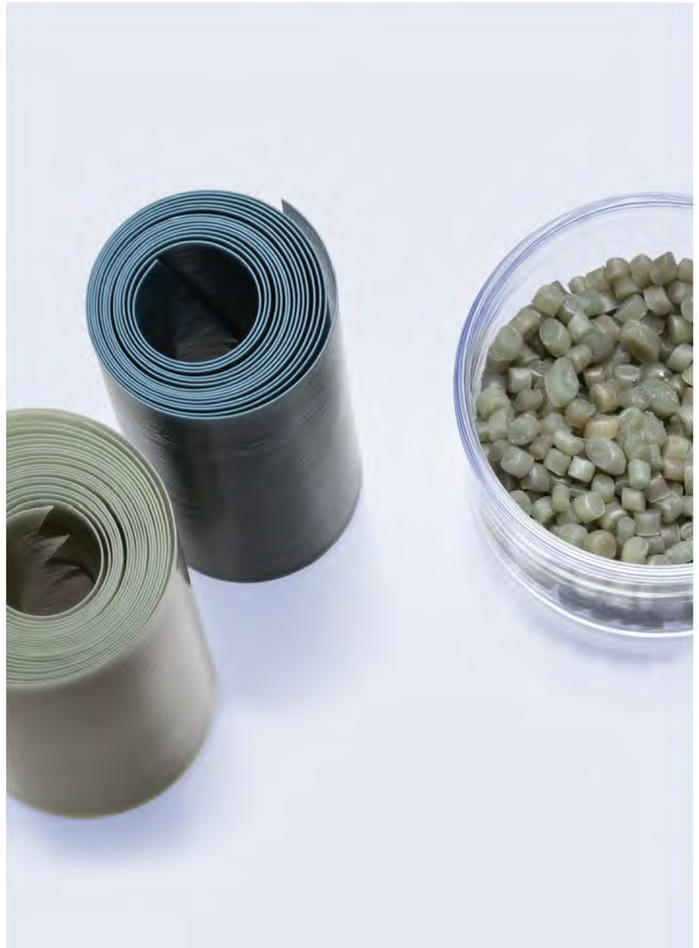
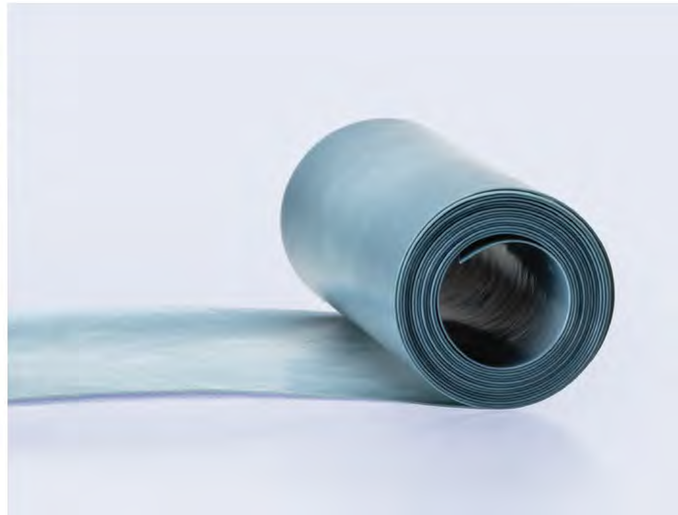
Polymer Processing

E-Book



Anton Paar



Plastic processing enables the creation of materials and components for automotive, healthcare, packaging, construction, and consumer goods.

The process involves the transformation of raw plastic materials into finished or semi-finished products using various techniques, each designed to meet customer-, application-, and regulatory requirements.

Plastics play an essential role in industrial and consumer applications due to their versatility, lightweight nature, durability, and cost-effectiveness. From household appliances to aerospace components, plastic materials deliver innovative solutions that traditional materials like metal and glass often cannot match.

While plastics offer many benefits, they also pose challenges related to environmental impact and recyclability. As global sustainability becomes a priority, the plastics processing industry is evolving, with companies adopting innovative technologies to reduce waste, enhance recyclability, and improve energy efficiency.

Plastics are broadly categorized into thermoplastics and thermosets:

- **Thermosets** undergo a chemical change during molding, making them rigid and non-recyclable. Examples include epoxy resins, phenolic resins, and polyurethane (PU)
- **Thermoplastics** can be melted and reshaped multiple times. Examples include polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polystyrene (PS)

This article and the following analytical methods focus on applications in the field of characterization of processing-relevant properties of thermoplastics and their related utilization e.g.:

- Polyethylene (PE): Used in packaging, piping, and plastic bags
- Polypropylene (PP): Found in automotive parts, textiles, and medical applications
- Polyvinyl chloride (PVC): Used for pipes, medical tubing, and window frames
- Polystyrene (PS): Common in packaging, disposable utensils, and insulation
- Polyethylene terephthalate (PET): Widely used in beverage bottles and food containers

Understanding these materials' properties is vital for selecting the appropriate plastic for any application and predicting its behavior during processing.
Key mass processing methods in plastics technology include the following techniques:

Injection molding is one of the most widely used plastic processing methods. It involves melting plastic pellets and injecting them into a mold cavity under high pressure. This technique is ideal for mass production of high-precision parts, such as electronic housings, medical devices, and automotive components.

Extrusion is a continuous process where plastic is melted and forced through a product-specific shaped die to create long, uniform products like pipes, tubing, sheets, and films. This method is widely used in packaging and construction industries.

Blow molding is used to create hollow plastic products like bottles and containers. It involves heating plastic until it becomes moldable and then inflating it inside a mold to achieve the desired shape.

Thermoforming involves heating a plastic sheet until it is soft and then forming it over a mold. This method is commonly used in the packaging industry for creating trays, clamshells, and disposable cups.

Rotational molding, or rotomolding, is used to produce large, hollow plastic parts such as tanks, playground equipment, and kayaks. This process involves heating and rotating a mold to evenly distribute the plastic material.

In addition to the established techniques and common plastics described above, new trends and developments in plastics processing can also be observed. Thus, 3D printing, e.g., has revolutionized plastic processing in the last decade by enabling rapid prototyping and on-demand manufacturing. This technology allows for greater design flexibility and reduced material waste compared to traditional methods and enables the production of plastic parts from a quantity of one.

Trends and drivers of change

Demand for environmentally friendly plastics is growing, leading to innovations in biodegradable and bio-based plastics. Materials such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA) are gaining popularity in sustainable packaging and medical applications.

The integration of automation and artificial intelligence (AI) in plastic processing enhances efficiency, reduces defects, and optimizes production lines. Smart sensors, robotic arms, and AI-driven analytics are becoming standard in modern manufacturing facilities.

In addition to these new technical possibilities and the associated challenges and necessary research efforts, the plastics industry is also facing a number of social and political challenges. One of the biggest challenges in plastic processing is waste management. Recycling initiatives, including mechanical recycling, chemical recycling, and closed-loop systems, aim to create a circular economy where plastics are continuously reused instead of discarded. Reducing energy consumption in plastic processing is essential for cost savings and environmental sustainability. Advances in energy-efficient machinery, heat recovery systems, and renewable energy integration help manufacturers reduce their carbon footprint. Governments worldwide are implementing stricter regulations on plastic production and waste management. Compliance with these regulations requires manufacturers to adopt sustainable practices, invest in eco-friendly materials, and adhere to safety standards.

Analytics to manage change

The diverse aspects of plastic processing, from material selection and processing techniques to sustainability considerations and industry regulations, all rely on a fundamental understanding of material behavior. The key to managing these complex plastic value chains lies in plastic analytics, which acts as the overarching framework connecting all these elements. The interaction between material composition, processing conditions, and final

product properties is highly intricate, with multiple influencing factors and interdependencies. To optimize performance, improve efficiency, and ensure consistent product quality, plastic analytics is indispensable. By applying scientific methods to analyze plastics at different stages – raw material characterization, in-process monitoring, and final product assessment – manufacturers gain indispensable insights. These insights allow for predictive adjustments, enhanced material efficiency, and sustainable production solutions, making plastic analytics the most important basis for establishing a comprehensive understanding of material and process behavior in plastic processing.

The following reports and studies highlight the benefits of integrating process technology with plastics analytics, using the extrusion process as an example. Extrusion is a complex system that relies on various auxiliary devices for operation and material handling. Understanding the properties of raw materials, the processing behavior of the plastic, and the characteristics of the extrudate is crucial for designing and optimizing the extrusion process.

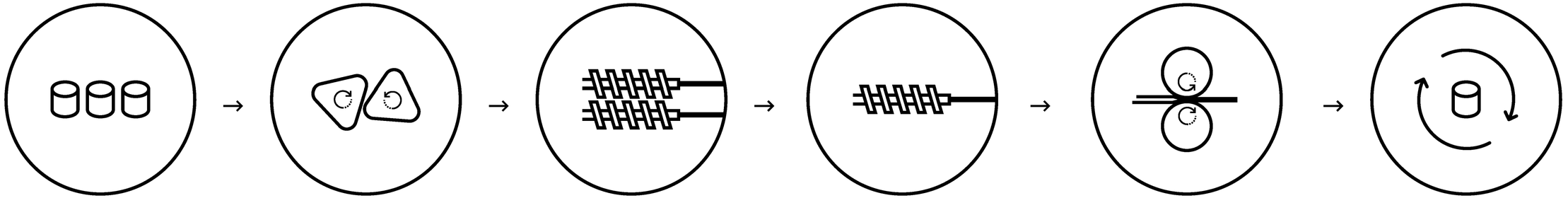
The examples presented here can also be applied to all other processing techniques, as similar challenges relating to process-induced morphologies such as crystallization, thermal resistance, and many more arise in all plastics processing methods.

This e-book is dedicated to the extrusion of flat films as a special area of this plastics processing method. Plastic film extrusion is a highly complex process that requires precise process control, extensive material knowledge, and cutting-edge technology. The selection of the polymer alone significantly affects the final properties of the film. Factors such as viscosity, melting behavior, and the use of additives must be carefully considered to achieve the desired mechanical, optical, and barrier properties. The extrusion process itself involves precise temperature and pressure control, ensuring uniform film thickness and structural integrity.

Plastic films, including packaging films, are sophisticated, high-tech products rather than simple materials. They often consist of multiple layers, each designed to fulfill a specific function, such as providing mechanical strength, oxygen or moisture barriers, or heat sealing. Advanced co-extrusion and lamination technologies enable the combination of different polymers, enhancing performance while maintaining minimal material usage. Additionally, modern plastic films integrate functionalities like anti-fog coatings, UV resistance, or recyclability features, further demonstrating their complexity. Their production demands not only advanced machinery but also in-depth expertise in polymer science, processing technology, and sustainability considerations.

Extruded films and thin strips, along with injection-molded films, are commonly used as source materials for test specimen preparation in plastics analysis. This is one reason why this e-book focuses on plastics analysis using the cast film extrusion process.

Polymer processing value chain



Raw materials	Recipe development	Compounder: pellet production	Extrusion: film production	Final product production	Recycling
FTIR spectroscopy	Lab-scale mixing	Twin-screw extrusion	Single-screw extrusion	FTIR spectroscopy	FTIR spectroscopy
Raman spectroscopy	FTIR spectroscopy	Rheological analysis	Raman spectroscopy	Zeta potential analysis	Dilute viscometry
Rheological analysis	Rheological analysis	Raman spectroscopy	Rheological analysis	Nanoindentation testing	Microwave digestion
Moisture analysis	Twin-screw extrusion	Gas pycnometry	FTIR spectroscopy	Rheological analysis	
Microwave digestion		Dilute viscometry			

5

Production of Final Product (e.g. Packaging Film)

6

Recycling

7

Anton Paar Solutions

1

Raw Materials (Plastic Pellets)

Key Facts

FTIR spectroscopy

Quick pass or fail quality checks of incoming materials

Rheological analysis

Optimization of processing conditions, tool design, and quality control

Water-selective moisture analysis

Moisture measurement and drying time prediction in packaged polymers

Raman spectroscopy

Quick incoming goods control based on their chemical fingerprint

Microwave digestion

Elemental impurity detection in raw materials affecting mechanical properties

Raw materials for impeccable quality

Polymer analysis of raw materials is critical in ensuring that the entire plastic processing value chain functions optimally, meeting both quality standards and evolving regulatory requirements. In this critical phase, where plastic granulate is examined prior to further processing, advanced analytical techniques are employed to assess the chemical composition, detect impurities, and verify the physical properties of the materials. These analyses – ranging from Fourier-transform infrared spectroscopy (FTIR) and chromatography to Raman spectroscopy, rheological investigations, and thermal analysis – provide a comprehensive picture of the raw material's integrity. By identifying even trace contaminants or degradation products at an early stage, manufacturers can prevent downstream processing issues that may compromise the mechanical strength, durability, and safety of the final plastic products.

Sustainability and control of composition

The increasing emphasis on sustainability and circular economy practices in today's market makes precise polymer analysis indispensable. As industries strive to reduce waste and enhance recycling processes, understanding the exact composition of plastic granulate is crucial for effective reprocessing. This not only minimizes environmental impact but also optimizes resource usage by ensuring that only high-quality, contaminant-free materials enter the production cycle. In addition, rigorous raw material control helps companies comply with both national and international environmental regulations, thereby reducing the risk of costly recalls or sanctions.

From offline to real-time analytics

The integration of real-time monitoring and state-of-the-art analytical equipment into production lines has further elevated the importance of polymer analysis. By enabling continuous quality assessment, these technologies help swiftly identify deviations from standard specifications, thereby reducing production downtime and associated costs. In a competitive global market, maintaining a consistent quality of raw materials translates directly into improved product performance and customer satisfaction. Furthermore, the data acquired through comprehensive polymer analysis can feed back into research and development initiatives, fostering innovations that lead to new material formulations and processing techniques.

In summary, the importance of polymer analysis in raw material control cannot be overstated. It is a cornerstone of quality assurance in plastic processing, ensuring that the initial building blocks are of the highest standard. By facilitating early detection of potential issues, enhancing compliance with stringent regulatory frameworks, and supporting sustainable manufacturing practices, polymer analysis not only safeguards the integrity of the production process but also contributes significantly to economic efficiency and environmental responsibility.

1.1 Incoming goods control with FTIR

Incoming goods inspection serves as a critical checkpoint in the polymer processing industry, ensuring that raw materials such as polymers and additives meet specific requirements before entering production processes.
The FTIR spectrometers Lyza 3000 and Lyza 7000 can perform verification measurements and interpret them automatically, presenting the user with a simple pass/fail result immediately without the need for expertise in the field of spectroscopy.

Material verification with FTIR

FTIR spectrometers can be used for material verification by comparing the sample spectrum against a reference spectrum. An FTIR spectrum consists of characteristic absorption patterns, corresponding to the molecular vibrations unique to the sample's chemical composition. Matching the spectra verifies the material's identity, while deviations can indicate impurities, defects, or nonconformity to standards.

The result of a verification is a hit quality index (HQI) using a Pearson correlation coefficient. The HQI is used to determine the degree to which two spectra match. The closer the HQI hit is to 100.00, the better the match. For incoming goods quality control, the HQI must have a high number above HQI 95.00 (depending on the material and the accepted raw material variation).
Reference spectra must be collected directly in the production facility at the point of incoming goods control. Batches of high quality are taken for the measurement of reference spectra, which are then used in the verification process. This way, customer-specific materials can be used for quality verification, and acceptance limits can be defined by the user depending on requirements.

Measurement cell

For typical polymers, an FTIR spectrometer using ATR (attenuated total reflectance) is industry-standard – the sample does not need to be prepared for analysis; it only needs to be loaded onto the ATR crystal for the measurement.

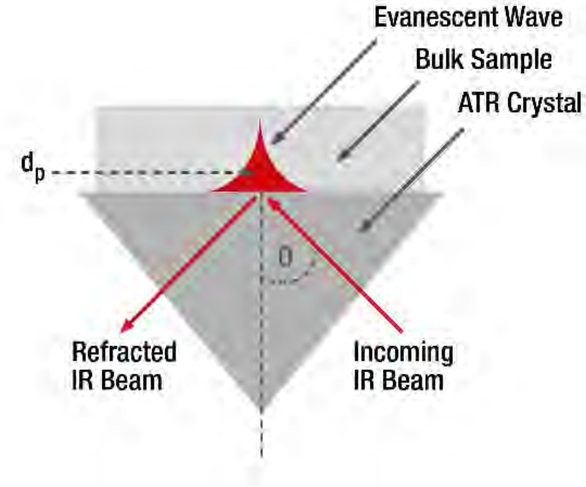


Figure 1: Schematic figure of attenuated total reflectance.

The IR light penetrates the sample to a depth of a few micrometers, where specific wavelengths are absorbed while the remaining light is reflected. The spectrum is generated only from the small interaction of light and sample. To ensure reproducible results, the sample must be firmly secured against the ATR crystal. A pressure clamp must be used to place the test sample properly on the ATR crystal.

Verification measurement

A pellet of raw material was measured with a diamond ATR cell. The measurement parameters are summarized in Table 1.

Spectral resolution	4 cm^{-1}
Number of scans	24
Zero padding	1
Spectral type	Absorbance
Apodization	Blackman-Harris

Table 1: Measurement parameters used for the verification measurement.

The acquired FTIR spectrum was compared against the reference spectrum of LDPE, the target material. Operators may use a predefined method which makes it extremely fast and less error-prone to perform such a verification.

Figure 2 displays the result of a passed material verification with an HQI of 98.69 and a set HQI threshold of 95.00.

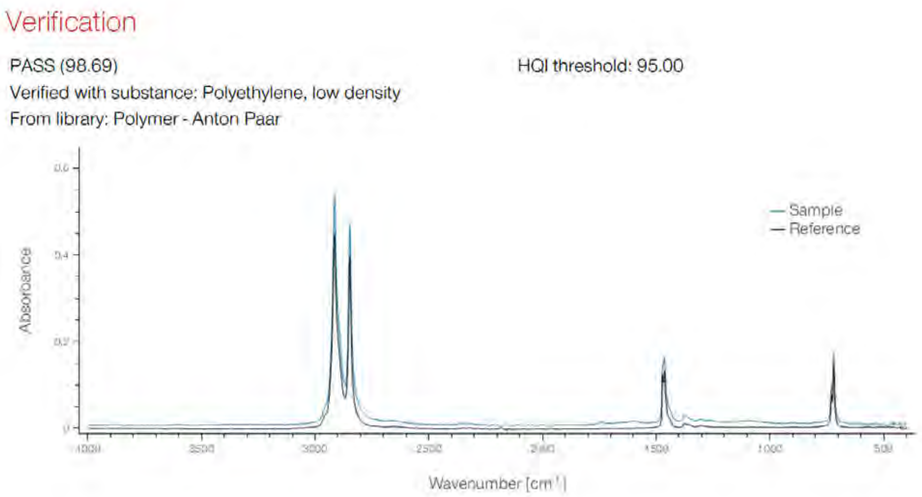


Figure 2: Result of a passed LDPE material verification with an HQI of 98.69.

FTIR is the ideal tool for reliable and quick incoming goods inspection due to its user-friendliness and measurement times of under a minute. With minimal sample preparation, FTIR is particularly well-suited for industries requiring fast and non-destructive quality checks, enhancing overall process efficiency.

Instruments suitable for these measurements
Lyza Series

1.2 Identification and quantification of polymers and their monomeric composition

The production of final polymer products involves compounding pellets from homopolymer raw materials, incorporating a blend of multiple polymers and additives. The recipe determines the quality-relevant properties of the final product, derived from both customer and regulatory requirements.

Copolymers, composed of two or more different monomers in their backbone, require precise composition control to achieve the desired material properties such as strength, processability, brittleness, liquid- and gas-barrier properties, recyclability, and toxicity.

Effective quality control starts with the proper qualification of the process input. This prevents errors originating from raw material composition, picking, handling, and dosing right at the outset.

The ability to identify individual polymers and quantify monomer content in copolymers is also essential for process optimization and output assessment. In the event of quality deviations, elucidating potential compositional changes is essential for prompt and rigorous root-cause analysis, thereby facilitating the timely implementation of corrective measures.

Raman spectroscopy provides a fast, non-destructive, and highly specific method for both polymer identification and quantification.

With Raman, chemical identification can be done through transparent or translucent packaging (like plastic bags, films, and containers). Alternatively, a fiber probe can be pierced or immersed into a bag or container. samples do not have to be taken to the lab and can be measured at-site with mobile Raman devices, with clear result output on the screen for decisions (not only spectra).

Identification of polymer components

Raman spectrometers are typically equipped with a factory library and support third-party spectral databases for immediate use.

For a fast material identity check, the instrument carries out an automatic comparison of the measured spectrum with a reference spectra database in the library. Within seconds, it delivers a clear pass/fail result based on the hit quality index (HQI) – a measure of match accuracy between the sample and the reference.

What underlying mechanisms are involved during the measurement process?

Each polymer exhibits a unique Raman fingerprint, allowing for direct differentiation between individual polymer components in a mixture. The fingerprint region (700 cm^{-1} to 1,700 cm^{-1}) contains characteristic vibrational bands associated with different functional groups. This enables rapid automatic identification of individual polymers, even without spectroscopic knowledge.

Figure 3 shows that each polymer exhibits its own characteristic pattern and that different polymers can easily be distinguished.

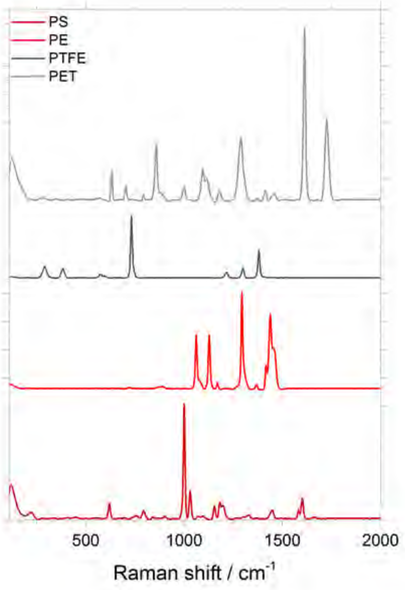


Figure 3: Comparison of the Raman spectra of the four polymers exemplarily studied in this chapter.

Characteristic functional groups of each polymer lead to characteristic vibrational bands which are mostly found above 900 cm^{-1}. For example, PET is the only polyester of the four substances and exhibits the characteristic carbonyl stretching band at 1,725 cm^{-1}.

Polymers with similar functional groups exhibit bands at similar positions. PS and PET, e.g., both exhibit a benzene ring and therefore show a characteristic band around 1,600 $cm^{-1,}$ which is related to the C-C stretching within the ring. Except for PTFE that does not contain any hydrogen atoms, the Raman spectra of the polymers studied here exhibit bands characteristic of deformation vibrations of CH_2 or CH_3.

Quantification of monomer content in copolymers

A Raman spectrum contains relatively few but distinct peaks, which enables direct determination of polymer composition in mixtures, as well as the ratio of repeating units in copolymers.

Quantifying a selected copolymer in a blend involves developing a linear regression model. Once established, the Raman spectrometer automatically calculates and displays the relevant concentration during routine analysis.

Developing the quantification method is straightforward: Characteristic peaks for different components are selected, correlations between relative concentrations and peak sizes are established, and the corresponding formula is saved on the instrument.

Ethylene content in ethylene-vinyl alcohol (EVOH) copolymer

Raman spectroscopy was applied to a series of ethylene-vinyl alcohol (EVOH) copolymer (see Figure 4) samples with varying ethylene content ranging from 24 % to 48 %. A calibration model for determining the ethylene concentration in unknown samples was established.

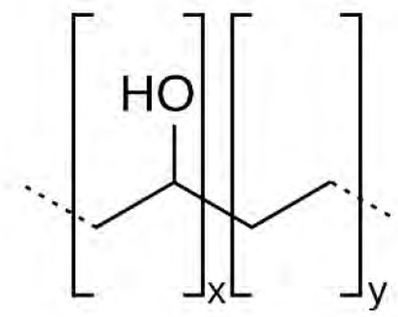


Figure 4: Structural formula of the ethylene-vinyl alcohol copolymer.

1. Raman spectra were acquired from EVOH pellets.
2. Specific spectral regions were selected, focusing on the vibrational bands corresponding to the ethylene and vinyl alcohol units (see Figure 5).
3. As the ethylene content increases, characteristic Raman bands associated with ethylene moieties become more prominent, while those of vinyl alcohol show relative intensity reductions.
4. To quantify these changes, peak intensity ratios are calculated, and a linear regression model is developed (see Figure 6).

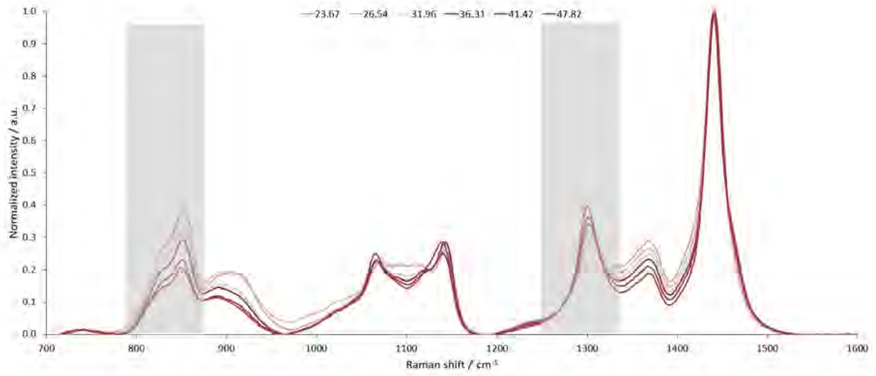


Figure 5: Structural formula of the ethylene-vinyl alcohol copolymer.

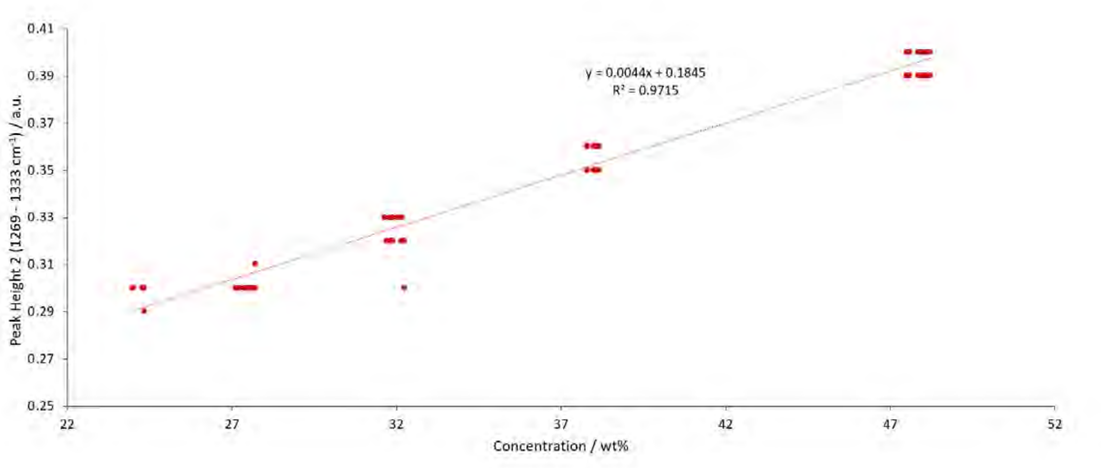


Figure 6: Calibration curve with the normalized height of Peak 2 plotted against the actual concentration.

The strong correlation between Raman spectral features and ethylene concentration allows for accurate quantification of EVOH compositions.
To validate the approach, test samples with known ethylene content were measured, and the Raman results were compared to NIR reference values. The deviations between the two methods were below 1 %, confirming the reliability of Raman spectroscopy for monomer quantification in copolymers.
This method offers a rapid, non-destructive alternative to traditional techniques, making it highly suitable for both quality control and research applications in polymer manufacturing.

Advantages of Raman spectroscopy

- At-site: Process input qualification to avoid errors from raw material, picking, and dosing, eliminating the need to take samples to the lab, and enabling real-time process optimization
- Mobility: Compact instruments with a battery option and fiber probe ensure easy on-site measurements anywhere on the production line or in the warehouse
- In-line and laboratory use: Suitable for industrial process development, production process monitoring, and quality control applications
- Non-destructive: Preserve material integrity while testing actual process input and output directly without the need for special sample preparation
- Chemical sensitivity: Distinguish compositional variations and avoid material non-conformities
- All qualification levels: Easy to interpret information without spectroscopy knowledge
- Traceability: Spectra saved for subsequent analysis or root cause analysis in case of deviations

Conclusion

Raman spectroscopy is a reliable technique for identifying polymers and quantifying monomer composition in copolymers. By leveraging the unique spectral fingerprints of different polymers and monomer units, it delivers rapid, precise analysis – enabling effective quality control, ensuring compliance of process inputs and output materials, and guiding process development and optimization.

Instruments suitable for these measurements
Cora 5001

1.3 Time-temperature superposition (TTS) and master curves

To select the appropriate polymer for a product or the correct process parameters and process design for its production, several key factors must be considered. When choosing a polymer, the mechanical properties as a function of temperature are particularly important. For pure polymers, this information can be found in technical data sheets. However, if blends are used, these properties can vary significantly depending on the polymers involved and their mixing ratio. This aspect is examined in Section 3.5 using the example of PMMA/PC blends.

However, the requirements for polymers are not limited to the final product properties in terms of thermomechanical behavior. The properties of the molten polymer are also of crucial importance. Different processing methods require different characteristics of the polymer melt. For example, in the extrusion of profiles or pipes, the melt must exhibit a certain stability so that the products maintain their shape after exiting the extrusion tool. In such cases, polymers with higher viscosity are typically used. Conversely, for injection molding applications, lower-viscosity melts are preferable, especially when thin-walled parts need to be produced.

The rheological properties of polymers are also of great significance when designing processing tools such as injection molds, extrusion dies, and melt distributors.

Furthermore, when designing tools and processes, the temperature dependence of the viscoelastic properties plays a crucial role. To analyze this relationship and to enable the prediction of flow behavior, so-called master curves are often created using the time-temperature superposition (TTS) method. In this section, such a master curve is developed for LDPE, and the process is described in detail.

The rheological investigations on LDPE were conducted using a rheometer. For sample temperature control, an electric heating plate and a corresponding active hood were used. To prevent thermal-oxidative degradation of the polymer, the hood was purged with nitrogen. Measurements were performed using a parallel-plate measuring system with a diameter of 25 mm.

Rheological testing can also be conducted fully automated using the HTR 7000 (high-throughput rheometer) from Anton Paar. This system automates the entire workflow, including sample loading, trimming, measurement execution, and optionally cleaning of the measuring system. The fully automated trimming tool with disposable blades, which are handled by the six-axis robot as well, performs the trimming process in order to achieve the highest reproducibility for the measurement results. This allows for continuous, efficient rheological characterization of up to 60 samples without manual intervention, making it particularly useful for extended testing routines. The implementation of the HTR 7000 increases lab safety, provides results of the highest reproducibility, and ensures data integrity for a digitalized lab. It can also significantly shorten the time-to-market for new formulations.

To create a master curve, multiple frequency tests at different temperatures must be carried out. For the frequency test, both the deformation and the frequencies need to be specified. When selecting the deformation, it is crucial to ensure that it falls within the linear viscoelastic range. This range can be determined using an amplitude sweep, which is not shown here.

When choosing the frequency range and the number of measurement points, time is a key factor. Low frequencies result in long measurement durations, which can become very time-consuming if multiple temperatures need to be tested. Additionally, there is a risk that the sample may undergo changes due to thermal-oxidative processes during the measurements. However, in the case of the thermally very stable LDPE tested here, time was not a critical factor. Therefore, a frequency sweep with 13 measurement points between 100 rad/s and 0.1 rad/s was performed.

Using a loop function in the rheometer software, the same measurement can be easily repeated at different temperatures. For this, the start and end temperatures, as well as the increment, must be specified. In this example, a start temperature of 160 °C, an end temperature of 210 °C, and an increment of 5 °C were chosen, resulting in 11 loop iterations.

In Figure 7, the measured complex viscosity curves are shown. As expected, an increase in temperature results in a shift of the complex viscosity towards lower values. Figure 8 presents the storage and loss modulus curves. For better clarity, only every second temperature step (in 10 °C increments) is displayed in this diagram.

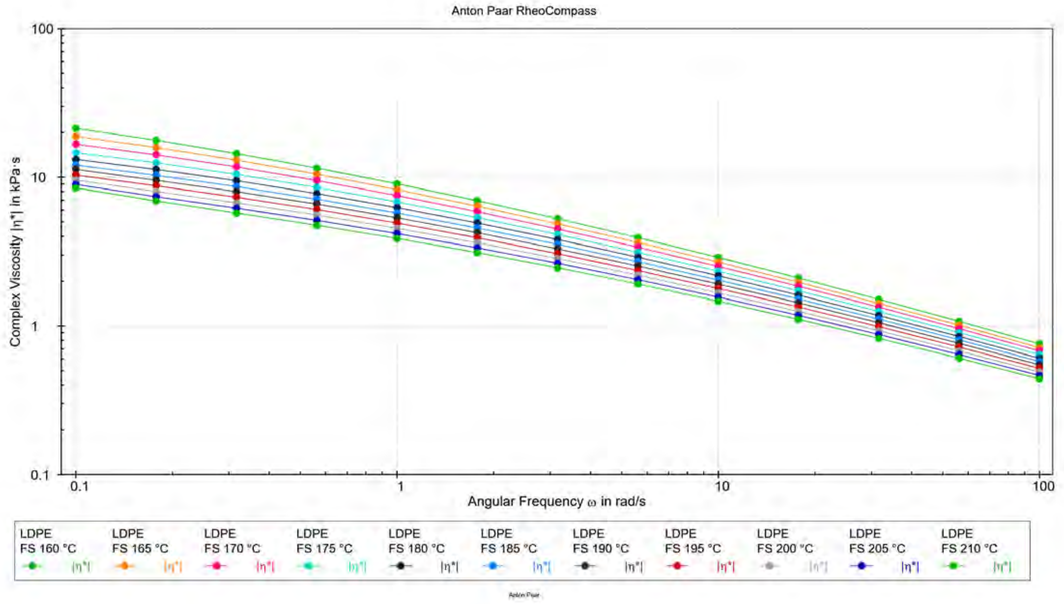


Figure 7: Complex viscosity curves as a function of angular frequency measured at temperatures between 160 °C and 210 °C.

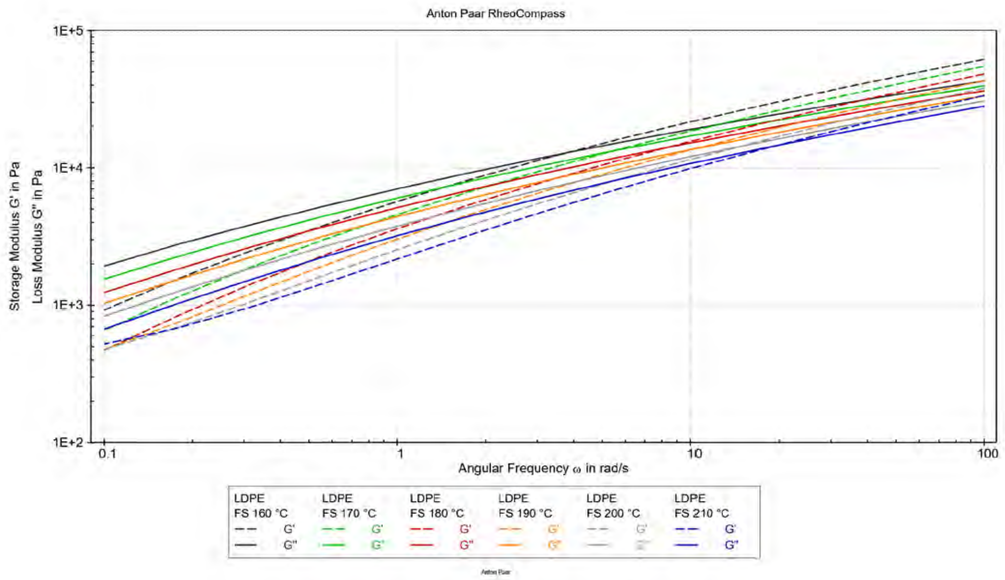


Figure 8: Storage (G') and loss (G") moduli as a function of angular frequency measured at temperatures between 160 °C and 210 °C.

