Polymer Char

Is your polyolefin resin performing as expected?

B. Monrabal, A. Ortín, P. del Hierro. Polymer Char, Valencia, Spain.

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

Newly Developed Resins are More Challenging to Control in Production Plants.

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.

Same Resins, Different Performance?

Within the Polyethylene (PE) family, the added information is essential especially in the case in dual reactor resins, as with pipe and blow molding products, or in the broad spectrum of linear lowdensity 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 an unequivocal characterization of the resin chemical structure. These techniques, which in the past demanded operation expertise and sophisticated equipment, are available today with a simplified design for quality control purposes (GPC-QC).

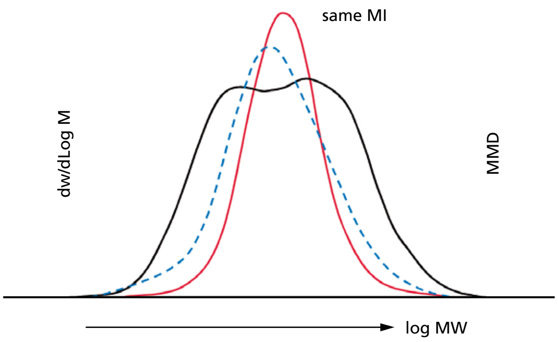

Figure 1.- Three different resins with the same Melt Index but completely different MWD and thus, different performance.

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 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).

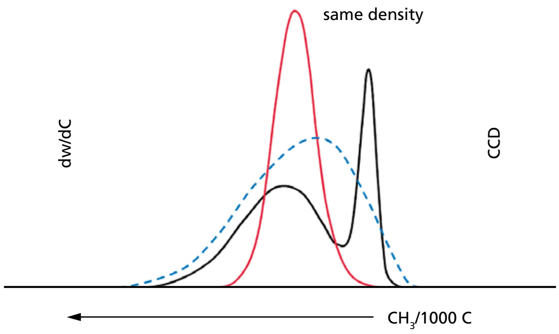

Figure 2.- Three different PE resins with the same density but completely different CCD and thus, different performance.

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 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 or additional parameters 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.

GPC-QC

Intrinsic Viscosity Analyzer (IVA)

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 the 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 the 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.

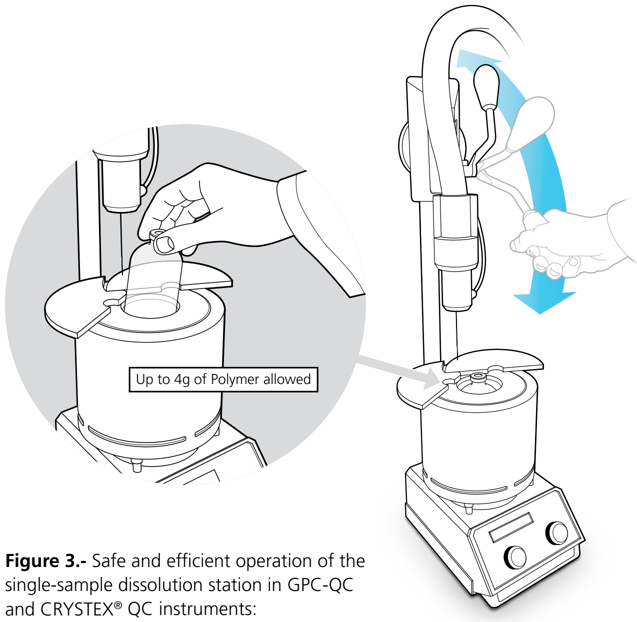

Figure 3.- Safe and efficient operation of the single-sample dissolution station in GPC-QC and CRYSTEX® QC instruments:
1) Remove the previous bottle and place a new one with an approximate sample weight.
2) Manual Injection and press START.

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 a four-gram 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. CRYSTEX® 42 is a version of CRYSTEX® QC with a 42-vial high-temperature autosampler available when requiring control of multiple samples, which are considered of reasonable homogeneity.

	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 165ºC

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

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

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.

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

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 a 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.

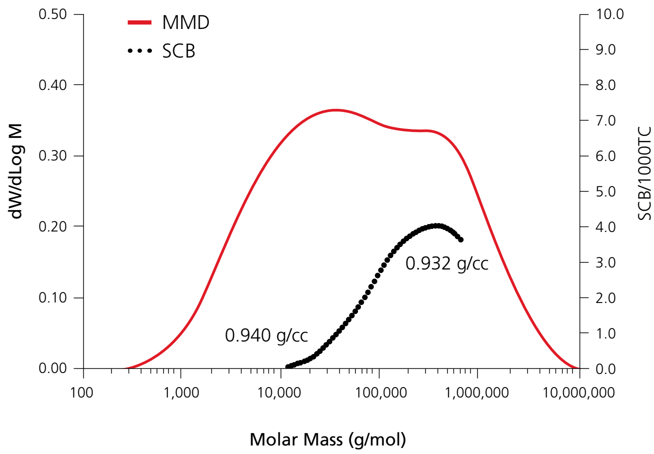

Figure 4.- MMD and short chain branching (SCB) frequency measured by GPC-QC for a bimodal HDPE. The density of each of the modes was calculated from an average of the SCB frequency in each molar mass range.

