Hyperzone PE Process Technology
A new polyethylene technology for the plastics industry

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Abstract

LyondellBasell introduces a new polyolefin process, *Hyperzone* PE Technology, which produces high density polyethylene (HDPE) resin with exceptional characteristics. This technology utilizes three distinct reaction zones in two reactors, which enables the production of tailored polymer structures to meet customers' demanding processing and product requirements. LyondellBasell is currently constructing a world-scale *Hyperzone* PE plant at our La Porte, TX facility with an annual capacity of 1.1 billion pounds (500,000 metric tons). Start-up is planned for 2019.

Introduction

For over 70 years, LyondellBasell and its predecessor companies have developed new products and processes that serve as the bedrock of the chemical industry. LyondellBasell is the global leader in the development and licensing of polyolefin processes and related catalysts.

Today's global annual polyethylene consumption is about 100 million metric tons, which continues to grow above GDP levels in the coming years. Polyethylene will continue to be the most widely used plastic resin in the world, benefitting from its low costs, easy processability and recyclability. Continuous innovation in polymerization catalyst performance as well as improved polymerization process technology will further drive polymer product performance.

Of all 3 main polyethylene segments (LDPE, LLDPE and HDPE), HDPE is the most widely used resin. Major applications like high molecular weight film, blow molding, injection molding and pipe have strong global demand.

The HDPE markets have evolved in history due to the capabilities of the different catalyst technologies. The vast majority of the HDPE products are produced by either chromium or Ziegler Natta catalysts. Ziegler Natta based commodity products like high molecular weight film, injection molding and small blow molding offer superior mechanical properties compared to their counterparts based on chromium catalysts. The products based on Ziegler Natta catalysts tend however to show a narrower processing window, caused by either the different rheological behavior or lack of homogeneity of the product. HDPE commodity and specialty resins are typically produced in a single reactor as well as in a cascaded reactor setup. HDPE commodity resins based on chromium catalysts show excellent processability on customer machines, but suffer from rather poor mechanical properties in case of high molecular weight film or an inferior resistance against environmental stress cracking (ESCR) in case of blow molding products. Specialty HDPE resins based on chromium catalysts like products for plastic fuel tank, intermediate bulk containers (IBC) and tight head drum are valued by converters due to the excellent processability and surface finish and show a good ESCR/impact balance. Ziegler Natta specialty HDPE products such as for pipe and caps and closures show an excellent ESCR/impact balance combined with good processability during extrusion. Here multimodality is key to obtaining this balance of properties, which is achieved using a reactor cascade setup.

Hyperzone PE technology is a new technology that will be able to serve all HDPE markets using LyondellBasell proprietary Ziegler Natta catalyst technology.

Reactor technology

The *Hyperzone* PE technology consists of a reactor cascade of 2 gas phase reactors. The first reactor is a fluidized bed gas phase reactor where the low molecular weight fraction of the final product is produced. The product leaving the first reactor is discharged into a MultiZone Circulating Reactor (MZCR), which produces the medium and high molecular weight fractions of the product. Comonomer is fed to the process to control the final density and stiffness of the product and can be targeted to the high molecular weight fraction of the product to obtain superior ESCR performance, see figure 1.

The fluidized bed reactor combined with the MZCR enables the *Hyperzone* PE process to produce multimodal HDPE products using only 2 reactors in cascade. The MZCR reactor is a circulating fluidized bed reactor combining a riser operating in fast fluidization regime and a downer operating as a packed moving bed. At the top of the downer, a barrier can be introduced allowing to operate the riser and downer at a different gas composition thereby producing a different molecular weight in each reactor zone, figure 2.

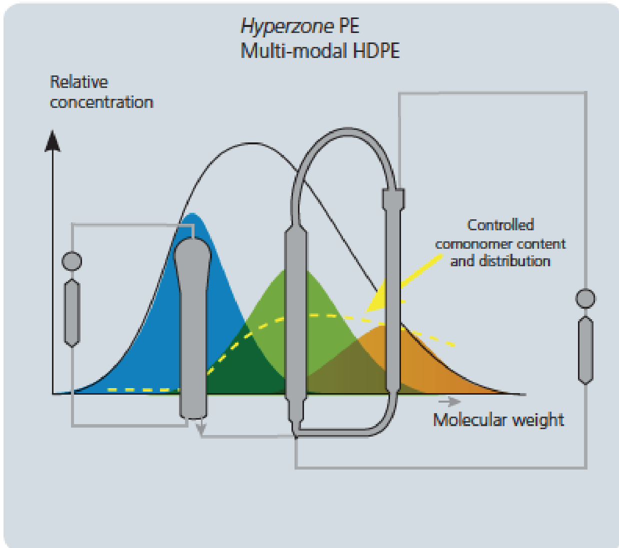

Figure 1. Unique 3 in 2 cascade reactor setup.