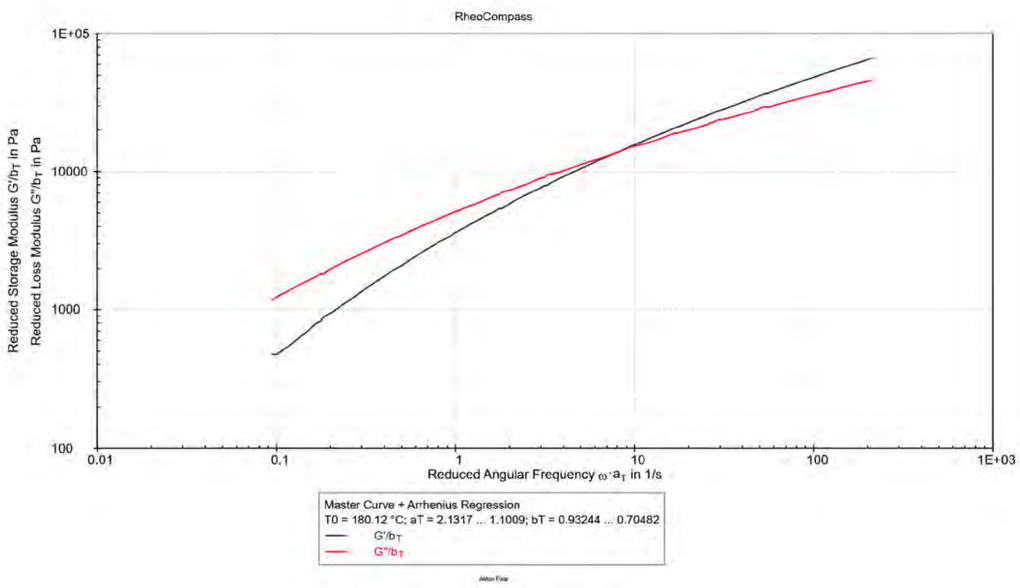


Figure 9: Master curve of LDPE for a reference temperature of 180 °C using the WLF regression mode.

Based on the measured data, master curves can now be calculated. Several options are available in the software for this purpose: The data can be simply shifted to a desired reference temperature, or the creation of a master curve can be combined with a regression model based on Arrhenius or the WLF approach, which also provides the shift factors at and bt.

Figure 9 shows a master curve with Arrhenius regression for a reference temperature of 180 °C.

Rheological master curves are an essential tool in polymer processing, as they allow for a detailed prediction of flow and deformation behavior over a broad time and frequency range. Using the time-temperature superposition (TTS) method, the viscoelastic properties of polymers can be evaluated to optimize processing conditions, tool design, and quality control. Master curves play a crucial role in extrusion, where they help determine viscosity stability to ensure dimensional accuracy in profiles and pipes, as well as in injection molding, where they aid in selecting materials with suitable flow behavior for thin-walled parts. They are also valuable in specialized processes such as fiber spinning, film blowing, and blow molding, where an understanding of melt strength

and elongational properties is critical to prevent defects. For such analyses, specialized tools like the Sentmanat Extensional Rheometer (SER) and Universal Extensional Fixtures (UXF) can be used in combination with an MCR Rheometer to directly obtain additional insights into the elongational behavior of polymers.

In this study, a master curve for LDPE was successfully developed based on frequency sweep measurements at different temperatures. The shift factors were determined using Arrhenius regression, demonstrating the temperature dependence of LDPE's viscoelastic behavior. The results confirm that TTS is a reliable method for extending experimental data and predicting polymer behavior under various processing conditions. By applying these insights, polymer selection and process optimization can be significantly improved, ensuring better control over material performance in industrial applications.

Instruments suitable for these measurements
MCR Evolution Rheometer Series
SmartMelt Series

1.4 Moisture content check of polymers and drying time prediction

Residual moisture in polymer granulates or finished components can severely impact processability and product quality. When material suppliers do not provide clear guidelines on drying times, or when there is uncertainty about whether the packaged polymer requires drying at all, measuring the moisture content becomes a crucial step. This use case presents a comprehensive approach to determining moisture levels in polymers – particularly when packaging conditions, storage times, or variations in raw material supply introduce unknown moisture uptake. By leveraging water-selective moisture analysis via the calcium-hydride method, processors gain a reliable basis for deciding whether drying is necessary and, if so, for how long it should be performed.

Importance of measuring moisture content in packaged polymers

In polymer processing, moisture can cause:

- Hydrolytic degradation of sensitive polymers (e.g., polyamides, polycarbonates)
- Surface defects (e.g., streaks, voids) in injection-molded parts
- Variations in viscosity leading to unstable processing parameters
- Compromised mechanical and optical properties in the final product

Moisture uptake may occur during shipping, long-term storage, or due to improper packaging conditions. When processors receive a batch of material without a precise drying recommendation – or if it is unclear whether the material has picked up moisture – direct measurement is the only way to accurately assess the need for drying. Measuring moisture is especially important for polymers that must be dried below specific thresholds (e.g., <0.02 % for certain polycarbonates) to avoid processing defects.

Water-selective measurement with the calcium-hydride method

The calcium-hydride method (DIN EN ISO 15512:2019, Method E) provides a water-selective approach by reacting the liberated water vapor with calcium hydride. In brief:

- The sample is heated under vacuum, causing moisture to evaporate
- The evaporated water reacts with calcium hydride to form hydrogen gas
- A pressure sensor detects the resulting increase in hydrogen pressure
- The instrument calculates the exact water content from the measured pressure change, temperature, and internal volume

Because only water reacts with calcium hydride, solvents or plasticizers do not interfere. This ensures high selectivity and eliminates overestimation of moisture content due to volatile non-water substances.

Relevance for packaged polymers

Unlike methods based purely on weight loss (e.g., gravimetric), the calcium-hydride approach directly targets water, which is the main culprit in processing issues. Even if a polymer package contains additives, colorants, or other volatiles, the result specifically reflects water content. This is especially beneficial

when dealing with recycled or composite materials where multiple unknown components could otherwise skew measurements.

Experimental setup

Moisture analyzers with water-selective capabilities employ the calcium-hydride method for rapid, repeatable analysis. This technique quickly releases moisture from polymers and delivers measurements that remain unaffected by ambient conditions.

The calcium hydride reagent reacts exclusively with water, generating hydrogen. sample preparation:

- Weighing a small amount of the polymer (commonly 5 g to 60 g)
- Placing the sample in the measuring cup along with a spoonful of fresh calcium hydride

Vacuum and heating:

- The measuring cup is evacuated, removing ambient humidity
- The sample is heated to the predefined measurement temperature (e.g., 160 °C or higher, depending on the polymer)

Reaction and measurement:

- As the sample releases water, it reacts with calcium hydride to produce hydrogen
- A pressure transducer detects the hydrogen buildup, calculating the total moisture content

Data interpretation:

- The instrument displays the measured moisture as % H_2O, ppm H_2O, or mg H_2O
- Built-in thresholds can indicate whether the measured moisture exceeds acceptable limits for processing

Decision on drying:

- If moisture levels exceed the recommended threshold (e.g., 0.02 % for polycarbonate), the material must be dried
- Operators can reference standard drying times for a selected polymer or consult guidelines from built-in databases
- If the measured moisture is already below the critical limit, no additional drying is required, saving energy and reducing cycle time

Benefits and context for polymer processing

Energy and cost savings

Measuring moisture before drying prevents unnecessary energy consumption by avoiding superfluous drying cycles. In many facilities, drying ovens run continuously, representing a major cost factor. Targeted, on-demand drying helps streamline operations.

Consistent product quality

Real-time knowledge of moisture content ensures that only material with acceptable residual moisture enters extrusion or injection molding. This consistency minimizes scrap rates, rework, and customer complaints related to dimensional inaccuracies or surface defects.

Adherence to standards

The calcium-hydride method, as outlined in DIN EN ISO 15512:2019, is internationally recognized. Using a standards-compliant method simplifies audits and fosters trust in quality assurance processes.

Process optimization

Should the measured moisture be high, the drying cycle can be optimized by adjusting temperature, time, or air flow. Conversely, if the moisture content is already low, production can begin without delay – reducing lead times and improving throughput.

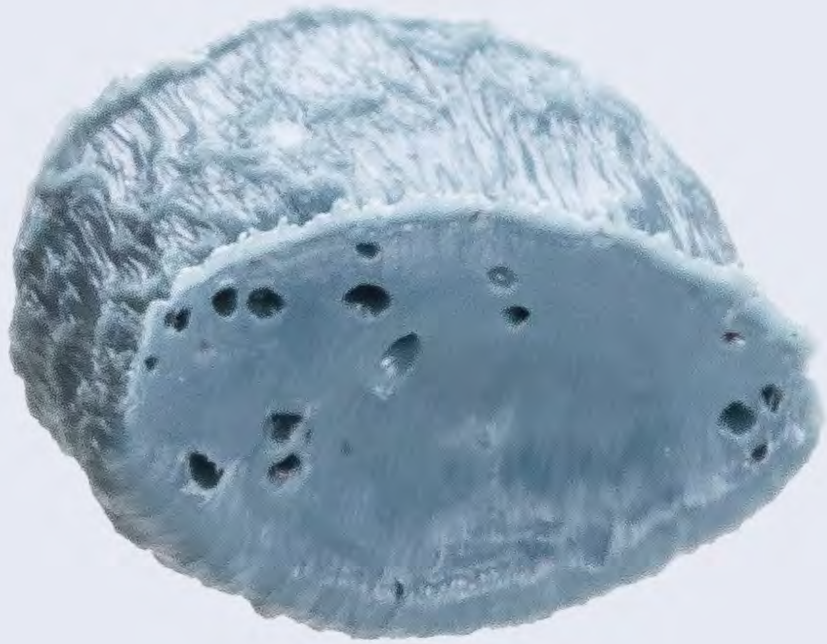
Avoiding over-drying of polymers

Excessive drying of polymers can lead to material degradation, impacting mechanical properties and processing behavior. Over-dried polymers may become brittle, suffer molecular weight reduction, or exhibit poor melt flow characteristics. Monitoring moisture levels accurately prevents unnecessary drying.

Conclusion

When suppliers do not specify drying times – or if there is uncertainty about moisture in packaged polymer materials – direct, water-selective measurement is the key to making well-informed decisions. Water-selective moisture analyzers, which implement the calcium-hydride method in compliance with DIN EN ISO 15512:2019, provide a robust and user-friendly solution. By accurately quantifying water content, processors can confidently determine whether drying is needed, specify the optimal drying duration, and ultimately ensure the highest possible product quality. This approach aligns with the broader goal of efficient resource use, reduced operational costs, and minimized scrap rates, thereby supporting sustainable and economically sound polymer processing practices.

Instruments suitable for these measurements
Brabender Aquatrac-V



1.5 Microwave digestion of polymer samples for elemental analysis

Ensuring polymer quality and consistency starts with the purity of raw materials. Elemental impurities – such as heavy metals, excess catalysts, or unintended additives – can undermine mechanical properties, durability, and safety. For example, heavy metals pose environmental and health risks, while residual catalysts disrupt downstream processes and affect product stability. By rigorously monitoring these impurities, manufacturers ensure regulatory compliance and uphold product quality, safeguarding both producers and end-users.

Effective incoming goods control is, therefore, essential to maintaining high manufacturing standards. Elemental analysis plays a key role in this process, identifying and quantifying trace elements and potential contaminants that could compromise polymer integrity.

Why elemental analysis matters for polymer scientists

Elemental analysis provides critical insights into the composition of raw materials used in polymer processing. Understanding the levels of specific elements allows manufacturers to:

- **Ensure compliance with regulations** such as RoHS (Restriction of Hazardous Substances) and REACH (Registration, Evaluation, Authorisation, and Restriction of Chemicals)
- **Prevent contamination issues** that could lead to discoloration, degradation, or other quality defects
- **Optimize formulations** for specific applications, balancing performance characteristics with safety requirements

Key contaminants and their impact include:

- **Heavy metals** such as cadmium (Cd), lead (Pb), and arsenic (As): Toxic and environmentally hazardous, requiring strict monitoring to meet safety standards
- **Iron (Fe):** Commonly introduced during manufacturing, elevated levels can cause discoloration or degradation
- **Copper (Cu) and zinc (Zn):** Often originating from catalysts or stabilizers, these elements can affect oxidative stability, optical or thermal properties, or recyclability
- **Silicon (Si), aluminum (Al), magnesium (Mg), calcium (Ca), sodium (Na), and potassium (K):** Trace elements from fillers or additives that can influence thermal stability, mechanical strength, or processability

Monitoring these elements is crucial for preventing disruptions in polymer production and ensuring material integrity.

Overcoming challenges in polymer digestion

Polymers are highly durable, making them resistant to chemical breakdown during elemental analysis. Additional challenges arise from:

- **Additives, pigments and fillers:** These components can complicate digestion, leaving insoluble residues that compromise analytical accuracy
- **Chemical diversity:** Polyolefins like polypropylene (PP) or polyethylene (PE) are easier to digest, while chemically resistant polymer types like PET or PEEK require higher temperatures for a complete digestion

Traditional wet digestion methods often fall short, leaving residues or requiring excessive processing time. Microwave digestion offers a superior alternative, providing complete and efficient decomposition of even complex polymer samples.

Using microwave digestion to prepare for accurate analysis

Microwave-assisted acid digestion has become the gold standard for preparing polymer samples for techniques like inductively coupled plasma optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS). By ensuring complete sample decomposition, microwave digestion minimizes matrix effects and enhances detection limits, enabling accurate quantification of even trace contaminants.

Microwave digestion:

- **Complete digestion:** Thoroughly breaks down polymers, eliminating carbon residues that could cause interferences during OES /MS analysis
- **Reproducibility:** Consistent results across a wide range of sample types
- **Efficiency:** Faster processing compared to traditional methods, saving time without compromising reliability

Microwave-assisted acid digestion and elemental analysis of a low-density polyethylene (LDPE) sample

The sample (200 mg) was weighed directly into one SVT50 digestion vessel, and 8 mL of nitric acid (HNO_3) and 0.05 mL of hydrofluoric acid (HF) were added. The microwave digestion program consisted of a ramp step to 90 °C over five minutes, a subsequent ramp step to 200 °C over 25 minutes, followed by a hold step at 220 °C for 10 minutes, with temperature control set to average. After digestion, 0.5 mL of HCl was added to the solutions to stabilize certain elements, such as As, for analysis. The digested solutions were transferred to 50 mL tubes and diluted to 50 mL with deionized water. Prior to filling the tubes, 1 mL of a 100 ppm yttrium (Y) solution was added as an internal standard to each sample.

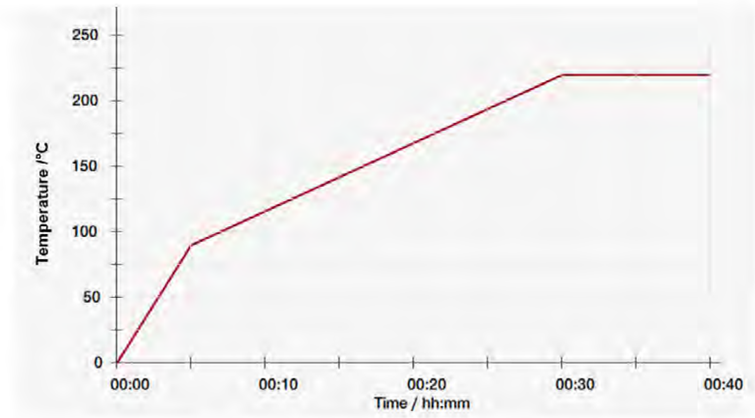


Figure 10: Multiwave 5001 temperature program for digestion of LDPE.

Results and discussion

Elemental analysis was performed using an ICP-OES instrument (iCAP PRO, Thermo Fisher Scientific) operating in axial mode. Calibration was performed using the multi-element standard solution, for accurate quantification of the elements of interest. Due to the unavailability of certified reference materials, the received values for Si should be regarded as indicative values.

Table 2 presents selected elements found in ICP-OES analysis of the digested HDPE sample.

For all elements, values below the limit of detection for the ICP-OES method were obtained, reflecting the high purity of the polymer samples. The presence of a significant amount of Si can be assigned to, e.g., catalyst carrier materials or certain additives.

Sample / Element	Fe	Zn	Cr	Cu	As	Cd	Pb	Si	Al	Mg	Ca	Na	K
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	g/kg	mg/kg	mg/kg	mg/kg	mg/kg
LDPE	<3	<3	<5	<3	<8	<3	<10	0.7	<8	<5	<0.1	<8	<3

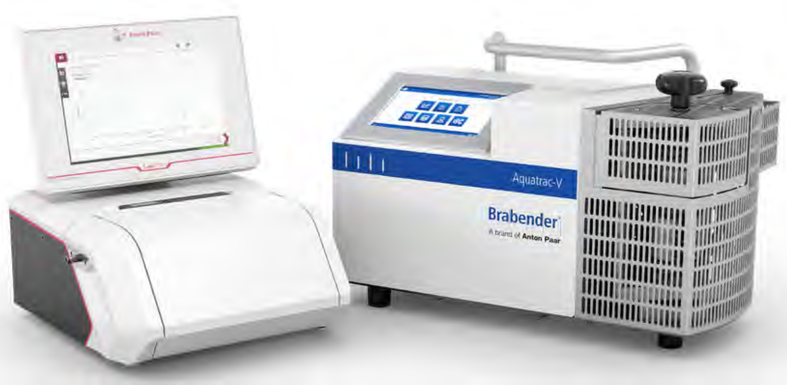
Table 2: Selected elements found in ICP-OES analysis of the supplied LDPE sample (Si indicative value).

Conclusion

Elemental analysis is a cornerstone of quality control in polymer manufacturing, ensuring compliance, consistency, and safety. Microwave digestion systems simplify this critical step by delivering complete, reproducible sample preparation. Advanced features, such as precise temperature control and SmartVent technology, enable the digestion of challenging materials, supporting accurate and consistent ICP-OES analysis.

For polymer scientists, robust elemental analysis not only guarantees material quality but also enhances production efficiency and customer trust. By incorporating microwave digestion into their workflows, manufacturers can confidently meet regulatory requirements and uphold the highest standards of quality assurance.

Instruments suitable for these measurements
Multiwave 5001
Multiwave 7101/7301/7501



Brabender Aquatrac-V

Lyza Series

Power Duo

Ensuring Raw Material Quality with Moisture Analysis and FTIR Spectroscopy

Facing quality issues from excess moisture and material impurities? Brabender Aquatrac-V and Lyza 7000 work together to safeguard your injection molding process. With precise on-site moisture control and rapid FTIR material verification, this duo minimizes defects and ensures consistent, high-quality production.

2

Recipe Development

Key Facts

Laboratory mixer

Process-focused formulation and lab-scale test batch production

FTIR spectroscopy

Fast quantification of additives in polymers for compound development

FTIR spectroscopy

Composition verification for accurate formulation, improved material properties, and enhanced reliability

Rheological analysis

Visualization and quantification of property changes resulting from formulation variations

Viscometry
twin-screw extrusion

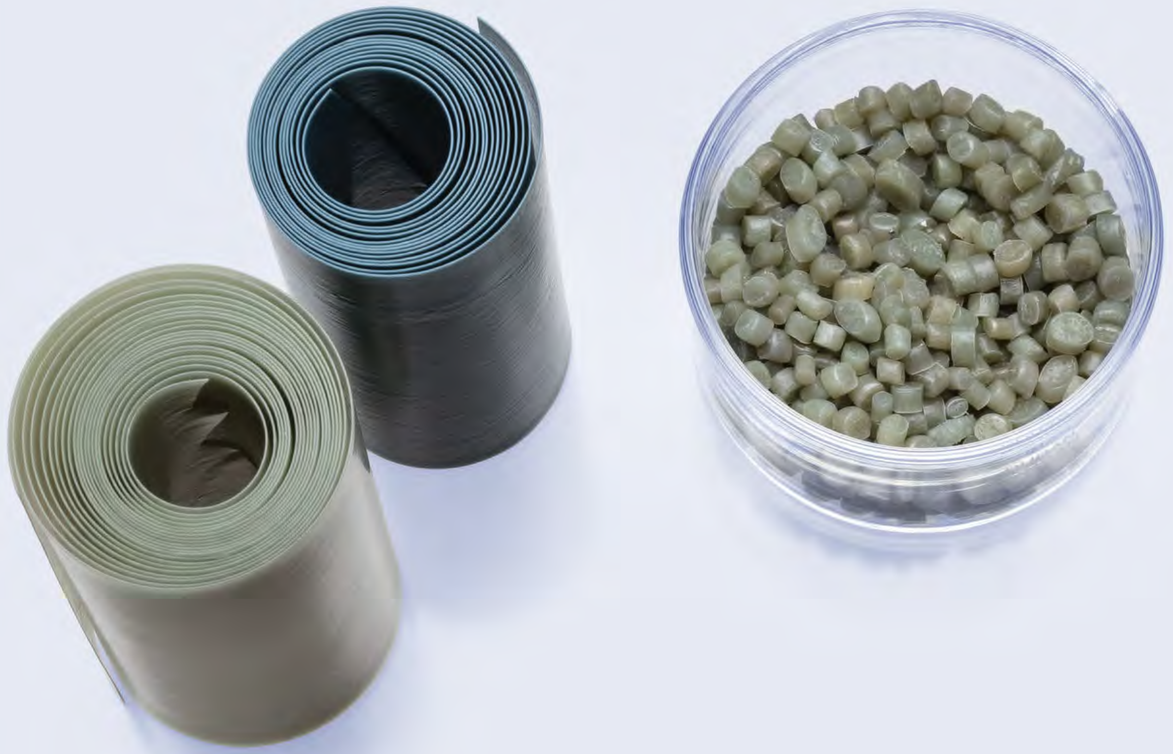
Comprehensive viscosity measurements across a broad shear rate range

Recipe development

The development of plastic formulations involves carefully selecting and combining various polymers, additives, and fillers to achieve desired properties such as strength, flexibility, heat resistance, or chemical stability. This process requires a deep understanding of material science, as well as extensive testing and optimization to meet specific application requirements. Additives like plasticizers, stabilizers, and flame retardants enhance performance, while reinforcing fillers improve mechanical properties.

The evaluation of the miscibility of different polymers in a polymer blend is crucial, as it directly influences the mechanical properties of the final material. Incompatible polymers may lead to phase separation, negatively affecting strength, toughness, and durability. By carefully selecting polymer combinations and using compatibilizers when necessary, manufacturers can optimize the blend’s performance for specific applications. Understanding the interactions between polymers and their impact on mechanical behavior is essential for developing high-quality, reliable plastic formulations.

Polymer analysis tests are essential for evaluating polymer formulations in the early stages of development.



2.1 Blending: Compatibility and process window

Laboratory mixers are primarily used for analyzing and developing plastics, rubber, and other chemical mixtures. They operate based on the internal mixer principle and consist of a mixing chamber with two counter-rotating mixing blades. During operation, raw materials such as polymers, additives, and fillers are introduced into the mixing chamber. The rotating blades generate shear and pressure forces, homogenizing and mechanically processing the material. The chamber is temperature-controlled, and the blade speed can be adjusted to simulate different mixing conditions. Throughout the process, key parameters such as torque and temperature are continuously measured to analyze the material properties. Once the desired mixing time is reached, the material is discharged for further processing or analysis. Anton Paar's Brabender mixers are widely used in research, quality control, and material development to optimize the processing properties of new formulations.

The Plastogram provides real-time insights into the processing behavior of materials during mixing (Figure 11). It is a graphical representation of torque (Nm) over time, recorded as the material undergoes shear and thermal influence inside the mixing chamber.

During the mixing process, the torque curve indicates viscosity changes due to, e.g., plasticization and changing flow behavior in general. A typical Plastogram consists of several distinct phases depending on the type of investigation and the analyzed plastic – e.g., an initial rise in torque as the material resists deformation, peaks that represents the maximum resistance (gelation, crosslinking), and a gradual decline as the material becomes more homogenized and stable.

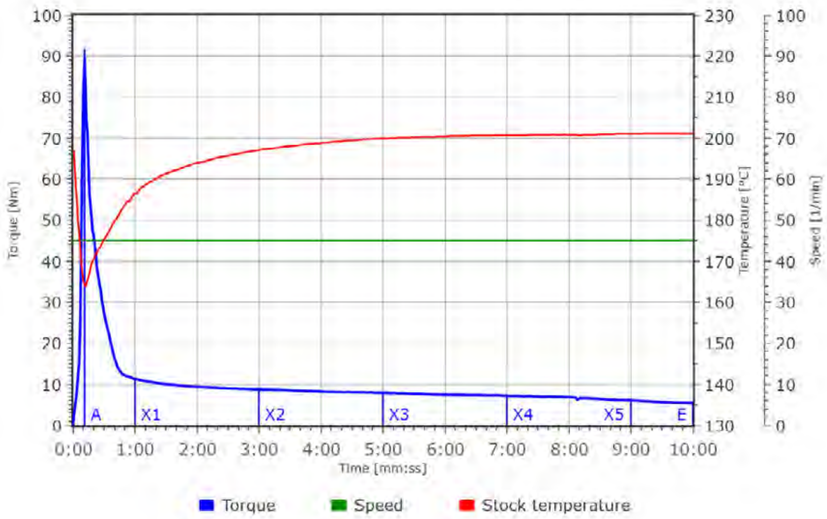


Figure 11: Plastogram of a mixing test of a thermoplastic material.

By analyzing the Plastogram, researchers and engineers can assess critical properties such as processing stability, filler dispersion, degradation behavior,

and the impact of additives. This information is essential for optimizing formulations, improving quality control, and predicting how a material will perform in industrial applications.

Another advantage of evaluating the processability of a compound using laboratory mixers is the small sample size required for analysis. Depending on the type of mixer, small sample volumes are needed, making it an ideal method for early-stage material development. This is particularly beneficial when working with novel materials that are only available in limited quantities or when dealing with expensive components. The ability to assess key processing properties with minimal material consumption allows for efficient formulation optimization while keeping costs and material waste low.

Laboratory mixers are also suitable for rapid quality control by testing a sample from a material batch or material delivery against a reference. This is becoming increasingly important in times of rising recyclate usage, as recycled materials often show greater fluctuations in composition and processing behavior.

Instruments suitable for these measurements
Brabender MetaStation with Measuring Mixer 30/50/350

2.2 Chemical characterization through functional group analysis

Functional group analysis using Fourier-transform infrared (FTIR) spectroscopy is a powerful technique for characterizing the chemical composition of materials, particularly in polymer science. By identifying specific functional groups, FTIR spectroscopy provides insights into the molecular structure, composition, and chemical interactions within polymers. This analytical approach plays a crucial role in polymer recipe development, where precise control over monomer selection, crosslinking, and functionalization is essential for tailoring material properties.

In polymer formulation, FTIR spectroscopy helps verify the presence of target functional groups, assess reaction completeness, and detect unwanted byproducts. This enables researchers to optimize synthesis parameters, enhance polymer performance, and ensure consistency in production.

To determine the quantity of poly(methyl methacrylate) (PMMA) and polycarbonate (PC) in a mixture, FTIR spectroscopy can be used to identify and quantify their characteristic functional groups. PMMA exhibits strong absorption bands associated with ester carbonyl (C=O) stretching around 1,725 cm^{-1}, while PC shows distinctive carbonate (C=O) stretching near 1,770 cm^{-1}. By applying quantitative analysis techniques, the relative concentrations of PMMA and PC can be accurately determined, enabling precise composition analysis of the polymer blend.

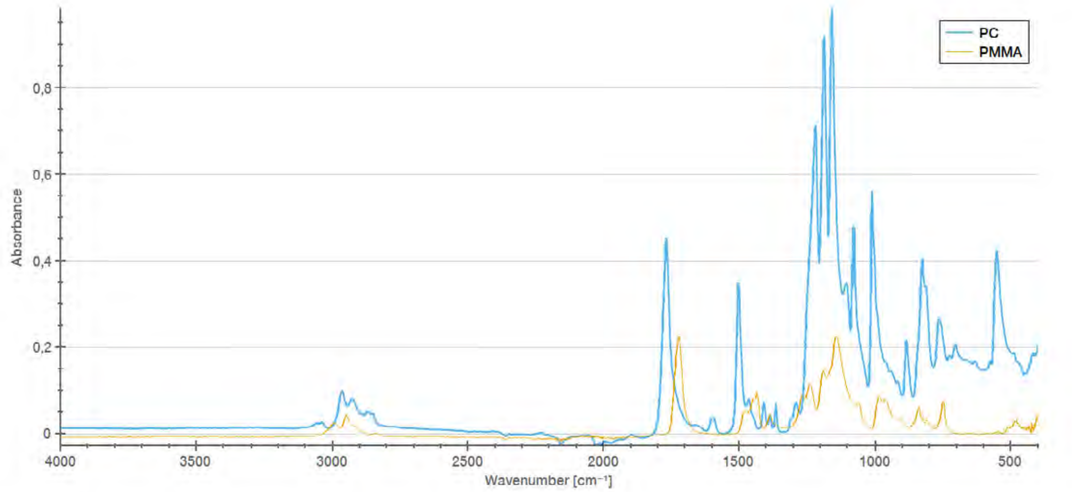


Figure 12: FTIR spectra of pure PC (blue) and pure PMMA (orange).

To evaluate the composition of a PMMA/PC mixture (70 wt % / 30 wt %), FTIR spectroscopy can be used to quantify each polymer based on their characteristic absorption bands. Pure PMMA and PC spectra serve as references to establish calibration models for quantitative analysis. By measuring the intensity ratios of the ester carbonyl (PMMA around 1,725 cm^{-1}) and carbonate (PC around 1,770 cm^{-1}) peaks, the actual composition of each mixture can be determined. This approach ensures the accuracy of the blending process and verifies whether the targeted polymer ratios were achieved.

Quantitative composition determination

A product recipe (recipe 1) was formulated to achieve a composition of 70 wt % PMMA and 30 wt % PC.

The FTIR measurements were performed with a Pike IRIS diamond ATR cell and the measurement settings as shown in Table 3.

Spectral range	400 cm^{-1} to 4,000 cm^{-1}
Scans	24
Spectral resolution	4 cm^{-1}
Apodization	Blackman – Harris
Zero padding	1
Result spectrum	Absorbance

Table 3: Measurement settings for FTIR spectrometer.

For detailed interpretation the spectra were baseline corrected (1-point baseline at 1,560 cm^{-1}). The maximum peaks in defined areas were used for calculation of the quantitative ratios between PC and PMMA. The flank of the carbonate (C=O) stretching peak of PC in the range of 1,775 cm^{-1} to 1,777 cm^{-1} slightly overlaps the carbonyl (C=O) stretching peak of PMMA in the range of 1,724 cm^{-1} to 1,726 cm^{-1} (see Figure 13).

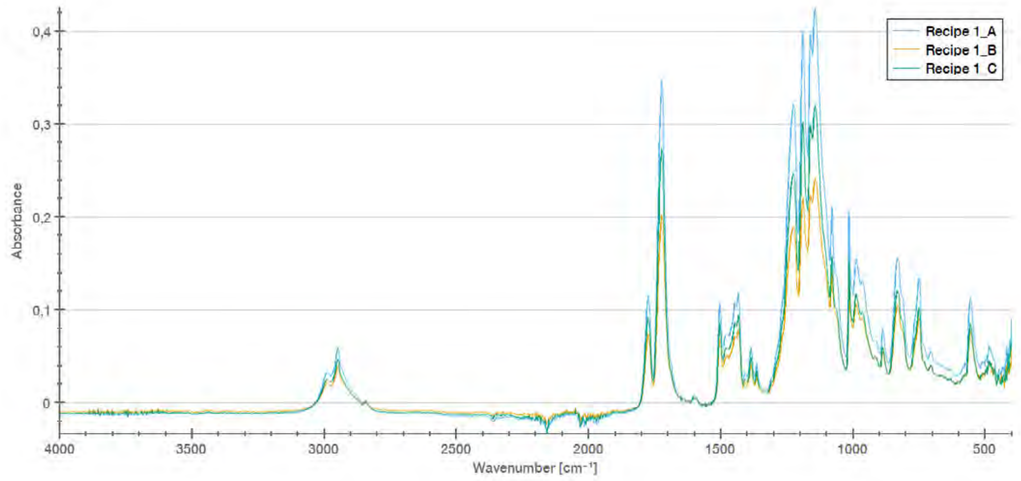


Figure 13: FTIR spectra of the mixture of recipe 1 (PMMA/PC 70 wt % / 30 wt %) measured in triplicate (A, B, C).

To compensate for the influence of this peak overlap on the maximum height of the PMMA peak, a flank disentanglement ratio was defined. The flank disentanglement ratio can be calculated based on the ratio of the PC peak intensity in the area of the maximum peak intensity of the PMMA peak (0.09) and the maximum PC peak intensity (0.48) (see Figure 16). The resulting flank disentanglement ratio is 0.19.

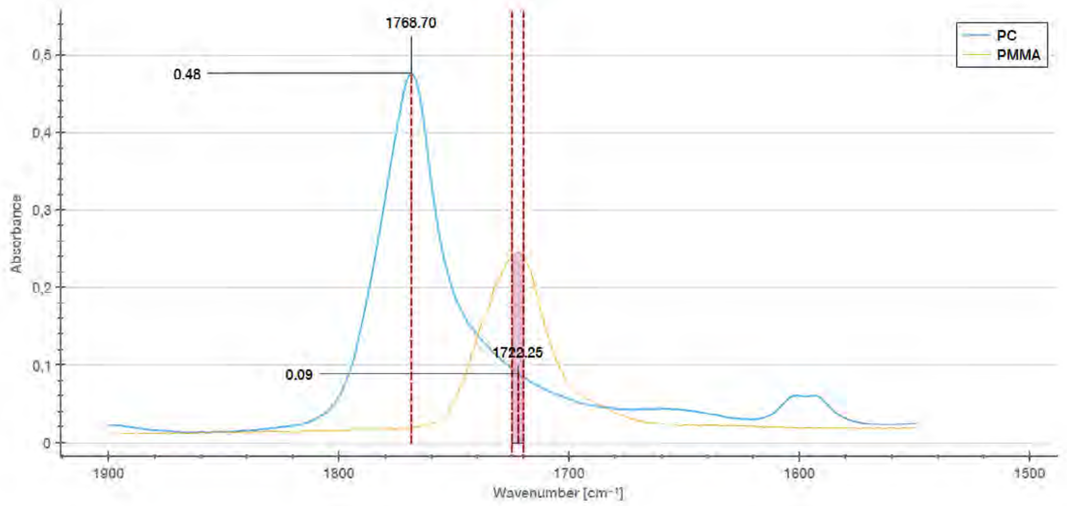


Figure 14: Spectral overlap of the characteristic ester carbonyl peak (PMMA) at around 1,725 cm^{-1} and the carbonate peak (PC) at around 1,770 cm^{-1}. The peak intensity used for the calculation of the flank disentanglement ratio is marked in red.

The PMMA peak intensity was corrected by subtracting the PC peak intensity multiplied by the flank disentanglement ratio (Equation 1).

Equation 1:

$$Peak\ height_{PMMA\ corrected} = Peak\ height_{PMMA} - (Peak\ height_{PC} * flank\ disentanglement\ ratio)$$

A known 50/50 wt % mixture of PMMA/PC was used in order to calculate normalization factors for both materials before measuring unknown samples. The normalization factors were calculated by dividing the known 50 wt % concentrations with the corresponding maximum peak intensities. The resulting normalization factors (793 for PC and 194 for PMMA) were applied for the calculation of the normalized peak heights, as presented in Equation 2 and Equation 3.

Equation 2:

$$Peak\ height_{PC\ normalized} = Peak\ height_{PC} * normalization\ factor_{PC}$$

Equation 3:

$$Peak\ height_{PMMA\ normalized} = Peak\ height_{PMMA\ corrected} * normalization\ factor_{PMMA}$$

The relative concentration of PMMA and PC in the produced polymer was calculated according to Equation 4 and Equation 5.

