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Advances in Polyethylene Analysis by NMR

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Introduction

Nuclear Magnetic Resonance (NMR) was first invented in the 1950s at Harvard University and Stanford University. Since then, the use of NMR has grown widely over the years in the areas of science, medicine, quality control and industrial process monitoring. The use of on-line NMR analysis for polyethylene (PE) production was first demonstrated in 1990 at multiple PE manufacturing sites in Canada. These initial installations included analysis of PE powder from a gas phase reactor and PE pellets from a solution reaction process. Since these pioneering efforts, more than 200 process NMR systems have been installed in the polyolefin industry worldwide. The most recent innovations in NMR technology have resulted in a third generation of process NMR systems. This latest technology further extends NMR as a powerful analytical tool and provides the polyethylene industry with the ability to measure real-time multiple polymer resin properties in powder or pellet form. The improvements have yielded faster analysis times, improved measurement resolution, greater on-line reliability, easier installation, and lower overall cost of ownership. These advances and the resulting benefits are outlined in this paper.

Early Process NMR Efforts

The first generation on-line NMR systems developed were used primarily in the agricultural industry and minerals industry. These large analyzer systems were engineered to be rugged for industrial use and had only basic NMR capability. However, they proved useful as a process technology due to the fact that calibrations were robust and stable over long periods of time (several years), and the system hardware was reliable.

NMR offers excellent operational performance because, unlike optical techniques, NMR measures the entire sample located in the probe and is not effected by color or particle size. In the next phase of technology development, significant configuration requirements were needed in order to utilize NMR technology in the polyolefin industry. In particular, challenging sampling handling requirements, safety requirements, and international certifications needed to be addressed. These challenges were resolved early in the development of process NMR systems. The resulting products were accepted by the polymer industry including polyethylene plants as reliable and effective tools that provided routine and accurate analysis of on-line PE resin properties. The first of these systems was installed at Dupont St. Clair River site in Canada (now Nova Chemicals). Commissioned in 1990, this industrial NMR analyzer has been in operation, 24 hours per day and 7 days per week, for more than 14 years performing more than 1 million on-line measurements with an estimated uptime of >98 %. Dozens of other second generation on-line NMR systems are still in operation and being supported by **progression, inc**.

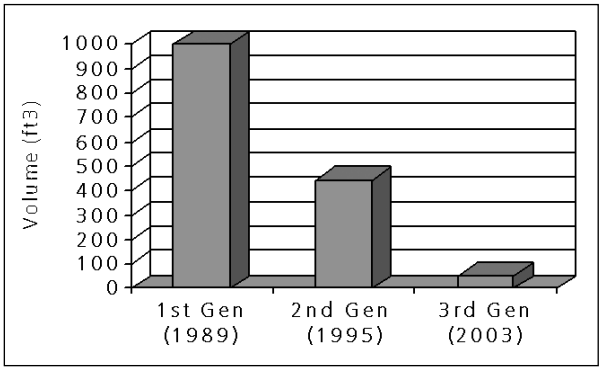

Figure 1: NMR system size reduction through innovation

Continued Innovation and Improvement

The team at **progression** is dedicated to the continued advancement and development of process NMR technology. Since the first generation technology introduction more than 10 patents have been granted in the area of process NMR related to polymers and other applications. These additional innovations have established the state-of-the-art third generation NMR for on-line polyolefin analysis.

As a result of electronic technology advances and re-engineering the physical size (volume) of process NMR systems has been reduced by 95%. This is shown in the graph of Figure 1.

Central to the many recent advances that have taken place is the improved data analysis methodology. **progression** has made vast improvements using the patented data analysis methods for translating raw NMR spectra from polymer samples to properties of interest such as density, crystallinity and melt index. These developments have led to 30% greater resolution of polymer property determination compared with the original data analysis techniques. An example of such improvement is shown in Figures 2 and 3. Figure 2 shows calibration performance for density using original (older) calibration methods. Figure 3 shows the same samples calibrated with the new data techniques. The methods for such data analysis are summarized in Appendix I.