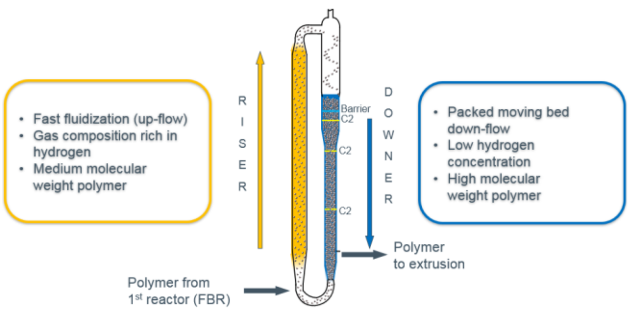

Figure 2. Functioning of the MZCR.

The concept of the MZCR reactor was first introduced by LyondellBasell for the *Spherizone* PP process [1], where the MZCR serves as first reactor in a reactor cascade to produce high quality PP products.

The MZCR reactor addresses a key weakness of traditional cascaded processes, such as Innovene S (Ineos), Hostalen (LyondellBasell), BorStar (Borealis) and Martech ADL (CPchem). All these processes consist of a reactor train of 2 or more reactors, each of them operating at different temperatures, pressures, hydrogen concentration, solids concentration, average residence time, etc. The reactors used in these technologies (loops, fluidized beds and stirred tank reactors) can be considered as continuous stirred tank reactors (CSTR). Therefore, the catalyst which is fed to the first reactor of the cascaded setup, will experience a residence time distribution in each reactor. This means that the composition of the particles leaving the last reactor of the cascaded setup, will have an intrinsic inhomogeneity, see figure 3. Since the molecular weight of the polymer produced in each reactor can be very different, such products risk to have gels or non-molten material in the final product. Since polymer particles produced in the MZCR circulate around the riser and downer, an intimate mixing of both materials is achieved. Layers of these different fractions build up with each pass around the reactor, resulting in a homogenous dispersion of the very-high molecular weight fractions with the rest of the material. Operating the MZCR of the *Hyperzone* PE process in monomodal mode, could lead to a similar homogeneity challenge as traditional cascaded processes. However, most of the *Hyperzone* products are produced using the full potential of the *Hyperzone* PE process and products produced with this setup at large scale pilot plant level have demonstrated a superior product homogeneity. Product homogeneity plays a key role for HDPE applications, since it impacts surface finish but also helps to exploit the full potential of the broad molecular weight distribution.

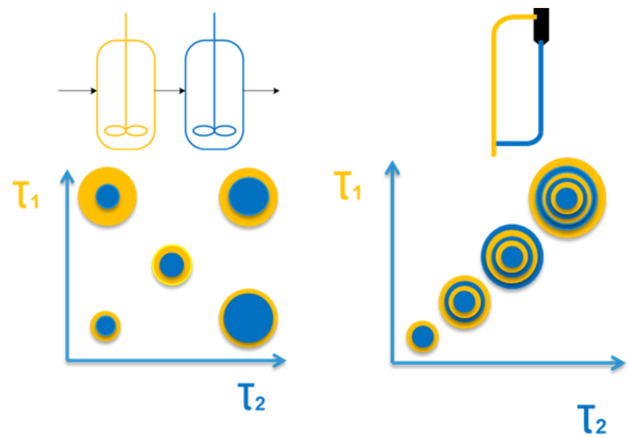

Figure 3. Intrinsic homogeneity due to reactor setup.

Polymer powder flowability, polymer size and bulk density plays a crucial role in the operation of the polymerization technology. In the downer solids concentrations close to the bulk density of the polymer are achievable. In the riser, operating under fast fluidization conditions, solids concentrations of 40% can be obtained. Polymer is discharged from the bottom of the downer where the polymer density is the highest thereby minimizing the energy required for recovering the discharged gasses. The reactor, being it essentially two interconnected pipes, has a higher efficiency of reactor volume compared to a traditional fluidized bed reactor due to the absence of a reactor dome. The riser of the reactor has a limited temperature gradient due to the high level of back mixing. This is in contrast to the downer, which operates essentially in adiabatic mode. The temperature in the bottom of the downer can be controlled by applying an appropriate solids circulation rate. Liquid injections at the top of the downer as barrier and along the downer to disperse additional ethylene feeding points further facilitate the removal of reaction heat.

The functioning of the barrier injected at the top of the downer is explained in figure 4. In the downer, polymer powder flows downward as a packed bed. The pressure balance of the MZCR is operated in such a way to ensure gasses in the downer will move downward as well. In case no barrier would be fed to the downer, the hydrogen concentration in the riser and downer would be essentially the same. In case a barrier is fed, the MZCR can be operated in a multimodal way allowing the polymer particles to grow in the downer at a much lower hydrogen concentration. By selecting the proper split of reaction between the fluidized bed reactor, riser and downer as well as hydrogen concentration in each reaction zone, a tailor made molecular weight distribution can be generated for each product application.

