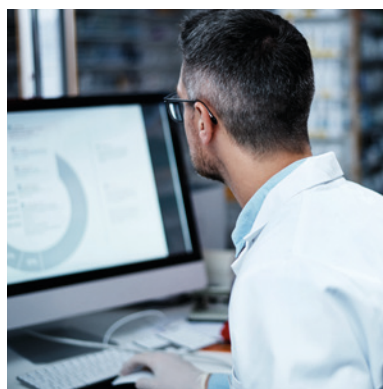


Quality and Process control in PE and PP Manufacturing

Separation Solutions for Plants and QC Laboratories



Polymer Char

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SEPARATION SOLUTIONS FOR PLANTS AND QC LABORATORIES



MOLAR MASS DISTRIBUTION

GPC-QC

Simplified and fully-automated GPC instrument for control laboratories in polyolefin production plants. Provides robust and precise Molar Mass Distribution data for process control, in a simplified and automated workflow, for one sample at-a-time in 30 minutes (Page 29).



INTRINSIC VISCOSITY

IVA

Fully-automated instrument for the Intrinsic Viscosity analysis of all polymeric materials, even the very challenging ones that can require temperatures of up to 200°C for dissolution. The autosampler allows up to 42 samples to be sequentially analyzed without user intervention (Page 39).



AMORPHOUS FRACTION

CRYSTEX® QC

Complete automation of the Soluble Fraction measurement in polypropylene while quantifying the ethylene content and intrinsic viscosity in the whole sample, and the soluble and crystalline fractions. Analysis of one sample at-a-time in approximately 2.5 hours (Page 15).



CRYSTEX® 42

This instrument shares the same analytical concept as CRYSTEX® QC, but it uses a high-temperature autosampler with 42 positions, ideal for a central laboratory, where large batches of pelletized, more homogeneous samples need to be analyzed in sequence (Page 25).



CHEMICAL COMPOSITION DISTRIBUTION

CEF QC (upcoming)

A simplified CEF for production plants to obtain the complete chemical composition distribution curve for one sample in less than 1h (incl. dissolution). The Density results facilitate a direct correlation with traditional process controls. The instrument can be operated as a CEF, TREF or TGIC (Page 49).

An Overview

IS YOUR POLYOLEFIN RESIN PERFORMING AS EXPECTED?

The introduction of single-site catalysts and the use of multiple reactors in the polyolefins industry has opened new routes to design resins with the desirable microstructure to optimize performance in specific applications. While this is good news for manufacturing, it presents a greater challenge for quality control because the currently used parameters show only partial information of the resin microstructure.

Melt Index (MI) and density are common parameters in process control and product definition that represent average molar mass and average composition respectively. However, with today's sophisticated industrial resins, these parameters are very far from defining resin performance. A set of analytical techniques has been recently developed to detail additional parameters relevant to the resin performance.

Will a competitor resin with the same Melt Index and density perform equally? I am recycling polyolefin resins. How can I optimize my product's performance? The resin I have used in the past is now performing/processing differently. Why?

Within the Polyethylene (PE) family, the added information is essential, especially in the case of dual reactor resins, as with pipe and blow molding products, or in the broad spectrum of linear low density polyethylene (LLDPE) resins.

Figure 1 shows three different PE that, in spite of having the same Melt Index, they have completely different Molar Mass Distribution (MMD), and thus, completely different performance and processing behavior. This reveals that a separation technique such as Gel Permeation-Size Exclusion Chromatography (GPC/SEC) is needed to have unequivocal characterization of the resin chemical structure. These techniques, which in the past demanded operation expertise and sophisticated equipment, are available today with simplified design for quality control purposes (GPC-QC). A similar situation is that of PE copolymers, such as the three LLDPE resins shown in Figure 2. They all have the same comonomer content, expressed with the density parameter, but reveal completely different Chemical

Melt Index and density have not changed, so why is the “same” resin performing differently?

Composition Distribution (CCD) and thus, different performance and processing behavior. Once more, this shows that a separation technique is demanded to have unequivocal characterization; in this case, using Temperature Rising Elution Fractionation (TREF), Crystallization Analysis Fractionation (CRYSTAF) or Crystallization Elution Fractionation (CEF).

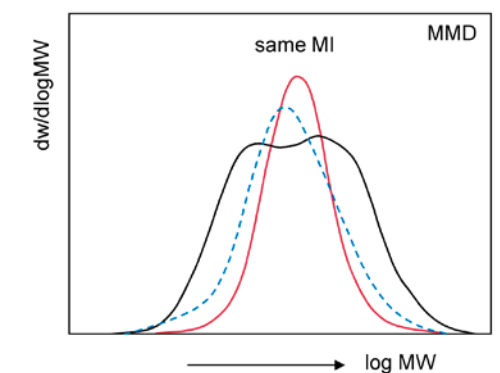


Fig 1. Three different resins with the same Melt Index but completely different MWD and thus, different performance.

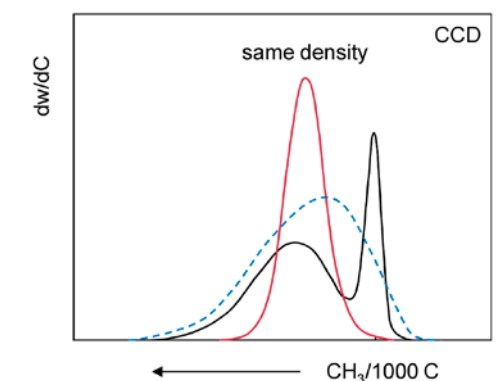


Fig 2. Three different PE resins with the same density but completely different CCD and thus, different performance.

Improving Performance by Fully Revealing the Resin Microstructure

Although MMD and CCD represent the most significant microstructural information, on occasions, this data alone is not enough due to the interdependence of molar mass and composition. A good example is that of Pipe resins, which contain small amounts of comonomer but for good performance, the comonomer (branching) is required to be incorporated within the larger molecules. The analysis of branching at different molar masses can be today obtained in a quality control lab by a simplified but sensitive GPC system with an additional IR composition sensor (GPC-QC IR5).

Within the Polypropylene (PP) family, the most demanding structure is that of heterophasic or High-Impact Polypropylene (HIPP). The routine analysis of the amorphous content (“xylene solubles”) is important but the analysis of the ethylene content and intrinsic viscosity in the two phases (crystalline and amorphous) provides additional information that can be critical to optimize the product’s performance. All these parameters can now be obtained automatically with the new CRYSTEX® instrumentation based on a TREF (Temperature Rising Elution Fractionation) separation process (CRYSTEX® QC and CRYSTEX® 42).

No Longer a Nice-to-have, Now a Must-have in Production

The increasing throughput of the new polyolefin manufacturing plants and the incorporation of complex multiple reactor-catalyst processes demand a closer control of the microstructure to prevent product variation with significant losses in off-grade production. The analysis of average properties such as MI, density, and amorphous fractions by rheological or spectroscopic techniques, although important in stable process conditions, on many occasions is not enough.

The measurement of the distributions by separation techniques such as GPC-QC or CRYSTEX® QC is required. This is especially important during grade changes, where reaching the desired microstructure in the shortest possible time is crucial to reduce off-grade production. Simplified separation techniques capable of obtaining results in short time are essential.

The industry has also shown an increased interest and production of very high and Ultra High Molar Mass (UHMW) resins in the last years. However, a full characterization of these resins is a challenging task and demands method and materials adaptation to prevent precipitation of the resin in the analytical process. The GPC-QC at low flow rate, has been developed to analyze the MMD of very high molar mass resins, one at a time. Additionally, a dedicated Intrinsic Viscosity Analyzer (IVA) was also designed to automatically analyze multiple samples of UHMW resins through a capillary relative viscometer without memory effects or plugging.



Newly developed resins are increasingly challenging to control in production plants.

Unparalleled
Separation of the
Soluble Fraction in PP

CRYSTEX® QC is a fully-automated instrument that separates crystalline and amorphous fractions by means of a proprietary Temperature Rising Elution Fractionation (TREF) column where a small aliquot of homogeneous polymer solution is crystallized, in di- or tri-chlorobenzene (o-DCB / TCB), on a support under reproducible and well-controlled conditions. The polymer solution is loaded into the column at elevated temperature; it is crystallized to near ambient temperature with no flow and then solvent is moved through the column to elute the amorphous soluble material towards the online detectors. Finally, the column temperature is increased again to re-dissolve the crystalline material which is eventually eluted to the detectors.