Equation 4:

$$c_{rel\ PC} = \frac{Peak\ height_{PC\ normalized}}{Peak\ height_{PMMA\ normalized} + Peak\ height_{PC\ normalized}}$$

Equation 5:

$$Conc_{PMMA} = \frac{Peak\ height_{PMMA\ normalized}}{Peak\ height_{PMMA\ normalized} + Peak\ height_{PC\ normalized}}$$

The calculated relative concentrations of PMMA and PC are summarized in Table 4.

Sample	PMMA [wt %]	PC [wt %]
Recipe 1_A	59.1	40.9
Recipe 1_B	61.6	38.4
Recipe 1_C	59.7	40.3

Table 4: Calculated relative PMMA and PC concentrations.

Conclusion

The FTIR analysis successfully determined the PMMA/PC ratios in the prepared mixtures, revealing deviations from the expected compositions. This ratio directly influences the polymer's mechanical, thermal, and optical properties, affecting strength, flexibility, and resistance to environmental conditions. Precise control over the composition ensures product consistency, enhances performance, and meets specific application requirements. By utilizing FTIR for composition verification, manufacturers can optimize formulation accuracy, improve material properties, and enhance overall product reliability.

Instruments suitable for these measurements
Lyza Series

2.3 FTIR quantification of calcium carbonate additive in polyethylene

Accurate quantification of calcium carbonate ($CaCO_3$) in linear low-density polyethylene (LLDPE) is essential for achieving optimal material properties. FTIR spectroscopy provides a rapid, non-destructive method for determining $CaCO_3$ content, supporting efficient quality control. Since $CaCO_3$ is commonly added to LLDPE to enhance performance and cost-effectiveness, the ability to quickly and reliably measure its concentration is invaluable.

Creation of a quantification calibration for determination of $CaCO_3$

To quantify an analyte of unknown concentration using FTIR spectroscopy, establishing a calibration curve is essential. Six LLDPE calibration standards with varying $CaCO_3$ concentrations were analyzed using a PIKE IRIS Diamond ATR cell, and a linear calibration model was constructed. The measurement settings are provided in Table 5.

Number of scans	12
Spectral resolution	2 cm^{-1}
Apodization	Blackman-Harris
Zero padding	1
Spectral type	Absorbance

Table 5: Measurement settings for FTIR spectrometer.

The measured FTIR spectra were plotted to identify spectral areas that show a correlation with the increasing $CaCO_3$ concentration (see Figure 15).

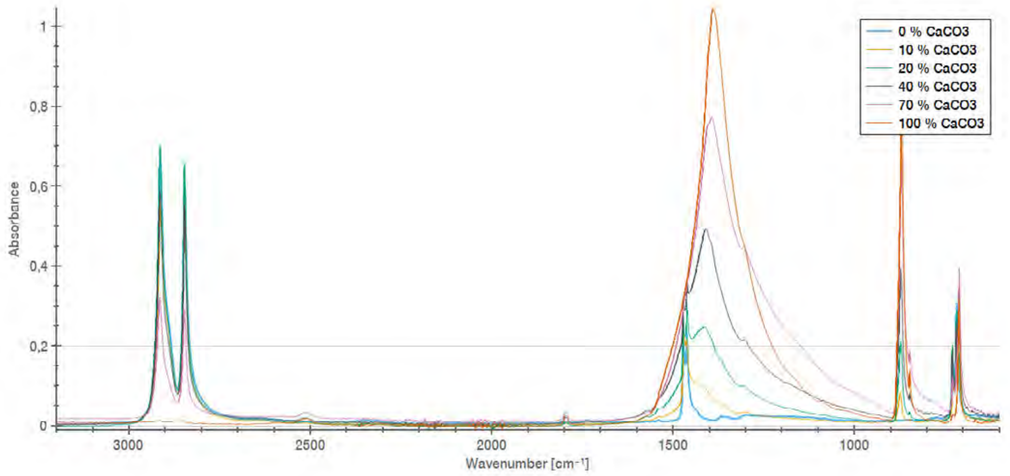


Figure 15: FTIR spectra of LLDPE with different additive concentrations of $CaCO_3$ (see legend). Several peaks show a correlation with the increasing $CaCO_3$ concentration. The peak around 870 cm^{-1} was chosen for further analysis.

$CaCO_3$ shows several absorption peaks, but specifically the carbonate out-of-plane bending at around 870 cm^{-1} showed the best correlation with the actual $CaCO_3$ concentration. The FTIR spectra were baseline corrected (2-point minima at 750 cm^{-1} to 800 cm^{-1} and 900 cm^{-1} to 950 cm^{-1}) and then used for the creation of a calibration model.

The absorbance of the peak at 870 cm^{-1} to 875 cm^{-1} increased with increasing $CaCO_3$ content (see Figure 16).

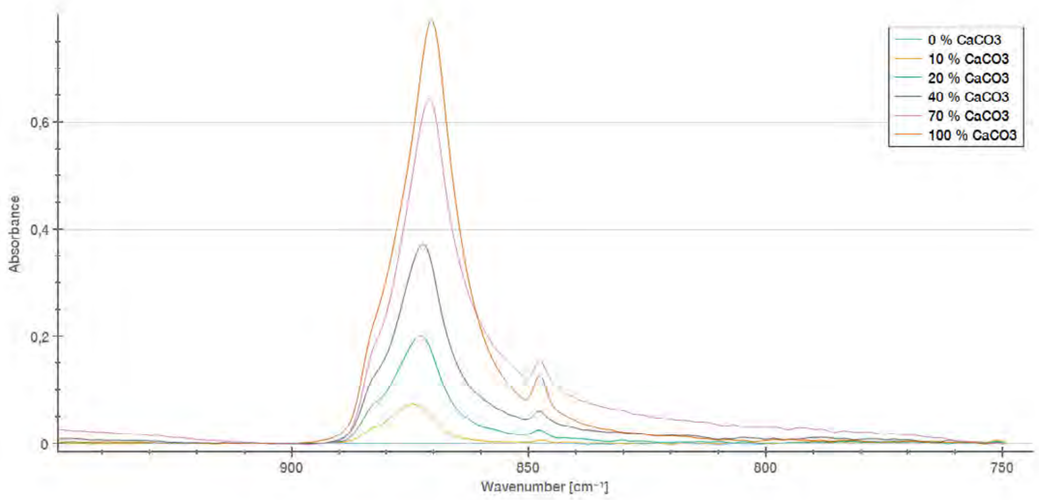


Figure 16: Absorbance increase with increasing $CaCO_3$ content (see legend). FTIR spectra shown in the wavenumber range from 750 cm^{-1} to 950 cm^{-1}.

The peak maxima were automatically calculated by the software in the given range and a linear calibration model was created in correlation with given $CaCO_3$ concentrations (0 %, 10 %, 20 %, 40 %, 70 %, 100 %).

A linear calibration with a good fit (r^2 = 0.9876) was obtained from the quantification model (see Figure 17).

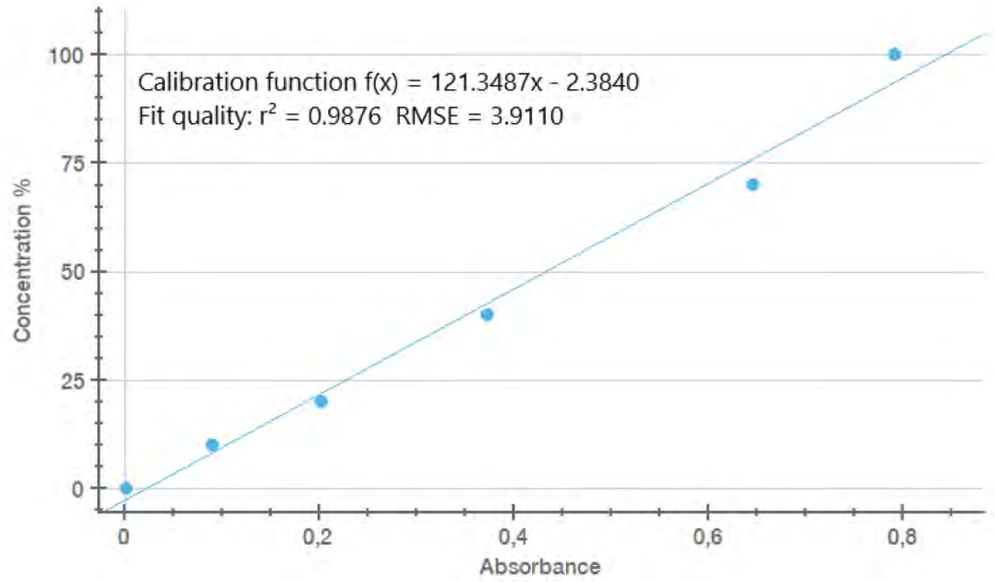


Figure 17: Linear calibration function correlating max. absorbance at 870 cm^{-1} to 875 cm^{-1} and % $CaCO_3$ concentration.

By using this calibration curve LLDPE samples with unknown concentrations of $CaCO_3$ additive can be measured in order to obtain the % $CaCO_3$.

FTIR spectroscopy facilitates fast quantification of $CaCO_3$ additives in polymers.

Instruments suitable for these measurements
Lyza 7000

2.4 Recipe development in polymer processing

To meet the often highly specific requirements of various applications, polymers are typically not used as pure materials, but are instead blended with various additives or other polymers. Depending on the type of additive, this can have a wide range of effects on the final product and its properties. By combining different components, it is possible to create a tailor-made material for a specific application.

The mixing of individual components is usually carried out in a compounder, where the materials can be precisely dosed and homogeneously blended. In this continuous process, a new plastic granulate is produced, which can then be further processed into an end-product with the desired properties.

Since the production of such polymer blends in a continuous extrusion process on a compounding line requires a relatively large amount of material, and material changes are both material- and time-intensive, the use of mixers is often preferable for material development. Mixers allow the preparation and comparison of samples from different material combinations with low material consumption and minimal cleaning effort.

This report investigates the miscibility of two polymers, polymethyl methacrylate (PMMA) and polycarbonate (PC), using DMA, as well as the effects of different mixing ratios on mechanical and thermal behavior.

For the experiments conducted in this report, the four materials listed in Table 6 were compared:

	Sample 4B	Sample 4C	Sample 4D	Sample 4E
PC (%)	0	30	50	70
PMMA (%)	100	70	50	30

Table 6: Investigated material formulations.

For the investigation of the influence on thermomechanical behavior, dynamic mechanical analysis (DMA) under tensile loading was performed. This mechanical characterization was carried out using a rheometer, equipped with a lower linear drive and a convection temperature device. The specimens were fixed using a solid rectangular fixture (SRF).

The measurement of the temperature-dependent dynamic mechanical behavior of the samples was conducted at a constant oscillatory strain of 0.1 % and a frequency of 1 Hz. The samples were heated at a constant heating rate of 2 K/min.

Figure 18 presents the measured storage modulus (E') and loss factor curves (tan(δ)) for the different materials. The influence of the mixing ratio is clearly visible in the storage modulus curves (solid lines), particularly at the temperature where the material softens (glass transition region, indicated by the drop in the

curve). For pure PMMA (Sample 4B, dark blue curve), this transition begins at approximately 100 °C. In the sample containing 30 % PC (Sample 4C), a small step appears in the temperature range 105 °C to 115 °C, which can be attributed to the glass transition (Tg) of PMMA. However, the 30 % PC content significantly stabilizes the material, as seen in the second plateau extending up to about 140 °C. At this temperature, the glass transition region of PC begins.

For Sample 4D (50:50 mixture), a similar trend is observed, although the step associated with the PMMA phase's glass transition is smaller, resulting in higher modulus values in the second plateau. The drop of the storage modulus due to the PC glass transition occurs in a similar temperature range. In Sample 4E (70 % PC content), the influence of PMMA's glass transition on the storage modulus becomes almost negligible, and the second glass transition shifts by approximately 5 °C to higher temperatures.

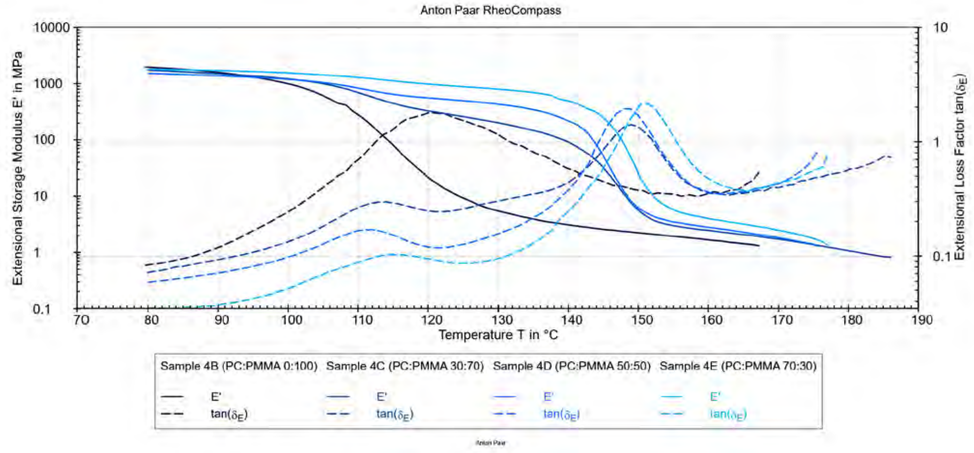


Figure 18: Impact of the composition of PC/PMMA blends on their thermo-mechanical properties.

The fact that the blends of PC and PMMA exhibit two glass transition temperatures (Tg) indicates that these two polymers do not fully mix but instead form two separate phases. In contrast, blends of miscible polymers, such as PMMA and polystyrene (PS), show only a single glass transition, which depends on the mixing ratio and lies between the Tg values of the pure polymers.

A similar trend can be observed in the loss factor curves, where the first Tg in Sample 4E becomes more clearly distinguishable. Comparing the individual peaks of the different samples, it is evident that they do not shift uniformly to higher temperatures with increasing PC content. This effect is particularly noticeable when looking at the first peak, corresponding to the Tg of PMMA.

	Sample 4B	Sample 4C	Sample 4D	Sample 4E
Tg 1 (°C)	120.2	113.0	112.0	114.7
Tg 2 (°C)	-	149.0	147.9	151.3

Table 7: Glass transition temperatures (Tg) of the investigated material formulations.

In a 50:50 PC/PMMA blend, the glass transition temperatures of both phases may be lower than in asymmetric mixtures such as 70:30 or 30:70. This may be explained by the maximized phase interface in the 50:50 blend, which leads to stronger intermolecular interactions and increased mobility of the polymer chains. Additionally, there may be limited molecular intermixing at the phase boundaries, which reduces the stiffness of the individual phases. In asymmetric mixtures, one polymer phase dominates, resulting in weaker interfacial effects and Tg values closer to those of the pure polymers.

As demonstrated in this example with PC and PMMA, various additives also influence the dynamic-mechanical and thermal properties of polymers. Particularly in the case of complex formulations designed for specific applications, careful formulation development, such as that carried out using mixers, is crucial. DMA measurements enable straightforward visualization and quantification of property changes resulting from formulation variations.

Instruments suitable for these measurements
MCR 702e MultiDrive

2.5 Accurate material modeling

Viscosity measurement in polymer processing is essential for evaluating the flow behavior of melts under real processing conditions. A highly effective method for in-line viscosity determination involves the use of slit and round capillary dies mounted on an extruder, allowing for continuous measurement of the material's rheological properties during extrusion. This setup provides real-time insights into the processability of polymers without the need for separate laboratory testing.

The principle of operation is based on forcing the polymer melt through a defined capillary die – either a round capillary with a cylindrical channel or a slit die with a flat, rectangular channel. In the simplest design with a round capillary and only one pressure sensor (Figure 19), the melt flows through the die, the pressure sensors positioned before the capillary measure the pressure drop (ΔP), and the volumetric flow rate (Q) is determined based on the extruder's screw speed and die dimensions. Using these parameters, the shear rate (γ) is calculated from the die geometry, and the apparent viscosity (η) is determined using the Hagen-Poiseuille equation. This method enables precise viscosity measurement at different shear rates, reflecting the material's flow behavior under actual processing conditions.

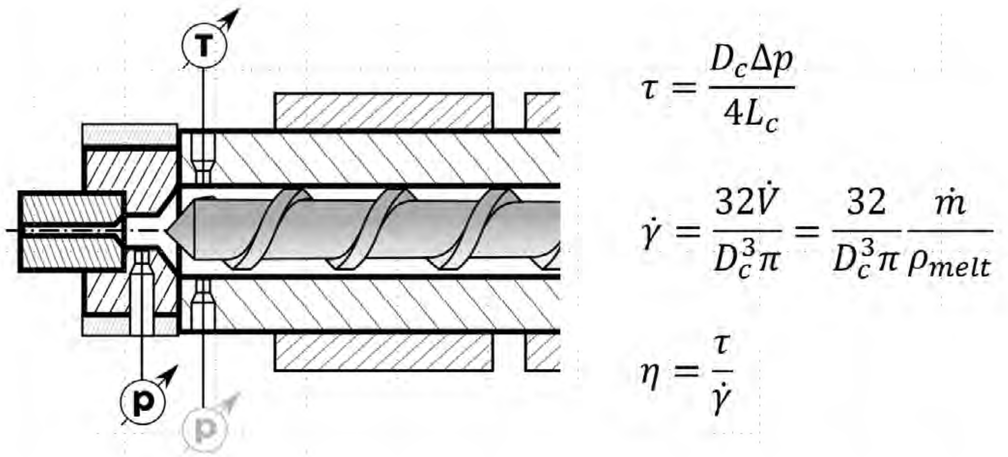


Figure 19: Schematic representation of a viscosity measurement with round capillary die.

When measuring viscosity with a round capillary die, corrections are necessary to account for entrance pressure losses (Bagley correction), non-Newtonian flow behavior (Rabinowitsch correction), and possible wall slip effects, which can lead to underestimations. These adjustments ensure accurate viscosity values but add complexity to the measurement.

A slot capillary die offers advantages by minimizing the effort regarding the necessary data corrections (Figure 20). Additionally, it better represents real processing conditions, especially for film and sheet extrusion, leading to more reliable viscosity data with fewer necessary adjustments.

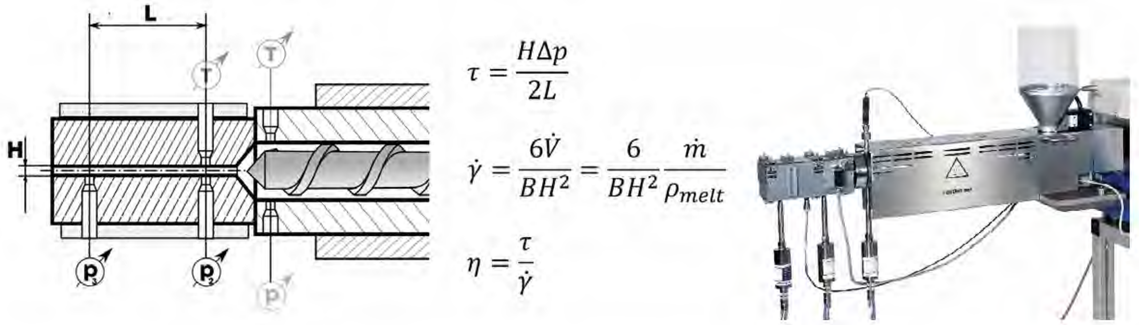


Figure 20: Schematic representation of a viscosity measurement with slot capillary die.

The viscosity curve of polymer melts typically exhibits shear-thinning behavior, meaning that viscosity decreases with increasing shear rate. Extrusion-based measurements target the medium to high shear rate range – approximately 100 s^{-1} to 10,000 s^{-1} – which is directly relevant to industrial processes such as extrusion and injection molding (Figure 21).

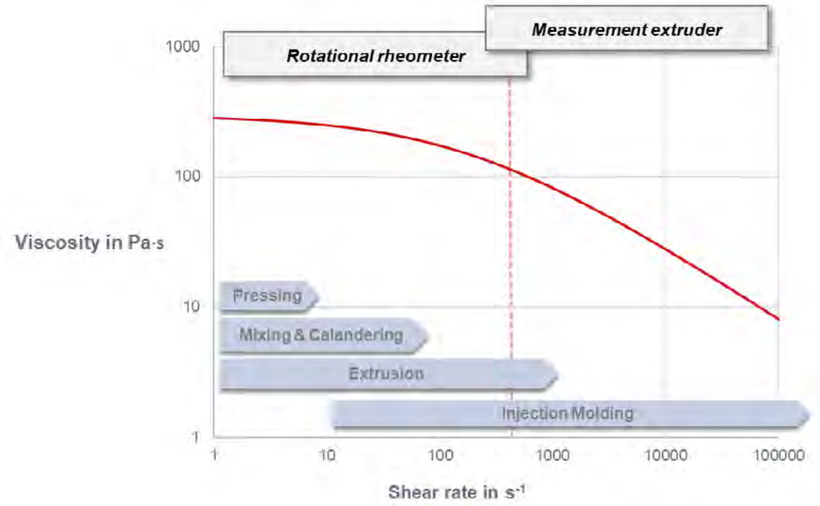


Figure 21: Mapping of the plastic processing processes to the shear rate ranges of a viscosity curve.

Compared to traditional laboratory capillary viscometers, viscosity measurement with an extruder offers advantages like real-time monitoring, enabling immediate process adjustments to optimize material flow and quality. Second, measurements are performed under actual processing conditions, ensuring higher accuracy and eliminating the need for subsequent measurements.

Overall, the use of slit and round capillary dies in combination with an extruder provides a highly efficient and practical solution for monitoring polymer viscosity in production environments. By delivering continuous, real-time data, this method helps manufacturers maintain consistent material quality, optimize processing parameters, and improve overall efficiency in polymer processing.

Combining a rotational with an extrusion capillary rheometer provides a comprehensive understanding of a polymer's flow behavior across a wide range of shear rates (Figure 22). Rotational rheometers are ideal for measuring viscosity at low shear rates (typically 0.01 s^{-1} to 100 s^{-1}) – relevant for material characterization, storage, and handling.

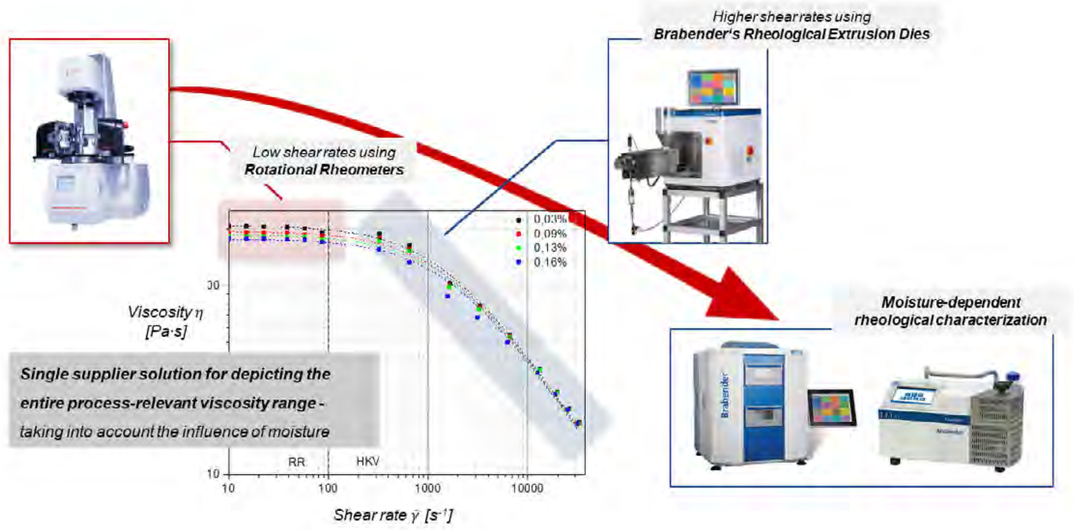


Figure 22: Combined analyses using rotational rheometers and capillary die measurements with an extruder.

By correlating data from both methods, a complete viscosity curve can be established, spanning low to high shear rates. This allows for accurate material modeling, enabling better predictions of flow behavior in industrial applications. The combination also improves process optimization, as insights from rotational rheometry help in understanding molecular structure and elasticity, while capillary rheometry provides data for processing performance and die design. This integrated approach enhances material selection, formulation adjustments, and quality control, ensuring optimal performance in production environments.

Instruments suitable for these measurements
Brabender TwinLab 12/20/30
Brabender Single-Screw Extruder 19/25

MCR Evolution Series

Brabender MetaStation

Power Duo

Optimizing Polymer Formulations through Rheology and Extrusion

Achieving high-performance plastic formulations is hindered when mixing, extrusion, and rheological testing are siloed – leading to inhomogeneous blends, variable mechanical properties, and delayed timelines. An integrated workflow ensures optimal dispersion of polymers, additives, and fillers, precise viscosity characterization across relevant shear rates, and comprehensive rheological evaluation. This streamlined approach boosts process efficiency and consistency, and accelerates product development.

3

Compounder: Extrusion (Twin-Screw) to Produce a Pellet

Key Facts

Twin-screw extrusion

Industrial and research-driven laboratory extrusion for material and process development

Rheological analysis

Information for process and tool design across a wide range of material combinations

Twin-screw extrusion

Upscaling of production from 60 g/h to 100 kg/h

Extrusion-Raman combination

Real-time polymer composition monitoring for consistent extrusion and in-process blend adjustments

Gas pycnometry

Fast density measurement to create datasheet specifications

Dilute viscometry

PBT grade determination for fast quality control

Compounder: Extrusion (twin-screw) to produce a pellet

Compounding is a crucial process in polymer science and plastic technology, allowing manufacturers to customize materials by blending polymers with additives, fillers, and colorants. This enables the production of plastics with specific properties such as strength, flexibility, heat resistance, and color. It is particularly important in industries like the automotive industry, the medical industry, and packaging, where material properties need to be tailored to meet specific demands. Compounding also supports sustainability by incorporating recycled materials and optimizing performance through various additives.

An important part of plastic material development projects is the application of lab-scale extruders which are specifically designed for small batch production and research. Their ability to provide precise control over mixing, temperature, and shear makes them ideal for experimenting with different formulations.

One of the key benefits of using laboratory-scale twin-screw extruders is their versatility. They can handle a variety of materials – from powders and pellets to molten polymers – enabling researchers to test a broad range of compounds. Additionally, the ability to adjust processing parameters such as screw speed, temperature, and pressure allows for fine-tuning of the process, helping to achieve optimal material properties. Importantly, these lab-scale systems allow for easy scaling from small batches to larger-scale production, ensuring that formulations can be efficiently transferred to pilot or full-scale extruders with minimal adjustments. This makes them a valuable tool for material development, quality control, and the production of high-performance plastics.

3.1 Twin-screw extrusion – laboratory scale

A typical laboratory compounding line consists of several key components that work in concert to mix, melt, and process polymer materials effectively. The heart of the compounding line is the so-called processing unit, which is designed to blend the polymer with additives efficiently. The process unit contains a pair of screws for conveying the plasticized masses and a heated cylinder which surrounds them and brings energy into the system in the form of heat. The intermeshing screws of the extruder create shear forces that promote uniform melting and mixing, ensuring that additives are well-dispersed and that the final compound exhibits consistent properties. Laboratory extruders that are equipped with multiple zones for temperature control allow regulation of the process conditions along different stages of the extrusion process.

In addition to the extruder, the laboratory compounding line typically includes a feeding system, which supplies the raw materials to the extruder. These systems can typically be configured for precise feeding of powders, pellets, liquids, or master batches, depending on the nature of the material being processed. Accurate dosing of additives is crucial for achieving the desired formulation, so feeding systems often feature loss-in-weight feeders, which ensure precise control over the input of each material. The feeding system also helps prevent material wastage by ensuring that the proper proportions of polymer and additives are maintained throughout the process.

In extrusion processes, material feeding is not limited to loss-in-weight feeders. Various other feeding systems are typically used to introduce materials into the extruder efficiently. These include different types of vertical force feeders, which ensure consistent material flow into the extruder screw. Additionally, side feeders are commonly employed to introduce fillers, additives, or reinforcements at specific points along the extrusion process. Furthermore, pumps are often used for feeding liquids or pasty materials directly into the extruder, ensuring precise dosing and homogeneous mixing.

Another critical component of a laboratory compounding line is the cooling and pelletizing system. After the polymer has been extruded and mixed with the additives, it is usually in a molten state and must be rapidly cooled to solidify. This cooling process is often done through a water bath or air cooling system. Once the compound has cooled, it is typically cut into small pellets using a pelletizer. These pellets are then ready for further testing, such as rheological analysis, mechanical testing, or processing trials. The pelletizing system allows for uniform sizing of the material, ensuring that it can be handled easily in subsequent processing steps.

To ensure that the produced compounds meet required specifications, laboratory compounding lines can be equipped with various monitoring and control systems. These systems can measure and control parameters such as temperature, pressure, screw speed, and torque, providing real-time feedback on the processing conditions. Additionally, these systems include online sensors to analyze the material's properties during the extrusion process, such as melt flow index or viscosity. Continuous monitoring ensures that any deviations from the desired processing conditions are detected and corrected quickly.

Additional software provides comprehensive data acquisition, enabling efficient collection, visualization, and analysis of process parameters. With customizable dashboards, users can tailor their workspace to display relevant data and insights. These systems typically support the integration into different IT structures, allowing for remote access, seamless data sharing, and smooth interaction with other systems. Automated reporting simplifies documentation and analysis by generating detailed reports.

Besides common features like system modularity and diversity of the extrusion line setup, the clam shell-design of the extruder barrel offers major advantages. This innovative design allows the barrel to be easily opened, enabling direct access to the extrusion process. This is particularly beneficial for process optimization, material development, and troubleshooting, as it allows users to visually inspect the material flow, detect irregularities, and make immediate adjustments. The ability to open the barrel also simplifies the cleaning process, reducing downtime between tests and ensuring reproducible conditions.

Moreover, the clam shell design facilitates quick screw configuration changes, making it possible to test different screw geometries and processing conditions efficiently. This flexibility is essential for R&D applications, where precise control over process parameters is key to achieving optimal results.

In addition, the clam shell design solution enables sampling along the screw for analysis in subsequent plastic analytical studies, such as those in this e-book. After stopping the process and opening the barrel, samples can be taken from inside the processing unit. Since the screws are not removed from the extruder before this, the local compounding conditions in the various areas of the screws remain unaffected.

In conclusion, the integration of these features with advanced data acquisition and analysis capabilities positions twin-screw extruders as a highly versatile and precise platform for both industrial-scale and research-oriented extrusion processes.

Instruments suitable for these measurements
Brabender TwinLab 12/20/30

3.2 Upscaling of production

Upscaling from a laboratory-scale twin-screw extruder, such as one with a throughput of 60 g/h, to an industrial, pilot-scale, twin-screw extruder with a throughput of up to 100 kg/h involves a complex but essential process of scaling both the equipment and the process parameters. While the laboratory extruder provides valuable data on material behavior, small-scale formulations, and optimal processing conditions, the transition to a larger system requires careful consideration of factors such as shear rate, temperature control, screw design, and material handling. One of the main challenges is maintaining consistent material properties across the larger scale while ensuring uniform distribution of additives and efficient mixing at higher throughput rates.

The upscaling process typically involves adjustments to the extruder's screw configuration, barrel design, and processing conditions. The larger extruder must be capable of handling a significantly higher volume of material while maintaining similar levels of mixing and dispersion achieved in the lab-scale system. Moreover, the residence time of the material inside the extruder must be carefully managed to avoid degradation or inconsistencies in the final product. In this context, simulations and trials on the pilot scale are often conducted to fine-tune parameters and ensure that the transition from laboratory to industrial scale results in reproducible, high-quality products. Ultimately, the goal of upscaling is to ensure that the performance, material properties, and production efficiency are consistent across the small-scale and full-scale systems.

Instruments suitable for these measurements
Brabender TwinLab 12/20/30

3.3 Compound density analysis for evaluating blending efficiency

Density is a fundamental property in polymer technology that provides critical insights into the composition, structure, and processing behavior of materials. It is particularly important in the evaluation of polymer blends and compounds, as it allows manufacturers to assess the efficiency of mixing and the consistency of material properties. In polymer processing, such as extrusion and injection molding, density directly influences mechanical properties, weight, and overall performance of the final product. A deviation between the theoretical (calculated) and actual (measured) density may indicate voids, impurities, or incomplete blending, which can affect the mechanical integrity of the polymer. Density measurements also play a crucial role in quality control, ensuring that materials meet industry specifications and perform as expected in their respective applications.

A gas pycnometer is an instrument used to determine the true or skeletal density of solid and porous materials. This method is based on gas displacement and follows the principles of Archimedes' displacement law in a gaseous medium.

The measurement process involves placing the polymer sample in a sealed sample chamber of known volume. The device then introduces an inert gas (typically helium or nitrogen) into the chamber at a controlled pressure. Helium is preferred due to its small atomic size, which allows it to penetrate even the smallest pores and provide an accurate volume measurement. However, for polymers, nitrogen is recommended, as helium may penetrate the solid structure of low-density polymers and organic materials. The gas expands into a second chamber of known volume, and the resulting pressure change is measured. Using the known volume of the chambers and the ideal gas law, the instrument calculates the skeletal volume of the sample. By dividing the sample mass by its measured volume, the precise density is determined.

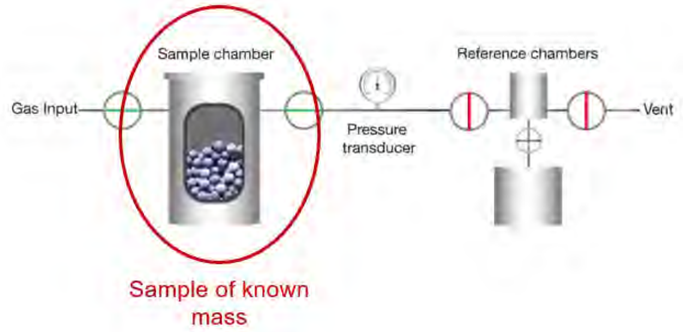


Figure 23: MCR Evolution Series and Brabender MetaStation.

This technique is highly accurate and reliable, making it ideal for characterizing polymeric materials, particularly in assessing the efficiency of blending processes. This enables manufacturers to detect inconsistencies in density, ensuring optimal material performance in various industrial applications.

Table 8 presents skeletal density values for a polymer compound consisting of polycarbonate (PC) and polymethyl methacrylate (PMMA) at different

blend ratios. The data includes both measured densities (obtained using the Anton Paar Ultrapyc gas pycnometer) and calculated densities (theoretical values based on the rule of mixtures). The measured skeletal density of PC is 1.2054 g/cm³, while PMMA has a skeletal density of 1.1919 g/cm³. These values serve as reference points for calculating the expected densities of the blends. The measured and calculated densities for the 70 % PC, 50 % PC, and 30 % PC blends are very close to the theoretical value, but slight deviations exist. The measured densities follow the expected trend, decreasing as the PC content decreases and the PMMA content increases.

Sample	Density measured	Density calculated
PC	1.2054	n.a.
PMMA	1.1919	n.a.
70 % PC	1.1999	1.2014
50 % PC	1.1969	1.1987
30 % PC	1.1954	1.1956

Table 8: Densities of a PC-PMMA compound in various mixing ratios determined experimentally and according to mixing rules.

The differences between measured and calculated densities provide insight into the blending process. The calculated densities assume perfect mixing without microstructural effects, voids, or phase separation. However, the measured densities are consistently slightly lower than the theoretical values, suggesting minor closed porosity, imperfect interfacial adhesion between the polymers, or slight variations in processing conditions during extrusion. These small deviations indicate that the extrusion process resulted in relatively homogeneous mixing, but some microscopic voids or phase boundaries may still exist. If the deviation were larger, it could imply poor mixing, air entrapment, or phase incompatibility between PC and PMMA.

