ABB MEASUREMENT & ANALYTICS | WHITE PAPER

Efficient quality control of PET properties during container blow moulding process through near-infrared analysis

The ability to perform reliable quality attribute measurements of polyethylene terephthalate (PET) preforms or blown bottles is critical in the packaging and bottling industry.

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01 Plastic bottles in a beverage factory

Abstract

Intrinsic viscosity (IV), moisture content, crystallization, co-monomer content and wall thickness determine the behaviour of PET packaging along all stages of manufacturing, transport, storage, and consumption. It is essential to control these quality attributes during manufacturing to ensure production efficiency and prevent product defects. Many laboratory methods can determine the state of these parameters, but most require specialized equipment, time, operator expertise, and solvents or reagents for some analysis. Consequently, some testing is outsourced or performed infrequently, thus reducing the full potential of a thorough quality check. This white paper demonstrates the use of Fourier-transform near-infrared spectroscopy (FT-NIR) as a simple, accurate and non-destructive alternative technique for fast determination of multiple properties linked to PET packaging characteristics. It illustrates the advantages of replacing multiple testing procedures with a multi-property analysis tool to monitor critical production parameters for PET-based products at the laboratory or production site.

Introduction

In stretch blow moulding, homogeneity, preform consistency and production environment stability are essential. During production, any fluctuation could propagate ahead and potentially cause disruptions in the process or defects in the product. Production conditions and perfect control of PET chemistry during the process is therefore a priority. Depending on the container, precise sets of parameters linked to the PET chemistry must be scrupulously monitored.

The requirements for the container and for the PET resin of which it is made derive largely from its contents and the filling method. Carbonated beverages build up pressure within the container and thus stress its walls, which then need to be stiff and creep resistant. Microbiologically sensitive beverages are sometimes hot filled to sterilize the container and closure. These containers need to exhibit enhanced crystallization to yield the necessary thermal stability. Other microbiologically sensitive products are filled under aseptic conditions. The container is then sterilized either at moderate temperatures, before being introduced into the aseptic filling environment, or even already stretch blow moulded under aseptic conditions.

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01 PET containers and preform

Those along with other containers with non-carbonated contents, do not need to withstand high pressures and temperatures, and can be noticeably lightweight. Yet, limitations in injection moulding can restrict the preform geometry for those lightweight applications, which entails high stretching ratios and demands the use of a resin with adequate properties. For most applications, good gas barrier properties are sought to meet the desired shelf life of the packaged goods. This is especially true with the trend of declining container weights and consequently reduced thickness, which implies faster permeant transfer rates. In PET containers, this mostly concerns carbon dioxide loss for carbonated beverages and oxygen ingress for sensitive products.

To generate the required properties, the preform or blow moulding processes must be finely tuned and controlled. The properties of plastic bottles must be tailored to their use (water, bioactive liquids, carbonized liquids) during production. As a result, monitoring and analysis of the bottles' properties must be constant and precise. We will be discussing the merits and shortfalls of the different monitoring techniques in comparison with the MB3600-CH80 PET Packaging Analyzer developed by ABB and based on FT-NIR technology. This reliable and versatile analytical solution can be used for off-line measurements in a laboratory or at-line within a manufacturing area. An immediate insight into material properties and processing conditioning on both preform and finished PET containers can enable an improved understanding of the process, providing feedback on the selected process settings or indicating the need to make process adjustments.

Monitoring PET properties and classic testing methods
To achieve the desired properties, for each PET container, five key PET attributes must be controlled and monitored: intrinsic viscosity, moisture content, crystallinity, co-monomer content and wall thickness.