The analytical workflow is also very simple: all the analyst is required to do is put an approximate amount of sample in a disposable bottle, place it in the stirred-heated plate, and lower a handle to pierce the bottle's septum with a needle (Figure 3). The automated process proceeds under computer control, including filling of the bottle with pre-heated solvent, controlling the dissolution time, temperature and stirring and taking an aliquot of the solution from the bottle into the instrument column.



Fig. 3 Safe and efficient operation of the single-sample dissolution station in GPC-QC and CRYSTEX® QC instruments: 1) Remove the previous bottle and place a new one with an approximate sample weight; 2) Manual Injection and press START.

The amorphous/crystalline fractions are quantified with a sensitive filter-type Infrared (IR) detector that delivers equivalent values to the xylene solubles test, obtained with outstanding precision. In addition, the IR detector measures the ethylene incorporation in the case of copolymers. The integration of a capillary viscometer provides an automated measurement of intrinsic viscosity of the whole sample and both amorphous and crystalline fractions.

Table 1 shows data obtained from seven replicate analyses using four grams of sample for a set of three polypropylene products with average standard deviations shown for each type of measurement. No additional experimental effort is required, since all the data is collected by the IR and viscometer detectors during the automated analysis, with one equipment in a single 2-hour experiment.

	Soluble Fraction			Crystalline Fraction		Whole Sample	
	%weight	Ethylene %	Int. Visc.*	Ethylene %	Int. Visc.*	Ethylene %	Int. Visc.*
Sample A	4.06	14.8	0.96	3.4	2.74	4.2	2.86
Sample B	2.73	16.3	0.90	3.9	2.33	4.4	2.30
Sample C	7.66	53.9	1.67	2.8	2.04	6.9	2.01
std	0.07	1.7	0.07	0.26	0.08	0.6	0.09

*Intrinsic Viscosity measured with TCB at 165

Table 1. Analysis of amorphous/crystalline fractions of three PP products by CRYSTEX® QC.

The GPC-QC instrument is built with the same single-sample dissolution station described above, and simplified hardware design including only one valve at high temperature, an external HPLC pump and robust detectors, which help in achieving the required level of reliability and minimizing potential downtime. The main detector is infrared, which provides a concentration signal based on absorbance of total CH, being very appropriate for a QC environment thanks to the fast stabilization time, stable baseline and good sensitivity. In addition, IR detection provides complementary information on chemical composition (short-chain branching, comonomer content) along the MMD.

GPC for Quality Control and Process Control in PE and PP Manufacturing

The analytical workflow is quite simple and requires minimum manual work. When a sample of polymer is received in the laboratory, it is weighed into a disposable bottle which is placed into the dissolution station oven. Then the analyst lowers a handle to insert the needle through the septum. The analysis is started from the computer and proceeds automatically according to the pre-set method conditions. Once the analysis is finished, the chromatograms are processed to generate the MMD and any calculated parameters of interest. When a new sample comes in, a new bottle is prepared with it and the analyst just discards the previous one placing the new one in the station. Following this workflow, the GPC-QC can be operated continuously with a cycle time of one hour or less, which is found appropriate for controlling the start-up of reactors, or when a change of grade is conducted. Once the process is stable, production may need to be controlled at a slower pace, one or several times per day.

An application example is provided in Figure 4 for a bimodal high-density polyethylene made in a dual-reactor process. A lower molar mass high-density component is typically produced, together with a second component of larger molar mass with a small amount of added comonomer. That balance results

in enhanced mechanical properties, such as ESCR, for pipe applications. From a single GPC-QC analysis, and in less than one hour with minimum operator intervention, it is possible to obtain an estimation on the density being produced in each of the two reactors (based on measured SCB level), as well as the molar mass and the weight fraction of each component.

The level of control on the process is thus, greatly enhanced over the alternative methods based on bulk properties (MI and density).

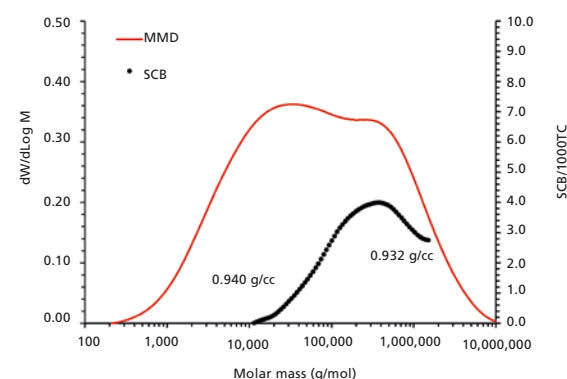


Fig 4. MMD and short chain branching (SCB) frequency measured by GPC-QC for a bimodal HDPE. The density of each of the modes was calculated from an average of the SCB frequency in each molar mass range.

Measuring Intrinsic Viscosity for All Polymeric Materials

The optimized dissolution and separation processes open the door to high-temperature GPC analysis within 30 minutes in most cases, including the sample preparation step with an efficient dissolution process under nitrogen atmosphere, and less than one hour even for the most difficult products. This is a step forward in this kind of technology and enables its practical application in manufacturing plants as a process control /quality control tool.

The Intrinsic Viscosity Analyzer, IVA, is a dedicated instrument for determination of intrinsic viscosity of polymeric materials, based on the same QC platform.

The relative viscosity of a dilute polymer solution with reference to the pure solvent is measured by means of a robust serial capillary viscometer. From it, the intrinsic viscosity of the polymer can be calculated using a single-point estimation method. Due to the popularity of dilute solution viscosity measurements and the availability of such methods in many laboratories, the IV of polymers has been traditionally used to specify and to control the production grades.

Different polymers in various solvents have been analyzed in this system, including PAN (polyacrylonitrile) in DMF (N,N-dimethylformamide), PET polyethylene

terephthalate) in phenol/o-DCB, PLA (polylactic acid) in TCB as well as polypropylene and polyethylene (even high and ultra-high molar mass) in TCB and o-DCB. The intrinsic viscosity results obtained by the IVA are in good agreement with reference methods (ISO 1628-3:2010 f.i.) in all cases.

References:

- Automated Soluble fraction analysis in PP (CRYSTEX® QC) – The Column (LC/GC), November 2013
- Soluble fraction analysis in polypropylene for QC (CRYSTEX® QC) LCGC – LCGC EU and NA The Applications Notebook, December 2013
- Gel Permeation Chromatography (GPC) for Process Control and Quality Control – The Column (LC/GC), September 2015
- Solution Viscosity in Polymeric Materials by IVA – Petro Industry News, April/May Issue 2015

Soluble Fraction for Polyolefin Production Plants



CRYSTEX[®] QC

RELIABLE AND AUTOMATED INSTRUMENT FOR SOLUBLE FRACTION DETERMINATION IN QUALITY CONTROL LABORATORIES OF POLYPROPYLENE PLANTS

CRYSTEX® QC is a step forward in technology for automating the Soluble Fraction determination in polypropylene and other polyolefin resins. This is a reliable instrument for continuous operation in the manufacturing plant laboratory, with minimum bench space and utilities requirements.

This is a modern alternative to the traditional wet chemistry method based on xylene solubility, known for being very time consuming and for requiring constant manual handling of solvent at high temperature. In comparison, CRYSTEX® QC is very easy to operate and obtains the amorphous phase content in a shorter time. It also eliminates the need to handle solvent manually and it operates with less flammable solvents than Xylene (TCB or oDCB), increasing the safety level in the laboratory.

The only manual task required is to put a representative amount of sample (up to 4g) in a disposable bottle, without the need of accurate weighing. The instrument then automates the entire analysis process, including precise dosing of solvent, sample dissolution, separation of the soluble fraction from the crystalline matrix, and analysis by the online detectors. This whole process takes 2.5 hours.

The crystalline and amorphous fractions are separated through a crystallization and re-dissolution temperature cycle within a proprietary TREF column. Precise quantification is achieved by means of an infrared detector that also delivers ethylene content information. Moreover, the instrument measures intrinsic viscosity by means of a built-in dual capillary viscometer. All results (concentration, ethylene content and intrinsic viscosity) are obtained for the whole sample, the amorphous fraction, and the crystalline fraction.



CRYSTEX® QC KEY FEATURES

Fully-automated analysis of the soluble (amorphous fraction) in polypropylene and other polyolefins.

A sample can be analyzed every 2.5 hours (including dissolution) without manual operation.

No need for accurate weighing of sample or manual solvent handling. No external filtration or solvent evaporation required.

Additional measurement of ethylene content and intrinsic viscosity for the amorphous fraction, the crystalline fraction, and whole sample.