Since density is a key material property affecting mechanical performance, these results confirm that the blending process was largely successful. Minor process optimizations, such as adjusting extrusion temperature, shear rate, or processing speed, could further reduce density deviations. Overall, the density measurements confirm a well-mixed polymer compound suitable for further material evaluation and application testing.

Instruments suitable for these measurements
Ultrapyc Series

3.4 In situ monitoring of polymer blends during extrusion

Blending of polymers such as polycarbonate (PC) and polymethyl methacrylate (PMMA) is key to achieving the specified mechanical, optical, and thermal properties of final polymer products. These include, e.g., strength, optical clarity, and impact resistance.

The actual properties vary with the relative concentrations of the constituent polymers in the blend. The correct composition needs to be ensured by proper dosing/mixing according to the formulation. This process can be subject to errors, e.g. wrong input materials, operator errors in picking and dosing materials by volume or weight, inhomogeneous mixing, or compromised material integrity.

Controlling the relative concentration of each component during extrusion is critical for process development, scale-up to production, and ensuring consistent material properties during production cycles for customers, as well as regulatory compliance. Please see Chapter 1.2, “Identification and quantification of polymers and their monomeric composition,” for a description of setting up quantification methods.

In situ process monitoring using Raman spectroscopy enables real-time quantification of polymer composition. This improves analytical efficiency and eliminates the time lag and costs associated with post-extrusion offline analysis. This shortens the development cycles by allowing immediate modifications and eliminating the need for reprocessing during process design. In case of product deviations during production, the error can be replicated in the lab extruder with direct analytical data from Raman to create the best corrective action.

Real-time composition monitoring of PC/PMMA blend

This example demonstrates the application of Raman spectroscopy for real-time concentration determination of a PC/PMMA blend during extrusion.

A Raman spectrometer fiber probe was placed directly after the round strand die head of a twin-screw extruder for real-time measurement of the polymer strand before cooling and pelletization, as seen in Figure 24.

Figure 24: Experimental setup with the Raman probe directly outside of the dye head with the polymer strand being cooled in a water bath and pelletized.

The Raman system operated at 1,064 nm excitation wavelength, with an exposure time of 9.9 s. Measurements were recorded every 20 s. An averaging feature which automatically takes the average value from three measurements was applied for improved accuracy.

Alternatively, monitoring can be performed directly inside the die head of the extruder using a Raman probe, for in situ process insights.

Three relative concentrations were varied over time: 30 % PC / 70 % PMMA, 50 % PC / 50 % PMMA, and 70 % PC / 30 % PMMA.

Results

The Raman spectra collected during extrusion showed clear changes as the PC/PMMA ratio varied. At the start of the process, the signal was dominated by PMMA contributions, and the quantification model confirmed a stable 30 % PC concentration with minimal fluctuations.

As the blend ratio changed to 50 % PC / 50 % PMMA, it can be seen in the spectra after 13 minutes that the measured concentration is slightly lower than the expected 50 % (as seen in Figure 25). This implies that the transition phase was not long enough to achieve a fully stabilized mixture before advancing to the next composition of 70 % PC / 30 % PMMA.

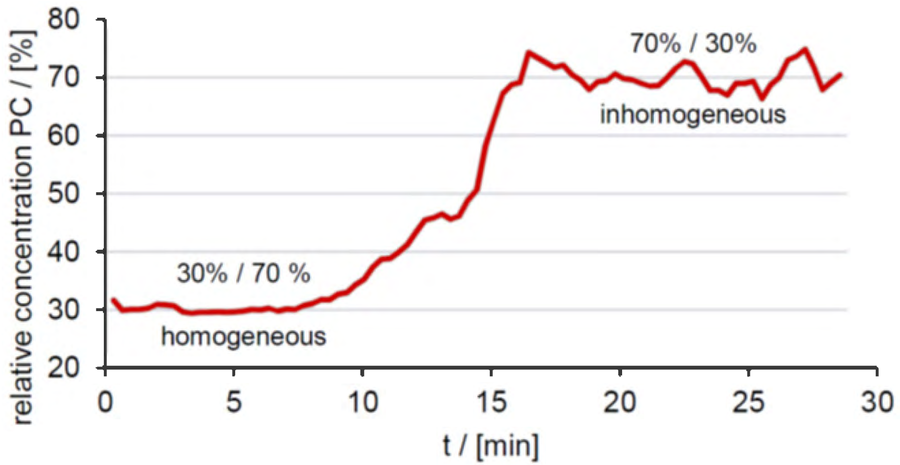


Figure 25: Concentration determined out of the Raman spectra over time.

For the 70 % PC / 30 % PMMA stage, significantly larger fluctuations in the Raman signal were observed. This indicates that the mixing process was not as uniform, leading to variations in polymer concentration within the extruded strand. Offline pellet measurements confirmed these findings, showing that the samples with 70 % PC were not homogeneous, further supporting the in-line Raman observations.

By applying quantification models on the instrument, the relative PC/PMMA concentrations were determined directly from the Raman spectra, allowing real-time composition tracking.

Advantages of Raman spectroscopy for in-line polymer composition monitoring

In situ and real-time:

- Shortened development cycle by eliminating post-extrusion offline testing and reprocessing
- Better control over process design parameters with real-time feedback
- Optimized processing parameters/extruder settings to avoid production issues
- Scale-up from lab to production: Validate and create better processing models and predictive simulations with enhanced knowledge of polymer interactions
- Root-cause analysis: Replicate production defects to pinpoint root cause and take corrective action
- Material knowledge base: Enhanced understanding of copolymer interactions
- Direct results: Easy-to-interpret results displayed directly on device screen

Conclusion

Raman spectroscopy has proved to be a powerful tool for in situ and real-time monitoring of polymer composition during extrusion. This study demonstrates the feasibility of quantification of PC and PMMA concentrations by analyzing Raman spectral features at key vibrational bands.

Integrating a Raman spectrometer with a fiber probe into the extruder allows a reduction in process and material development times and costs, as well as enhanced process and quality control, and material consistency, to give users a competitive edge.

Instruments suitable for these measurements

Cora 5001

Brabender Single-Screw Extruder 19/25

Brabender TwinLab 12/20/30

3.5 Optimizing material formulations, processes, and tool designs for tailor-made polymers

To meet specific product requirements, base polymers are often modified through blends and additives such as fillers, stabilizers, and modifiers. The wide range of possible combinations enables tailor-made materials but also presents significant challenges in formulation development.

As described in section 2.4, the solid-state properties of PC/PMMA blends were examined using dynamic mechanical analysis (DMA). In contrast, this section focuses on their flow behavior during processing. The resulting rheological properties are fundamental for defining the process window, designing extrusion dies, and configuring screw elements.

The investigation of the rheological properties of the pure polymers and their blends (70:30, 50:50, and 30:70) was conducted using a rotational rheometer, equipped with a combination of an electric heating plate and an active hood. The measurements were performed using a parallel-plate measuring system with a diameter of 25 mm.

Amplitude sweeps were performed before the frequency sweeps to determine the linear viscoelastic range (LVER), but are not discussed in detail here. Based on these tests, a strain amplitude of 1 % was selected for frequency sweeps ranging from 628 rad/s to 0.1 rad/s, conducted at a temperature of 240 °C for all samples. To counteract thermooxidative degradation of the polymers, all tests were performed in an inert gas atmosphere (nitrogen).

In Figure 26, the complex viscosity of the pure polymers PC and PMMA is plotted as a function of angular frequency, while Figure 29 shows the storage and loss moduli of both materials. These comparisons clearly highlight the different viscoelastic behavior of the two base polymers. The zero viscosity of PMMA is significantly higher at just over 11 kPas compared to approximately 3 kPas for PC. However, the plateau extends to significantly higher frequencies for PC, leading to a crossover point where, above approximately 55 rad/s, the complex viscosity of PC becomes higher than that of PMMA. This is a crucial factor for process and tool design. This demonstrates a significant advantage of rheological measurements over the commonly used MFR (melt flow rate) in the plastics industry, which is a single-point measurement and cannot capture such effects.

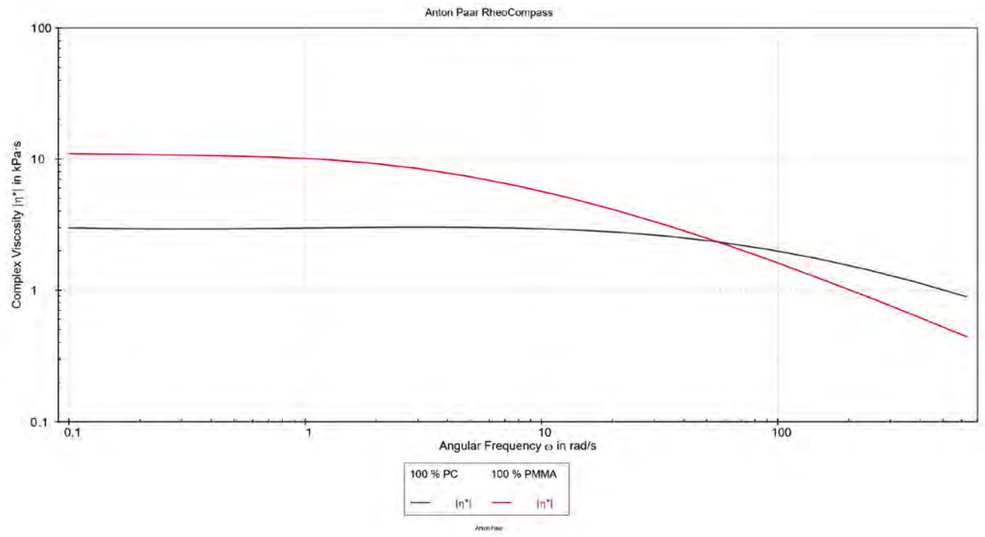


Figure 26: Complex viscosity curve of PC and PMMA, measured at 240 °C.

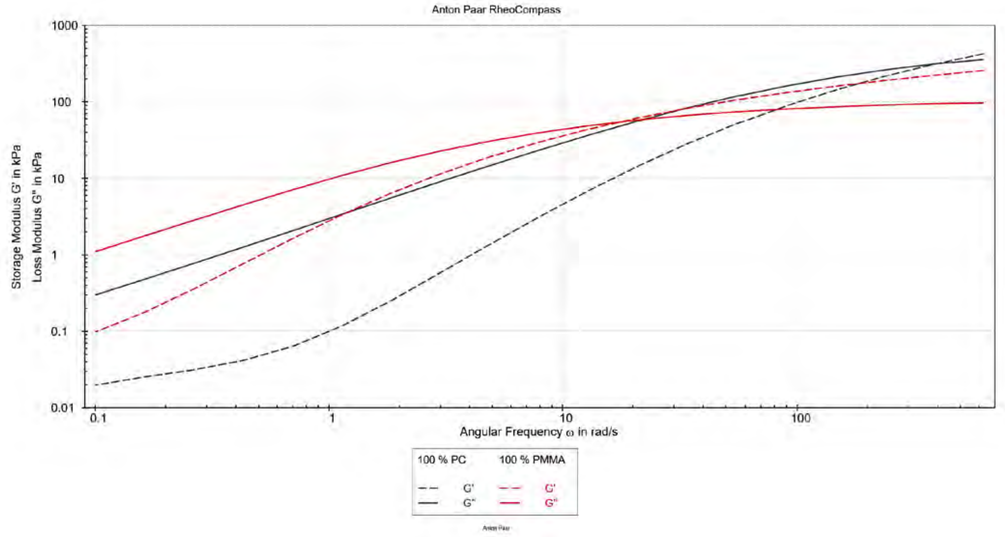


Figure 27: Storage and loss modulus curves of PC and PMMA, measured at 240 °C.

A comparison of G' and G" in Figure 27 provides insights into the ratio of viscous and elastic behavior of the melt at a given frequency. Here, G' represents the storage modulus, indicating elastic behavior, while G" represents the loss modulus, indicating viscous behavior. Significant differences can be observed in this comparison. One particularly interesting aspect is the crossover point (G' = G"), which marks the transition frequency where the material shifts from viscous-dominant to elastic-dominant behavior.

Figure 28 and Figure 29 present the curves for all five samples. These figures highlight the significant influence of polymer blend ratios on the viscoelastic behavior of polymer melts. Rheological measurements are essential for better material understanding and optimal process and tool design. Since the crossover points are not clearly visible due to the number of curves in Figure 29, they are summarized in Table 9.

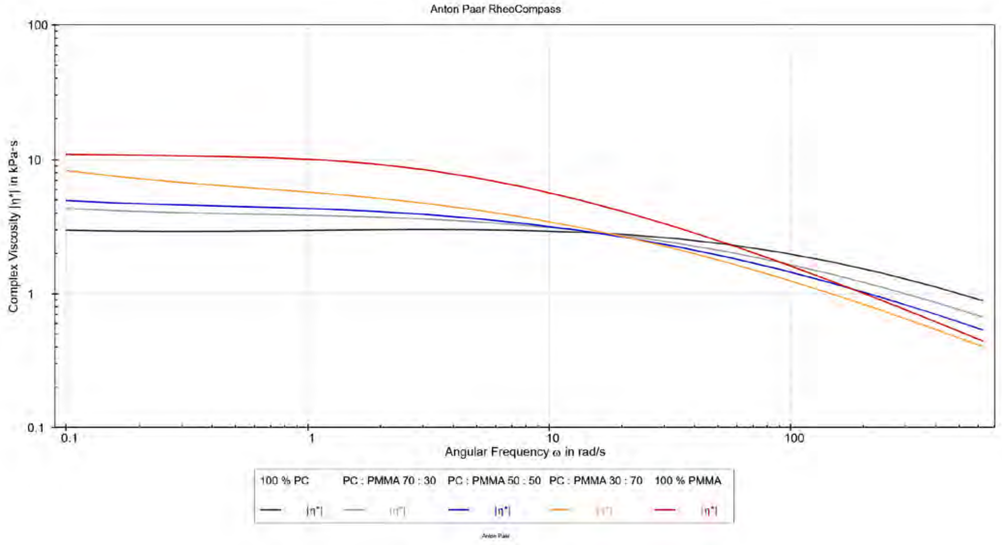


Figure 28: Comparison of the complex viscosity curves of the five analyzed materials, measured at 240 °C.

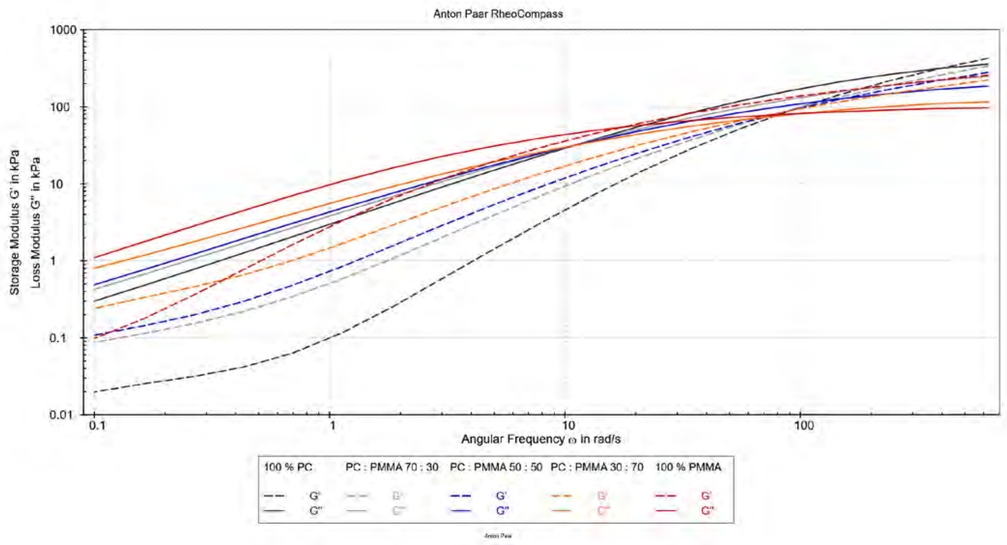


Figure 29: Comparison of the storage and loss modulus curves of the five analyzed materials, measured at 240 °C.

The values in Table 9 show a clear trend: as the PMMA content increases, both the modulus values and the frequencies at which these intersection points occur decrease significantly.

	100 % PC	70:30	50:50	30:70	100 % PMMA
G'=G" (kPa)	314	193	128	70.3	54.2
ω (rad/s)	391	250.9	152.1	61.8	17.4

Table 9: Cross-over points of the investigated material formulations.

These data provide valuable insights. For example, it can be observed that:

- Lower crossover frequency: The material exhibits viscous behavior over a broader frequency range, resulting in easier flow and reduced elasticity
- Lower modulus values: The melt is softer and less structurally resistant, indicating easier processability, such as for injection molding or extrusion
- Processing implications: As the PMMA content increases, the material's flowability improves, but its shape stability after processing may decrease

This example is just one of many applications where rheology is crucial for material development and its relevance to polymer processing. As mentioned earlier, any additive can influence the viscoelastic behavior of melts, which can be analyzed in a similar manner. However, some processes, such as the production of foamed polymers, involve gas loading of the melt. This also affects viscosity, processability, etc. However, measuring the solubility of gases and their impact on viscoelastic behavior cannot be easily performed using a conventional plate-plate setup with a heating plate, as there is no way to apply pressure. For such applications, a pressure cell, enabling rheological measurements under defined pressure and temperature conditions is required. Thus, rheometers can provide valuable information for process and tool design across a wide range of material combinations used in various areas of plastics processing.

Instruments suitable for these measurements
SmartMelt Series

3.6 Measuring intrinsic viscosity for optimized plastic processing

The term “plastics” describes a wide range of materials such as PET, PBT, PVC, and PA, to name a few. Plastics are composed of polymers, which are macromolecules made up of repeating units of monomers (Figure 30). The type of monomer and the final size/chain length of the polymer determine the properties of the material and therefore the type of application.

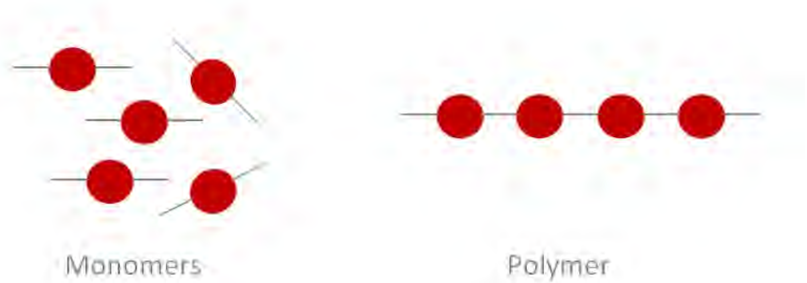


Figure 30: Polymers consisting of repeating monomer units.

During processing, mechanical stress can induce structural modifications in polymers, typically manifested as changes in molecular chain length. Depending on the degree of structural modifications, the properties of the final product may diverge significantly from those of the raw materials, potentially rendering the product unsuitable for its intended application.

Monitoring polymer properties by assessing specific quality parameters is fundamental across various fields, including research and development, polymer manufacturing, and processing:

- Characterization of raw materials and finished products
- Optimization of chemical and physical properties
- Design of polymerization plants
- Defining process parameters
- Quality control of raw materials and finished products
- Avoiding production of defective batches

One technique that can be used for quality control is dilute solution viscometry. Polymers are diluted in appropriate solvents, and the viscosity of the pure solvent is related to the viscosity of the polymer solution. This gives the relative viscosity, a basic parameter from which several others can be calculated. The most relevant is intrinsic viscosity, which is related to the molar mass of a polymer.

Intrinsic viscosity measurements of polybutylene terephthalate (PBT) were conducted, with comprehensive details provided on the sample preparation procedures.

Samples and sample preparation

The intrinsic viscosity [mL/g] of the PBT resin and the final PBT product was measured because the final product showed poor performance in its application (material fracture under load). The samples and chemicals used are described in Table 10.

Sample and chemicals	Chemical description
Sample	Polybutylene terephthalate (PBT), raw material and end product
Solvent 1	Dichloroacetic acid (DCA), for dissolving the polymer and cleaning
Solvent 2	Ethanol for removing the acid from the system before drying

Table 10: Samples and chemicals employed in testing.

The samples were prepared according to ISO 1628-5, a common test method for determining the viscosity of thermoplastics.

The raw material was supplied as small pellets, whereas the final product, being a single piece, was crushed before testing.

> **Tip: Shredding or milling can shorten the dissolution process by creating a larger surface area. It also results in increased homogeneity.**

0.250 g of the sample was weighed into a 50 mL graduated flask and the weight was recorded (d = 0.1 mg). A magnetic stirring rod and approximately 25 mL of DCA were added and the flask was plugged. For dissolution, the sample was stirred for 60 min on a hot plate set at 100 °C with stirring function. After approximately 60 min, the sample was completely dissolved and the flask was removed from the hot plate and cooled to room temperature.

> **Tip: Dissolution times may vary depending on polymer type and material size. Always check that the polymer solution is clear and that no residues are visible.**

After removing the stirring rod, the flask was filled with DCA to a final volume of 50 mL, resulting in a final concentration of 0.005 g/mL. To avoid concentration gradients, the flask was shaken thoroughly prior to measurements. The solvent blank was processed in the same manner as the sample. Each of the samples was dissolved three times.

> **Tip: Sample preparation is a critical step. Errors here can lead to incorrect results and/or poor repeatability.**

Measurement

For all measurements, a rolling-ball viscometer in flow-through mode was used.

- Capillary: 1.8 mm glass
- Ball material: gold-coated steel
- O-rings: Kalrez

Tip: A chemical resistance upgrade kit can be ordered that includes a batch of gold-coated balls and Kalrez® O-rings for improved chemical resistance.

Product settings

- Product: Polymer single concentration
- Temperature: 25 °C
- Measurement cycles: 3
- Manual angle: 30°
- Distance: long
- Variation coefficient: 0.3 %

Results

Each sample was filled and measured in triplicate: All polymer parameters were automatically calculated from the pure solvent and polymer solution run times.

Table 11 shows the results for the raw material and the final PBT product expressed in relative and intrinsic viscosity [mL/g].

Differences were found in the intrinsic viscosity of the two materials. This suggests that changes in the polymer structure occur during the manufacture of the final product. This structural change is likely to result in unsatisfactory performance of the final product.

Sample type	Relative viscosity [Mean ± 1 σ (RSD %)]	Intrinsic viscosity [Mean ± 1 σ (RSD %)]
Raw material	1.33 ± 0.02 mL/g (1.1 %)	58.1 ± 1.9 mL/g (3.2 %)
End product	1.39 ± 0.02 mL/g (0.1 %)	68.4 ± 2.1 mL/g (3.1 %)

Table 11: Relative and Intrinsic viscosity of the raw material and the end product.

To check the quality of the measurement, two parameters are of interest: the FW/BW deviation and the variation coefficient (see Table 12).

– The FW/BW deviation is the deviation between the run time of a forward measurement (e.g. +70° angle) and a backward measurement (e.g. -70° angle).

– The variation coefficient gives the repeatability of the run time between measurement cycles.

Sample type	Variation coefficient [%]	FW/BW deviation [%]
Raw material	≤0.35	≤0.37
End product	≤0.28	≤0.26

Table 12: Variation coefficient and FW/BW deviation as measurement quality indicators.

Conclusion

Dilute solution viscometry is the perfect solution for determining the properties of polymers and detecting changes in their structural behavior.

References

[1] ISO 1628-5, Plastics – Determination of the viscosity of polymers in dilute solution using glass capillary viscometers – Part 5: Thermoplastic polyester (TP) homopolymers and copolymers

Instruments suitable for these measurements
Lovis 2001

Brabender TwinLab 12/20/30

Cora 5001

Power Duo

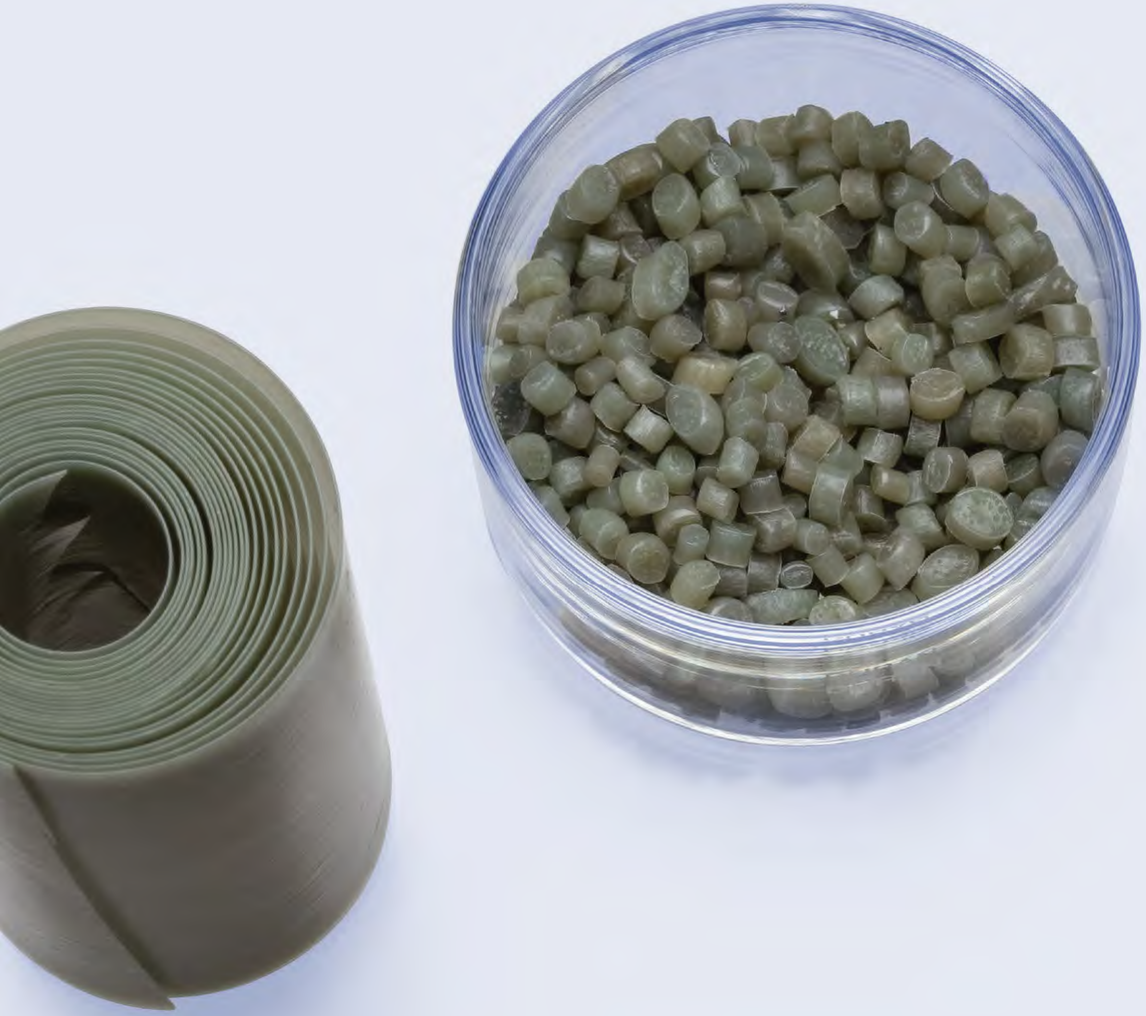
Ensure Consistent Polymer Quality with Real-Time Raman Control

Precise dosing in PC/PMMA blending is critical, as minor deviations during extrusion affect quality. Brabender TwinLab extruders with Cora 5001 enable real-time, in situ monitoring, allowing immediate corrections and faster development, and ensuring compliance.

4

Extrusion (Single Screw) to Produce a Film

Key Facts



Single-screw extruder

Material melting and shaping

Raman spectroscopy

Real-time extrusion crystallization monitoring

Raman-rheology combination

Real-time crystallization monitoring

Single-screw extruder
Raman spectroscopy

Real-time extrusion consistency monitoring

Rheological analysis

Process control for achieving desired product properties with special focus on crystallinity

FTIR spectroscopy

Fast, reliable inspection of intermediate products

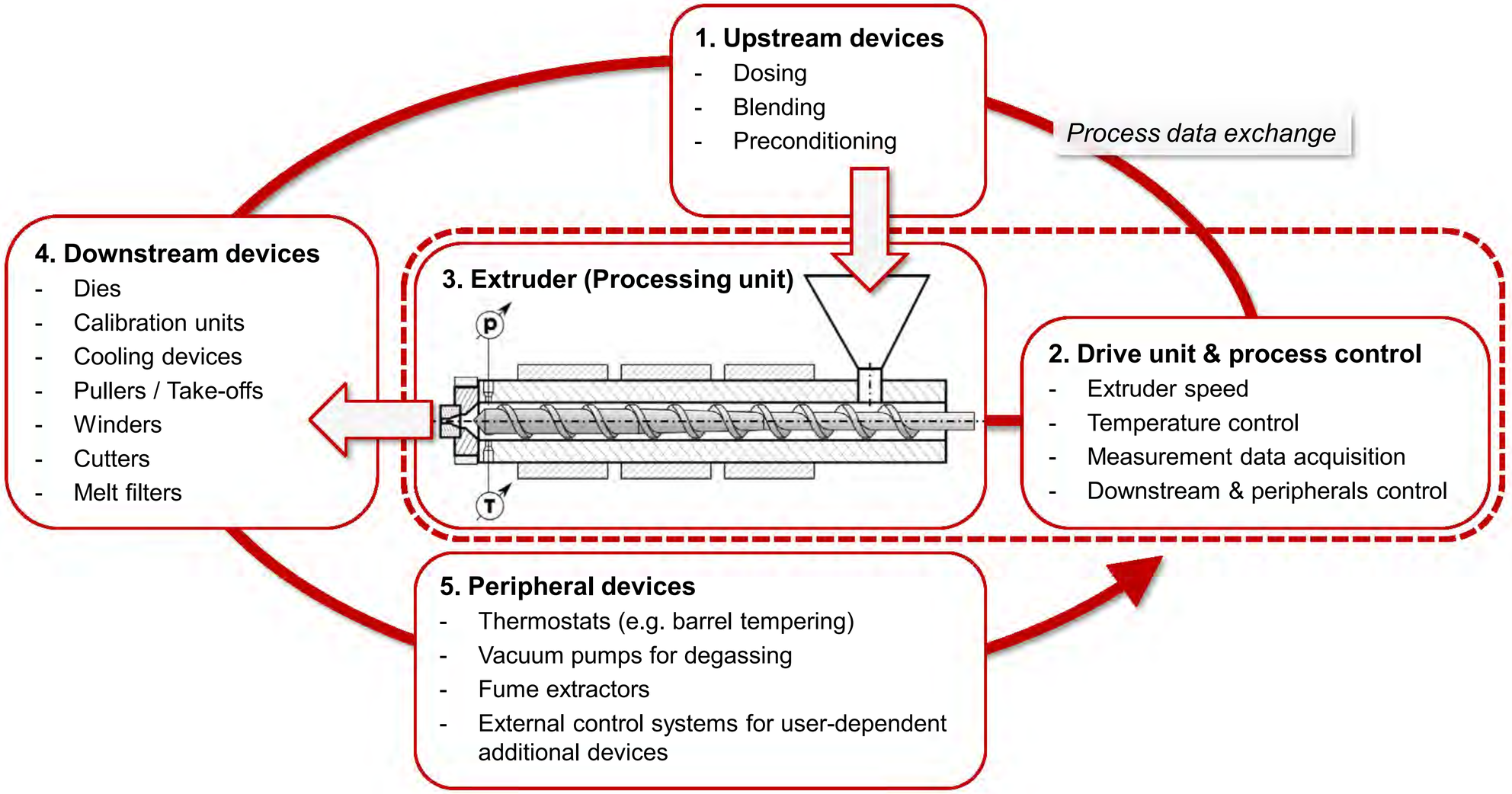


Figure 31: Schematic system illustration of an extrusion process with surrounding equipment.

Extrusion (single screw) to produce a film

Single-screw extrusion is commonly used for the production of semi-finished products, such as sheets, films, pipes, and profiles, from thermoplastics and other polymer-based materials. The process enables continuous material processing and shaping into defined geometries. Single-screw extruders perform melting, homogenization, and conveying efficiently, making them suitable for stable and cost-effective large-scale production. Compared to twin-screw extruders, they offer less flexibility for material modifications but are well-suited for established formulations and applications requiring consistent and stable production conditions.

Cast film extrusion is a process within single-screw extrusion used for producing thin, flat films with precise thickness control. In this chapter, the molten polymer is extruded through a flat die and immediately cast onto a cooled, rotating chill roll to rapidly solidify the film. This process allows for high production speeds and ensures uniform film thickness. Cast film extrusion is widely used for packaging films, protective films, and technical applications, offering advantages such as high transparency, smooth surface quality, and excellent mechanical properties. Compared to blown film extrusion, it provides better thickness uniformity and is often preferred for applications requiring precise optical and mechanical characteristics.

In cast film extrusion, polymer analysis methods such as differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and rheology are essential for ensuring material quality and process stability. These analytical techniques provide critical insights into the thermal, chemical, and rheological properties of the polymer, which directly impact the extrusion process and the final film properties. FTIR and Raman spectroscopy allow for the identification of polymer compositions, additives, and possible material degradation, which is crucial for maintaining consistency in film production. Rheological measurements provide information on the viscosity and flow behavior of the melt, which influence process stability, film thickness distribution, and overall mechanical performance.

In addition to these analytical techniques, optical film inspection plays a crucial role in detecting defects such as streaks, pinholes, gels, or thickness variations in real-time. Modern inspection systems, based on line scan camera technology, enable continuous monitoring and immediate process adjustments, minimizing material waste and improving production efficiency.

By combining polymer analysis and optical inspection, manufacturers can optimize material selection, detect process deviations early, and ensure that cast films meet high-quality standards in terms of mechanical, optical, and functional properties.

4.1 Optical film quality analysis

The principle of optical film inspection is based on the continuous monitoring of the film surface using high-resolution line scan cameras. As the extruded film moves through the production line, these systems capture detailed images and analyze them in real-time to detect defects such as gels, streaks, holes, thickness variations, and contamination (Figure 32).

Figure 32: Exemplary defects in a plastic film according to ASTM D7310 – 21.

Advanced image processing algorithms evaluate the captured data, distinguishing between acceptable surface variations and critical defects. Depending on the system configuration, transmitted light, reflected light, or laser-based techniques can be used to identify different types of imperfections. Upon defect detection, the system triggers alarms, flags affected areas, and provides real-time feedback for immediate process adjustments. This approach maintains consistent film quality while minimizing material waste.

Figure 33 illustrates a film quality analysis (FQA) system used for inspecting extruded films. It depicts a line scan camera that continuously captures images of the moving film. The scanning process occurs across the film's width while it advances along its length. The camera records line scan images, which are then stitched together to form a parcel of data. These parcels allow for detailed, step-by-step analysis of the film's surface, detecting potential defects such as impurities, bubbles, or irregularities (Figure 33). This method enables real-time quality control, ensuring that deviations in film quality are identified immediately, allowing for prompt adjustments in the extrusion process.

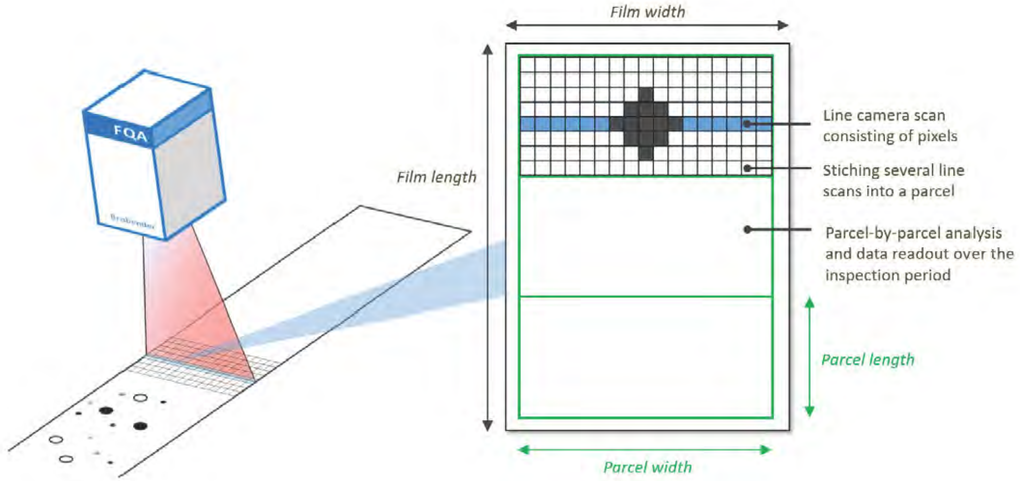


Figure 33: Defect detection and digitalization of contamination in plastic films.

