Advanced Ziegler-Natta catalyst tools to empower polypropylene innovators

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Abstract

GRACE has developed advanced internal donor, external donor, support and process aids technologies that afford enhanced value for polypropylene (PP) producers, converters, brand owners and ultimately consumers. These advanced Ziegler-Natta (ZN) building blocks make possible innovation in the polypropylene (PP) industry to address the needs of the highly complex PP market. This presentation reviews some of these technologies and showcases how GRACE ZN catalyst technology enables innovative product features such as ultra-high clarity thermoformed parts, low temperature no-break and high MFR reactor TPO injection molding grades for automotive and low blooming injection molded articles for packaging applications.

Introduction

W.R. GRACE (GRACE hereafter) is the leading third party PP catalyst supplier licensor of polypropylene (PP). This leadership position is the result of targeted acquisitions that have afforded the broadest catalyst portfolio in the industry and, most importantly, because of GRACE's relentless commitment to catalyst innovation that can enable our customers globally. In this connection, GRACE's innovation approach is to understand and address market needs. In the SPE PO 2015 Conference, we presented GRACE's four market themes pictorial that has become our innovation compass [**1**] for catalyst development efforts. Figure 1 shows those four innovation themes that revolve around developing: (i) stronger materials that enable down-gauging (lighter theme); (ii) materials with rheological features that make it possible to increase fabrication rates (faster); (iii) materials with less catalyst residuals, lower Volatile Organic Compounds (VOC) content, lower taste and odor by avoiding peroxide cracking and non-Phthalate based (cleaner); and (iv) materials with higher transparency (clearer). These themes are still the dominant innovation drivers in 2016.

Market drivers are a key part of the innovation process, but technology capability is critical to being able to provide solutions that enable PP producers, converters and brand owners. In this regard, GRACE has developed a ZN catalyst technology platform that enables catalyst innovation to address market known and unknown needs.

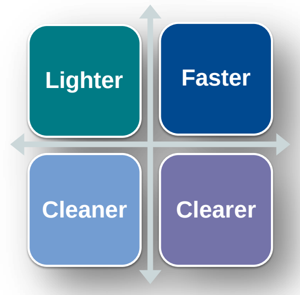

Figure 1: Innovation themes that drive the PP industry since 2005 (market research by GRACE).

This paper discusses tools that GRACE uses to enable catalyst technology development and provides several examples of PP innovation enabled by GRACE catalyst technology.

GRACE ZN Tools

GRACE has built a PP catalyst innovation tool box over the last 10 years that has made us the leading third party supplier globally. Figure 2 shows a high level view of the tool box that GRACE uses to address product needs for different applications and process requirements for the different processes used by PP producers (UNIPOL® PP, SPHERIPOL, INNOVENE, NOVOLEN, HYPOL, SPHERIZONE …). Some more details of these options are provided later in the text. The selection of catalyst components has a substantial influence on PP products that can be made and also on the operability and the cost in use of the PP manufacturing units. Regarding the former, how the catalyst is built will influence MFR capability, isotacticity range, Molecular Weight Distribution (MWD), ethylene-propylene rubber (EPR) content capability and ethylene distribution. Catalysts can be assembled to address the commodity markets, or differentiated spaces or both (the ideal concept of one catalyst for all applications). In relation to how the catalyst components listed in Figure 2 can affect plant operability and cost in use, this is done by tailoring catalyst productivity, catalyst life time and catalyst particle size.

The internal donor captures much of the attention of research groups in academia and industry. It is certainly a key element of the ZN technology, but other elements (support, external donors and process aids) are also critical to providing the desired performance. GRACE has developed internal donor technology that is considered as the 6th generation catalyst platform because of very high productivities, broad XS capability, excellent H_2 response and best in class operability. This platform was discovered by using high throughput tools that have allowed GRACE to have access to an extensive library of internal donors that will enable constant innovation in years to come. Figure 3 shows a “shotgun” plot of polydispersity index (PDI) versus XS that includes a large number of the internal donors in the GRACE library and highlights the ability that GRACE has to be the industry leading innovator. The CONSISTA® catalyst commercialized in 2012 for the UNIPOL® PP process is one of the points in this plot. It should be noted that all internal donors in Figure 3 are non-phthalate in nature.