For Process/QC laboratories in production plants.

Compatible with other polyolefin materials such as LDPE, and adaptable to other solubility tests (heptane or hexane solubles).



CRYSTEX® QC

APPLICATION NOTE

The Classic Gravimetric Procedure

Soluble Fraction Analysis in Polypropylene: Characterization of the whole polymer, amorphous and crystalline fractions in a Quality Control Laboratory

Introduction

The analysis of the amorphous fraction in polypropylene resins is considered a fundamental task in the production of polypropylene; it provides a measurement of the small amounts of undesirable low tacticity and low molar mass fractions in the homopolymer resins, which have significant influence on the polymer properties and processing. The presence of amorphous fraction is required for certain applications, as in the case of high-impact polypropylene copolymer resins. The incorporation of the amorphous material is usually done within the same production plant in a second stage of the polymerization process by adding ethylene to the continuous reaction, which results in the formation of amorphous ethylene-propylene copolymer.

The continuous measurement of the overall amount of this rubbery fraction, which can range between 0 and 30% of the total polymer, is essential for plant control in order to obtain the desired specifications and performance of the polymer resin. In addition to the measurement of the total rubber percentage

(soluble fraction), the analysis of its molar mass and ethylene content are of major importance in this type of manufacturing process.

Historically, the amorphous or soluble content has been measured by solubility in xylene using manual wet chemistry methods, as described in the next section, which demand significant manpower, solvent volume, and analysis time. Later on, it was shown that the amorphous content in polypropylene can be measured by crystallization (1) and a method was prepared based on the Crystallization Analysis Fractionation (CRYSTAF) technique (2-4).

A new approach has now been developed to analyze polypropylene samples, one at a time, in Quality Control plant laboratories. CRYSTEX® QC consists on a fully automated system based on a proprietary Temperature Rising Elution Fractionation (TREF) column where a small aliquot of homogeneous polymer solution is crystallized on a support under reproducible and well-controlled conditions. The amorphous fraction is measured with a highly sensitive filter-type Infrared (IR) detector delivering equivalent values to the xylene solubles measurement, obtained with outstanding precision.

In addition to measuring the amorphous or soluble fraction percentage, CRYSTEX® QC quantifies the ethylene incorporation and intrinsic viscosity in the original sample and in both, the amorphous and crystalline fractions. Total analysis time per sample is approximately two hours.

Natta and coworkers (5) were among the first to understand the importance of separating the polypropylene produced according to stereo regularity. In those years (1950s) fractionation was only accessible by extraction, using a Soxhlet apparatus with solvents of different boiling points. The atactic polymer was obtained by the extraction in boiling ether, the stereo block fraction corresponded to the material which was insoluble in boiling ether but soluble in boiling heptane, and the isotactic fraction was what remained insoluble in those solvents. Most importantly in these extraction procedures was the determination of the amorphous atactic fraction, although reproducibility was not as good as desired.

A few years later (1960s), a new approach was proposed by P.M. Kamath, L. Wild (6) and others, by fully dissolving the sample in a good solvent and allowing it to precipitate according to its crystallizability. Carrying out the test in this manner and establishing

the equilibrium in the opposite direction provided a significant advantage over the extraction procedure:

The amorphous fraction did not have to migrate from the interior of the solid material to the surface, which could be influenced by the size of the particles and the molecular structure of the matrix. Solvent selection was not so important in this procedure, and from a variety of solvents, xylene was chosen due to the ease of filtration of the crystallized polymer and ease of drying. This procedure, which they named Fractional Crystallization, resulted in a significant improvement in reproducibility over the extraction method and it showed that separation was barely affected by molar mass or by the initial concentration in a rather broad range.

The Fractional Crystallization approach finally evolved into the current standard procedures (7-8) which can be summarized as follows:

“The polypropylene is dissolved in hot xylene, then cooled under controlled conditions down to 25°C, which results in the precipitation of the insoluble fraction. The soluble matter remains in the xylene. The suspension is filtered and an aliquot of the solution is then evaporated, dried and the residue weighed.” (7-8)



Fig 1. Schematic representation of the analytical steps required in the classic gravimetric method for the determination of the xylene solubles.

A schematic analytical process is depicted in Figure 1. This procedure, which we will refer to as the classic gravimetric method, has been extensively used in the industry and has proven to be of great value to the manufacturing of polypropylene (PP). The analysis of the xylene soluble with this approach however, demands significant manpower, solvent consumption, and an analysis time of around five to six hours. Just as significant is the fact that the precision of the method suffers from the required controlled precipitation conditions as discussed in the ASTM and ISO methods. In the last years, new methods have been developed to quantify the amorphous fraction attempting to overcome previous time-consuming procedures by automating the analytical process and, at the same time, provide extended characterization of the amorphous and crystalline phases.

Automated Crystallization methods

The classic gravimetric method, as discussed above, is based on a crystallization process where the crystalline matrix is segregated from the amorphous soluble fraction by cooling the solution according to a specified method with a fixed crystallization temperature and time. The selection of solvent did not

appear to be of significant importance as the intention is to separate two different polymer phases quite apart in crystallinity as shown in Figure 2, where the soluble fraction corresponds to the distinctive peak in a PP resin characterized by TREF or CRYSTAF analysis.

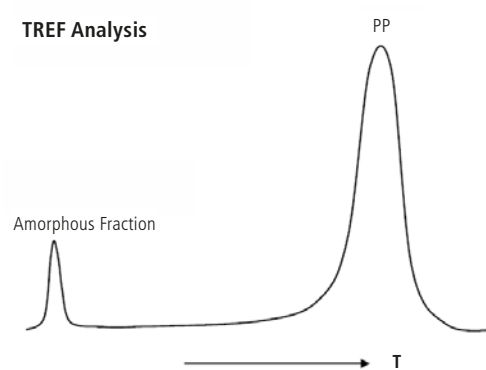


Fig 2. Chemical Composition Distribution of a polypropylene copolymer analyzed by TREF where the amorphous and crystalline fractions are well segregated.

In the early 2000s, it was shown that the amorphous content in polypropylene can be measured by an automated crystallization technique (1) and a method (CRYSTEX®) was developed based on CRYSTAF (2-4) using a chlorinated solvent (di or tri-chlorobenzene) combined with the use of an IR detector.

The correlation with the classic gravimetric method was excellent for a wide selection of PP resins as shown in Figure 3, while obtaining better reproducibility thanks to the full automation of CRYSTEX®.

An extension of the CRYSTEX® technique for application in quality control laboratories of polypropylene plants has now been developed. The new analytical process, named CRYSTEX® QC, is based on TREF, rather than the CRYSTAF approach, with the intention of speeding up the analysis of a single sample while maintaining the system's same capability to measure intrinsic viscosity and ethylene incorporation. The new method analyzes one sample at a time and is capable to dissolve up to 4 g of sample, thus, minimizing error due to the poor homogeneity of powder samples.

The schematics of the system are presented in Figure 4. The only task done by the analyst consists in putting

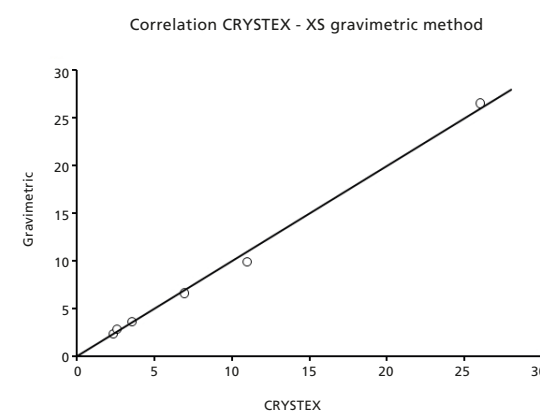


Fig 3. Correlation between the xylene solubles ISO/ASTM methods and the new crystallization approach.

an approximate amount of sample into a bottle, placing the bottle in an oven, lowering a handle to pierce the bottle's septum, and initiate the automated run. There is no need of weighing the sample since the IR detection of the full solution will provide accurate measurement of the amount of resin used, (which does not need to be in a dry form as residual water will not be detected by the IR). The IR detector is used to measure as well, the concentration of the amorphous and crystalline fractions and their ethylene incorporation. The crystallization in a TREF column, on an inert support, eliminates the filtration step, and the integration of a capillary viscometer provides an automated measurement of intrinsic viscosity of the whole sample and both amorphous and crystalline fractions.