Detected defects are systematically classified and visually represented, enabling a detailed analysis of film quality. This classification is based on three critical aspects. First, the Standard Size Classes categorize defects into 10 size ranges based on their dimensions, such as 19 µm to 100 µm or 101 µm to 200 µm, with the number of particles per square meter recorded for each class (Figure 34). This tabular representation provides a quantitative

assessment of defect distribution across different size ranges. Second, the histogram size classes offer a real-time statistical evaluation by visualizing the defect size distribution in a histogram. Different defect types, such as black specks, gels, and holes, are distinguished using color coding, making it easy to identify patterns. Finally, the time history classes use a line chart to display the occurrence of defects over time, allowing for time-dependent analysis. This helps detect trends or process irregularities, offering insights into potential disruptions or material-related issues. By combining tabular data, histograms, and time-series graphs, this system ensures comprehensive quality monitoring, enabling quick identification and resolution of defect sources in the production process.

Figure 34: Statistical evaluation of film quality analysis and classification of defects.

Optical film inspection is essential for maintaining high product quality, especially as the use of recycled materials increases. Recycled polymers often have variable compositions and may contain impurities, gels, or black specks, which can affect the film's performance. Real-time defect detection ensures consistent quality, allowing manufacturers to identify and eliminate contaminations before they impact production.

With recycled content, process conditions must be precisely controlled, and optical inspection helps optimize parameters, reducing waste and costs. It also supports sustainability efforts by enabling higher recycled material usage while ensuring compliance with industry standards. As demand for closed-loop recycling grows, optical inspection remains a key technology for balancing quality, efficiency, and environmental responsibility in modern film production.

Instruments suitable for these measurements
Brabender FQA Film Quality Analyzer

4.2 In situ monitoring of polymer melting and crystallization

Polyethylene (PE) is a widely used thermoplastic with applications ranging from packaging materials to high-performance engineering components. As a semi-crystalline polymer, its processing behavior is highly dependent on melting and crystallization transitions, which influence its mechanical properties, flow characteristics, and final material performance. Understanding these transitions in real-time is crucial for process optimization and quality control in polymer manufacturing.

While rheometers provide details on the macroscopic visco-elastic behavior of crystallization processes, Raman spectroscopy adds the underlying molecular information.

By tracking temperature-dependent spectral changes, Raman spectroscopy enables the identification of structural variations between the amorphous and crystalline states of polyethylene, which cannot be determined by rheometry.

This level of understanding is crucial in optimizing material properties such as strength, flexibility, permeability, processing behavior, and recyclability. The molecular level information governing the visco-elastic behavior shortens research- and optimization cycles. It is also valuable for determining the root causes and corrective actions in case of deviations from the desired material specifications.

Monitoring crystallization in LDPE and HDPE

Crystallization behavior was monitored via the example of low-density polyethylene (LDPE) and high-density polyethylene (HDPE), as they exhibit distinct crystallization characteristics due to differences in their molecular branching.

Experimental set-up

The measurements were performed using a Raman spectrometer in combination with a rheometer equipped with a Peltier temperature device and a plate-plate measuring geometry.

Raman spectra were collected in real-time while the material was undergoing heating and cooling cycles in the rheometer as well as mechanical oscillation at a constant frequency of 1 Hz.

At high temperatures, when the sample is in melt state, a strain of 1 % was applied and the strain was logarithmically reduced with decreasing temperature, so that at the lowest temperature a strain of only 0.01 % was applied.

The polyethylene samples were heated to 130 °C (LDPE) and 150 °C (HDPE) to ensure a homogeneous molten phase before cooling at a controlled rate of 1 K/min until 80 °C and 100 °C, respectively. During crystallization, Raman spectra were recorded at 30 s intervals with an exposure time of 10 s, an excitation wavelength of 785 nm, and a laser power of 450 mW, providing continuous molecular-level insights into the phase transition process.

Temperature-dependent spectral changes and structural transitions

The transition from crystalline to the amorphous phase was clearly visible in the Raman spectra, showing distinct shifts and intensity variations in C–C stretching and CH_2 deformation bands.

As can be seen in Figure 35, characteristic bands associated with the trans-conformations of polyethylene chains (e.g., at 1,064 cm^{-1}) weakened, broadened, and shifted to higher wavenumbers during melting. This indicates the disruption of the ordered crystalline lattice. Simultaneously, bands characteristic of the amorphous phase (e.g., 1,081 cm^{-1} and 1,304 cm^{-1}) became more prominent, confirming the transformation to a less-ordered polymer structure. Consequently, crystallinity can be monitored using Raman spectroscopy, either independently of or alongside rheological data.

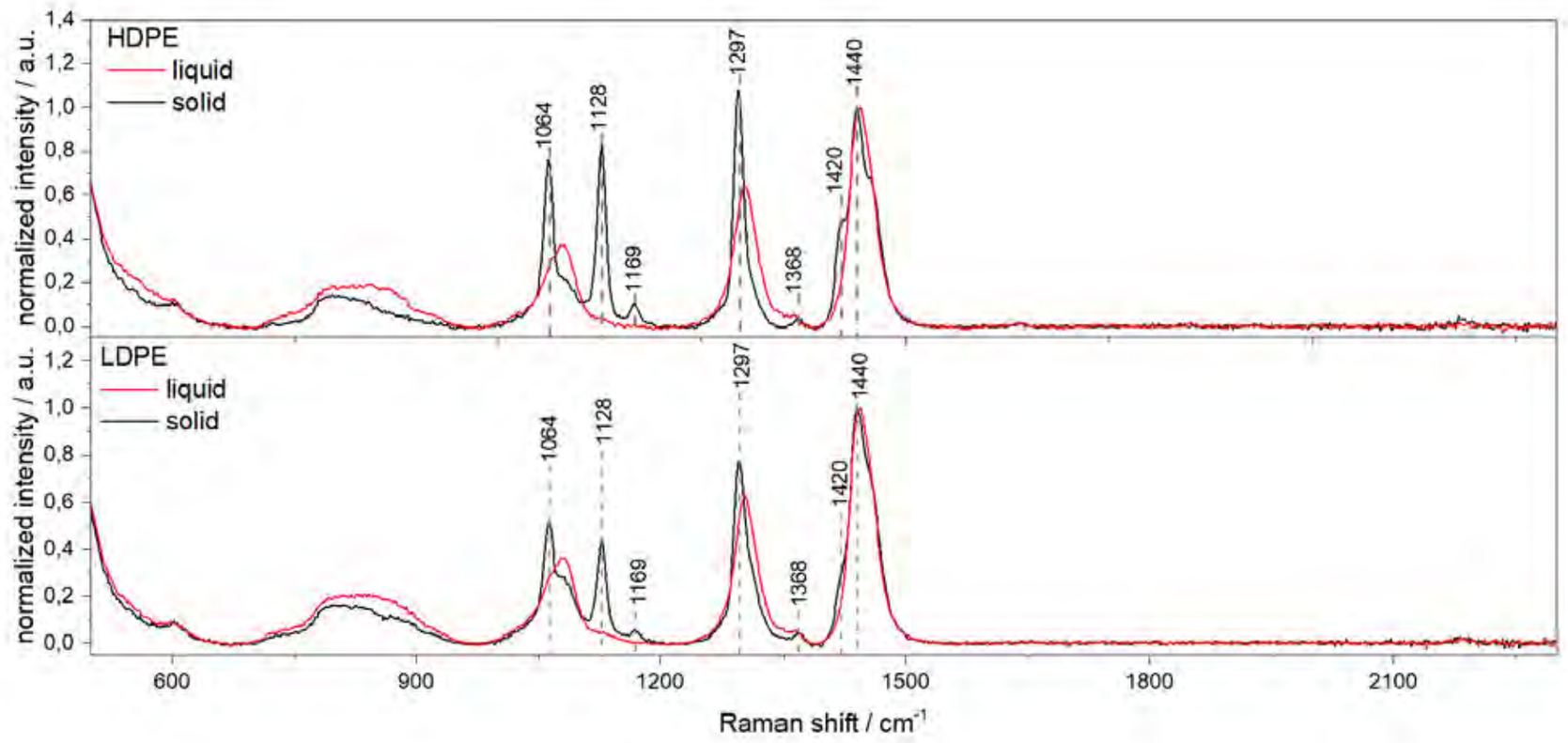


Figure 35: Raman spectra of HDPE (above) and LDPE (below) in the liquid (red) and solid (black) state. All spectra were normalized to the maximum of the CH_2 band around 1,440 cm^{-1}.

Upon cooling, the spectral trends were reversed, with the gradual reappearance of crystalline-phase peaks. However, the crystallization behavior of LDPE and HDPE differed significantly: HDPE exhibited a sharp increase in crystalline content at around 113 °C, while LDPE showed a more gradual, delayed crystallization process, suggesting hindered crystal formation due to its branched structure. With this information, the amount of branched chains could be quantified using the Rheo-Raman combination.

Interestingly, the Raman-derived crystallization temperature was found to be slightly lower than the corresponding rheological transition temperature, suggesting that molecular-level ordering (detected via Raman) occurs before macroscopic mechanical changes become evident. This indicates that PE first

undergoes a transition from the amorphous liquid to an amorphous solid state, and later on starts to crystallize. This highlights the complementary nature of Raman spectroscopy and rheology, with Raman providing early-stage molecular insights into polymer phase transitions.

Advantages of Raman spectroscopy for monitoring polymer phase transitions

- **Measurable molecular insights:** Obtain thorough evidence explaining the physical behavior of materials, for better material models and process design, as well as efficient root cause analysis of defects and corrective actions
- **Real-time process monitoring:** Continuously track polymer transformations during production and process development for stricter quality control and material/batch consistency
- **Reduced waste and costs:** Detect subtle phase transitions before they manifest in bulk material properties, to avoid bigger quality issues and cost impacts
- **In situ and non-destructive:** Raman spectroscopy provides molecular insights in situ without altering material structure during measurements, for better accuracy and live process control

Conclusion

This study demonstrates the effectiveness of Raman spectroscopy for in situ monitoring of polyethylene phase transitions, providing real-time molecular insights into melting and crystallization. The results confirm that temperature-dependent spectral shifts correlate directly with structural transformations, enabling precise detection of phase transitions.

This information is crucial for optimizing crystallization, melting, and flow properties, which allows better process development and precise control over polymer processing. Manufacturers can use the insights to enhance product consistency, prevent defects, and fine-tune processing conditions for superior performance of the final product, such as films, fibers, and molded components.

Instruments suitable for these measurements
MCR Evolution Rheometer and Cora 5001

4.3 Effect of crystallinity on the dynamic mechanical properties of PEEK films

In semi-crystalline polymers, many properties strongly depend on the crystallinity of the polymer. For example, the degree of crystallinity plays a crucial role in determining optical properties, such as transparency, and is directly correlated with the mechanical and thermal performance of the final product. Crystallinity, in turn, is strongly influenced by the thermal history of the product, particularly the cooling process. Slow cooling allows crystals to grow, leading to products with a higher degree of crystallization. Conversely, if a semi-crystalline polymer is cooled very rapidly, the crystals have little to no time to grow, which can result in low crystallinity or even amorphous products. Controlled cooling is therefore a crucial process step to achieve the desired product properties.

This report examines the relationship between crystallinity and the resulting dynamic mechanical properties of PEEK films. The critical step in film extrusion for this purpose is cooling on the take-off roll. This can be controlled by adjusting the take-off speed and/or the roll temperature.

The following samples were compared:

Sample	Roller temperature	Draw-off speed	Expected crystallinity
3B	110 °C	5 m/min	Very low
3D	125 °C	2 m/min	Medium
3G	145 °C	0.8 m/min	High

Table 13: Samples and corresponding processing conditions.

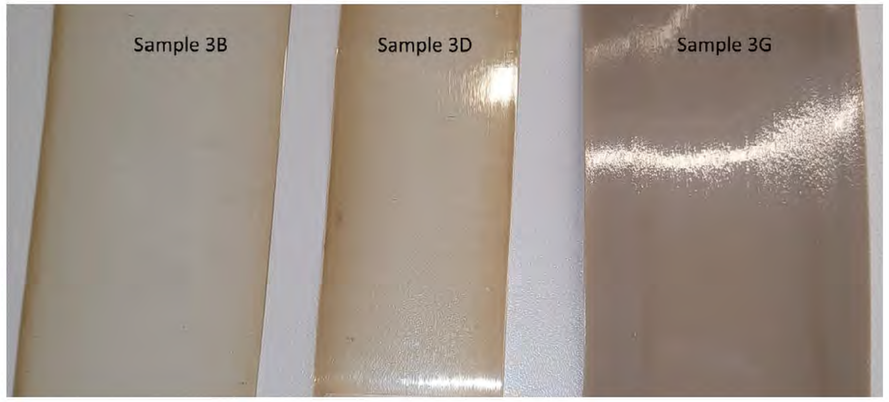


Figure 36: Impact of the processing conditions on the optical properties of the three investigated samples.

In Figure 36, the three films are shown. The optical difference is clearly visible, with Film 3B standing out the most, as it is significantly more transparent than the other two. This suggests an almost amorphous structure. From these films, test specimens with a length of 35 mm and a thickness of 10 mm were cut. The thickness of each film was determined before the measurement and entered into the rheometer software.

The mechanical characterization was carried out using a rheometer equipped with a lower linear drive, a convection temperature device (CTD), and a low-temperature option with liquid nitrogen to achieve temperatures as low as -160 °C. Solid rectangular fixtures (SRF) were used as the measuring system.

The investigation of the dynamic mechanical properties of the PEEK films was performed at a constant oscillatory strain of 0.1 % and a frequency of 1 Hz over a temperature range from 75 °C to 350 °C (or until sample failure). The heating rate for the experiments was set to 2 K/min.

Figure 37 shows the thermograms of Sample 3B (solid lines), which is expected to have the lowest crystallinity, and Sample 3D (dashed lines), which is expected to have a medium crystallinity. A striking feature of the curves is the irregular and atypical behavior of the moduli and the loss factor in the temperature range between approximately 140 °C and 170 °C. This range corresponds well to the expected glass transition region (Tg) of semi-crystalline PEEK.

It is therefore suspected that the amorphous regions, which should be relatively pronounced in this case, initially soften. This leads to a sharp decrease in the storage modulus (E', black curves) and a peak in the loss modulus (E", red curves). At a temperature of approximately 150 °C, the decrease in E' slows significantly before a strong increase is observed again at temperatures above 160 °C. This suggests that recrystallization occurs during the measurement.

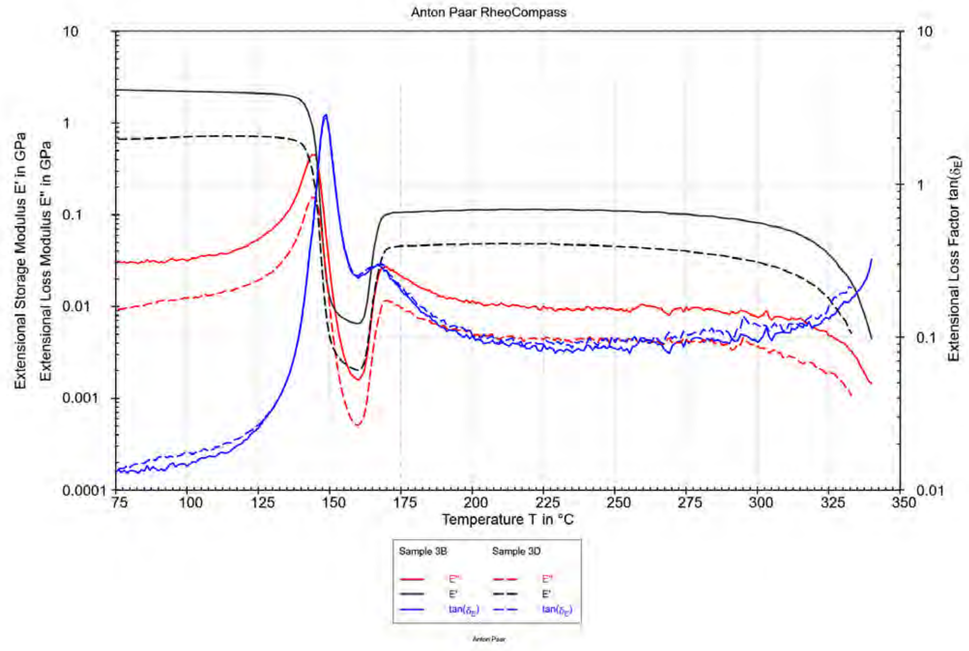


Figure 37: Thermogram of samples 3B and 3D.

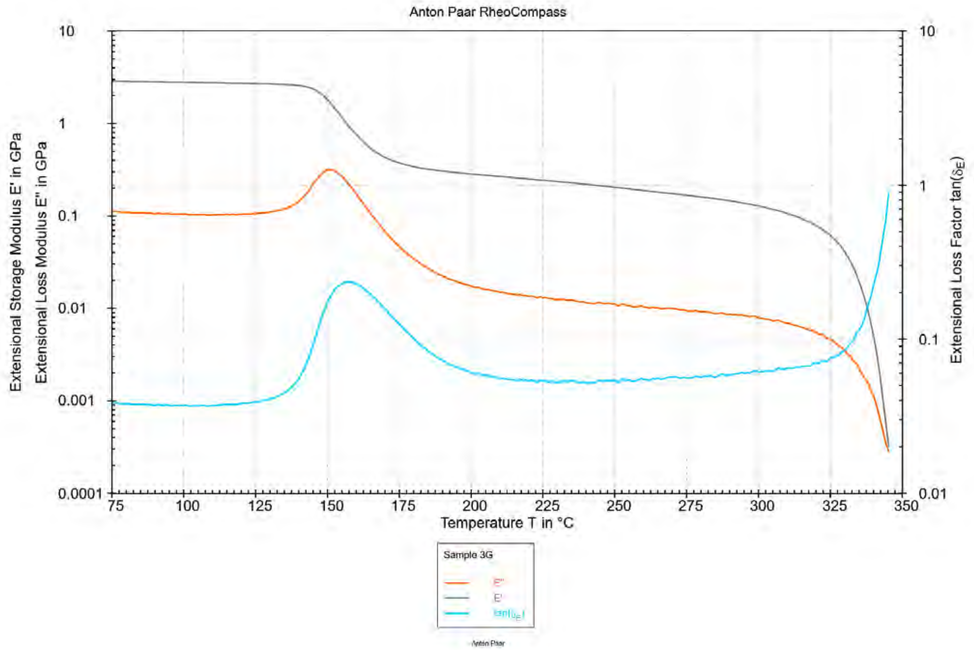


Figure 38: Thermogram of Sample 3G.

The measurement shown in Figure 38 for Sample 3G, which has the highest crystallinity due to the slow cooling during processing, confirms this assumption.

Due to the significantly higher degree of crystallization, no irregularities in the curve progression can be observed in the temperature range between 140 °C and 170 °C. Instead, a clearly identifiable glass transition region forms, characterized by a distinct step in the storage modulus curve and well-developed peaks in E" and tan(δ).

To support the hypothesis of recrystallization, an additional experiment was conducted on Sample 3D. The test procedure was slightly modified: before the actual measurement, the sample was heated to 170 °C, held at this temperature for 30 min, and then cooled back down to 75 °C. Once this temperature was reached, the measurement was started in the same manner as for all other samples.

Figure 39 shows the thermogram of the recrystallized Sample 3D. Although the curve progression is not identical to that of Sample 3G – likely due to differences in thermal history and cooling conditions – the irregularities in the curves between 140 °C and 170 °C are no longer present. Instead, typical modulus behavior is again observed in this range. The increase in E' at temperatures above 175 °C suggests that further crystallization effects are occurring.

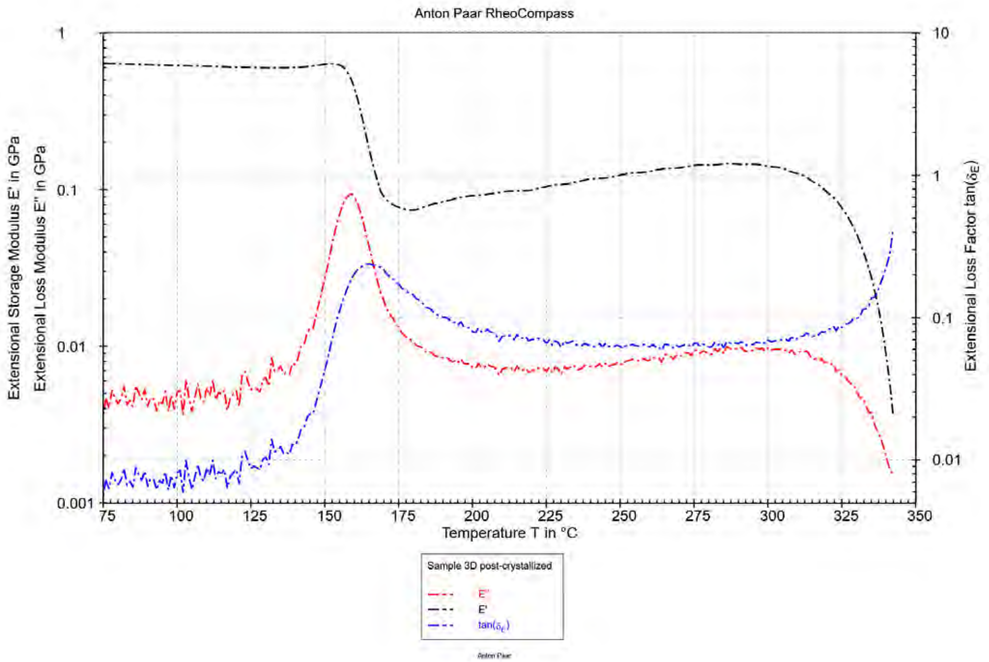


Figure 39: Thermogram of Sample 3D after a 30 min post-curing step at 170 °C.

The results of these experiments demonstrate how crucial process control is for achieving the desired product properties and how significantly crystallinity, which is highly process-dependent, can alter the properties of the same polymer.

Instruments suitable for these measurements
MCR 702e MultiDrive

4.4 Real-time Raman spectroscopic monitoring of crystallinity during extrusion

Crystallinity is a key structural property of polymers that significantly influences their mechanical, optical, and barrier properties. During film extrusion, crystallinity is affected by processing parameters, particularly the draw-off speed, which controls the rate at which the extruded film is stretched and cooled. Changes in crystallinity can be caused by material composition, process parameters, or ambient factors, which may lead to non-conformity of the output product. With offline analysis, such defects or deviations can go unnoticed until the end of the process cycle, leading to increased costs and wastage of time.

Therefore, real-time monitoring and control of crystallinity are a building block towards a state-of-the-art quality control system ensuring quick alerts and timely corrective actions before deviations can cause damage. Real-time data collection ensures that the product output is continuously assessed throughout the production cycle and data is collected for future analyses, when needed.

A Raman spectrometer with a fiber probe can be directly mounted on the film haul-off unit. This allows for continuous monitoring of the crystallinity during production with results directly displayed on the instrument screen.

LDPE and PEEK film crystallinity monitoring

Two widely used polymers in film extrusion – low-density polyethylene (LDPE) and polyetheretherketone (PEEK) – were examined. Their markedly different material properties are closely correlated with variations in their crystallinity.

Experimental setup

A Raman spectrometer was installed directly on a film haul-off unit of the extrusion line. The probe was positioned at the top, after the film passes through the cooling drums (Figure 40).

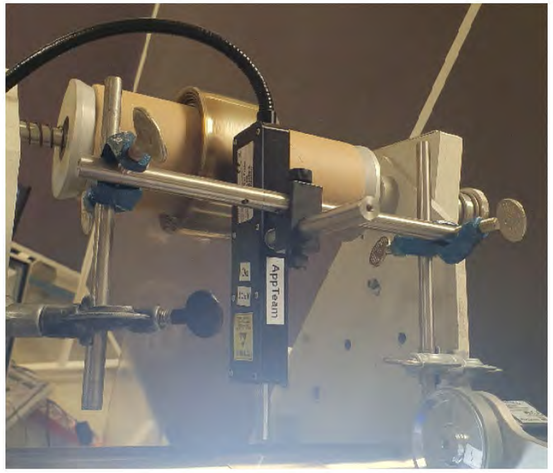


Figure 40: Raman probe installed on the haul-off unit measuring the extruded drawn film.

The Raman spectrometer was set to detect characteristic signals of LDPE and PEEK using a fixed exposure time of 4.9 s and a laser power of 450 mW. An excitation wavelength of 785 nm was used for LDPE and 1064 nm for PEEK, leveraging dual wavelength ability to reduce the fluorescence and obtain optimal signals.

Measurements were recorded continuously every 10 s throughout the extrusion process to determine the impact of draw-off speed variations on crystallinity.

Effect of draw-off speed on crystallinity in LDPE

The data in Figure 41 clearly shows up to which draw-off speed the process can be accelerated without changing the crystallinity of the product. While small changes of up to 5 m/min did not show any detectable change in crystallinity, at speed changes of 10 m/min there was a prominent decrease in crystallinity, as can be seen by the change in Raman signal in Figure 41 at around the 28 min mark.

Specifically, the intensity ratio between crystalline and amorphous bands in the LDPE spectrum was reduced, indicating a lower degree of molecular ordering. The crystallinity was calculated using formula (1) [Kida et al.]. This reduction in crystallinity can be attributed to the reduced time available for polymer chains to organize into a crystalline structure before solidification.

$$\chi_c = \frac{I_{1418}}{0.46(I_{1298}+I_{1305})}$$

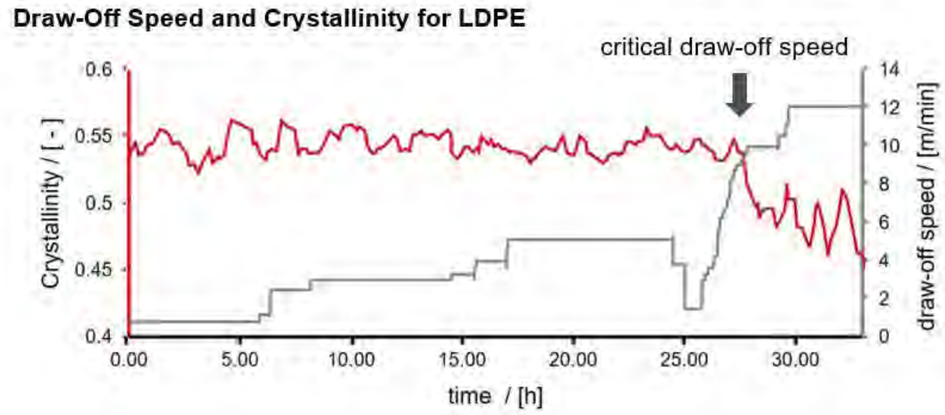


Figure 41: Draw-off speed and crystallinity for LDPE.

Effect of draw-off speed on crystallinity in PEEK

In contrast to LDPE, data collected for PEEK shows a more pronounced reduction in crystallinity with increasing draw-off speed in the range up to 2.5 m/min. Increasing the draw-off speed to 4 m/min did not further reduce crystallinity, as indicated by the plateau reached after 10 min in Figure 42. This suggests that PEEK reaches a critical cooling rate at a draw-off speed of 2.5 m/min, at which a change in the degree of crystal-ordering occurs. At draw-off speeds above and below this critical draw-off speed, the crystal order remains stable at different levels.

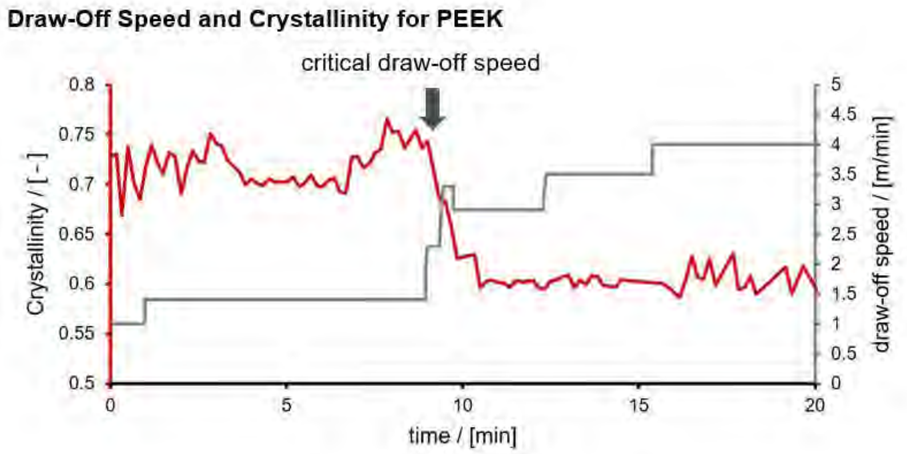


Figure 42: Dependence of crystallinity on draw-off speed for PEEK.

As there is no commonly used formula to determine the PEEK crystallinity, a more generalized formula was chosen. For assessing the crystalline phase, the spectral peak at 1,144 cm^{-1} was selected, while the peak at 1,598 cm^{-1} represents the amorphous phase. The calibration constant k was set to 1:

$$\chi_c = \frac{I_{cr}}{k\,(I_{cr} + I_{am})} = \frac{I_{1144}}{I_{1144} + I_{1598}}$$

Advantages of Raman spectroscopy for in-line monitoring

- **Faster formulation development:** Eliminate dependence on time-consuming, post-extrusion offline analysis and reprocessing by using real-time data
- **Optimized process design:** Better control the process parameters with live tracking of the effect of variations on process parameters or material composition
- **Seamless scale-up from lab to production:** Simulate processing conditions with deeper molecular insights to optimize material recipes as well as process parameters
- **Non-destructive and in situ:** Get immediate feedback on polymer crystallinity without change in material structure or interference with the extrusion process
- **Efficient root-cause analysis and corrective action:** Locate the precise source as well as reason for defects, to take the right corrective action without relying on trial-and-error methodology

Conclusion

Raman spectroscopy has proven to be an effective tool for better understanding polymer morphology, as seen with live monitoring of crystallinity during LDPE and PEEK film extrusion. Based on the Raman data, the critical speeds at which crystallinity changes occur can be determined. This information is important to determine and design process parameters like the draw-off speed for optimal final product quality, even with variation in other process or ambient conditions.

By detecting crystallization inconsistencies, molecular orientation shifts, and process defects on the fly, Raman spectroscopy ensures faster formulation development, reduced material waste, and seamless scale-up to production. It is the key to smarter, faster, and more precise polymer processing.

Instruments suitable for these measurements
Cora 5001
Brabender Single-Screw Extruder 19/25
Brabender TwinLab 12/20/30

4.5 In-line monitoring of polymer phase transitions during extrusion

Understanding the structural changes of polymers during extrusion is essential for optimizing process parameters and ensuring consistent material properties. Until now, there had been no analytical access to the molecular transformations occurring inside an extruder, which remained a ‘black box.’ Only the end-product could be analyzed ex situ and after the extrusion process was completed. This added to development times as well as material consumption and costs, owing to multiple reprocessing cycles until optimal material properties and process parameters were established.

Understanding the phase transitions in the extruder helps define process parameters and extruder settings during scale-up to production. In situ monitoring of the molecular transformations with a Raman spectrometer with a fiber probe placed directly inside an extruder provides analytical data to shorten development cycles, and optimize process parameters and speed, as well as ensure final product quality. In case of deviations from production quality, root cause analysis can be faster and based on analytical evidence rather than assumptions.

Monitoring LDPE phase transitions during extrusion

Experimental setup

A Raman spectrometer fiber probe was positioned within the die head of the single-screw extruder for continuous monitoring of the polymer melt within the processing zone (see Figure 43).

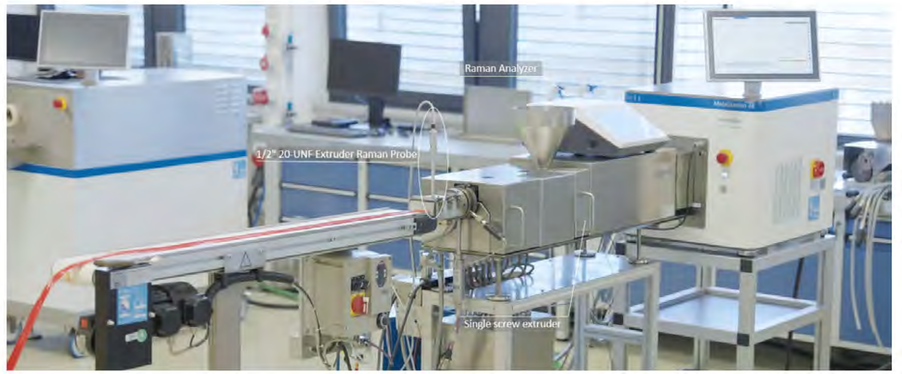


Figure 43: Raman spectrometer fiber probe installed in the extruder die head to monitor temperature variations.

Effect of temperature on Raman spectra of LDPE

The measurements demonstrated correlations between temperature variations and changes in spectral features (see Figure 44).

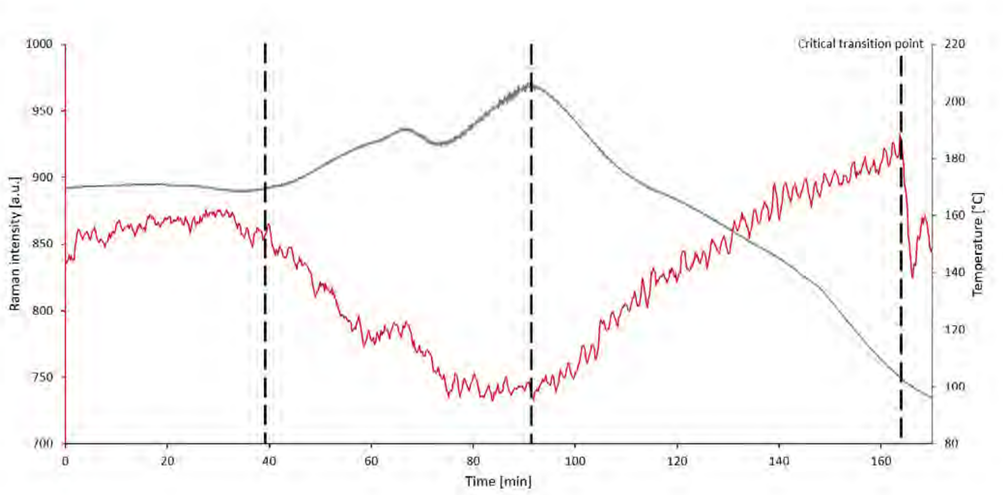


Figure 44: Raman peak intensity at 1,080 cm^{-1} and temperature over time.

The Raman peak intensity at 1,080 cm^{-1} shows an inverse relationship with temperature.

Peak intensity and temperature are plotted over time in Figure 44. As the extruder temperature increased after 40 min, the peak intensity decreased, reaching a maximum and minimum, respectively, at 92 min. This clearly indicates a temperature-induced structural modification in LDPE.

As the temperature moved below 120 °C (at 164 min) the intensity of the peak at 1,080 cm^{-1} dropped off steeply, indicating a distinct structural transition. These changes are consistent with transformation from an amorphous liquid to an amorphous solid state, marking a critical phase boundary in the polymer's processing behavior.

The continuous spectral monitoring confirmed that temperature fluctuations directly impact molecular organization, reinforcing the potential of Raman spectroscopy as a tool for detecting real-time structural changes within the extruder. The spectra of the three marked times in Figure 45 are compared to show the differences in intensity with the monitored peak at 1,080 cm^{-1}.