Intrinsic viscosity (IV): A fundamental characteristic of PET resins, the IV, which is a measure for the chain length or molecular weight in polyester, reflects the material's melting point, crystallinity, and tensile strength. With higher IV, the stiffness and creep resistance of the resin increase, which improves, for example, stability, burst pressure and thermal expansion behaviour. High IV resins are typically only used for packaging carbonated beverages. In contrast, for lightweight containers intended for non-carbonated contents where mechanical requirements are reduced, a low IV resin is utilized. The IV also facilitates the flow of the PET resin in injection moulding and its stretching behavior in stretch blow moulding.
The increasingly common addition of recycled PET content in preforms can also influence its final properties. The recycling process will affect the polymer chain length, and possible variations in the quality or quantity of the recycled PET fraction in a preform will be noticeable. Of note, the susceptibility of PET to degradation in injection moulding affects IV. A minor drop in IV is associated with melt processing, mainly through hydrolysis and thermal degradation. In both cases, the result includes shortened polymer chains. Incorrect processing such as improper drying or exposure to high temperatures for a prolonged time will subsequently show an exceptional drop in IV. Due to its marked influence on processing, it is important to maintain a precise level of IV to ensure a stable production process. The traditional measuring methods of IV levels require solvents (solution viscometry) or are based on a melt flow index determination. The methods are lab-based and do not offer a real-time solution for process control managers. The third method is a physical extrusion test method (analysis is made on the degradation rate of the resin) that has the advantage of being relatively fast (20 minutes). But the process lacks the versatility needed for an effective process control scheme.

Moisture content: The hygroscopic nature of PET not only entails the risk of hydrolytic degradation in injection moulding but also directly impacts other resin properties. Moisture is readily absorbed from the environment into the preforms and the rate of absorption depends on the storage temperature. Maximum moisture content is determined by the relative humidity in the storage environment. As a result of increasing water content in the resin, both glass transition and cold crystallization will shift towards lower temperatures. Besides the thermal properties, moisture will also affect the physical properties of PET by reducing orientation and crystallization during stretching, especially when stretching at higher temperatures. Monitoring moisture content is therefore critical to guarantee a stable and efficient production process. Methods such as Karl-Fischer titration, thermogravimetry, calcium hydride analysis or microwaves are either time consuming, require reagents, are operator dependent, imprecise, or, like thermogravimetry, are sensitive to hydrolytic degradation at high temperatures. Used as standalone tools or in combination, these methods are time consuming and do not offer a fast and reliable data source for high input production processes.

Crystallinity: Chain crystallinity is an important property for PET-based containers. It affects their mechanical properties, their thermal stability in hot-filling and barrier properties (often correlated to the shelf life of the package's contents). The manufacturing process of PET containers by stretch blow moulding largely determines the crystallinity therein. Crystallinity can be measured in a laboratory using X-ray diffraction, density measurements or calorimetric techniques, but those methods are sometimes inaccurate. Besides, they are slow and require chemical consumables, which means results are not always available in time to be included in a certificate of analysis for end users. Some tests require specialized equipment, time, repeated measurements, operator expertise and the availability and proper handling and storage of chemicals. Depending on ease of implementation, some tests can only be carried out hourly, upon changing formats, once per shift or even less frequently.

Co-monomer content: Co-monomers in PET are used to control its thermal properties and crystallization behaviour. Next to IV, their presence and concentration are decisive in the choice of a PET resin for an application. Commonly, co-monomer concentration is determined by gas chromatography after chemical extraction. The equipment and operator expertise necessary is often a complication for most bottling plants. The simplicity of the MB3600-CH80 and its ease of use is a welcome relief at these facilities.

Wall thickness: Wall thickness distribution is relevant in both preforms and PET containers. It allows assessing the stability of the previous production process and will influence all subsequent processing. The observation of both the distribution and tolerances in axial and circumferential direction is usual. Existing measurement tools for wall thickness include ultrasonic thickness gauges and depth sensors, segment weight measurement, hall effect probe, infrared (IR) beam broadband attenuation, and magneto static gauges, among the wide and diverse range of tools. These solutions are either fast but inaccurate or slow and problematic to set up. They can also require expensive implementation procedures, such as the IR beam broadband attenuation technology. Finding the right technology is a challenge, especially if the device must be integrated into an already clogged test and analysis tool infrastructure.