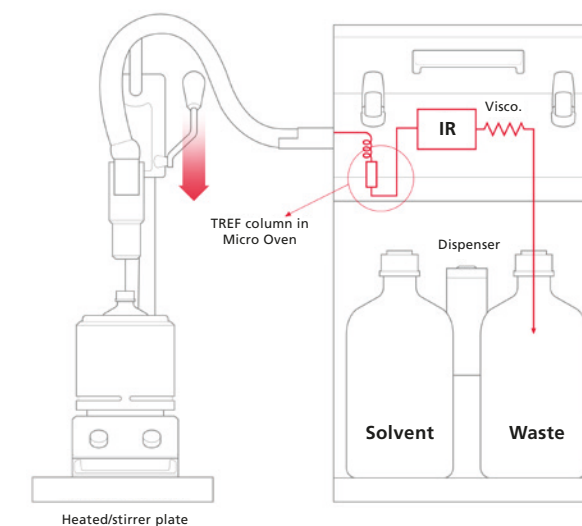


Fig 4. Schematic diagram of the new CRYSTEX® QC instrument.

Automated Crystallization Methods

A major advantage of this approach is that the crystallization step is done with a small but representative aliquot of the solution and takes place in a packed column where the crystallization kinetics are fast and very well-controlled; thus, providing very reproducible results. The overall analytical process lasts two hours including automated solvent dispensing into the bottle to dissolve the sample, and column cleaning in order to be ready for the next sample analysis.

Once the powder or pelletized polymer is put into the bottle and the automated run is initiated, the analysis proceeds as follows:

- a) Filling the disposable bottle up to 100 or 200 mL with preheated solvent at 160°C (depending on whether pellets or powder samples are analyzed) and initiate stirring. The deep vortex formed in the dissolution process prevents the polymer from sticking to the glass walls and speeds up dissolution.
- b) An aliquot of the solution is pumped through the TREF column at 160°C towards the detectors to measure the whole sample concentration, ethylene incorporated and intrinsic viscosity (first eluted peak in Figure 5).
- c) A new aliquot of the solution is injected into the middle of the column at 160°C, the flow is stopped and the column temperature is reduced rapidly down

to controlled ambient temperature, staying there for an specified amount of time to precipitate the crystalline fraction; the column is then flushed to elute the amorphous soluble fraction peak (second peak in Figure 5). The ratio of this peak area by the one of the whole sample provides the soluble percentage in the sample. As the soluble material passes through the IR and Viscometer detectors, the ethylene content and intrinsic viscosity of this fraction are also measured.

d) Temperature is raised rapidly up to 160°C with stop flow to re-dissolve the crystalline fraction and after a pre-set time of a few minutes, this fraction is eluted through both IR and viscometer detectors.

e) The column is washed and the instrument remains ready for a new sample analysis.

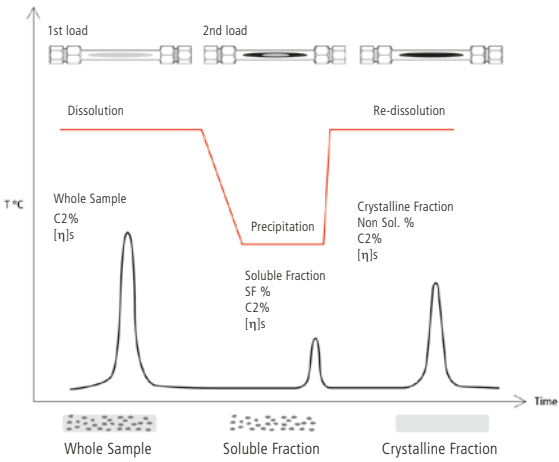


Fig 5. Schematic diagram of the new CRYSTEX® QC instrument.

Full analytical results are obtained in two hours, including not only the soluble fraction percentage, but also the ethylene content and intrinsic viscosity of whole sample, as well as of the soluble and crystalline fractions. Reproducibility in the soluble fraction percentage determination is remarkable; typically standard deviation (std) is lower than 0.1%, as seen in Table 1, much lower than indicated for the standard gravimetric methods.(7) In the same Table, whole sample ethylene and intrinsic viscosity are also reported, along with standard deviation (std) values. The precision achieved, also in those determinations, proves the reliability of this method.

	Soluble Fraction		Ethylene Content		Intrinsic Viscosity*	
	%	std	%	std	dL/g	std
Sample A	4.06	0.04	4.2	1.0	2.86	0.12
Sample B	2.73	0.05	4.4	0.4	2.30	0.04
Sample C	7.66	0.12	6.9	0.3	2.01	0.12

*Intrinsic Viscosity measured TCB at 165°

Table 1. Soluble fraction, total ethylene content and Intrinsic Viscosity for three different PP products. Data obtained from seven replicate analyses using 4 g of sample.

	Ethylene Content				Intrinsic Viscosity*			
	Soluble Fraction		Crystalline Fraction		Soluble Fraction		Crystalline Fraction	
	%	std	%	std	dL/g	std	dL/g	std
Sample A	14.8	2.1	3.4	0.3	0.96	0.06	2.74	0.11
Sample B	16.3	1.5	3.9	0.2	0.90	0.11	2.33	0.02
Sample C	53.9	1.4	2.8	0.3	1.67	0.05	2.04	0.12

*Intrinsic Viscosity measured TCB at 165°

Table 2. Ethylene content and Intrinsic Viscosity in the amorphous/soluble and the crystalline fractions for three different PP products. Same analysis as in Table 1.

Conclusions

CRYSTEX® QC is a new method to measure the soluble fraction in polypropylene resins that has been developed based on a TREF crystallization approach. The analytical process is fully automated with no need of weighing, filtration or solvent handling. This new method is especially interesting for quality control (product and process) in polypropylene plants.

The total analysis time is two hours, and samples are analyzed one at a time in disposable bottles. The total volume consumption is as low as 180 mL for a 2-g sample analysis. The analysis of 4 g of resin in the form of powder can be done for enhanced sample representativeness.

Besides the soluble fraction (equivalent to xylene solubles), CRYSTEX® QC measures automatically and simultaneously, the ethylene content and intrinsic viscosity in both amorphous and crystalline fractions, and in the whole sample.

The possibility to measure a sample in two hours allows a fast response in process control during product grade changes reducing off grade production. The new system can be used with other polyolefin type resins as well.

References

- 1) B. Monrabal , Encyclopedia of Analytical Chemistry, John Wiley & Sons, 2000 pages 8074-8094.
- 2) L. Romero, B. Monrabal, A. Ortín, Pittcon 2001 U.S.A.
- 3) A.. Ortín, B. Monrabal, M. D. Romero, LCGC Europe Vol 19 Issue Suppl., March 2006, 32.
- 4) A. Ortín, L. Romero, B. Monrabal. Polyolefin Characterization (ICPC) November 7 - 10, Shanghai, China 2010
- 5) G. Natta et al. Chim. e Ind. (Milano) 39, 275, 1957
- 6) P.M. Kamath and L. Wild, Polymer Engineering & Science, 6, Issue 3, 213–216, 1966
- 7) ASTM standard D5492-10, ASTM
- 8) ISO standard 6427, 1992, ISO standard 16152, 2005



CRYSTEX® 42

HIGH-THROUGHPUT SYSTEM FOR SIMULTANEOUS MEASUREMENT OF THE SOLUBLE FRACTION, ETHYLENE CONTENT AND INTRINSIC VISCOSITY

CRYSTEX® 42 is a high-throughput and fully-automated approach for obtaining the soluble fraction in polypropylene and other polyolefin resins. It is based on the same TREF separation concept as CRYSTEX® QC, in which the sample is loaded into a TREF column twice. The first injection serves to measure the whole polymer and the second one remains within the column for a crystallization ramp that results in the separation of the soluble from the crystalline fraction.

CRYSTEX® 42 incorporates a high temperature autosampler with 42 positions to analyze samples in 20mL vials (max. sample amount of 160mg). This system eliminates the need to handle solvent manually and it operates with less flammable solvents than Xylene (TCB or oDCB), increasing the safety level in the laboratory.

Results are very precise thanks to its full automation and to its integrated infrared detector (IR4), which measures precisely the amount of sample analysed as well as providing ethylene content information. Moreover, for a truly complete analysis, the instrument measures intrinsic viscosity by means of a built-in dual capillary viscometer. All results (concentration, ethylene content, and intrinsic viscosity) are obtained for the whole sample, the soluble fraction, and the crystalline fraction.

While CRYSTEX® QC was designed to be installed in each production plant to monitor in real time the process analyzing a significant amount of powder sample (up to 4g), CRYSTEX® 42, thanks to the incorporation of the high temperature autosampler, becomes a perfect complement to be used in a central lab, where large batches of pelletized, more homogeneous samples need to be analyzed.



