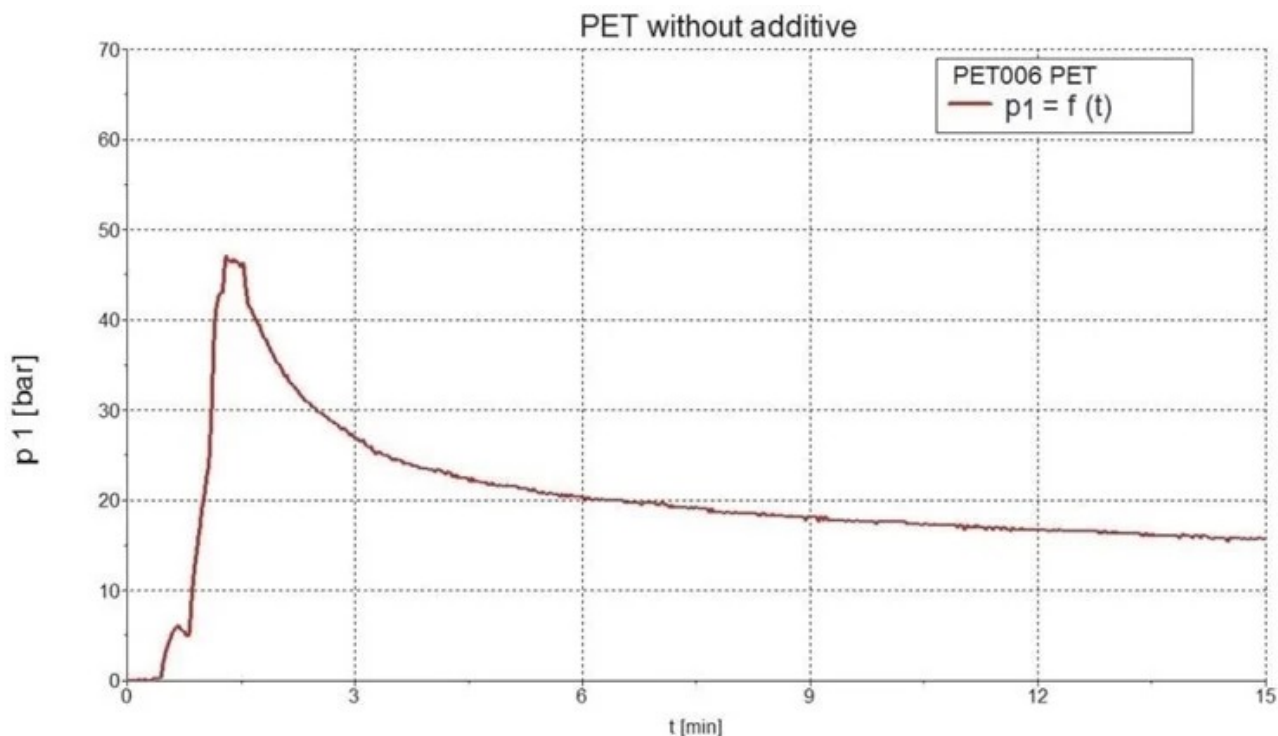


Figure 5. Pressure dependence of PET with no additives.