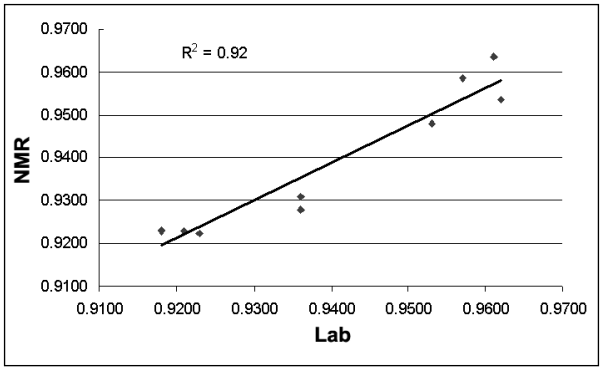

Figure 2: Density calibration using early methods

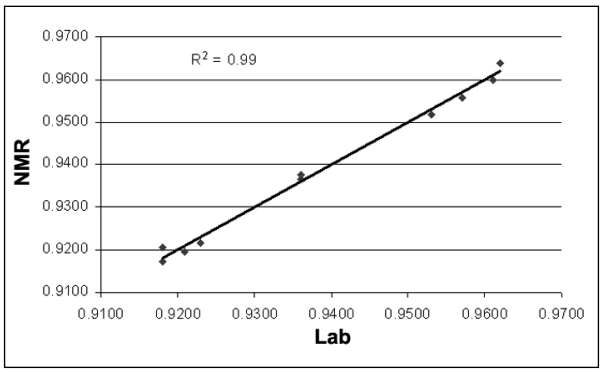

Figure 3: Density calibration using advanced data analysis

The resulting new NMR data analysis methods also yielded improved system repeatability performance as shown in Figure 4.

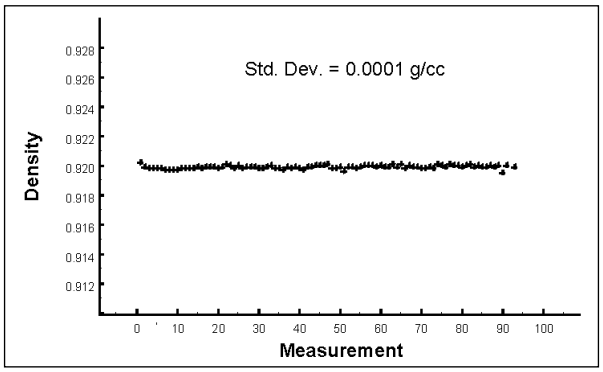

Figure 4: Standard deviation of repeat NMR density analysis

Other improvements and corresponding benefits of the third generation NMR technology are outlined in Table 1.

One such advancement is the ability to include an internal reference standard as part of a process NMR system. This internal reference can be used as an ISO test sample and automatically checked each shift or each week depending on the plant protocol. This development has helped **progression** customers to use process NMR technology for final classification and product release.

Advancement	**Benefit**
50% lower total	Economic payback improved by factor of 2
Internal reference standard	Useful for ISO qualifications and verification
Full bidirectional DCS communications	Improved plant integration
Internet/modem capable	Fast/low cost remote support
Open architecture software	Flexible for use with various APC platforms

Table 1

The innovation of the third generation system has been endorsed by an R&D 100 Award for the MagModule II™ on-line NMR technology. This international award is given by *R&D Magazine* to the top 100 most technically significant new products introduced in a given year.

Polyethylene Process Benefits

The use of process NMR has been demonstrated with most polyethylene production process technologies including the following:

- Borstar (Borealis)
- Horizontal Loop (USI)
- Hostalen (Basell)
- Innovene (BP)
- Lupotech G (Basell)
- Lupotech T (Basell)
- Mitsui CX
- Sclairtech I (Nova)
- Sclairtech II (Nova)
- Slurry Loop (ChevronPhillips)
- Spherilene (Basell)
- Tubular/ Autoclave
- Unipol (Univation)

In all cases, the analysis is non-destructive, and samples taken from the process (in either a powder or pellet form) can be returned back to the process. The key value to customers is that fast, reliable resin property data are measured directly on the polyethylene resin and used to improve real-time process control.

As a result, process NMR customers have been able to demonstrate vast improvements in reaction process control during transitions as well as improved consistency during steady-state operation. Users have also been able to reduce the traditional laboratory manual analysis in favor of automated real-time analysis. Process data examples are shown in Figures 6 and 7.