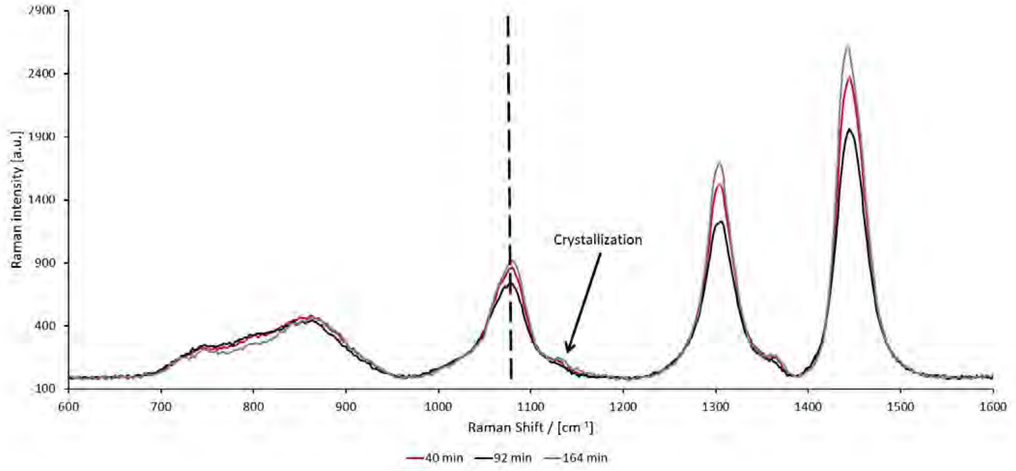


Figure 45: Raman spectra of LDPE at time stamps 40 min, 92 min, and 164 min.

Advantages of in-line monitoring of LDPE phase transitions during extrusion using Raman spectroscopy

- **Thermal optimization:** Identify critical transition points at different positions in the extruder for optimized temperature regulation to better control the polymer properties
- **Structural consistency and reproducibility:** Design processes based on temperature-spectra correlations to ensure a stable molecular structure throughout the process and across batches
- **Faster formulation development and scale-up to production:** Cut down process and recipe development times by gaining real-time process insights and eliminating dependence on offline testing as well as multiple process simulation iterations
- **Custom recipes:** Develop new formulations or tailor properties for polymers or their blends by controlling crystallinity
- **Non-destructive and in situ:** Monitor the polymer accurately and in situ, without altering its chemical structure or requiring special sample preparation

Conclusion

This study demonstrates the effectiveness of in-line Raman spectroscopy for tracking phase transitions in LDPE directly inside the extruder in real-time. The observed relationship between temperature and spectral changes is a valuable indicator of molecular dynamics within the melt.

This knowledge can be used to fine-tune cooling rates, develop new material recipes, tailor material properties, and scale up new formulations to production, as well as ensure material consistency by setting correct process parameters, and performing data-based root cause analysis and corrective action.

Instruments suitable for these measurements
Cora 5001
Brabender Single-Screw Extruder 19/25
Brabender TwinLab 12/20/30

4.6 Optimizing quality control for intermediate products

Fourier transform infrared spectroscopy (FTIR) is a crucial analytical tool for quality control in the polymer industry, particularly for intermediate products. Ensuring the consistency and purity of these intermediates is essential to maintaining the desired properties of the final polymer products. By implementing FTIR-based quality control, manufacturers can prevent defects, reduce production costs, and enhance product performance, ensuring compliance with industry standards and customer expectations.

Material verification with FTIR

FTIR spectroscopy is used for material verification by comparing a sample spectrum to a reference spectrum. Each FTIR spectrum contains characteristic absorption patterns that reflect the molecular structure of the material. A match confirms identity, while deviations may indicate impurities or nonconformity.

The hit quality index (HQI) depicts how good the fit of sample and reference spectrum is, based on the Pearson correlation coefficient. Values close to 100.00 indicate a strong match, with values above 95.00 typically accepted for quality control purposes (depending on the material and accepted variation). Reference spectra, collected from high-quality batches during intermediate product inspection, ensure accurate verification.

Verification measurement

As quality control of the intermediate product, the produced PEEK film was measured with a diamond ATR cell. The measurement parameters are summarized in Table 14.

Spectral resolution	4 cm^{-1}
Number of scans	24
Zero padding	1
Spectral type	Absorbance
Apodization	Blackman-Harris

Table 14: Measurement parameters used for the verification measurement.

The obtained FTIR spectrum was analyzed using the instrument’s software function “Verification” with the spectrum of the ideal intermediate PEEK product as a reference. A predefined method with a defined quality criteria HQI threshold can be used, allowing operators to conduct verification analyses quickly and with minimal risk of errors. The verification process results in an analysis report, including a pass/fail statement, and the plotted spectra of sample and reference, as well as the calculated HQI, as shown in Figure 46.

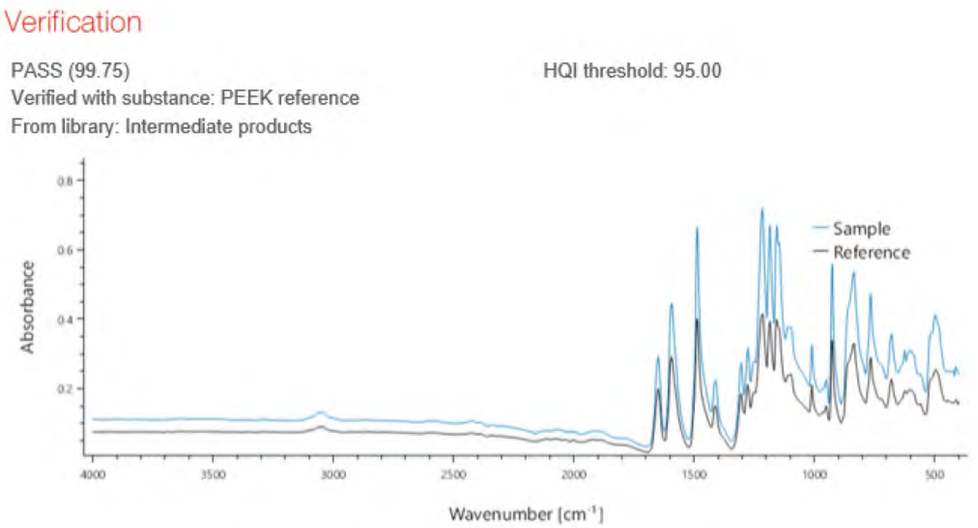


Figure 46: Result of a passed PEEK material verification with an HQI of 99.75.

FTIR is a highly efficient tool for fast, reliable inspection of intermediate products, offering ease of use and measurement times of under a minute. Requiring minimal sample preparation, it is particularly beneficial for industries that require rapid, non-destructive quality checks to ensure material conformity. By streamlining the verification process, FTIR enhances overall efficiency and helps maintain consistent product standards.

Instruments suitable for these measurements
Lyza Series

MCR Evolution

Cora 5001

Power Duo

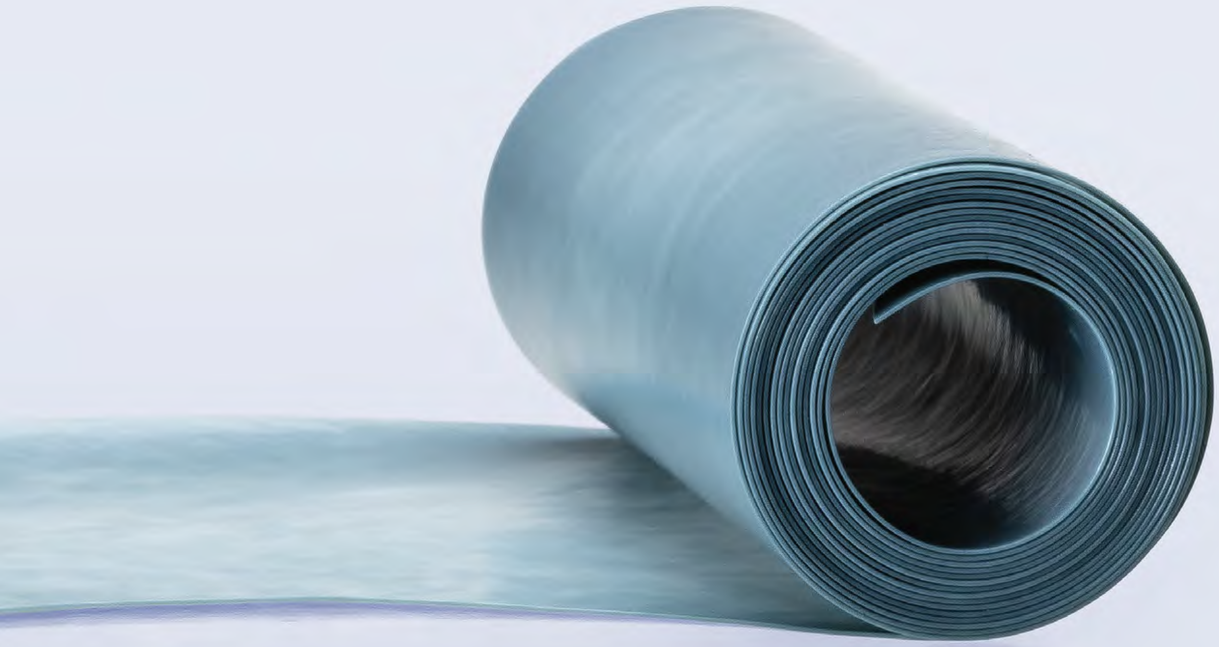
Film Quality and Process Stability via Raman – Rheology Integration

Understanding molecular changes during melting and crystallization is key to polymer processing. The combined MCR Evolution rheometer and Cora 5001 Raman spectrometer enable real-time, in situ analysis of mechanical and chemical properties under processing conditions – accelerating development, optimizing processes, and improving quality control.

5

Production of Final Products (e.g. Packaging Film)

Key Facts



FTIR spectroscopy

Assessing crystallinity in PEEK materials derived from ASTM F2778-09

Zeta potential analysis

Quantification of surface modifications and support for complementary surface analysis techniques

FTIR spectroscopy

Accurate material differentiation, aiding in material verification and preventing misapplication in critical industries

Nanoindentation testing

Mechanical strength evaluation to assess material

Rheological analysis

Detection of the impact of process parameters like roller temperature and draw-off speed on the properties of an LDPE film

Production of final product

The production of high-quality final products, such as packaging films, relies on a combination of precise material selection, optimized processing conditions, and strict quality control measures. The choice of polymers and additives plays a crucial role in determining the film's mechanical strength, barrier properties, and optical clarity. In particular, multilayer extrusion techniques are often used to enhance functional performance, such as moisture and gas barrier protection.

The technical implementation of the extrusion process requires careful control of melt temperature, local processing pressures inside the extrusion line, and cooling rates to ensure uniform film thickness and consistency. In blown film extrusion, bubble stability and air ring design influence the final film properties, while in cast film extrusion, chill roll temperature management is key to achieving smooth surface quality. Additionally, proper winding and tension control prevent defects such as wrinkles and uneven rolls, which are critical for further processing and end-use applications.

With the increasing demand for sustainable solutions, recyclability and the use of biodegradable materials have become essential considerations in packaging film production. Mono-material films and advanced formulations aim to meet both performance and environmental requirements. By optimizing process parameters and material composition, manufacturers can produce films that offer the necessary strength, flexibility, and protective properties while aligning with modern sustainability trends.

5.1 Crystallinity assessment of polymer films according to ASTM F2778-09

PEEK (polyetheretherketone) is a high-performance polymer belonging to the polyaryletherketone (PAEK) family. It is known for its exceptional mechanical, thermal, and chemical properties, making it ideal for demanding applications in industries such as the aerospace, medical, and automotive industries.
PEEK polymer films were produced; they are typically used as semiconductor components, insulation layers for extreme thermal and environmental conditions, or biocompatible films for implants.

Importance of crystallinity determination
Determining the crystallinity of PEEK is important because the degree of crystallinity significantly impacts its physical, mechanical, and thermal properties.

Higher crystallinity typically improves tensile strength, stiffness, and hardness, making the material more suitable for demanding structural applications. Highly crystalline PEEK has a higher melting temperature (around 340 °C) and better thermal stability. This makes it suitable for high-temperature environments.
PEEK's exceptional chemical resistance is linked to its crystalline regions, which are less accessible to chemical attack compared to the amorphous regions.
The crystallization rate and degree of crystallinity influence how PEEK behaves during manufacturing processes like injection molding, extrusion, and 3D printing.

By assessing crystallinity, manufacturers and researchers can optimize PEEK for specific applications, ensuring performance and reliability.

Principle of crystallinity determination with FTIR
PEEK exhibits distinct spectral features in the FTIR (Fourier transform infrared) spectrum due to its aromatic and carbonyl functional groups. The differences in molecular ordering between crystalline and amorphous regions cause variations in the absorption intensities and positions of certain characteristic bands. By comparing the intensity of these bands, the crystallinity can be semi-quantitatively estimated.

Based on ASTM F2778-09 the crystallinity index (CI) can be determined by calculating the ratio of the height between the absorption peaks near 1,305 cm^{-1} and 1,280 cm^{-1}. With this crystallinity index the ASTM standard provides an equation to convert the CI to % crystallinity [1].

Crystallinity index and correlation with % crystallinity
The crystallinity index (CI) is calculated by dividing the measured absorption peak height HA (maximum peak around 1,305 cm^{-1}) by the measured absorption peak height HB (maximum peak around 1,280 cm^{-1}).

Equation 6: Calculation of the crystallinity index CI with HA (max. abs. around 1,305 cm^{-1}) and HB (max. abs. around 1,280 cm^{-1}).

$$CI = \frac{HA}{HB}$$

HA is the peak height corresponding to carbonyl linkages, while HB is primarily influenced by the diphenyl ether groups of the PEEK molecular chain. According to ASTM F2778-09 the CI is related to percent crystallinity through the following formula:

Equation 7: Calculation of % crystallinity using the CI.

$$\%\ Crystallinity = \frac{CI - 0.728}{1.549} \times 100$$

This equation was derived from CI measurements of samples with known crystallinity from WAXS (wide-angle X-ray scattering) as reference measurements [1].

Measurements of PEEK films

The produced PEEK films were measured with ATR-FTIR (attenuated total reflectance FTIR). The FTIR spectrometer was equipped with a Pike IRIS diamond ATR cell and each sample film was directly applied onto the diamond ATR crystal. In order to generate the best contact with the crystal and to guarantee optimal signal intensity, the built-in pressure clamp was applied to press the sample film onto the diamond ATR crystal.

The FTIR spectra were collected in a spectral range of 400 cm^{-1} to 4,000 cm^{-1} with 24 scans and a spectral resolution of 4 cm^{-1}. Figure 47 shows an example FTIR spectrum of a PEEK film, which gives a characteristic fingerprint of the measured sample.

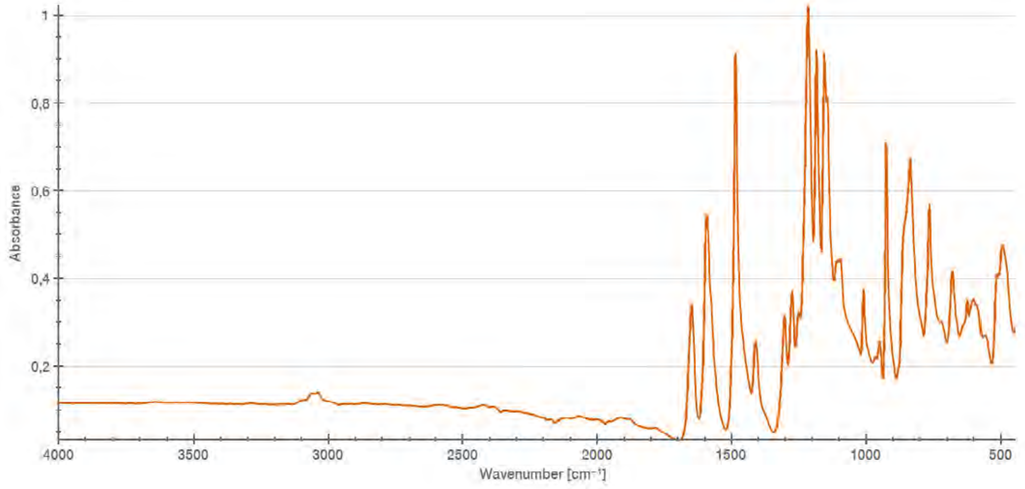


Figure 47: ATR-FTIR spectrum of a PEEK polymer film measured from 400 cm^{-1} to 4,000 cm^{-1} with a diamond ATR cell.

Spectral processing and calculation

The selected samples showed different optical appearance and had a different degree of crystallinity, which should be determined with the FTIR measurements.

The measured spectra were processed based on ASTM F2778-09. The spectral range was reduced to 1,000 cm^{-1} to 1,400 cm^{-1}. A two-point minima baseline correction in the ranges of 1,000 cm^{-1} to 1,080 cm^{-1} and 1,340 cm^{-1} to 1,375 cm^{-1} was performed.

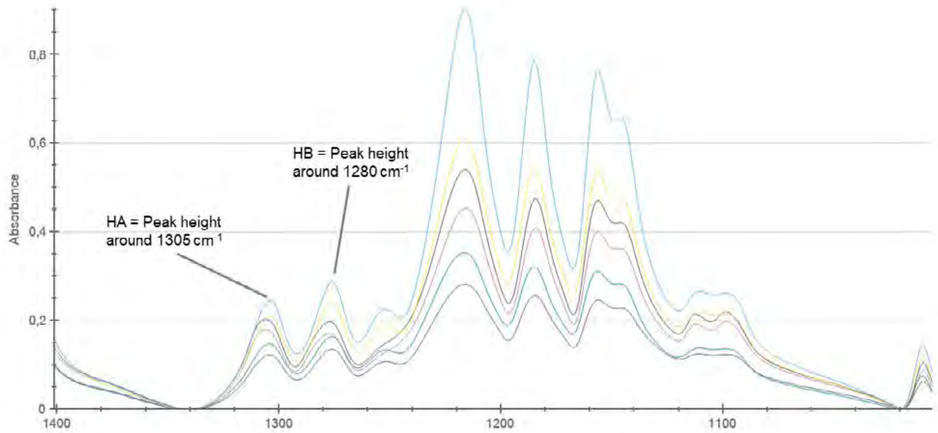


Figure 48: Measured ATR-FTIR spectra of PEEK polymer films with different crystallinity shown in a wavenumber range from 1,000 cm^{-1} to 1,400 cm^{-1}. HA and HB peak according to ASTM F2778-09 are marked in the plot. PEEK film in an amorphous state (blue and yellow curve), a crystalline state (black and pink curve), and in a transition state between amorphous and crystalline (green and violet curve).

The processed spectra were used to read out the HA and HB values at the peak maxima near 1,305 cm^{-1} and 1,280 cm^{-1} as described in the standard. The exact peak maxima were detected by using the wavenumber ranges 1,295 cm^{-1} to 1,315 cm^{-1} and 1,270 cm^{-1} to 1,290 cm^{-1} (see Figure 49).

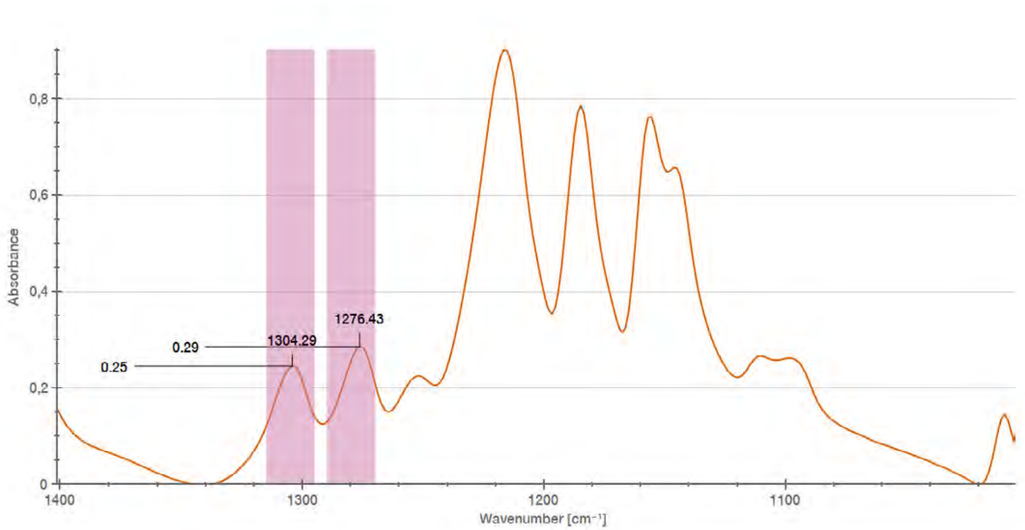


Figure 49: The intensity analysis function applied to the Amorphous #2 spectrum. The colored ranges mark the peak areas of interest.

Six different PEEK samples were chosen for the analysis: two amorphous samples, two crystalline samples, and two samples in a transition state. The goal was to semi-quantitatively determine the degree of crystallinity of the PEEK samples.

Sample	HA [a.u.]	HB [a.u.]	CI	% crystallinity
Amorphous #1	0.2095	0.2387	0.8777	9.7
Amorphous #2	0.2451	0.2856	0.8582	8.4
Transition #1	0.1470	0.1637	0.8980	11.0
Transition #2	0.1228	0.1350	0.9096	11.7
Crystalline #1	0.2031	0.1969	1.0315	19.6
Crystalline #2	0.1786	0.1706	1.0469	20.6

Table 15: Results for HA and HB read out of the processed FTIR spectra. The corresponding CI and % crystallinity were calculated according to the equations provided in ASTM F2778-09.

The calculated degree of crystallinity can be linked to the state of the analyzed sample, as summarized in Table 15.

The amorphous samples had a crystallinity of around 9 %, those in a transition state around 11 %, and those in a crystalline state around 20 %.

FTIR is a robust analytical technique for assessing crystallinity in polymeric materials. This approach involves the identification and evaluation of specific absorption bands within the spectra, which are directly influenced by the degree of crystallinity. Crystallinity induces characteristic alterations in the spectral features, thereby enabling quantification and analysis of the crystalline content in polymer samples.

[1] American Society for Testing and Materials (ASTM). (2009). ASTM F2778-09: Standard Test Method for Measurement of Percent Crystallinity of Polyetheretherketone (PEEK) Polymers by Means of Specular Reflectance Fourier Transform Infrared Spectroscopy (R-FTIR). West Conshohocken, PA: ASTM International. https://doi.org/10.1520/F2778-09

Instruments suitable for these measurements
Lyza Series

5.2 Enhanced measurement sensitivity

Perfluoroalkoxy (PFA) and polytetrafluoroethylene (PTFE) are both fluoropolymers with similar chemical structures, but their differences in processing, mechanical properties, and thermal stability make it crucial to distinguish between them, especially in applications demanding precise material performance. Even small amounts of PFA in a PTFE blend make a difference in the processability, mechanical properties, and surface finish of the material. FTIR transmission analysis provides high spectral resolution, allowing for precise identification of characteristic absorption bands unique to each polymer. This method ensures accurate differentiation, aiding in material verification and preventing misapplication in critical industries.

Measurement with ATR or transmission mode?

Polymer films can be measured either with an ATR (attenuated total reflectance) cell or in transmission. The latter has the advantage of higher sensitivity, allowing the detection of peaks of potential contaminants that would not be visible in an ATR spectrum due to their lower signal intensities.

One point to consider when measuring a polymer film in transmission mode is that it can completely absorb certain infrared wavelengths, resulting in saturated and broadened peaks and the loss of valuable information in the region of these peaks. However, additional peaks may appear that are not visible in ATR spectra, indicating the presence of contaminants. This makes transmission the measurement principle of choice when peaks of compounds present at low levels need to be detected.

PTFE film creation and measurement

A polymer pellet sample was measured with an FTIR spectrometer equipped with a Pike IRIS Diamond ATR. Afterwards, a film was created by placing a small amount of the polymer sample in the Pike PIXIE press for one min at a force of two tons. The resulting film was measured in the pellet holder in transmission. The measurement parameters are summarized in Table 16.

Spectral resolution	4 cm^{-1}
Number of scans	24
Zero padding	1
Spectral type	Absorbance
Apodization	Blackman-Harris

Table 16: Measurement parameters used for the polymer sample measurement.

While the spectrum measured with ATR shows the characteristic PTFE peaks, the spectrum measured in transmission, although oversaturated in large parts of the spectrum, reveals the presence of the distinctive PFA peak at around 995 cm^{-1} (Figure 50).

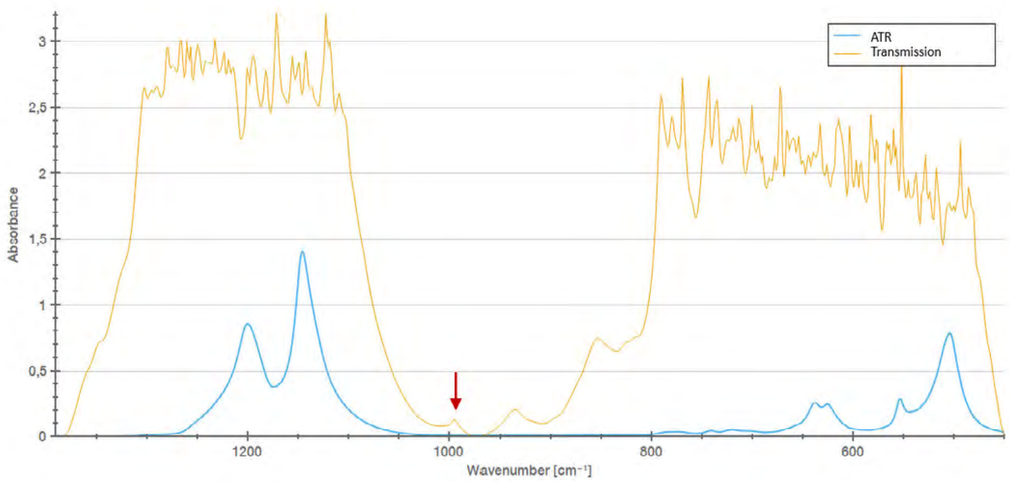


Figure 50: Comparison of the PTFE sample measured as a pellet with ATR (blue) and as a film in transmission (orange) with the characteristic PFA peak at 995 cm^{-1} is marked with an arrow.

The creation of a PTFE film allowed the detection of PFA in transmission, which was not possible with an ATR measurement.

Instruments suitable for these measurements
Lyza Series

5.3 Dynamic mechanical analysis: Effects of roller temperature and draw-off speed on polymer film properties

The properties and performance of polymer-based products such as sheets, foils, and films are significantly influenced by the conditions under which they are processed. The extrusion process, as well as stretching and cooling of the extruded product, determine not only the final geometry but also key material properties such as mechanical strength, optical clarity, and thermal stability. A fundamental understanding of polymer rheology, dynamic mechanical analysis (DMA), and the correlation between flow behavior and process parameters is essential for optimizing production and achieving high-quality products.

An important factor in process design is uniaxial stretching, commonly used to enhance mechanical properties and tailor shrinkage behavior in polymer films. Stretching aligns polymer chains, inducing anisotropy in the material. This orientation increases tensile strength in the stretch direction while affecting flexibility and shrinkage characteristics. The degree of molecular alignment determines the film's response to thermal exposure, a key consideration for applications such as packaging and high-performance technical films. The effect of stretching (or orientation) on the mechanical and shrinking behavior of a film will be investigated in this report using the example of an LDPE film.

Another parameter that plays a major role in defining the structure of semi-crystalline polymers is the cooling speed. Rapid cooling leads to a more amorphous morphology, which results in increased transparency but also alters mechanical strength, transition temperatures, and thermal resistance. Conversely, slower cooling allows for enhanced crystal growth, improving stiffness and thermal stability but potentially reducing optical clarity. To meet the required product properties of semi-crystalline polymers, the cooling speed must be carefully selected.

A further area of interest is the surface quality of extruded polymer products. An unfavorable combination of polymer, processing conditions, and die design may, e.g., lead to surface defects such as the shark skin effect or even melt fracture, significantly reducing product quality. To avoid such defects, it is important to monitor the Deborah number, which correlates the relaxation time of a polymer (determined by the rheological behavior of the polymer at the processing conditions) and the characteristic process time (defined by the geometry of the nozzle and the process speed). This aspect will not be shown with a practical example.

The influence of processing conditions on the properties of extruded polymer films is shown using the example of an LDPE film. During the extrusion experiments, parameters such as roller temperature and draw-off speed were varied, and the resulting films were analyzed using dynamic mechanical analysis. This mechanical characterization was carried out using a rheometer equipped with a lower linear drive, a convection temperature device, and a low-temperature option using liquid nitrogen to reach temperatures down to -160 °C.

For the tests, strips with a length of 35 mm and a width of 10 mm were cut from the film both in the extrusion direction (0°) and perpendicular to it (90°). Due to different processing conditions, the film thickness varied from sample to sample and was determined before each measurement and entered into the rheometer software. Solid rectangular fixtures (SRF) were used as the measuring system. To investigate the dynamic mechanical properties under tensile loading, the sample was heated with a ramp of 2 K/min, starting at -160 °C until failure at approximately +100 °C, while being subjected to a defined oscillatory strain.

The measured DMA curves of the different samples were relatively similar in some cases but all followed a clearly recognizable trend. This trend can be correlated with the expected changes in crystallinity due to variations in roller temperature and stretching caused by draw-off speed. For better clarity, this report presents the effects using two extreme cases as examples: Sample 1a (cooler draw-off roller and low uniaxial stretching) and Sample 1f (warmer draw-off roller and strong stretching).

Figure 51 shows that the glass transition temperature Tg (evaluated based on the peaks of tan(δ)) shifts slightly from 128.66 °C for Sample 1a to 129.76 °C. Additionally, it can be observed that the decrease in the damping factor shifts to slightly higher temperatures for Sample 1f. This minor change is attributed to a (likely only slight) variation in the sample's crystallinity, which can be explained by the different cooling rates of the polymer film on the roller.

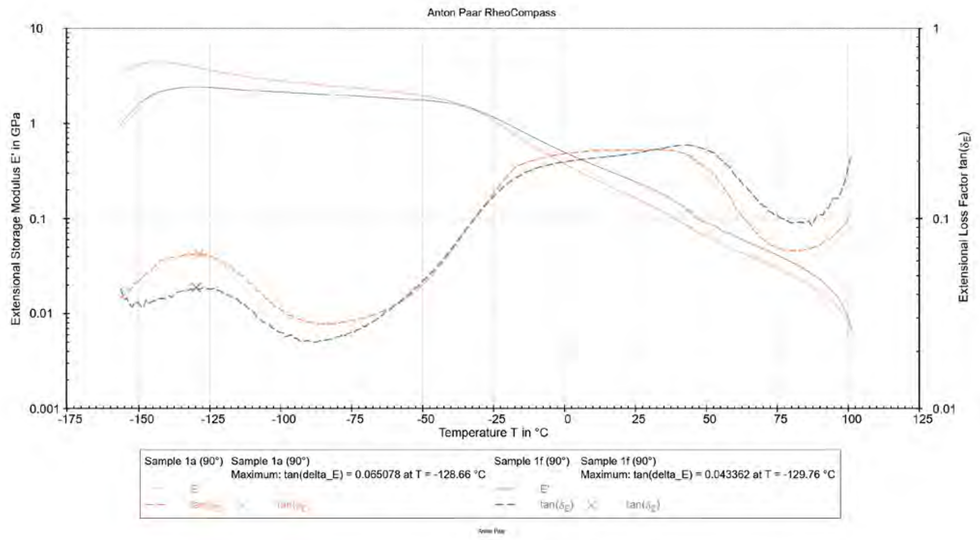


Figure 51: Storage modulus E' and extensional loss factor of an almost unstretched and quickly cooled LDPE film (Sample 1a) and a highly orientated and slowly cooled LDPE film (Sample 1f).

In Figure 52, the thermograms of Sample 1a in the extrusion direction (0°) and perpendicular to it (90°) are compared. It is evident that the influence of the processing direction is negligibly small and has no significant impact on the thermomechanical properties of the product. Since the draw-off speed for Sample 1a was set to a low value, this result was expected.

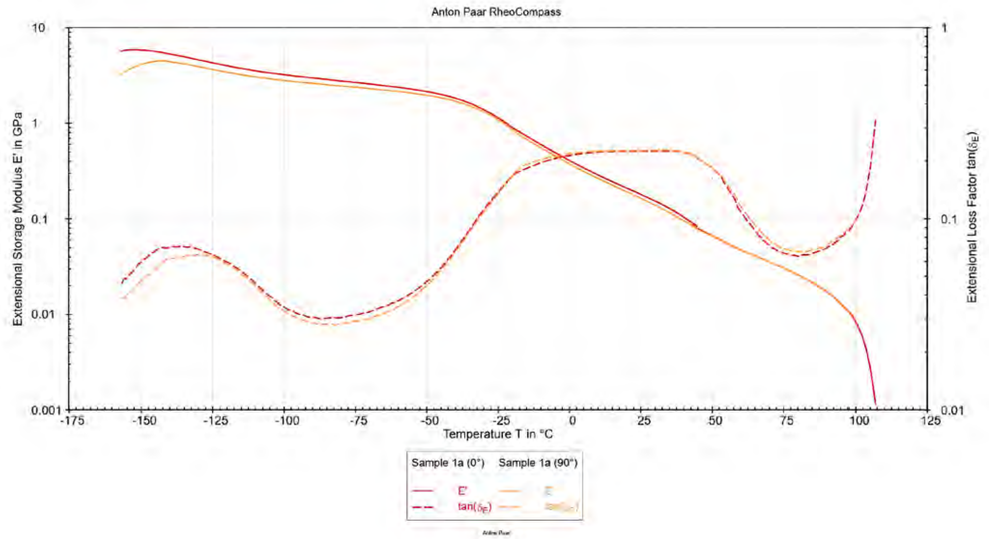


Figure 52: Impact of the sample direction on the thermo-mechanical properties of film 1a.

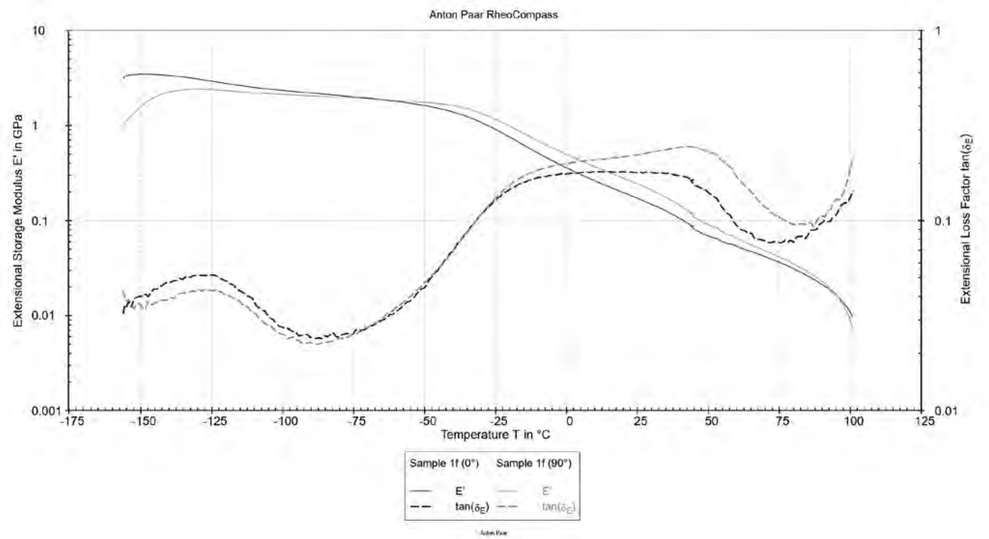


Figure 53: Impact of the sample direction on the thermo-mechanical properties of film 1f.

When looking at the same comparison for the stretched Sample 1f (Figure 53), clear differences can be observed. The extrusion direction or stretching direction (0 °) has a significant influence on the storage modulus E', as well as on the damping behavior of the polyethylene film.

Furthermore, the effects of stretching and orientation, which result from different draw-off speeds, were investigated.