PET without additives

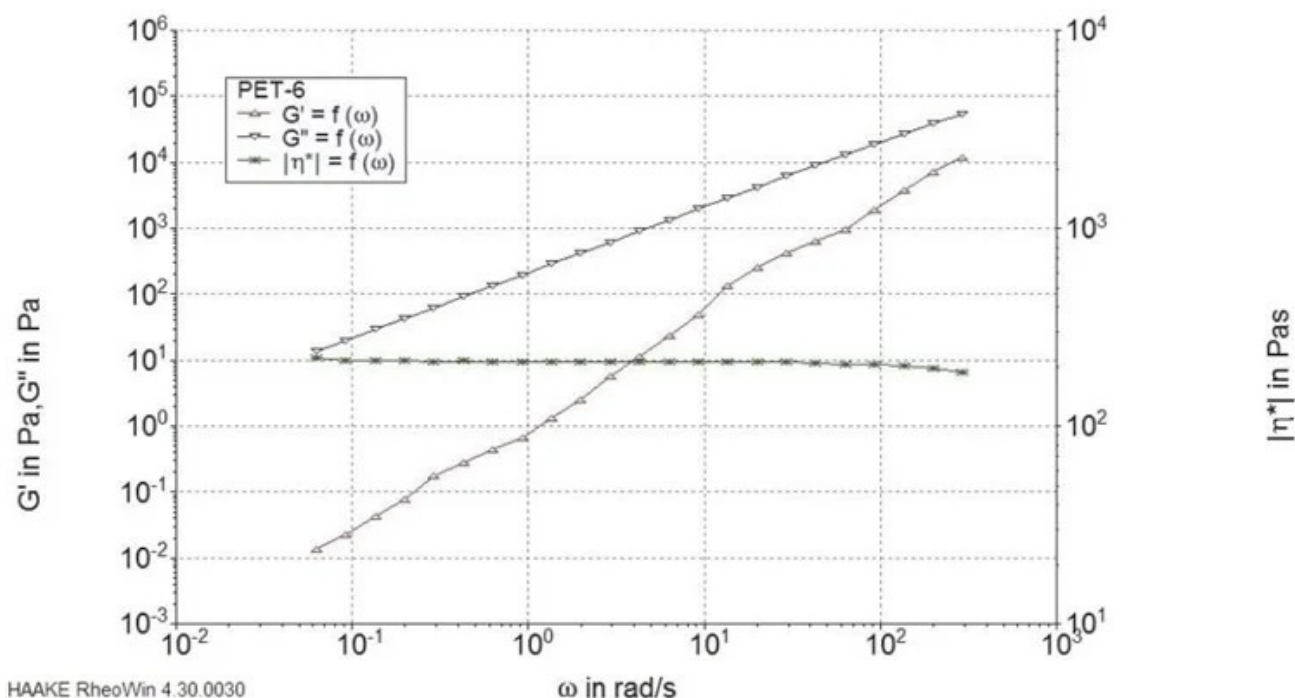


Figure 6. Frequency sweep of PET with no additives.

Figure 7 shows the PET with 1% 1,2,4-Benzenetricarboxylic anhydride after the loading peak, a pressure increase which correlates with the condensation reaction of the PET. After 15 minutes, the pressure continues to increase with a value of approximately 15 bar. Compared to the plain PET it is marginally less of an indication of a lower viscosity.