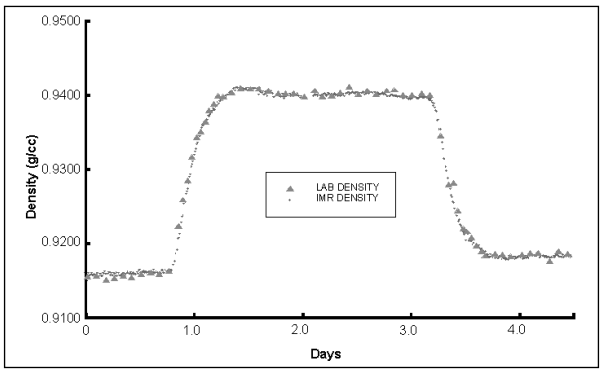

Figure 6: On-line density analysis by NMR compared with lab results

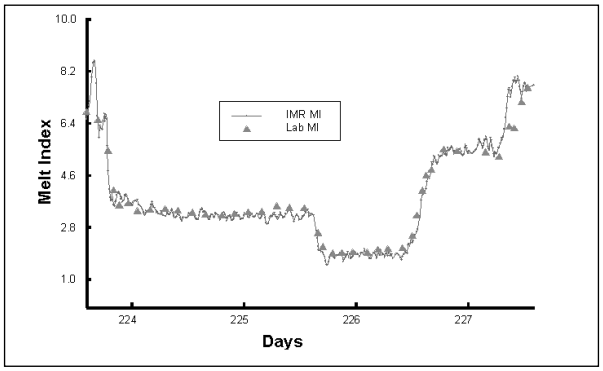

Figure 7: On-line melt index analysis by NMR compared with lab results

The simultaneous multi-property analysis is completed in about 6 minutes time. The analysis is done directly on a slip stream of resin taken from the process soon after the reaction. The ability to directly determine the resin properties by analysis of PE resin allows operators or APC systems to adjust process conditions more efficiently to optimize product properties and production parameters. This is especially evident during product transitions and any process upset conditions when the direct measurement of PE resin is most critical.

Figure 8 shows the improvement a commercial PE producer was able to achieve using the continuous feedback from process NMR to significantly reduce polyethylene Melt Index (MI) variance.

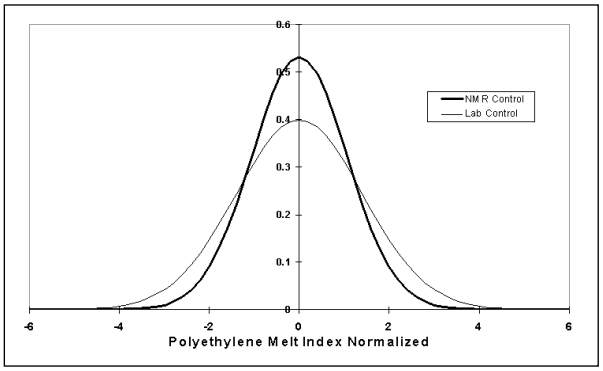

Figure 8: MI consistency improvement with NMR control

ASTM Crystallinity Method

New developments in process NMR have resulted in the growing interest of the direct measurement of polymer crystallinity by NMR. In fact a group of polyolefin producers in North America has initiated a new ASTM effort to promote NMR crystallinity as a new reference standard for the classification of PE, PP and other polymer materials. ASTM Subcommittee D20.70 has already drafted a method and is in the process of conducting industry-wide round robin testing during 2005.

Some NMR crystallinity data are shown in Figure 9. The data are generated using PE pellets from several PE process technologies. As expected the relationship between density and crystallinity is quite clear. The determination of polymer crystallinity by NMR is a direct measurement and requires no calibration. The technique measures the number of hydrogen protons of the polymer that are crystalline and those that are not crystalline. The percentage of crystalline material is then calculated directly. The analysis of polyethylene crystallinity can be added to all existing

process NMR systems supplied by progression with no hardware of software modifications.