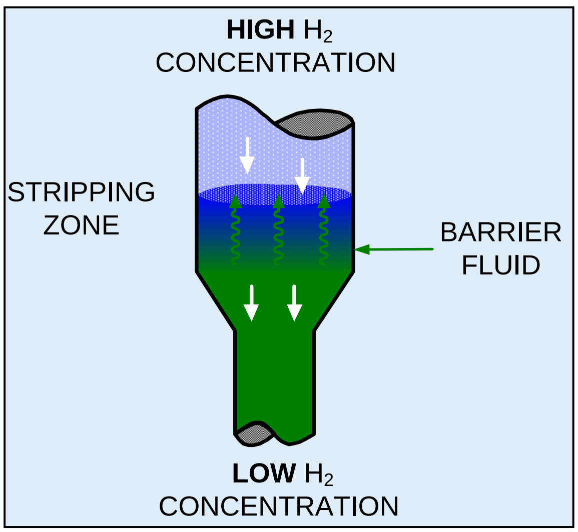

Figure 4. The barrier concept.

Pushing the boundaries of HDPE product properties

The great flexibility of the *Hyperzone* PE technology to control the molecular weight distribution as desired, targeted comonomer distribution as well as a step change in product homogeneity has been demonstrated at large scale pilot plant level. Products for all major HDPE applications have been developed and tested at customers.

In the blow molding segment, products have been developed that show an outstanding ESCR/Stiffness/ Impact balance combined with proven processability on all typical extrusion blow molding platforms. Figure 5 shows an example of the ESCR performance of the *Hyperzone* IBC grade versus the current bench mark grade based on a chromium catalyst system. *Hyperzone* PE offers the possibility to control the weight swell of the resin, thereby designing a resin with more forgiving wider die gaps if desired by the customer. The *Hyperzone* resin offers not only a very low gel level and higher ESCR performance but also higher stiffness, higher impact resistance at higher HLMI (i.e. improved processability). This combination allows the customer to run lower cycle times and at lower weight of the final article for the same functionality.

Figure 7 shows the ESCR performance of a small blow molding grade versus the chromium benchmark grade in the market. Again, the superior ESCR performance while keeping the processability similar to the ones customers used to see for such chromium grades, see figure 8. Bimodal small blow molding grades based on Ziegler Natta catalysts typically offer great ESCR performance over chromium based grades, but typically don't process well on high shear reciprocating blow molding machines. Internal and external trials on all typical equipment used in the industry has shown that *Hyperzone* blow molding resins show a processability comparable to that of a typical Chromium based resin combined with a very low gel level for a smooth surface finish.

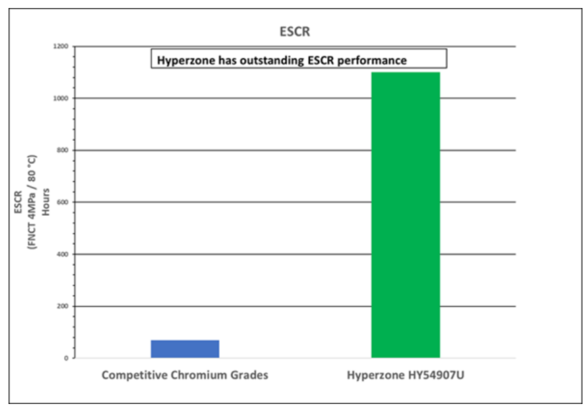

Figure 5. ESCR performance of the *Hyperzone* IBC grade versus chromium based bench mark grades.

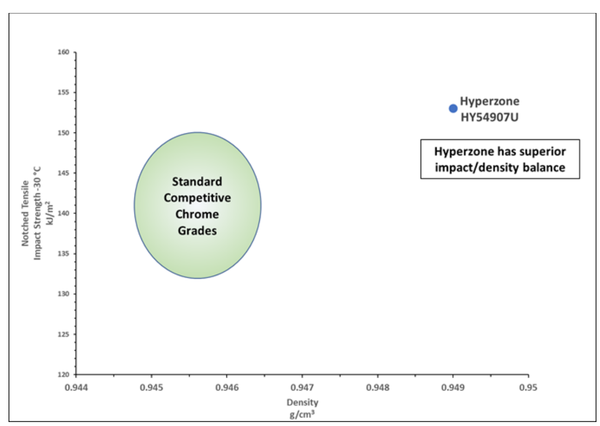

Figure 6. IBC Impact / Stiffness performance versus chromium based bench mark grades.