PET with 1% 1,2,4-Benzenetricarboxylic anhydride

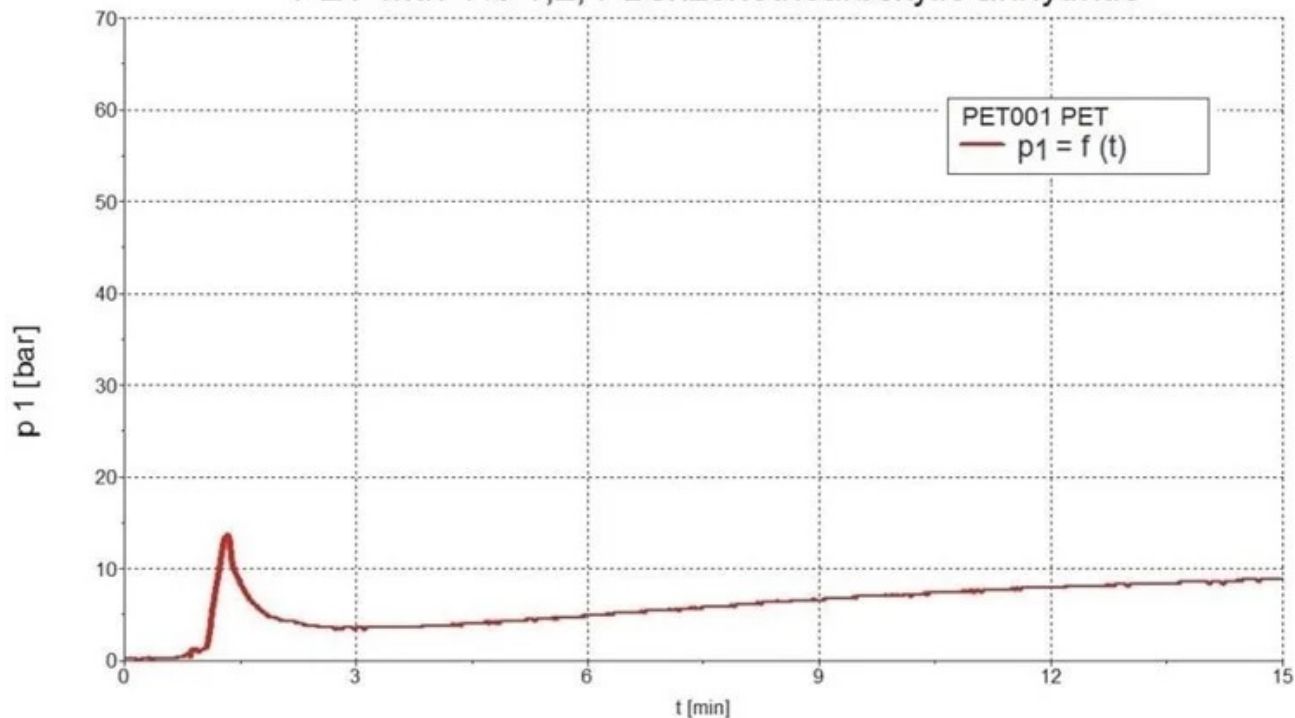


Figure 7. Pressure dependence of PET with 1% 1,2,4-Benzenetricarboxylic anhydride.

A look at the frequency sweep in Figure 8 for the same sample illustrates that G' and G'' are getting closer. This goes along with a lower δ of approximately 85° at low frequencies. The PET gains more elasticity. The $|\eta^*|$ is 150 Pas at low frequencies. Compared to the plain PET, the additive is accountable for the lower pressure and the lower $|\eta^*|$ on the one hand, but on the other hand the additive brought about a reaction of the PET.