Traditional analysis tools are complex and time consuming

One observation that can be made is that most of the testing relates to the PET containers and only a smaller portion covers preform and resin quality aspects. Also, while some tests are not connected to significant investments and operator training, others may require specialized equipment, time, repeated measurements to increase accuracy, operator expertise, and the availability and proper handling and storage of chemicals. As a result, testing frequency is influenced. Depending on feasibility, some tests will be carried out hourly, upon changing formats, once per shift or even less frequently. With today's high line output speeds, the risk associated with detecting a defect too late is even higher as more and more production volume is handled between measurements. Of note, even current efficient analysis solutions, being specialized monitoring instruments, lack versatility. As a result, data correlation is more complex and time consuming.

In this context, additional insight would be beneficial but is effectively unreachable. A closer look at preform and resin properties has the potential to detect defects that may only become visible after transforming them into a container or further down the production chain. Immediate insight into material properties and processing conditioning on both preform and finished PET containers can enable an improved understanding of the process, providing feedback on the selected process settings or indicating the need to adjust them. Monitoring these parameters would facilitate an enhanced view on the state of the process chain and allow for its stabilization and further optimization.

The MB3600-CH80 PET Packaging Analyzer: an easy-to-use multi-property monitoring solution for PET container manufacturers and end-users

01 MB3600-CH80 PET Packaging Analyzer

FT-NIR technology overview

The MB3600-CH80 PET Packaging Analyzer is built around FT-NIR technology. Near-infrared (NIR) technology provides information on chemical composition of samples, usually liquid or solid. In addition, the technology also provides information on some physical attributes of the sample. It enables multi-property determination on a complex sample or mixture through a single measurement: the NIR spectrum. NIR technology is widely used in food, chemicals, refining, pharmaceutical and semiconductor industries. As a correlative technique, it requires preliminary calibration of the analyzer (spectrometer) against a reference method for each property of interest. The calibration step consists of establishing a numerical relationship between the NIR spectrum of a sample and its assay value as measured by a reference method. This usually involves some mathematical modelling and the use of chemometric algorithms that maximize the covariance between spectral features and the property of interest.

Once calibrated, the FT-NIR analyzer can be used for routine analysis for the more time-consuming reference methods that were discussed previously. The analyzer will exhibit similar accuracy (*i.e.*, reproducibility) as the reference method against which it was calibrated and will typically provide superior precision (*i.e.*, repeatability) as the technique is free of any operator-related error. NIR measurements are performed in seconds and do not require sample dilution or complex handling. Laboratory NIR measurements can be performed on intact samples by operators with no analytical background. Remote real-time NIR process measurements can also be performed in situ with the use of insertion probes or cells connected to the analyzer via fibre optics. FT-NIR analysis offers the prospect of conducting frequent testing of important quality parameters without the need for highly trained personnel and multiple pieces of specialized equipment on site, and without the need for consulting external service laboratories. This is ideal for in-house R&D projects and for quality control.