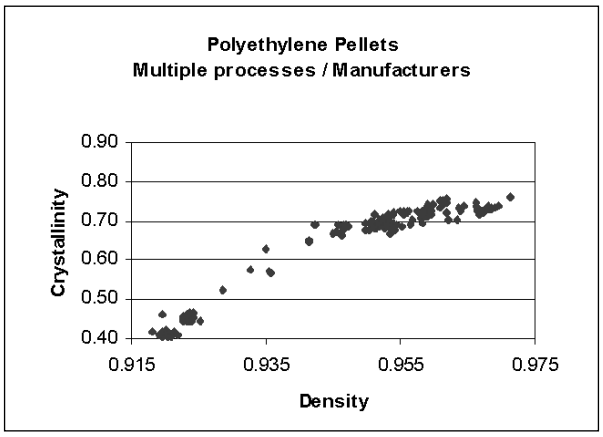

Figure 9

Summary

The advancements in PE analysis by NMR during the past 15 years have resulted in vast improvements in the state-of-the-art. These developments have provided greater performance in terms of resolution, number of properties measured and faster analysis times. In addition, the newer NMR technology has become more flexible with plant communications and smaller in physical size. These combined benefits with the lower overall cost have provided both new and existing PE production plants with an attractive process control tool to improve plant efficiency and overall operational profit. Process NMR is already widely used in the PE industry at the present time and will continue to grow in utilization due to these important advancements.

Appendix I
Magneflow Theory of Operation

The measurement of polymer properties is based on two fundamental properties of NMR:

1) The amplitude of the NMR signal is proportional to the quantity being measured.
2) The shape of the NMR signal is closely related to the morphology of the substance being measured.

The first property is the basis of most "benchtop" NMR systems, typically used in the food and agricultural industries (fat content measurements, oil in seeds, etc.) and the measurement of "spin finish" in the synthetic fiber industry.

The second property is of significance in the measurement of polyolefins, since polymer morphology is a fundamental important polymer property. Figure 10 shows the NMR signal of different polyethylene samples with different density values.

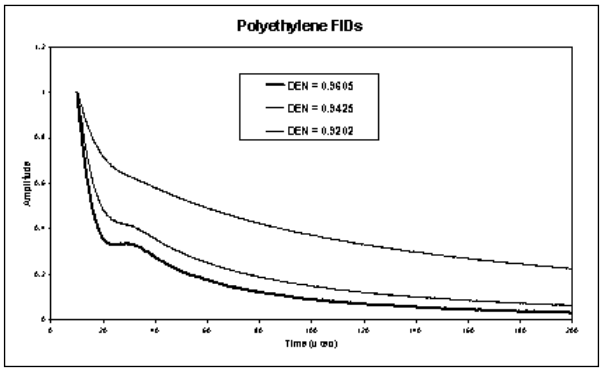

Figure 10

The shape of the NMR signal (known as a Free Induction Decay or FID), is very well understood in terms of how it reflects the morphology of the material. The NMR signals of crystalline material decay very fast, often in less then 20 microseconds. Amorphous material on the other hand, because of the more random and increased mobility of the molecules, decay much more slowly and in pure liquids can actually be several seconds long!

The analysis of low-resolution solid-state NMR signals is most efficiently performed using curve "deconvolution" or curvefitting techniques. NMR theorists have long known that NMR signals of polyolefins can be resolved into three main components:

1) Fast Gaussian
2) Slow Gaussian
3) Exponential

These are shown below in Figure 11.

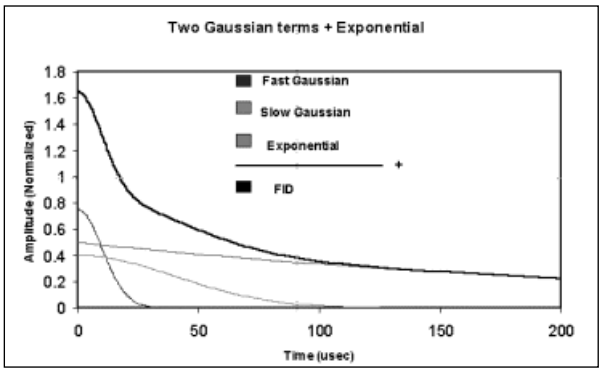

Figure 11: Typical polyethylene FID

The fast gaussian term represents the crystalline (isotactic) region of the polymer, whereas the exponential component reflects the amorphous (atactic) region. The slow gaussian curve depicts what is commonly referred to as the "interfacial" region.

This mathematical technique thus converts the NMR signal "shape" into a set of numbers reflecting amplitudes and time constants which are then be used in calibration procedures.

Calibration Techniques

The most effective calibration technique to correlate the changes in the NMR signal shapes to standard laboratory measurement values is the use of multi-variate regression analysis. Of these, the technique of choice is that of chemometrics using the PLS (Partial Least Squares) method. This is essentially the use of advanced statistical analysis, in which all the input variables obtained from the NMR measurements are used in combinations to yield the most effective regression model. This model is then used to predict resin properties of unknown samples.