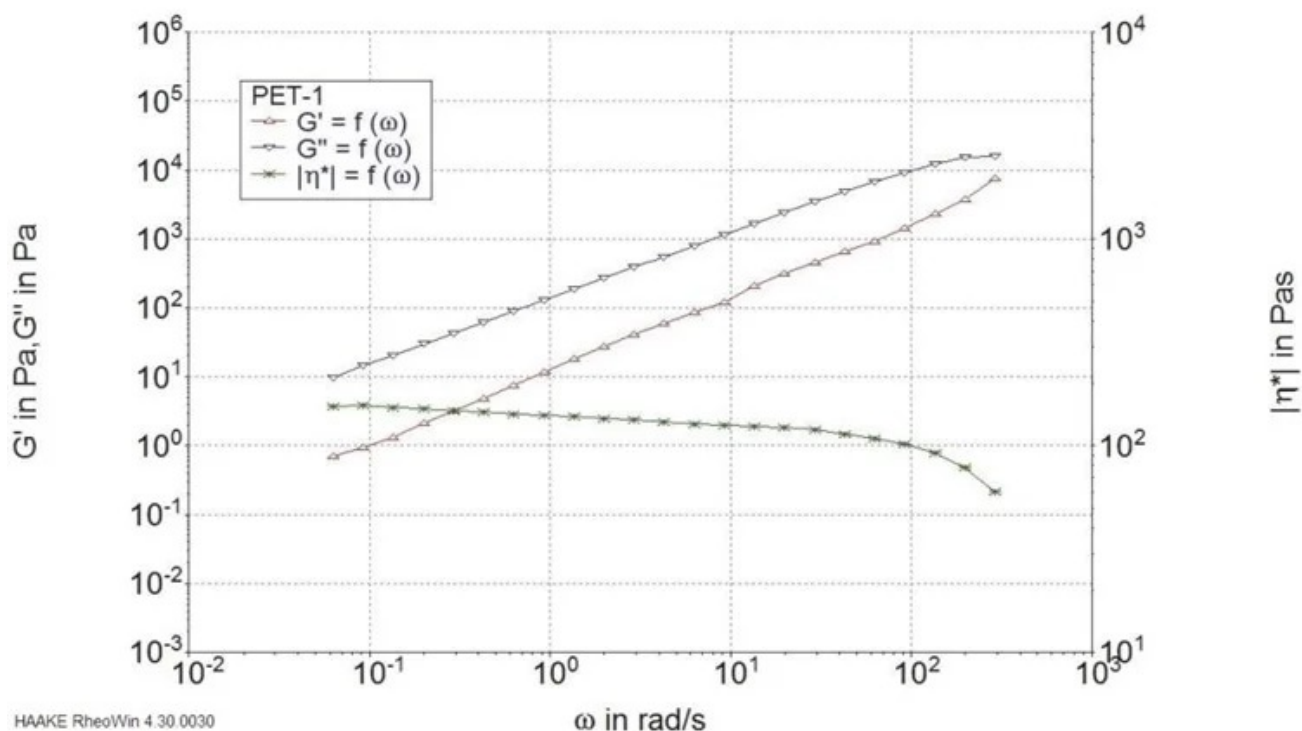


Figure 8. Frequency sweep of PET with 1% 1,2,4-Benzenetricarboxylic anhydride.

The pressure dependence of PET with 1% 1,2,4-Benzenetricarboxylic anhydride and 1% meta-Dioxazolinebenzene in Figure 9 illustrates the pressure decrease, and afterward an increase after the loading peak. The end pressure with 55 bar is considerably higher compared to the plain PET and the compound with 1% 1,2,4-Benzenetricarboxylic anhydride as an additive. The pressure fluctuation at the end of the test is because of a rubbery morphology. The frequency sweep in Figure 10 illustrates the common trend of G' and G'' for a viscoelastic material. The $|\eta^*|$ with nearly 2800 Pas is over 10 times higher compared to the plain PET and the compound with PET and 1% 1,2,4-Benzenetricarboxylic anhydride as an additive. An observation of the change of δ from 88° at low to 52° at high frequencies shows a higher elastic behavior coming near the crossover. The mixture of both additives reveals first a decomposition of the PET followed by a reaction to build up a new structure. It is very likely that the molecular weight is considerably higher. The rise in pressure and $|\eta^*|$ correlates well in comparison to the tests of plain PET and the compound

with 1% 1,2,4-Benzenetricarboxylic anhydride.