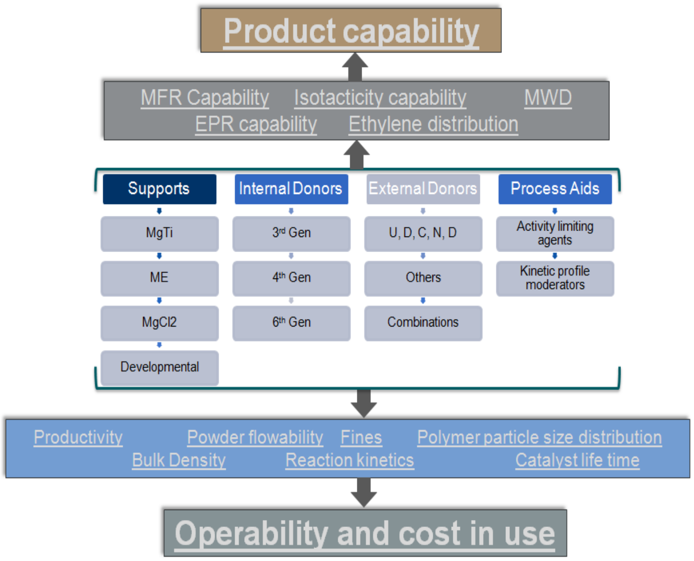

Figure 2: GRACE catalyst innovation tool box and product and process properties impacted.

Other recent innovations that are also very exciting from an innovation perspective is the discovery activity moderators that provide high flexibility to meet the needs of different processes used in the industry.

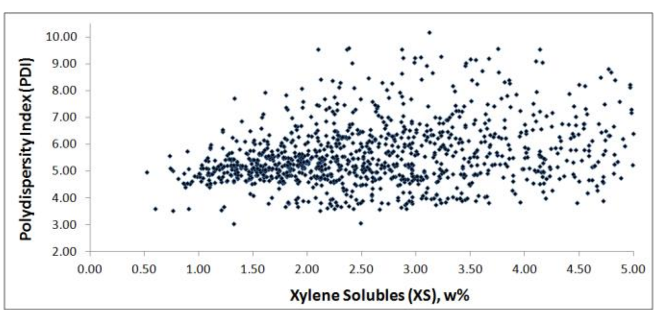

Figure 3: Shotgun plot that shows GRACE’s internal donor capability. All internal donors in this plot are non-phthalate in nature.

Showcases

Ultra-clear PP thermoformed articles

The food packaging industry is looking for PP offerings that can provide enhanced clarity and top load of thermoformed articles to compete with PET. The main drivers for this interest are that PET has very high density and it is difficult to process.

Ethylene random copolymers (e-RCP) do not seem to meet the requirements that are given in Figure 4 for a deep drawn article (cup). Grace has developed a butene random copolymer (b-RCP) based on 6th generation catalyst technology to address this market need. The key working hypothesis for this development work is that GRACE’s 6th generation catalyst affords a more random distribution of both comonomer which translates into smaller crystal domains that translates into lower haze. In addition, b-RCP affords higher modulus which translates into higher top load.

Figure 5 shows the results obtained for a number of e-RCP and b-RCP with and without clarifier. It is important to note that thermoformed cups were made and analyzed at the Milliken Research Center in Spartanburg, South Carolina (see Appendix for details). As can be seen from Figure 5, only the cups made with clarified b-RCP fall inside the performance requirements of this development.

This enhanced behavior could be explained as a result of the pending ethyl groups in b-RCP been more prompt to participate in the lamellar crystalline phase rather than in the amorphous phase which can result in faster crystallization rates vs e-RCP. Faster crystallization rates can help freeze the orientation introduced during the thermoforming step which, in turn, can translate into increased modulus. In addition, the presence of advanced clarifiers can decrease crystal size to sub-micron levels, which combined with a lower concentration of amorphous phase can lead to enhanced haze. The latter effect could be related to a lower concentration of refractive index change interfaces.