For this purpose, the deformation of the film was measured during a temperature ramp (heating rate also 2 K/min) under a low constant tensile force of 0.1 N. In Figure 54, it can be observed that deformation becomes measurable in all samples upon reaching an elevated temperature. For both films examined perpendicular to the extrusion direction (90°), as well as for the nearly unstretched Sample 1a (0°), the deformation is positive. This means that as soon as the film softens, it is elongated under the low tensile force.

The different temperatures at which these elongation effects are measured are likely due to the varying sample thickness. Thickness plays a dual role in this case: on the one hand, the applied stress decreases with increasing thickness, and on the other hand, thicker films soften or begin to melt more slowly. This leads to the shift in deformation observed in Figure 54.

In contrast, when examining the deformation behavior of the stretched sample 1f in the extrusion direction (0°), a negative trend can be seen as soon as the sample softens sufficiently to relieve the internal stresses introduced during processing. In this case, the sample contracts – it shrinks.

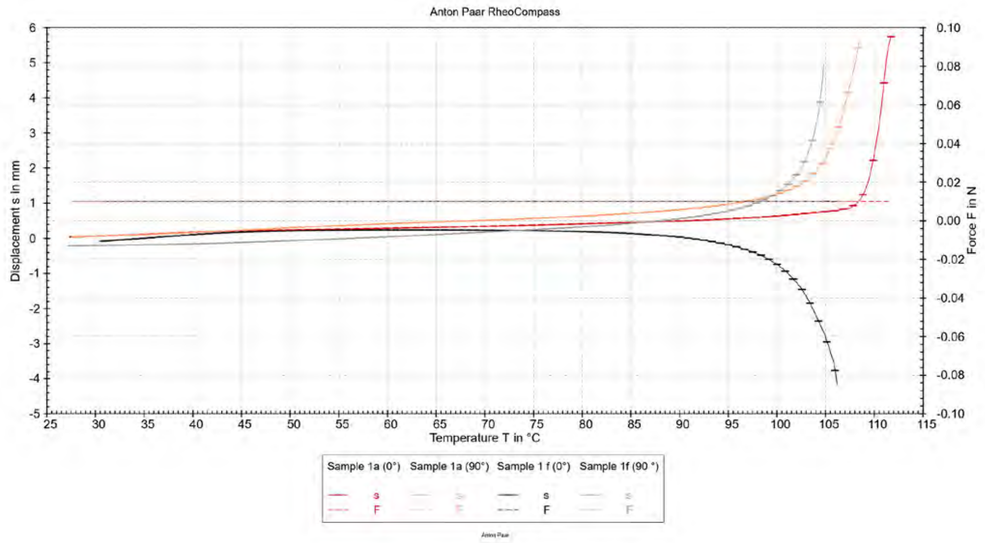


Figure 54: Effect of stretching and sample direction on the shrinkage behavior of LDPE films.

This example clearly demonstrates the impact that processing conditions can have on a product such as a plastic film, leading to the development of a completely invisible preferential direction.

Instruments suitable for these measurements
MCR 702e MultiDrive

5.4 Zeta potential analysis for evaluating film-environment interactions

Many applications of polymer films require surface modification to enhance their performance in specific environments. These modifications aim to increase their affinity toward merging materials (e.g., printing, painting, lamination, adhesion), to improve compatibility with specific environments (e.g., biocompatibility, hemocompatibility), or to introduce functional chemical groups (e.g., coatings for antimicrobial activity). Such modifications – achieved through physical treatments (e.g., Corona discharge, plasma activation) or chemical reactions (e.g., alkaline etching, grafting) – alter the outermost surface of the film. Analytical confirmation of successful modification requires a surface-sensitive parameter and a corresponding measurement technique.

A variety of analytical methods can detect functional groups on material surfaces, each providing complementary information with different levels of complexity. Commonly employed methods iclude attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). These methods differ in lateral resolution and penetration depth into the bulk material. In addition to these spectroscopic techniques for dry samples, water contact angle and the zeta potential measurements probe interfacial properties in aqueous environments. While the water contact angle reflects the hydrophobicity and wettability (by water) of the material surface, the zeta potential serves as an indicator for surface and interfacial charge.

The zeta potential

The zeta potential is defined as the electric potential (in Volts or millivolts) at the solid-water interface. It is caused by a charge distribution at this interface that differs from the charge (ion) distribution in the bulk aqueous solution. The surface and interfacial charge is triggered by the interaction of water with the material surface chemistry and attracts charge carriers in solution (ions) primarily of opposite charge. The interfacial charge may be modelled by a capacitor at the nanoscale as shown in the schematics of Figure 55A.

The zeta potential itself is a calculated parameter and requires the measurement of a so-called electrokinetic effect. In general, an electrokinetic effect is generated by the action of an external force on the solid-water interface that provokes a relative motion of solid and water phases. A frequently used effect is the electrophoretic mobility to assess the zeta potential of colloidal dispersions such as a (nano-) particle suspension or an emulsion. For colloidal dispersions like nanoparticles or emulsions, zeta potential is derived from electrophoretic mobility: an electric field causes charged particles (or emulsion droplets) to move, and their velocity is measured using laser scattering techniques (Figure 55B). The resulting zeta potential distribution typically features a peak value representing the net charge at the particle-water interface. The sign of this value indicates whether charges are positive or negative, while its magnitude predicts dispersion stability.

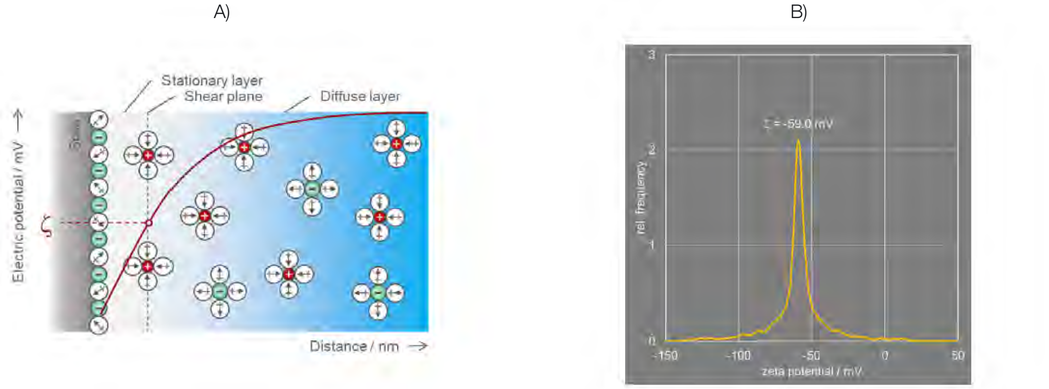


Figure 55: A) Model of the electric double layer representing the charge distribution and the zeta potential ζ at the solid-water interface. (B) Zeta potential distribution for a polymer particle dispersion determined from electrophoretic mobility measurement.

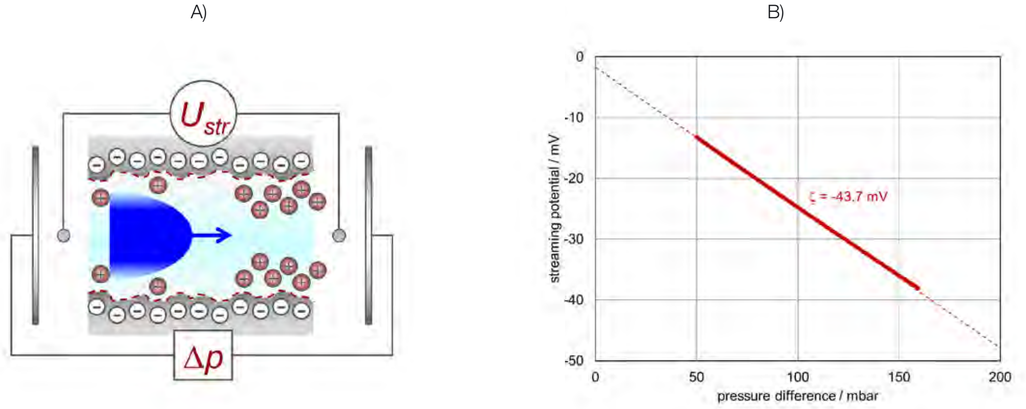


Figure 56: A) Schematic principle of the streaming potential measurement in a rectangular flow channel. B) Linear dependence of streaming potential on applied pressure for an LDPE foil.

Different to colloidal dispersions, the zeta potential of macroscopic solid materials such as polymer films is determined from the measurement of the streaming potential. This method involves flowing liquid through a narrow channel formed by two adjacent film surfaces (Figure 56A). The distance between adjacent film surfaces is small compared to the sample size (here: 20 mm x 10 mm film size, 0.1 mm channel height). A pressure (mechanical force) is applied to the aqueous test solution and the subsequent flow of liquid moves the excess of interfacial charge. Charge separation along the length of the flow channel initiates an electric potential (the so-called streaming potential). A pressure-driven liquid flow moves interfacial charges along the channel length, creating an electric potential – the streaming potential – which is used to calculate zeta potential (Figure 56B).

The polymer-water interface

As shown in Figure 57, pristine polymer films exhibit negative zeta potentials at neutral pH [1]. Common to all polymers is also a nearly linear relationship between zeta potential and pH in mid-range values and isoelectric points near pH 4, where the zeta potential equals zero. In other words, at this material-specific pH, charge reversal occurs, which makes knowledge of the isoelectric point important for the optimization of processes at the solid-water interface (electrostatic forces may switch from attractive to repulsive and vice versa). The zeta potential values recorded near pH 4 follow a linear trend with a negative slope (dashed lines). This slope becomes steeper as the material's hydrophobicity increases, following the order: PMMA (least hydrophobic) < LDPE < PTFE (most hydrophobic).

Unlike materials with a high density of functional groups, the formation of charge at the pristine polymer-water interface cannot be explained by a deprotonation of acidic groups or a protonation of basic groups due to acid-base reactions of these groups with water. Instead, the mechanism of charge formation involves the accumulation of hydroxide (OH-) and hydronium ions (H_3O+) at the polymer surface [2]. This explanation is derived from an empirical observation of the effects of different compositions of the aqueous solution (type of salt, salt concentration, pH) on the zeta potential. The accumulation of these ions is triggered by the hydrophobic character of polymers, which also shows responsibility for the correlation between the zeta potential and the water contact angle.

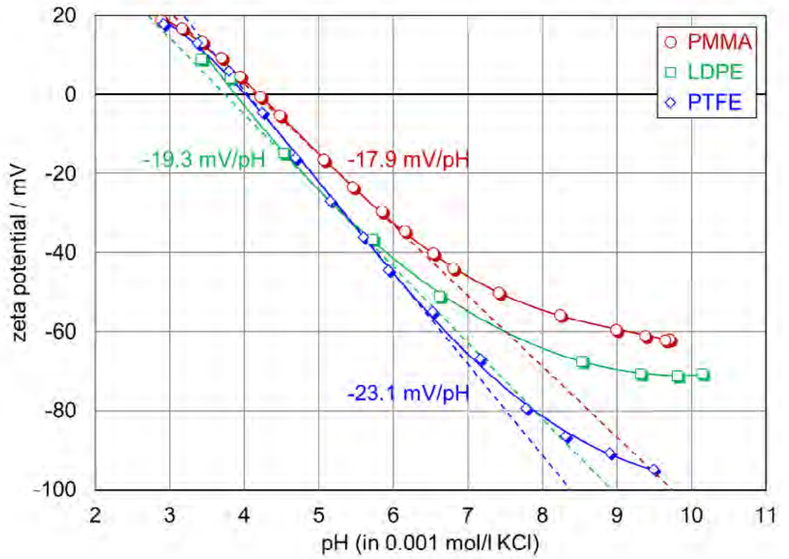


Figure 57: pH dependence of zeta potential for a series of pristine polymer films. The negative slope in the linear range of $\zeta = f(pH)$ increases with hydrophobicity.

Effect of surface treatment

The correlation between the zeta potential and the water contact angle is best observed for a series of polymer films that experience surface modification at increasing treatment time or intensity. Figure 58A shows how photochemical treatment of low-density polyethylene (LDPE) with UV irradiation in an SO_2 atmosphere introduces sulfonic acid groups (–SO_3H), which deprotonate easily due to their highly acidic nature [3].

The titration curve evolves from linear for untreated LDPE to sigmoidal after treatment. Furthermore, the isoelectric point shifts significantly from pH 4 to below pH 2 after one minute of treatment. With longer treatment times, hydrophilicity increases (as indicated by decreasing water contact angles in Figure 58B), but the plateau region at higher pH shifts toward less-negative values.

This counterintuitive trend, where increased functionalization reduces negative zeta potential, is explained by a transition in charging mechanisms: from ion adsorption on untreated surfaces to deprotonation of acidic groups on treated surfaces. Additionally, hydrophilic surfaces attract water molecules that suppress effective charge density.

By combining zeta potential analysis with complementary techniques like water contact angle measurements, researchers can gain a comprehensive understanding of polymer surface properties – enabling precise control over material performance across diverse applications.

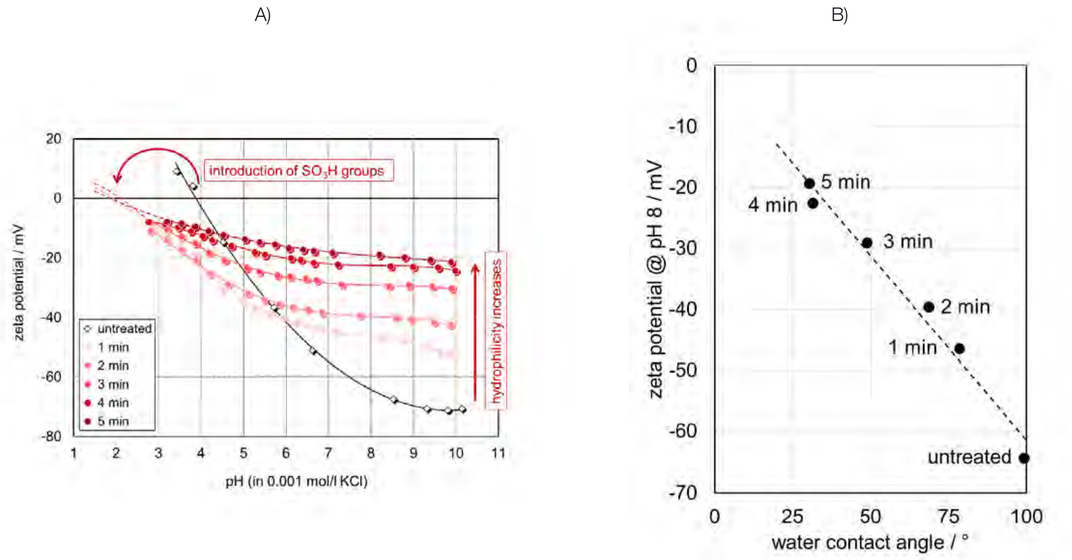


Figure 58: A) Effect of photochemical treatment of polyethylene on the zeta potential and isoelectric point. B) Correlation between zeta potential and water contact angle for the series of pristine and treated PE films.

Implementing function into polymer surfaces

Zeta potential is useful in detecting the activity of additives embedded in the bulk polymer after the compounding extrusion process. For example, chitosan, a cationic polysaccharide with functional amine groups, is widely used due to its antimicrobial properties.

Figure 59A demonstrates the effect of blending polypropylene (PP) with varying concentrations of chitosan. The isoelectric point shifts from pH 4 for pristine PP film (0 % chitosan) to pH 8 for chitosan in solution. For the chitosan solution, the isoelectric point is determined via a pH scan of the zeta potential and electrophoretic mobility measurements. Figure 59B further reveals that the surface concentration of chitosan – indicated by the isoelectric point – scales almost linearly with its concentration in the PP bulk. Empirical studies have shown a correlation between the isoelectric point of polymer surfaces functionalized with amine groups and their antimicrobial activity, particularly in suppressing bacterial and fungal growth [4].

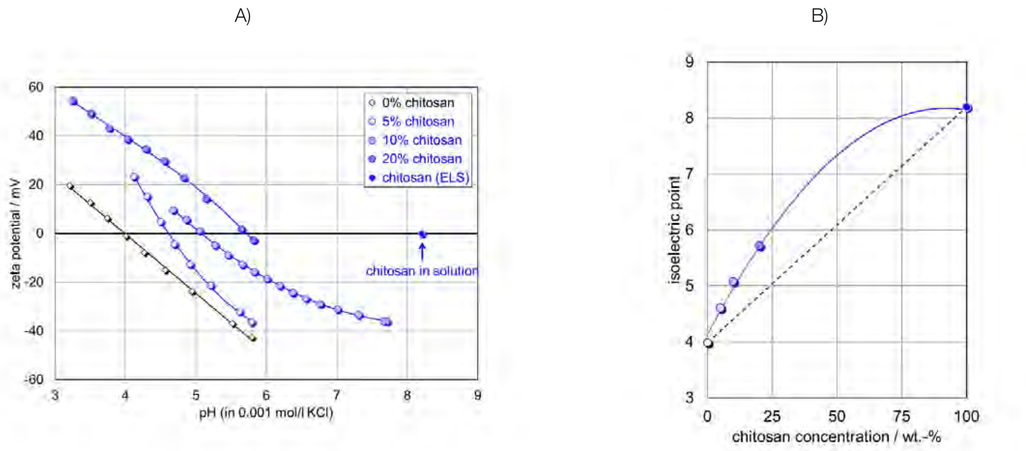


Figure 59: A) pH dependence of zeta potential for plates of polypropylene compounded with different concentrations (wt.-%) of chitosan. B) Correlation between the isoelectric point and the bulk concentration of chitosan.

Another method for equipping polymer films with antimicrobial and antioxidant functionality involves coating them with biopolymers such as chitosan-polyphenol nanoparticles [5]. For this approach, polyethylene (PE) surfaces are activated using UV-ozone treatment prior to the application of the biopolymer to enhance the adhesion of the coating to the polymer film, preferably by covalent bonds. The zeta potential results in Figure 60 suggest that chitosan becomes partially encapsulated by the polyphenols extracted from thyme and cinnamon. This conclusion arises from the lower isoelectric point of PE films coated with chitosan-polyphenol nanocolloids compared to a coating with pure chitosan.

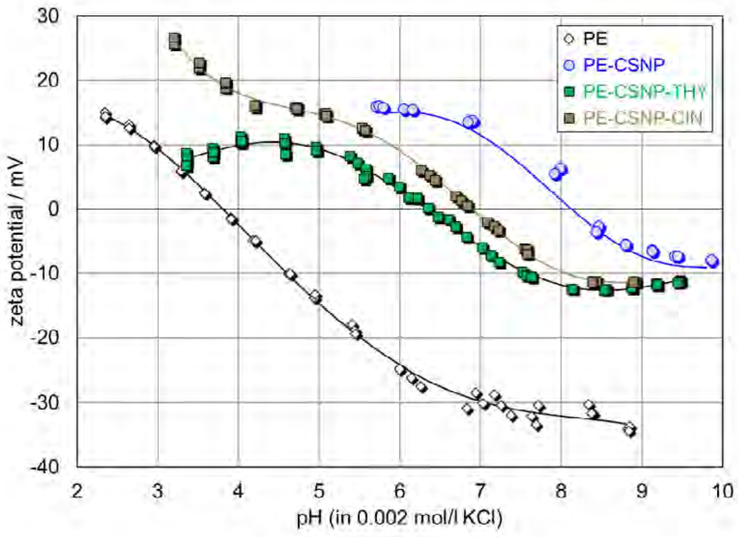


Figure 60: Polyethylene foil coated with different compositions of chitosan-polyphenol nanoparticles. Polyphenols are extracted from thyme and cinnamon.

Recycled polymers behave differently

Pristine and recycled grains of LDPE were extruded into semitransparent foils, and their zeta potential was analyzed using streaming potential measurements. A pH scan revealed characteristic trends typical of nearly pristine polymer surfaces (Figure 61A). Regardless of the LDPE grain source, zeta potential exhibited a linear dependence on pH, with an isoelectric point at pH 3.3 ± 0.2. The deviation of the isoelectric point from the expected range of pH 4 ± 0.2 may be attributed to additives in recycled LDPE – such as dyes (blue and green) – or surface residues from auxiliary agents used during extrusion (the polymer foils were simply rinsed with deionized water prior to the zeta potential analysis to preserve the technical conditions of these foils). Zeta potential analysis clearly differentiates between foils extruded from pristine LDPE and recycled LDPE grains, as well as between sources of recycled LDPE (blue vs. green). Poly(ether ether ketone), PEEK, a polymer distinct from polyolefines, was also analyzed and compared to pristine and recycled LDPE foils. The slopes of zeta potential vs. pH curves suggest an increasing hydrophobicity of the polymer foils in the series LDPE-B, recycled (blue color) < LDPE-C, recycled (green color) < PEEK < LDPE-A, pristine.

Note that a dilute phosphate buffer solution (PBS) was selected as the background electrolyte for the zeta potential analysis and the pH scan. Unlike unbuffered aqueous solution containing monovalent salts such as KCl, the dilute PBS stabilizes the aqueous solution at its native pH 7.2 (for the selected buffer composition). This stabilization reduces measurement uncertainty caused by variations in electrolyte pH, ensuring reproducibility.

Furthermore, PBS allows single-point zeta potential analysis at pH 7.2 – clearly distinguishing surface properties among different polymer foils (Figure 61B). For example, repeated scans for LDPE-B foil showed deviations of ±2.4 mV at pH 7.2, close to the repeatability value of ±1.3 mV observed for pristine LDPE foil.

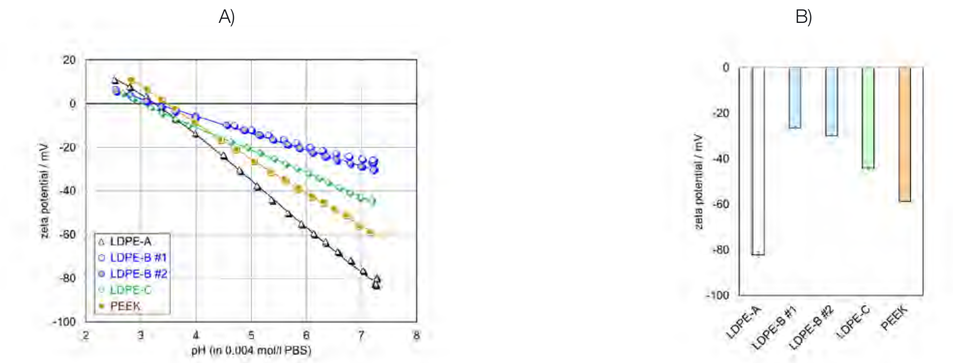


Figure 61: (A) pH dependence of zeta potential for extruded foils of pristine (LDPE-A) and recycled (LDPE-B, LDPE-C) polyethylene and poly(ether ether ketone) foils. (B) Zeta potential for polymer foils at pH 7.2.

Conclusion

The zeta potential is a critical property of the solid-water interfaces that reflects interfacial charge distribution. It governs electrostatic interactions between the material surface and solutes in aqueous environments. For colloidal dispersions of nanoparticles, electrostatic repulsion among these particles determines dispersion stability. For macroscopic solids, electrostatic forces influence solute interactions – important for applications involving aqueous environments. Beyond representing surface charge and driving electrostatic interactions, the zeta potential also serves as a descriptor of the outermost surface chemistry. It helps to qualify and quantify surface modifications while complementing related analytical techniques.

References

[1] Luxbacher, T. The ZETA Guide, Anton Paar GmbH, 2014
[2] Zimmermann, R., Dukhin, S., Werner, C., J. Phys. Chem. B 105 (2001) 8544-8549
[3] Temmel, S., Kern, W., Luxbacher, T., Prog. Colloid Polym. Sci. 132 (2006) 54-61
[4] Kelly, A.M., Kaltenhauser, V., Mühlbacher, I., et al., Macromol. Biosci. 13 (2013) 116-125
[5] Fras Zemljic, L., Plohl, O., Vesel, A., et al., Int. J. Mol. Sci. 21 (2020) 495

Instruments suitable for these measurements
SurPASS 3
Litesizer DLS Series

5.5 Micromechanical mapping of LDPE via nanoindentation to assess property gradients

The mechanical properties of polymeric foils and polymeric materials in general are crucial in determining their strength, flexibility, barrier performance, and durability across various applications. Their resistance to tearing, puncturing, and stretching ensures reliability in packaging, industrial coatings, and protective films, while their flexibility allows for efficient processing and adaptability in wrapping, lamination, and sealing. Mechanical integrity is essential for maintaining barrier properties against gases, moisture, and UV radiation, particularly in food packaging and electronic insulation. Additionally, these properties influence adhesion, impact resistance, and long-term stability under environmental stress, making them vital for applications ranging from medical films to automotive components. By optimizing mechanical characteristics, manufacturers ensure efficiency, product longevity, and suitability for demanding industrial and commercial uses.

The following case study demonstrates the use of matrix nanoindentation mapping in order to determine mechanical properties distribution in an LDPE sample. The study focused on an injection-molded LDPE sample which showed increased porosity at a specific location. A grid of nanoindentation tests was set up in order to measure the gradient of mechanical properties from the dense area of the sample towards the more porous area (Figure 62 and Figure 63). The matrix indentation method allows for the localized characterization of mechanical properties in a large area. The test highlighted a significant decrease in mechanical properties linked to the increased porosity of the material.

Furthermore, nanoindentation allows for a quantitative analysis of the impact of the porosity on the mechanical properties of the material.

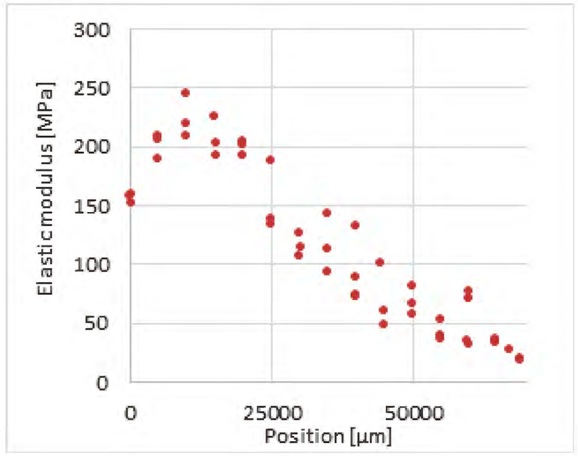


Figure 62: Elastic modulus measured from the dense area towards the porous area.

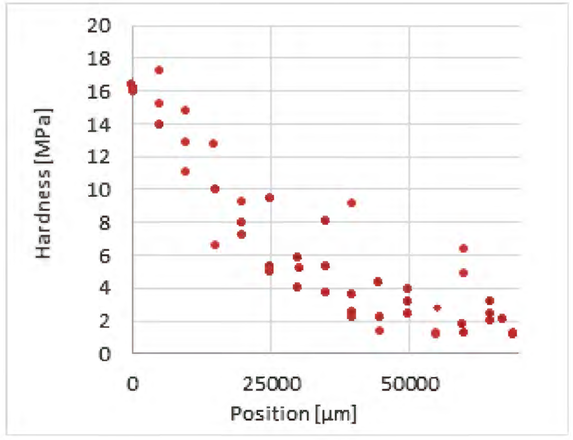


Figure 63: Hardness measured from the dense area towards the porous area.

Evolution of viscoelastic properties in thin polyacrylate films at elevated temperature

Nanoindentation can also contribute to investigation of viscoelastic properties of polyacrylate films and coatings at an elevated temperature. Viscoelastic properties of thin films can be determined by using a dynamic mechanical analysis (DMA) method applied to nanoindentation. The nanoindentation DMA consists in superimposing a small oscillating load on a predefined constant load profile (Figure 64).

The main viscoelastic features can be determined: storage and loss moduli, and tan δ, which provides information about the fraction of the viscous phase.
A typical example where the evolution of viscoelastic properties at elevated temperatures must be known is polyacrylate foils and films used for protection of OLED panels. We performed a series of nanoindentation DMA measurements using a heating sample stage. Four types of 40 µm thin polyacrylate foils were heated up to 120 °C (Figure 64) and at each temperature step their viscoelastic properties were measured. This method allows the user to determine the influence of temperature on the mechanical and viscoelastic behavior of their thin films, offering a detailed measurement of elastic modulus (Figure 65) and tan δ (Figure 66), loss modulus, and storage modulus. The measurement at various temperatures helped estimate the glass transition temperature of the polyacrylate foil, thus providing important information about the mechanical properties of the polyacrylate foils in different environments.

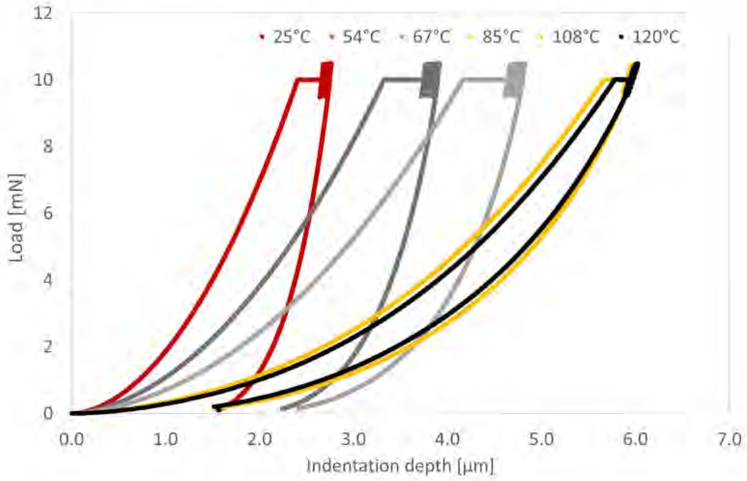


Figure 64: DMA load-displacement curves at different temperatures.

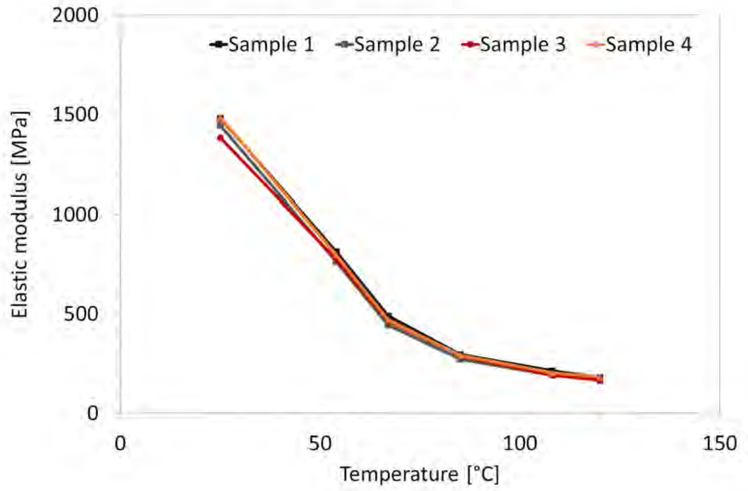


Figure 65: Evolution of elastic modulus as a function of temperature.

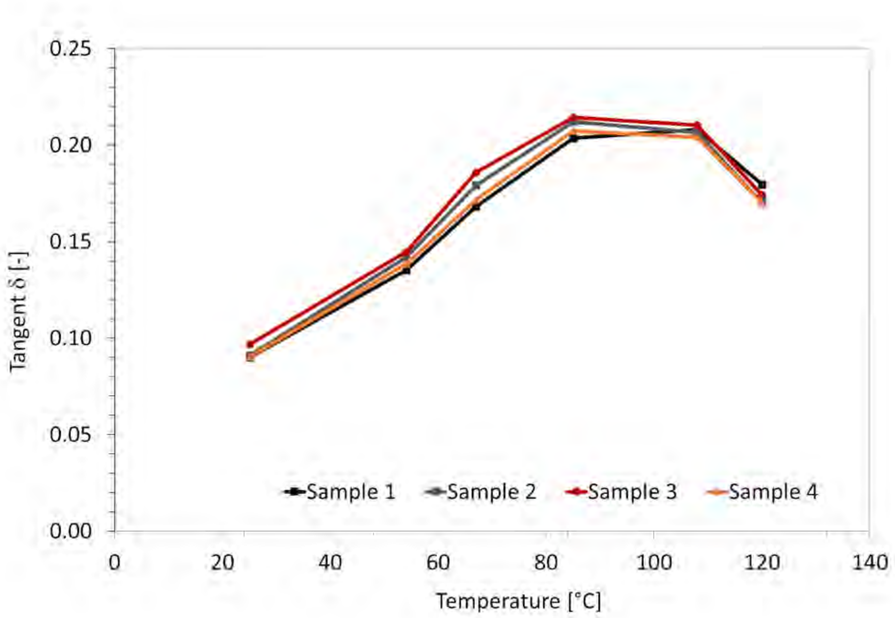


Figure 66: Evolution of tangent delta as a function of temperature.

Comparison of the viscoelastic properties of polymer thin films of different composition

Viscoelastic properties of several polymer film samples of different composition, thickness, and application used in the microelectronic industry were investigated by dynamic nanoindentation. This method is a straightforward and consistent way to measure even very thin foils (thickness higher than ~ 10 µm) where the material can be reliably tested on a very small scale and in very small amounts or volume.

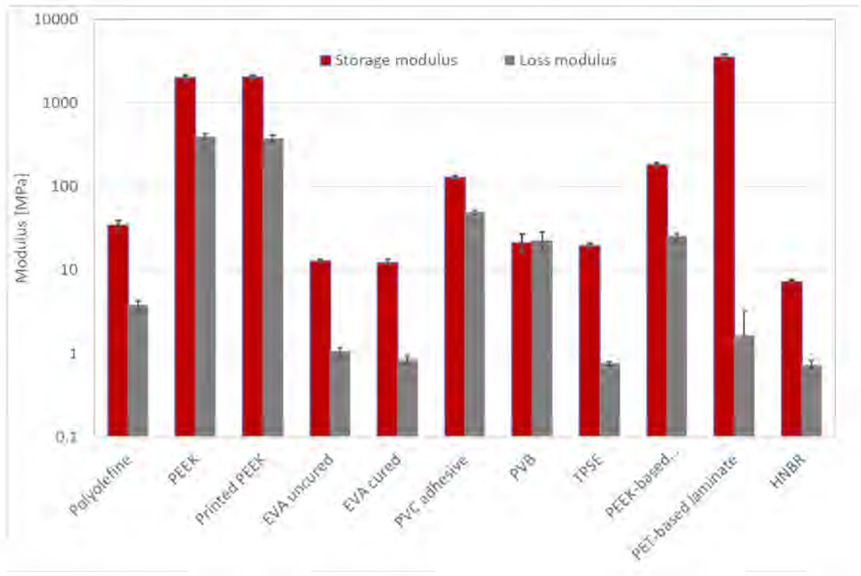


Figure 67: Viscoelastic properties of the tested foil samples.

The DMA nanoindentation results provide an important overview of the viscoelastic properties of the different materials. This also serves as a demonstration of the wide range of polymeric material including PEEK, PVC, and PET that nanoindentation can easily characterize (Figure 67). The nanoindentation method has proved to be a fast, reliable method to measure challenging samples in cases where other measurement methods are difficult to apply or the sample preparation is complicated.

Investigation of the scratch resistance and elastic recovery in self-healing polymeric foils

Elastic recovery describes the ability of a material to recover from non-permanent damage. Different types of polymeric foils and coatings use this property to enhance resistance against wear and tear, and thus are often called self-healing. This study demonstrates the use of a scratch tester to compare the ability of the self-healing polymers to recover compared to conventional polymers. For this, scratch tests were performed on both self-healing and conventional polymeric foils and the true penetration depth during the scratch was recorded. After the scratch, the so-called residual depth (the depth left in the polymer after the load was released) was recorded by scanning the surface after using the same tip but a very low load.