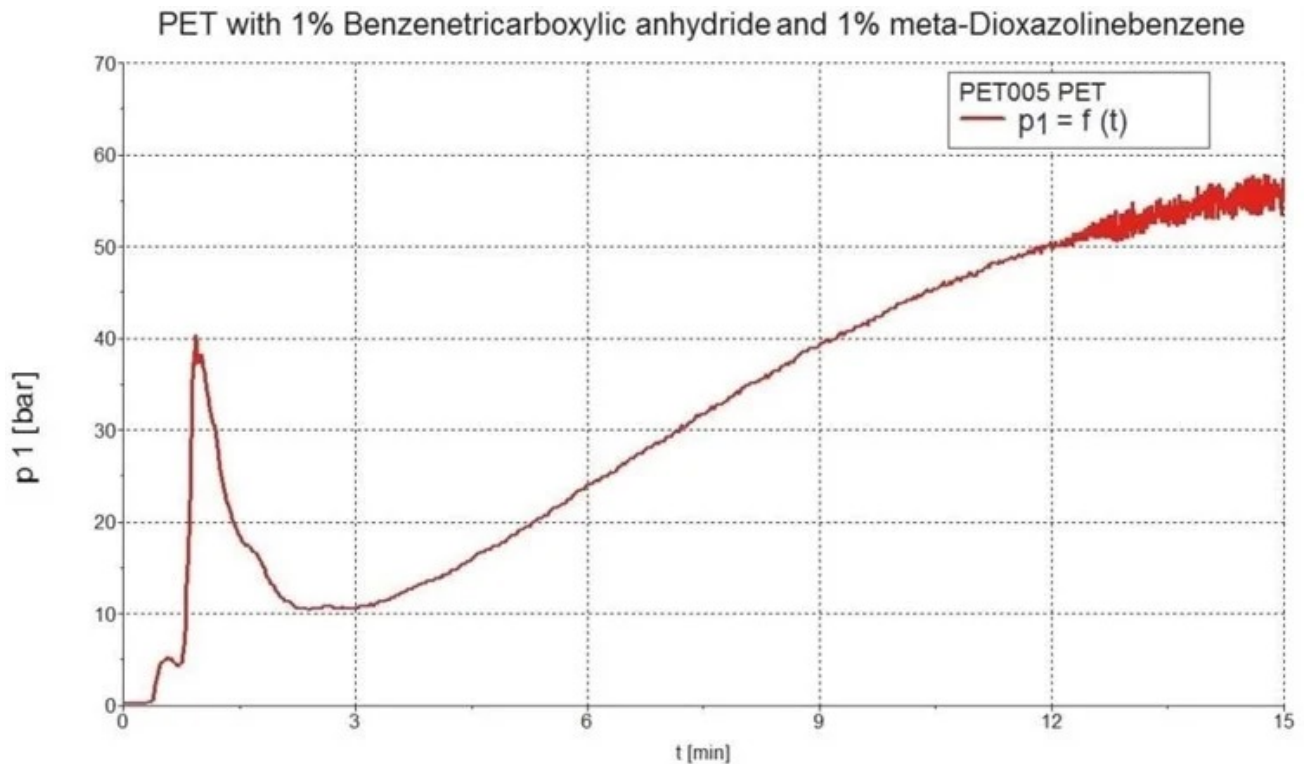


Figure 9. Pressure dependence of PET with 1% 1,2,4-Benzenetricarboxylic anhydride and 1% meta-Dioxazolinebenzene.

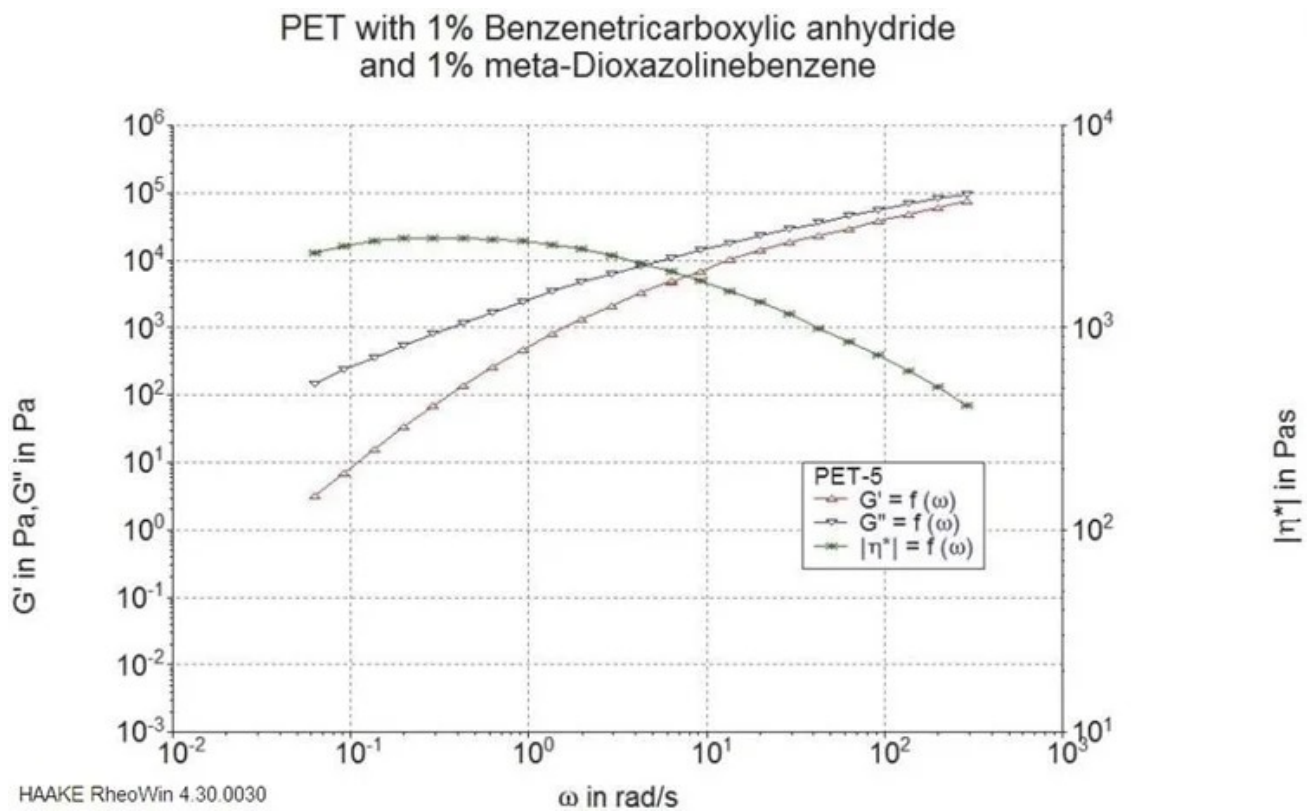


Figure 10. Frequency sweep of PET with 1% 1,2,4-Benzenetricarboxylic anhydride and 1%

