Fully Automated Instrument for Solution Viscosity in Polymeric Materials.

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The IVA® – Intrinsic Viscosity Analyzer is a compact and fully automated instrument for measuring the intrinsic viscosity in a wide range of polymeric materials from ambient temperature up to 200°C. The process is entirely performed without user intervention nor handling any solvents including filling of vials and dissolution of the samples, thanks to an autosampler with capacity of up to 42 samples. At the core of the IVA®, a robust two-capillary viscometer collects relative viscosity data from which intrinsic viscosity is derived. The stainless steel capillaries design is self-cleaning and self-calibrating, ensuring reliable and reproducible data. Furthermore, the instrument adds safety to the process thanks to the full automation, thus IVA® becomes a practical and convenient alternative to manual or semi-automated methods.

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 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 [η]) 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 the IV is not a property of the polymer itself, as the molar mass is, but rather a property of the polymer solution, influenced by the solvent and the temperature.

The IVA® (Intrinsic Viscosity Analyzer) is a fully automated instrument 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 programmed independently from ambient to 200ºC, so that a wide range of polymers, even the most crystalline ones, can be analyzed with convenience and safety.

Figure 1. IVA® instrument, fully automated benchtop system for measuring intrinsic viscosity of polymeric materials soluble at room or elevated temperatures up to 200ºC, compatible with a variety of solvents. Autosampler including dissolution oven (left), instrument main unit with solvent / waste containers and detectors oven (center) and computer with control and data processing / reporting software (right).

Intrinsic viscosity determination

The IVA® instrument performs the polymer intrinsic viscosity measurement by means of a two-capillary relative viscosity detector, which concept was developed and patented by Dr. Wallace W. Yau in the 80s (US 4793174), as a robust method in contrast to temperature, pressure or solvent flow rate variations.

Capillary viscometers rely on the principle that the pressure drop (ΔP) due to the flow (Q) of a fluid across a capillary tubing of length L and radius r, is proportional to the absolute viscosity of the flowing fluid [η_{sp}], according to Poiseuille's law:

$$(1)\quad \Delta P = \frac{8QL}{\pi r^4}\eta$$

Absolute viscosity of fluids is important to many industries and can be measured using different types of capillary viscometers. However, in polymeric materials the interest is on the relative viscosity of a dilute polymer solution given that from it, the intrinsic viscosity of the polymeric material can be derived.

In the first place, the relative viscosity [η_{rel}] is defined as the ratio of the polymer solution viscosity to that of the pure solvent:

$$(2)\quad \eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}}$$

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 defined to remove that effect. The specific viscosity [η_{sp}] of the solution and the polymer intrinsic viscosity [η] are calculated according to the Equations:

$$(3)\quad \eta_{sp} = \eta_{rel} - 1$$

$$(4)\quad [\eta] = \lim_{C\to 0} \frac{\eta_{sp}}{C}$$

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 relative viscosity measured 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 obtain the extrapolated value. Among several models and equations, the Solomon-Ciutà Equation, which does not require additional parameters, can be used:

$$(5)\quad [\eta] = \frac{\sqrt{2\,(\eta_{rel} - 1 - \ln \eta_{rel})}}{C}$$

In the serial viscometer design implemented in the IVA® instrument, two stainless steel capillaries 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 polymer dilute 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 (Equation 6). An instrumental constant is easily measured by 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.

$$(6)\quad \eta_{rel} = K\frac{\Delta P_{solution}}{\Delta P_{solvent}}$$

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 pulsations) or thermal effects are cancelled out directly by the reference capillary, resulting in very high sensitivity and long-term stability.

Figure 2. IVA autosampler oven (left), equipped with a built-in shaker motor with different power levels, and diagram of nitrogen purging system for the vials atmosphere (right).

IVA® – Intrinsic Viscosity Analyzer

The IVA® constitutes a precise and convenient approach to IV measurement, due to the automation of all the analytical procedures, from vials filling to reporting of results. Samples are put in solid form into 20 mL vials and brought to the instrument 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, the instrument takes care of adding solvent to the vials, controlling the dissolution time per vial, injecting each solution and rinsing of the capillary lines. Thanks to the compact design without cold spots, the solution travels safely throughout all the system without any risk of precipitation. 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, the Sample Care protocols successfully implemented by Polymer Char in other analytical applications, are also part of the IVA® method. Those include the ability to purge the vial atmosphere with an inert gas (Nitrogen) before dissolution starts, and minimizing 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.