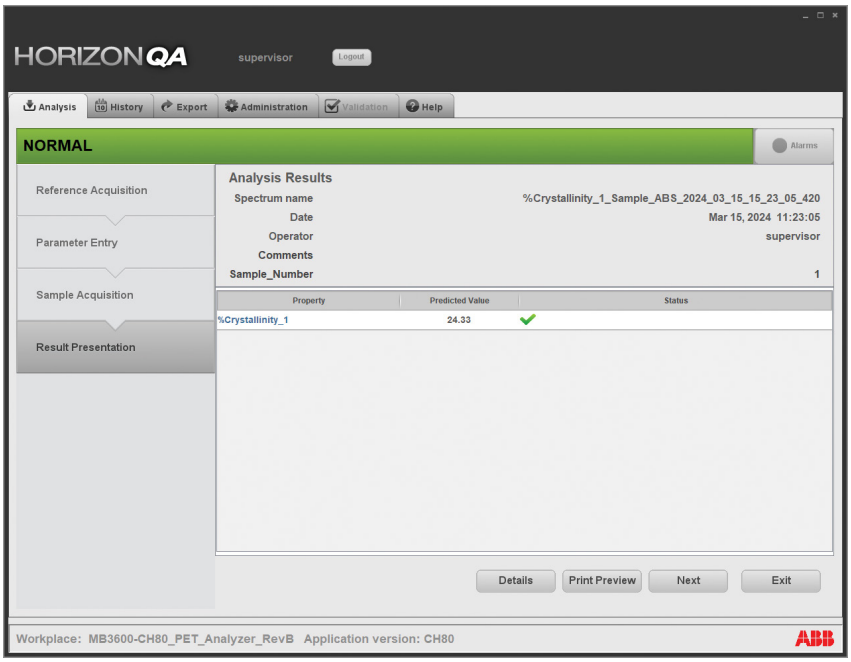
The ABB PET Packaging Analyzer is a precise, versatile, robust, and non-destructive solution

FT-NIR analyzers, like the ABB MB3600-CH80, represent a class of NIR spectrometers in which an interferogram of the sample is generated using the Michelson interferometer principle. The spectral information is then retrieved by applying a mathematical transformation (Fourier transform) to the interferogram. The combination of speed, versatility, ease of use, analytical performance, and stability of FT-NIR technology has contributed to its success in different industries. The ABB MB3600-CH80 analyzer is a multi-property measuring solution that can be used for research and development (R&D) or quality analysis purposes in laboratories, and they are used online or inline for real-time control and determination of the process end points. Results are generated in seconds.

The unique qualities of ABB's FT-NIR based analysis tool makes it the multi-property solution to monitor time sensitive processes, often in real time, and without the need for multiple analysis tools, lab validation, or chemicals. This is how the ABB MB3600-CH80 analyzer can monitor each of the PET package critical production parameters.

Intrinsic viscosity: The FT-NIR spectrum contains information on sample molecular weight, chain length and conformation. Since IV is a value of molecular weight, NIR-based analysis of PET samples is fast and extremely precise once the equipment is calibrated. Since the FT-NIR analysis process is non-intrusive, it is therefore an ideal inline analysis solution.

Crystallinity: This parameter is largely determined by chain length, stereoregularity, presence of polar groups and degree of substitution on the chains. All those effects are present in the FT-NIR spectrum. This enables the fast and simple analysis of crystallinity through FT-NIR spectroscopy, even by an operator without analytical background.



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01 HorizonMB QA software interface

Moisture: Being one of its strongest absorbers, water has a strong infrared signature. This quality makes FT-NIR technology and ideal tool to determine moisture levels rapidly and precisely in PET based packages, without having to rely on imprecise, complex, or time-consuming analysis methods. Moisture concentrations can vary depending on environmental factors and the effects on crystallinity of the PET package can be dramatic and are well documented. A fast analysis tool such as the MB3600-CH80 analyzer becomes a powerful must-have process and quality control tool for any PET-based plastic bottle manufacturer, without the need for sample tampering. It also constitutes a fast and easy way to monitor property degradation over time of PET bottles in storage, without any chemicals required.

Co-monomer content: As an alternative to complex traditional measuring methods, FT-NIR co-monomer assay on PET samples is straightforward. The FT-NIR spectrum carries qualitative information (frequency of different absorption bands) and quantitative information (height of the bands) which enable precise analysis of the percentage of co-monomers present in a PET sample. FT-NIR composition analysis can be performed on intact samples and does not require any solvent extraction or column preparation.

Wall thickness: Variations in PET packaging wall thickness between samples will translate into different intensities (absorbance values) at similar band positions of the FT-NIR spectrum. Those intensity variations can be quantified and directly correlated to wall thickness. It is therefore possible to add wall thickness to the list of PET properties that can be rapidly and reliably determined with a single FT-NIR measurement.