CRYSTEX® 42 KEY FEATURES

Fully-automated analysis of the soluble fraction in polypropylene and other polyolefins.

Additional analysis of ethylene content and intrinsic viscosity for the amorphous fraction, the crystalline fraction and whole sample.

Fully-automated process of consecutive samples: No need for accurate weighing of the sample or manual solvent handling. No external filtration and no solvent evaporation required.

Dissolution and full analysis of the first sample completed in 3 hours. Following samples results are obtained every 2 hours.

Compatible with other polyolefin materials such as LDPE and adaptable to other solubility tests (heptane or hexane solubles).



HT GPC for Process Control and Quality Control in PE and PP Production



GPC-QC

SIMPLIFIED AND FULLY-AUTOMATED HIGH-TEMPERATURE GPC INSTRUMENT AIMED AT CONTROL LABORATORIES IN THE POLYOLEFIN INDUSTRY

GPC-QC is a compact, high-temperature GPC instrument for quality control in polyolefin manufacturing lines. The instrument has a simple and reliable approach based on Polymer Char's recently developed QC platform, to provide robust and precise Molar Mass Distribution for process control.

For quality control purposes, the industry has traditionally relied on physical parameters related to an average of the MMD, such as melt flow index (MFI) and density. These parameters are not enough when producing complex multiple reaction products, some of them having multimodal MMD. It is in these occasions when GPC-QC can provide significant value by measuring the whole MMD.

GPC-QC delivers the complete Molar Mass Distribution for one sample through a simplified workflow, while keeping a fully automated sample preparation and an analysis free of manual solvent handling throughout the entire process. The complete analysis takes 30 minutes including dissolution.

The IR detection, implemented in the instrument through Polymer Char's integrated IR4 or IR5 MCT detectors, is highly stable, contributing to the overall reliability of the instrument. The IR detector also provides simultaneous chemical composition information, which is key for controlling the production of heterogeneous resins.

Moreover, for a truly complete analysis, the instrument can also measure intrinsic viscosity by means of a built-in dual capillary viscometer that can be incorporated as an additional feature.



GPC-QC KEY FEATURES

Full automation of the entire analytical process.

One sample analyzed in 30 minutes including dissolution.

IR4 or IR5 MCT detectors for Concentration and Short Chain Branching information.

Optional incorporation of a dual-capillary viscometer.

Simple and reliable design for Quality Control environments.

Comprehensive results (MMD, SCB, IVD).

Outstanding precision thanks to the full automation and the detectors' robustness.



GPC-QC

APPLICATION NOTE

Design Principles and Operation

Introduction

Polyolefin (PO) constitutes the largest volume industrial polymer group in the world in terms of economic impact and production. They are used for making a wide range of commercial products that touch nearly every aspect of our daily lives, such as automobile parts, pipes, packaging films, household bottles, and many more. PO as a group includes high-density and low-density polyethylene (HDPE, LDPE), polypropylene (PP), ethylene-propylene (EP) rubber, and linear low density (LLDPE) copolymers of ethylene with alpha olefins (propylene, 1-butene, 1-hexene, 1-octene). They are poly-disperse materials, meaning that a single product is made of a range of chains with different chain-lengths and possibly different chemical compositions when more than one monomer type is used in the synthesis. Moreover, different molecular architectures (linear or branched) and stereo-structures (tacticity in PP) are also possible in these products. All that complexity, together with the semi-crystalline nature of most PO materials, helps to understand the expanding application range of these products.

A range of reactor configurations and catalyst systems are used nowadays by different manufacturers to produce thousands of tons of polyethylene and polypropylene every year, in huge petrochemical

complexes around the world. Even if the material being produced is in fact characterized by a distribution of molar masses (MMD) and possibly a distribution of chemical compositions (CCD), due to historical and practical reasons, the production is typically controlled based on bulk properties, which can be measured with relatively simple equipment. Melt flow rate (MFI) is maybe the most important of such bulk parameters, being related mainly to the average molar mass. Density, which is more related to the average of chemical compositions, is another parameter typically used for controlling the reactor and the product.

With the development of more complex PO, such a multimodal polyethylene or heterophasic PP, and the requirement for a more uniform production and tighter specification ranges demanded by a global and competitive market, the classical approach of relying on bulk physical properties for control of the manufacturing process starts to find its limits. A new paradigm needs to be implemented based on acquiring complete information about the full distributions that characterize the products, in order to replace or complement the control based on single average parameters.

Gel permeation chromatography (GPC/SEC) is extensively used in the industry's analytical laboratories to obtain the MMD. The requirement of high temperature operation, given the semi-crystalline nature of polyolefin, together with the inherent complexity of the technique and fragility of columns, has prevented in the past the availability of MMD analysis as a routine process control tool in the manufacturing plant laboratory. In order to fulfill this need in the industry, a compact GPC-QC instrument has been developed to provide robust and precise MMD data for process control. In addition to a high-reliability hardware design, the operation workflow has been simplified while keeping full automation of sample dissolution and analysis.

Given that the application for GPC-QC follows the process changes in manufacturing, there are no batches of samples coming together to be analyzed. Instead, the analysis of a single sample of the material produced at a particular time is required, in a continuous operation cycle. That means there is no need for an auto-sampler, but a single dissolution station optimized to shorten the dissolution time is used instead. This is a fundamental difference in the design for QC, compared to the instrumentation dedicated to research.

A simplified hardware design including only one valve at high temperature, an external HPLC pump and robust detectors, helps in achieving the required level of reliability and minimizing potential downtime. The main detector is infrared, which provides a concentration signal based on absorbance of total CH, being very appropriate for the QC environment thanks to the fast stabilization time, stable baseline and good sensitivity.

Depending on the process homogeneity, a significant amount of sample may be required to obtain a good representativeness, so large capacity vials of 100 or 200 mL are used compared to the typical 2 – 10 mL used in research grade instruments. Up to 200 mg of polymer can be dissolved for analysis, although 50 mg is the typical sample size.

The analytical workflow is quite simple and requires minimum manual work. When a sample of polymer is received in the laboratory, it is weighed into the vial and a small magnetic bar is placed (a small amount of a flow rate marker, or internal standard, can be added to the vial). The vial is placed in the dissolution station oven. Then the analyst lowers a handle to insert the needle into the vial through the septum.

Results
and Discussion

The analysis is started from the computer, and proceeds automatically according to the pre set method conditions. Once the analysis is finished, the chromatograms are processed to generate the MMD and any calculated parameters of interest. When a new sample comes in, a new vial is prepared with it and the analyst just discards the previous one placing the new one in the station. Following this workflow, the GPC-QC can be operated continuously with a cycle time of one hour or less, which is found appropriate for controlling the start-up of reactors, or when a change of grade is conducted. Once the process is stable, production may need to be controlled at a slower pace, several times per day.

Precision in the molar mass results is key in the application of this technology in manufacturing control, so some experiments were conducted to assess whether the performance was satisfactory. A series of replicate analyses of an LLDPE material (density 0.868 g/cm³) were performed in a GPC-QC instrument, using typical analysis conditions: mobile phase was 1,2,4-trichlorobenzene (TCB) with 300 ppm of butylhydroxytoluene (BHT) as antioxidant, chromatographic pump flow rate of 2.0mL/min, column and detectors temperature 150°C, injection 200 µL, and the column was a PL Rapide H 150 x 7.5 mm (Agilent, Waldbronn, Germany). For sample preparation, 40 mg of polymer were put in the vial

and filling volume was set to 80 mL taken from the same reservoir as the mobile phase, dissolution time was 60 minutes at 160°C with 400 rpm stirring. The IR detector concentration chromatograms are shown in Figure 1 (left) for the seven replicates, which overlay perfectly. It should also be noted that the separation was achieved in a time slightly over 2 minutes. The total analysis time can be reduced to around 3 minutes, and solvent consumption to around 50 mL per sample.

The good precision in the collected chromatograms is translated to the calculated MMD as seen in the same Figure (right). The molar mass averages M_w and M_n from all individual distributions are presented in Table 1, together with the poly-dispersity index calculated as the ratio M_w/M_n . This index is related to the broadness of the distribution, and that information is not available when only bulk properties are measured. The precision in the molar mass averages and poly-dispersity index expressed as standard deviation (std) and relative standard deviation (RSD %) is remarkable for GPC analysis.