No solvent needs to be handled by the analyst at any moment and no vapors are released to the atmosphere given all the system is airtight at all times. Thus, a higher standard in safety and health is set thanks to the IVA® fully automated approach.

For increased safety level, the instrument is equipped with three vapor sensors in different compartments, in order to detect any potential leaks of solvent and stop the analysis in such event. Over-temperature protection, as well as heater failure protections are included into the instrument dedicated electronics as well as monitoring software.

Results and Applications

The viscosity measurement is performed by the built-in two-capillary viscometer placed inside of an oven with extremely precise and stable temperature control (0.01°C). The instrument fluidic design is rather simple, having a single valve inside the oven, which results in high reliability.

The IV results obtained by IVA® are in good agreement with the ISO 1628-3:2010 method, as can be verified in Figure 3, for a series of polypropylene samples with medium to high viscosity values, analyzed in TCB at 150°C.

An infrared (IR) detector is optionally incorporated 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, and can be dissolved in solvents that are IR transparent. An important group in this category are polyolefins, such as polyethylene and polypropylene as well as copolymers.

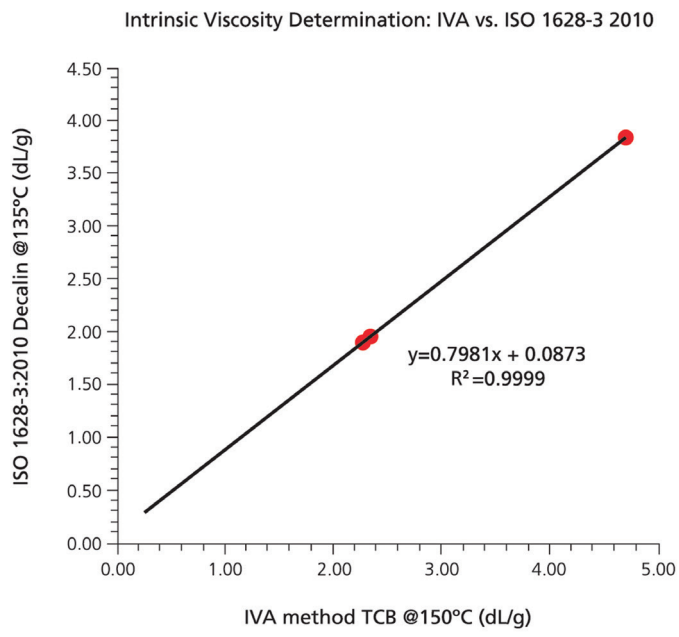

Figure 3. Correlation of intrinsic viscosity (IV) values obtained using the IVA® instrument compared to IV determined according to standard method ISO 1628-3:2010 for a set of polypropylene samples. IVA® was run in tri-chlorobenzene at 150°C, using solutions prepared at 1mg/mL; the ISO method was performed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

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 specific viscosity [η_{sp}] of the solutions.

Three different materials were analyzed at a low concentration level of 0.25 or 0.15 mg/mL in TCB, for limiting the viscosity of the solutions. 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.

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.

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

Other UHMWPE materials from industry, even with higher viscosities ranging from 30 to 50 dL/g, were also successfully analyzed in the IVA® instrument. The dissolution time was increased up to 3 hours and, in the extreme cases, the measurement flow rate was reduced in order to keep the backpressure in the system within acceptable range. The estimated molar mass averages from IV determination were in excess of 10 million g/mol, beyond the typical application range of high temperature Gel Permeation or Size Exclusion Chromatography (GPC/SEC). As it happens in many cases of industrial interest, viscometry was the only path to characterize and rank those products according to their molar mass.

Conclusion

A new fully automated Intrinsic Viscosity Analyzer (IVA®) has been developed to fulfill the need in the industry for an efficient, precise and safe approach to dilute solution viscosity determinations. A wide range of polymers soluble from ambient to 200°C can be analyzed in a variety of solvents.

The instrument performs all the needed steps without user intervention nor solvent handling throughout the whole process for up to 42 samples, paying special attention to the sample condition and minimizing degradation.

The two-capillary serial design is self-cleaning and self-calibrating, which ensures long term, robust and precise viscosity results, removing the need for manual rinsing or cleaning. When applicable, the IR detection helps in improving the accuracy and precision of the method. Measurement of intrinsic viscosities in excess of 30dL/g for UHMWPE was achieved with convenience.