Conclusion

The use of FT-NIR technology to perform precise determination of several PET packaging quality attributes such as IV, moisture content, crystallinity, co-monomer content, and wall thickness revolutionizes traditional monitoring solutions for PET-based bottle and packaging manufacturers.

FT-NIR analysis of PET packaging is an information-rich approach that allows correlating several important chemical and physical properties of each sample to its NIR spectrum. Once the FT-NIR analyzer has been calibrated against the different reference methods for a set of PET properties, the obvious benefit of its implementation is that it can replace all those reference methods for routine analysis of new samples in a quality control laboratory and opens the opportunity to perform on-site PET bottle analysis during the routine bottle manufacturing process. The instrument permits extremely fast (in seconds) simultaneous determination of multiple properties for all new samples, with accuracy comparable to the traditional laboratory methods and often with superior precision. Also, FT-NIR analysis is non-destructive and can easily be performed by operators without analytical background. Furthermore, this approach does not require any chemical reagent, waste disposal or analytical expertise. No sample or instrument preparation is required, and the measurements are totally non-destructive. As a result, the number of routine analyses can be significantly increased, while the cost per analysis is reduced compared to traditional laboratory methods.

The MB3600-CH80 analyzer is shipped with starter calibration for percent crystallinity. ABB's renown staff of application scientists will work with each customer to ensure the calibration meets the needs of the laboratory. The same application scientists will work with laboratory personnel to create customised calibrations for additional properties. ABB simplifies the entire user experience. The plot below highlights the agreement between the laboratory results and the MB3600-CH80 results. The crystallinity FT-NIR measurement accuracy is excellent and the MB3600-CH80 will outperform the laboratory when the same sample is run 10-15 times.

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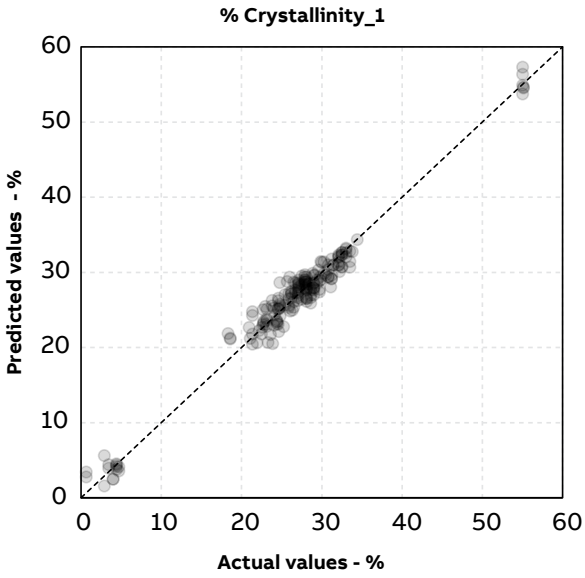
01 Predicted and actual values chart according to crystallinity percentage

The main benefits of FT-NIR technology for PET packaging analysis lies in its unique combination of versatility, precision, and ease of use. The latest generations of FT-NIR analyzers are also extremely robust and virtually maintenance-free as they do not require any consumables or preventive maintenance. The technology is also modular. For instance, an FT-NIR analyzer can be initially used in a laboratory for single property determination (often crystallinity or IV) and later upgraded with the addition of new calibration models for additional PET properties. This is done by uploading new calibration models in the software. In addition, previously stored sample spectra can be evaluated using new added calibrations to increase data space for deeper analysis. With a single analyzer, it is also possible to perform analyses on different samples types (e.g., intact bottles or preforms, pellets, liquid samples) by using different sampling interfaces and accessories that are easily swappable. From moisture levels to crystallinity, the ABB MB3600-CH80 analyzer offers a powerful and complete solution for all PET packaging manufacturers.



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