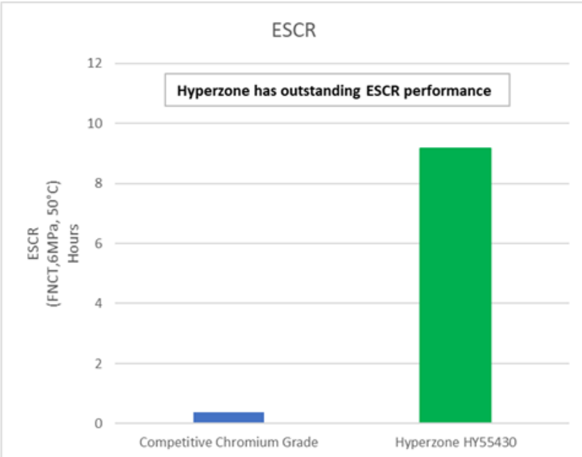

Figure 7. ESCR performance versus the chromium based small blow molding bench mark grade.

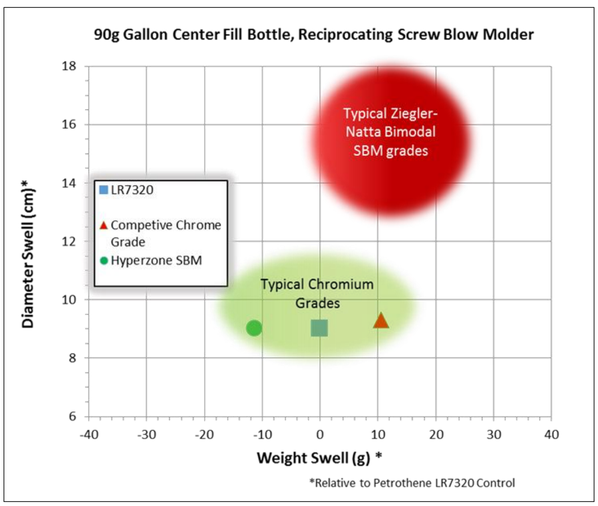

Figure 8. Diameter Swell versus the chromium-based bench mark grades as well typical Ziegler Natta bimodal grades.

Another important product segment to be addressed is pressure pipe. HDPE material have been dominating this market due its outstanding slow crack growth resistance (SCGR) / Impact / Creep balance. *Hyperzone* introduces a new product for pressure pipe applications that combines good SCGR performance (figure 9), good processability and a step out resistance to rapid crack propagation (figure 10).

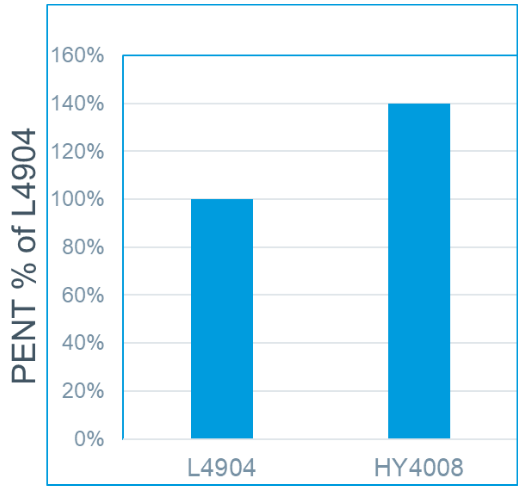

Figure 9. SCGR performance versus *Alathon* L4904.

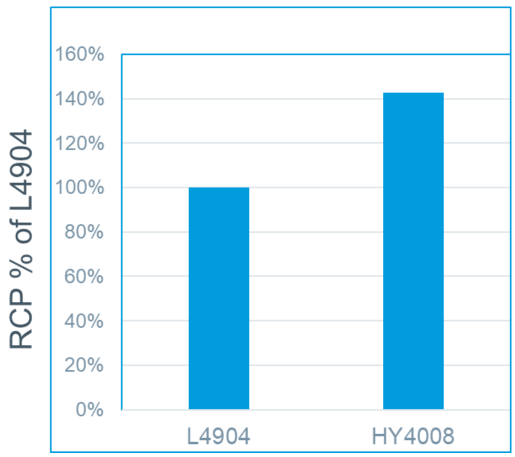

Figure 10. Resistance to rapid crack propagation versus *Alathon* L4904.

Conclusions

Hyperzone PE is a new HDPE technology that combines a unique set of reactors capable of stretching the envelop of product capabilities. LyondellBasell is currently constructing a world-scale *Hyperzone* PE plant at the La Porte, TX facility with an annual capacity of 1.1 billion pounds (500,000 metric tons). Start-up is planned for 2019.

References

1. M. Covezzi, G. Mei, *Chemical Engineering Science*, **56**, 4059 (2001)