Conclusion

The HAAKE MiniLab Micro Compounder is a suitable instrument to screen the effects of various additives. Only a small quantity of sample (7 g) is needed. Just viewing the pressure dependence provides a first revelation of the functionality of the additives. The time required for one test is reasonable. If additional rheological or other physical tests have to be done, the transfer of the polymer melt into the [HAAKE MiniJet Pro System](#) is possible. Different test specimens can be prepared rapidly and are reproducible. Additional studies on the molecular weight and distribution, either by comprehensive rheological tests for example Time Temperature Superposition compared with GPC data, could really establish the assumptions.



This information has been sourced, reviewed and adapted from materials provided by Thermo Fisher Scientific – Materials & Structural Analysis.

For more information on this source, please visit [Thermo Fisher Scientific – Materials & Structural Analysis](#).

Product Catalog

Evolution One/One Plus UV-Vis Spectrophotometers

For routine, complex research and advanced applications, including current compliance, the Thermo Scientific™ Evolution™ One/One Plus UV-Vis Spectrophotometer series brings together reliable, versatile hardware, a broad range of accessories, with easy-to-use, easy-to-learn Thermo Scientific™ Insight™ Pro Software.

Nicolet iS50 FTIR Spectrometer

Solve analytical challenges with ease using the Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer, featuring purpose-built accessories and integrated software — making it an all-in-one materials analysis workstation.

Nicolet Summit FTIR Spectrometer

Confidently identify sample components and rapidly verify materials with less effort so you can make critical decisions fast. Use the compact Thermo Scientific™ Nicolet™ Summit™ FTIR Spectrometer to quickly see pass/fail QC results on the multi-colored LED LightBar located on the front of the instrument.

ARL QUANT'X EDXRF Spectrometer

Get composition data on virtually any sample in minutes. The Thermo Scientific™ ARL™ QUANT'X EDXRF Spectrometer provides major, minor, and trace element quantification across the broadest range of samples, including bulk solids, granules, loose or pressed powders, fused beads, thin films, pastes, and liquids.

ARL EQUINOX 100 X-ray Diffractometer

Get a dedicated XRD instrument designed for QA/QC, academic, and routine X-ray diffraction applications with the compact, affordable Thermo Scientific™ ARL™ EQUINOX 100 X-ray Diffractometer.

HAAKE MARS Rheometers

This highly flexible Modular Advanced Rheometer System (MARS) provides accuracy, easy handling, and many application-oriented solutions for material characterization.

HAAKE MARS iQ Rotational Rheometer

Thermo Scientific™ HAAKE™ MARS™ iQ Rotational Rheometers ensure intuitive, reliable and flexible rheological measurements.

Product Catalog

HAAKE PolyLab OS Modular Torque Rheometer

The Thermo Scientific™ HAAKE PolyLab OS is a state-of-the-art measuring mixer and extruder system that is focused on the specific needs in research and development.

HAAKE MiniLab 3 Micro Compounder

Find unmatched flexibility in designing today's products for tomorrow's world. The Thermo Scientific™ HAAKE™ MiniLab 3 Micro Compounder provides extrusion specifications and online rheology measurements for pilot and scale-up projects across a range of compounded materials.

HAAKE MiniJet Pro Piston Injection Molding System

Eliminate worries of limited material quantities and produce various sample geometries using the Thermo Scientific™ HAAKE™ MiniJet Pro Piston Injection Molding System.



ARL EQUINOX 100 X-ray
Diffractometer



Nicolet iS50 FTIR Spectrometer



HAAKE MiniLab 3 Micro Compounder

Get in touch at [thermofisher.com/contactus](https://www.thermofisher.com/contactus)