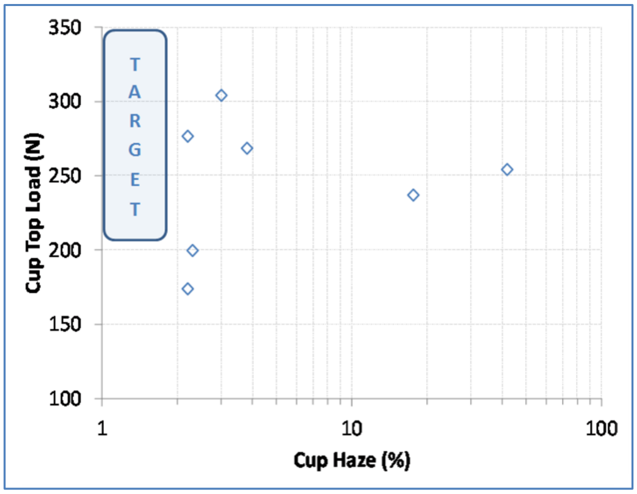

Figure 4: Pictorial representation of target cup top load and haze. The blue diamond's correspond to cups produced with commercial ethylene random copolymers (e-RCP).

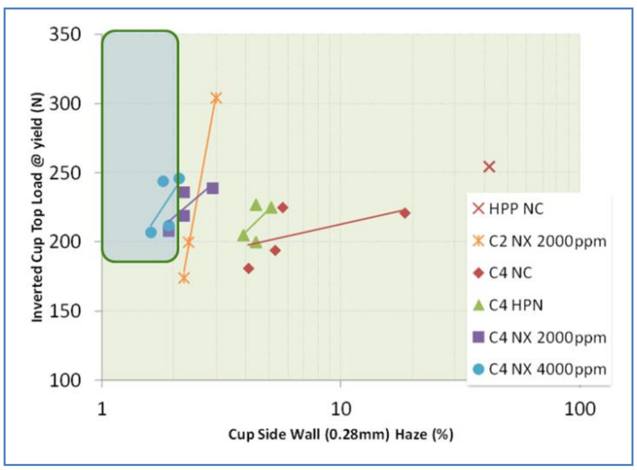

Figure 5: Cup top load versus side wall haze for the different prototypes tested in this development study.NC = no clarifier; HPN = HPN 600ei; NX = NX8000; C2 = ethylene-RCP; C4 = butene-RCP.

High MFR in-reactor TPO's

One of the trends in the automotive industry is high melt flow rate (MFR) in-reactor TPO to enable shorter injection molding cycle time of large intricate parts. TPO is defined here as an impact copolymer (ICP) that shows no break behavior. The no break requirement is temperature dependent and the industry speaks about room temperature, 0 °C, -20 °C and -30 °C no break performance. The main design parameters for no-break performance are EPR content (EPR^c) and EPR particle size distribution. EPR^c is limited by powder flowability that is controlled by catalyst technology and process hardware considerations. In this example, EPR^c is limited to 33 w%. The EPR particle size distribution is controlled by thermodynamic and kinetic factors. The latter relate to the compatibility of the two phases which can be moderated by adjusting the ethylene content in the EPR and the former depends on shear forces in the extruder and viscosity differences between rubber (discontinuous) and matrix (continuous) phases. This has been described generically by Taylor's empirical relationship of domain break up (eq. [1])

$$d \propto \frac{G}{\gamma} \frac{\eta_R}{\eta_M} \qquad \textbf{...[1]}$$

Where $\underline{d}$ is the EPR average particle size, $\underline{\eta}$ is the EPR (R) or the matrix (M) viscosity, $\underline{G}$ is the HPP/EPR interfacial tension and $\underline{\gamma}$ is the shear rate. The viscosity ratio η_R/η_M can be converted to a ratio of the TPO MFR (MFR^T) and the MFR of the matrix (MFR^M) and this ratio is denoted in this paper as β/α ratio.