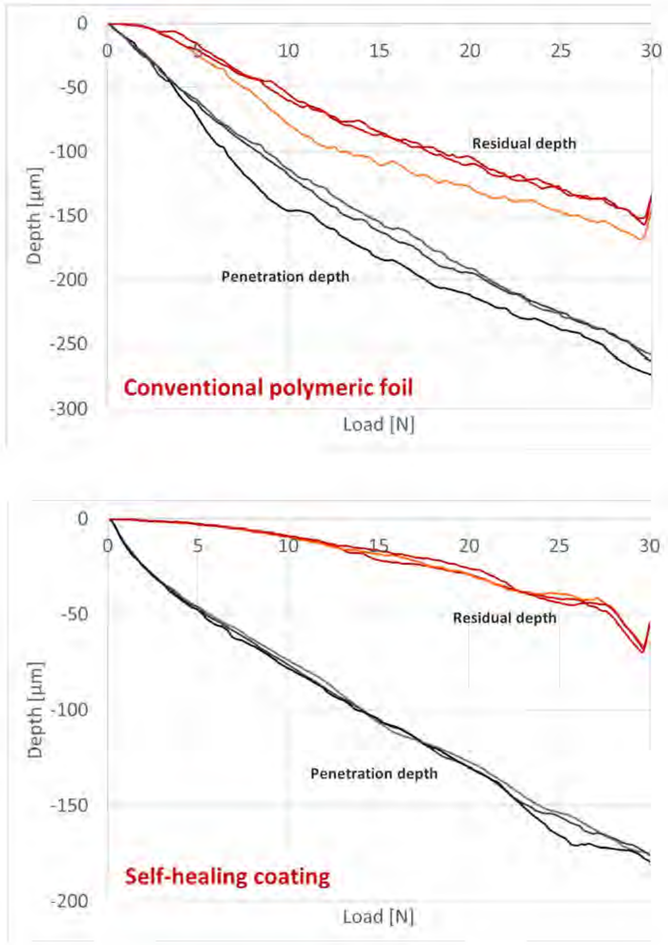


Figure 68: Comparison of penetration and residual depth of the conventional polymer (top) and self-healing paint (bottom).

The difference between the penetration depth recorded during the scratch (under load, dark grey line in Figure 68) and the residual depth (after unloading, red line in Figure 68) shows how much the material recovers from the deformation caused by the scratch. The lower the residual depth, the better the elastic recovery and self-healing. The scratch test method, with precisely measured depth during the scratch using the pre-scan procedure and post-scan for precise measurement of the residual depth, highlights the differences in elastic recovery between a conventional polymeric foil and a self-healing polymeric foil.

Instruments suitable for these measurements
Nanoindentation Tester NHT³

SurPASS 3

NHT³ Nanohardness Tester

Power Duo

Optimize Advanced Materials With Surface and Mechanical Analysis

High-performance materials demand precise analysis of surface and mechanical properties. Anton Paar's SurPASS 3 electrokinetic analyzer measures zeta potential for insights into surface charge, modification, and particle interactions, while the NHT³ nanohardness tester assesses nanoscale hardness and elasticity. Together, they provide complementary data to enhance material performance, durability, and process efficiency – essential for applications in packaging, medical devices, and structural films.

6

Recycling

Key Facts

FTIR spectroscopy

Fast, reliable, non-destructive method to ascertain polymer identity and purity

Dilute solution viscometry

Suitability check of recycled polymers for the intended application (dilute solution viscometry)

Microwave digestion

Preparation for elemental analysis of the recycled LDPE samples reveals various sources of impurities

Recycling

Today’s manufacturing processes are increasingly being developed in the direction of recycling raw materials or must undergo changes due to international regulation to create more sustainable value chains. The use of recycled materials in lab extrusion presents several challenges, particularly due to the variability in the properties of recyclates. Unlike virgin polymers, recyclates come from different sources, leading to heterogeneity in their composition. This can result in contamination, such as inks or adhesives, and degradation of the polymer’s molecular structure, reducing its mechanical properties like strength and flexibility. As a result, the behavior of recyclates during extrusion can be unpredictable, making the process more complex compared to working with virgin materials.

Moreover, the extrusion process is sensitive to parameters like temperature, screw speed, and pressure, which need to be adjusted for recyclates to achieve desired performance. However, higher temperatures can lead to further degradation, highlighting the need for precise control. This is where polymer analytics becomes critical. Analytical techniques such as viscometry and FTIR help understand the recyclate’s properties before, during, and after extrusion. These methods identify degradation, contamination, and processing behavior, enabling optimization of extrusion parameters.
By understanding the recyclate’s structure and properties, researchers can adjust processing conditions and select appropriate additives to enhance performance, ensuring high-quality results. Polymer analytics is essential for overcoming the challenges posed by recyclates and ensuring the production of consistent, high-performance recycled plastic products.

6.1 FTIR-based purity evaluation of recycled LDPE polymers

Fourier transform infrared spectroscopy (FTIR) is a powerful, widely used analytical technique for characterizing polymers. It enables the identification of functional groups, chemical structures, and contaminants by measuring the absorption of infrared radiation across different wavelengths. In the context of recycled polymer raw materials, FTIR plays a crucial role in determining the degree of purity and assessing the quality of the recycled feedstock.

Spectral fingerprint of native and recycled polymers

Samples

The samples of interest consist of five batches of recycled low-density polyethylene (LDPE). Due to their origin, additives and dyes are certainly present. As the materials come from recycled films, coating materials or fillers may also be included.

- Sample V1: Recycled raw material in pellet form (Batch V1), light green-turquoise
- Sample V2: Recycled raw material in pellet form (Batch V2), light green-turquoise-yellow
- Sample V3: Recycled raw material in pellet form (Batch V3), light olive-beige
- Sample V4: Recycled raw material in pellet form (Batch V4), light green-yellow
- Sample V5: Recycled raw material in pellet form (Batch V5), light gray-blue

Sample V5 of recycled LDPE polymer as well as native LDPE were used for the production of polymer films. Three different LDPE polymer films were created in this experiment (pure native LDPE, pure recycled LDPE (Sample V5) and a 50 % / 50 % mixture of native and recycled LDPE (Sample V6)).
The produced polymer films were measured with a diamond ATR cell.
The measurement parameters are summarized in Table 17.

Spectral resolution	4 cm^{-1}
Number of scans	24
Zero padding	1
Spectral type	Absorbance
Apodization	Blackman-Harris

Table 17: Measurement parameters diamond ATR-FTIR.

The spectral characteristics of the FTIR measurements (see Figure 69) for the three different samples are pretty identical at a first glance, however, when having a closer look, the recycled LDPE polymer shows peaks that are not visible in the native LDPE.

Those peaks can be seen in the range from 800 cm^{-1} to 1,800 cm^{-1} (see Figure 70) and can be interpreted according to functional groups.

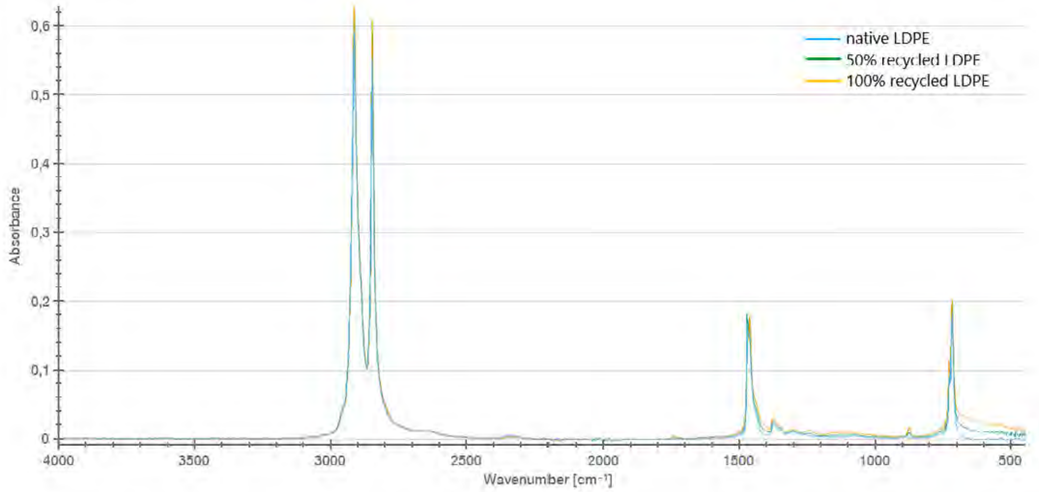


Figure 69: Spectra of native (blue curve), 50 % recycled (green curve), and 100 % recycled (orange curve) polymer were measured.

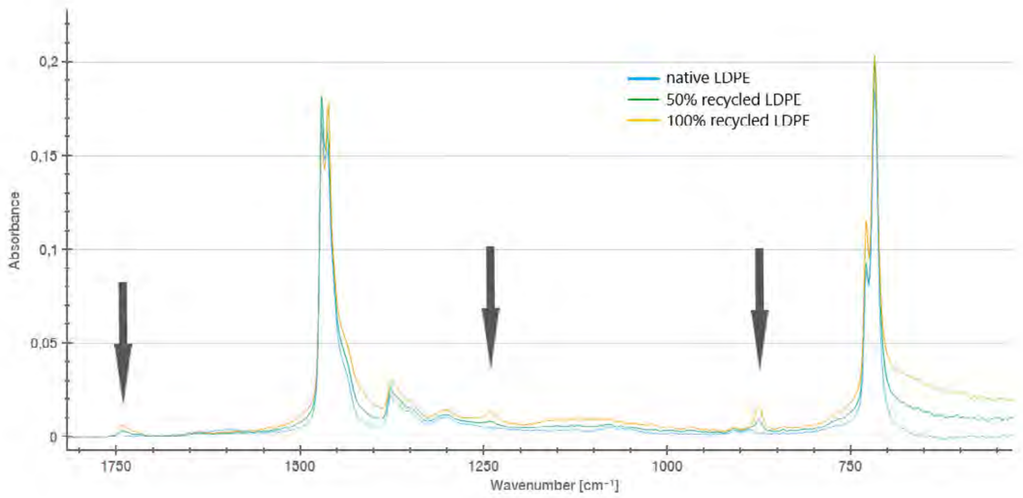


Figure 70: LDPE polymer film spectra of native (blue curve), 50 % recycled (green curve), and 100 % recycled (orange curve) polymer depicted in a wavenumber range from 550 cm^{-1} to 1,800 cm^{-1}. Characteristic differences can be identified near 875 cm^{-1}, 1,240 cm^{-1}, and 1,740 cm^{-1} (see arrows). The 100 % recycled polymer (orange curve) shows the most characteristic peaks, the 50 % recycled polymer (green curve) shows correspondingly weaker signals at the same positions.

Interpretation of the FTIR absorption bands

An absorption band near 875 cm^{-1} can be observed in a variety of materials and is often associated with carbonate fillers ($CaCO_3$). Calcium carbonate commonly shows a characteristic absorption band near 875 cm^{-1}, originating from the out-of-plane bending mode of the carbonate ion.

Because multiple materials can exhibit a band near 875 cm^{-1}, context and comparison to reference spectra are crucial for correct identification. If the sample is known to contain fillers, $CaCO_3$ is a prime candidate.

An absorption band near 1,240 cm^{-1} is commonly associated with various types of C–O stretching vibrations. In polymers and related materials, some of the most frequent causes include:

Ester groups (e.g., PET, other polyesters)

- The asymmetric stretching of the C–O–C bond in ester linkages often appears between 1,230 cm^{-1} and 1,260 cm^{-1}
- Polyethylene terephthalate (PET), e.g., shows a characteristic strong band around 1,240 cm^{-1}

Ether linkages

- If the polymer or compound contains ether groups (–C–O–C–), you may see a band in the 1,200 cm^{-1} to 1,250 cm^{-1} region

Fluoropolymers

- In materials containing $–CF_2$ or $–CF_3$ groups (e.g., PTFE, PVDF), absorbances can appear in this range due to the characteristic C–F stretching modes

Aromatic polycarbonates

- Polycarbonates can exhibit an absorption band near 1,240 cm^{-1} related to the aromatic carbonate structure (aromatic C–O stretching)

A strong absorption band near 1,740 cm^{-1} is commonly associated with the stretching vibration of carbonyl (C=O) groups. In polymer and organic chemistry contexts, the most frequent cause includes ester groups. They are found in polyesters such as PET (polyethylene terephthalate), PBT (polybutylene terephthalate), PMMA (polymethyl methacrylate), and various acrylates.

Without more detailed information about the samples and the composition of the recycled material, it cannot be determined with certainty what contamination is present in the recycled polymer.

It can be clearly seen that there is an impurity present in the recycled polymer (see Figure 70), however, a precise interpretation is not possible without further knowledge. The pure recycled polymer shows the strongest absorption peaks near 875 cm^{-1}, 1,240 $cm^{-1,}$ and 1,740 cm^{-1}, whereas the pure native LDPE does not show peaks at these positions. The 50 % recycled polymer shows accordingly weaker signals at the same positions.

FTIR spectroscopy is integral to the quality control of recycled polymer raw materials, offering a fast, reliable, non-destructive method to ascertain polymer identity and purity.

Instruments suitable for these measurements
Lyza Series

6.2 Elemental analysis of recycled LDPR samples

Recycled low-density polyethylene (LDPE) is increasingly used in the plastics industry to promote sustainability and reduce environmental impact. However, recycling processes can introduce various impurities and contaminants, which may affect the properties and usability of the recyclate. This chapter discusses the elemental analysis results for a series of recycled LDPE samples (V1–V5) and their potential implications.

Samples

The samples of interest consist of five batches of recycled low-density polyethylene (LDPE). Due to their origin, additives and dyes are certainly present. As the materials come from recycled films, coating materials or fillers may also be included.

- Sample V1: Recycled raw material in pellet form (Batch V1), light green-turquoise
- Sample V2: Recycled raw material in pellet form (Batch V2), light green-turquoise-yellow
- Sample V3: Recycled raw material in pellet form (Batch V3), light olive-beige
- Sample V4: Recycled raw material in pellet form (Batch V4), light green-yellow
- Sample V5: Recycled raw material in pellet form (Batch V5), light gray-blue

Sample / element	**Fe** mg/kg	**Zn** mg/kg	**Cr** mg/kg	**Cu** mg/kg	**As** mg/kg	**Cd** mg/kg	**Pb** mg/kg	**Si** mg/kg	**Al** mg/kg	**Mg** mg/kg	**Ca** mg/kg	**Na** mg/kg	**K** mg/kg
V1	227 ± 16	65 ± 2	38 ± 3	<3	<8	<3	<10	0.8	116	80	1.6	76	21
V2	338 ± 37	69 ± 2	60 ± 7	<3	<8	<3	<10	1.0	95	89	1.3	66	19
V3	165 ± 15	66 ± 1	26 ± 2	<3	<8	<3	<10	1.1	94	98	2.0	63	19
V4	80 ± 8	74 ± 2	9 ± 2	<3	<8	<3	<10	1.9	108	75	1.3	72	21
V5*	428 ± 44	88 ± 3	70 ± 7	38 ± 1	<8	<3	<10	1.3	202	126	3.4	98	35

Table 18: Selected elements found in ICP-OES analysis of the supplied recycled LDPE samples (see indicative value).
*Digestion not complete – grey-white residues remained.

Figure 71: LDPE polymer films of native (blue curve), 50 % recycled (green curve), and 100 % recycled (orange curve) polymer were measured.

Analytical methodology

The digestion and analysis of the recycled LDPE samples were performed following the methodology detailed in Chapter 1.5. The results are presented in Table 18. Notably, Sample V5 could not be fully digested and a grey-white residue remained which was subjected to further analysis with XRD.

Elemental composition of recycled LDPE

The elemental analysis revealed significant variation in the concentration of elements across the samples. While the original LDPE sample (chapter 1.5.) showed no detectable levels of most elements (<3 mg/kg for Fe, Zn, Cr, Cu, As, Cd, Pb), the recycled samples exhibited higher concentrations of certain metals:

- Arsenic (As), cadmium (Cd), and lead (Pb): No detectable levels of these problematic elements were found in any of the samples
- Iron (Fe): The levels ranged from 80 mg/kg in V4 to 428 mg/kg in V5, likely originating from machinery wear during the recycling process or residual pigments and additives
- Zinc (Zn): Concentrations ranged from 65 mg/kg to 88 mg/kg. Zinc may stem from stabilizers (e.g., zinc stearate) or residues from prior usage, as it is often used in packaging materials or coatings
- Chromium (Cr): Detected at significant levels in V5 (70 mg/kg) and lower concentrations in other samples. Chromium could be linked to pigments, especially in colored plastics, or residual contamination during recycling
- Aluminum (Al), magnesium (Mg), calcium (Ca), sodium (Na), potassium (K) and silicon (Si): These elements are likely associated with fillers or contaminants introduced during the recycling process. V5, in particular, exhibited elevated levels of aluminum (202 mg/kg) and magnesium (126 mg/kg). For silicon, increased contents were found in particular in Sample V4, which could stem from certain fillers, such as talcum.

Unique properties of Sample V5

Sample V5 (see Figure 71) differed markedly from the others in multiple key aspects: its color and appearance, as well as its composition. Unlike the greenish tones of V1–V4, V5 exhibited a pale blue color, suggesting the presence of specific pigments. Additionally, digestion of V5 resulted in a gray-white residue, which X-ray diffraction (XRD) identified as titanium dioxide (TiO_2), indicating the presence of pigments or additives commonly used to impart whiteness or UV resistance in plastics. Another notable distinction was the presence of copper (38 mg/kg), which was uniquely detected in V5. This could stem from pigments such as copper phthalocyanine (a common blue pigment used in plastics processing), other additives, or contamination during the recycling process. Since elevated copper levels can influence the recyclate's thermal and mechanical properties, they may need to be considered for its end-use applications.

Summary and conclusion

Elemental analysis of the recycled LDPE samples reveals various sources of impurities. Machinery wear is indicated by elevated Fe and Al levels, suggesting abrasion from processing equipment. Pigments and additives, such as Ti (titanium dioxide), Zn, and Cr, likely originate from stabilizers or colorants used in the original manufacturing process. Fillers and contaminants, including Mg, Ca, Na, and K, may stem from prior industrial or consumer applications where these elements were introduced.

These impurities can significantly impact the mechanical and thermal properties of recycled polymers, potentially limiting their applications. The distinct pale blue color and titanium dioxide content in Sample V5, e.g., suggest a different material origin or treatment compared to the greenish V1–V4 samples, which may affect its suitability for certain uses.

Understanding the elemental composition of recycled LDPE is crucial for optimizing recycling processes, improving material quality, and ensuring compliance with industry standards. The unique characteristics of Sample V5 emphasize the need for detailed analysis to assess recyclate suitability and maintain consistent material performance.

Instruments suitable for these measurements
Multiwave 5001
Multiwave 7101/7301/7501

6.3 Intrinsic viscosity analysis of raw materials and recycled products

The properties and applications of a polymer are primarily determined by the type of monomer used and the final molecular size or chain length, which is true for both newly produced (virgin) as well as recycled polymers. Structural changes in polymers, often resulting from mechanical stress, typically lead to variations in chain length. These changes can significantly alter the properties of the final product compared to the original raw materials. Consequently, recycled polymers may not always be suitable for their intended applications.

Controlling the quality and performance of recycled polymers is crucial and serves several purposes, including:

- Characterizing raw materials and finished products
- Defining recycling process parameters
- Ensuring quality control of incoming and recycled materials
- Identifying defective batches

Dilute solution viscometry is a reliable technique for polymer quality control. This method involves dissolving polymers in suitable solvents and measuring the viscosity of both the pure solvent and the polymer solution. From the ratio of these viscosities, known as relative viscosity, intrinsic viscosity can be calculated – an important parameter directly related to the average molar mass of a polymer.

Example: Determining the intrinsic viscosity of PET bottle flakes
Polyethylene terephthalate (PET) bottle flakes were prepared following the relevant sections of ISO 1628-5. Sample preparation is a critical step, as errors can compromise downstream measurement accuracy. PET flakes were precisely weighed and dissolved in dichloroacetic acid (DCA). The exact concentration was noted, as accurate concentration is critical for final calculations. Typically, solutions with a concentration of 5 mg/ml are used for such measurements.

The measurements involve these steps:

- Measuring the runtime of pure DCA solvent
- Measuring the runtime of the polymer solution
- Comparing runtimes to automatically calculate viscosity parameters

Measurements were performed using a flow-through filling setup with a 30° inclination angle and the calculation mode Single Concentration. The adjustable capillary angle helps mitigate the effects of shear-thinning behaviour often observed in polymer solutions. Alternatively, a zero-shear scan (ZSS) can be applied. This method involves measuring the sample at multiple inclination angles and extrapolating the results to a theoretical zero-shear viscosity, providing even more accurate viscosity readings. In addition to the Single Concentration mode, users can measure multiple concentrations and calculate intrinsic viscosity using the integrated calculation formulas. In this case, the intrinsic viscosity of the PET samples was determined using the calculation methods according to Billmeyer, Deb-Chatterjee and Solomon-Ciuta.

Intrinsic viscosity	Billmeyer	Deb-Chatterjee	Solomon-Ciuta
	PET-BF	PET-BF	PET-BF
Mean value [dL/g]	0.762	0.797	0.771
Std. dev. [dL/g]	0.001	0.001	0.001
Std. dev. [%]	0.09	0.09	0.09
2 Std. dev. [%]	0.17	0.18	0.17

Table 19: Mean intrinsic viscosity values and standard deviations for PET bottle flakes (PET-BF) using different calculation methods.

Conclusion

Dilute solution viscometers offer a precise, reliable solution for evaluating intrinsic viscosity and related polymer properties, thereby enabling the early detection of potential quality issues, in an easily understandable and practical manner. Its high precision and minimal sample requirements make it an especially valuable asset for quality control in polymer recycling.

Instruments suitable for these measurements
Lovis 2001

7

Anton Paar Solutions

Lyza Series

The Lyza series FTIR spectrometers transform industry standards: Guided workflows, combining measurement, processing and spectral analysis in an automated method, allow users with minimal experience to perform QC measurements in just three steps, for a quick pass/fail result. Measure hundreds of sample types – from solid to liquid or gaseous – and switch effortlessly between measurement cells, thanks to the versatile modular cell concept.

Find out more
www.anton-paar.com/eb-polymer-lyza

Cora 5001

Cora 5001 is a Raman analyzer for the quick and reliable identification of substances based on their chemical fingerprint, or for the monitoring of chemical changes. Choose the Fiber model for flexible analysis outside the instrument via a probe or the Direct model which analyzes samples in a closed compartment and is certified as laser class 1 – for ultra-safe use. The guided analysis procedure means Cora 5001 is suitable for operation with only minimal training.

Find out more
www.anton-paar.com/eb-polymer-cora

MCR Evolution Rheometer and Cora 5001

The Rheometer-Raman setup is the perfect symbiosis of rheology as a mechanical – and Raman as a molecular – spectroscopy method. The relationship between the mechanical behavior obtained from the rheometer and structural parameters deducted from the Raman spectra is important for a better understanding of changes in the chemical functionality and microstructure of various materials and their influence on processing and applications.

Find out more
www.anton-paar.com/eb-polymer-mcr-cora

MCR Evolution Rheometer Series

The MCR Evolution series is the result of consistent thinking and rethinking, of continuous development based on decades of experience, and of the feedback of more than 10,000 satisfied customers. The combination of innovative and thousandfold field-proven technology with the modular design represents the benchmark in its class. With 200+ accessories, the MCR Evolution rheometer series gives you endless possibilities for rheological investigations and material characterization.

Find out more
www.anton-paar.com/eb-polymer-mcr

MCR 702e MultiDrive

The high-end model: Alongside all standard rheological test modes it can be equipped with an additional lower drive unit. This means that you can perform rheological tests with two torque transducers and drive units at once – opening up multiple possibilities for your research. There are no limitations regarding the test modes used, measuring systems, accessories, and temperature devices, and no limitations on measurement precision.

Find out more
www.anton-paar.com/eb-polymer-mcr-702e

SmartMelt Series

The SmartMelt series is the choice for polymer melt rheology at the highest level. Experience unmatched performance, precise temperature control via actual sample temperature measurement, comprehensive shear-rheology testing, and seamless compliance with ASTM D4440. Designed for efficiency, SmartMelt ensures quick training, fast measurements, and dependable outcomes.

Find out more
www.anton-paar.com/eb-polymer-smartmelt

HTR 7000

The HTR automation series offers an optimized analysis workflow for rheological investigations based on Anton Paar's MCR 702 rheometer. The extensive set of features and the built-in flexibility make it the ideal choice for sophisticated and high-throughput R&D or QC work.

Find out more
www.anton-paar.com/eb-polymer-htr-7000

Brabender MetaStation

A versatile, modular drive unit and torque rheometer for determining the processability and material characteristics of different plastics and plastifiable substances, compliant with key ASTM standard methods. Tailor it to your specific PVC, rubber, or thermoset testing needs, using our portfolio for varied blade geometries, mixer sizes, and temperature control. In addition to batch-wise compounding and mixing, continuous processes are also possible via the use of single- and double-screw extrusion attachments of different scales.

Find out more
www.anton-paar.com/eb-polymer-metastation

Brabender Single-Screw Extruder 19/25

Minimize downtime when it comes to establishing new materials and current processes with the Brabender Single-Screw Extruder's lab-scale design whilst also avoiding blocking your production extruders. It comes in two different options: compact, i.e. stand-alone operation is possible, and in a modular setup. The modular system construction opens up comprehensive materials analysis options. Depending on the application, you have a broad range of configuration options at your disposal: The solution leaves the way open for expansion options, such as connecting a Brabender Twin Screw Extruder or mixer.

Find out more
www.anton-paar.com/eb-polymer-extruder

Brabender Aquatrac-V

The only instrument on the market that determines the water-selective, residual moisture in plastics in compliance with DIN EN ISO 15512:2019. With an accuracy of 0.0001 % (H_2O resolution), Brabender Aquatrac-V is ready for both QC in the lab and process control. Since it uses the globally recognized calcium hydride method, it offers reliable measurements that you can access from any device. It can also prepare dried polymer samples for Melt Flow Rate (MFR) determination, meaning no specialized labs or hazardous chemicals are needed.

Find out more
www.anton-paar.com/eb-polymer-aquatrac

Brabender TwinLab

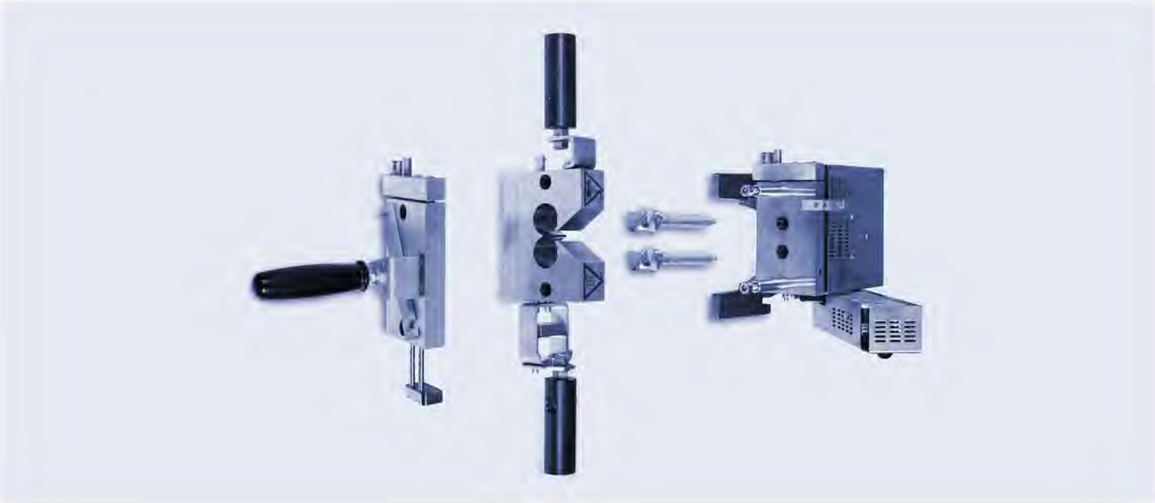
The Brabender TwinLab series provides various configurations to process everything from liquids to pellets. Streamline your material testing for lab and pilot-scale setups, and optimize your extrusion production process. MetaBridge operating software ensures intuitive device control, paired with comprehensive features and data analytics. It lets you access data from any device at any time. Brabender TwinLab's smart clam shell design makes the liner easy to access and clean.

Find out more
www.anton-paar.com/eb-polymer-twinlab

Brabender FQA Film Quality Analyzer

The Brabender FQA Film Quality Analysis System represents an additional follow-up device for the optical evaluation of the quality of blown and cast films. This is particularly suitable for use in the development of virgin plastics as well as quality assurance in the processing of films with recycled or biopolymer content.

Find out more
www.anton-paar.com/eb-polymer-film-quality-analyzer



Brabender Measuring Mixer 30/50

Designed for easy handling and cleaning, featuring a bipartite or tripartite mixer bowl. It offers flexible heating and cooling options, including liquid-based temperature control or an electric heater. Precise and consistent temperature regulation is ensured by three independent heating zones, allowing operating temperatures of up to 500 °C with electrical heating. The mixer's versatility is enhanced by its quickly removable and interchangeable mixer blades, making it adaptable to various applications.

Find out more
www.anton-paar.com/eb-polymer-mixer-30-50

Multiwave 5001

This microwave reaction platform provides digestion of a broad array of samples (varying in difficulty or volume), acid leaching, solvent extraction, evaporation, microwave-induced O_2 combustion, sample drying, and synthesis. Furthermore, it comes with a comprehensive, interactive method library, a customizable, intuitive user interface, and modern sensor technology, together with easy-to-handle compact rotors.

Find out more
www.anton-paar.com/eb-polymer-multiwave-5001

Multiwave 7101/7301/7501

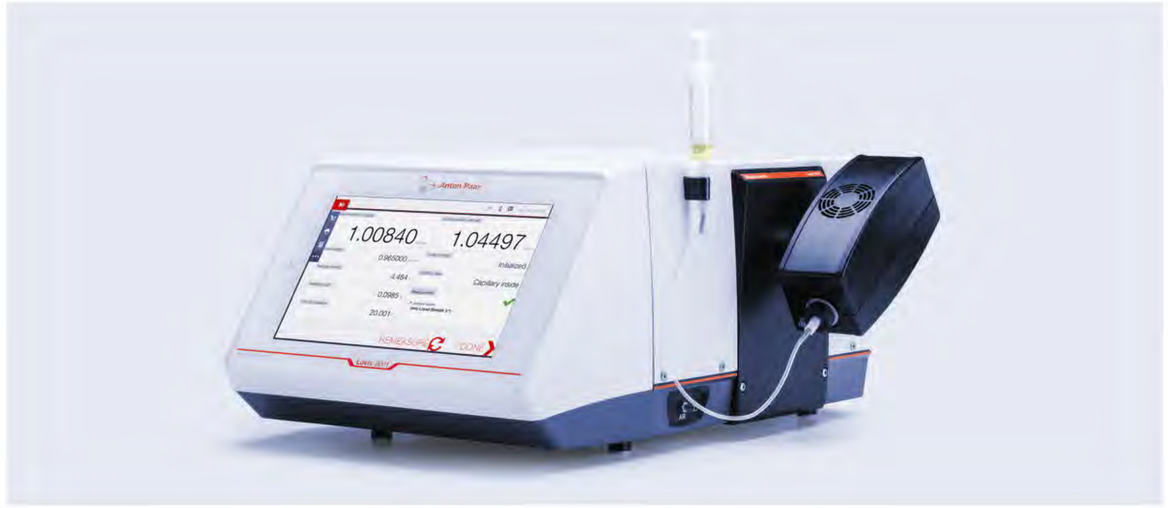
When over 40 years of experience in pressurized acid digestion meet advanced microwave technology, a high-performance microwave digestion system is the outcome. The Multiwave 7101/7301/7501 series delivers the next level of performance, working at up to 300 °C and up to 199 bar. This ensures complete digestions of all kinds of samples, such as food, environmental, polymer, cosmetic, pharmaceutical, geological, chemical, and petrochemical samples, in the same run.

Find out more
www.anton-paar.com/eb-polymer-multiwave

Ultrapyc Series

Ultrapyc gas pycnometers measure the true and skeletal density of solids to track their purity and porosity. Measurements take less than 10 minutes, so they are perfect to control the quality of your solid materials throughout the manufacturing process. The PowderProtect mode enables measurements of fine powders without instrument contamination and the built-in Peltier temperature control ensures superior thermal stability with no external temperature control bath required.

Find out more
www.anton-paar.com/eb-polymer-ultrapyc



Lovis 2001

This falling-ball viscometer features an adaptable measurement angle, ensuring pinpoint precision, especially for low-viscosity or shear-sensitive liquids. Plus, it delivers polymer-specific parameters, such as intrinsic viscosity, K-value, and average molar mass with minimal sample volume, in just 30 seconds to three minutes. The Peltier thermostat ensures quick, energy-efficient temperature control (5 °C to 100 °C) for precise results across various sample types. An optional setup extends the range to -40 °C, making it a versatile choice for labs.

Find out more
www.anton-paar.com/eb-polymer-lovis

SurPASS 3 Series

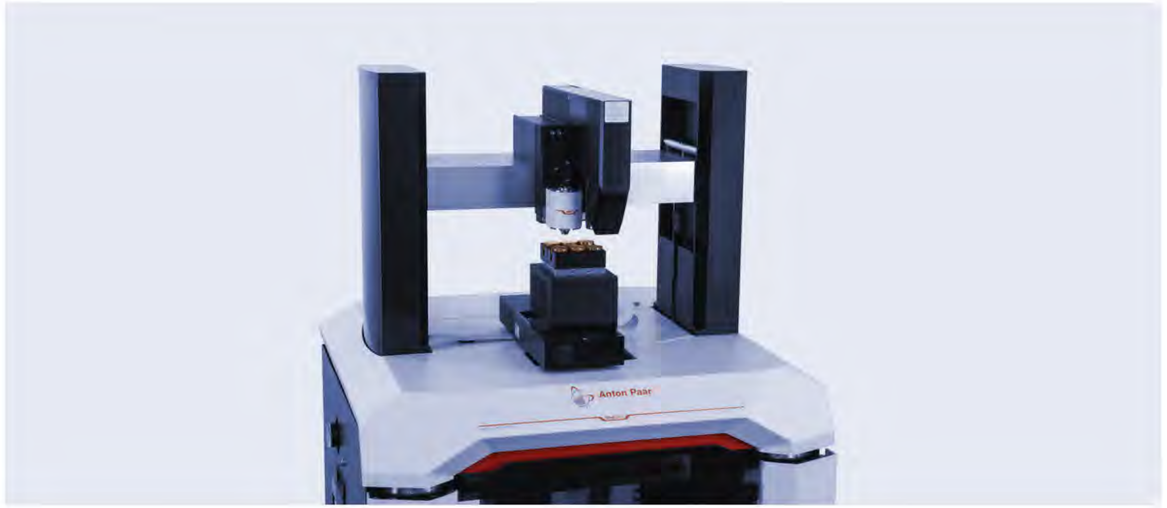
The SurPASS 3 series features fully automated zeta potential analysis of macroscopic solids under real-life conditions. As electrokinetic analyzers, they employ the classic streaming potential and streaming current method for direct analysis of the surface zeta potential. The zeta potential is related to the surface charge at a solid/liquid interface and is a key parameter for understanding surface properties and developing new specialized materials.

Find out more
www.anton-paar.com/eb-polymer-surpass-3

Litesizer DLS Series

Delivers best-in-class particle sizing with automatic angle selection to prevent errors, while MAPS technology yields the highest-possible peak resolution. Continuous transmittance monitoring detects sedimentation and agglomeration during measurement, enhancing measurement reliability. Unique to our system, cmPALS and Omega Cuvette improve zeta potential accuracy and repeatability by addressing aging effects and minimizing electrical gradient.

Find out more
www.anton-paar.com/eb-polymer-litesizer-dls



Nanoindentation Tester NHT³

Designed for measuring hardness, elastic modulus, creep, and other surface properties from the nanometer to the micrometer scale. Its force ranges from 0.1 mN to 500 mN for maximum versatility. With the unique top surface referencing technique, an instrumented indentation measurement can be made immediately without waiting for thermal stabilization. The “Quick Matrix” indentation mode allows high throughput (up to 600 measurements per hour).

Find out more
www.anton-paar.com/eb-polymer-nht3

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