Tribute to Giulio Natta: Industrial Chemisty

"R&D in polimeric materials"

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Ferrara took 3 years to industrialize Prof G. Natta discovery.
First world polypropylene plant was started in 1957, after 36 month of research and development, in the petrochemical complex present in the "Ferrarese" area.
In the polyolefin field this plant still historical benchmark for many innovation projects.

The plant was producing homo- and co- polymers at lower gum content, as of today only one reactor remains; it has been restored as monument and testimony of the brilliant initiative.

Annual polypropylene production is estimated in 33 million tons per year and still increasing by yearly 5%, well above actual GDP grow trend of the industrialized countries.

Research after the basic discovery had been the key factor for this enormous achievement, Basel R&D center in Ferrara, dedicated to G Natta, it was and still is a reference and the principal sponsor.

Catalytic systems that within the new generations increased the yield and the isotactic index came from a slow evolution of the product and process developed in the 60s & the 70s.

In particular the isotactic index was at the base of the primary evolution, if we can name it in that way, in fact modulus, impact strength of PP and its co-polymer is strictly related to the catalyst. Plant couldn't be simplify and its cost couldn't be reduced due to the high production of atactic by product.

A big step happened in the 70s with the 4th generation catalyst, which allowed thinking of a different type of process.
Yield and isotactic index allow to eliminate the solvent used to separate the by product and lower the cost.
Spheric morphology of the catalyst and of the polymer became the most important parameter for the advantageous design of the unitary processes.
The new born process based on these performances was the Sheripol. The commercial success of this technology since 1982 was astonishing: more then 90 plant had been build in the world leading to 49% volume of PP produced with this process.
Reason of the success was the lower investment cost, but also cost in use.
All the units for separation and recovery of the by product were eliminated together with the solvent.
The unstoppable expansion of the PP were in reality due to the new process and the new catalyst that allow to take advantage of the versatility of the polymer, enabling its utilization in more application specially for the property achieved with the control of the structure.

While Sheripol process hadn't reach is pivotal point, in the 90s the Catalloy process development begun.
This process consist in a system of 3 reactors in series that allow to utilize different polymer matrix with the objective to obtain polymers "alloy" "in situ."

The three gas phase reactors completely separated allow in series to obtain on the same particles different polymer compositions and to achieve extreme sophisticated targets.

The technological advantage is shown in the following slide, which demonstrates the wide range of property of the polymers versus traditional process.
In specific, the automotive sector, known for its high technological content, got the main advantage for this technology, bringing to 40 kg the content of PP per car produced.

In the second part of the 90s base research on catalyst had been never stopped, even with the leadership obtained with the 4th generation ones, although it enlarged the field of structures that could be obtained finding again two different catalytic systems, di-ether and succinates, which still under industrial development in this years.
Basic research on catalyst stills the engine for developing PP even after 50 years.

Research in parallel with the catalyst, better taking advantage on it, in the second half of the 90s give itself a very ambitious target: overcame the Spheripol process.
A new reactor type, never applied with polyolefin has been taken in consideration: gas phase recirculating bed.
This moved the base exigencies from mechanical simplicity and low energy consumption to the ability to build up “a material with a new principle”: polymer does not pass two reactors in series, but recycled in two zones of the same apparel at different reaction composition.
The scheme conceptually overcame the previous technology reducing the domain of material generated per cycle favouring product homogeneity.
The two zone connected are riser and downcomer (or downer).
Each zone has its own fludodinamic and though a barrier fluid different gas composition can be obtained leading to a generation of different material.

Increasing the frequency of the cycles, so the passage between both ambient, ease the capacity to obtain more uniform, homogeneous materials with better property. New process has been named Spherizone.

Today the Spherizone process in its complete aspect, which include gas phase reactors at the end of the principal one is an industrial reality in Brindisi, where the first Spheripol, built in the 1982, has been retrofitted to achieve 160 kt/y with this new technology.

Driving force for the research was again the expansion of property of PP.
Changing to Spherizone, with the new catalytic systems, rigid characteristics, ratio impact/rigidity, creep, melt strength, can be increased enormously.

The new technology, Spherizone, have the potential to allow another development in the market of the PP resins, renewing more traditional application such as BOPP and fibres.