For the implementation of this new technology in manufacturing plants for process control, the total cycle time, from sample reception to delivery of results, is a crucial parameter. Thanks to the use of a single fast-GPC column and increased pump flow rate, the actual GPC separation is performed in less than three min. However, the polymer needs to be brought in solution before analysis, which in the case of most PO, it is considered a time-consuming process. The single-vial dissolution station in the GPC-QC was optimized in order to shorten the dissolution time, by ensuring good heat-transfer to the vial and providing

injection	Mw (g/mol)	Mn (g/mol)	Mw / Mn
15-0365	190,158	46,638	4.08
15-0364	189,939	47,122	4.03
15-0363	189,840	46,936	4.04
15-0362	190,592	47,155	4.04
15-0361	191,754	47,057	4.07
15-0360	190,258	47,335	4.02
15-0359	190,630	47,622	4.00
average	190,453	47,124	4.04
std	647	308	0.03
RSD (%)	0.34%	0.65%	0.68%

Table 1. Summary of molar mass averages and poly-dispersity index showing excellent precision obtained by GPC-QC.

vigorous stirring. Besides that, the vial is filled with preheated solvent, so no additional time is required to increase its temperature once in the vial. The optimized dissolution and separation processes opens the door to HT-GPC analysis within 30 minutes in most cases, including the sample preparation step, and less than one hour even for the most difficult products. This means a breakthrough in this kind of technology and enables the practical application in manufacturing plants as a process control /quality control tool.

Additional detection to enhance the information gained by GPC-QC: chemical composition by IR and viscometry

The use of an IR detector in these instruments can also generate useful information on the chemical composition of the sample being analyzed. This is relevant in the case of copolymers, which account for a large part of the PO produced nowadays, such as LLDPE, some HDPE and also the important group of EP copolymers.

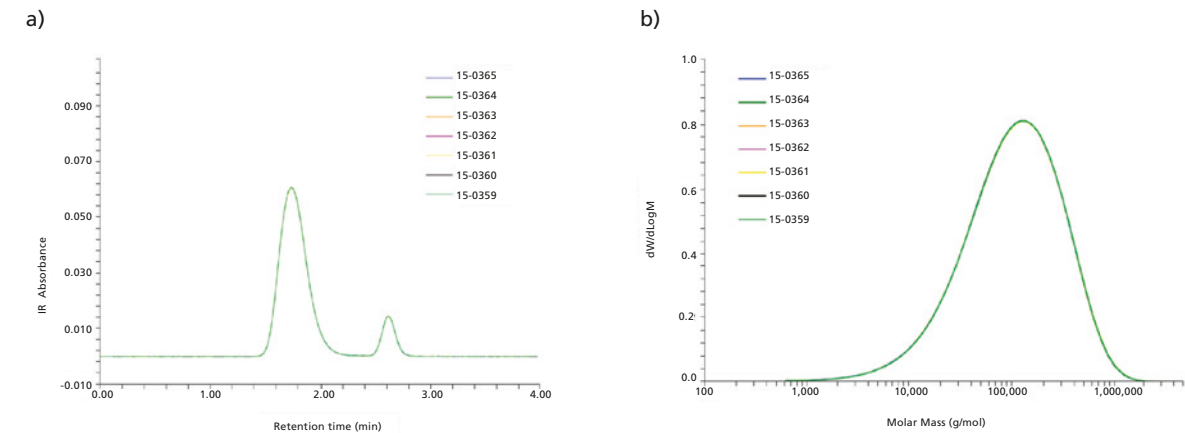


Fig. 1. Chromatograms (left) and molar mass distribution (right) for seven injections of a PE sample, showing excellent precision in the injection and analysis process in GPC-QC. Smaller peak at 2.6 min is a flow rate marker.

The information generated by the IR detector can be translated to either comonomer weight fraction or to density units for a given product range. A single value representing the bulk composition/density can be reported, but possible variations along the molar mass distribution can also be measured in the case of heterogeneous multicomponent resins.

An example is provided in Figure 2 for a bimodal HDPE made in a dual-reactor process. A lower molar mass high-density component is typically produced, together with a second component of higher molar mass with a small amount of added comonomer. That balance results in enhanced mechanical properties, such as ESCR, for pipe applications. From a single GPC-QC analysis, and in less than one hour with minimum operator intervention, it is possible to obtain an estimation on the density being produced in each of the two reactors, as well as the molar mass and the weight fraction of each component. The level of

control on the process is thus greatly enhanced over the alternative methods based on bulk properties (MI and density).

All that capability is readily available using the GPC-QC technology, given that the built-in IR detector can deliver it without any analytical complexity. In order to obtain quantitative results from the IR, a simple calibration can be used with a small set of reference products with known chemical composition.

When required, a 2-capillary serial viscometer can be included in GPC-QC to collect data on the polymer intrinsic viscosity and its distribution, and also on long chain branching. Intrinsic viscosity is more directly related to the processing behavior and properties of the polymer and so it may be preferred in some cases as an alternative to molar mass. The 2-capillary serial design used in GPC-QC is robust and well suited for this environment.

It can be said that GPC-QC is a very powerful tool for process control and QC, given that by means of a GPC separation, it provides enhanced and more detailed information than the bulk property methods used nowadays. In order to optimize the application of this technology, specific data processing procedures, based on multivariate analysis or modeling may be developed, targeted to a given process or product range. Additionally, robust data processing methods, based on viscosity distribution, are being developed as a means to enhance the precision and long-term reliability of GPC-QC as a process control tool.

Conclusions

The control of the reactors for manufacturing of PE and PP is nowadays still based on measuring physical properties of the bulk material (Melt Index, density), which is quite limited information on the product itself. An enhanced, more refined, control on the process and the product can be realized by using more complete information given by the molar mass distribution (MMD).

Instrumentation specifically aimed at measuring the MMD in a manufacturing plant laboratory has been developed. It has been proved that the total cycle time, including the sample dissolution step can be reduced to around 30 minutes, well in line with the process control requirements.

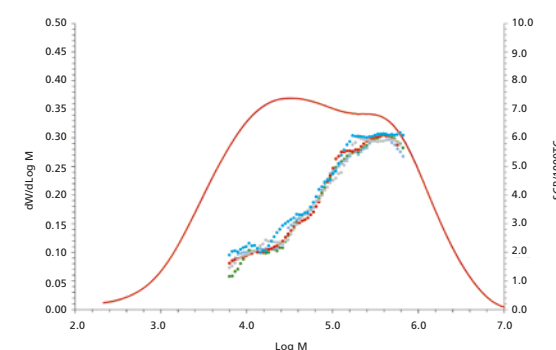


Fig. 2. MMD and short chain branching (SCB) frequency measured by GPC-QC for a bimodal HDPE. The density of each of the modes was calculated from an average of the SCB frequency in each molar mass range.

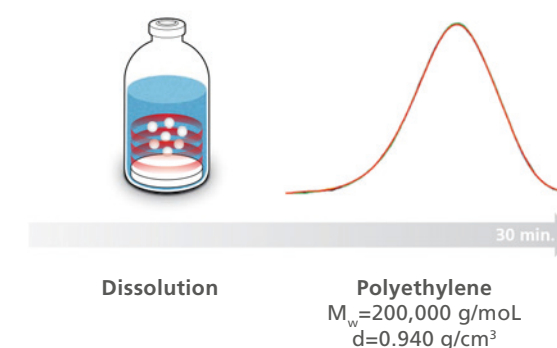
Important Applications for GPC-QC

Reproducibility of this technology is very good in both average molar mass and poly-dispersity index (RSD around 0.5%). Additional detection of chemical composition, which can be related to density, is given by the built-in IR detector, while an online viscometer can also be incorporated.

Important applications for GPC-QC are:

- Pilot plants
- Plant start-ups
- Monitoring grade changes in multi-reactor processes
- Monitoring the microstructure of pipe resins
- Processors laboratories

MMD and SCB results of a bimodal HDPE sample
Overlay of 5 injections



Intrinsic Viscosity Determination for Polymeric Materials



IVA

FULLY-AUTOMATED INSTRUMENT FOR DETERMINATION OF INTRINSIC VISCOSITY IN POLYMERIC MATERIALS

A reliable and automated instrument for intrinsic viscosity analysis of polymeric materials in solution. Intrinsic viscosity can be seen as an indirect measurement of the average molar mass and, as a result, it provides valuable information within any polymer characterization process.

IVA integrates in a reduced footprint, a robust dual-capillary relative viscometer combined with a high temperature autosampler with a capacity for 42 samples. IVA can analyze a wide range of polymers with IV values from 0.5dL/g up to over 40dL/g, such as polyolefins, PET, PAN, PMMA, and others, by using almost any organic solvent.