Figure 6 shows the master lines of MFR^T versus MFR^M for different β/α ratios. The typical β/α working range is from 1 to 3 with most products being in the 1.5 to 2.5 bracket. It is apparent from this Figure 6 that a $MFR^T = 20$ g/10 min will require a MFR^M of 20 g/10min for $\beta/\alpha = 1$, of ~ 40 g/10min for $\beta/\alpha = 2$ and of ~ 100 g/10min for $\beta/\alpha = 3$. Higher MFR^T will demand even higher MFR^M. To make this kind of MFR^T, it is necessary to use a catalyst with enhanced MFR response. The Grace 6th generation catalyst platform provides this capability and enables high MFR^T in-reactor TPO. Figure 7 shows the room temperature izod as a function of MFR for a number of 6th generation catalyst based r-TPOs at three β/α ratios (modeled values obtained from empirical correlations). All these r-TPO's in Figure 7 exhibit the same EPR^c (33 w%).

It appears from Figure 7 that room temperature no-break r-TPO's having a MFR as high as 30 g/10 min can be produced with GRACE catalyst technology.

Low blooming technology e-RCP

The third and final showcase included in this paper is the development of low blooming RCP technology for food packaging applications. Blooming is a thin layer of chemical products that migrate to the part as a function of service temperature and time. The research work done for this development showed that blooming is primarily related to PP oligomers and other ethylene-propylene chains and not to additives used in this application. This thin layer changes the optical properties of the part (increases haze) and this is the way performance is measured (see additional details in Appendix). The GRACE 6th generation catalyst enables the control of XS in RCP to achieve ratios of XS to ethylene content (Et) (XS/Et) even < 1 at certain Et levels. Figure 8 shows the level of haze change after treating molded parts to 55 °C temperature for 24 hours as a function of the XS/Et ratio. A haze change of 15 % is considered acceptable by brand owners in this application. space. As can be seen from this Figure, the RCP materials that fall within the acceptable range are those with an XS/Et ratio < 1.5.

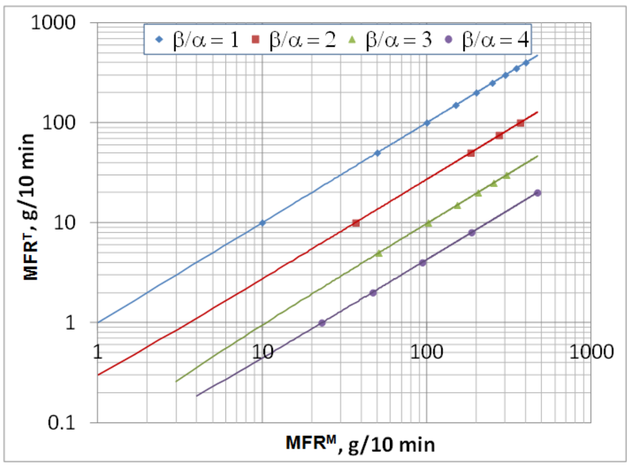

Figure 6: MFR^T versus MFR^M for different β/α ratios.

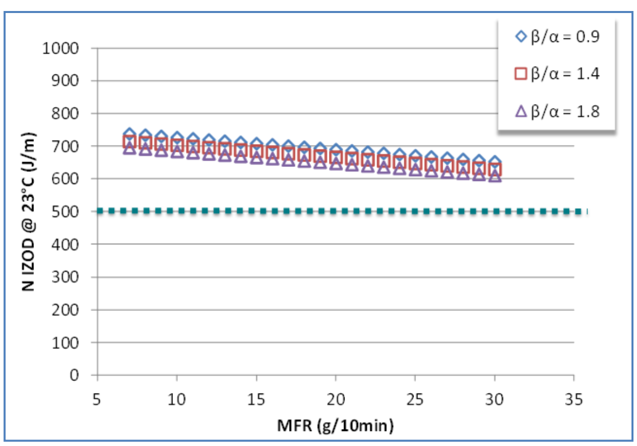

Figure 7: Room temperature izod as a function of MFR for modeled r-TPO's (empirical correlations done on 6^{th} generation based TPO's). EPR^c is 33 w% for all modeled systems in the graph.