Measuring Intrinsic Viscosity of All Polymeric Materials.

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 singlepoint 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 of Polymeric Materials by IVA - Petro Industry News, April/May Issue 2015.

Solutions for Polyolefin Characterization

CRYSTAF: An instrument designed for intensive use in the analysis of the Chemical Composition Distribution in Polyolefins.

TREF: A completely automated apparatus for the analysis of the Chemical Composition Distribution in Polyolefins. It provides complementary information to CRYSTAF data in the analysis of some complex resins.

CRYSTAF-TREF: CRYSTAF and TREF techniques are available in the same equipment for a full Chemical Composition Distribution characterization.

CEF: A high throughput equipment to analyze the Chemical Composition Distribution in Polyolefins, using a new approach combining CRYSTAF and TREF separation mechanisms.

PREP mc²: An automated instrument to perform semipreparative fractionation according to composition by TREF or CRYSTAF, or molar mass.

PREP C20: New column-based preparative fractionation instrument, capable to fractionate up to 20 grams of polymer.

CRYSTEX® QC: A truly automated system based on TREF-separation concept for soluble fraction measurement ethylene content and intrinsic viscosity in PP/PE plants control.

CRYSTEX® 42: A high-throughput and easy to use system for simultaneous measurement of the soluble fraction, ethylene content and intrinsic viscosity in a fully automated process for up to 42 samples.

IVA: Reliable and automated instrument for Intrinsic Viscosity Analysis of polymers with dissolution temperature up to 200ºC.

GPC-IR®: Advanced High Temperature GPC for the analysis of Molar Mass Distribution in Polyolefins. Fully automated sample preparation and filtration. Triple detector (IR, VS, LS) plus composition.

GPC-QC: High Temperature GPC instrument for Quality and Process Control in Polyolefin production plants.

CFC: A fully automated Cross Fractionation Chromatograph (TREF+GPC) for the analysis of Bivariate distribution in Polyolefins.

GPC One® Software: The most comprehensive GPC/SEC Calculations Software integrating all detectors' signals.

Data Unit 200: Versatile signals acquisition device to link any vendor GPC instrument with Polymer Char's GPC One®.

TGIC: An adsorption high temperature HPLC technique for the analysis of low crystallinity Polyolefins.

SGIC 2D: An adsorption high temperature HPLC technique combined with GPC and infrared detection for the analysis of composition and molar mass interdependence of Polyolefin resins.

IR4: Integrated reliable and simple to use infrared (IR) detector to measure concentration and composition.

IR5 MCT: Integrated and modern IR detector with an MCT element (thermoelectrically cooled) for high sensitivity analysis.

Analytical Services: Polymer Char laboratory, a global reference in the field, counts on the latest technologies for Polyolefin Characterization.

Company Profile

Polymer Char is devoted to the development of state-of-the-art instrumentation for Polyolefin Analysis.

The company offers the broadest and most modern range of instruments and services for polymer analysis and more specifically, for the structural characterization of Polyolefins, such as Molar Mass Distribution (GPC-IR®, GPC-QC, GPC One®), Chemical Composition Distribution (CRYSTAF, TREF, CEF), Bivariate Distribution by Cross-Fractionation Chromatography (CFC), High Temperature HPLC (TGIC, SGIC 2D), Soluble Fraction Determination (CRYSTEX®, CRYSTEX® QC and CRYSTEX® 42), Preparative Fractionation (PREP mc², PREP C20), Intrinsic Viscosity (IVA) or integrated Infrared Detection (IR4, IR5 MCT).

Polymer Char is also well known for its advanced approach to virtual instrumentation software that, together with excellent remote control capabilities and its strong commitment to Customer success, places the company at the leading edge on instrumentation diagnostics and technical support.

Together with its global network of partners and distributors, Polymer Char supplies, trains and supports Customers worldwide. The company provides analytical services in 35 countries and its instruments are present today in over 20 countries within the Americas, Europe, Africa, Middle East and Asia Pacific, predominantly serving Polymer Producers and Processors, Government and Academic Research Laboratories, Contract Research Organizations, Analytical and Testing Laboratories, and Chemical Instrumentation Manufacturers.

In the last two decades and with an annual investment of up to 20% of its manpower resources on R&D, Polymer Char has played a key role in the development of most of the existing Polyolefin analysis technologies, such as CRYSTAF, CRYSTEX®, CEF, CFC, and GPC with IR detection. Each new project, each new analysis, underpins Polymer Char as the Polyolefin Characterization Company.

GENERALITAT VALENCIANA IMPIVA MINISTERIO DE CIENCIA E INNOVACIÓN MINISTERIO DE INDUSTRIA, TURISMO Y COMERCIO EUROPEAN UNION European Regional Development Funds

Several Polymer Char's R&D projects have counted on the financial support of IMPIVA, the Spain's Ministries of Science and Innovation and of Industry and Trade; and the European Union, with its Funds for Regional Development within the FEDER operational program of the Valencian Community 2007-2013.