The principle of a relative viscometer is simple: the pressure-drop across a stainless-steel capillary tubing caused by the flow of polymer solution is compared to the one produced by the solvent, which is measured simultaneously by a twin reference capillary. The relative viscosity of polymer solution is derived from the ratio of pressure, and the intrinsic viscosity is calculated taking into account the injected mass.

Unlike the glass capillaries used in Ubbelohde viscometers, the IVA capillaries and tubing do not require manual washing or rinsing, and provide robust and precise viscosity values over time.

When using IVA, the analyst places the vials with polymer into the autosampler's external tray, where they stay at room temperature until they are scheduled for analysis under software control. Then the instrument takes the vials into the dissolution oven, fills them with solvent and starts shaking. Dissolution temperature, shaking intensity, non-oxidative atmosphere with nitrogen, and time are accurately controlled so that the analyst can select the optimum conditions to achieve full dissolution while minimizing thermal degradation.

The analysis of polyolefins and other polymers containing significant C-H content can be further improved by the incorporation of the optional Infrared detector IR4 to accurately quantify the injected polymer mass, which results in improved precision and accuracy of intrinsic viscosity determination.

IVA KEY FEATURES

Full-automation of dissolution and analysis processes.

No manual solvent handling.

High temperature autosampler for dissolution of samples in the same instrument.

Self-cleaning design based on dual capillary relative viscometer.

High precision achieved by automation.

Up to 42 samples can be analyzed sequentially.

Analysis of high and ultrahigh molar mass polymers.

Compatible with most organic solvents such as decalin, chloroform, tetrahydrofuran, tri-chlorobenzene, and others.



IVA

APPLICATION NOTE

New research leads to the development of an automated and versatile technique for solution viscosity determination of a wide range of polymeric materials in different solvents, from ambient temperature up to 200°C.

Introduction

The determination of the solution viscosity of polymeric materials is very important to the industry, both to research and manufacturing, since it can be used to estimate the molar mass, providing important information relating to the physical properties of polymers. The relative viscosity of a dilute polymer solution to that of the pure solvent itself is measured and from it, the intrinsic viscosity (IV or $[\eta]$) of the polymer is calculated. Due to the popularity of dilute solution viscosity measurements and the availability of those methods in many manufacturing laboratories, the IV of polymers has been traditionally used to specify and to control the production grades. It must be noted however, that IV is not a property of the polymer itself, as molar mass is, but rather a property of the polymer solution, influenced by the solvent and temperature.

The recently developed technique is an automated process for viscosity measurements of polymeric materials in solution. It is compatible with typically

used organic solvents such as decalin, tetralin, tri-chlorobenzene (TCB) and ortho-dichlorobenzene among many others. Dissolution temperature and analysis temperature can be set independently, from ambient to 200°C, so that a wide range of polymers, even the most crystalline ones, can be analyzed with convenience and safety with this alternative approach.

Intrinsic Viscosity Determination

The proposed new method performs the polymer intrinsic viscosity measurement by means of a two-capillary relative viscosity detector, which concept was developed and patented by Yau in the 80s (US 4,793,174), as a robust method in contrast to temperature, pressure or solvent flow rate variations.

Capillary viscometers rely on the principle that under a forced flow (Q), the pressure drop (ΔP) due to a fluid traveling along a capillary tubing of length L and radius r , is proportional to the absolute viscosity of the flowing fluid $[\eta]$, according to Poiseuille's law:

$$\Delta P = \frac{8QL}{\pi r^4} \eta$$

Absolute viscosity of fluids is important to many industries and can be measured using different types viscometers. However, in polymeric materials the interest is on the relative viscosity of a dilute polymer solution compared to that of the pure solvent, given that from it, the intrinsic viscosity, related to molar mass of the polymeric material, can be derived. In the first place, the relative viscosity $[\eta_{rel}]$ is defined as:

$$\eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}}$$

This is a dimensionless quantity which represents to what extent the added polymeric material increases the viscosity of the solvent. The relative viscosity of the solution is proportional to the amount or concentration (C) of polymer it contains, while the intrinsic viscosity is independent of concentration. The specific viscosity $[\eta_{sp}]$ of the solution and the polymer intrinsic viscosity $[\eta]$ are calculated according to the Equations:

$$\eta_{sp} = \eta_{rel} - 1$$

$$[\eta] = \lim_{C \rightarrow 0} \frac{\eta_{sp}}{C}$$

The intrinsic viscosity has units of inverse density (dL/g for instance). It is defined at the limit of infinite dilution (zero concentration), and sometimes calculated by extrapolation of data at different concentration levels. A more practical and efficient approach is based on a single-point relative viscosity measurement, taken at a defined concentration low enough to eliminate the need for extrapolation, or using a model equation to estimate the extrapolated value. Among several models and equations, the Solomon-Ciutà Equation, which does not require additional parameters, can be used:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_{rel})}}{C}$$

A serial viscometer design has been implemented for the new method: two pieces of capillary tubing are connected in series in such a way that the first one experiments the flow of pure solvent while the second one simultaneously receives the flow of the dilute polymer solution. The pressure drop across each capillary is measured continuously as a function of time by high sensitivity differential pressure transducers. According to Equations (1) and (2), the relative viscosity is proportional to the ratio of differential pressures, being independent of the flow rate. An instrumental constant is easily measured by

Results and Applications

flowing pure solvent through the two capillaries. The constant is automatically measured with every injection thus, compensating for small, long-term variations in capillaries (self-calibrating). It also accounts for differences in tubing dimensions, so in this design, it is not required that the capillaries stay accurately matched.

The relative viscosity is calculated as a function of time as the injected solution goes through the system, and any influence of flow-rate variations (such as high frequency pump pulsations) or thermal effects are cancelled out directly by the reference capillary, resulting in very high sensitivity and long-term stability.

An automated technique for Intrinsic Viscosity Analysis

The proposed method constitutes a precise and convenient approach to IV measurement, due to the automation of all the analytical procedures, from filling of vials to the reporting of results. Samples are put in solid form into 20 mL vials and brought to an autosampler tray with capacity of 42 vials. The operator enters the samples identification data, selects the analytical method and starts the analysis that proceeds unattended until all the vials defined in the instrument run queue are analyzed. Under software control,

solvent is added to the vials, controlling the dissolution time per vial, injecting each solution and rinsing of the capillary lines. The solution travels safely throughout all the system without any risk of precipitation because there are no cold spots. A new run can be immediately started after finishing the previous one, achieving a throughput of 40 samples a day in standard operation conditions.

In order to maintain the polymeric sample integrity along the dissolution and measurement processes, *Sample Care* protocols have been implemented as part of the method. Those include the ability to purge the vial atmosphere with an inert gas (Nitrogen) before dissolution starts, and controlling accurately the time spent at high temperature by keeping every vial inside of the oven only for the programmed dissolution time. The vials remain in an external tray at room temperature until the scheduling software requests their transfer to the dissolution oven. Efficient heat transfer to the vial, together with preheating of the solvent prior to delivery to the vial, help in shortening the time required for dissolution. Oxidative and thermal degradation is thus minimized, ensuring that accurate intrinsic viscosity is measured even for the most challenging ultra-high molar mass materials, or oxidation-prone polymers, such as polypropylene.

Different polymers in various solvents have been analyzed in this system, including PAN (polyacrylonitrile) in DMF (N,N-dimethylformamide), PET in phenol:o-DCB, PLA in TCB as well as polyolefins in TCB and o-DCB. Even if the procedure or conditions in this new system were different, the IV results obtained were in good agreement with reference methods (ISO 1628-3:2010 f.i.) in all cases, as shown in Figures 1 and 2 for two of the systems considered.

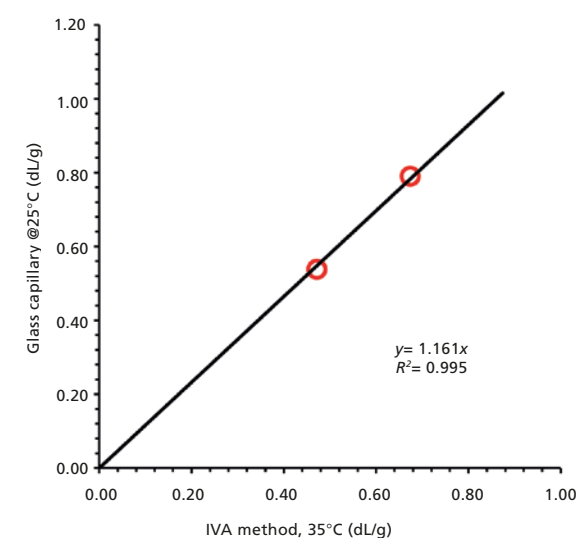


Fig. 1. Correlation of intrinsic viscosity (IV) values obtained using the IVA method compared to IV determined using a traditional glass capillary setup for a set of PET samples. In both cases a mixture of phenol:o-DCB (2:3, m:v) was used while temperatures were 35°C and 25°C respectively.