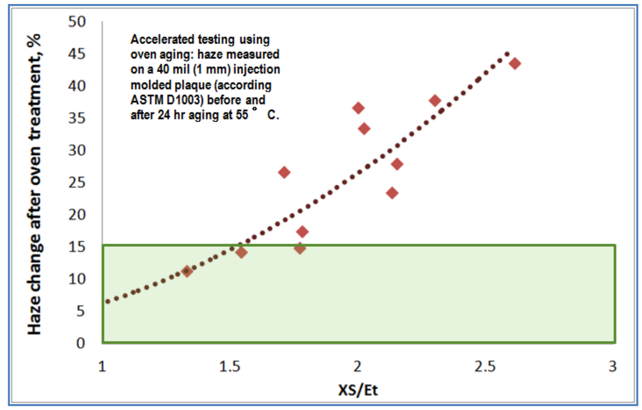

Figure 8: % change in haze after oven treatment as a function of the XS/Et ratio for different RCP prototypes studied in this showcase.

Conclusions

Grace has developed advanced internal donor, external donor, support and process aids technologies that afford enhanced value for PP producers, converters, brand owners and ultimately consumers. These advanced ZN building blocks make it possible to address the needs of the highly complex PP market. This presentation showcased how GRACE ZN catalyst technology enables innovative product features such as ultra-high clarity thermoformed parts, low temperature no-break and high MFR reactor TPO injection molding grades for automotive and low blooming injection molded articles for packaging applications.

Acknowledgements

The authors would like to thank Milliken for making available to GRACE their sheet extrusion and thermoforming lines as well as testing labs for the development work of the ultra-clear RCP.

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Appendix

Raw materials

R-TPO, e-RCP and b-RCP were made in GRACE pilot plant set ups.All materials were formulated with anti-oxidants (Irganox 1010 and Irgafos 168) and an acid scavenger (calcium stearate or ZnO or DHT4A). HPN 600ei and NX8000 were kindly provided by Milliken. Additives were dispersed in the polymers using lab twin screw extruders.

Methods

Properties tested are shown in Table 1 as well as the standard methods used. The r-TPO and low blooming projects testing was performed in GRACE Labs.

Table 1: Properties tested and test methods

Property	Method
Flexural Modulus, MPa	ASTM D790
Notched Izod Impact, J/m	ASTM D256
MFR, g/10 min	ASTM D1238
XS, w%	ASTM D5492
Haze in injection molded plaques	ASTM D1003

XS were measured with a Viscotek instrument equipped with Flow Injection Polymer Analyzer. Sample preparation is very similar to what is described in the ASTM method D5492.

Ethylene content in the r-TPO, b-RCP, and e-RCP, ethylene content in the r-TPO EPR and r-TPO EPR content were measured with FTIR methods developed for GRACE catalysts systems.

Blooming on e-RCP 1 mm plaques was measured by placing the molded plaques in an oven at 55 °C for 24 h and measuring haze before and after the oven treatment and calculating the % change.

The b-RCP thermoforming work was conducted at the Milliken lab in Spartanburg, South Carolina. An in-line sheet forming and thermoforming process was used to produce deep draw cups. Cast-sheet was produced by feeding PP formulated pellets to a sheet forming line. The line is composed with three major sections (1) a single screw extruder (2) a coat hanger-manifold die and (3) a water bath and a set of chill-rolls. The 1.9 mm thick sheet was fed into an Illig RDM-54K solid phase former equipped with upper and lower infrared ceramic heaters. Sheet forming and thermoforming were set at similar conditions for all samples each time. The molded cups were 139 mm tall and 500 ml in volume with a mouth diameter of 93 mm and a bottom diameter of 59 mm. Cup optics were measured at the same height where wall thickness is around 275 μm. Wall thickness reduction is about 7 fold at this location. Clarity and haze were measured with a BYK Gardner Plus haze meter using ASTM method D1003-11.