The following slide shows the current range of expansion of PP, that can be reach with this technology: new range of products, as the utilization of resins already developed with previous technology: a variety and a combination of different property in continuous development, something that 20 years ago wasn’t imaginable.

The technology evolution has been the undoubtedly the engine of the development of PP, as shown in by the increase utilization of this material in Europe in the last 20 years, following the research breakthrough as Spheripol and subsequently the Catalloy.
In fact PP have more then double the presence in the principle segment of the market.

The subsequent slides demonstrate how PP is the most used product versus the fractionation of the other plastics types. As testimony of its versatility, the capacity to satisfy market request: cost, performances, workability.

I would like to conclude showing the milestones that the research centre in Ferrara, dedicated to G. Natta, has achieved in the polyolefin field with continuity since the years of the discovery; I believe the best gift from Ferrara's researcher to his memory.

Tribute to Giulio Natta – Milano, October 6th 2003

"Development of research and new technologies in the field of polymeric materials"

Ing. Massimo Covezzi, Basell Poliolefine Italia S.r.l.

The Polypropylene (PP)

Polypropylene (PP) – Thermoplastic resin obtained by propylene polymerization.

PP has a wide range of properties and is used in the sectors of packaging, house accessories, fibers, films and also in automotive and electric industries.

The three main PP families are:

- Homopolymer: characterized by high thermal resistance and good stiffness, useful in a wide range of applications;
- Heterophaic copolymers, obtained by incorporation of several comonomers; they have good impact strength performances and are opaque;
- Random copolymers, obtained by the introduction of ethylenic bonds in the polymer chain; they have good optical properties, useful in transparent packaging.

Types of Polypropilene Products (PP)

Moplen, Pro-fax

- Homoplymer polypropylene, random copolymer and copolymer with an high impact, based on Ziegler-Natta catalyst

Metocene

- Family of resins based on single-site metallocene catalysts

Adstif

- Polypropylene with high crystallinity and high stiffness

Clyrell

- Highly transparent polyolefinic resins with an high impact strength

Pro-fax Ultra

- High performances polypropylene resins

Advanced Polyolefins (APO)

Advanced polyolefins (APO) – Family of advanced Basell polyolefins with a wide range of applications.

The two principal APO families are:

- Compounds: obtained with a variety of additives: rubber that confer softness and elasticity, talc and mineral charge that confer rigidity, glass fibers that confer stability and heat resistance.
- Catalloy resins: directly obtained in the reactor; they are polymeric alloys (not mixtures) and are more homogeneous than compound. They grant better performances, better workability and recycling.

Types of Advanced Polyolefins (APO)

Catalloy resins

- Available with the commercial name of Adflex, soft and flexible, and Adsyl, low temperature welding resins. They can be soft and flexible, but also strong and stiff.

Hifax

- Materials with an high impact strength. Materials for external applications on cars, including materials for bumpers (HSBM). Materials for cables and yarn and applications which need fire-proofing properties.

Hostacom

- Materials strenghthened with glass fibers and mineral charges. Materials designed for hose hold appliances. Materials to be used for internal parts and under bonnet in cars construction.

Types of Advanced Polyolefins (APO)

Hostalen PP

- Materials based on high molecular weight polypropylene, used for pipes and slabs.

Poly(1-butene) (PB-1)

- Seal-peel resins, used for the modification of films, for heat adhesive and generally for the modification of polyolefins. Such resins are also used in piping.

Moplen

- Product suited for covering by extrusion.

Types of licensing & Catalysts Products

Process technology

Spheripol

- Process for the production of polypropilenehomopolymer, random and heterofasic copolymer

Spherilene

- Gas phase process for LLDPE and HDPE production

Hostalen

- Slurry process at low pressure for mono- and bimodal HPDE production.

Lupotech T

- Process with high pressure tubular reactor for the production of homopolymer LPDE and copolymer EVA.

Lupotech G

- Fluidized gas phase process for LLDPE and HDPE production.

Types of Licensing & Catalyst Products

Catalysts

Avant ZN

- Titanium high yield Ziegler-Natta catalysts for highly stereoregular polypropylene production.

Avant Z

- Titanium high yield Ziegler-Natta catalysts for the production of linear low- and high density polyethylene with a large/narrow molecular weight distribution.

Avant C

- Chromium catalyst for high and medium density polyethylene production.

Avant M

- Zirconium metallocenic catalyst for polypropylene and polyethylene production.