A factor to keep in mind when comparing different methods to evaluate IV in polymeric materials is the effect of shear rate on the observed viscosity. Methods based on glass capillaries are driven by gravity and operate under low shear condition, while forced flow, used in this new method, may work at higher shear rates. Typically when shear rate increases the observed viscosity decreases, so keeping constant shear rate may be advantageous in order to get consistent results.

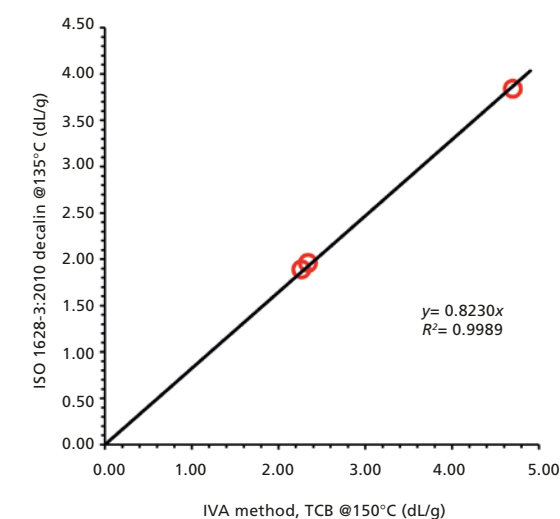


Fig. 2. Correlation of intrinsic viscosity (IV) values obtained using the IVA method compared to IV determined according to standard method ISO 1628-3:2010 for a set of polypropylene samples. IVA was run in tri-chlorobenzene at 150°C, using solutions prepared at 1 mg/mL; the ISO method was performed in decalin at 135°C with solutions at 1-1.5 mg/mL. The linear correlation is excellent as proved by the high R^2 value.

A study was conducted for a set of PE materials spanning a very wide range in IV, in order to compare the observed viscosity at two different flow rates. Results depicted in Figure 3 show that an excellent correlation was found, and therefore a high flow rate determination can be performed in order to reduce the analysis time, and still obtain data comparable to lower shear conditions. The analysis time per sample was reduced from half an hour to 4 minutes with the increased flow rate.

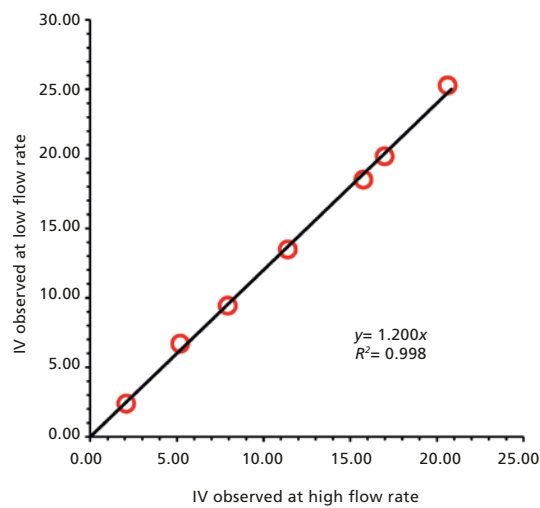


Fig. 3. Observed intrinsic viscosity for a series of polyethylene materials, in tri-chlorobenzene at 150°C, using high and low flow rate through the two-capillary viscometer.

Application example: Intrinsic Viscosity of UHMWPE

Maybe one of the most challenging polymers for analysis is ultra-high molar mass polyethylene (UHMWPE). Those are high crystallinity materials with extremely high values of IV, only soluble at elevated temperatures in organic solvents. Special care must be taken in sample preparation to prevent degradation, which would reduce the apparent viscosity, and also in the analysis, given the high viscosity of the $[\eta_{sp}]$ solutions.

Dissolution temperature and time must be chosen so that the polymer dissolves completely but also to give the very long molecular chains enough time to disentangle completely and obtain reliable viscosity values. In Figure 4, data collected after 90 minutes or 180 minutes of dissolution show that longer time is required to achieve that full disentanglement condition; otherwise, the intrinsic viscosity is underestimated. When the polymer stays at elevated temperature for such long time, a nitrogen atmosphere is also required to prevent oxidative degradation which also decreases the observed viscosity as seen in the same Figure 4.

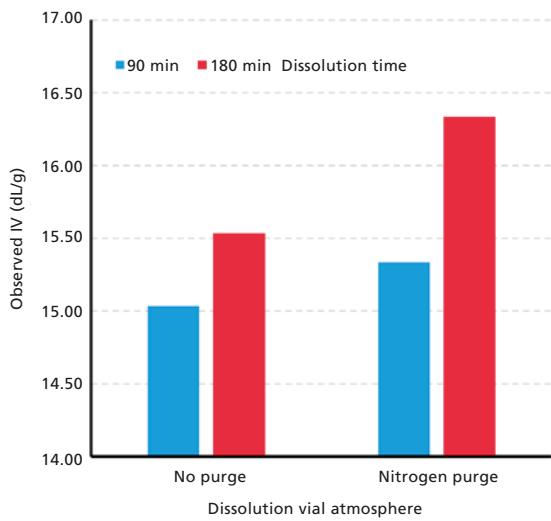


Fig. 4. Observed viscosity for an UHMWPE sample with different dissolution time, with and without nitrogen purge of the dissolution vial.

An infrared (IR) detector can be optionally used for online accurate quantification of the injected mass, which otherwise needs to be entered as weighed using an analytical balance. The IR detector is suitable for detection of polymers with aliphatic CH groups, dissolved and analyzed in solvents that are IR transparent, such as the important class of polyolefins (polyethylene, polypropylene and copolymers), in TCB or o-DCB.

A technique that is proven to be efficient, precise, and safe

Conclusions

A new technique has been developed for dilute solution viscosity that is proven to be efficient, precise and safe. A wide range of polymers soluble from ambient to 200°C can be analyzed in a variety of solvents.

The proposed method takes an automated approach, and performs all the needed steps without user intervention nor solvent handling throughout the whole process, paying special attention to the sample condition, minimizing the degradation, as well as to laboratory health and safety considerations. Appropriate dissolution time control and purging of the vial atmosphere with nitrogen both help in enhanced reliability of the data, by reducing degradation possibilities. The application of a fixed forced flow rate for the IV determination maybe also help in improving consistency of data by keeping constant shear in all determinations, while increased flow rate provides a net gain in efficiency while maintaining good correlation of the method with lower shear values.

When applicable, the online IR detection helps in improving the accuracy and precision of the method, through the direct quantification of the true amount of sample injected.

In order to demonstrate the advantage in precision when applying online IR quantification compared to the offline balance, three different high molar mass PE materials were analyzed at a low concentration level of 0.25 or 0.15 mg/mL in TCB. Dissolution time was 1 hour with gentle shaking, at 140°C under nitrogen atmosphere, in order to minimize thermal and oxidative degradation. Results are presented in Table 1, together with standard deviation, when using the IR detector for quantifying the injected mass, and when using the nominal weight given by the analytical balance, in the IV calculation. An improvement in the precision is clearly seen when the actual mass measured by the IR detector is considered, given it eliminates any errors associated with handling small amounts of polymer by the operator, but also due to the possible presence of non-soluble particles.

Sample	IV (dL/g)	std (IR)	std (balance)
A	11.38	0.2	0.7
B	21.00	0.4	2.6
C	28.67	0.7	3.8

Table 1. Intrinsic viscosity (IV) for three industrial UHMWPE samples analyzed by IVA in TCB at 140°C. Standard deviation based on 6 replicates when using the measured injected mass by IR, or using the nominal mass given by the analytical balance.

Chemical Composition Distribution for Quality Control



CEF QC

The latest development in Polymer Char's Quality Control portfolio, a Crystallization Elution Fractionation instrument for Process Control in production plants. This instrument delivers the chemical composition distribution for one sample in less than 1 hour (including dissolution). The density results are also provided to facilitate a direct correlation with the traditional process control data in the plant. The instrument can be operated as a CEF, TREF or TGIC.

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